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DEFECT CHEMISTRY AND CHARACTERIZATION OF $Hg_{1-x}Cd_xTe$

By H. R. Vydyanath
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Final Report

February 1982

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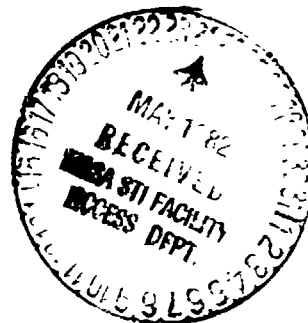
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16. Abstract

Single-crystal samples of undoped and doped $Hg_{1-x}Cd_xTe$ were annealed at varying temperatures and partial pressures of Hg. Hall effect and mobility measurements were carried out on these samples after quenching to room temperature. Based on the variation of the carrier concentration and the carrier mobility as a function of the partial pressure of Hg temperature, and dopant concentration, defect models have been established for the doped and the undoped crystals. These models indicate that the native acceptor defects in both $Hg_{0.8}Cd_{0.2}Te$ and $Hg_{0.6}Cd_{0.4}Te$ are doubly ionized and the native donor defects are negligible in concentration, implying that p-to-n conversion in these alloys occurs due only to residual donors. Incorporation mechanisms of copper, indium, iodine and phosphorus have been investigated. Copper and indium appear to occupy only Hg lattice sites acting as single acceptor and single donor, respectively; whereas, iodine is found to act as a single donor occupying only Te lattice sites. A large concentration of indium is found to be incorporated as In_2Te_3 with only a small fraction acting as donors. In crystals doped with iodine, a large fraction of iodine is found to be paired with the native acceptor defects. Results on crystals doped with phosphorus indicate that phosphorus behaves amphoterically, acting as a donor on Hg lattice sites and as an acceptor interstitially on Te lattice sites. A majority of the phosphorus is found to be present as neutral species formed from the pairing reaction between phosphorus on Hg lattice sites and phosphorus in interstitial sites. Equilibrium constants for the intrinsic excitation reaction, as well as for the incorporation of the different dopants and the native acceptor defects, have all been established. These constants satisfactorily explain all the experimental results in the undoped as well as the doped crystals.

As a result of the work performed on this program, it is possible to predict the nature and concentration of defects obtained in $Hg_{1-x}Cd_xTe$ compounds as a function of the annealing temperature, partial pressure of Hg, and dopant concentration. It is now possible to vary the concentration of defects controllably as a function of the crystal preparation conditions and in turn correlate the physical characteristics, such as carrier lifetime and carrier concentrations with defect centers in the crystals.

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SECTION 1
FOREWORD

This technical report covers the work performed by Honeywell Electro-Optics Operations, Lexington, Massachusetts from December 18, 1978 to February 17, 1982 under the NASA sponsored program entitled "Defect Chemistry and Characterization of (Hg,Cd)Te" on Contract NAS8-33245. The objective of this program is to study and formalize the defect chemistry of (Hg,Cd)Te and to evaluate and select characterization methods for the material.

The principal investigator is Dr. H. R. Vydyanath, providing the overall technical direction for the program. Technical assistance during the various phases of the program has been provided by D. A. Nelson, J. C. Donovan, P. Crickard, A. Barnes, and R. C. Abbott. R. A. Lancaster and D. A. Nelson generously furnished all the crystals required for the program.

8203-01

SECTION 2
INTRODUCTION

$Hg_{1-x}Cd_xTe$ is a variable bandgap alloy semiconductor extensively used for infrared applications. Detector performance close to the theoretical limits imposed by infrared imaging systems requires extreme control for compositional uniformity, carrier concentration, and carrier lifetime. The program deals with the study of the nature and concentration of the lattice defects incorporated into $Hg_{1-x}Cd_xTe$ alloys as a function of the physiochemical conditions of preparation; namely, the temperature, the partial pressures of the constituent elements, and/or the concentration or the activity of the dopant being incorporated.

Undoped, donor-doped, and acceptor-doped $Hg_{1-x}Cd_xTe$ samples are annealed at various temperatures in suitable Hg atmospheres. The samples are quenched to room temperature from the high temperatures. Hall effect and resistivity measurements are carried out at 77 K to determine the carrier concentrations and mobilities. The variation of the carrier concentrations as a function of the partial pressure of Hg and/or the dopant concentration is used to arrive at defect models for the doped and the undoped crystals.

At the end of the 36 month period of the program, significant accomplishments have been made toward understanding the nature of lattice defects and the mode of incorporation of different dopants. For the first time in literature, the defect structures of undoped $Hg_{0.6}Cd_{0.4}Te$ (s) undoped, copper doped, indium doped, iodine doped, and phosphorus doped $Hg_{0.8}Cd_{0.2}Te$ (s) have all been established. The native acceptor defects have been found to be doubly ionized both $Hg_{0.6}Cd_{0.4}Te$ (s) and $Hg_{0.8}Cd_{0.2}Te$ (s). Native donor defects are found to be negligible in concentration in these alloys and the origin of p-type to n-type conversion has been shown to be due to residual foreign donors and not due to native donor defects.

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Of the dopants studied, copper and indium have been found to occupy only Hg lattice sites acting with single acceptor and donor electrical activities respectively, whereas iodine is found to act as a single donor occupying only Te lattice sites. A large concentration of indium is found to be incorporated as In_2Te_3 with only a small fraction acting as donors. Crystals doped with iodine are found to be saturated with the metal iodide with a large fraction of iodine being paired with the native acceptor defects. Results on crystals doped with phosphorus indicate that phosphorus behaves amphoterically acting as a donor on Hg lattice sites and as an acceptor interstitially on Te lattice sites. Thermodynamic constants have been established for the incorporation of the native defects as well as the different dopants. These constants satisfactorily explain all the experimental results.

The following presentations and publications have resulted from the work performed throughout the duration of this program

1. H. R. Vydyanath, D. A. Nelson, et al, "$(Hg_{1-x}Cd_x)Te$ Material Studies," Proceedings of the IRIS Detector Specialty Group Meeting, Minneapolis, MN, 15-17 June 1979, p. 29.

2. H. R. Vydyanath, D. A. Nelson, and R. A. Lancaster, "Defect Chemistry and Characterization of $(Hg_{1-x}Cd_x)Te$," J. of Electrochem. Soc. 126, 371C (1979).

3. H. R. Vydyanath, "Defect Studies in $Hg_{0.8}Cd_{0.2}Te$," Presented at the Conference on the "Crystal Growth and Characterization of II-VI Compounds," University of Lancaster, U. K., 14-16 April 1980.

4. H. R. Vydyanath, "Lattice Defects in Semiconducting $Hg_{1-x}Cd_xTe$ Alloys," I-Defect Structure of Undoped and Copper Doped $Hg_{0.8}Cd_{0.2}Te$, J. Electrochem. Soc. 128, 2609 (1981).

5. H. R. Vydyanath, "Lattice Defects in Semiconducting $Hg_{1-x}Cd_xTe$ Alloys," II-Defect Structure of Indium Doped $Hg_{0.8}Cd_{0.2}Te$, J. Electrochem. Soc. 128, 2619 (1981).

6. H. R. Vydyanath, J. C. Donovan, and D. A. Nelson, "Lattice Defects in Semiconducting $Hg_{1-x}Cd_xTe$ Alloys," III-Defect Structure of Undoped $Hg_{0.6}Cd_{0.4}Te$, J. Electrochem. Soc. 128, 2625 (1981).

7. H. R. Vydyanath, D. A. Nelson, J. C. Donovan, P. Crickard, and R. C. Abbott, "Role of Lattice Defects in Undoped and Doped $Hg_{1-x}Cd_xTe$ Alloys," HCT Workshop, Minneapolis, MN, 28-30 October 1981.

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8. H. R. Vydyanath, D. A. Nelson, R. C. Abbott, J. C. Donovan, and P. Crickard, "Point Defects in Undoped and Doped $Hg_{1-x}Cd_xTe$ Alloys," Materials Research Society Annual Meeting, Boston, MA, 16-19 November 1981.

9. H. R. Vydyanath and F. A. Kroger, "Doping Behavior of Iodine in $Hg_{0.8}Cd_{0.2}Te$," J. Electronic Materials, 11, 111 (1982).

10. H. R. Vydyanath and R. C. Abbott, "Mode of Incorporation of Phosphorus in $Hg_{0.8}Cd_{0.2}Te$," (Submitted to Appl. Phys. November 1981).

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SECTION 3
TECHNICAL DETAILS

Hall effect and electrical resistivity measurements were the main tools utilized in characterizing the defects in the present program. The variation in the carrier concentration and carrier mobility in the crystals-- cooled to room temperature subsequent to anneals at high temperatures under different partial pressures of Hg--was used to arrive at defect models in the undoped as well as the doped crystals. This section, dealing with the work performed from December 18, 1978 to February 17, 1982, presents the technical details of the work in the form of five papers which were submitted for publication in scientific literature. Of these, four have already been published in the journals of Electrochemical Society and Electronic Materials. The fifth one has been submitted to the Journal of Applied Physics and has not yet been published. The details of the publications; the titles, the authors' names, the name of the journal and the page numbers are furnished below.

1. H. R. Vydyanath, "Lattice Defects in Semiconducting $Hg_{1-x}Cd_xTe$ Alloys," I-Defect Structure of Undoped and Copper Doped $Hg_{0.8}Cd_{0.2}Te$, J. Electrochem. Soc. 128, 2609 (1981).

2. H. R. Vydyanath, "Lattice Defects in Semiconducting $Hg_{1-x}Cd_xTe$ Alloys," II-Defect Structure of Indium Doped $Hg_{0.8}Cd_{0.2}Te$, J. Electrochem. Soc. 128, 2619 (1981).

3. H. R. Vydyanath, J. C. Donovan, and D. A. Nelson, "Lattice Defects in Semiconducting $Hg_{1-x}Cd_xTe$ Alloys," III-Defect Structure of Undoped $Hg_{0.6}Cd_{0.4}Te$," J. Electrochem. Soc. 128, 2625 (1981).

4. H. R. Vydyanath and F. A. Kroger, "Doping Behavior of Iodine in $Hg_{0.8}Cd_{0.2}Te$," J. Electronic Materials, 11, 111 (1982).

5. H. R. Vydyanath and R. C. Abbott, "Mode of Incorporation of Phosphorus in $Hg_{0.8}Cd_{0.2}Te$," (Submitted to J. Appl. Phys. November 1981).

The papers describe the background material, the experimental details and the analyses of the data. Defect models for undoped $Hg_{0.8}Cd_{0.2}Te$ and $Hg_{0.6}Cd_{0.4}Te$, as well as for copper, indium, iodine and phosphorus doped $Hg_{0.8}Cd_{0.2}Te$ have been proposed. Thermodynamic constants for the incorpor-

ation of the native defects, dopant defects and the intrinsic excitation process have all been arrived at. These constants satisfactorily explain the experimental results in the undoped as well as the doped crystals.

8203-01

3.1   DEFECT CHEMISTRY AND CHARACTERIZATION OF UNDOPED AND COPPER DOPED $Hg_{0.8}Cd_{0.2}Te$

8203-01

Lattice Defects in Semiconducting $Hg_{1-x}Cd_xTe$ Alloys

I. Defect Structure of Undoped and Copper Doped $Hg_{0.8}Cd_{0.2}Te$

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ABSTRACT

Undoped $Hg_{0.8}Cd_{0.2}Te$ crystals were subjected to high temperature equilibration at temperatures ranging from 400° to 655°C in various Hg atmospheres. Hall effect and mobility measurements were carried out on the crystals quenched to room temperature subsequent to the high temperature equilibration. The variation of the hole concentration in the cooled crystals at 77 K as a function of the partial pressure of Hg at the equilibration temperatures, together with a comparison of the hole mobility in the undoped samples with that in the copper-doped samples, has yielded a defect model for the undoped $Hg_{0.8}Cd_{0.2}Te$ crystals, according to which, the undoped crystals are essentially intrinsic at the equilibration temperatures and the native acceptor defects are doubly ionized. Native donor defects appear to be negligible in concentration, implying that the p-to-n conversion in these alloys is mainly due to residual foreign donor impurities. The thermodynamic constants for the intrinsic excitation process as well as for the incorporation of the doubly ionized native acceptor defects in the undoped crystals have been arrived at. Copper appears to be incorporated on metal lattice sites acting as a single acceptor with little compensation. Results on the heavily copper-doped samples indicate that the quench from the equilibration temperatures was imperfect resulting in a large fraction of the copper precipitating during the quench. From results of experiments where the cooling rate from the equilibration temperatures was intentionally varied in the undoped samples, a qualitative correlation was established between the quenching efficiency and the presence of macroscopic defects such as voids and inclusions in the samples.

The importance of the pseudobinary semiconducting $Hg_{1-x}Cd_xTe$ alloys as a useful infrared detector material has long been recognized (1, 2). The bandgap of these alloys is variable depending on the proportions of HgTe and CdTe present in them; the variable bandgap makes these alloys suitable for infrared detector applications over a wide spectral range.

Considerable deviations from stoichiometry arise in these alloys prepared at elevated temperatures; these deviations result in electrically active point defects which in turn influence the carrier concentration and the lifetime in the material. Very little information exists on the systematic investigation of the nature of defects and the variation of the concentration on of these defects in these alloys as a function of the physicochemical conditions of preparation. In fact, much disagreement prevails regarding the origin of p-type to n-type conversion in these alloys (2-5).

As part of a program aimed at investigating the defect structure of the undoped $Hg_{1-x}Cd_xTe$ alloys as well as the mode of incorporation of dopants, the present paper reports on the study of the undoped and copper-doped $Hg_{0.8}Cd_{0.2}Te$.

Based on the results of Hall effect and mobility measurements on the undoped and copper-doped crystals quenched to room temperature subsequent to high

temperature equilibration, defect models for the undoped and copper-doped $Hg_{0.8}Cd_{0.2}Te$ have been arrived at. Thermodynamic constants for the intrinsic excitation constant and the incorporation of the native acceptor defects have been evaluated. These constants satisfactorily explain the electrical data in the undoped as well as the copper-doped crystals.

Experimental

Starting material.—The compositional uniformity of the $Hg_{1-x}Cd_xTe$ alloy samples used in the investigation was $x = 0.2 \pm 0.005$. Most of the experiments were carried out with starting material that was free of macroscopic defects such as precipitates, pores, and Hg or Te inclusions; in a few experiments where the intent was to establish the effect of macroscopic defects on the efficiency of quenching the high temperature equilibrium, material with a relatively high density of voids and inclusions was used. In order to assure ourselves that equilibrium was attained at temperatures as low as 400°-460°C within reasonable annealing periods (2-3 weeks), and also to increase the efficiency of quenching the high temperature equilibrium, the thickness of most of the $Hg_{0.8}Cd_{0.2}Te$ samples used in the present investigation was restricted to ≤ 0.04 cm. The residual donor or acceptor concentration in the starting undoped $Hg_{0.8}Cd_{0.2}Te$ material was $\cong 10^{16}$ cm^{-3}

Copper doping.— Doping to different concentrations of copper was obtained by evaporating various amounts of copper on to the surface of the undoped samples and subsequently diffusing in the copper in a known atmosphere of Hg. Copper concentration obtained in the doped samples was determined by atomic absorption analysis carried out by Photometrics, Incorporated, Lexington, Massachusetts.

It is to be noted that the samples used for copper diffusions at temperatures below 400°C had been previously annealed at 250°C for several months in order to reduce the native acceptor defect concentration to less than 10^{16} cm^{-3}. Since copper has a high diffusivity in Hg$_{1-x}$Cd$_x$Te alloys (6-7), diffusion times of 6-8 weeks were found adequate for uniform doping of samples (0.04 cm thick) at temperatures below 400°C; uniform doping at these temperatures was confirmed by sequentially lapping away the material from both sides of the samples and making certain that the hole concentrations did not change.

High temperature annealing.— Prior to the anneals, crystals were cleaned in organic solvents followed by a Br-methanol etch and a final rinse in DI water. Annealing experiments in various partial pressures of Hg were carried out in evacuated quartz ampuls containing a small amount of Hg also, to obtain the desired Hg vapor pressure. In those experiments where the desired Hg pressure was high enough, an isothermal setup was used where the free Hg and the Hg$_{0.8}$Cd$_{0.2}$Te samples were kept at the same temperature; the vapor pressure of Hg in such a setup depended on the amount of free Hg in the ampul and the volume of the ampul. In experiments where the desired Hg pressure was low a two-temperature zone setup was used; the Hg$_{0.8}$Cd$_{0.2}$Te crystals were kept at the higher temperature end of the ampul and the free Hg at the lower temperature end; the vapor pressure of Hg obtained corresponded to the saturation pressure of Hg at the lower temperature and was independent of the amount of Hg in the ampul. The limits of Hg pressure, within which the solid is stable at a given temperature, were obtained from the partial pressure-temperature data for HgTe (8) and Hg$_{1-x}$Cd$_x$Te alloys (9-10).

Equilibration periods ranging from 16 to 24 hr were used for annealing at temperatures of 500°C or greater and a two week equilibration was used for annealing temperatures of 460° and 400°C. Subsequent to the anneals, samples were rapidly quenched in ice water, to freeze in as much of the high temperature equilibrium as possible; in a few cases the samples were air cooled from the equilibration temperatures.

Electrical measurements.— Hall effect and resistivity measurements were made using the van der Pauw method (11). Magnetic field strengths of 400 and 4000G were used for the measurement of the Hall coefficient.

Results

Only those Hall coefficient measurements where the Hall coefficient R_H did not vary with varying magnetic field strength, (400-4000G) were used in evaluating the hole concentrations in the crystals. This ensured that the samples did not show mixed conduction (12) and the carrier concentration was given by

$$\frac{1}{|R_H|q}$$

Figure 1 shows the variation of the Hall coefficient as a function of the temperature of measurement for the undoped samples equilibrated at different temperatures under known partial pressures of Hg and quenched to room temperature. It is evident from the figure that at temperatures exceeding 145 K the contribution from the intrinsic carriers becomes important, whereas at temperatures between 77 and 145 K the Hall coefficient is temperature independent indicating that the native
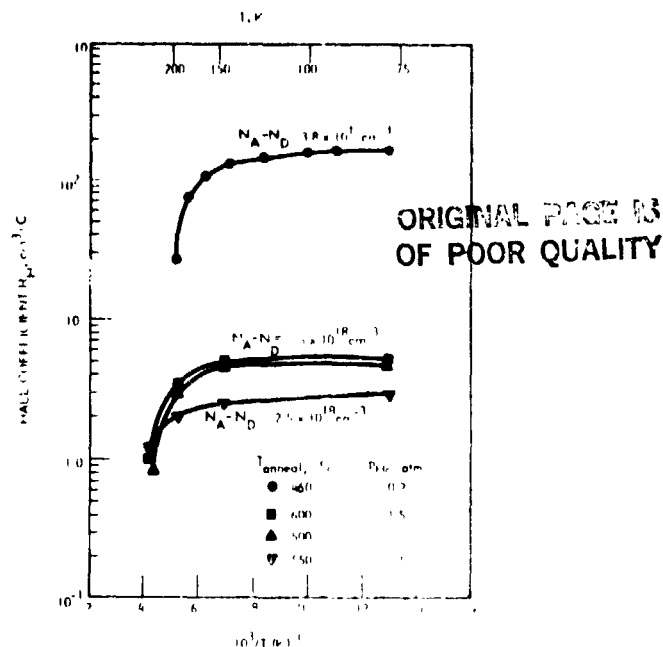

Fig. 1. Hall coefficient as a function of measurement temperature for undoped Hg$_{0.8}$Cd$_{0.2}$ samples equilibrated at the indicated temperatures and partial pressures of Hg and quenched to room temperature.

acceptors are completely ionized at 77 K for concentrations ranging from 10^{17} to 10^{18} cm^{-3}. Based on this inference, all the Hall effect measurements on the undoped samples were carried out at 77 K, and the resulting hole concentration was assumed to give a measure of the native acceptor defect concentration incorporated at the higher equilibration temperatures.

Figure 2 shows the hole concentrations at 77 K as a function of the partial pressure of Hg for the undoped crystals annealed at various temperatures and quenched to room temperature. The samples are invariably p-type for all partial pressures of Hg (throughout the existence region) at temperatures greater than 400°C and the hole concentration is roughly inversely proportional to the partial pressure of Hg, p_{Hg}. Phase boundary limits at each temperature are indicated by arrows in the figure. The solid lines
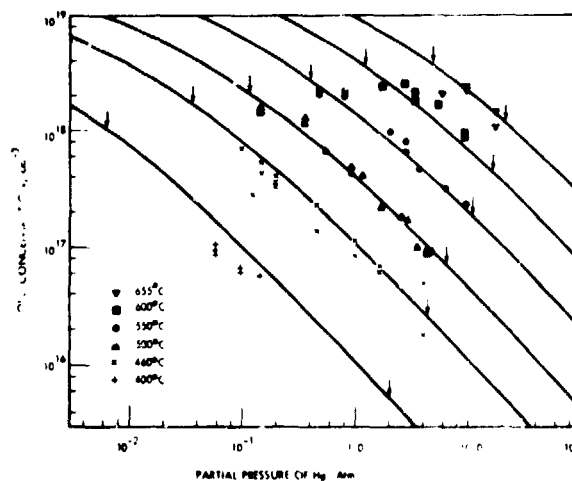

Fig. 2. Hole concentration at 77 K as a function of the partial pressure of Hg for undoped Hg$_{0.8}$Cd$_{0.2}$ crystals annealed at various equilibration temperatures and quenched to room temperature; solid lines correspond to the values calculated on the basis of the defect model discussed in the text.

shown in the figure correspond to the hole concentrations calculated on the basis of the defect model for the undoped crystals, to be discussed later.

Figure 3 shows the variation of the Hall coefficient as a function of the temperature of measurement for crystals doped with different copper concentrations. Just as with the undoped crystals, most of the copper present in the electrically active form appears to be completely ionized between 77 and 145 K, and at temperatures greater than 145 K the contribution from the intrinsic carriers becomes significant. The total amount of the electrically active copper concentration in the samples was inferred from the hole concentrations obtained at 145 K.

Figure 4 shows the hole mobility at 77 K for the undoped crystals as a function of the hole concentration. The data indicate that the hole mobility decreases with increase in hole concentration. Figure 5 shows the hole mobility at 77 K in various copper-doped samples. The temperatures at which the various copper diffusions were done are also indicated in the figure. It is apparent from Fig. 4 and 5 that the copper-doped samples
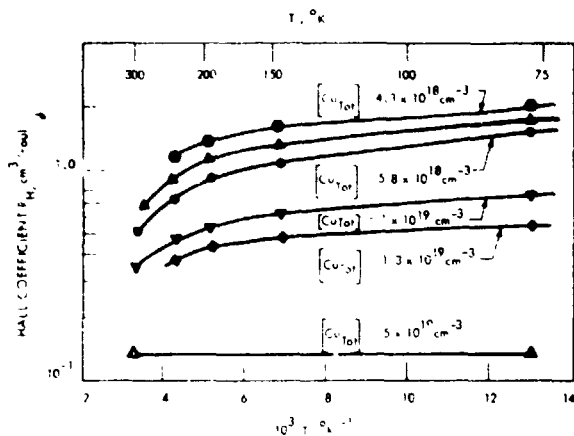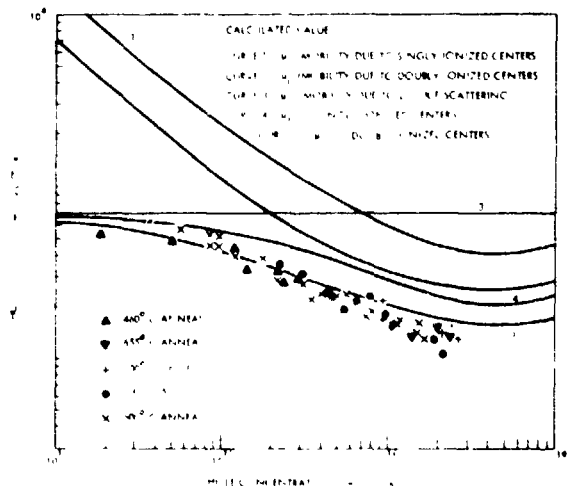
Fig. 5. Experimental and calculated hole mobility at 77 K as a function of the hole concentration for copper-doped $Hg_{0.8}Cd_{0.2}$ crystals; curves 1 and 2 show the calculated mobility due to impurity scattering (curve 1 for singly ionized centers and curve 2 for doubly ionized centers), line 3 shows the mobility due to lattice scattering, and curves 4 and 5 show the overall mobility calculated by reciprocally combining the impurity scattering mobility (curve 4 for singly ionized centers and curve 5 for doubly ionized centers) See Appendix A for details of calculations.

have higher hole mobilities than the undoped samples containing similar hole concentrations. The mobilities calculated on the basis of the combined ionized impurity and lattice scattering are also shown in the figures.

Figure 6 compares the electrical conductivity at 77 K obtained in the undoped crystals containing a relatively large concentration of voids and inclusions ($\sim$1000 per cm^2) with those containing a negligible concentration of these (≤ 20 per cm^2) subsequent to anneals at 500°C in different partial pressures of Hg and air cooled or quenched to room temperature; the voids and inclusions in the samples were approximately 10-30 μm in diameter, and depending on how the bulk crystals were grown, the inclusions were either Hg rich or Te rich. Figure 7 shows the electrical conductivity at 77 K, obtained in the undoped crystals containing a large concentration of voids and inclusions and which were air cooled to room temperature subsequent to anneals at 500°C in different partial pressures of Hg. Figures 6 and 7 clearly show that the electrical conductivity variations as a function of the partial pressure of Hg are similar for undoped crystals with and without voids and inclusions that were quenched to room tem-

Fig. 3. Hall coefficient as a function of measurement temperature for copper-doped $Hg_{0.8}Cd_{0.2}$ crystals.

Fig. 4. Experimental and calculated hole mobility at 77 K as a function of the hole concentration for undoped $Hg_{0.8}Cd_{0.2}$ crystals; curves 1 and 2 show the calculated mobility due to impurity scattering (curve 1 for singly ionized centers and curve 2 for doubly ionized centers), line 3 shows the mobility due to lattice scattering, and curves 4 and 5 show the overall mobility calculated by reciprocally combining the impurity scattering mobility and the lattice scattering mobility (curve 4 for singly ionized centers and curve 5 for doubly ionized centers). See Appendix A for details of calculations.
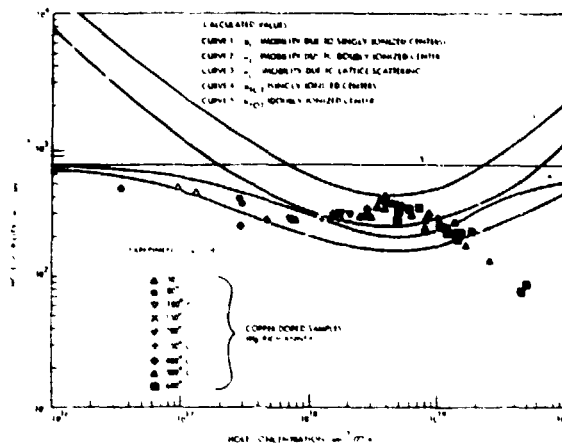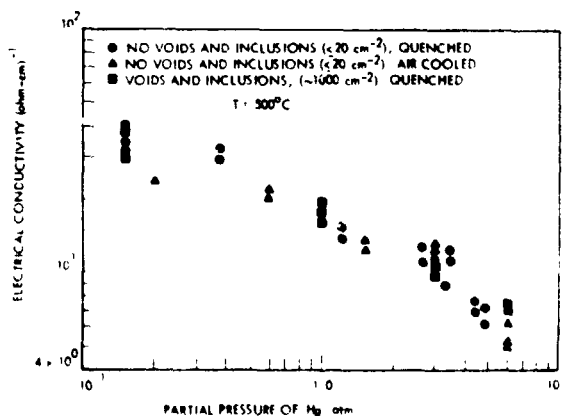
Fig. 6. Electrical conductivity at 77 K for various sets of undoped $Hg_{0.8}Cd_{0.2}Te$ crystals containing different concentrations of voids and inclusions, and quenched or air cooled subsequent to anneals in different Hg pressures at 500°C.
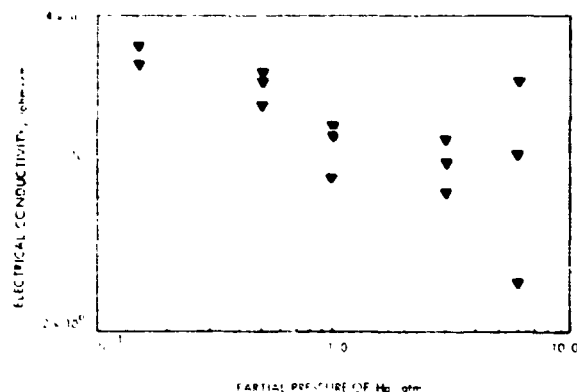
Fig. 7. Electrical conductivity at 77 K for undoped $Hg_{0.8}Cd_{0.2}Te$ crystals containing a large concentration of voids and inclusions and air cooled subsequent to anneals in different Hg pressures at 500°C.

perature subsequent to equilibration at 500°C; the results are also similar for the undoped crystals containing virtually no voids and inclusions and which were air cooled from 500°C. However, considerable scatter is obtained in the results for the undoped crystals containing a large concentration of voids and inclusions and which were air cooled from 500°C.

Discussion

Defect equilibria —The way in which the concentrations of defects vary as a function of the physicochemical conditions of preparation (temperature, partial pressure of Hg or partial pressure of Te_2, and/or the dopant concentration) can be arrived at by utilizing the quasichemical approach developed by Kröger and Vink (13). The quasichemical approach has been used in many binary compounds to establish defect models (14). In such an approach, atomic and electronic defects are considered as chemical species and defect formation reactions along with the corresponding mass action relations are formulated. The concentrations of all the defect species comprising the electroneutrality condition and the dopant balance equation (for the doped crystals) are then expressed in terms of the relevant mass action constants and the concentration of one defect species. This results in equations containing the various mass action constants and the concentrations of one single defect species, numerical solution will then yield the concentration of this defect species for given values of the mass action constants. Once the concentration of one defect species is determined the concentrations of all the other defect species can be evaluated via the mass action relations.

Defect formation reactions and mass action relations for various defect species are listed in Table I. The defect notations are according to the scheme of Kröger and Vink (13, in which the major symbol indicates the

defect, the subscript denotes the type of lattice site occupied, and the superscript indicates the charge. Superscripts prime (') and dot ( ) stand for effective negative and positive charges, respectively, while a cross (x) stands for a neutral charge. Thus V''_{Hg} indicates a doubly negatively ionized vacant lattice site of Hg. Square brackets indicate concentrations expressed as site fractions. The native acceptor defect species considered in this paper are the vacancies of Hg instead of the interstitials of Te. Electrical measurements cannot distinguish between the two species and hence the results will be the same if interstitials of Te are considered as the native acceptor defect species instead. Recent work on the defect structure of CdTe (15, 16) determined by Hall effect and tracer self-diffusion data indicates the presence of appreciable concentrations of Te interstitials in addition to the vacancies of Cd. Although the results of the present work showed no evidence of presence of any native donor defects such as Hg_i or V_{Te}, etc. in any appreciable concentration, Table I includes these defects also for purposes of later discussion in the paper.

Defect state in the cooled crystals.—Ideally, in situ high temperature physical property measurements and measurements on the crystals quenched from the equilibration temperatures should both be used to arrive at defect states prevailing at the high temperature as well as in the cooled crystals, much information regarding precipitation of atomic defects during quenching can be obtained by correlating the defect state in the cooled crystals with that obtained at the equilibration temperatures. CdTe (15-19) is only one of the few materials that has been studied extensively from such a viewpoint. In the present work, however, the defect state in the cooled crystal shall be used to derive information regarding the defect state prevailing at the equilibration temperatures.

While attempting to deduce the high temperature defect state of the crystals from measurements on the crystals quenched to room temperature from the high temperature physicochemical conditions, a few assumptions are made. The assumptions are (i) that the electrons and the holes recombine during cooling, (ii) that all the atomic defects at the high temperature are frozen in, and (iii) that the intrinsic carrier concentration $n_i = K_i^{1/2}$ at the measurement temperature << concentration of the electrically active atomic defects so that the Fermi level is pinned at the defect level and the carrier concentration in the cooled crystals gives the concentration of the atomic defects corresponding to the high temperature equilibrium. The first assumption is always satisfied and the third one is also satisfied as long as the carrier concentration measurement temperature is low enough for n_i to be low. The second assumption requires that the crystals be quenched fast enough that the precipitation of the atomic defects is not given rise to.

Approximation to the electroneutrality condition and dopant balance condition.—When the electroneutrality

Table I   List of the defect formation reactions, mass action constants, electroneutrality condition, and dopant balance equation

Reaction	Mass action relation
1 $O \rightarrow e' + h^\cdot$, E_i	$K_i = [e'] [h^\cdot]$
2 $Hg^x_{Hg} \rightarrow V''_{Hg} + 2h^\cdot + Hg(g)$; H''_{VHg}	$K''_{VHg} = [V''_{Hg}] [h^\cdot]^2 p_{Hg}$
3 $V''_{Hg} \rightarrow V'_{Hg} + h^\cdot$; $E_{a,i}'$	$K_{a,i}' = [V'_{Hg}] [h^\cdot] / [V''_{Hg}]$
4 $V'_{Hg} \rightarrow V^x_{Hg} + h^\cdot$, $E_{a,i}^x$	$K_{a,i}^x = [V^x_{Hg}] [h^\cdot] / [V'_{Hg}]$
5 $(Hg_xCd_{0.2})Te (S) \rightarrow 0.8 (Hg(g) + 0.2 Cd(g) + 1/2 Te_2(g))$; $H_{Hg_{0.8}Cd_{0.2}Te}$	$K_{(Hg_{0.8}Cd_{0.2}Te)} = p_{Hg}^{0.8} p_{Cd}^{0.2} p_{Te_2}^{1/2}$
6 $O \rightarrow V''_{Hg} + V^\cdot_{Te}$; H'_s	$K'_s = [V''_{Hg}] [V^\cdot_{Te}]$
7 $Hg^x_{Hg} \rightarrow V^x_{Hg} + Hg^\cdot_i$; H'_F	$K'_F = [V^x_{Hg}] [Hg^\cdot_i]$
8 $Hg(l) \rightarrow Hg(g)$; H_{Hg}	$K_{Hg} = p_{Hg} / a_{Hg}$
9 $Te(l) \rightarrow 1/2 Te_2(g)$, H_{Te}	$K_{Te} = p_{Te_2}^{1/2} / a_{Te}$
10 Electroneutrality condition $[e'] + [Cu'_{Hg}] + [V'_{Hg}] + 2[V''_{Hg}] = [h^\cdot] + [Cu_i^\cdot] + [Hg_i^\cdot] + 2[Hg_i^{\cdot\cdot}] + 2[V^{\cdot\cdot}_{Te}]$	
11 Copper balance equation $[Cu'_{Hg}] + [Cu_i^\cdot] = [Cu_{tot}]$	

condition and the dopant balance equation (Table I) are approximated by only the dominant members (20), one can obtain the variation of the defect concentrations as a function of p_{Hg} and the total copper concentration (for copper-doped crystals) in the form

$$\text{Concentration} \propto p_{Hg}{}^r \, [Cu_{tot}]^s$$

where r and s are small integers or fractions.

Table II lists the exponents of p_{Hg} and $[Cu_{tot}]$ for the variation of the concentrations of the different defects for various approximations to the electroneutrality condition.

Native acceptor defects.—The fact that the hole concentration in the undoped crystals is proportional to $p_{Hg}{}^{-1}$ (Fig. 2) indicates that the crystals are essentially intrinsic at the high temperature (Table II, electroneutrality approximation $[e'] = [h^{\cdot}]$); however, as can be noted from Table II, for a situation where the crystal is intrinsic, all the native acceptor defects vary as $p_{Hg}{}^{-1}$ irrespective of the charge state of the defects. In order to establish the charge state of the native acceptor defects dominant in the undoped crystals the electrical characteristics of the undoped and the acceptor doped crystals will be compared. Figure 4 shows that the hole mobilities in the undoped crystals at 77 K decrease with an increase in the hole concentration indicating that the contribution of ionized impurity scattering to the hole mobilities is substantial. If so, the fact that a majority of the copper-doped crystals shown in Fig. 5 have higher mobilities than the undoped crystals indicates that the ionized impurity scattering is less in the copper-doped crystals; the results can be explained if copper is a single acceptor occupying Hg lattice sites and the native acceptor defects in the undoped crystals are doubly ionized. Based on the theory of ionized impurity scattering (21) for comparable hole concentrations. the mobilities due to ionized impurity scattering in the copper-doped crystals containing x number of singly ionized copper centers can be expected to be twice that in the undoped crystals containing $x/2$ number of the doubly ionized native

acceptor defect centers. Also, in those crystals where the electrically active copper concentration exceeds the intrinsic carrier concentration at the annealing temperatures, thus extrinsically doping them, the native acceptor defect concentration decreases with an increase in the copper concentration as a consequence of the mass action effect. As can be seen from Table II, as soon as the crystals become extrinsic with copper doping and the electroneutrality approximation becomes $[Cu'_{Hg}] = [h^{\cdot}]$, the doubly ionized native acceptor defects decrease in proportion to the square of the copper concentration in the crystals ($[V''_{Hg}] \propto [Cu_{tot}]^{-2}$). This is shown schematically in Fig. 8. Hence. in samples doped with copper to greater than the intrinsic carrier concentration, the concentration of the doubly ionized native acceptor defects is considerably depressed. If the native acceptor defects were singly ionized, their concentration would decrease in an inverse linear proportion to $[Cu_{tot}]$ as soon as the copper concentration exceeds the intrinsic carrier concentration (Table II and Fig. 8); however, the hole mobility of such samples should be no different from that of the undoped crystals for comparable hole concentrations. It may be argued that the larger hole mobility in the heavily copper-doped samples (Fig. 5) may result from shorting paths due to the high concentrations of copper; however, the fact that the hole mobility in the copper-doped samples decreases for hole concentrations in excess of 10^{19} cm^{-3} (Fig. 5) rules out this explanation. It should also be noted from Fig. 4 and 5 that the hole mobilities are essentially the same for both the copper-doped and the undoped samples when the hole concentration is less than 10^{17} cm^{-3}. This result indicates that ionized impurity scattering is probably less significant for hole concentrations less than 10^{17} cm^{-3}. Hole mobilities calculated by reciprocally combining the mobility due to lattice scattering and the mobility due to ionized impurity scattering (see Appendix A for details) are also shown in Fig. 4 and 5 for the cases of singly ionized and doubly ionized scattering centers; clearly, for the undoped crystals, the agreement between the experimental values and the calculations is better for the case of the doubly ionized scattering centers, whereas for the copper-doped crystals the agreement is better for the case of the singly ionized scattering centers. It should be noted that the

Table II. Variations of the defect concentrations as a function of p_{Hg} and/or copper concentrations for various approximations to the electroneutrality condition

Type of defect and approximation to the electro- neutrality condition	$[\,] \propto p^r{}_{Hg}[Cu_{tot}]^s$		Hole concentration in the cooled crystals	
	r	s	r	s
1. $[e'] = [h^{\cdot}] = \sqrt{K_i}$	0	0		
$[V''_{Hg}]$	−1	0	−1	0
$[V'_{Hg}]$	−1	0	−1	0
$[Hg^{\cdot}_i]$	+1	0	+1	0
$[Hg^{\cdot\cdot}_i]$	+1	0	+1	0
$[V^{\cdot\cdot}_{Te}]$	+1	0	+1	0
$[Cu'_{Hg}] = [Cu_{tot}]$	0	1	0	1
2. $[Cu'_{Hg}] = [Cu_{tot}] = [h^{\cdot}]$	0	1	0	1
$[V''_{Hg}]$	−1	−2		
$[V'_{Hg}]$	−1	−1		
$[Hg^{\cdot}_i]$	+1	+1		
$[Hg^{\cdot\cdot}_i]$	+1	+2		
$[V^{\cdot\cdot}_{Te}]$	+1	+2		
$[Cu'_{Hg}] = [Cu_{tot}]$	0	1		
3. $[h^{\cdot}] = 2[V''_{Hg}]$	−1/3	0	−1/3	0
$[e']$	+1/3	0		
$[V'_{Hg}]$	−2/3	0		
$[Hg^{\cdot}_i]$	+2/3	0		
$[Hg^{\cdot\cdot}_i]$	+1/3	0		
$[V^{\cdot\cdot}_{Te}]$	+1/3	0		
$[Cu'_{Hg}] = [Cu_{tot}]$	0	1		
4. $[V''_{Hg}] = [V^{\cdot\cdot}_{Te}] = \sqrt{K'_s}$	0	0		
$[e']$	1/2	0		
$[h^{\cdot}]$	−1/2	0		
$[V'_{Hg}]$	−1/2	0		
$[Hg^{\cdot}_i]$	+1/2	0		
$[Hg^{\cdot\cdot}_i]$	0	0		
$[Cu'_{Hg}] = [Cu_{tot}]$	0	1		
5. $[V'_{Hg}] = [Hg^{\cdot\cdot}_i] = \sqrt{K''_r}$	0	0		
$[e']$	1/2	0		
$[h^{\cdot}]$	−1/2	0		
$[V''_{Hg}]$	−1/2	0		
$[Hg^{\cdot}_i]$	+1/2	0		
$[Hg^{\cdot\cdot}_i]$	0	0		
$[V^{\cdot\cdot}_{Te}]$	0	0		
$[Cu'_{Hg}] = [Cu_{tot}]$	0	1		

Fig. 8. Schematic variation of $[e']$, $[h^{\cdot}]$, $[Cu'_{Hg}]$, $[V''_{Hg}]$ (or $[Te''_i]$), $[V'_{Hg}]$ (or $[Te'_i]$), and $[Hg^{\cdot}_i]$ (or $[V^{\cdot\cdot}_{Te}]$) as a function of the electrically active copper concentration in Hg$_{0.8}$Cd$_{0.2}$Te at a fixed temperature and partial pressure of Hg

Brooks-Herring expression (21) used for calculating the mobility due to ionized impurity scattering is applicable only for nondegenerate semiconductors and hence the mobility calculations shown in Fig. 4 and 5 for hole concentrations in excess of 10^{19} cm^{-3} should not be deemed significant; for such large carrier concentrations impurity banding effects also become important.

Absence of compensation in the undoped and copper-doped crystals.—Absence of compensation in the undoped as well as the copper-doped crystals of Hg$_{0.8}$Cd$_{0.2}$Te is evidenced by a few inferences. First, the hole mobilities in the undoped crystals are only dependent on the hole concentration and are independent of the temperature of anneal; if there was any compensation by native defects, the concentration of these defects would be expected to be exponentially dependent on temperature and the mobility dependence on the hole concentration would not have been nearly as linear as shown in Fig. 4. Second, if the undoped crystals had a considerable concentration of native donor defects compensating the native acceptor defects the concentration of these native donor defects would have considerably increased via the mass action effect as soon as the copper concentration exceeded the intrinsic carrier concentration and the crystal became extrinsic (Table II and Fig. 8). Since the copper-doped crystals, in fact, have higher mobilities than the undoped crystals for comparable hole concentrations, the undoped and the copper-doped crystals seem to be uncompensated and the native donor defect concentration in Hg$_{0.8}$Cd$_{0.2}$Te seems to be negligible. Absence of compensation also has been established in Hg$_{0.6}$Cd$_{0.4}$Te (22).

Origin of p-type to n-type conversion.—In the absence of any systematic defect studies in Hg$_{1-x}$Cd$_x$Te various reasons for p-type to n-type conversion have been proposed (2-5, 23, 24). Reynolds *et al.* (23) observed that the Hg$_{0.8}$Cd$_{0.2}$Te crystals annealed under Hg-saturated conditions converted to n-type below 360°C and the electron concentration was independent of temperature of anneal below 360°C. The temperature independence of the electron concentration under Hg-saturated conditions led them to conclude that the crystals were n-type due to residual donors in the crystals and not due to any native donor defects. Similar inferences and conclusions were reported recently by Bartlett *et al.* (24) for Hg$_{0.8}$Cd$_{0.2}$Te. Schmit and Stelzer (25) observed that their undoped Hg$_{0.6}$Cd$_{0.4}$Te samples also turned n-type at temperatures below 350°-400°C under Hg-saturated conditions. Also the conversion temperatures were different for different samples. Although the temperature independence of the electron concentration in the undoped crystals of Hg$_{0.8}$Cd$_{0.2}$Te (23, 24) and Hg$_{0.6}$Cd$_{0.4}$Te (25) for Hg-saturated conditions does not, by itself, rule out the n-type conversion to be due to native donor defects (see Appendix B), the fact that the different samples in the experiments of Schmit and Stelzer (25) converted to n-type at different temperatures indicates that the conversion in these samples was due to residual foreign donors in the crystals, the samples with a higher residual foreign donor concentration being able to convert to n-type at a higher temperature. Also it was noticed in the present work that certain of the p-type samples (10^{15}-10^{16} cm^{-3}) did not convert to n-type even when annealed in Hg-saturated conditions at temperatures below 350°C. If the n-type conversion occurs due to native donor defects the inability to convert some of these samples is difficult to explain. In these samples the residual acceptor impurity concentration exceeded the residual donor impurity concentration and hence p-type to n-type conversion was not possible at any temperature. These arguments support our conclusion in the previous section that the native donor defects in Hg$_{0.8}$Cd$_{0.2}$Te are negligible in concentration; (probably

much less than 10^{15} cm^{-3} at 350°-400°C). The conversion to n-type in Hg$_{0.8}$Cd$_{0.2}$Te, as well as Hg$_{0.6}$Cd$_{0.4}$Te does not appear to be due to native donor defects. The assumption that the p-type to n-type conversion in Hg$_{1-x}$Cd$_x$Te alloys occurs due to native donor defects appears erroneous (2-5), and such a conversion only occurs due to residual donor impurities; also the conversion is only possible for samples with residual donor impurity concentration exceeding the residual acceptor impurity concentration in the crystals.

Correlation of the quenching efficiency with the presence of voids and inclusions.—Results of Fig. 6 and 7 indicate that the electrical conductivity variations in the cooled crystals at 77 K as a function of the partial pressure of Hg at the equilibration temperatures can be a sensitive function of the cooling rate, particularly for samples containing a large concentration of voids and inclusions ($\sim$ 1000 per cm^2). For samples containing a relatively small concentration of voids and inclusions ($\leq$ 20 per cm^2) the results are approximately the same except under very low Hg pressures where the air-cooled samples have smaller electrical conductivity than the quenched samples (Fig. 6). Electrical conductivity, rather than hole concentration, has been plotted in Fig. 6 and 7 for ease of comparison of the results of different anneals; for instance, some of the air-cooled samples showed mixed conductivity due to the formation of thin n-type inversion layers formed by a reduction in the hole concentration due to precipitation of native acceptor defects during cooling and/or partial type conversions of the samples. When such layers are thin, the overall conductivity is still dominated by holes ($p\mu_p > n\mu_n$) even if the Hall coefficient is negative ($n\mu^2_n > p\mu^2_p$), hence electrical conductivity for such samples was assumed to reflect the bulk crystal properties better than the Hall effect results. It can be inferred from Fig. 6 and 7 that the cooling rate obtained from air cooling the samples is not high enough to retain the high temperature equilibrium in the samples containing a large concentration of voids and inclusions, thus resulting in a reduction of the concentration of the native acceptor defects at 500°C. The diffusion distances for equilibration are lower in the presence of a large concentration of voids and inclusions, hence crystals containing a large concentration of these can come to equilibrium at an intermediate temperature between 500°C and room temperature during air cooling, whereas crystals containing fewer of them retain the high temperature equilibrium to a greater degree. It should also be noted from Fig. 7 that quenching in ice water is fast enough for crystals containing a large concentration of voids and inclusions to retain the 500°C equilibrium. Although experiments with varying cooling rates were not undertaken at higher temperatures it is reasonable to assume that the effect of the presence of voids and inclusions on the quenching efficiency is greater at temperatures higher than 500°C and lower at lower temperatures.

Analysis of the carrier concentration in the undoped crystals.—In the detailed analysis of the carrier concentration in the cooled crystals, the complete electroneutrality condition is considered. In order to distinguish the high temperature state of the crystal from the low temperature state of the crystal (cooled crystals) subscripts HT (high temperature) and LT (low temperature) are used.

For the undoped crystals, knowing that the native acceptor defects are doubly ionized and that the native donor defects are negligible in concentration and neglecting the influence of residual donors and acceptors, the complete electroneutrality condition becomes

$$[e']_{HT} + 2[V''_{Hg}]_{HT} = [h\cdot]_{HT} \qquad [1]$$

Expressing $[e']$ and $[V''_{Hg}]$ in terms of the mass action

constants defined in Table I, we obtain

$$(K_i|[h^.])_{HT} - (2K''_{VHg}|[h^.]^2 p_{Hg})_{HT} = [h^.]_{HT} \quad [2]$$

or

$$[h^.]_{HT}^2 - (K_i[h^.])_{HT} = 2(K''_{VHg}|p_{Hg})_{HT}$$

The concentration of holes obtained in the cooled crystals is given by

$$[h^.]_{LT} = 2[V''_{Hg}]_{HT} = (2K''_{VHg}|[h^.]^2 p_{Hg})_{HT}$$

$$[h^.]_{HT} = (2K''_{VHg}|p_{Hg})_{HT}^{1/2}|[h^.]_{LT}^{1/2} \quad [3]$$

Combination of [2] and [3] with some simplification gives

$$[h^.]_{LT}^{3/2} (2K''_{VHg}|p_{Hg})_{HT}^{1/2} + (K_i)_{HT} [h^.]_{LT}$$

$$= (2K''_{VHg}|p_{Hg})_{HT} \quad [4]$$

For given values of K_i and K''_{VHg} at various temperatures, the solution of Eq. [4] gives the hole concentration in the cooled crystals as a function of p_{Hg}. By a procedure of trial and error, the values of K_i and K''_{VHg} were optimized at each temperature to give the best fit between the experimentally observed hole concentrations and the calculated values. The calculated values are shown in Fig. 2 as solid lines. The agreement between the experimental values and the calculations appears to be within limits of experimental error.

Mass action constants K_i and K''_{VHg} determined from the present investigation (valid for temperatures between 400° and 655°C) are given by

$$K_i = 5.77 \times 10^{-4} \exp (-0.57 \text{ eV}/kT) \text{ (Site Fr)}^2 \quad [5]$$

and

$$K''_{VHg} = 7.9 \times 10^2 \exp (-2.24 \text{ eV}/kT) \text{ (Site Fr)}^3 \text{ atm} \quad [6]$$

Noting that there are 1.26×10^{22} molecules/cm^3 in $Hg_{0.8}Cd_{0.2}Te$, we get

$$K_i = 9.16 \times 10^{40} \exp (-0.57 \text{ eV}/kT) \text{ cm}^{-6} \quad [7]$$

and

$$K''_{VHg} = 1.58 \times 10^{69} \exp (-2.24 \text{ eV}/kT) \text{ cm}^{-9} \text{ atm} \quad [8]$$

Both K_i and K''_{VHg} influence the absolute values of the carrier concentration obtained in the cooled crystals and the variation of the carrier concentration as a function of p_{Hg}. From Table II, it can be seen that the hole concentration in the cooled crystals (equal to twice the concentration of the doubly ionized native acceptor defects at the anneal temperature) is expected to be proportional to p_{Hg}^{-1} for crystals which are intrinsic, whereas it is expected to be proportional to $p_{Hg}^{-1/3}$ for crystals which are extrinsic with the situation $[h^.] = 2[V''_{Hg}]$ at the high temperature. Thus, for a given value of K''_{VHg}, if the chosen K_i value was such that $[V''_{Hg}]$ was comparable in concentration to $[e']$ and $[h^.]$, at the high temperature, the power dependence of the calculated hole concentration in the cooled crystals was between $-1/3$ and -1. On the other hand, if the chosen K_i values were high compared to the hole concentration in the cooled crystals, the calculated hole concentration varied strictly as p_{Hg}^{-1}. The absolute values of the calculated hole concentration depended both on K_i and K''_{VHg}. In order to show how sensitive the calculated hole concentrations are to the variation in the K_i values at the anneal temperatures, the hole concentrations in the cooled crystals were calculated as a function of p_{Hg} for K_i values 25% higher and 25% lower than given by expression [7] for K_i. The calculated hole concentrations in the cooled crystals for K_i values given by the expression as well as for K_i values ± 25% are shown for $T = 500°C$ in Fig. 9, the K''_{VHg} value in the calculations was kept
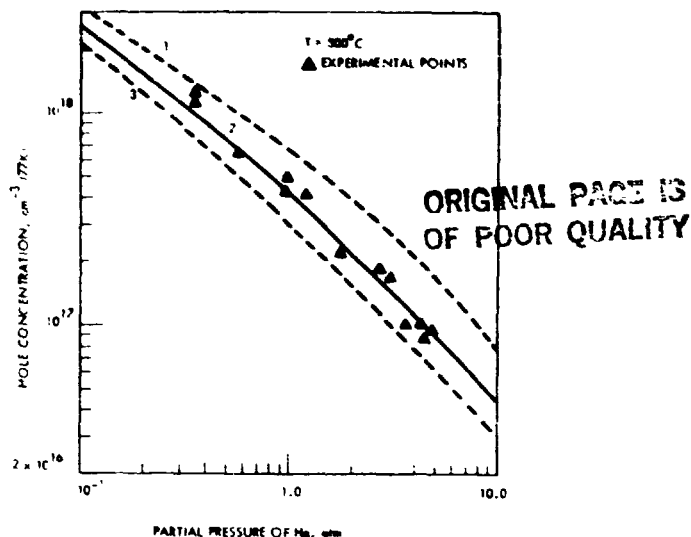

PARTIAL PRESSURE OF Hg, atm

Fig. 9. Defect model calculations of the hole concentrations at 77 K for undoped $Hg_{0.8}Cd_{0.2}Te$ annealed at 500°C in various partial pressures of Hg and quenched to room temperature; solid line 2 represents calculations using K_i values given by expression [7] of the text, whereas the dashed lines 1 and 3 correspond to calculations using K_i values differing from those of expression [7] by ±25%; experimental points are also shown for comparison.

constant as given by expression [8]. It appears that ±25% variations in K_i do not affect the calculations adversely.

Assuming simple parabolic conduction and valence bands and nondegenerate semiconductor statistics the expression for K_i is written as

$$K_i = 2(m_e m_h)^{3/2} (\pi kT/h^2)^3 \exp (- E_g/kT) \text{ cm}^{-6} \quad [9]$$

where m_e and m_h are the effective masses of electrons and holes, respectively, and E_g is the energy gap. $E_g = E_g(0) + aT$ where $E_g(0)$ corresponds to the energy gap at 0 K. A linear increase of the energy gap with increase in temperature has been verified by various researchers for temperatures up to 400 K (26-30). To the author's knowledge, no measurements on the energy gap or the intrinsic carrier concentration at temperatures much in excess of 400 K exist in the literature. If we assume the linear temperature dependence of the gap to hold good at temperatures greater than 400 K, with $E_g(0) \sim 0.1$ eV (3) and inclusion of the T^3 term in the exponent term (Eq. [9]), we get 0.32 eV for the enthalpy associated with K_i. This value is lower than the value of 0.57 eV found from the present investigation expressions [5] and [7]). The possible nonparabolicity of the bands at the higher temperatures and a nonnegligible temperature dependence of the effective masses of carriers may account for the higher enthalpy associated with K_i given by expression [7].

The dependence of the calculated hole concentrations in the cooled crystals on the value of K''_{VHg} can be judged by the inspection of Eq. [4] which indicates that for crystals which are intrinsic at the annealing temperature, the second term on the left-hand side dominates, with the result that the hole concentration in the cooled crystals is proportional to the value of K''_{VHg}/K_i. As a result it is not hard to realize that for given values of K_i the hole concentrations in the cooled crystals depend on K''_{VHg} in just the opposite way as they did with K_i for fixed K''_{VHg} values. Thus, just as ±25% variations in K_i did not adversely affect the calculations (Fig. 9), we believe similar variations can be tolerated in the value of K''_{VHg}.

3-10

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From the present work the enthalpy for the reaction

$$Hg_{Hg}{}^x \rightarrow V''_{Hg} + 2h^{\cdot} + Hg(g)$$

has been established to be 2.24 eV.

For comparison with CdTe, the enthalpy associated with the reaction

$$Cd_{Cd}{}^x \rightarrow V''_{Cd} + 2h^{\cdot} + Cd(g)$$

is evaluated to be 4.72 eV (15). The higher enthalpy associated with a similar defect reaction for CdTe is reasonable in view of the fact that CdTe has a larger melting point and bandgap than $Hg_{0.8}Cd_{0.2}Te$ and, hence, stronger bonding.

Table III summarizes the values of some of the mass action constants defined in Table I. Included in the table are the values of K_i and K''_{VHg} applicable for $T = 400°$-$655°C$ as well as the K_i value applicable for $T = 27°$-$400°C$.

The mass action constants K_i and K''_{VHg} established from the present work can explain the results on indium-doped (31), Iodine-doped (32) and phosphorus-doped $Hg_{0.8}Cd_{0.2}Te$ (33) satisfactorily.

Defect isotherms for undoped $Hg_{0.8}Cd_{0.2}Te$.—Once the values of K_i and K''_{VHg} are known, it is possible to calculate the concentrations of various defects as a function of p_{Hg} at any given temperature. Such a defect isotherm for $T = 500°C$ is shown in Fig. 10. As can be seen from the figure, the crystal is essentially intrinsic except at low Hg pressures at higher temperatures where native acceptor defects begin to become comparable in concentration to intrinsic carriers.

Hole concentration in undoped $Hg_{0.8}Cd_{0.2}Te$ *under Hg-saturated and Te-saturated conditions*.—The highest and the lowest Hg pressures in the experimental data indicated by arrows in Fig. 2, correspond to the Hg pressure under Hg-saturated conditions and the Hg pressure under Te-saturated conditions, respectively (8-10). Figure 11 shows the hole concentration variation in the cooled crystals as a function of temperature of equilibration for Hg-saturated and Te-saturated conditions. The temperature dependences of the hole concentration are given by

[h·] (Hg saturated)

$$= 1.54 \times 10^{24} \exp(-1.13 \text{ eV}/kT) \text{ cm}^{-3}$$

and

[h·] (Te saturated)

$$= 2.36 \times 10^{20} \exp(-0.314 \text{ eV}/kT) \text{ cm}^{-3}$$

Isohole concentration plot for $Hg_{0.8}Cd_{0.2}Te$.—Knowledge of K_i and K''_{VHg} permits us to calculate hole concentrations in the cooled crystals as a function of the physicochemical conditions of preparation, namely, p_{Hg} and T. Such a plot is shown in Fig. 12. As can be seen from Fig. 12, the undoped material is p-type throughout the existence region for all temperatures as long as the residual foreign acceptor concentration is greater than the residual foreign donor concentration in the crystals. This figure is different from the isocarrier concentration plot reported in Ref. (2, 4) where

Table III. Values of the parameters for the equilibrium constants
$K = K_0 \exp(-H/kT)$ defined in Table I

Equilibrium constant	K_0 (Site Fr. atm)	H (ev)		Source
1. K_i	5.77×10^{-4}	0.57	}	This work
2. K''_{VHg}	7.9×10^{8}	2.24		(400°-655°C)
3. K_i	1.4×10^{-4}	0.354		(27°-400°C)
4. K_{Hg_0}	2.75×10^{6}	2.06		Ref. (10)
5. K_{H_2}	7.84×10^{4}	0.62		
6. K_{Te}	1.82×10^{4}	1.27	}	Ref. (8)

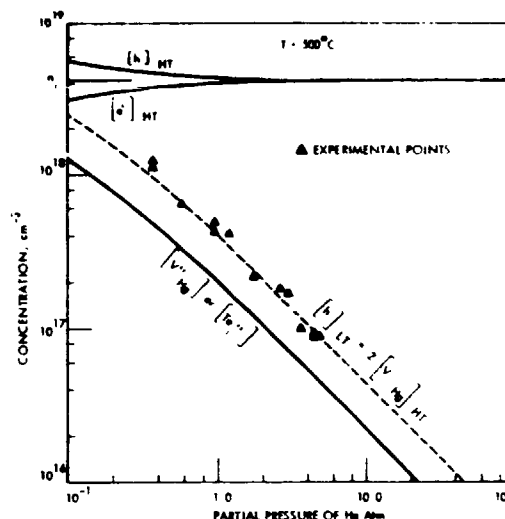There are 1.26×10^{22} molecules/cm³ in $Hg_{0.8}Cd_{0.2}Te$

Fig. 10. Calculated defect concentrations as a function of the partial pressure of Hg at the equilibration temperature of 500°C; dashed line represents the calculated hole concentration in the cooled crystals at 77 K; experimental points are also shown for comparison.
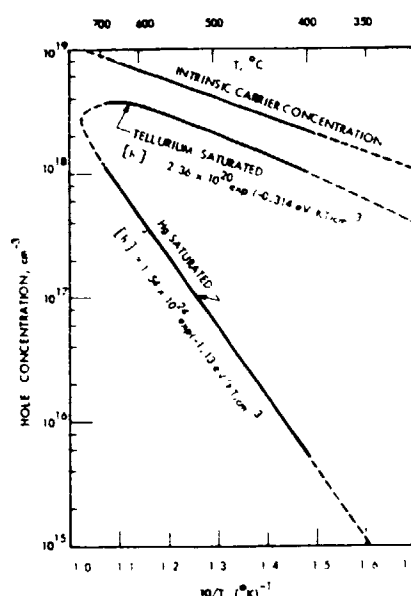

Fig. 11. Calculated hole concentration lines at 77 K as a function of temperature for undoped $Hg_{0.8}Cd_{0.2}Te$ equilibrated in Hg-saturated and Te-saturated conditions and quenched to room temperature. Calculations for temperature ranges outside the experimental work reported in this paper are shown dashed; intrinsic carrier concentration as a function of temperature is also shown

p-type to n-type conversion was attributed to native donor defects. It can also be seen that the highest deviation from stoichiometry (or the highest hole concentration in the cooled crystals) attainable in undoped $Hg_{0.8}Cd_{0.2}Te$ is $< 3 \times 10^{16}$ cm^{-3}.

Defect isotherms for copper-doped $Hg_{0.8}Cd_{0.2}Te$.—With the assumption that all of the electrically active copper is present as Cu'_{Hg}, defect concentrations as a function of the electrically active copper concentration and p_{Hg} can be calculated. As before, we define high temperature and low temperature states of the crystal using subscripts HT and LT, respectively. The complete electroneutrality condition and the copper balance equation are
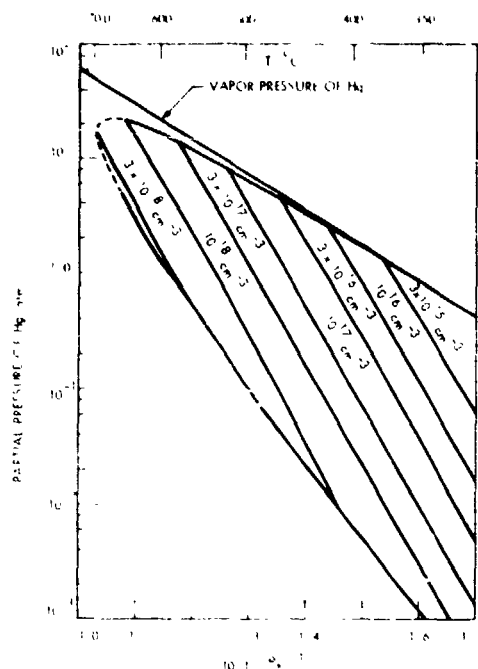
Fig. 12. Calculated isohole concentration lines at 77 K for $Hg_{0.8}Cd_{0.2}Te$ as a function of the partial pressure of Hg and temperature of equilibration.
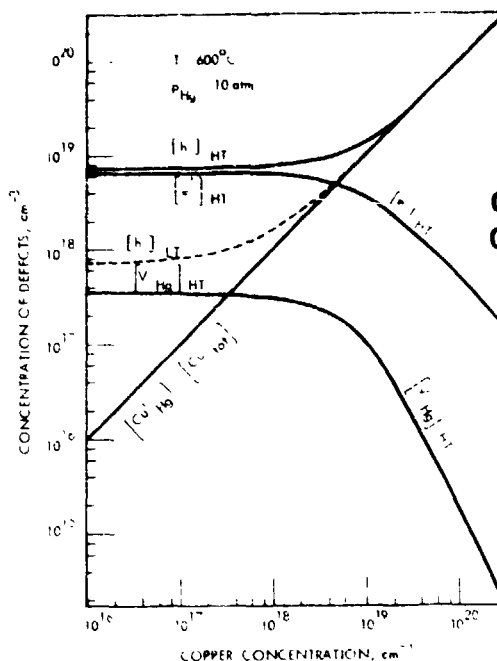

Fig. 13. Calculated defect concentrations as a function of the electrically active copper concentration in the crystals at the equilibration temperature of 500°C and $p_{Hg} = 3$ atm; dashed line corresponds to the calculated hole concentration in the cooled crystals at 77 K.

$$[e']_{HT} + 2[V''_{Hg}]_{HT} + [Cu'_{Hg}] = [h\ ]_{HT} \quad [10]$$

and

$$[Cu'_{Hg}]_{HT} = [Cu_{tot}]_{HT} \quad [11]$$

In terms of the mass action constants K_1 and K''_{VHg}, the electroneutrality condition is rewritten as

$$(K_1/[h\ ])_{HT} + 2(K''_{VHg}/[h\ ]^2 p_{Hg})_{HT}$$
$$+ [Cu_{tot}] = [h\ ]_{HT} \quad [12]$$

or

$$[h\ ]_{H1}^3 - [h\ ]_{HT}^2 [Cu_{tot}]$$
$$- K_1[h\ ]_{HT} = 2(K''_{VHg}/p_{Hg})_{HT} \quad [13]$$

In the cooled crystals, the hole concentration is given by

$$[h\ ]_{1T} = 2[V''_{Hg}]_{HT} + [Cu\ _{Hg}]_{HT}$$
$$= 2[V''_{Hg}]_{H\bar{1}} + [Cu_{tot}]_{HT} \quad [14]$$

or, expressing $[V''_{Hg}]$ in terms of K''_{VHg} and $[h\ ]$, we get

$$[h\ ]_{LT} = (2K''_{VHg}/[h\ ]^2 p_{Hg})_{HT} + [Cu_{tot}]_{HT} \quad [15]$$

With the knowledge of the mass action constants K_1 and K''_{VHg} established for the undoped crystals, defect concentrations ($[V''_{Hg}]$, $[h\ ]_{HT}$, $[h\ ]_{LT}$, etc.) as a function of copper concentration for a fixed p_{Hg} or as a function of p_{Hg} for fixed copper concentration can be calculated from Eq. [13] and [15]. Figure 13 shows the defect isotherm for $T = 500°C$ and $p_{Hg} = 3$ atm as a function of the total copper concentration in the crystal. Similarity between Fig. 8 and 13 is to be noted. While Fig. 8 is drawn with approximation to the neutrality condition, Fig. 13 has been drawn with the consideration of the complete electroneutrality condition.

Imperfect quench for heavily copper-doped samples. —The electrically active copper concentration in various samples as inferred from the Hall effect measurements was found to be lower than the total copper concentration in the samples inferred from atomic absorption analysis (Table IV) From arguments in the previous sections, compensation by native donor de-

fects or by copper interstitials (acting as donors) is ruled out as the explanation. On the other hand, precipitation of copper during quenching or the solubility limit of copper at the equilibration temperatures can explain the discrepancy. If the explanation is one of the solubility limit, it is hard to reason why samples having total copper concentration less than 10^{19} cm^{-3} also show electrically active copper less than the total amount of chemically inferred copper concentrations. Owing to the high diffusivity of Cu in $Hg_{1-x}Cd_xTe$ (6, 7), we are inclined to believe that precipitation of copper as CuTe or Cu₂Te during quenching results in the electrically active copper (as found by Hall effect measurements) to be less than that obtained by chemical analysis. The fact that the fraction of electrically active copper decreases for higher and higher copper concentrations (as determined by chemical analysis) also supports the view that precipitation occurs during quenching since the diffusion distance between copper atoms for precipitation to occur can be expected to decrease as $[Cu_{tot}]^{-3}$. Efforts to improve the quenching efficiency by breaking open the ampuls and quenching the samples directly in water did not result in any improvement. It appears that the high diffusivity of copper results in an imperfect quench from the equilibration temperature. If we believe that precipitation occurs during quenching, the solubility of electrically

Table IV. Comparison of the concentrations of electrically active copper and the total amount of copper (as determined from atomic absorption analysis) for samples doped with copper at 500 and 600°C

Temperature (°C)	Total copper concentration (cm⁻³) (atomic absorption)	Electrically active copper concentration (cm⁻³) (Hall effect)
500	3.4 × 10⁰	10¹⁰
500	1.6 × 10¹⁰	5 × 10¹⁰
500	8.7 × 10¹⁰	4.3 × 10¹⁰
600	2.2 × 10¹⁰	5 × 10¹⁰
600	4.8 × 10¹⁰	1.3 × 10¹⁰
600	3 × 10¹⁰	10¹⁰
600	8.6 × 10¹⁰	4.8 × 10

active copper at $T = 500°\text{-}600°\text{C}$ appears to be in excess of 10^{20} cm^{-3}.

Conclusion

Lattice defect models for undoped and copper-doped $Hg_{0.8}Cd_{0.2}Te$ have been established via Hall effect and mobility measurements on crystals equilibrated under different partial pressures of Hg at high temperatures and quenched to room temperature. According to the models, native donor defects are negligible in concentration, native acceptor defects are doubly ionized, and copper acts as a single acceptor occupying Hg lattice sites. Equilibrium constants for the intrinsic excitation constant, as well as the incorporation of the doubly ionized native acceptor defects, have been established.

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APPENDIX A

Calculations of Hole Mobility at 77 K in Undoped and Copper-Doped $Hg_{0.8}Cd_{0.2}Te$

The decrease of hole mobility at 77 K with an increase in the hole concentration in the undoped crystals (Fig. 4) indicates that the contribution of ionized impurity scattering to the mobility at 77 K is not negligible.

For a nondegenerate semiconductor with parabolic bands, the mobility due to ionized impurity scattering as given by the Brooks-Herring expression (21) is

$$\mu_I = 2^{7/2}\,\pi^{-3/2}\,(kT)^{3/2}\,(\epsilon_0\epsilon_s)^2\,(m_0)^{-1/2}\,(m^*/m_0)^{-1/2}$$

$$\times\ N_I^{-1}\left\{\ln(1+b) - \frac{b}{1+b}\right\}^{-1} \quad [A\text{-}1]$$

where

$$b = \frac{24 m_0\,(m^*/m_0)k^2\,(\epsilon_0\epsilon_s)}{e^2\,\hbar^2\,p'} \quad [A\text{-}2]$$

and

$$p' = p + (N_A - N_D - p)\,(p + N_D)/N_A \quad [A\text{-}3]$$

In expressions [A-1], [A-2], and [A-3], k is the Boltzmann's constant, T is the temperature, ϵ_0 is the free space permittivity, ϵ_s is the static dielectric constant, m_0 is the free electron mass, (m^*/m_0) is the effective mass ratio of holes, N_I is the number of scattering centers given by the total number of ionized donors and acceptors, e is the electronic charge, and $\hbar$ is Planck's constant. With $T = 77$ K, (m^*/m_0) (holes) $= 0.7$ (34), $\epsilon_s = 17.5$ (3) the expression for the mobility due to ionized impurity scattering becomes

$$\mu_I = 8 \times 10^{20}\,N_I^{-1}\left\{\ln(1+b) - \frac{b}{1+b}\right\}^{-1} \quad [A\text{-}4]$$

and

$$b = 9.42 \times 10^{18}/p' \quad [A\text{-}5]$$

In general

$$N_I = ([A'] + [D\ ]) + 4([A''] + [D\ ]$$
$$+\ 9([A'''] + [D\ ]) + \ldots \quad [A\text{-}6]$$

where $[A']$, $[A'']$, $[A''']$, etc. are the concentrations of the singly charged, doubly charged, and triply charged acceptors; a similar definition holds for the donor concentrations $[D\ ]$, $[D\ ]$, $[D\ ]$, etc. The multiplying factors of 4, 9, etc. in Eq. [A-6] arise because the centers are doubly ($z = 2$) and triply ($z = 3$) charged, etc. For the case where the undoped and the copper-doped crystals are not compensated (as discussed in the main text) we have

$$N_I = [A'] + 4[A''] + \ldots \quad [A\text{-}7]$$

Since the defects are completely ionized at 77 K in both the undoped and the copper-doped crystals (see main text for details), $p' = p$ (77 K) for the undoped as well as the copper-doped crystals. Using Eq. [A-4] and [A-5], μ_I was calculated as a function of p (77 K) for the case of (i) $N_I = [A'] = p$ (77 K) (dominance of singly charged centers) and (ii) $N_I = 4[A''] = 2p$ (77 K) (dominance of doubly charged centers).

The calculated mobilities due to ionized impurity scattering for the cases of the dominances of the singly charged centers and dominance of the doubly charged centers are shown as dashed lines in Fig. 4 and 5. Extrapolating the hole mobility due to lattice scattering to be 700 cm²/Vsec at 77 K the overall hole mobility as a function of the hole concentration at 77 K was calculated by reciprocally combining the mobility due to ionized impurity scattering and that due to lattice scattering

$$1/\mu_{TOT} = \frac{1}{\mu_{lattice}} + \frac{1}{\mu_{ionized}} = \frac{1}{700} + \frac{1}{\mu_{ionized}} \quad [A\text{-}8]$$
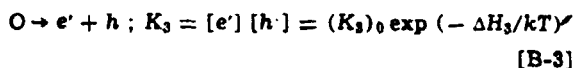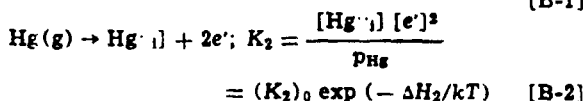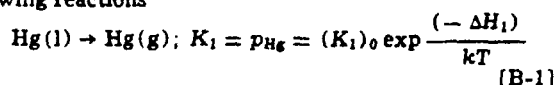
The calculated overall hole mobility as a function of the hole concentration is shown in Fig. 4 and 5 as solid lines.

APPENDIX B

Temperature Independence of the Native Donor Defect Concentration

Results of Reynolds *et al.* (23) on $Hg_{0.8}Cd_{0.2}Te$ and of Schmit and Stelzer (25) on $Hg_{0.6}Cd_{0.4}Te$ indicate that the crystals turn n-type below 300°-350°C under Hg-saturated conditions and the electron concentration under Hg-saturated conditions remains independent of the anneal temperature.

If the conversion is thought to be due to some sort of native donor defects, it remains to explain under what circumstances the temperature independence could arise. For an explanation of this we consider the following reactions

$$Hg(l) \rightarrow Hg(g);\ K_1 = p_{Hg} = (K_1)_0 \exp\frac{(-\Delta H_1)}{kT} \quad [B\text{-}1]$$

$$Hg(g) \rightarrow Hg\cdot_i] + 2e';\ K_2 = \frac{[Hg\cdot_i]\,[e']^2}{p_{Hg}}$$

$$= (K_2)_0 \exp\,(-\Delta H_2/kT) \quad [B\text{-}2]$$

$$0 \rightarrow e' + h\cdot;\ K_3 = [e']\,[h\cdot] = (K_3)_0 \exp\,(-\Delta H_3/kT) \quad [B\text{-}3]$$

Two electroneutrality approximations can be considered:

Case 1: $[e'] \sim [h\cdot] = \sqrt{K_3}$.

Case 2: $[e'] \sim 2\,[Hg\cdot_i]$.

Case 1: $[e'] = [h\cdot]$. From Eq. [B-2], $[Hg\cdot_i] = K_2\,p_{Hg}/[e']^2$. Substituting $[e'] = [h\cdot] = \sqrt{K_3}$ from [B-3] and for p_{Hg} from [B-1], we get

$$[Hg\cdot_i] = \frac{K_1 K_2}{K_3}$$

$$= \frac{(K_1)_0 (K_2)_0}{(K_3)_0} \exp\left(\frac{-\Delta H_1 - \Delta H_2 + \Delta H_3}{kT}\right)$$

If $\Delta H_3 = \Delta H_1 + \Delta H_2$, $[Hg\cdot_i]$ will be independent of temperature and the electron concentration under Hg-saturated conditions will be independent of temperature in the cooled crystals.

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Case 2: $[e'] \sim 2\,[\text{Hg}_i]$

From [B-2],

$$[\text{Hg}_i] = K_2\, p_{\text{Hg}}/[e']^2$$

$$= K_2\, p_{\text{Hg}}/4\,[\text{Hg}_i]^2$$

or

$$[\text{Hg}_i] = (K_2\, p_{\text{Hg}}/4)^{1/3}$$

$$= \left(\frac{(K_2)_0 (K_1)_0}{4} \right)^{1/3} \exp\left(\frac{-\Delta H_1 - \Delta H_2}{3kT} \right)$$

Thus if $\Delta H_1 = -\Delta H_2$, $[\text{Hg}_i]$ will be independent of temperature and the electron concentration in the cooled crystals under Hg-saturated conditions will also be independent of temperature.

It should be noted that while Hg$_i$ are considered for the native donor defects here, the arguments are similar if V$_{\text{Te}}$ are considered instead.

REFERENCES

1. W. D. Lawson, S. Nielson, E. H. Putley, and A. S. Young, *J. Phys. Chem. Solids,* **9** (1959).
2. D. Long and J. L. Schmit, "Semiconductors and Semimetals," Vol. 5, R. K. Willardson and A. C. Beer, Editors, p. 234, Academic Press, New York (1970).
3. R. Dornahaus and G. Nimtz, "Solid State Physics," Vol. 78, Springer-Verlag, New York (1976).
4. R. A. Farrar, G. J. Gillham, R. Bartlett, and M. Quelch, *J. Mater. Sci.,* **12**, 836 (1977).
5. R. F. Brebrick and J. P. Schwartz, *J. Electron. Mater.,* **9**, 485 (1980).
6. A. I. Andrievskii, A. S. Teodorvich, and A. D. Shneider, *Sov. Phys. Semicond.,* **7**, 1112 (1974).
7. E. S. Johnson and J. L. Schmit, *J. Electron. Mater.,* **6**, 25 (1977).
8. R. F. Brebrick and A. J. Strauss, *J. Phys. Chem. Solids,* **26**, 989 (1965).
9. J. P. Schwartz, T. Tung, and R. F. Brebrick, *This Journal,* **128**, 438 (1981).
10. T. Tung, L. Golonka, and R. F. Brebrick, *ibid.,* **128**, 451 (1981).
11. L. J. van der Pauw, *Philips Tech. Rev.,* **20**, 220 (1959).
12. R. A. Smith, "Semiconductors," Cambridge University Press (1968).
13. F. A. Kröger and H. J. Vink, "Solid State Physics III," F. Seitz and D. Turnbull, Editors, p. 307, Academic Press, New York (1956).
14. F. A. Kröger, "The Chemistry of Imperfect Crystals," second revised edition, Vol. 2, Chap. 14-16, North Holland (1974).
15. S. S. Chern, H. R. Vydyanath, and F. A. Kroger, *J. Solid State Chem.,* **14**, 33 (1975).
16. S. S. Chern and F. A. Kröger, *ibid.,* **14**, 44 (1975).
17. D. de Nobel, *Philips Res. Rep.,* **14**, 361 (1959).
18. F. A. Selim, V. Swaminathan, and F. A. Kröger, *Phys. Status Solidii A,* **29**, 465 (1975).
19. V. Swaminathan, F. A. Selim, and F. A. Kröger, *ibid.,* **30**, 721 (1975).
20. G. Brouwer, *Philips Res. Rep.,* **9**, 366 (1954).
21. H. Brooks, *Phys. Rev.,* **83**, 879 (1952); *Adv. Electron. Electron Phys.,* **7**, 156 (1955).
22. H. R. Vydyanath, J. Danovan, and D. A. Nelson, *This Journal,* **128**, 2625 (1981).
23. R. A. Reynolds, M. J. Brau, H. Kraus, and R. T. Bate, *J. Phys. Chem. Solids,* **32**, Suppl. 1, 511 (1971).
24. B. E. Bartlett, P. Capper, J. E. Harris, and M. J. T. Quelch, *J. Cryst. Growth,* **49**, 600 (1980).
25. J. L. Schmit and E. L. Stelzer, *J. Electron. Mater.,* **7**, 65 (1978).
26. J. D. Wiley and R. N. Dexter, *Phys. Rev.,* **181**, 1181 (1969).
27. M. W. Scott, *J. Appl. Phys.,* **40**, 4077 (1969).
28. J. L. Schmit and E. L. Stelzer, *ibid.,* **40**, 4865 (1969).
29. Y. Nemrousky and E. Finkman, *ibid.,* **50**, 8107 (1979).
30. C. Verie, *Phys. Status Solidii,* **17**, 889 (1966).
31. H. R. Vydyanath, *This Journal,* **128**, 2619 (1981).
32. H. R. Vydyanath and F. A. Kröger, *J. Electron. Mater.,* **10**, No. 1 (1982).
33. H. R. Vydyanath and R. C. Abbott, Submitted to *J. Appl. Phys.*
34. M. W. Scott, E. L. Stelzer, and R. J. Hager, *J. Appl. Phys.,* **47**, 1408 (1976).

8203-01

3.2 DEFECT CHEMISTRY AND CHARACTERIZATION OF INDIUM DOPED $Hg_{0.8}Cd_{0.3}Te$

Lattice Defects in Semiconducting $Hg_{1-x}Cd_xTe$ Alloys

II. Defect Structure of Indium-Doped $Hg_{0.8}Cd_{0.2}Te$

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ABSTRACT

Hall effect measurements were carried out on indium-doped $Hg_{0.8}Cd_{0.2}Te$ crystals quenched to room temperature subsequent to equilibration at 500° and 600°C under various partial pressures of Hg. All the indium-doped crystals were n-type under moderate to high partial pressures of Hg whereas they were p-type at very low Hg pressures. The concentration of electrons obtained in the cooled crystals was lower than the intrinsic carrier concentration at the equilibration temperatures. Also the electron concentration was much lower than the indium concentration in the crystals and was found to increase with increasing Hg pressures at the equilibration temperatures and with increase in the total indium present in the crystals. These inferences have led to a defect model according to which most of the indium is incorporated as $In_2Te_3(S)$ dissolved in $Hg_{0.8}Cd_{0.2}Te(S)$ with only a small fraction of indium acting as single donors occupying Hg lattice sites. Based on such a model, calculated electron concentrations in the cooled crystals as a function of indium concentration and partial pressure of Hg are in agreement with the experimentally observed values.

The role of indium as a donor and its influence on the native defect structure has been investigated in

CdS (1-2) and CdTe (3-4). However, such a systematic investigation into the mode of incorporation of indium and its influence on the native defects has not so far been carried out for $Hg_{1-x}Cd_xTe$ alloys. The defect structure of undoped $Hg_{0.8}Cd_{0.2}Te$, the thermo-

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dynamic constants for the incorporation of the native acceptor defects, and the intrinsic excitation constant in $Hg_{0.8}Cd_{0.2}Te$ have been established in the preceding paper (5) hereafter referred to as part I. The present work was undertaken to study the behavior of indium in $Hg_{0.8}Cd_{0.2}Te$ as a function of the physicochemical conditions of preparation (p_{Hg}, T, indium concentration, etc.) and to explain the properties of the indium-doped crystals with the knowledge of the defect structure of the undoped crystals (5).

Experimental

Indium was evaporated onto the surface of the undoped $Hg_{0.8}Cd_{0.2}Te$ crystals ($x = 0.2 \pm 0.005$) and the indium was diffused in at 600°C and $p_{Hg} = 10$ atm and at 500°C and $p_{Hg} = 3$ atm. Diffusion times of 24 hr at 600°C and 7 days at 500°C into samples of thickness ≤ 0.04 cm were found to be adequate for the homogeneous diffusion of indium. The concentration of indium in each sample was determined from atomic absorption analysis carried out by Photometrics, Incorporated, Lexington, Massachusetts. The residual impurity concentration in the starting undoped $Hg_{0.8}Cd_{0.2}Te$ was $\leq 10^{16}$ cm^{-3}. The thicknesses of the samples were minimized as much as possible in order to improve the quenching efficiency from the equilibration temperatures as well as to assure thermodynamic equilibrium within reasonable equilibration times. The equilibration procedure in various Hg atmospheres is similar to that described in part I. Subsequent to the equilibration, the samples were quenched to room temperature; in a few cases the samples were air cooled to room temperature from the equilibration temperatures. The samples were lapped, polished, and etched in Br-methanol solution. Hall effect and electrical resistivity measurements were made using the van der Pauw method (6). Magnetic field strengths of 400 and 4000G were used for the Hall effect measurements.

Results

As mentioned in part I, only those Hall effect results which did not vary with the magnetic field and thus showed no mixed-type conduction were used in evaluating the carrier concentrations in the samples using the expression

$$n = \frac{1}{R_H q}$$

The Hall effect data on all the samples doped to reasonable concentrations of indium and annealed at medium to high partial pressures of Hg showed n-type conductivity and the electron concentration in the samples at 77 and 300 K did not vary much, indicating that the indium was all ionized at 77 K. Figures 1 and 2 show the electron concentration in the cooled crystals as a function of the total indium present in the samples at $T = 500°$ and 600°C for various partial pressures of Hg. From the figures, it is apparent that the electron concentration in the samples increases with an increase in the total indium concentration in the samples and also increases as the partial pressure of Hg at the equilibration temperatures increases. It is to be noted that although the electron concentration is a function of the total indium present in the crystals, the electron concentration is much lower than the total amount of indium present in the crystals.

Figure 3 shows the electron mobility at 77 K in various indium-doped samples as a function of the electron concentration. These mobilities are lower than values reported for $Hg_{0.8}Cd_{0.2}Te$ samples containing low donor concentrations (7).

Figure 4 shows a comparison of the electron concentration obtained at 77 K as a function of the partial pressure of Hg at 500°C for crystals that were doped with various indium concentrations and were air
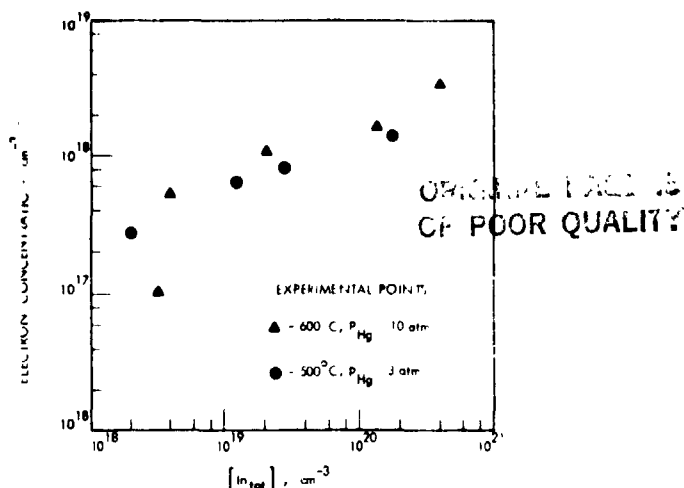

Fig. 1. Electron concentration at 77 K as a function of the total indium concentration for $Hg_{0.8}Cd_{0.2}Te$ crystals annealed at 500° and 600°C under the indicated partial pressures of Hg and quenched to room temperature.
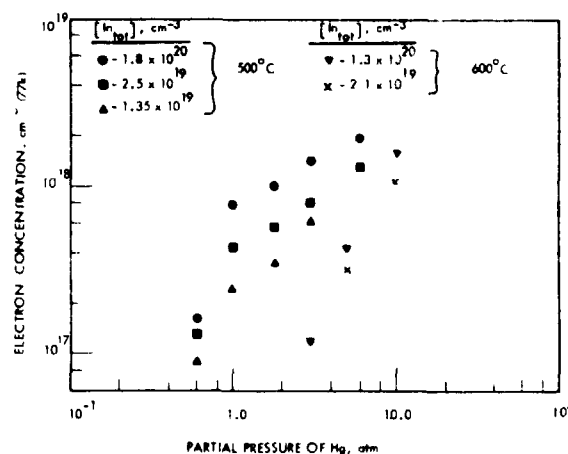

Fig. 2. Electron concentration at 77 K as a function of the partial pressure of Hg for $Hg_{0.8}Cd_{0.2}Te$ crystals doped with various amounts of indium and annealed at 500° and 600°C and quenched to room temperature.

cooled or quenched to room temperature. It appears from the results that higher electron concentrations are obtained in the air-cooled samples than in the quenched samples, the deviations between the two sets of samples being greater at lower Hg pressures.

Discussion

The approach utilized in arriving at a defect model for the indium-doped $Hg_{0.8}Cd_{0.2}Te$ is similar to that used for the undoped and copper-doped $Hg_{0.8}Cd_{0.2}Te$ in part I. Also any defect model that is established to explain the experimental results in the indium-doped crystals should be consistent with the observations in the undoped and the copper-doped crystals of part I.

Choice of a defect model.—Based on the value of the intrinsic excitation constant K_i arrived at for $Hg_{0.8}Cd_{0.2}Te$ (part I) for temperatures between 400°–655 C, data shown in Fig. 1 and 2 indicate that the electron concentration obtained in the cooled crystals is much less than the intrinsic carrier concentration at the equilibration temperatures.

Three different models can be considered to explain the electron concentration data shown in Fig. 1 and 2.

In the first model considered, a fraction of the indium is assumed to be present as singly positively
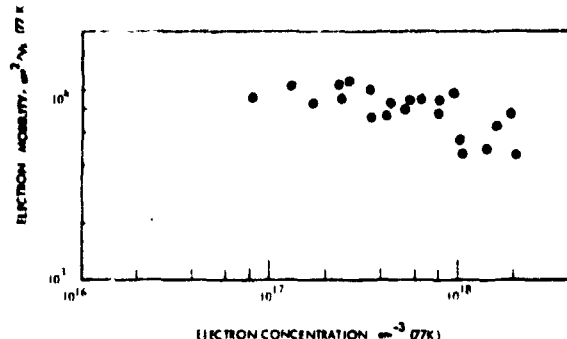
Fig. 3. Electron mobility at 77 K as a function of the electron concentration in indium-doped Hg$_{0.8}$Cd$_{0.2}$Te crystals.

charged donors occupying Hg lattice sites while the rest of it is assumed to be present as negatively charged associates of singly positively charged indium on Hg lattice sites and doubly negatively charged native acceptor defects. Most of the indium is assumed to be self-compensated as given by the electroneutrality approximation

$$[\text{In}^{\cdot}_{\text{Hg}}] = [(\text{In}_{\text{Hg}}V_{\text{Hg}})'] = [\text{In}_{\text{tot}}]/2$$

For such a model the dependence of [e'] on [In$_{\text{tot}}$] and p$_{\text{Hg}}$ is inferred from the reaction

$$2e' + \text{In}^{\cdot}_{\text{Hg}} + \text{Hg}^{x}_{\text{Hg}} \rightarrow (\text{In}_{\text{Hg}}V_{\text{Hg}})' + \text{Hg}(g)$$
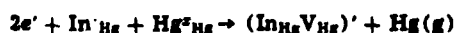
and the mass action constant

$$K_{(\text{In}_{\text{Hg}}V_{\text{Hg}})} = [(\text{In}_{\text{Hg}}V_{\text{Hg}})']p_{\text{Hg}}/[e']^2[\text{In}^{\cdot}_{\text{Hg}}] \quad [1]$$

with

$$[(\text{In}_{\text{Hg}}V_{\text{Hg}})'] = [\text{In}^{\cdot}_{\text{Hg}}] = [\text{In}_{\text{tot}}]/2$$

$$[e'] \propto [\text{In}_{\text{tot}}]^0 p_{\text{Hg}}^{1/2} \quad \text{from [1]}$$

Although this model qualitatively explains the weak donor activity of indium it predicts an independence of electron concentration as a function of the total indium present in the samples, contrary to the results shown in Fig. 1 and 2.

In the second model considered, most of the indium is assumed to be present as neutral triplets (In$_{\text{Hg}}$V$_{\text{Hg}}$In$_{\text{Hg}}$)^x formed by the association of two singly positively charged indium donor species on Hg lattice

sites with a doubly negatively charged native acceptor defect; a small fraction of the indium is assumed to be present unassociated on Hg lattice sites acting as donors.

The reaction of interest is

$$2e' + 2\text{In}^{\cdot}_{\text{Hg}} + \text{Hg}^{x}_{\text{Hg}} \rightarrow (\text{In}_{\text{Hg}}V_{\text{Hg}}\text{In}_{\text{Hg}})^x + \text{Hg}(g)$$

and the mass action relation is given by

$$K_{(\text{In}_{\text{Hg}}V_{\text{Hg}}\text{In}_{\text{Hg}})^x} = [(\text{In}_{\text{Hg}}V_{\text{Hg}}\text{In}_{\text{Hg}})^x]p_{\text{Hg}}/[e']^2[\text{In}^{\cdot}_{\text{Hg}}]^2$$

$$[2]$$

Since we know that the electron concentration obtained in the cooled crystals is less than the intrinsic carrier concentration at the equilibration temperatures, the electroneutrality condition at the equilibration temperatures can be approximated by

$$[e'] = [h^{\cdot}] = \sqrt{K_i}$$

and for [(In$_{\text{Hg}}$V$_{\text{Hg}}$In$_{\text{Hg}}$)^x] = [In$_{\text{tot}}$]/2 as the approximation to the indium balance equation [In$^{\cdot}_{\text{Hg}}$] $\propto$ [In$_{\text{tot}}$]$^{1/2}$p$_{\text{Hg}}^{1/2}$ at the equilibrium temperatures. Although this model qualitatively explains the variation of electron concentration as a function of the indium in the crystals and the partial pressure of Hg at the equilibration temperatures, the calculated electron concentration in the cooled crystals considering the complete neutrality condition shows a much steeper dependence on p$_{\text{Hg}}$ than observed experimentally. Also, the model predicts the crystals will turn p-type even at Hg pressures close to saturation pressures, contrary to the results of Fig. 2.

The third model considered is one where most of the indium is assumed to be present as In$_2$Te$_3$ dissolved in Hg$_{0.8}$Cd$_{0.2}$Te, with a small fraction of In on Hg lattice sites acting as donors. The dependence of the electron concentration on the indium in the crystals and p$_{\text{Hg}}$ can be inferred from the reaction describing the incorporation of In$_{\text{Hg}}$ from the In$_2$Te$_3$(S) dissolved in Hg$_{0.8}$Cd$_{0.2}$Te.

The reaction of interest is

$$\text{In}_2\text{Te}_3(S) + \text{Hg}(g) \rightarrow \text{Hg}^{x}_{\text{Hg}} + 2\text{In}^{\cdot}_{\text{Hg}} + 2e' + 3\text{Te}^{x}_{\text{Te}}$$

The mass action relation is given by

$$K_{(\text{In}_2\text{Te}_3 - \text{In}_{\text{Hg}})} = [\text{In}^{\cdot}_{\text{Hg}}]^2[e']^2/a_{\text{In}_2\text{Te}_3}p_{\text{Hg}} \quad [3]$$

where $a_{\text{In}_2\text{Te}_3}$ is the activity of In$_2$Te$_3$(S).

For

$$[e'] = [h^{\cdot}] = \sqrt{K_i} \gg [\text{In}^{\cdot}_{\text{Hg}}]$$

from relation [3]

$$[\text{In}^{\cdot}_{\text{Hg}}] \propto a_{\text{In}_2\text{Te}_3}^{1/2}p_{\text{Hg}}^{1/2} \propto \gamma_{\text{In}_2\text{Te}_3}^{1/2}X_{\text{In}_2\text{Te}_3}^{1/2}p_{\text{Hg}}^{1/2} \quad [4]$$

where $\gamma_{\text{In}_2\text{Te}_3}$ and $X_{\text{In}_2\text{Te}_3}$ stand for the activity coefficient and the mol fraction of In$_2$Te$_3$(S) dissolved in (Hg$_{0.8}$Cd$_{0.2}$)Te(S).

In the cooled crystals at 77 K

$$[e']_{77\text{K}} = [\text{In}^{\cdot}_{\text{Hg}}] - 2[V''_{\text{Hg}}] \propto X_{\text{In}_2\text{Te}_3}^{1/2}p_{\text{Hg}}^{1/2}$$

$$\propto [\text{In}_{\text{tot}}]^{1/2}p_{\text{Hg}}^{1/2} \quad [5]$$

Hence, the dependence of e' in the cooled crystals on the indium concentration in the samples and the partial pressure of Hg at the equilibration temperatures is explainable.

A defect situation where the crystal is saturated with the dopant has been observed for iodine-doped CdS (8) where CdI$_2$(S) was present as a pure second phase; however, the concentration of the iodine donor species on sulfur lattice sites was independent of the activity of CdI$_2$(S), a_{CdI_2} since a_{CdI_2} was taken to be unity for pure CdI$_2$(S). In the present case, if the In$_2$Te$_3$(S) does not dissolve in Hg$_{0.8}$Cd$_{0.2}$Te(S) but re-
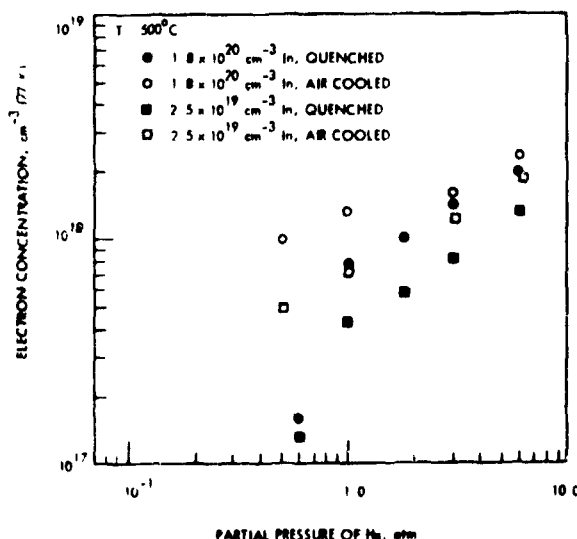

Fig. 4. Electron concentration at 77 K as a function of the partial pressure of Hg for crystals doped with different indium concentrations and quenched or air cooled subsequent to equilibration at 500°C.

mains as a pure second phase, the activity of $In_2Te_3(S)$ becomes unity and the electrically active fraction of indium [$In\cdot_{Hg}$] becomes independent of the activity of In_2Te_3 and in turn becomes independent of the amount of $In_2Te_3(S)$ or the total amount of indium present in the crystals (Eq. [3]-[5]) contrary to our experimental observations (Fig. 1 and 2). However, if $In_2Te_3(S)$ dissolves in $Hg_{0.8}Cd_{0.2}Te(S)$, the activity of $In_2Te_3(S)$, $a_{In_2Te_3}$, becomes a variable, increasing with increasing amount of the dissolved $In_2Te_3(S)$ and reaching a value of unity when the solubility limit is reached, and $In_2Te_3(S)$ becomes a pure second phase. For such a situation, the electrically active fraction of indium [$In\cdot_{Hg}$] becomes a function of the activity of $In_2Te_3(S)$ and thereby a function of the amount of $In_2Te_3(S)$ or the total amount of indium present in the crystals (Eq. [3]-[5]); the electron concentration in the cooled crystals which is directly proportional to the amount of the electrically active indium becomes a function of the total indium present in the crystals (Eq. [5]). Hence the dissolution of $In_2Te_3(S)$ in $Hg_{0.8}Cd_{0.2}Te(S)$ is an essential requirement in explaining the dependence of the electron concentration in the cooled crystals on the total indium present in the crystals. It should also be mentioned at this stage that if indium in interstitial sites is considered to be the donor species instead of indium on Hg lattice sites the incorporation reaction is written as

$$In_2Te_3(S) + 3Hg(g) \rightarrow 2In\cdot_i + 2e' + 3Hg^x_{Hg} + 3Te^x_{Te}$$

and the mass action constant

$$K = [In\cdot_i]^2[e']^2 / a_{In_2Te_3} p_{Hg}^3$$

for an intrinsic crystal with $[e'] = [h\cdot] = \sqrt{K_i}$

$$[In\cdot_i] \propto p_{Hg}^{3/2} a_{In_2Te_3}^{1/2}$$

The electron concentration in the cooled crystals for such a situation can be expected to be dependent on p_{Hg} much more than experimentally observed. Also, such a model predicts that the crystals turn p-type at Hg pressures close to saturation pressures contrary to the experimental results (Fig. 1 and 2). Thus, in addition to the requirement that $In_2Te_3(S)$ be in solid solution of $Hg_{0.8}Cd_{0.2}Te(S)$ the requirement that the majority of the electrically active indium be present substitutionally on Hg lattice sites rather than in interstitial sites must also be satisfied in order to explain the experimental results.

The fact that the experimental results require that In_2Te_3 be in solution of $Hg_{0.8}Cd_{0.2}Te$ up to about 1-2 mol percent (m/o) is not unreasonable. HgTe, CdTe, and In_2Te_3 all have zinc blende structures with not too largely different lattice parameters (6.45A for HgTe, 6.47A for CdTe, and 6.15A for In_2Te_3) and, in fact, it has been established by Woolley et al. (9) and Spencer (10) that amounts of up to 15 m/o In_2Te_3 dissolve in HgTe and the energy gap increases with increasing In_2Te_3 concentration somewhat significantly beyond about 5 m/o. We assume however, that in our experiments for In_2Te_3 concentration less than 1 m/o, the influence on the energy gap of $Hg_{0.8}Cd_{0.2}Te$ is negligible. The assumption appears justified since no drastic variation in the concentration of carriers is encountered with increasing indium concentration in the crystal. Pure In_2Te_3 is known to be p-type with an energy gap of 0.5 eV (10) and in fact one of the samples that was doped to 5×10^{21} atoms/cm^3 of indium showed excessive In_2Te_3 formation and the sample was p-type.

Preliminary x-ray and Auger analysis data also seem to support the model of indium being present as $In_2Te_3(S)$ dissolved in $Hg_{0.8}Cd_{0.2}Te(S)$. Auger analysis of the surface of a sample containing greater than 10^{21} cm^{-3} of indium indicated the surface to be rich in

indium and tellurium and the composition corresponded to In_2Te_3. X-ray analyses indicated evidence of lattice parameter changes with an increase in the concentration of indium from 3×10^{19} cm^{-3} to 3×10^{20} cm^{-3} with no evidence of the presence of a second phase, whereas clear evidence of the presence of a second phase was obtained in samples containing greater than 10^{21} cm^{-3} of indium. Although not entirely conclusive, these data seem to support the idea that $In_2Te_3(S)$ is soluble in $Hg_{0.8}Cd_{0.2}Te$ from 1 to 5 m/o at 500°-600°C.

Analysis of the carrier concentration in the cooled crystals.—Denoting the high temperature defect state by subscript HT, the complete electroneutrality condition and the indium balance equation can be written as

$$[e']_{HT} + 2[V''_{Hg}]_{HT} = [In\cdot_{Hg}]_{HT} + [h\cdot]_{HT} \quad [6]$$

and

$$[In\cdot_{Hg}]_{HT} + 2[In_2Te_3]_{HT} = [In_{tot}] \quad [7]$$

Expressing all the quantities in the electroneutrality condition [6] in terms of the mass action constants defined in part I, we get

$$[e']_{HT} + 2K''_{VHg}[e']_{HT}^2/K_i^2 p_{Hg} = [In\cdot_{Hg}] + K_i/[e']_{HT}$$

or

$$2[e']_{HT}^3 K''_{VHg}/K_i^2 p_{Hg} + [e']_{HT}^2$$
$$- [In\cdot_{Hg}][e']_{HT} - K_i = 0 \quad [8]$$

Owing to the narrow bandgap of $Hg_{0.8}Cd_{0.2}Te$, the correctness of the assumption of $K_i = [e'][h\cdot] =$ constant for a fixed temperature for large donor or acceptor concentrations is arguable. Since all our experimental results have shown systematic variations of carrier concentrations as a function of the imposed physicochemical conditions in accordance with the mass action approach, we feel our assumption is a valid one.

In the crystals quenched to room temperature from the equilibration temperatures

$$[e']_{77 K} = [In\cdot_{Hg}]_{HT} - 2[V''_{Hg}]_{HT}$$

or

$$[e']_{77 K} = [In\cdot_{Hg}] - 2K''_{VHg}[e']_{HT}^2/K_i^2 p_{Hg} \quad [9]$$

values of the mass action constants K_i and K''_{VHg} are given by (part I)

$$K_i = 9.16 \times 10^{40} \exp(-0.57 \text{ eV}/KT) \text{ cm}^{-6} \quad [10]$$

and

$$K''_{VHg} = 1.58 \times 10^{43} \exp(-2.24 \text{ eV}/KT) \text{ cm}^{-9} \text{ atm} \quad [11]$$

with the knowledge K''_{VHg} and K_i (Eq. [8]) gives $[e']_{HT}$ and $[V''_{Hg}]$ as a function of $[In\cdot_{Hg}]$ for various partial pressures of Hg.

The product of the mass action constant defined by Eq. [3] and the activity of $In_2Te_3(S)$, $K_{(In_2Te_3-In\cdot_{Hg})}a_{In_2Te_3}$ and $[e']_{77 K}$ are also immediately obtained as a function of $[In\cdot_{Hg}]$ from Eq. [3] and [9], respectively. Comparison of the calculated $[e']_{77 K}$ as a function of $[In\cdot_{Hg}]$ with the experimental values of Fig. 1 gives the concentration of the electrically active fraction of indium as a function of the total indium present in the crystals as shown in Fig. 5. Values of $K_{In_2Te_3-In\cdot_{Hg})}a_{In_2Te_3}$ calculated earlier as a function of $[In\cdot_{Hg}]$ can then be related to the total indium concentration in the crystals and in turn to the amount of In_2Te_3 present in the crystals from the indium balance Eq. [6]. Figure 6 shows $K_{(In_2Te_3-In\cdot_{Hg})}a_{In_2Te_3}$ as a function of $[In_2Te_3]$ present in the crystals. Since the slope of the curves on the log-log scale is different from unity, it appears that the activity coefficient of $In_2Te_3(S)$ dissolved in $Hg_{0.8}Cd_{0.2}Te(S)$ is not constant, but varies with the amount of $In_2Te_3(S)$. Once the values of $K_{(In_2Te_3-In\cdot_{Hg})}a_{In_2Te_3}$ as a function of $In_2Te_3(S)$ are
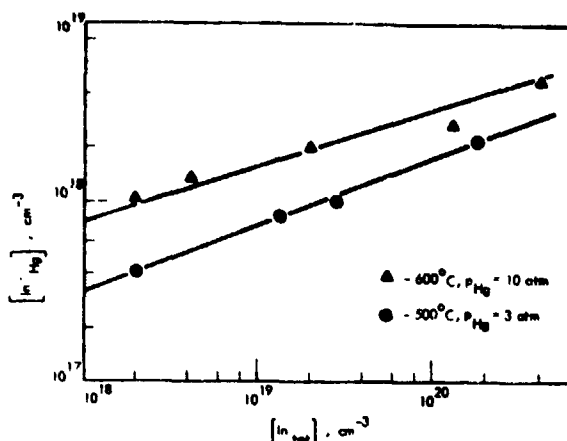
Fig. 5. Concentration of electrically active indium as a function of the total indium present in the crystals subsequent to equilibration at 500°C, p_{Hg} = 3 atm and at 600°C, p_{Hg} = 10 atm.
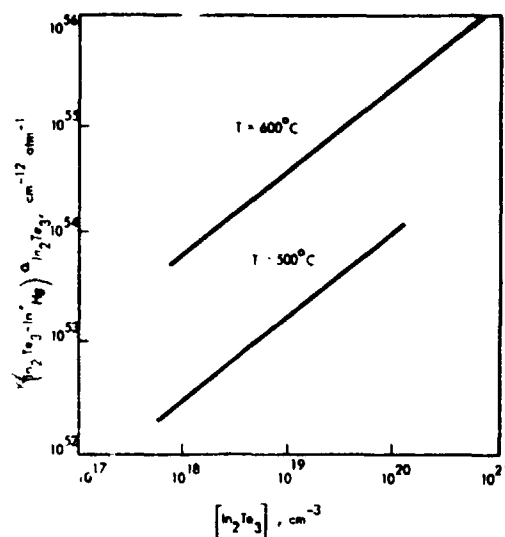

Fig. 6. Calculated value of the product of the mass action constant $K_{(In_2Te_3-In\,Hg)}$ and the activity of $In_2Te_3(S)$ in solution of $Hg_{0.8}Cd_{0.2}Te(S)$ (=$[In\,Hg]^2[e']^2/p_{Hg}$; expression [3] in the text) as a function of the concentration of In_2Te_3 present in the indium-doped crystals subsequent to equilibration at 500° and 600°C.

known from Fig. 6, it is possible to calculate $[e']_{77\,K}$, $[e']_{HT}$, $[V''_{Hg}]_{HT}$, $[In\,Hg]$, and $[In_2Te_3]$ as a function of $[In_{tot}]$ and p_{Hg} from Eq. [3], [7], [8], and [9].

Figures 7 and 8 show the calculated defect concentrations at T = 500°C, p_{Hg} = 3 atm, and T = 600°C, p_{Hg} = 10 atm as a function of the indium concentration in the crystals. Calculated values of the carrier concentrations in the cooled crystals are also shown along with the experimental values. The agreement between the calculated values and the experimental ones appears satisfactory. The figures also predict that the crystal is essentially intrinsic with most of the indium being present as In_2Te_3 with only a small fraction present as single donors occupying Hg lattice sites. The concentration of the native acceptor defects is essentially constant in the figures since the partial pressure of Hg is kept constant and the crystals essentially intrinsic.

Figure 9 shows the calculated defect concentrations at T = 500°C as a function of the partial pressure of Hg for a fixed indium concentration in the crystal. It can be noticed from the figure that although the total indium concentration is fixed in the crystal, the amount of the electrically active indium varies as a function of the partial pressure of Hg as predicted from the in-
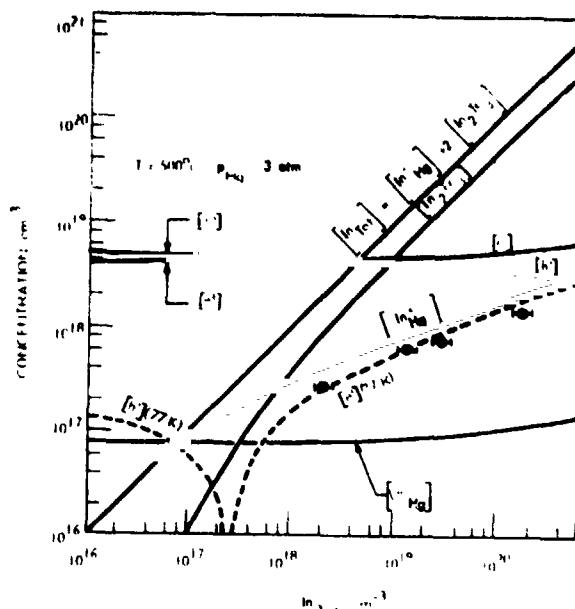

Fig. 7. Calculated defect concentrations ($[e']$, $[h\cdot]$, $[V''_{Hg}]$, $[In\cdot_{Hg}]$, and $[In_2Te_3]$) as a function of the total indium present in the indium-doped $Hg_{0.8}Cd_{0.2}Te$ crystals subsequent to equilibration at 500°C and p_{Hg} = 3 atm; dashed lines show the calculated carrier concentrations obtained in the cooled crystals at 77 K; experimental points are also shown for comparison.
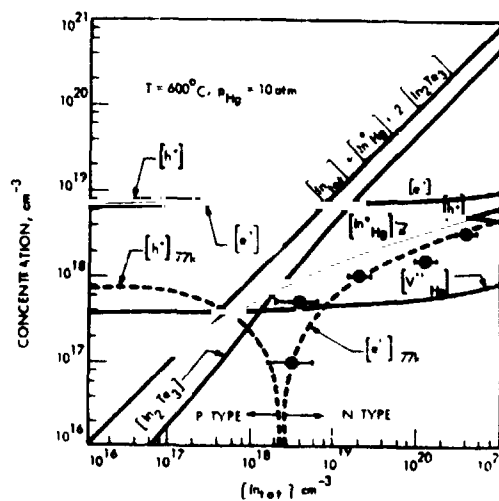

Fig. 8. Calculated defect concentrations ($[e']$, $[h\cdot]$, $[V''_{Hg}]$, $[In\,Hg]$, and $[In_2Te_3]$) as a function of the total indium present in the indium-doped $Hg_{0.8}Cd_{0.2}Te$ crystals subsequent to equilibration at 600°C and p_{Hg} = 10 atm; dashed lines show the calculated carrier concentrations obtained in the cooled crystals at 77 K; experimental points are also shown for comparison.

corporation reaction for In_{Hg} from $In_2Te_3(S)$ (Eq. [3]). The concentration of the native acceptor defects ($[V''_{Hg}]$) also varies in Fig. 9 since the partial pressure of Hg is a variable. The calculated electron concentration values at 77 K as a function of p_{Hg} are in agreement with the experimental values shown in the figure. The p to n transition in the cooled crystals (Fig. 7 through 9) occurs when $[In\,Hg]$ = $2[V''_{Hg}]$.

Figures 10 and 11 show the calculated electron concentrations at 77 K for various indium concentrations in the crystals at T = 500° and 600°C as a function of p_{Hg}. Agreement between the calculated values and the experimental ones appears satisfactory.
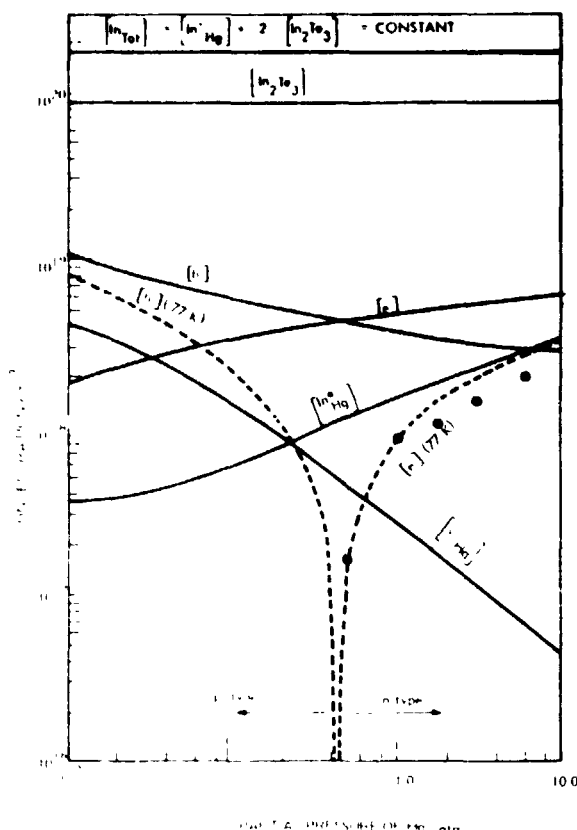
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Fig. 9. Calculated defect concentrations ([e'], [h], [V"$_{Hg}$], [In$_{Hg}$], and [In$_2$Te$_3$]) as a function of the partial pressure of Hg at the equilibration temperature of 500°C for a fixed indium concentration of 1.8 × 10^{20} cm^{-3} in Hg$_{0.8}$Cd$_{0.2}$Te crystals; dashed lines show the calculated carrier concentrations obtained in the cooled crystals at 77 K; experimental points are also shown for comparison.

It is interesting to note from Fig 8 through 11 that even for very high indium concentrations the crystals turn p-type under low Hg pressures thus demonstrating the complexity of dopant incorporation in defect semiconductors.

Effect of cooling rate on the electron concentration. —The results of Fig. 4 indicate that the electron concentration obtained in the indium-doped samples which are air cooled from 500°C is higher than in the ones quenched from 500°C, the deviation being greater at lower Hg pressures This implies that the native acceptor defects frozen in the air-cooled samples is lower than in the quenched samples, thereby increasing the electron concentration in the samples air cooled from the equilibration temperatures. It is not presently clear why the native acceptor defects rather than the indium atoms tend to precipi'ate out during air cooling.

Electron mobility in the indium-doped samples.— As shown in Fig. 3, the electron mobility at 77 K in the indium-doped samples is on the order of 10^4 cm^2/Vsec, decreasing to lower values for electron concentrations exceeding 10^{18} cm^{-3}. These values are an order of magnitude lower than reported previously (7) for low donor concentrations (<10^{15} cm^{-3}). The data shown in Fig 3 correspond to various indium-doped samples containing indium concentrations varying from approximately 5 × 10^{18} cm^{-3} to greater than 10^{20} cm^{-3}; these samples also contain doubly ionized native acceptor defects varying from 10^{17} cm^{-3} to 5 × 10^{17} cm^{-3} in concentrations corresponding to the
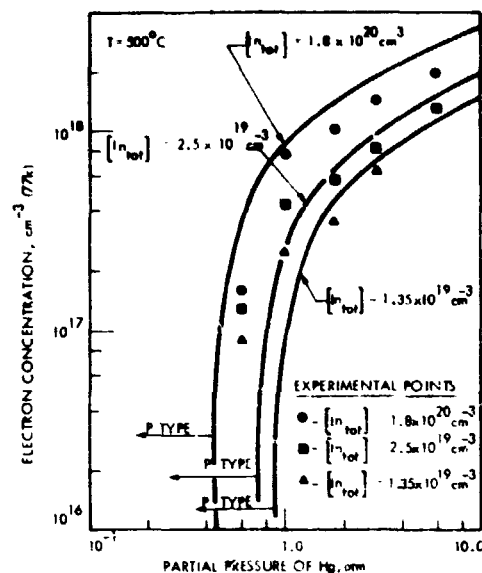

Fig. 10. Calculated electron concentration at 77 K in various indium-doped Hg$_{0.8}$Cd$_{0.2}$Te crystals as a function of the partial pressure of Hg after the crystals are annealed at 500°C and quenched to room temperature; experimental points are also shown for comparison.
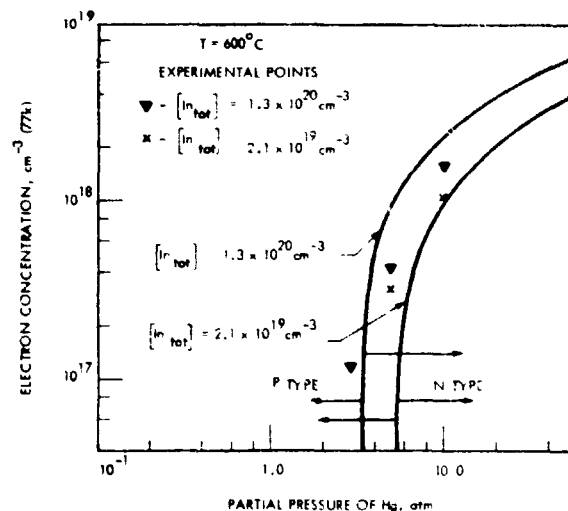

Fig. 11. Calculated electron concentration at 77 K in various indium-doped Hg$_{0.8}$Cd$_{0.2}$Te crystals as a function of the partial pressure of Hg after the crystals are annealed at 600°C and quenched to room temperature; experimental points are also shown for comparison.

annealing temperature of 500°-600°C under various partial pressures of Hg. The large electrically active indium concentrations (10^{17}-10^{18} cm^{-3}) and the compensating doubly ionized native defect concentrations probably account for the much lower mobilities.

Conclusion

A defect model for indium-doped Hg$_{0.8}$Cd$_{0.2}$Te has been established from Hall effect measurements on indium-doped crystals equilibrated under various partial pressures of Hg and temperatures and quenched to room temperature. According to the model, most of the indium is incorporated into the crystals as In$_2$Te$_3$(S) dissolved in Hg$_{0.8}$Cd$_{0.2}$Te(S) with only a small fraction being present as single donors occupying the Hg lattice.

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REFERENCES

1. V. Kumar and F. A. Kröger, *J. Solid State Chem.*, **3**, 387 (1971).
2. G. H. Hershman, V. P. Zlomanov, and F. A. Kröger, *ibid.*, **3**, 401 (1971).
3. S. S. Chern, H. R. Vydyanath, and F. A. Kröger, *ibid.*, **14**, 33 (1975).
4. S. S. Chern and F. A. Kröger, *ibid.*, **14**, 44 (1975).
5. H. R. Vydyanath, *This Journal*, **128**, 2609 (1981).
6. L. J. van der Pauw, *Philips Tech. Rev.*, **20**, 220 (1959).
7. W. Scott, *J. Appl. Phys.*, **43**, 1055 (1972).
8. H. R. Vydyanath, S. S. Chern, and F. A. Kröger, *J. Phys. Chem. Solids*, **34**, 1317 (1973).
9. J. C. Woolley and B. Ray, *ibid.*, **15**, 27 (1960b).
10. P. M. Spencer, *Br. J. Appl. Phys.*, **15**, 625 (1964).

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3.3   DEFECT CHEMISTRY AND CHARACTERIZATION OF UNDOPED $Hg_{0.6}Cd_{0.4}Te$

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Lattice Defects in Semiconducting Hg$_{1-x}$Cd$_x$Te Alloys

III. Defect Structure of Undoped Hg$_{0.6}$Cd$_{0.4}$Te

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ABSTRACT

Hall effect measurements were carried out on undoped Hg$_{0.6}$Cd$_{0.4}$Te crystals quenched to room temperature subsequent to equilibration at temperatures varying from 450° to 720°C under various partial pressures of Hg. The variation of the hole concentration as a function of the partial pressure of Hg indicates that the native acceptor defects are doubly ionized. Native donor defects are found to be negligible in concentration and the p-type to n-type conversion is shown to be due to residual donors and not due to native donor defects. Thermodynamic constant for the incorporation of the doubly ionized native acceptor defect has been established.

Schmit and Stelzer (1) have reported electrical data on Hg$_{0.6}$Cd$_{0.4}$Te crystals annealed at various temperatures under Hg-saturated and Te-saturated conditions. Brebrick and Schwartz (2) have recently analyzed these data on the basis of a defect model that assumes all the p-type crystals to be compensated by native donor defects and predicts the conversion of p-type to n-type in the crystals to be due to native donor defects. Conclusions of recent defect structure investigation in undoped Hg$_{0.8}$Cd$_{0.2}$Te (3) are in contradiction to those of Brebrick and Schwartz (2). Since an exact power dependence of the hole concentration on the partial pressure of Hg at the annealing temperatures is not possible to evaluate from the experimental results of Schmit and Stelzer (2), which were done under Hg-saturated and Te-saturated conditions only, the present work was undertaken to obtain additional electrical data at various intermediate partial pressures of Hg in addition to those of Schmit and Seltzer (1). These data have enabled us to establish a more precise power dependence of the hole concentration on the partial pressure of Hg at the annealing temperatures; the hole concentration in the cooled crystals has been found to vary as $p_{Hg}^{-1/3}$ indicating that the dominant native acceptor defects at the annealing temperatures are doubly ionized. Just as for undoped Hg$_{0.8}$Cd$_{0.2}$Te (3) the electrical data in Hg$_{0.6}$Cd$_{0.4}$Te have been explained satisfactorily on the basis that the native acceptor defects are doubly ionized, that the native donor defects are negligible in concentration, and that the conversion to n-type in Hg$_{0.6}$Cd$_{0.4}$Te

crystals is due to residual foreign donors. The dependence of the hole concentration on the partial pressure of Hg and the temperature of equilibration has led to the establishment of the thermodynamic constant for the incorporation of the doubly ionized native acceptor defect.

Experimental

The composition of the crystals used in the present work corresponded to $x = 0.4 \pm 0.005$. The residual impurity concentration was $<10^{16}$ cm^{-3}. In order to improve the efficiency of quenching the high temperature equilibrium, the thickness of the samples was restricted to <0.04 cm. Equilibration periods ranged from 24 hr at temperatures $>500°$C up to 2-3 weeks at 450°C. The procedure of equilibrating the samples in various Hg pressures and quenching the samples subsequent to equilibration is identical to that of part I (3). It should be mentioned here that while Schmit and Stelzer (1) used Te powder along with the samples for equilibration under Te-saturated conditions, we have used equivalent Hg pressures (4-6). Subsequent to the equilibration, the samples were quenched to room temperature. The samples were lapped, polished, and etched in Br-methanol solution. Hall effect and electrical resistivity measurements were made using the van der Pauw method (7). Magnetic field strengths of 400 and 4000G were used for the Hall effect measurements.

Results

As mentioned in part I (3) only those Hall effect results which did not vary with the magnetic field and, thus, showed no mixed-type conduction, were

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used in evaluating the hole concentrations in the samples using the expression

$$p = \frac{1}{R_{eq}}$$

Hall coefficient as a function of temperature of measurement is shown in Fig. 1 for undoped $(Hg_{0.6}Cd_{0.4})Te$ samples equilibrated at the indicated temperatures and partial pressures of Hg. It can be inferred from the figure that the ionization of the native acceptor defects appears to be complete around 190-200 K and at higher temperatures intrinsic carriers begin to become important. We have used hole concentration measurements at 192 K to infer the concentration of native acceptor defects present at the equilibration temperatures. Figures 2 and 3 show the hole concentration at 192 K as a function of the partial pressure of Hg for various equilibration temperatures ranging from 450° to 720°C. The hole concentration increases with decrease in the partial pressure of Hg, but more weakly than was found for $Hg_{0.8}Cd_{0.2}Te$ (part I) (3). In undoped $Hg_{0.8}Cd_{0.2}Te$ the hole concentration varied as p_{Hg}^{-1} (part I), whereas, results of Fig. 2 and 3 indicate that the hole concentration in undoped $Hg_{0.6}Cd_{0.4}Te$ varies as $p_{Hg}^{-1/3}$ and increases with increase in temperature.

Figures 4 and 5 show the mobility of holes at 77 and 192 K as a function of the hole concentration. The
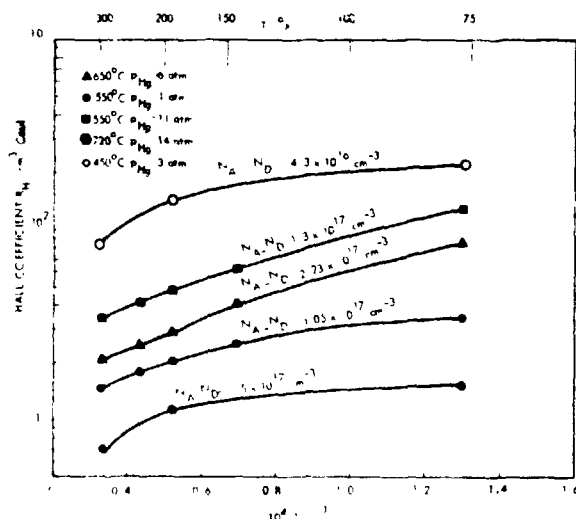

Fig. 3. Hole concentration at 192 K as a function of the partial pressure of Hg for undoped $Hg_{0.6}Cd_{0.4}Te$ crystals annealed at 500°, 650°, and 720°C and quenched to room temperature; solid lines correspond to the values calculated on the basis of the defect model.

Fig. 4. Hole mobility at 77 K as a function of the hole concentration for undoped $Hg_{0.6}Cd_{0.4}Te$.

Fig. 1. Hall coefficient as a function of measurement temperature for undoped $Hg_{0.6}Cd_{0.4}Te$ samples annealed at the indicated temperatures and partial pressures of Hg and quenched to room temperature.

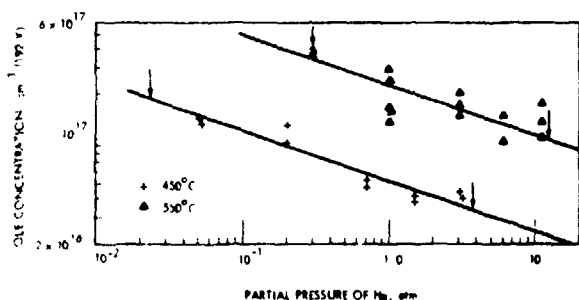Fig. 5. Hole mobility at 192 K as a function of the hole concentration for undoped $Hg_{0.6}Cd_{0.4}Te$.

hole mobilities at 77 K are lower than those obtained for $Hg_{0.8}Cd_{0.2}Te$ (part I) (3).

Discussion

The quasichemical approach used to arrive at the defect model has already been described in part I (3) and, hence, is not detailed here.

Native acceptor defects.—The fact that the hole concentration in the crystals is proportional to $p_{Hg}^{-1/3}$ (Fig. 2 and 3) indicates that the native acceptor defects are doubly ionized. The formation and ionization of these defects can be described by the following reaction and mass action relation

$$Hg^x_{Hg} \rightarrow V''_{Hg} + 2h^{\cdot} + Hg(g); \quad H''_{VHg} \quad [1]$$

$$K''_{VHg} = [V''_{Hg}] [h^{\cdot}]^2 p_{Hg} \quad [2]$$

Fig. 2. Hole concentration at 192 K as a function of the partial pressure of Hg for undoped $Hg_{0.6}Cd_{0.4}Te$ crystals annealed at 450° and 550°C and quenched to room temperature; solid lines correspond to the values calculated on the basis of the defect model.
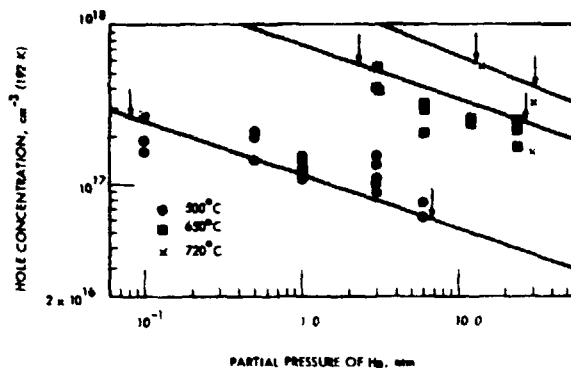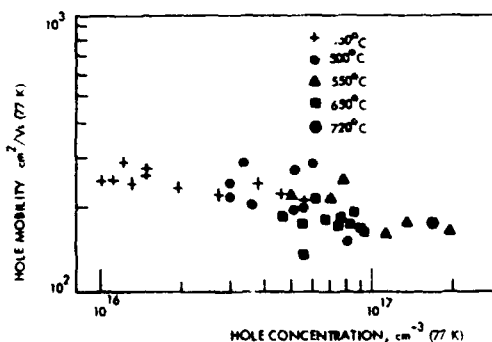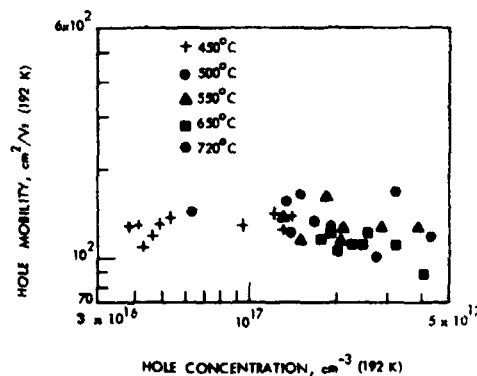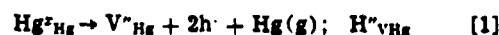
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If the electroneutrality condition is dominated by V''_{Hg} and $h^\cdot$ then we have

$$[h^\cdot] \approx 2[V''_{Hg}] > [e']$$

From expression [2] we get

$$[h^\cdot] = [2K''_{VHg}]^{1/3} p_{Hg}^{-1/3}$$

The dominance of V''_{Hg} at the equilibration temperatures implies that the undoped $(Hg_{0.6}Cd_{0.4})Te$ crystals are not intrinsic, unlike undoped $(Hg_{0.8}Cd_{0.2})Te$ crystals (part I), in $Hg_{0.6}Cd_{0.4}Te$, at the annealing temperatures

$$[h^\cdot] = 2[V''_{Hg}] > \sqrt{K_i} > [e']$$

whereas, in $Hg_{0.8}Cd_{0.2}Te$

$$2[V''_{Hg}] < [e'] = [h^\cdot] \sqrt{K_i} \quad \text{(part I)}$$

Thus, although the native acceptor aspects are doubly ionized in both $x = 0.2$ and $x = 0.4$ crystals, the dependence of the hole concentration on the partial pressure of Hg in the cooled crystals is different for the two compositions.

The fact that the intrinsic carrier concentration for the $x = 0.2$ material is higher than that for the $x = 0.4$ is a consequence of the lower bandgap for the $x = 0.2$ material.

Comparison of present experimental results with previous work.—Our experimental results differ from those of Schmit and Stelzer (1) at higher temperatures of equilibration as well as for Te-saturated conditions. We did not observe any decrease in the hole concentration at $T > 600°C$, as found by Schmit and Stelzer. Also, we obtain higher native acceptor defect concentrations (or higher hole concentrations) under Te-rich conditions than Schmit and Stelzer did. It is to be noted that the electrical data in Ref. (1) were obtained for crystals annealed in Hg vapor and Te_2 vapor, with Hg or Te being at the same temperature as $Hg_{0.6}Cd_{0.4}Te$. It is known that the saturation Hg pressure over $Hg_{0.6}Cd_{0.4}Te$ (4-6) is less than that of pure Hg itself, the difference being higher at temperatures greater than 500°C. Hence, by exposing the $Hg_{0.6}Cd_{0.4}Te$ crystals to saturated-Hg vapor at greater than 500°C, in the experiments of Schmit and Stelzer (1), compositional changes in the samples may have arisen. Also, similar arguments apply for anneals in saturated Te_2 vapor, reported in Ref. (1). In addition, it is also known (4-6) that the partial pressures of Te_2 over $Hg_{0.6}Cd_{0.4}Te$ under Te-saturated conditions are orders of magnitude lower than partial pressures of Hg under Te-saturated conditions. Hence, depending on the kinetics of the different equilibration processes and depending on the fact that during the heat-up of the samples and the tellurium source, the sample may not have stayed within the existence region, compositional changes for anneals under Te-saturated conditions may also have risen in the experiments of Ref. (1). In the present work, however, equilibrations under Te-saturated conditions were done in Hg vapor at equivalent partial pressures of Hg (4-6) rather than in Te_2 vapor. As discussed in part I, macroscopic defects such as voids, Hg or Te inclusions, etc. can affect the quenching efficiency of the crystals. Presence of these may also account for the lower hole concentrations obtained by Schmit and Stelzer (1).

p-type to n-type conversion in undoped $(Hg_{0.6}Cd_{0.4})Te$.—Schmit and Stelzer (1) found the undoped $(Hg_{0.6}Cd_{0.4})Te$ samples converted from p-type to n-type under Hg-saturated conditions at temperatures below about 350°C. The conversion temperatures for the two crystals that they experimented with were different and the electron concentration in both samples was independent of the equilibration temperature at temperatures below the conversion temperatures. If the p-type to n-type conversion is due to native donor defects, a temperature dependence of the electron concentration should be expected just as is observed for the hole concentration (1) unless the enthalpies associated with the vaporization of Hg(l), the intrinsic excitation constant, and the incorporation of the native donor defects are of such a sign and magnitude that the electron concentration in the cooled crystals is independent of the anneal temperature. For details see Appendix B of part I. However, if the conversion is due to native donor defects, the p-type to n-type conversion temperature should be the same for different samples as long as native donor defects are larger in concentration than the foreign donors. Thus, even if the temperature independence of electron concentration under Hg-saturated conditions can be explained on the basis of native donor defects, different conversion temperatures for different samples cannot be explained unless the conversion is due to foreign donor impurities present in the crystals. Hence, the concentration of native donor defects in undoped $(Hg_{0.6}Cd_{0.4})Te$ crystals appears to be negligible and, at least, less than 10^{15} cm^{-3} at 300°C.

Absence of compensation.—While attempting to explain the low experimental mobilities of holes in $(Hg_{0.6}Cd_{0.4})Te$, Scott et al. (8) assumed that all the undoped p-type samples were heavily compensated. This implied that the compensation mechanism in their crystals was probably a result of the dominance of either Schottky defects $([V''_{Hg}] = [V^{\cdot\cdot}_{Te}])$ or Frenkel defects $([V''_{Hg}] = [Hg^{\cdot\cdot}_i])$ (2). Evidence of any such compensation in our samples is lacking. Figure 4 indicates that the hole mobilities at 77 K vary (although only weakly) as a function of only the hole concentration in the crystals, irrespective of the partial pressure of Hg and the temperature of the anneal. If there was any compensation by native donor defects, the concentration of these defects can be expected to be exponentially dependent on temperature and the mobility dependence on the hole concentration would not have been as linear as shown in Fig. 4.

It should be pointed out that mobility results similar to those of Scott et al. (8) mentioned above, have been observed by others (9-14). For instance, electron and hole mobilities less than predicted by the Brooks-Herring expression for the ionized impurity scattering (9) have been reported by Reynolds et al. (10) for $(Hg_{0.8}Cd_{0.2})Te$. These authors explain the discrepancy to be due to the inadequacy of the Brooks-Herring formula for doping levels on the order of 10^{16} cm^{-3} in the n-type material and of 10^{16} cm^{-3} in the p-type material, and they choose not to invoke compensation as the reason. Ionized impurity mobility calculations at 77 K in degenerately doped n-type GaAs (11), n-type HgSe (12), and p-type Ge (13) at 77 K where the Brooks-Herring formula has considerably overestimated the mobilities due to ionized impurity scattering have also been reported. Recent calculations of Nishizawa et al. (14) for hole mobilities due to ionized impurity scattering in $(Hg_{0.82}Cd_{0.18})Te$ yielded values 4.5 times larger than the experimentally measured mobilities. According to these authors, the discrepancy between the theoretical and experimental mobilities of holes due to ionized impurity scattering is a common feature of many semiconductors. In view of these arguments it appears that more thorough calculations of hole mobilities in $Hg_{1-x}Cd_xTe$ alloys are needed.

Mass action constant K''_{VHg}.—Since the power dependence of the hole concentration on the partial pressure of Hg in the cooled crystals does not appear to be greater than 1/3, the only dominant species at the annealing temperatures appear to be the holes and

the native acceptor defects ($[e'] \ll [V''_{Hg}] = [h\cdot]/2$). Assuming that $[h\cdot] = 2[V''_{Hg}]$ at the high temperature as well as in the cooled crystals, from Eq. [2] we get

$$K''_{VHg} = ([h\cdot]^3/2)p_{Hg} \qquad [3]$$

Using a procedure of trial and error, an expression for K''_{VHg} in the form of $Ae^{-Q/kT}$ was arrived at, which best explained the experimental results of Fig. 2 and 3 at various temperatures. Greater emphasis was placed on the results at lower annealing temperatures with the assumption that results from the highest temperature anneals may suffer from a greater quenching inefficiency. The value of K''_{VHg} was evaluated to be

$$K''_{VHg} = 6.61 \times 10^{65} \exp(-2.29 \text{ eV}/kT)(cm^{-9} \text{ atm}) \quad [4]$$

or, in terms of site fractions, (there are 1.33×10^{22} molecules/cm^3 in Hg$_{0.6}$Cd$_{0.4}$Te)

$$K''_{VHg} = 0.279 \exp(-2.29 \text{ eV}/kT) \text{ site Fr}^3 \text{ atm} \quad [5]$$

The hole concentrations calculated based on this value of K''_{VHg} are shown in Fig. 2 and 3 as solid lines. The agreement between the experimental results and the calculated values appears satisfactory.

Since Hg$_{0.6}$Cd$_{0.4}$Te melts at a higher temperature than Hg$_{0.8}$Cd$_{0.2}$Te and has a greater bandgap, the enthalpy associated with the incorporation of the doubly ionized acceptor defect can be expected to be higher in $x = 0.4$ material than in $x = 0.2$ material. The enthalpy for $x = 0.4$ from Eq. [4] is 2.29 eV, whereas, that for $x = 0.2$ material established in part I is 2.24 eV.

Since the intrinsic carriers do not dominate the electroneutrality condition in $x = 0.4$ material for temperatures between 450°-720°C, evaluation of the intrinsic excitation constant $K_i = [e'][h\cdot]$ was not possible. However, from the results of Fig. 2 and 3 it appears that the intrinsic carrier concentration is less than 3×10^{16} cm^{-3} at 450°C and less than 3×10^{17} cm^{-3} at 720°C. These upper limits of the intrinsic carrier concentrations are lower than those extrapolated from the empirical expressions for n_i for $x = 0.4$ in literature (15).

Hole concentrations for anneals under Hg-saturated and Te-saturated conditions.—With the knowledge of the partial pressures of Hg under Hg-saturated and Te-saturated conditions (4-6) and the value of K''_{VHg} (expressions [4] and [5]) established in the previous section, the hole concentrations in the crystals cooled to room temperature after anneals at different temperatures can be calculated from Eq. [3]. Figure 6 shows the calculated hole concentrations under Hg-saturated and Te-saturated conditions. It is to be noted that the calculations assume the concentrations of the residual donors and acceptors to be negligible in comparison with the native defect concentrations at the anneal temperatures. Figure 6 shows the experimental results of the present work, as well as those of Schmit and Stelzer (1). It is clear from the figure that quenching inefficiencies or the presence of voids and inclusions in the material (part I) can cause scatter in the data, particularly at higher temperatures. Also, the decrease of hole concentration with increase in temperature at $T > 600°C$ for Hg-saturated conditions observed in Ref. (1) appears to arise from the quenching inefficiencies and is not a real effect since our results show a continuous increase in hole concentration with increase of temperature from 450° to 720°C. Residual impurity concentrations were neglected in the electroneutrality condition used to arrive at the hole concentration calculations detailed in the previous section. At lower temperatures of annealing the presence of residual donor concentrations can considerably affect the hole concentration in the sam-
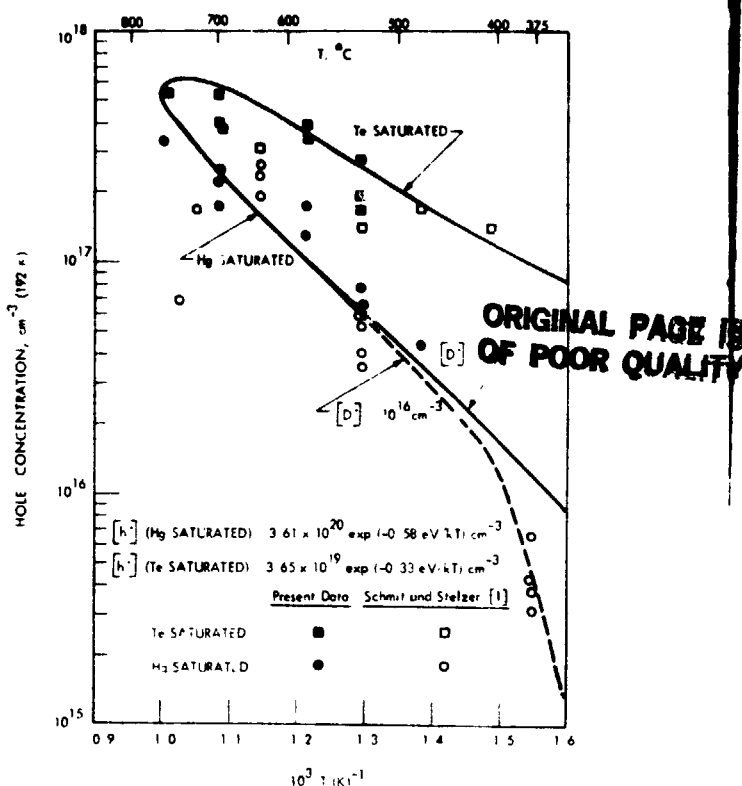

Fig. 6. Calculated hole concentration lines at 192 K as a function of annealing temperature for undoped Hg$_{0.6}$Cd$_{0.4}$Te equilibrated in Hg- and Te-saturated conditions.

ples. The Appendix details the calculation of the hole concentration in the crystals in the presence of residual donors. Such a calculation assuming a residual donor concentration of 10^{16} cm^{-3} is shown as a dashed line in Fig. 6. It is clear from the figure that the results of Ref. (1) at 375°C under Hg-saturated conditions can be explained if the crystals are assumed to have approximately 10^{16} cm^{-3} residual donors.

The expressions for the hole concentrations in the cooled crystals as a function of temperature for Hg-saturated and Te-saturated conditions are given by

$$[h] \text{ (Hg-saturated)} = 3.61 \times 10^{20}$$
$$\exp(-0.58 \text{ eV}/kT) \text{ cm}^{-3} \quad [6]$$

and

$$[h] \text{ (Te saturated)} = 3.65 \times 10^{19}$$
$$\exp(-0.33 \text{ eV}/kT) \text{ cm}^{-3} \quad [7]$$

Isohole concentration plot.—Hole concentration calculations as a function of the anneal temperature and the partial pressure of Hg as detailed in the two previous sections enable us to draw lines of constant deviation from stoichiometry as a function of temperature and partial pressure of Hg. A plot of such lines of constant hole concentration is shown in Fig. 7. The upper and lower Hg pressures within which the solid is stable at each temperature were obtained from references (4-6). Comparison of this plot with a similar one for Hg$_{0.8}$Cd$_{0.2}$Te (part I, Fig. 12) indicates that the concentration of native acceptor defects obtained in $x = 0.4$ material is lower than in $x = 0.2$ material. The temperature dependence of the hole concentration in the cooled crystals is also shallower for $x = 0.4$ than for $x = 0.2$ owing to the fact that the $x = 0.2$ crystals are intrinsic at the anneal temperatures, whereas the $x = 0.4$ crystals are not.
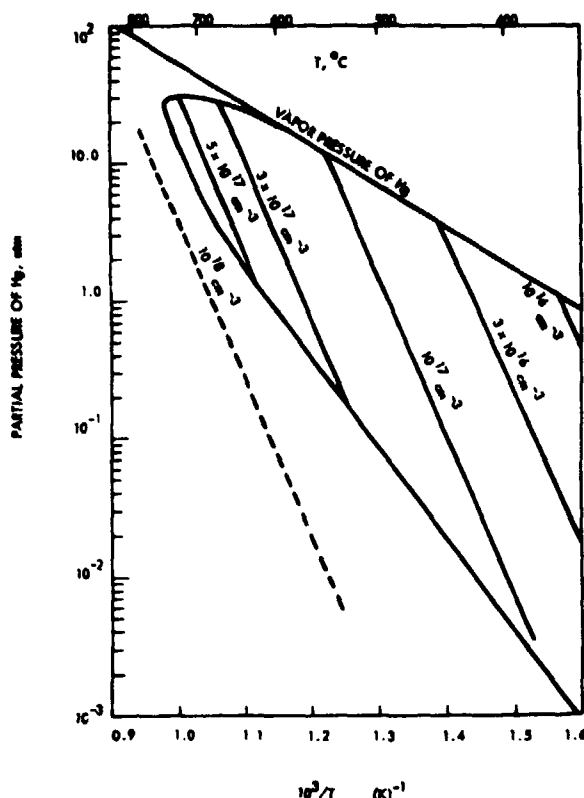
Fig. 7. Calculated isohole concentration lines at 192 K for Hg₀.₆Cd₀.₄Te as a function of the partial pressure of Hg and temperature of annealing.

Hole mobility in Hg₀.₆Cd₀.₄Te.—Figures 4 and 5 show that the hole mobility at 77 K decreases with increase in hole concentration whereas it is relatively independent of the hole concentration at 192 K indicating that the hole mobility at 192 K is almost completely dominated by lattice scattering whereas ionized impurity scattering contributes to the mobility at 77 K. The absolute hole mobility at 77 K as well as its dependence on the hole concentration in Hg₀.₆Cd₀.₄Te are less than in Hg₀.₈Cd₀.₂Te (part I) (3).

Conclusion

Based on the variation of the hole concentration as a function of the partial pressure of Hg in crystals annealed at various temperatures and quenched to room temperature, the dominant native acceptor defects in undoped Hg₀.₆Cd₀.₄Te have been established to be doubly ionized. The mass action constant describing the incorporation of the doubly ionized acceptor defect explains the experimental results satisfactorily.

Acknowledgments

APPENDIX

Hole Concentration Calculations in Hg₀.₆Cd₀.₄Te Containing Residual Donors

Electroneutrality condition:

High temperature

$$2[V''_{Hg}]_{HT} = [h\cdot]_{HT} + [D\cdot] \qquad [A-1]$$

Cooled crystals

$$[h\cdot]_{LT} = 2[V''_{Hg}]_{HT} - [D\cdot] \qquad [A-2]$$

Subscripts HT and LT in Eq. [A-1] and [A-2] refer to the high temperature and low temperature defect states, respectively; [D·] refers to concentration of residual donors in the samples, assumed to be always ionized and independent of anneal temperature.

Expressing the species in Eq. [A-1] and [A-2] in terms of the mass action constant $K''_{V_{Hg}}$ (Eq. [2] of main text) we get

$$2K''_{V_{Hg}}/([h\cdot]^2_{HT}p_{Hg}) = [h\cdot]_{HT} + [D\cdot]$$

or

$$[h\cdot]^3_{HT} + [h\cdot]^2_{HT}[D\cdot] = 2K''_{V_{Hg}}/p_{Hg} \qquad [A-3]$$

In the cooled crystals

$$[h\cdot]_{LT} = 2K''_{V_{Hg}}/([h\cdot]^2_{HT}p_{Hg}) - [D\cdot] \qquad [A-4]$$

with the knowledge of $K''_{V_{Hg}}$ (Eq. [2] of the main text) hole concentration in the cooled crystals can be calculated from Eq. [A-3] and [A-4] for various fixed residual donor concentrations in the crystals.

REFERENCES

1. J. L. Schmit and E. L. Stelzer, *J. Electron. Mater.*, **7**, 65 (1978).
2. R. F. Brebrick and J. P. Schwartz, *ibid.*, **9**, 485 (1980).
3. H. R. Vydyanath, *This Journal*, **128**, 2609 (1981).
4. R. F. Brebrick and A. J. Strauss, *J. Phys. Chem. Solids*, **26**, 989 (1965).
5. J. P. Schwartz, T. Tung, and R. F. Brebrick, *This Journal*, **128**, 438 (1981).
6. T. Tung, L. Golonka, and R. F. Brebrick, *ibid.*, **128**, 451 (1981).
7. L. J. van der Pauw, *Philips Tech. Rev.*, **20**, 220 (1959).
8. W. Scott, E. L. Stelzer, and R. J. Hager *J. Appl. Phys.*, **47**, 1408 (1976).
9. H. Brooks, *Phys. Rev.*, **83**, 879 (1952); *Adv. Electron. Electron Phys.*, **7**, 156 (1955).
10. R. A. Reynolds, M. J. Brau, H. Krause, and R. T. Bate, *J. Phys. Chem. Solids*, **32**, Suppl. 1, 511 (1971).
11. E. J. Moore, *Phys. Rev.*, **160**, 618 (1967).
12. J. G. Broerman, *ibid.*, **183**, 754 (1969).
13. D. M. Brown and R. Bray, *ibid.*, **127**, 1953 (1962).
14. J. Nishizawa, K. Suto, M. Kitanura, M. Sato, Y. Takase, and A. Ito, *J. Phys. Chem. Solids*, **37**, 33 (1976).
15. J. L. Schmit and E. L. Stelzer, *J. Appl. Phys.*, **40**, 4865 (1969).

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3.4 DEFECT CHEMISTRY AND CHARACTERIZATION OF IODINE DOPED $Hg_{0.8}Cd_{0.2}Te$

DOPING BEHAVIOR OF IODINE IN $Hg_{0.8}Cd_{0.2}Te$[†]

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Iodine doped single crystal samples of $Hg_{0.8}Cd_{0.2}Te$ were annealed at temperatures varying from 450 to 600°C in Hg vapor and quenched to room temperature. Hall effect measurements at 77 K on the crystals cooled to room temperature indicate the samples to be n-type after anneals at high Hg pressures whereas they turn p-type after anneals at low Hg pressures; the electron concentration increases with increase in Hg pressure. The results are explained on the basis that the crystals are saturated with $(Hg,Cd)I_2$, with the iodine being present as donors occupying tellurium lattice sites ($I_{Te}^{\cdot}$) and a fraction being present as $(I_{Te}V_{Hg})'$ species formed from the iodine on tellurium lattice sites ($I_{Te}^{\cdot}$) pairing with the doubly ionized native acceptor defects (V_{Hg}''). The solubility of the $I_{Te}^{\cdot}$ species increases with increase in Hg pressure, whereas that of the $(I_{Te}V_{Hg})'$ species increases with decrease in Hg

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pressure. Equilibrium constants for the incorporation of the iodine species as well as the pairing reaction have been established.

Key words: Iodine, Mercury Cadmium Telluride, II - IV compounds, doping, Hall effect, Defect, Electron mobility.

Introduction

With the emergence of $Hg_{1-x}Cd_xTe$ as a technologically useful infrared detector material,[1] it has become important to study in detail the nature of impurities and dopants in this material. As part of a program aimed at understanding the physicochemical properties of undoped and doped $Hg_{1-x}Cd_xTe$ compounds,[2] the defect structures of undoped $Hg_{0.8}Cd_{0.2}Te$, undoped $Hg_{0.6}Cd_{0.4}Te$, copper doped, and indium doped $Hg_{0.8}Cd_{0.2}Te$ were reported recently.[3-5] The present work was undertaken to extend such a defect structure investigation to iodine in $Hg_{0.8}Cd_{0.2}Te$. Halogens have been known to be donors occupying chalcogen lattice sites in II-VI compounds.[6] In the present work, the defect state prevailing in the iodine doped samples at the annealing temperatures is deduced from the Hall effect measurements on the crystals cooled to 77 K from the annealing temperatures. The results obtained are similar to those found for iodine doped CdS established from in situ high temperature Hall effect measurements previously;[7] iodine acts as a single donor occupying Te lattice sites with a fraction paired with the native acceptor defects. The crystals are saturated with the metal iodide which influences the incorporation of the iodine donor species on tellurium sites as well as the $(I_{Te}V_{Hg})'$ species, which result from the iodine on tellurium sites pairing with the doubly ionized native acceptor defects. The concentration of the $I_{Te}^{·}$ species increases with increase in the partial

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pressure of Hg, whereas that of the pair species
increases with decrease in the partial pressure of Hg.
The equilibrium constants evaluated for the incorpora-
tion of the isolated iodine species as well as the
iodin Hg vacancy pairs satisfactorily explain the
experimentally observed carrier concentration data.

Experimental

Iodine doped $Hg_{0.8}Cd_{0.2}Te$ crystal was grown by
the solid state recrystallization method.[8] The total
amount of iodine in the starting charge material was
approximately 10^{20} cm^{-3}. Single crystal slices of
$Hg_{0.8}Cd_{0.2}Te$ were cut from the larger boule. The
slices were lapped down to thicknesses of less than 0.04
cm and were subsequently polished, etched in Br metha-
nol, and rinsed in DI water. The samples were annealed
in evacuated quartz ampoules containing some Hg also to
obtain the desired Hg pressure.[3] The annealing experi-
ments were carried out within certain limits of partial
pressure of Hg set by the phase boundary limits for
$Hg_{0.8}Cd_{0.2}Te$ (S).[9] Typical anneal times used were
24 hours at temperatures of 600°C and higher, 3 days at
550°C, 7 days at 500°C, and 4 to 6 weeks at 450°C.
These equilibration periods appeared satisfactory for
the complete homogenization of the samples. Subsequent
to the anneals at the high temperatures, the ampoules
were quenched in ice water. Hall effect and electrical
resistivity measurements were made using the van der
Pauw technique.[10] Magnetic fields of 400 and 4000 gauss
were used for the Hall effect measurements.

Results

In order to ascertain an unambiguous evaluation of
the carrier concentration, only those measurements where
the Hall effect did not vary with the magnetic field

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were used in determining the carrier concentration in
the samples.[3] The carrier concentration was calculated
using the expression:

$$n \text{ or } p = \frac{1}{|R_H q|}$$

The hole concentration in the p-type samples and the
electron concentration in the n-type samples did not
vary with the temperature of measurement varying from
77 K to 145 K, thus indicating that the iodine donor
species as well as the iodine acceptor species and the
native acceptor defect species are all ionized at 77 K;
all the carrier concentration measurements were carried
out at 77 K to deduce the defect state at the annealing
temperatures.

Fig. 1 shows the carrier concentration at 77 K in
the iodine doped samples as a function of the partial
pressure of Hg at the various annealing temperatures.
It is apparent from the figure that the samples are
n-type under Hg rich conditions whereas they turn p-type
at lower Hg pressures similar to the observation in the
indium doped samples.[4] Also, the electron concentration
appears to increase with increase in the Hg pressure
just as was observed for the indium doped samples.[4]

Fig. 2 shows the electron mobility at 77 K as a
function of the electron concentration in the samples.
The magnitude of the electron mobility is similar to
that observed in the indium doped samples[4] for compara-
ble electron concentrations.

Discussion

Iodine can exist in two forms, namely as a single
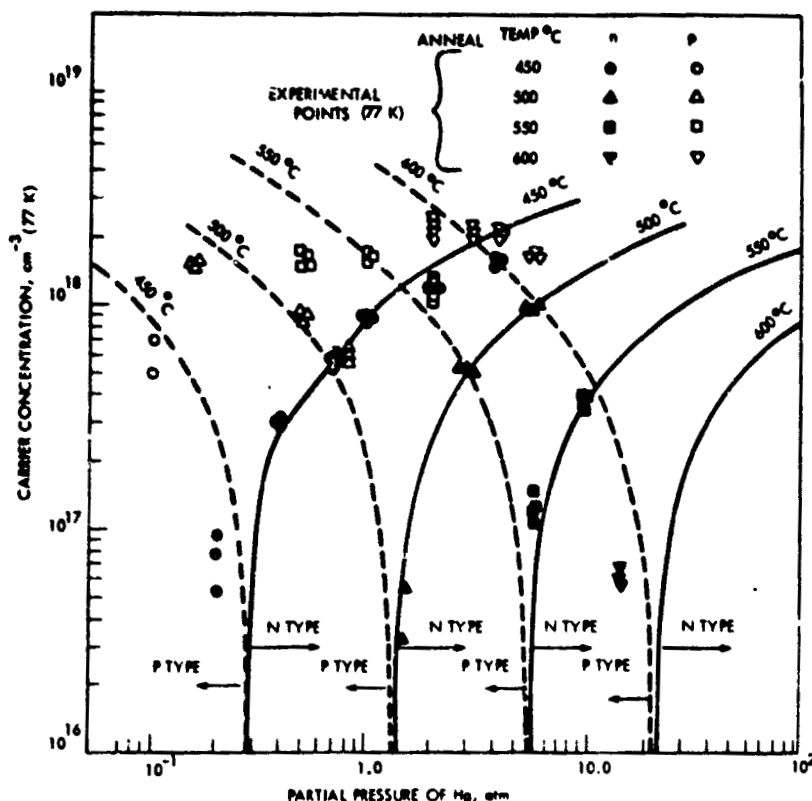donor occupying Te lattice sites I_{Te}^+ or paired with

Fig. 1. Carrier Concentration at 77 K as a Function
of the Partial Pressure of Hg for Iodine
Doped $Hg_{0.8}Cd_{0.2}Te$ Samples Annealed at
Various Temperatures and Quenched to Room
Temperature; Solid Lines Show the Calculated
Electron Concentrations While the Dashed Lines
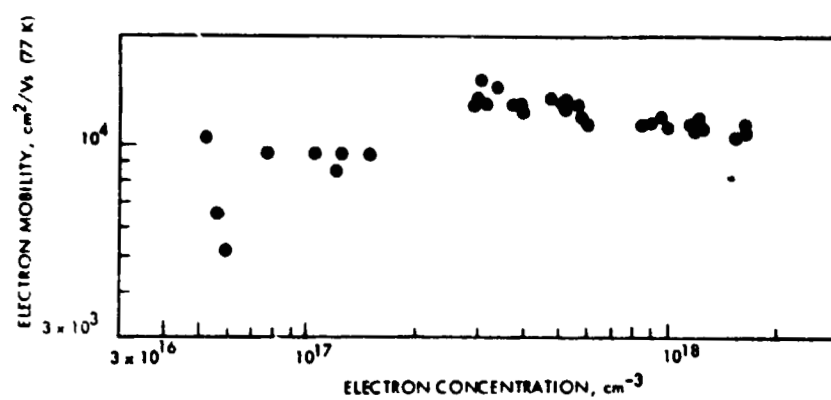Show the Calculated Hole Concentrations.

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Fig. 2. Electron Mobility at 77 K as a Function of the
Electron Concentration for the Iodine Doped
$Hg_{0.8}Cd_{0.2}Te$ Samples.

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the doubly ionized native acceptor defects as
$(I_{Te}V_{Hg})'$. The following inferences can be drawn
from the experimental data:

1. The concentration of iodine in the start-
   ing charge was on the order of 10^{20}
   cm^{-3}, whereas the maximum electron con-
   centration in the doped samples is only on
   the order of 10^{18} cm^{-3}.

2. The concentration of electrons obtained at
   77 K is less than the intrinsic carrier
   concentration[3] at the annealing tempera-
   tures.

3. The concentration of electrons increases
   with increase in the Hg pressures.

4. The hole concentration in the p-type sam-
   ples at low Hg pressures is close to that
   obtained in the undoped samples.[3]

Several defect situations can be considered to explain
the experimental data:

1. $[I_{Te}^{\cdot}] = [I_{TOT}]$ = constant and the
   crystal is intrinsic at the annealing
   temperatures. In the cooled crystals
   $[e'] = [I_{Te}^{\cdot}] \gg [V_{Hg}'']$. Such a model
   would predict an electron concentration
   independent of the partial pressure of Hg
   particularly at lower temperatures and
   higher Hg pressures for which conditions
   the native acceptor defect concentration
   is expected to be less than the concentra-
   tion of the electrons obtained in the
   crystals. The experimental data are in
   disagreement with this model.

2. $[I_{Te}^{\cdot}] = [(I_{Te}V_{Hg})'] = [I_{TOT}/2]$
and the crystal is intrinsic at the
annealing temperatures. In the crystals
cooled to 77 K, $[e'] = [I_{Te}^{\cdot}]$ minus
$[(I_{Te}V_{Hg})']$. This model predicts an
independence of the electron concentration
as a function of the partial pressure of
Hg particularly at the highest Hg pres-
sures contrary to the observed results.

3. The crystals are saturated with iodine
with the formation of $(Hg_{0.8}Cd_{0.2})I_2$
as the second phase. The concentration of
$I_{Te}^{\cdot}$ as well as $(I_{Te}V_{Hg})'$ depends on
the partial pressure of Hg with $[I_{Te}^{\cdot}]$
varying as $p_{Hg}^{+1/2}$ and $[(I_{Te}V_{Hg})']$
varying as $p_{Hg}^{-1/2}$. The incorpora-
tion reactions of interest are:

A. $Hg(g) + (Hg_{0.8}Cd_{0.2})I_2(S)$

$\longrightarrow 2\ I_{Te}^{\cdot} + 2e' + 1.8\ Hg_{Hg}^{X} + 0.2\ Cd_{Hg}^{X}$
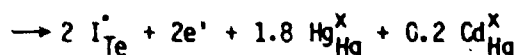
$$K_{I_{Te}} = \frac{[I_{Te}^{\cdot}]^2\ [e']^2[Hg_{Hg}^{X}]^{1.8}[Cd_{Hg}^{X}]^{0.2}}{p_{Hg}^{a}\ a_{(Hg_{0.8}Cd_{0.2})I_2}} \quad (1)$$

where $a_{(Hg_{0.8}Cd_{0.2})I_2}$ refers to the
activity of the $(Hg_{0.8}Cd_{0.2})I_2(s)$
phase.

As long as the partial pressure of Hg is
within the phase boundary limits for
$(Hg_{0.8}Cd_{0.2})Te(s)$[9] the composition can
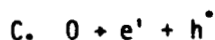be assumed to be constant and hence

$[Hg_{Hg}^{X}] = 0.8$ and $[Cd_{Hg}^{X}] = 0.2$

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$$\therefore K_{I_{Te}} = \frac{[I_{Te}^{\cdot}]^2 [e']^2}{2 p_{Hg} a_{(Hg_{0.8}Cd_{0.2})I_2}} \quad (2)$$
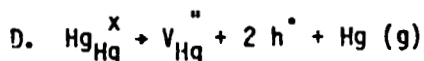
For an intrinsic crystal $[e'] = [h^{\cdot}] = \sqrt{K_i}$. Since the crystal is saturated with iodine and $(Hg_{0.8}Cd_{0.2})I_2$ exists as a pure second phase, $a_{(Hg_{0.8}Cd_{0.2})I_2}$, the activity of the metal iodide is unity and hence $[I_{Te}^{\cdot}] \, \alpha \, p_{Hg}^{1/2}$ from mass action relation (2).
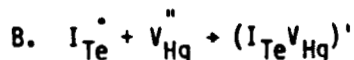
B. $I_{Te}^{\cdot} + V_{Hg}'' \rightarrow (I_{Te}V_{Hg})'$

$$K_{P(I_{Te}V_{Hg})'} = [(I_{Te}V_{Hg})'] \, \Big| \, [I_{Te}^{\cdot}] \, [V_{Hg}''] \quad (3)$$

C. $0 \rightarrow e' + h^{\cdot}$

$$K_i = [e'] [h^{\cdot}] \quad (4)$$

D. $Hg_{Hg}^x \rightarrow V_{Hg}'' + 2 h^{\cdot} + Hg \, (g)$

$$K_{VHg}'' = [V_{Hg}''] [h^{\cdot}]^2 \, p_{Hg} \quad (5)$$

combining mass action constants (2), (3), (4) and (5) we get

$$K_{P(I_{Te}V_{Hg})'} = \left\{ \frac{[(I_{Te}V_{Hg})'] \, p_{Hg}^{1/2} \, k_i^2}{2^{1/2} \, K_{I_{Te}}^{1/2} \, K_{VHg}'' \, [e'] \, a_{(Hg_{0.8}Cd_{0.2})I_2}^{1/2}} \right\} \quad (6)$$

For an intrinsic crystal with

$[e'] = [h^\bullet] = \sqrt{K_i}$ and
$a(Hg_{0.8}Cd_{0.2})I_2 = 1$ for a pure
second phase of $(Hg_{0.8}Cd_{0.2})I_2$

$[(I_{Te}V_{Hg})'] \propto p_{Hg}^{-1/2}$ from mass action relation (5).

This last model is similar to that established for
iodine doped CdS[7] where CdI_2 was assumed to be present
as a pure second phase. Similarity between the Indium
doping[4] and Iodine doping in $Hg_{0.8}Cd_{0.2}Te$ is also
worth noting. In the Indium doped crystals the samples
are intrinsic at the annealing temperature with the
electron concentration increasing with increasing Hg
pressure; however, in that case the dopant compound
In_2Te_3 is present as an unsaturated solid solution with
$a_{In_2Te_3}$ the activity of the metal telluride being
variable, whereas in the present case the solution of
$(Hg,Cd)I_2$ is saturated with $a_{(Hg_{0.8}Cd_{0.2})I_2} = 1$.

Analysis of the Carrier Concentration in the Cooled Crystals

The various species to be considered in the elec-
troneutrality condition are e', $h^\bullet$, V_{Hg}'', $I_{Te}^\bullet$ and
$(I_{Te}V_{Hg})'$.

The complete electroneutrality condition is written
as:

$$[e'] + 2[V_{Hg}''] + [(I_{Te}V_{Hg})'] = [I_{Te}^\bullet] + [h^\bullet] \qquad (7)$$

Expressing the various species in terms of the mass
action constants defined in relations 1 through 5 we
get:

$$[e'] + \frac{2K''_{VHg} \, p^{-1}_{Hg} \, [e']^2}{K_i^2} + \frac{2 \, K^{1/2}_{P(I_{Te}V_{Hg})'} \, K^{1/2}_{I_{Te}} \, K''_{VHg} \, [e']}{K_i^2 \, p_{Hg}^{1/2}}$$

$$- \frac{2^{1/2} K^{1/2}_{I_{Te}} \, p^{1/2}_{Hg}}{[e']} - \frac{K_i}{[e']} = 0 \qquad (8)$$

with some simplification we get:

$$\frac{[e']^3 \, 2K''_{VHg} \, p^{-1}_{Hg}}{K_i^2} + [e']^2 \left\{ 1 + \frac{2 \, K^{1/2}_{P(I_{Te}V_{Hg})'} \, K^{1/2}_{I_{Te}} \, K''_{VHg}}{K_i^2 \, p_{Hg}^{1/2}} \right\}$$

$$= 2^{1/2} \, K^{1/2}_{I_{Te}} \, p^{1/2}_{Hg} + K_i \quad . \qquad (9)$$

In the crystals cooled to 77 K

$$[e']_{77 \, K} \text{ or } [h^{\cdot}]_{77 \, K} = \left| [I^{\cdot}_{Te}] - 2[V''_{Hg}] - [(I_{Te}V_{Hg})'] \right| \qquad (10)$$

The concentrations $[V''_{Hg}]$, $[(I_{Te}V_{Hg})']$ and $[I^{\cdot}_{Te}]$
in Equation (10) are given by the second, third, and
fourth terms of Equation (8), respectively. Of the four
mass action constants in Equations (8) and (9), values

of the two constants K_i and $K_{V_{Hg}}''$ are known from the work on the undoped crystals[3] and are given by

$$K_i = 9.16 \times 10^{+0} \exp(-0.57 \text{ eV}/kT) \text{ cm}^{-6} \qquad (11)$$

$$K_{V_{Hg}}'' = 1.58 \times 10^{69} \exp(-2.24 \text{ eV}/kT) \text{ cm}^{-9} \text{ atm} \qquad (12)$$

The values of the constants $K_{I_{Te}}$ and $K_{p(I_{Te}V_{Hg})'}$ were optimized by a procedure of trial and error until the calculated carrier concentration as given by Equation (10) agreed best with the experimental results, as a function of the partial pressure of Hg at various temperatures. The values of the mass action constants $K_{I_{Te}}$ and $K_{p(I_{Te}V_{Hg})'}$ established from the present work are given by

$$K_{I_{Te}} = 2.8 \times 10^{63} \exp(1.434 \text{ eV}/kT) \text{ cm}^{-12} \text{ atm}^{-1} \qquad (13)$$

and

$$K_{p(I_{Te}V_{Hg})'} = 3.77 \times 10^{-21} \exp(0.445 \text{ eV}/kT) \text{cm}^3 \qquad (14)$$

or, in terms of site fractions (there are 1.26×10^{22} molecules cm^{-3} in $Hg_{0.8}Cd_{0.2}Te$)

$$K_{I_{Te}} = 1.1 \times 10^{-25} \exp(0.717 \text{ eV}/kT) \text{ site Fr}^4 \text{ atm}^{-1} \qquad (15)$$

and

$$K_{p(I_{Te}V_{Hg})'} = 47.5 \exp(0.445 \text{ eV}/kT) \text{ site Fr}^{-1} \qquad (16)$$

The calculated defect concentrations as a function of the partial pressure of Hg at various temperatures are shown in Figs. 3 through 6; the experimentally obtained

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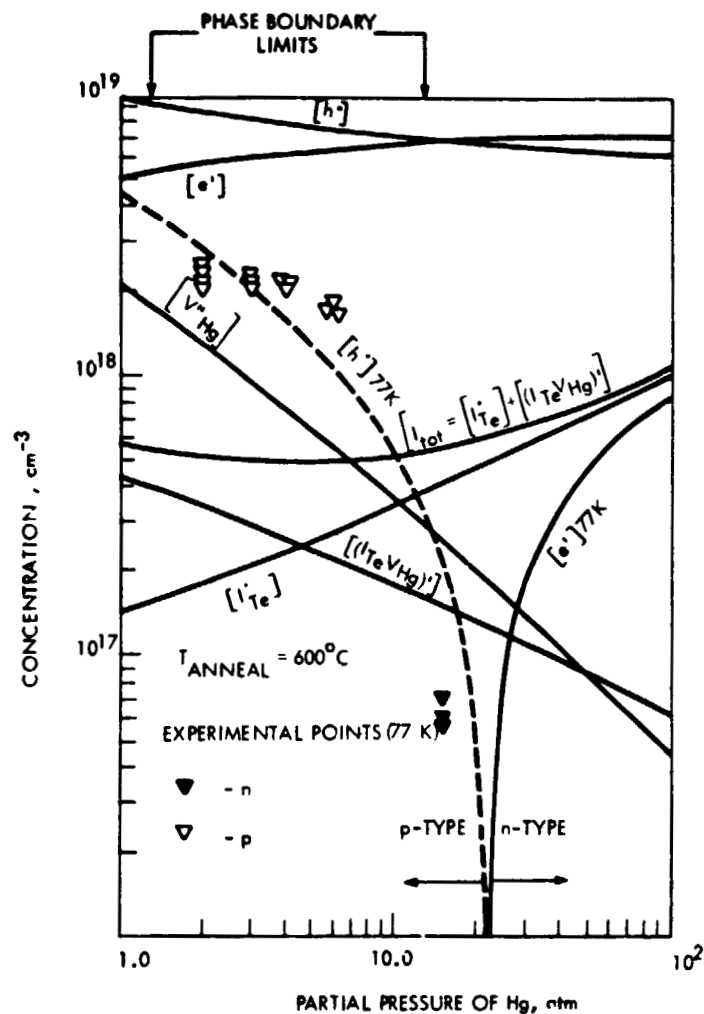
Fig. 3. Calculated Defect Concentrations ($[e']$, $[h^\cdot]$, $[I_{Te}^\cdot]$, $[(I_{Te}V_{Hg})']$ and $[V''_{Hg}]$) as a Function of the Partial Pressure of Hg for Iodine Doped $Hg_{0.8}Cd_{0.2}Te$ Annealed at 600°C and Quenched to Room Temperature; Calculated Electron and Hole Concentrations Expected at 77 K (indicated by solid and dashed lines respectively) are Also Shown Along with the Experimental Points.

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Fig. 4. Calculated Defect Concentrations ([e'], [h·],
[$I_{Te}^{·}$], [($I_{Te}V_{Hg}$)'] and [V''_{Hg}]) as a
Function of the Partial Pressure of Hg for
Iodine Doped $Hg_{0.8}Cd_{0.2}Te$ Annealed at 550°C
and Quenched to Room Temperature; Calculated
Electron and Hole Concentrations Expected at
77 K (indicated by solid and dashed lines
respectively) are Also Shown Along with the
Experimental Points.

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Fig. 5. Calculated Defect Concentrations ([e'], [h$^{\cdot}$],
[I$_{Te}^{\cdot}$], [(I$_{Te}$V$_{Hg}$)'] and [V"$_{Hg}$]) as a
Function of the Partial Pressure of Hg for
Iodine Doped Hg$_{0.8}$Cd$_{0.2}$Te Annealed at 500°C
and Quenched to Room Temperature; Calculated
Electron and Hole Concentrations Expected at
77 K (indicated by solid and dashed lines
respectively) are Also Shown Along with the
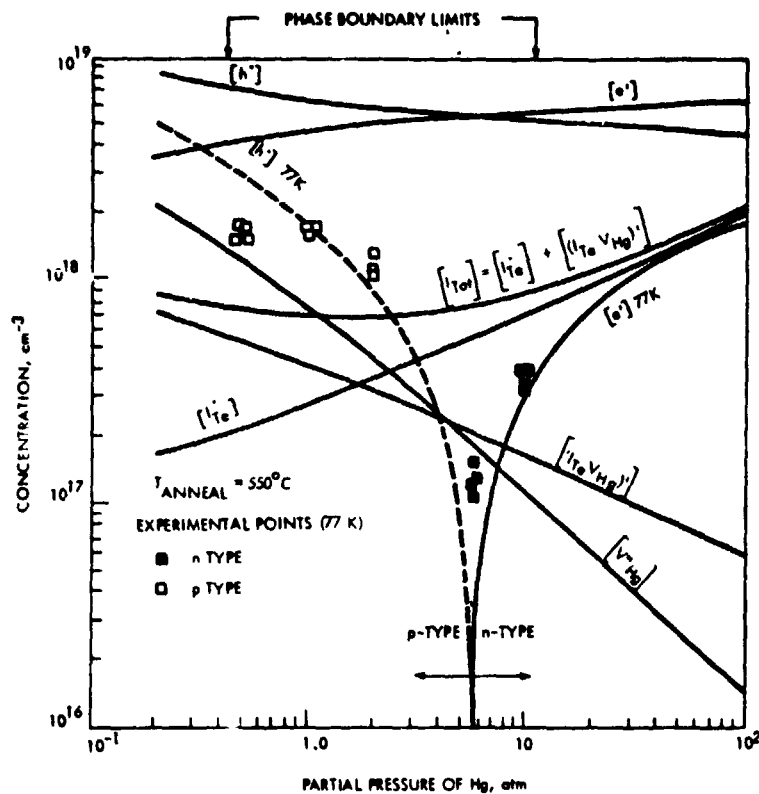Experimental Points.

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Fig. 6. Calculated Defect Concentrations ([e'], [h'],
[I$_{Te}$], [(I$_{Te}$V$_{Hg}$)'] and [V"$_{Hg}$]) as a
Function of the Partial Pressure of Hg for
Iodine Doped Hg$_{0.8}$Cd$_{0.2}$Te Annealed at 450°C
and Quenched to Room Temperature; Calculated
Electron and Hole Concentrations Expected at
77 K (indicated by solid and dashed lines
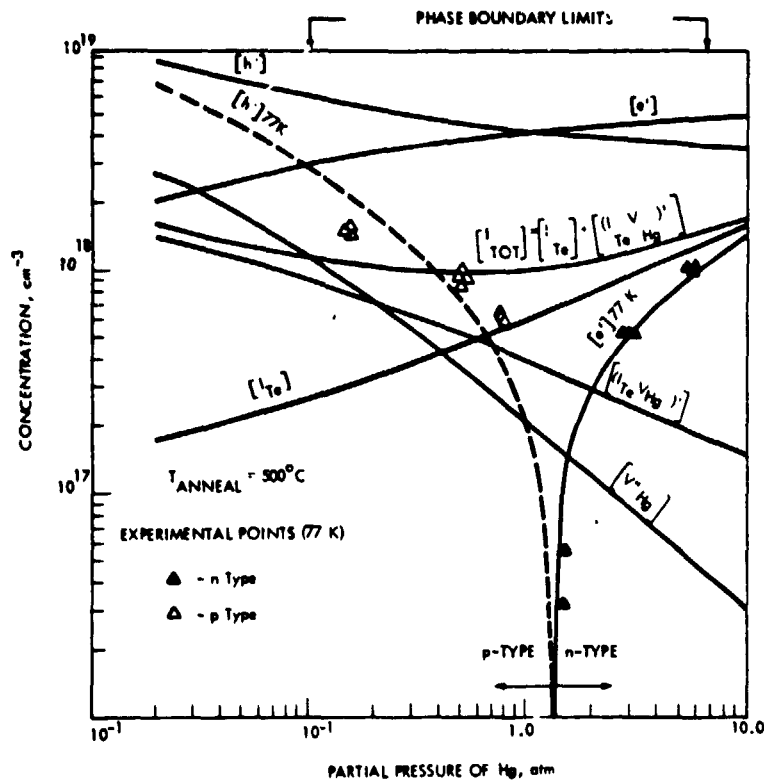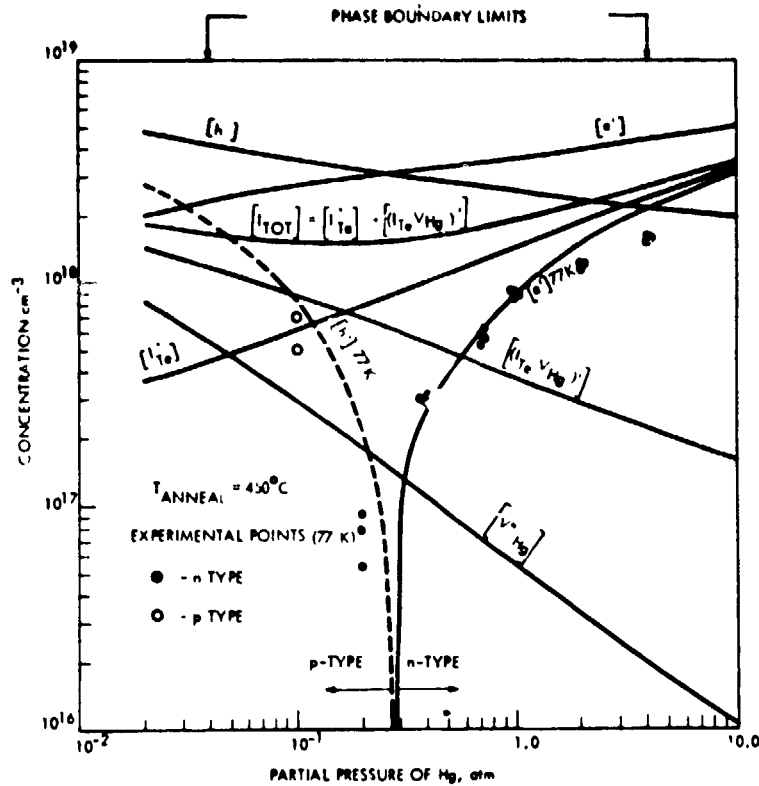respectively) are Also Shown Along with the
Experimental Points.

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carrier concentrations are also shown in the figures. The agreement between the calculated values and the experimental results appears satisfactory except near the p-n transition points. Inadequate quenching can explain the discrepancy somewhat. Near p-n transition $[I_{Te}^{\cdot}] = 2\ [V_{Hg}^{\shortmid\shortmid}] + [(I_{Te}V_{Hg})^{\shortmid}]$. If the quenching is inadequate, the sample may spend sufficient time at a lower temperature (between room temperature and the anneal temperature) where the pairing reaction between $I_{Te}^{\cdot}$ and $V_{Hg}^{\shortmid\shortmid}$ is promoted with the result that the partial pressure of Hg at which p-n transition occurs moves to lower Hg pressures. As can also be noted from the figures, the concentration of the iodine donor species increases with increase in the partial pressure of Hg whereas the opposite is true for the iodine acceptor species. The concentration of the native acceptor defects is essentially the same as in the undoped crystals[3] since the concentration of Iodine in the crystals is insufficient to make them extrinsic; the crystals are intrinsic just as the undoped crystals are under similar physicochemical conditions.[3]

Coulombic Value for the Enthalpy of Pairing
Between $I_{Te}^{\cdot}$ and $V_{Hg}^{\shortmid\shortmid}$

The pairing constant is written as:

$$K_p = K_p^\circ \exp\ (-Hp\ eV/kT)\ (Site\ Fr)^{-1} \qquad (17)$$

Hp, the enthalpy of pairing can be calculated on the basis of coulombic attraction between $I_{Te}^{\cdot}$ and $V_{Hg}^{\shortmid\shortmid}$

$$H_p = \frac{-2q^2}{\epsilon r} \quad (reference\ 11) \qquad (18)$$

where ϵ is the static dielectric constant, r is the distance between $I_{Te}^{\cdot}$ and $V_{Hg}^{\shortmid\shortmid}$. The factor 2 arises

because of the double charge on V_{Hg}''. For
$Hg_{0.8}Cd_{0.2}Te$, $\epsilon = 17.5^1$ and $r_{Hg-Te}' = 2.8$ A°
($\sqrt{3}/4$ times $a_0 = 6.46$ A). The calculated value based
on the coulombic calculations turns out to be

$$H_p = -0.581 \text{ eV}$$

This value is deemed to be close to the value of -0.445
eV [expressions (14) and (16)] calculated by us from the
experimental data.

Solid Solubility of Iodine in $Hg_{0.8}Cd_{0.2}Te$

The carrier concentration data shown in Fig. 1
indicate an increase of electron concentration at 77 K
with decrease in the annealing temperature for compara-
ble Hg pressures, implying an increase of the solubility
of the I_{Te}' species with decrease in temperature.
Fearing that complete equilibration may not have been
attained at the lower temperatures, (particularly with
regard to the Iodine species) Hall effect measurements
were carried out on several samples which were thermally
cycled from the lower temperature to higher temperatures
and vice versa; the resulting carrier concentrations
were independent of the prior thermal history thus con-
firming the validity of the experimental results of
Fig. 1 showing a negative temperature dependence of the
solubility of I_{Te} species in $Hg_{0.8}Cd_{0.2}Te$. The
negative temperature dependence of $[I_{Te}]$ arises from
the negative temperature dependence of the mass action
constant $K_{I_{Te}}$ (relation 15) which is not surprising
considering the large entropy of Hg (g) (reaction A). A
negative ΔH is also not surprising considering that Hg
without interaction as it is in Hg (g) is changed to Hg
interacting with Te when in solid solution (reaction A);

the entropy works the other way, decreasing the solubility with increasing temperature. The calculated defect isotherms shown in Figs. 3 through 6 do predict an increase of the total amount of Iodine in solid solution of $Hg_{0.8}Cd_{0.2}Te$ ($[I_{Tot}] = [I_{Te}^{\cdot}] +$ $[(I_{Te}V_{Hg})']$) with decrease in temperature thus accounting for the experimental results of Fig. 1.

Electron Mobility

The values of electron mobility shown in Fig. 2 for the iodine doped samples are comparable to those obtained for indium doped samples[4] for similar electron concentrations. The data in Fig. 2 appear to indicate that the mobility initially increases with decrease in electron concentration, and decreases with decrease in electron concentration for electron concentrations less than about 2×10^{17} cm^{-3}. A qualitative explanation for this can be elucidated from the defect concentration isotherms shown in Figs. 3 through 6. As can be noted from these figures, for electron concentrations greater than 2×10^{17} cm^{-3} the doubly ionized native acceptor defect concentration is negligible compared to the singly Ionized Iodine species and the mobility is essentially dominated by the Iodine species, and thus the mobility decreases with increasing electron concentrations originating from increasing iodine donor concentration. For electron concentrations less than 2×10^{17} cm^{-3}, the concentration of the doubly ionized native acceptor defects (V_{Hg}'') becomes dominant enough to contribute to ionized impurity scattering. Since these scatter four times more strongly than the singly ionized Iodine species, the electron mobility decreases with increase in the concentration of these native acceptor defects and thereby with decrease in electron concentration.

Conclusion

Iodine acts as a single donor occupying tellurium lattice sites (I_{Te}) and a large concentration exists as ($I_{Te}V_{Hg}$)' paired with the doubly ionized native acceptor defects. Equilibrium constants have been evaluated for the incorporation of the Iodine species as well as for the Iodine-native acceptor defect pairing.

Acknowledgement

REFERENCES

1. R. Dornahaus and G. Nimtz, Solid State Physics, Vol. 78, Springer-Verlag, New York (1976).

2. H.R. Vydyanath, "Defect Chemistry and Characterization of (Hg,Cd)Te" Semiannual technical report to NASA, George C. Marshall Space Flight Center, Alabama, under contract NAS8-33245, June 1980 (unpublished).

3. H.R. Vydyanath, Journal of Electrochemical Society (Dec. 1981 issue).

4. H.R. Vydyanath, Ibid, (December 1981 Issue)

5. H.R. Vydyanath, J.C. Donovan, and D.A. Nelson Journal of Electrochemical Society (Dec. 1981 issue).

6. M. Aven and S. Prener "Physics and Chemistry of II - VI Compounds" chapter 5, North Holland (1967); K. Zanio, "Semiconductors and Semimetals" Vol. 13 (Willardson and Beer Eds), Academic Press, New York, (1978) p. 129.

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7. H.R. Vydyanath, S.S. Chern, and F.A. Kröger, J. Phys. Chem. Solids 34, 1317 (1973).

8. D.A. Nelson, W.M. Higgins, and R.A. Lancaster, Proc. SPIE, 225, 48 (1980).

9. T. Tung, L. Golonka and R.F. Brebrick, Journal of Electrochemical Society 128, 451 (1981).

10. L.J. Van Der Pauw, Philips Tech. Rev. 20, 220 (1959).

11. F.A. Kröger "The Chemistry of Imperfect Crystals" Second revised edition, Volume 2, Chapter 10. North Holland (1974).

3.5   DEFECT CHEMISTRY AND CHARACTERIZATION OF PHOSPHOROUS DOPED
$Hg_{0.8}Cd_{0.2}Te$

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Mode of Incorporation of Phosphorus in $Hg_{0.8}Cd_{0.2}Te$*

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Single crystal samples of phosphorus doped $Hg_{0.8}Cd_{0.2}Te$ were annealed at temperatures varying from 450°C to 600°C in different partial pressures of Hg. Hall effect and mobility measurements were performed on the samples cooled to room temperature. All the samples were found to be p-type with the hole concentration being much less than the total amount of phosphorus present in the crystals. The hole concentration was found to increase with increase in partial pressure of Hg in contrast to the behavior observed in undoped crystals. Also, the hole concentration obtained in the doped samples at low Hg pressures was less than that in undoped crystals. The 77 K hole mobility of the doped samples was similar to that of undoped samples. All these inferences indicate that phosphorus behaves amphoterical'y in $Hg_{0.8}Cd_{0.2}Te(s)$ acting as a single acceptor occupying interstitial and tellurium lattice sites at high Hg pressures and as a single donor occupying Hg lattice sites at low Hg pressures; at intermediate Hg pressures, the majority of the phosphorus appears to be present as electrically neutral pairs formeᴗ from the association of the interstitial and substitutional phosphorus species, $(P_i P_{Hg})^X$. At low Hg pressures, a large fraction of the phosphorus appears to be present as $(P_{Hg}V_{Hg})'$ and $(P_{Hg}V_{Hg})^{..}$.

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Thermodynamic constants evaluated for the incorporation of the various phosphorus species satisfactorily explain the experimental results.

Key words: II-VI compounds, $Hg_{0.8}Cd_{0.2}Te$, phosphorus doping, hole mobility, defects, ionized impurity scattering.

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I. INTRODUCTION

The mode of incorporation of phosphorus in CdTe has been studied in detail by Selim and Kröger [1] who correlated their own electrical data with the diffusion and solubility data of Hall and Woodbury [2] to arrive at the defect state. According to their findings, phosphorus behaves amphoterically in CdTe acting as an accepter interstitially (P_i') and on Te lattice sites (P'_{Te}) and as a triple donor on Cd lattice sites ($P_{Cd}^{\cdots}$); at high phosphorus concentrations, a large fraction was found to be present as neutral associates $(P_{Cd}P_i)^X$. In this paper we have undertaken to examine the role of phosphorus in $Hg_{0.8}Cd_{0.2}Te$ via Hall effect and mobility measurements on phosphorus doped crystals quenched from 450-600°C subsequent to anneals in different partial pressures of Hg. The results indicate that the behavior of phosphorus in $Hg_{0.8}Cd_{0.2}Te$ is similar to that established for CdTe [1] except that all the electrically active phosphorus defect centers in $Hg_{0.8}Cd_{0.2}Te$ appear to be only singly ionized. At low Hg pressure, phosphorus is incorporated as a single donor occupying in lattice sites ($P_{Hg}^{\bullet}$) and at high Hg pressure as a single acceptor on interstitial sites (P_i') and Te lattice sites (P'_{Te}). At moderate Hg pressures, a large fraction is found to be present as neutral pairs $(P_{Hg}P_i)^X$. At low Hg pressures, electrically active associates $(P_{Hg}V_{Hg})'$ and $(P_{Hg}V_{Hg})^{\bullet}$ appear to be present in appreciable concentrations. The equilibrium constants established for the incorporation of the various phosphorus defects explain the experimental results satisfactorily.

II. **EXPERIMENTAL**

A. Preparation of the Phosphorus Doped Crystals
_____

A phosphorus doped $Hg_{0.8}Cd_{0.2}Te$ ingot was grown by the solid state recrystallization method [3]. Phosphorus corresponding to a concentration of $10^{19}cm^{-3}$ was added to the starting charge. Single crystal slices were then cut from the boule. The slices were lapped, polished, etched in Br methanol and rinsed in DI water prior to the anneals.

B. Hg Vapor Anneals
_____

The samples were annealed in evacuated quartz ampoules containing some Hg to obtain the desired Hg pressure [4]. In isothermal anneals, the partial pressure of Hg was dependent on the amount of Hg and the volume of the ampoule. In non-isothermal anneals, the partial pressure of Hg was determined from the temperature of the Hg. The limits of Hg pressure-with'n which $Hg_{0.8}Cd_{0.2}Te(s)$ is stable--were obtained from the partial pressure data of Tung et al. [5]. In order to assure ourselves of equilibration within reasonable annealing times, the sample thicknesses were restricted to less than 0.04 cm. Annealing times ranged from 72 hours at 550 to 600°C to 7 days at 500°C and approximately 4 to 6 weeks at 450°C. These annealing times appeared to be satisfactory for complete equilibration. Subsequent to the equilibration in Hg vapor, the ampoule containing the sample was quenched in ice water.

C. Electrical Measurements

Hall effect and electrical resistivity measurements were carried out using the Van der Pauw method [6]. Magnetic field strengths of 400 gauss and 4000 gauss were used for the measurement of the Hall coefficient.

D. Chemical Analysis

The concentration of phosphorus in the samples was mass spectrographically analyzed (Photometrics Inc., Woburn, Mass.) and the concentration determined from the analysis was close to what had been added to the starting charge within ± 20%.

III. Results

Only those Hall effect data where the Hall coefficient did not vary with the magnetic field were used in evaluating the carrier concentraion. This procedure ensured that the samples did not exhibit mixed conduction [7] and thus an unambiguous evaluation of the carrier concentration was possible. The carrier concentration was evaluated using the expression:

$$n \text{ or } p = \frac{1}{|R_H|q}$$

Figure 1 shows the Hall coefficient as a function of the temperature of measurement from temperatures below 77 K to 300 K for phosphorus doped samples annealed at various temperatures in different partial pressure of Hg. The data indicate that the phosphorus centers are all ionized at 77 K;
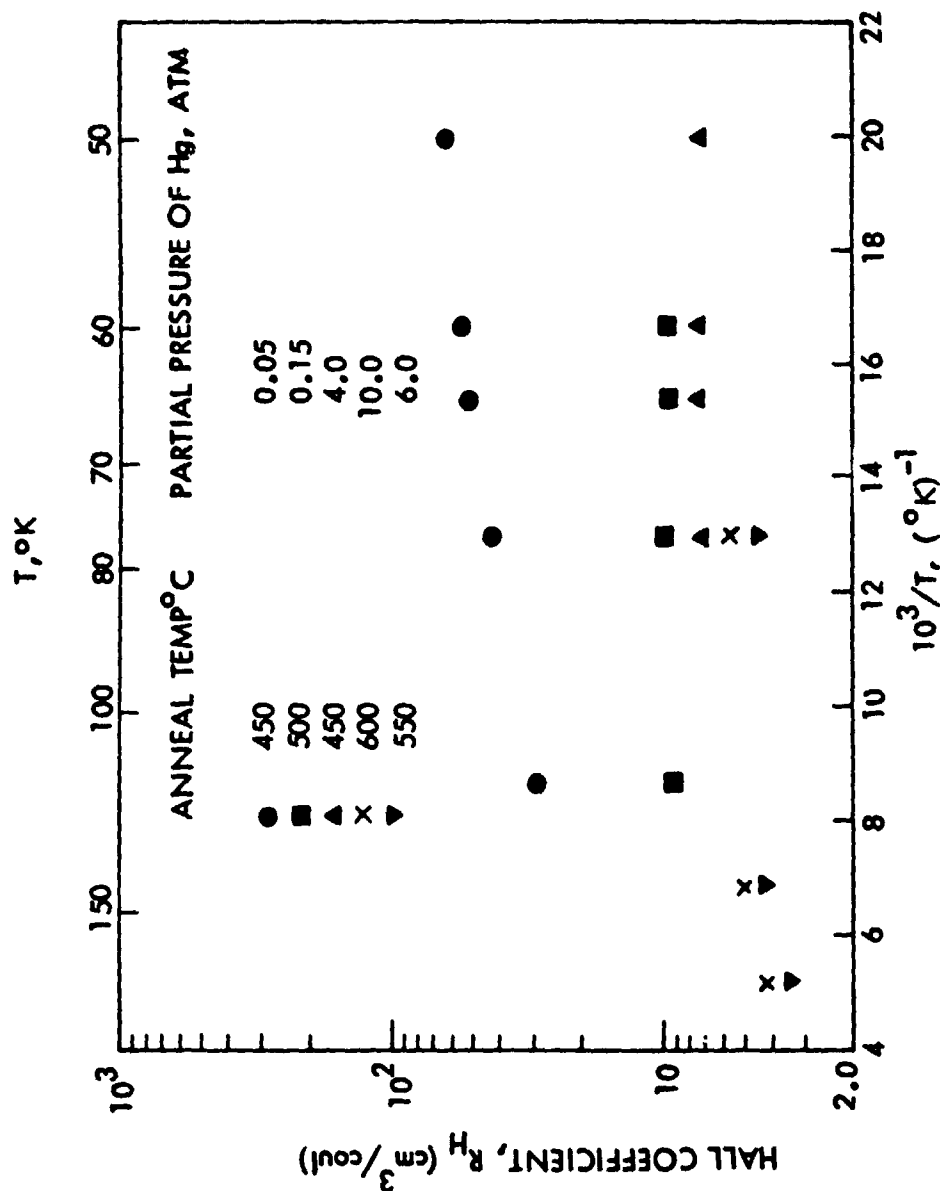
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Figure 1. Hall Coefficient as a Function of Temperature of Measurement for Phosphorus Doped (10^{19} cm^{-3}) $Hg_{0.8}Cd_{0.2}Te$ Crystals Annealed at Different Temperatures under Various Partial Pressures of Hg and Quenched to Room Temperature.

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therefore all the Hall measurements were carried out at 77 K and the resulting hole concentration was assumed to give a measure of the concentration of the defects at the higher annealing temperatures.

Figure 2 shows the hole concentrations obtained in samples doped with $10^{19} cm^{-3}$ of phosphorus which were annealed at various temperatures in different partial pressures of Hg; the data shown in Figure 2 are replotted in Figures 3 through 6 for different temperatures of anneal. Additional data shown in these figures include the hole concentration and hole mobility obtained in the undoped samples as well as the hole mobility in the phosphorus doped samples, all of which are plotted as a function of the partial pressure of Hg.

Several inferences can be made from the results of Figures 2 through 6. They are:

(1) The hole concentration in the phosphorus doped samples is lower than the total concentration of phosphorus in the samples and lower than the intrinsic carrier concentration for $Hg_{0.8}Cd_{0.2}Te(s)$ at the temperatures of annealing reported here [4].

(2) The hole mobility in the phosphorus doped samples increases with increasing partial pressure of Hg just as is the case for the undoped samples.
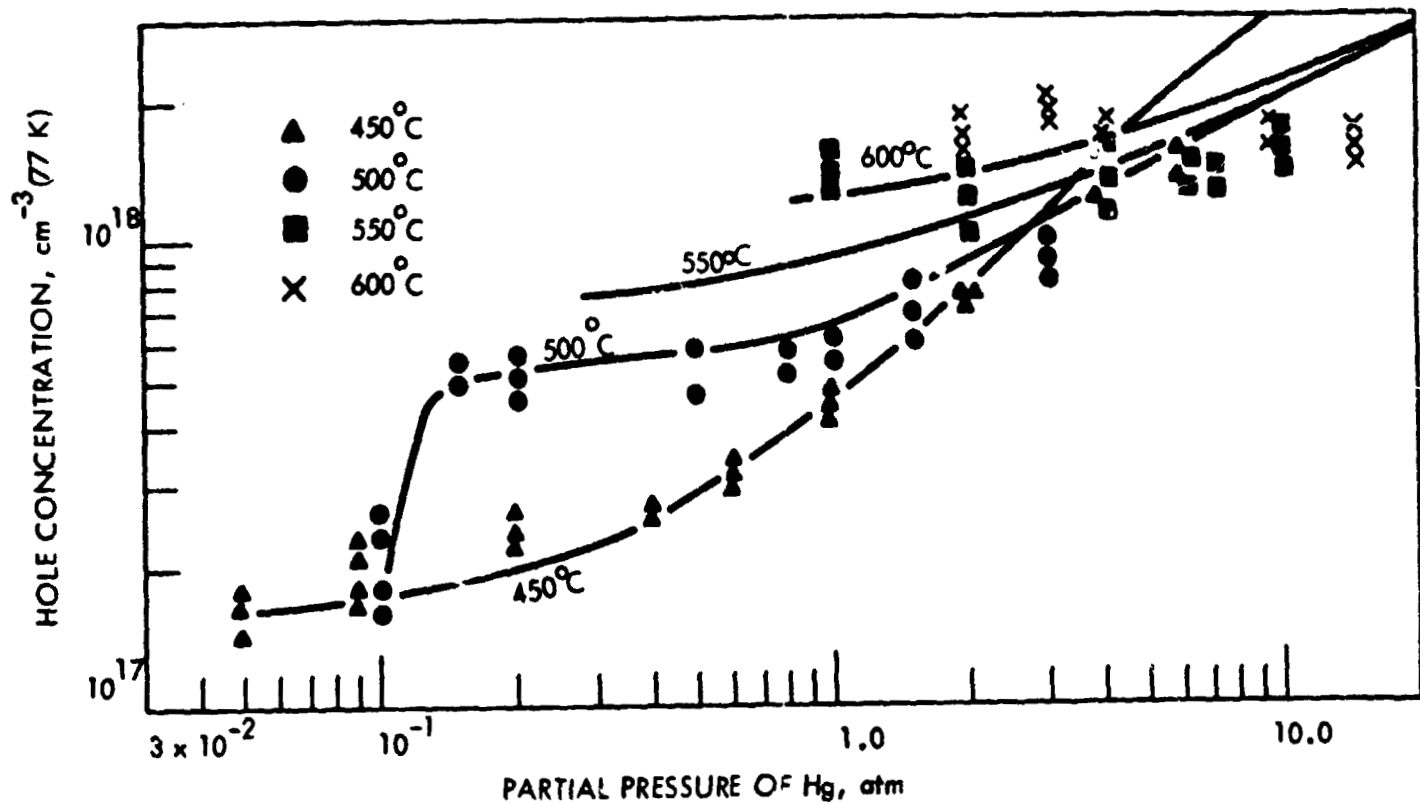
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Figure 2. Hole Concentration at 77 K as a Function of the Partial Pressure of Hg for Phosphorus Doped (10^{19} cm^{-3}) $Hg_{0.8}Cd_{0.2}Te$ Crystals Quenched to Room Temperature After Annealing at Different Temperatures.

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HOLE MOBILITY

UNDOPED

P DOPED

HOLE
CONCENTRATION

HOLE CONCENTRATION, cm^{-3} (77 K)

HOLE MOBILITY, cm^2/Vs (77 K)

10^{19}

10^{18}

10^{17}

10^{16}

10^2

10

EXPERIMENTAL
POINTS   P DOPED   UNDOPED
HOLE CONCENTRATION
(77 K)   ▲   ●
HOLE MOBILITY (77 K)   △   ○

T = 450°C; P DOPED
T = 460°C; UNDOPED

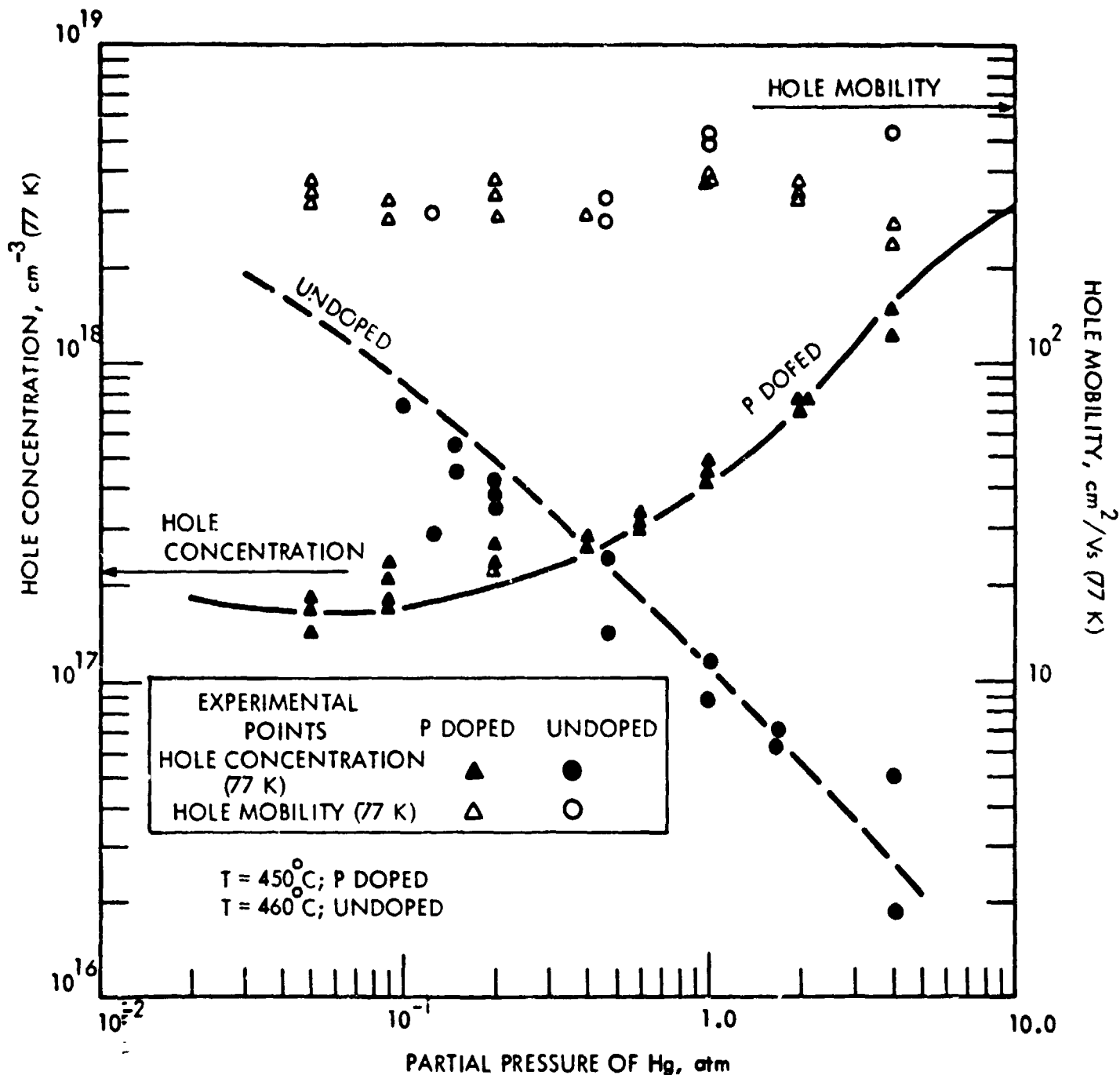10^{-2} 10^{-1} 1.0   10.0

PARTIAL PRESSURE OF Hg, atm

Figure 3. Hole Concentration and Hole Mobility at 77 K as a Function of
the Partial Pressure of Hg for Phosphorus Doped (10^{19}cm^{-3})
Hg$_{0.8}$Cd$_{0.2}$Te Crystals Quenched to Room Temperature After
Annealing 450°C. Similar data are shown for undoped samples
annealed at 460°C [Reference 4]. The solid and the dashed lines
show the calculated hole concentrations to be expected in the
doped and the undoped samples on the basis of the defect model.
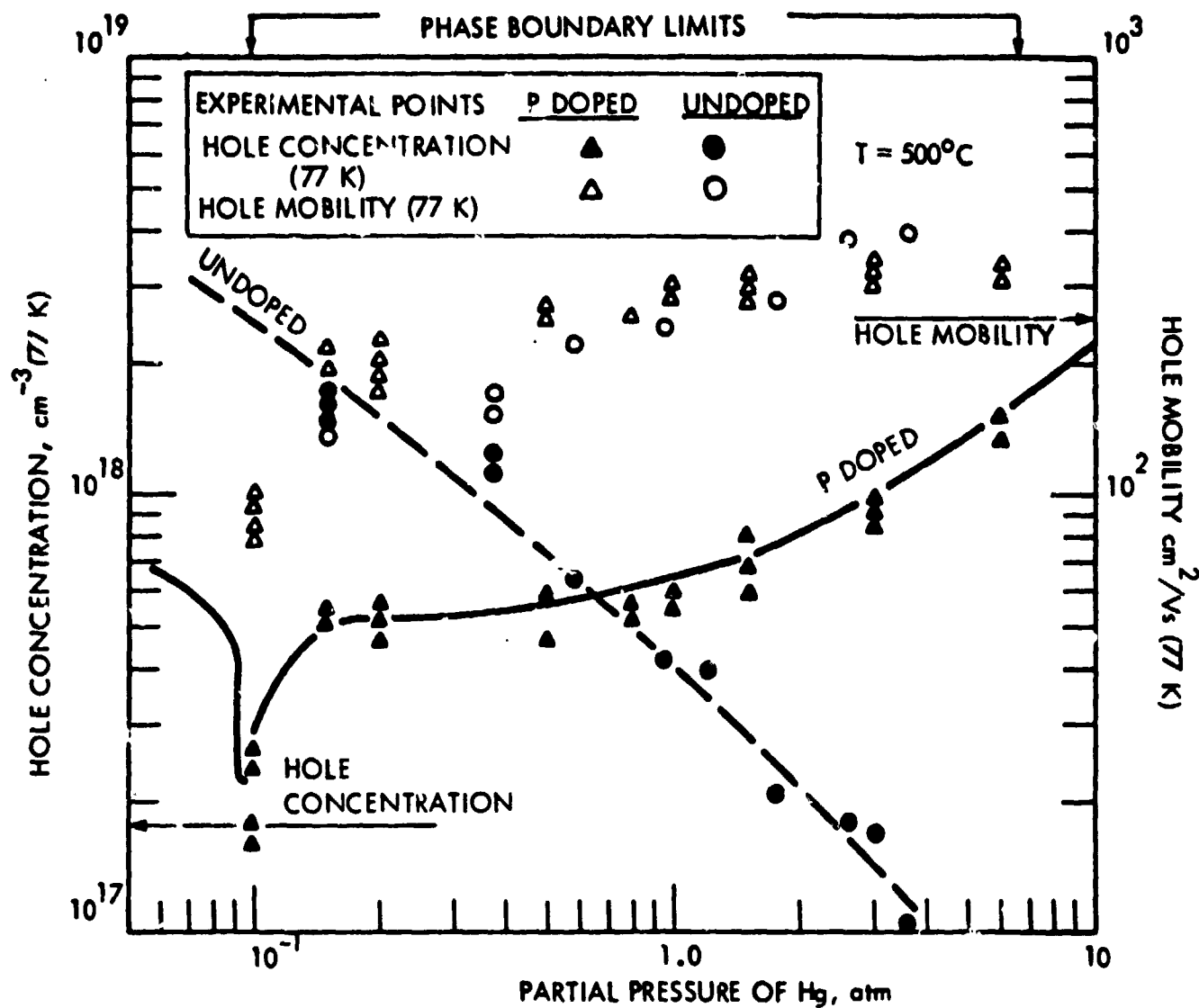
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Figure 4. Hole Concentration and Hole Mobility at 77 K as a Function of the Partial Pressure of Hg for Phosphorus Doped $(10^{19} cm^{-3})$ and Undoped [Reference 4] $Hg_{0.8}Cd_{0.2}Te$ Crystals Quenched to Room Temperature After Equilibration at $\sim 00°C$; the solid and the dashed lines show the calculated hole concentrations to be expected in the doped and the undoped samples on the basis of the defect model.
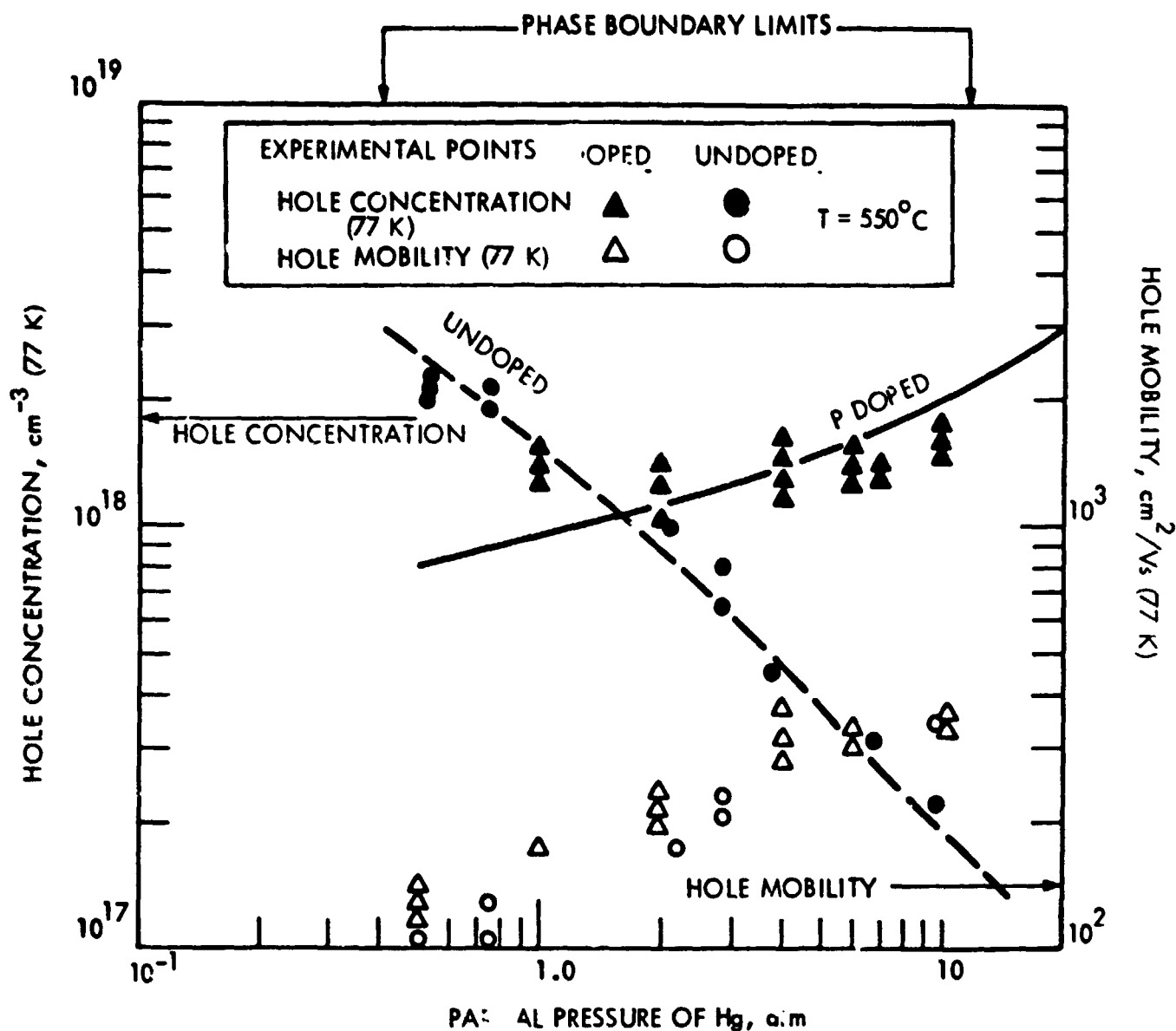
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Figure 5. Hole Concentration and Hole Mobility at 77 K as a Function of
the Partial Pressure of Hg for Phosphorus Doped $(10^{19}cm^{-3})$
and Undoped [Reference 4] $Hg_{0.8}Cd_{0.2}Te$ Crystals Quenched to
Room Temperature After Equilibration at 550°C; the solid and the
dashed lines show the calculated hole concentrations to be
expected in the doped an' the undoped samples on the basis of
the defect model.

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Figure 6. Hole Concentration and Hole Mobility at 77 K as a Function of
the Partial Pressure of Hg for Phosphorus Doped ($10^{19} cm^{-3}$)
and Undoped [Reference 4] $Hg_{0.8}Cd_{0.2}Te$ Crystals Quenched to
room Temperature After Equilibration at 600°C; the solid and the
dashed lines show the calculated hole concentrations to be
expected in the doped and the undoped samples on the basis of
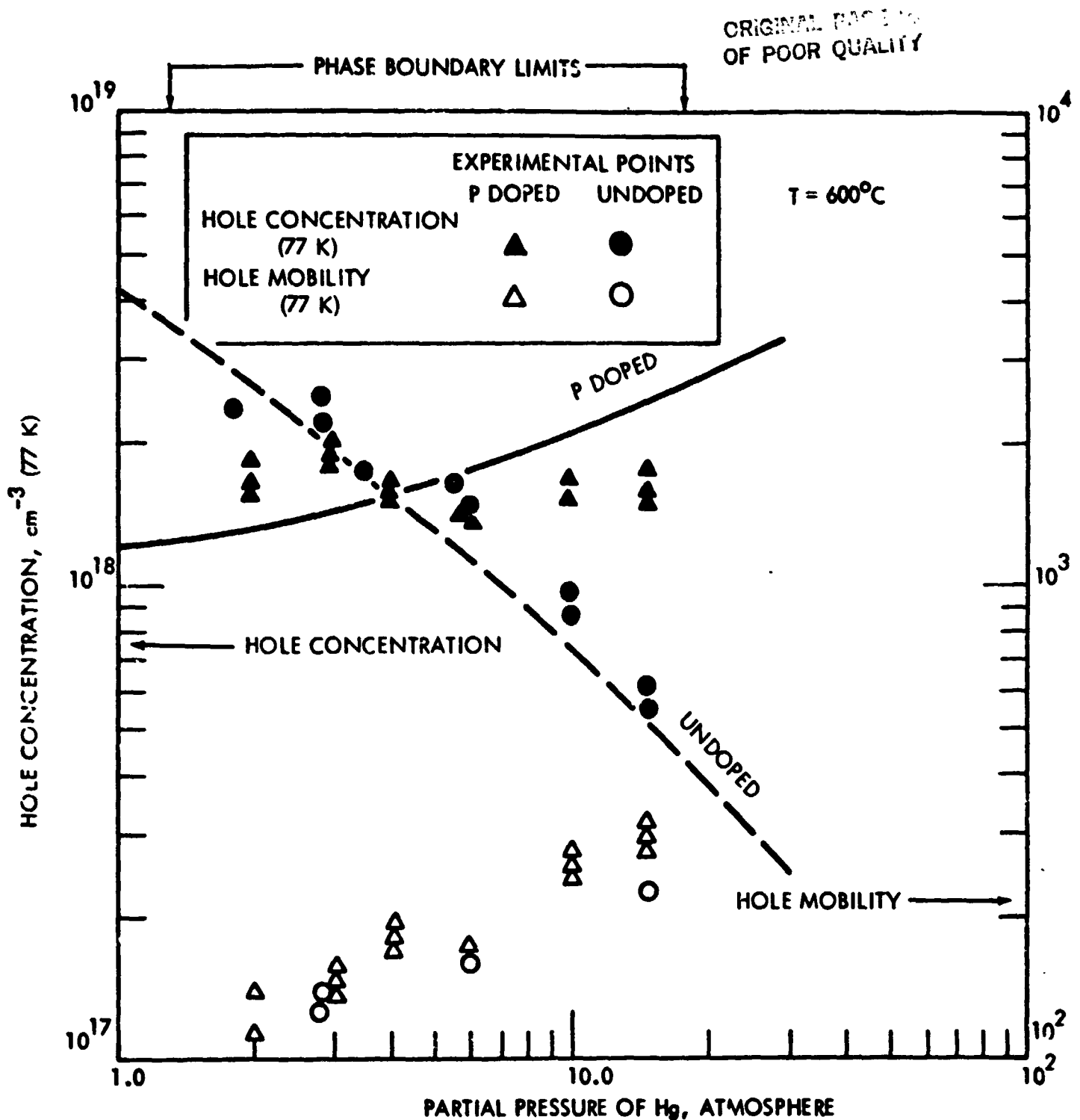the defect model.

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(3) The hole concentration in the phosphorus doped samples increases with increasing partial pressure of Hg; the hole concentrations at high Hg pressures are higher than found in the undoped crystals.

(4) The hole concentration in the samples annealed at 500°C and 450°C under very low Hg pressures is less than that obtained in the undoped samples for comparable annealing conditions.

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IV. DISCUSSION

A. Defect Equilibria

The way in which the concentration of defects varies as a function of the total phosphorus concentration in the crystals, temperature and partial pressure of Hg(g) (or partial pressure of $Te_2(g)$) is well described by the law of mass action approach pioneered by Kroger and Vink [8-9]. The defect structures of undoped $Hg_{0.8}Cd_{0.2}Te$ and $Hg_{0.6}Cd_{0.4}Te$, Indium doped and Iodine doped $Hg_{0.8}Cd_{0.2}Te$ have already been established using this approach [4,10-12]. In such an approach, the various defect formation reactions are formulated along with the respective mass action constants. All the species in the electroneutrality condition and the phosphorus balance equations are then expressed in terms of one of the phosphorus species, electrons or holes and the various mass action constants. For given values of the various mass action constants the solution of the electroneutrality and the phosphorus balance equations yields the concentration of all the defects as a function of the temperature of anneal, partial pressure of Hg and the concentration of phosphorus. Although exact solutions are sought using a fect model, the choice of the various possibilities is initially reduced by considering only the dominant members of the electroneutrality condition and approximating the phosphorus balance equation. When such approximations are used, simple solutions for the variation of the defects as a function of the partial pressure of Hg and phosphorus concentration fall out of the mass action relations; solutions will be of the form concentration $= p^r_{Hg}[P_{Tot}]^s$ where r and s are integers or fractions. The defect formation reactions along with the mass action relations, the electroneutrality condition and the phosphorus balance

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equation are all listed in Table I. Only those defects which were found to be important as a result of the present work are shown in Table I. Table II lists the exponents of the partial pressure of Hg and the phosphorus concentration for all the defects for various approximations to the electroneutrality condition and the phosphorus balance equation.

Table 1. DEFECT FORMATION REACTIONS, MASS ACTION RELATIONS, ELECTRONEUTRALITY CONDITION AND PHOSPHOROUS BALANCE EQUATION

Reaction | **Mass Action Relation**

1. $0 \to e' + h^\cdot$; $\qquad$ $K_i = [e'][h^\cdot]$

2. $Hg_{Hg}^x \to V_{Hg}'' + 2h^\cdot + Hg(g)$; $\qquad$ $K_{V_{Hg}'}' = [V_{Hg}''][h^\cdot]^2 \, p_{Hg}$

3. $2h^\cdot + (P_iP_{Hg})^x + Hg_{Hg}^x \to 2P_{Hg}^\cdot + Hg(g)$; $\qquad$ $K_{P_{Hg}} = [P_{Hg}^\cdot]^2 \, p_{Hg}/[h^\cdot]^2[(P_iP_{Hg})^x]$

4. $(P_iP_{Hg})^x + 3Hg(g) + 3Hg_{Hg}^x \to 2P_{Te}' + 2h^\cdot$; $\qquad$ $K_{P_{Te}} = [P_{Te}']^2 \, [h^\cdot]^2/[(P_iP_{Hg})^x] \, p_{Hg}^3$

5. $P_i' \to P_{Hg}^\cdot + (P_iP_{Hg})^x$; $\qquad$ $K_P(P_iP_{Hg})^x = [(P_iP_{Hg})^x]/[P_i'][P_{Hg}^\cdot]$

6. $P_{Hg}^\cdot + V_{Hg}'' \to (P_{Hg}V_{Hg})'$; $\qquad$ $K_P(P_{Hg}V_{Hg})' = [(P_{Hg}V_{Hg})']/[P_{Hg}^\cdot][V_{Hg}'']$

7. $(P_iP_{Hg})^x + 2h^\cdot + 3Hg_{Hg}^x \to 2(P_{Hg}V_{Hg})^\cdot + 3Hg(g)$; $\qquad$ $K(P_{Hg}V_{Hg})^\cdot = [(P_{Hg}V_{Hg})^\cdot]^2 \, p_{Hg}^3 \, / \, [(P_iP_{Hg})^x][h^\cdot]^2$

Electroneutrality Condition

$$[e'] + 2[V_{Hg}''] + [P_i'] + [P_{Te}'] + [(P_{Hg}V_{Hg})'] = [h^\cdot] + [P_{Hg}^\cdot] + [(P_{Hg}V_{Hg})^\cdot]$$

Phosphorus Balance Equation

$$[P_i'] + [P_{Hg}^\cdot] + [P_{Te}'] + [(P_{Hg}V_{Hg})'] + [(P_{Hg}V_{Hg})^\cdot] + 2[(P_iP_{Hg})^x] = [P_{Tot}]$$

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Table II. VARIATIONS OF THE DEFECT CONCENTRATIONS AS A FUNCTION OF p_{Hg} AND/OR PHOSPHORUS CONCENTRATIONS FOR VARIOUS APPROXIMATIONS TO THE ELECTRONEUTRALITY CONDITION AND PHOSPHORUS BALANCE EQUATION

Type of defect and approximation to the electroneutrality condition and phosphorus balance equation	$[\int \alpha\, p_{Hg}^{\,r}\, [P_{Tot}]^{\,s}]$	
	r	s
(1) $[e'] = [h^\bullet] = \mathcal{K}_i$ $[(P_i P_{Hg})^x] = [P_{Tot}]/2$	0	1
$[V_{Hg}'']$	-1	0
$[P_i^\bullet]$	$1/2$	$1/2$
$[P_{Hg}^\bullet]$	$-1/2$	$1/2$
$[P_{Te}']$	$3/2$	$1/2$
$[(P_{Hg}V_{Hg})']$	$-3/2$	$1/2$
$[(P_{Hg}V_{Hg})^\bullet]$	$-3/2$	$1/2$

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Table II VARIATIONS OF THE DEFECT CONCENTRATIONS AS A FUNCTION OF P_{Hg} AND/OR PHOSPHORUS CONCENTRATIONS FOR VARIOUS APPROXIMATIONS TO THE ELECTRONEUTRALITY CONDITION AND PHOSPHORUS BALANCE EQUATION(Cont.)

	r	s
$[e'] = [h^\cdot] = \sqrt{K_i}$	0	1
$[(P_{Hg}P_{Te})^x] = [P_{Tot}]/2$	-1	0
$[V''_{Hg}]$	0	1/2
$[P'_i]$	-1	1/2
$[P^\cdot_{Hg}]$	+1	1/2
$[P'_{Te}]$	-2	1/2
$[(P_{Hg}V_{Hg})']$	-2	1/2
$[(P_{Hg}V_{Hg})^\cdot]$		

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B. Choice of a Defect Model

Based on the fact that P belongs to group V, Hg to group II and Te to group VI, a number of different phosphorus species can be expected depending on the type of lattice sites occupied. These are:

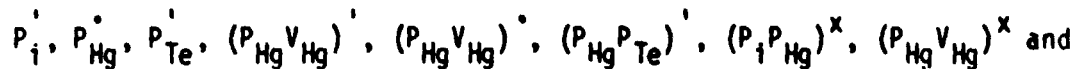|		
Interstitially	P_i', P_i'' ... P_i'''''	(Acceptors)
Substitutionally (occupying Hg lattice site)	$P_{Hg}^{\cdot}$, $P_{Hg}^{\cdot\cdot}$ and $P_{Hg}^{\cdot\cdot\cdot}$	(Donors)
Substitutionally (occupying Te lattice site)	P_{Te}'	(Acceptors)

Pairs - a) $(P_i P_{Hg})^X$, $(P_i P_{Hg})'$, $(P_i P_{Hg})^{\cdot}$

$(P_i P_{Hg})^{\cdot\cdot}$, $(P_i P_{Hg})''$, $(P_i P_{Hg})'''$, $(P_i P_{Hg})''''$

b) $(P_{Hg} V_{Hg})^X$, $(P_{Hg} V_{Hg})'$ and $(P_{Hg} V_{Hg})^{\cdot}$

c) $(P_{Hg} P_{Te})^X$, $(P_{Hg} P_{Te})^{\cdot}$ and $(P_{Hg} P_{Te})^{\cdot\cdot}$

The data shown in Figures 3 through 6 indicate that the hole mobility values obtained in the phosphorus doped samples are comparable to those in the undoped samples for similar partial pressures of Hg and temperatures of annealing even though at high Hg pressures, the hole concentrations in the phosphorus doped samples are higher than in the undoped samples. This inference already precludes the possibility of the presence of multiply electrically charged phosphorus species in large concentrations since such species can be expected to behave as much stronger scattering centers than the singly charged species,

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thus causing the hole mobility in the phosphorus doped samples to be considerably lower than the hole mobility in the undoped samples contrary to the experimental results. The species of interest are reduced to

$$P_i', \ P_{Hg}^{\bullet}, \ P_{Te}', \ (P_{Hg}V_{Hg})', \ (P_{Hg}V_{Hg})^{\bullet}, \ (P_{Hg}P_{Te})', \ (P_iP_{Hg})^X, \ (P_{Hg}V_{Hg})^X \ \text{and}$$

$(P_{Hg}P_{Te})^X$. The fact that the hole concentrations obtained in the phosphorus doped samples are much lower than the total phosphorus concentration in the samples (10^{19} cm^{-3}) indicates that most of the phosphorus is present as neutral species in the form of $(P_iP_{Hg})^X$, $(P_{Hg}V_{Hg})^X$ or $(P_{Hg}P_{Te})^X$. It is also to be noted that the hole concentrations obtained in the phosphorus doped samples (Figures 2 through 6) are smaller than the intrinsic carrier concentrations to be expected at the temperatures of anneal reported here [4].

The choice of a defect model is reduced to:

(1) $[e'] = [h^{\bullet}] = \sqrt{K_i} \neq f (p_{Hg})$ and $[(P_{Hg}P_{Te})^X] = [P_{Tot}/2]$

(2) $[e'] = [h^{\bullet}] = \sqrt{K_i} \neq f (p_{Hg})$ and $[(P_{Hg}V_{Hg})^X] = [P_{Tot}]$

and   (3) $[e'] = [h^{\bullet}] = \sqrt{K_i} \neq f (p_{Hg})$ and $[(P_iP_{Hg})^X] = [P_{Tot}]/2$

The expected power dependences of the various defects on the partial pressure of Hg for the above defect model situations are listed in Table II. Models 1 and 2 for which $[P_{Tot/2}] = [(P_{Hg}P_{Te})^X]$ or $[(P_{Hg}V_{Hg})^X]/2$ predict much stronger dependences of $[P_{Hg}^{\bullet}]$ on p_{Hg} and the search did not result in a consistent set of mass action constants for the incorporation of the various phosphorus species which could explain the experimental results of Figures 3

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through 6. The third defect model for which $[e'] = [h^\bullet] = \sqrt{K_i} \neq f(p_{Hg})$ and $[(P_i P_{Hg})^x] = [P_{Tot}]/2$ successfully explains the experimental results of Figures 3 through 6; for such a situation it can be deduced from the mass action relations of Table I that

$$[P_i'] \propto p_{Hg}^{1/2}, [P_{Hg}^\bullet] \propto p_{Hg}^{-1/2}, [P_{Te}'] \propto p_{Hg}^{3/2}, [(P_{Hg}V_{Hg})'] \propto p_{Hg}^{-3/2}$$

and $[(P_{Hg}V_{Hg})^\bullet] \propto p_{Hg}^{-3/2}$. These exponents are listed in Table II. It should be mentioned here that although our initial considerations for the electrically active phosphorus species were restricted to the simple species, P_i', $P_{Hg}^\bullet$ and P_{Te}', it was immediately realized that the experimental results warranted the introduction of the species $(P_{Hg}V_{Hg})'$ and $(P_{Hg}V_{Hg})^\bullet$ also.

The pairs $(P_{Hg}V_{Hg})^\bullet$ are formed from the association of the species $P_{Hg}^{\bullet\bullet\bullet}$ and V_{Hg}'' whereas $P_{Hg}^\bullet$ and V_{Hg}'' make up the pairs $(P_{Hg}V_{Hg})'$. The explanation for the presence of appreciable concentrations of $(P_{Hg}V_{Hg})^\bullet$ without the presence of large concentrations of isolated $P_{Hg}^{\bullet\bullet\bullet}$ species lies in the fact that the donor energy level of the $P_{Hg}^{\bullet\bullet}$ species (which upon ionization gives $P_{Hg}^{\bullet\bullet\bullet}$) may lie outside the forbidden gap (in the valence band) and pairing may bring its level to within the gap [13]. Examples of such level variations upon pairing have been found by us earlier for Cds: Ag [14] and Si: Se [15].

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C. DEFECT MODEL CALCULATIONS AND COMPARISON WITH EXPERIMENTAL RESULTS

In this section we examine the validity of the proposed defect model for phosphorus doped $Hg_{0.8}Cd_{0.2}Te$ from a comparison of the electrical data with those one calculates from the defect model. Although the defect model arrived at in the previous section took into consideration the mobility data also, it will become apparent from discussions in this section that the agreement between the experimental values and calculations (based on the defect model) is better for carrier concentration than for hole mobilities.

C.1 Analysis of the Carrier Concentration

According to the defect model deduced in the previous section, the phosphorus species of interest are P_i', $P_{Hg}^{\bullet}$, P_{Te}', $(P_{Hg}V_{Hg})'$, $(P_{Hg}V_{Hg})^{\bullet}$ and $(P_iP_{Hg})^x$.

The complete electroneutrality condition is written as:

$$[e'] + 2\,[V_{Hg}''] + [P_i'] + [P_{Te}'] + [(P_{Hg}V_{Hg})'] = [h^{\bullet}] + [P_{Hg}^{\bullet}] + [(P_{Hg}V_{Hg})^{\bullet}] \quad (1)$$

Expressing all the species in terms of $[h^{\bullet}]$, P_{Hg} and $[(P_iP_{Hg})^x]$ via the mass action relations listed in Table 1, we get:

$$\frac{K_i}{[h^{\bullet}]} + \frac{2\,K_{VHg}''}{P_{Hg}[h^{\bullet}]^2} + \frac{[(P_iP_{Hg})^x]^{1/2}\,P_{Hg}^{1/2}}{K_p\,(PiPHg)^x\,K_{P_{Hg}}^{1/2}\,[h^{\bullet}]}$$

$$+ \frac{K_{P_{Te}}^{1/2}\,P_{Hg}^{3/2}\,[(P_iP_{Hg})^x]^{1/2}}{[h^{\bullet}]}$$

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$$+ \frac{K_P (P_{Hg}V_{Hg})' K_{P_{Hg}} [(P_iP_{Hg})^X]^{1/2} K''_{VHg}}{[h^{\bullet}] P_{Hg}^{3/2}}$$

$$- [h^{\bullet}] - \frac{K_{P_{Hg}} [h^{\bullet}] [(P_iP_{Hg})^X]^{1/2}}{P_{Hg}^{1/2}}$$

$$- \frac{K^{1/2}_{(P_{Hg}V_{Hg})} \cdot [h^{\bullet}] [(P_iP_{Hg})^X]^{1/2}}{P_{Hg}^{3/2}} = 0 \qquad \text{-- (2)}$$

The phosphorus balance equation is written as:

$$[P_i'] + [P_{Hg}^{\bullet}] + [P_{Te}'] + [(P_{Hg}V_{Hg})'] $$

$$+ [(P_{Hg}V_{Hg})^{\bullet}] + 2 [(P_iP_{Hg})^X] = [P_{Tot}] \qquad \text{-- (3)}$$

The concentrations of the species P_i', P_{Te}', $(P_{Hg}V_{Hg})'$, $P_{Hg}^{\bullet}$ and $(P_{Hg}V_{Hg})^{\bullet}$ are respectively given by the III, IV, V, VII and VIII terms of equation (2).

The concentration of holes obtained in the crystals cooled to 77 K is given by:

$$P(77 \text{ K}) = [P_i'] + [P_{Te}'] + [(P_{Hg}V_{Hg})'] + 2 [V_{Hg}'']$$

$$— [P_{Hg}^{\bullet}] - [(P_{Hg}V_{Hg})^{\bullet}] \qquad \text{-- (4)}$$

(The assumption made here is that the electrons and holes recombine during quenching and only the atomic defects are frozen in [8-9].)

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The concentrations $[P_i']$, $[P_{Te}']$, $[(P_{Hg}V_{Hg})']$, $2\,[V_{Hg}'']$,

$[P_{Hg}^\bullet]$ and $[(P_{Hg}V_{Hg})^\bullet]$ in equation 4 are respectively given by the III,
IV, V, II, VII and VIII terms of equation (2).

Of the mass action constants K_i, K_{VHg}'', $K_{P_{Hg}}$, $K_{P_{Te}}$,
$K_{P(P_{Hg}V_{Hg})}'$ and $K_{(P_{Hg}V_{Hg})^\bullet}$, K_i and K_{VHg}'' are known from
earlier work on the undoped crystals [4] and are given by:

$$K_i = 9.16 \times 10^{40} \exp\,(-0.57\ eV/_{KT})cm^{-6} \qquad -- (5)$$

and

$$K_{VHg}'' = 1.58 \times 10^{69} \exp\,(-2.24\ eV/_{KT})cm^{9}\ atm \qquad -- (6)$$

With the knowledge of the constants K_i and K_{VHg}'' and $[P_{Tot}] = 10^{19}cm^{-3}$,
a procedure of trial and error was used to arrive at the values of the other
mass action constants such that a solution to equations 2 and 3 yielded hole
concentrations at 77 K (using equation 4) which agreed best with the
experimentally observed values; the concentrations of all the defects present
in the crystal are also immediately obtained from the various terms in equation
(2). The hole concentrations calculated from the defect model are shown in
Figures 3 through 6 as solid lines; the agreement between the calculation and
the experimental values appears satisfactory particularly at 450 C and 500 C.
The agreement is not as good at 550 C and 600 C probably due to quenching
inefficiency [4] at the higher temperatures. The calculated defect isotherms
for various annealing temperatures are shown in Figures 7 through 10. The
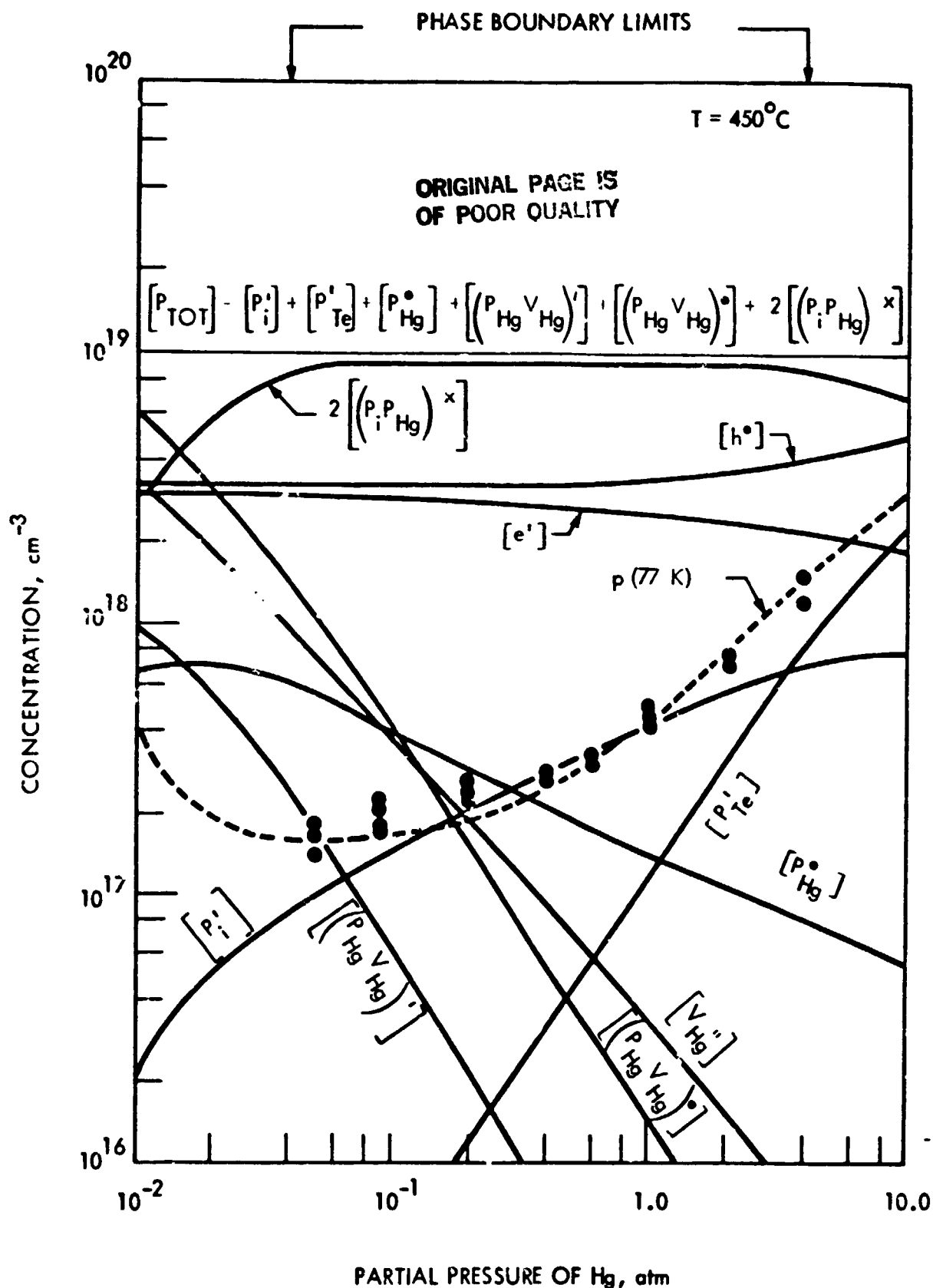
Figure 7. Calculated Concentrations of $[e']$, $[h\cdot]$, $[V_{Hg}'']$, $[F_i']$, $[P_{Te}']$, $[P_{Hg}^\bullet]$, $[(P_{Hg}V_{Hg})^\bullet]$, $[(P_{Hg}V_{Hg})']$ and $[(P_iP_{Hg})^x]$ as a Function of the Partial Pressure of Hg at 450°C; the expected hole concentration in the crystals cooled to 77 K is indicated as a dashed line along with the experimental results.
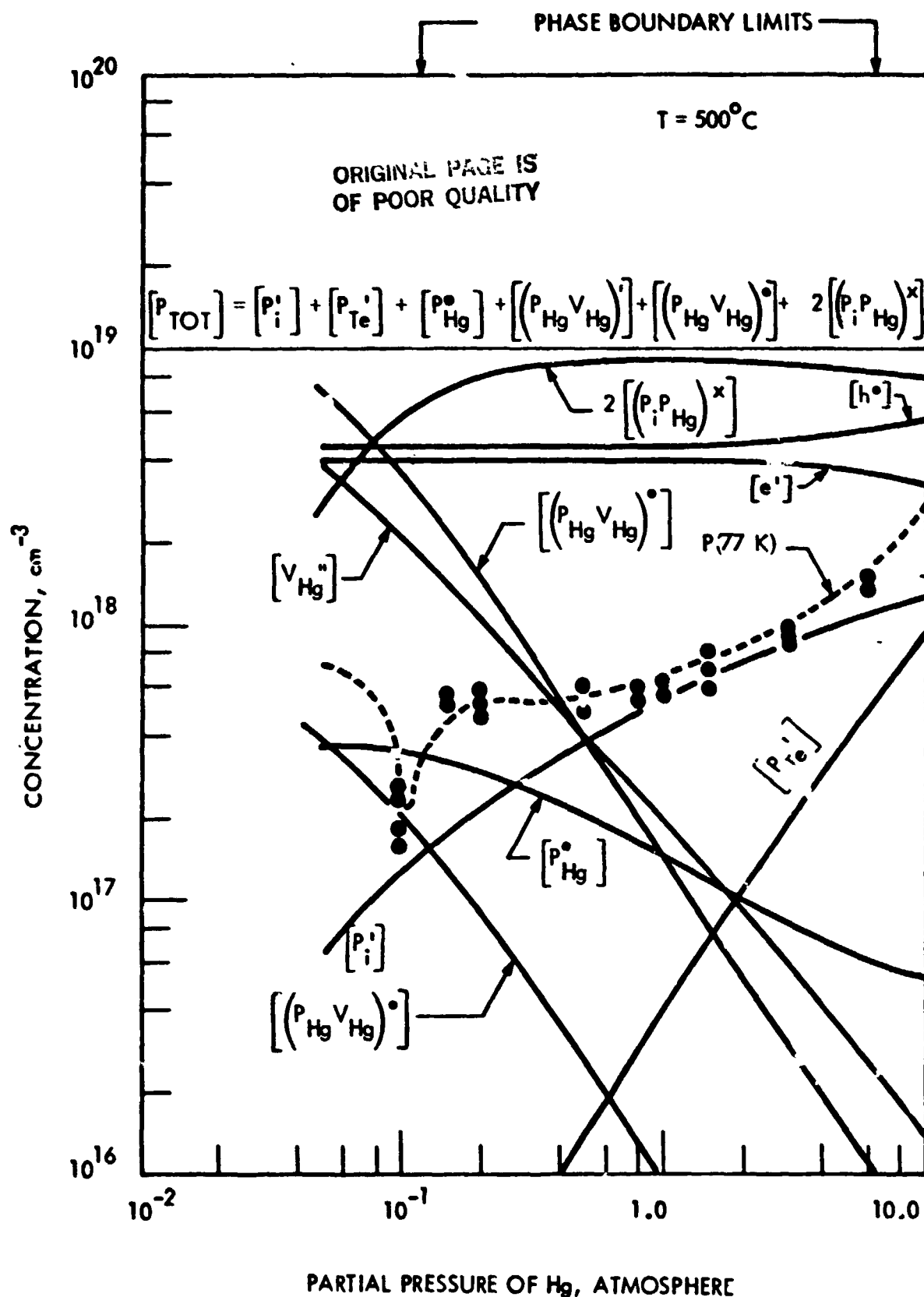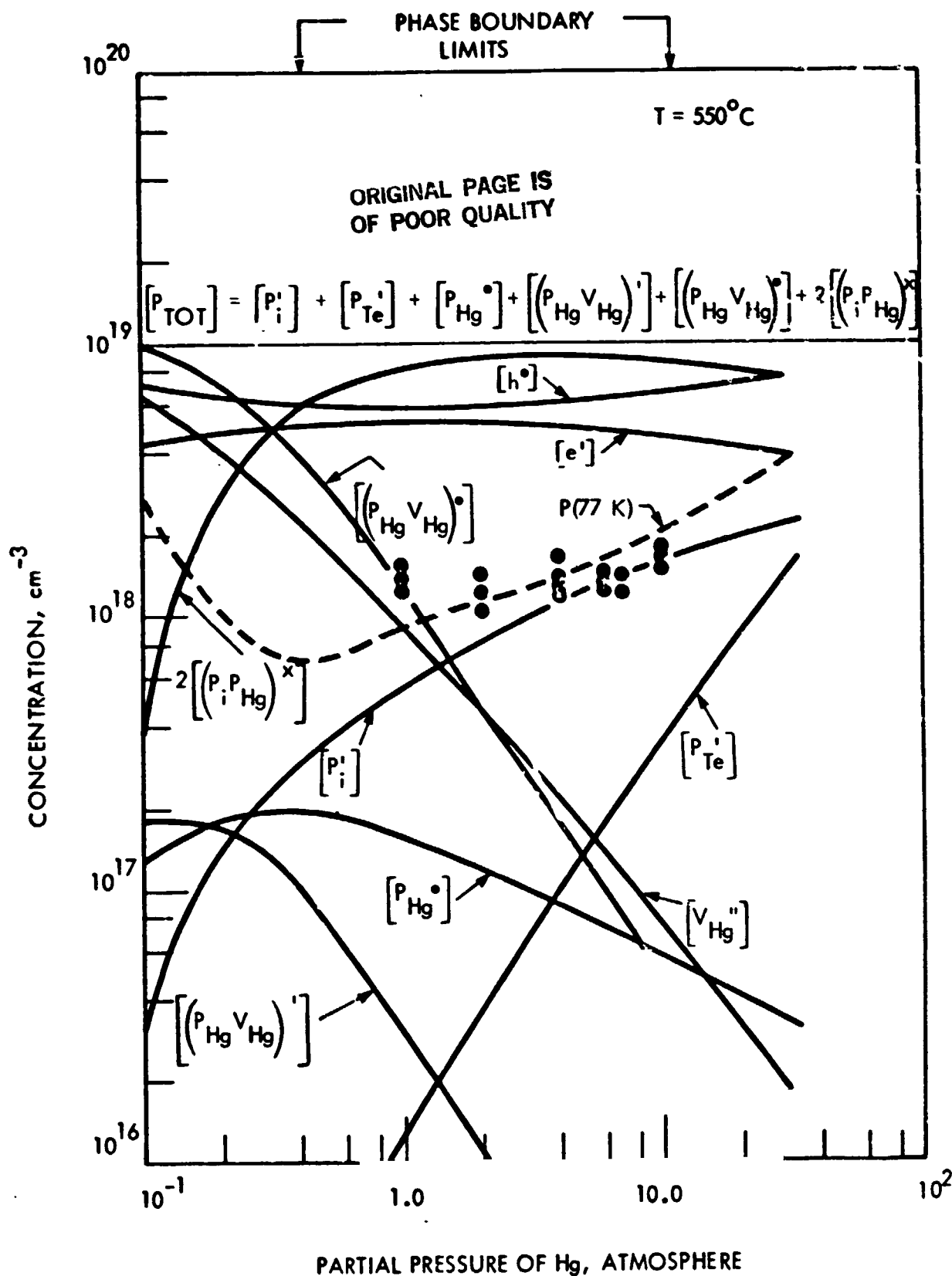
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Figure 8. Calculated Concentrations of $[e']$, $[h \cdot]$, $[V''_{Hg}]$, $[P_i']$, $[P_{Te}']$, $[P^{\cdot}_{Hg}]$, $[(P_{Hg}V_{Hg})^{\cdot}]$, $[(P_{Hg}V_{Hg})']$ and $[(P_iP_{Hg})^x]$ as a Function of the Partial Pressure of Hg at 500°C; the expected hole concentration in the crystals cooled to 77 K is indicated as a dashed line along with the experimental results.

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$$[P_{TOT}] = [P_i'] + [P_{Te}'] + [P_{Hg}^\bullet] + [(P_{Hg}V_{Hg})'] + [(P_{Hg}V_{Hg})^\bullet] + 2[(P_iP_{Hg})^x]$$

PARTIAL PRESSURE OF Hg, ATMOSPHERE

Figure 9. Calculated Concentrations of $[e']$, $[h\cdot]$, $[V_{Hg}'']$, $[P_i']$, $[P_{Te}']$, $[P_{Hg}^\bullet]$, $[(P_{Hg}V_{Hg})^\bullet]$, $[(P_{Hg}V_{Hg})']$ and $[(P_iP_{Hg})^x]$ as a Function of the Partial Pressure of Hg at 550°C; the expected hole concentration in the crystals cooled to 77 K is indicated as a dashed line along with the experimental results.
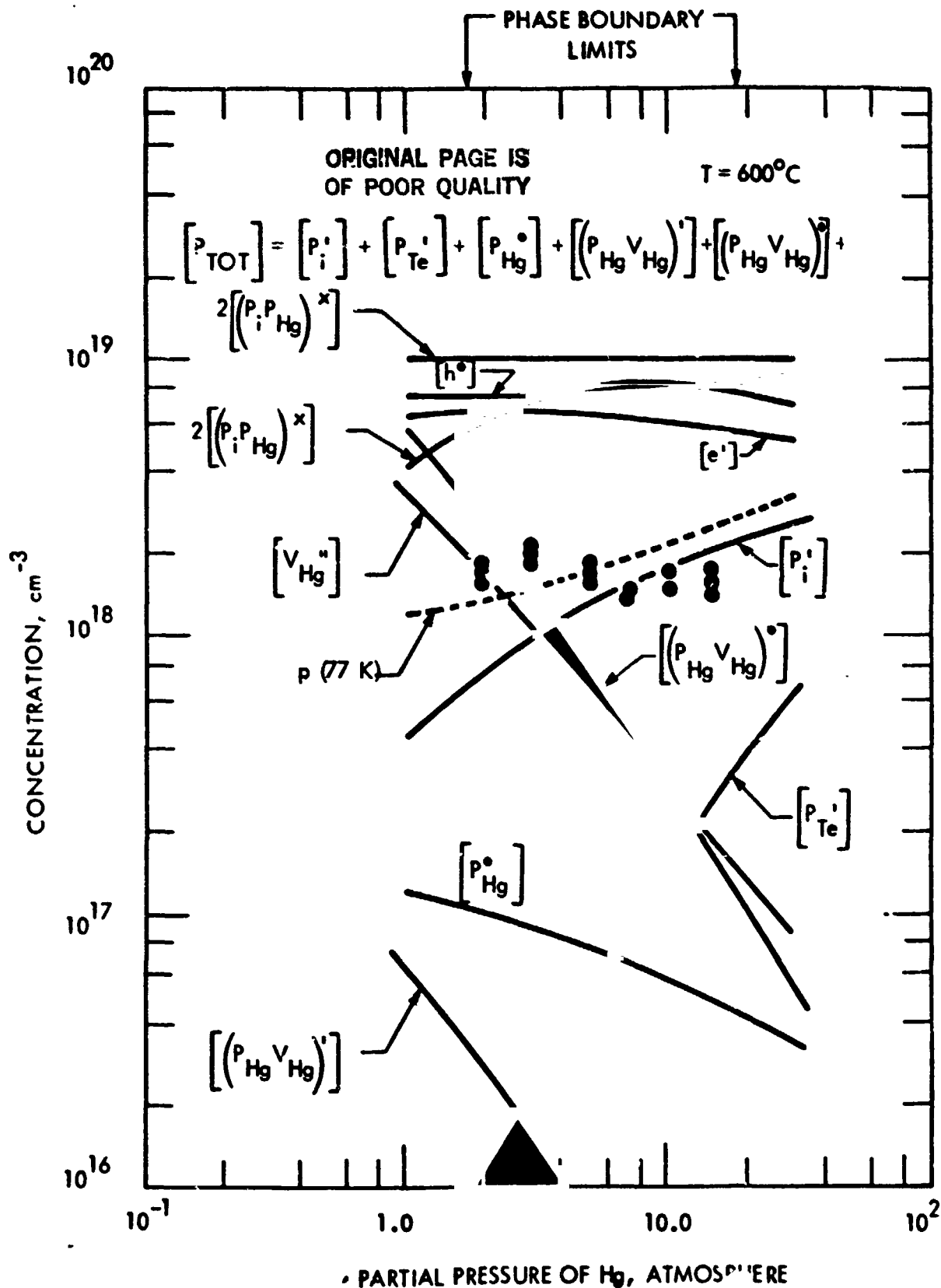
3-78

Figure 10. Calculated Concentrations of $[e']$, $[h\cdot]$, $[V''_{Hg}]$, $[P_i']$, $[P_{Te}']$, $[P^\bullet_{Hg}]$, $[(P_{Hg}V_{Hg})^\bullet]$, $[(P_{Hg}V_{Hg})']$ and $[(P_iP_{Hg})^x]$ as a Function of the Partial Pressure of Hg at 600°C; the expected hole concentration in the crystals cooled to 77 K is indicated as a dashed line along with the experimental results.

defect isotherms show the concentration of the electrons, holes and the various phosphorus defect species as a function of the partial pressure of Hg. The calculated hole concentrations expected at 77 K along with the experimental values are also indicated in the figures. It is apparent from the defect isotherms that the crystal is essentially intrinsic at the annealing temperature except at Hg pressures close to Hg saturated or Te saturated conditions indicated by the phase boundary limits in the figures. It should also be noted that most of the phosphorus is present as neutral $(P_iP_{Hg})^x$ almost throughout the existence region of the crystal except at Hg pressures close to the Hg saturation and Te saturation conditions where the electrically active phosphorus species become significant in concentration. The calculated hole concentrations at 77 K are extremely sensitive to the value of the total phosphorus concentration in the crystals at the lowest Hg pressures where the crystals are very closely compensated (Figures 7 through 10) and the hole concentration in the cooled crystals is much smaller than the concentration of the electrically active native as well as phosphorus defects.

The mass action constants for the incorporation of the various phosphorus species resulting from the present work are listed in Table III.

Table III. VALUES OF THE PARAMETERS FOR THE EQUILIBRIUM CONSTANTS

$K = K_o \exp(-H/KT)$ defined in Table 1.

EQUILIBRIUM CONSTANT	K_o (SITE FR., ATM)	H (EV)	SOURCE
1 K_i	5.77×10^{-4}	0.57	Ref. 4
2 K''_{VHg}	7.9×10^{2}	2.24	
3 Kp_{Hg}	1.36×10^{-2}	-0.360	This Work
4 Kp_{Te}	1.81×10^{-26}	-1.73	
5 $Kp(PiP_{Hg})^x$	1.76×10^{4}	-0.252	
6 $Kp(P_{Hg} V_{Hg})$	17	-0.36	
7 $K(P_{Hg} V_{Hg})$	2.1×10^{28}	4.29	

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C.2. Coulombic Values for the Pairing Constants $K_{P(P_i-P_{Hg})}x$ and $K_{i'(P_{Hg}V_{Hg})}$'

The pairing constant is given by $\overset{o}{K}_P = K_p \exp(-H_P/KT)$. The Coulombic value for the enthalpy of pairing is given by

$$H_P = \frac{-Z_1Z_2q^2}{\epsilon r} \quad [ref. 13] \tag{7}$$

Where Z_1 and Z_2 refer to the charges of the two species comprising the pair, and r to the distance between them.

Noting that $r_{P_i - P_{Hg}} = 3.23$ Å and

$$r_{P_{Hg} - V_{Hg}} = 4.5 \text{ Å}$$

$$H_{P(P_i P_{Hg})}x = -0.252 \text{ ev}$$

$$\text{and} \quad H_{P(P_{Hg}V_{Hg})}' = -0.36 \text{ ev}$$

while analyzing the Hall effect data, the constants $K_{P(P_i P_{Hg})}x$ and $K_{P(P_{Hg}V_{Hg})}$' were chosen such that their temperature dependences were close to the above coulombic values (Table III). The preexponent or the entropy term (K_P^o) is expected to be ~ 4.0 [13]. However, as can be noted from Table III, the preexponents needed to explain the experimental results are much larger than 4 particularly for $K_{P(P_i P_{Hg})}x$.

C.3. <u>Analysis of the Hole Mobility</u>

It is known from the results of previous work [4] that ionized impurity scattering contributes to the mobility of holes at 77 K in $Hg_{0.8}Cd_{0.2}Te$. Similar to the procedures used previously, [4] we have undertaken to calculate the hole mobility due to ionized impurity scattering which is then used to calculate the overall mobility by reciprocally combining the mobility due to lattice scattering with the mobility due to ionized impurity scattering. The number of ionized impurity scattering centers obtained at different Hg pressures for different temperatures of anneal as calculated from the defect model is shown in Figures 7 through 10.

For a non-degenerate semiconductor with parabolic bands the mobility due to ionized impurity scattering as given by the Brooks Herring Expression is

$$\mu_I = 2^{7/2} \pi^{-3/2} (kT)^{3/2} (\epsilon_0 \epsilon_s)^2 (m_c)^{-1/2} (m^*/m_0)^{-1/2} N_I^{-1} \left\{ \log_e (1+b) - \frac{b}{1+b} \right\}^{-1}$$

where $b = \dfrac{24 \, m_0 \, (m^*/m_0) \, k^2 \, (\epsilon_0 \epsilon_s)}{e^2 \, h^2 \, p'}$

$$\hspace{10cm} (8)$$

and $p' = p + (N_A - N_D - p) (p + N_D)/N_A$ $\hspace{3cm}$ (9)

In the ab. expressions, k is the Boltzmann's constant, T is the temprature, ϵ_0 is the free space permittivity, ϵ_s is the static dielectric constant, m_0 is the free electron mass, (m^*/m_0) is the effective mass ratio for holes, N_I is the number of scattering centers given by the total number of ionized donors and acceptors, e is the electronic charge and $\hbar$ is the planck's constant.

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with T = 77 K, (m^*/m_0) (holes) = 0.7 [16] ϵ_s = 17.5 [16] the expression for the mobility due to ionized impurity scattering becomes

$$\mu_I = 10^{21} N_I^{-1} \left\{ \log_e (1+b) - \frac{b}{1+b} \right\}^{-1} \qquad (10)$$

and $b = 1.05 \times 10^{19}/p'$ (11)

for undoped crystals $N_I = 4 \; [V''_{Hg}]$ (12)

for phosphorus doped crystals

$$N_I = [P_i'] + [P_{Te}'] + [P_{Hg}^\bullet] + [(P_{Hg}V_{Hg})'] + [(P_{Hg}V_{Hg})^\bullet] + 4 \; [V''_{Hg}] \qquad (13)$$

The multiplying factor of 4 for the species V''_{Hg} arises in expressions 12 and 13 for N_I since these centers are doubly charged (z=2) and hence four times as strong in scattering as the singly charged centers. Since the defects are completely ionized at 77 K in both the undoped crystals and the phosphorus doped crystals (Figure 1)

$p' = p$ (77 K) $= 2 \; [V''_{Hg}]$ (anneal temperature) for the undoped crystals

and $p' = p$ (77 K) $= [P_i'] + [P_{Te}'] + [(P_{Hg}V_{Hg})'] + 2 \; [V''_{Hg}] - [P_{Hg}^\bullet] - [(P_{Hg}V_{Hg})^\bullet]$

for the phosphorus doped crystals.

From the values of p (77 K) for the phosphorus doped crystals and the concentrations of all the defects as a function of the partial pressure of Hg as given by the defect isotherms of Figures 7 through 10, the hole mobility due to ionized impurity scattering was calculated by reciprocally adding the lattice mobility and the mobility due to ionized impurity scattering. From the results on undoped crystals, the hole mobility due to lattice scattering was assumed to be - 700 cm^2/vsec at 77 K for $Hg_{0.8}Cd_{0.2}Te$ [4]. The results are shown in Figures 11 through 14 where calculated hole mobility is shown as a function of the partial pressure of Hg for various temperatures of anneal; the experimentally measured hole mobilities are also shown in the figures. From the figures, it is apparent that the trend in the variation of the calculated hole mobility as a function of the partial pressure of Hg agrees with the experimental results for the phosphorus doped crystals as well as the undoped crystals. The calculated values for the phosphorus doped crystals decrease drastically at the lowest Hg pressures since the total number of charged defects increases rather strongly under Hg deficient conditions (Figures 7 through 10); in addition, the expected hole concentrations at these low Hg pressures are much lower than for the undoped crystals particularly at 450°C and 500°C. The reduced screening (due to the low hole concentrations) of the coulombic field of the ionized scattering centers along with the rather high concentration of charged defects explains the drastic decrease of the calculated hole mobility at the lowest Hg pressures. However, the experimental hole mobilities are larger than the calculated values at the lowest Hg pressures. The discrepancy can be qualitatively explained by assuming that a fraction of the charged phosphorus defects precipitates during cooling. More sophisticated calculations are needed to explain the results better.
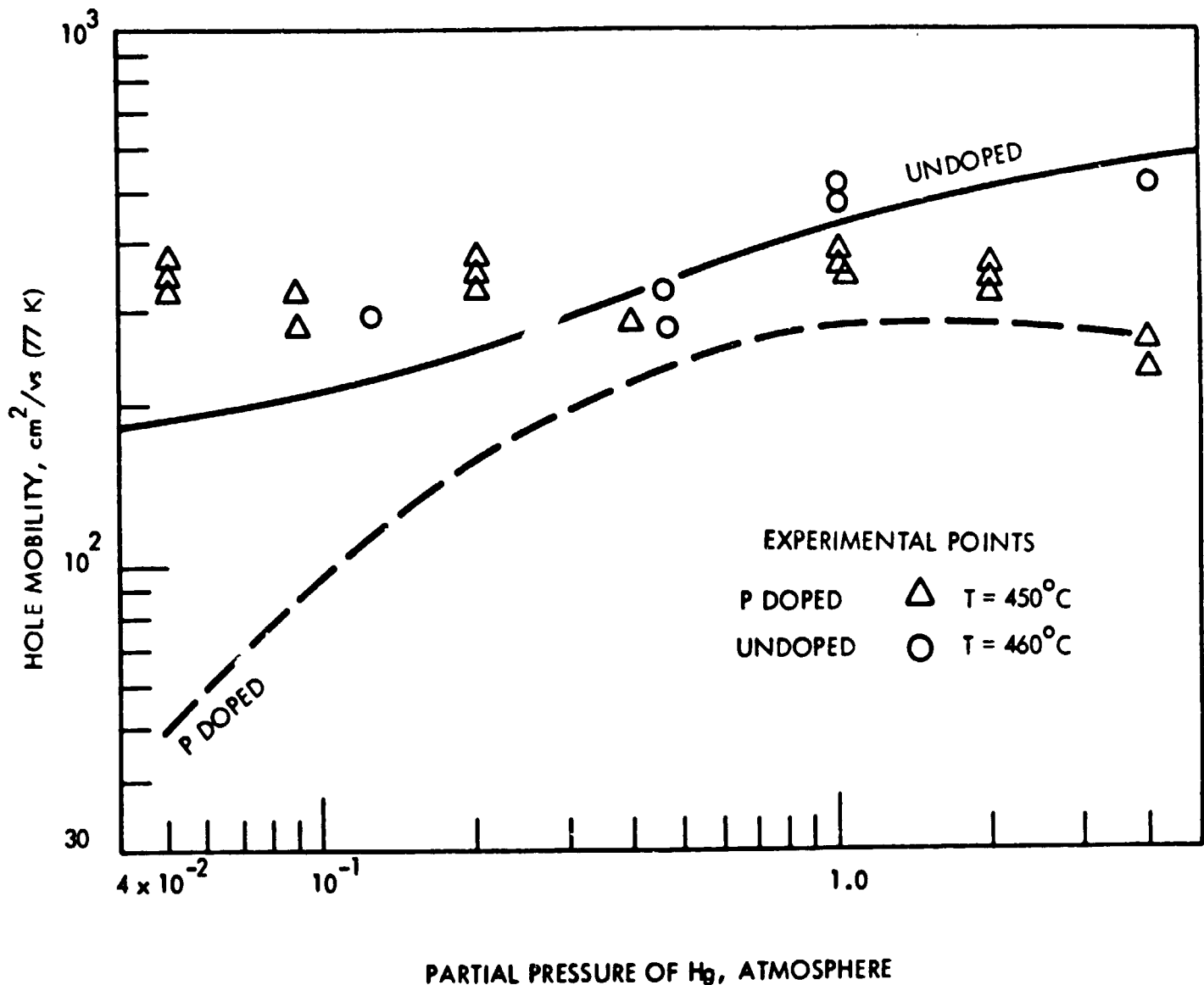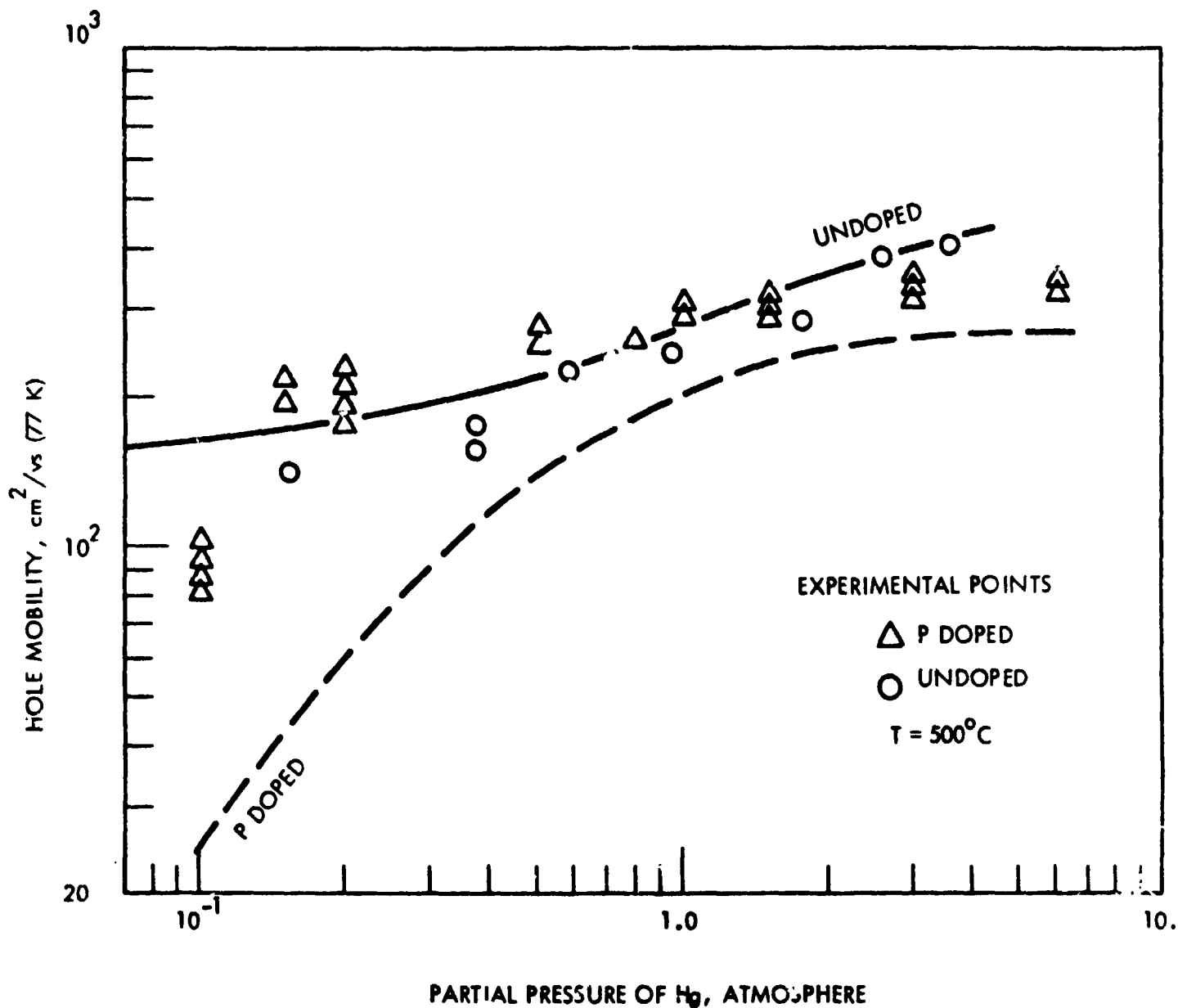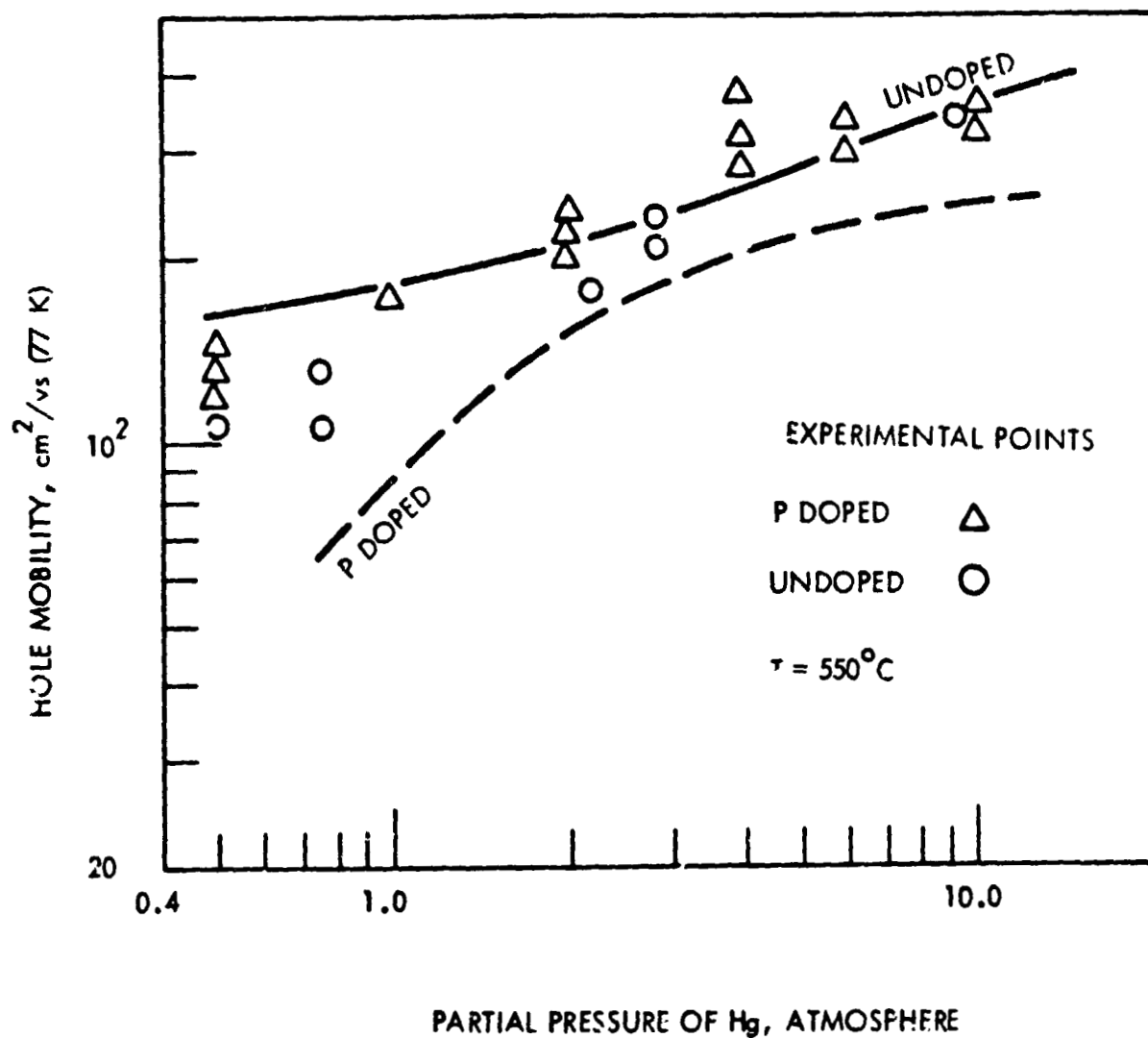
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Figure 11. Calculated Hole Mobility at 77 K as a Function of the
Partial Pressure of Hg for Phosphorus Doped ($10^{19}cm^{-3}$)
$Hg_{0.8}Cd_{0.2}$Te Samples Quenched to Room Temperature ..ter
Equilibration at 450°C; calculation for the und..ped crystals
after equilibration at 460°C is also shown along with the
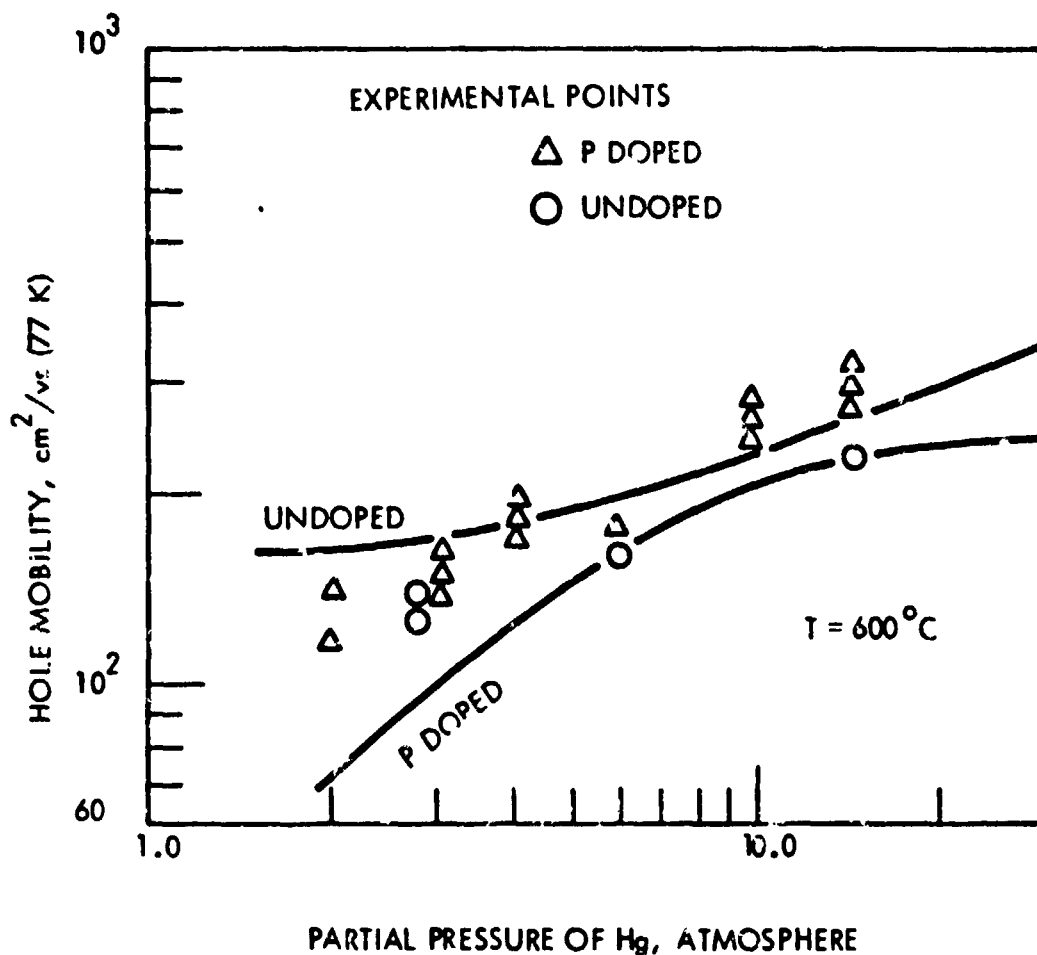experimental values for both the doped and the undoped
crystals.

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Figure 12. Calculated Hole Mobility at 77 K as a Function of the Partial Pressure of Hg for Phosphorus Doped ($10^{19} cm^{-3}$) and Undoped $Hg_{0.8}Cd_{0.2}Te$ Crystals Quenched to Room Temperature After Equilibration at 500°C; experimental values are also shown for comparison.

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Figure 13. Calculated Hole Mobility at 77 K as a Function of the
Partial Pressure of Hg for Phosphorus Doped ($10^{19}cm^{-3}$)
and Undoped $Hg_{0.8}Cd_{0.2}Te$ Crystals Quenched to Room
Temperature After Equilibration at 550°C; experimental
values are also shown for comparison.

8703-01

Figure 14. Calcul?ted Hole Mobility at 77 K as a Function of the Part?l Pressure of Hg for Phosphorus Doped ($10^{19}cm^{-3}$) and Undoped $Hg_{0.8}Cd_{0.2}Te$ Crystals Quenched to Room Temperature After Equilibration at 600°C; experimental values are also shown for comparison.

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D. Comparison with the Defect State in Phosphorus Doped CdTe

The defect model established in the present work for phosphorus doped $Hg_{0.8}Cd_{0.2}Te$ is very similar to the one established for phosphorus doped CdTe [1]. In both $Hg_{0.8}Cd_{0.2}Te$ and CdTe, phosphorus occupies interstitial and Te lattices acting as an acceptor while it acts as a donor occupying metal lattice sites. The difference however is that isolated phosphorus donor species are found to be triply ionized in CdTe [1] whereas in $Hg_{0.8}Cd_{0.2}Te$ it is found to be present only in the singly ionized state. Considering that the band gap of $Hg_{0.8}Cd_{0.2}Te$ is only 0.1 eV compared with the value of 1.6 eV for CdTe it is understandable that the energy levels of the doubly and triply ionized states of the phosphorus donor species could lie below the valance band edge in $Hg_{0.8}Cd_{0.2}Te$ whereas they lie within the gap in CdTe. In both $Hg_{0.8}Cd_{0.2}Te$ and CdTe a large concentration of phosphorus is found to be present as neutral pairs $(P_{Hg}P_i)^X$ and $(P_{Cd}P_i)^X$ respectively. At low Hg pressures a considerable fraction of phosphorus is found to be present as $(P_{Hg}V_{Hg})'$ and $(P_{Hg}V_{Hg})^{\cdot}$ in $(Hg_{0.8}Cd_{0.2})Te$ whereas similar species $(P_{Cd}V_{Cd})'$ and $(P_{Cd}V_{Cd})^{\cdot}$ have not been reported for CdTe [1].

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Phosphorus doped $Hg_{0.8}Cd_{0.2}Te$ single crystals were annealed at 450°C to 600°C in different partial pressures of Hg. Hall effect measurements were made on crystals quenched to room temperature after the anneals. The results are explained on the basis of a defect model in which phosphorus behaves amphoterically acting as a single acceptor in interstitial sites at high Hg pressures and occupying Te lattice sites (P_i' and P_{Te}') and as a single donor occupying Hg lattice sites ($P_{Hg}^{\bullet}$). Most of the phosphorous appears to be present as neutral pairs $(P_iP_{Hg})^X$ at moderate Hg pressures while a considerable fraction also exists paired with the native acceptor defects $(P_{Hg}V_{Hg})'$ and $(P_{Hg}V_{Hg})^{\bullet}$ at low Hg pressures. Equilibrium constants for the incorporation of the various phosphorous species have been evaluated.

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REFERENCES

1. F.A. Selim and F.A. Kröger, J. Electrochem. Soc. 124, 401 (1977).

2. R.B. Hall and H.H. Woodbury, J. Appl. Phys., 39, 5361 (1953).

3. D.A. Nelson, W.M. Higgins and R.A. Lancaster, Proc. SPIE 225, 48 (1980).

4. H.R. Vydyanath, J. Electrochem. Soc. 128, 2609 (1981).

5. T. Tung, L. Golinka and R.F. Brebrick, J. Electrochem. Soc. 128, 451 (1981).

6. L.J. van der Pauw, Philips Tech. Rev. 20, 220 (1959).

7. R.A. Smith, "Semiconductors" (Cambridge University Press), (1968).

8. F.A. Kröger and H.J. Vink, Solid State Physics III (Edited by F. Seitz and D. Turnbull) p. 307, Academic Press, New York (1956).

9. F.A. Kröger, "The Chemistry of Imperfect Crystals," Second Revised Edition, Volume 2, Chs 14 to 16. North Holland (1974).

10. H.R. Vydyanath, J.C. Donovan and D.A. Nelson, J. Electrochem. Soc. 128, 2625 (1981).

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REFERENCES (Cont.)

11. H.R. Vydyanath, J. Electrochem. Soc. 128, 2619 (1981).

12. H.R. Vydyanath and F.A. Kröger, J. Electronic Materials (Jan. 1982 issue)

13. Ref. 9, Ch. 10.

14. H.R. Vydyanath and F.A. Kröger, J. Phys. Chem. Solids 36, 509 (1975).

15. H.R. Vydyanath, J.S. Lorenzo and F.A. Kröger, J. Appl. Phys. 49, 5928 (1978).

16. R. Dornahaus and G. Nimtz, Solid State Physics, Vol. 78, Springer-Verlag, New York (1976).

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SECTION 4
SUMMARY

Single crystal samples of undoped and doped $Hg_{1-x}Cd_xTe$ were annealed at varying temperatures and partial pressures of Hg. Hall effect and mobility measurements were carried out on these samples after quenching to room temperature. Based on the variation of the carrier concentration and the carrier mobility as a function of the partial pressure of Hg, temperature and dopant concentration, defect models have been established for the doped and the undoped crystals. These models indicate that the native acceptor defects in both $Hg_{0.8}Cd_{0.2}Te$ and $Hg_{0.6}Cd_{0.4}Te$ are doubly ionized and the native donor defects are negligible in concentration, implying that p to n conversion in these alloys occurs due only to residual donors. Incorporation mechanisms of copper, indium, iodine and phosphorus have been investigated. Copper and indium appear to occupy only Hg lattice sites acting as single acceptor and single donor respectively, whereas iodine is found to act as a single donor occupying only Te lattice sites. A large concentration of indium is found to be incorporated as In_2Te_3 with only a small fraction acting as donors. In crystals doped with iodine a large fraction of iodine is found to be paired with the native acceptor defects. Results on crystals doped with phosphorus indicate that phosphorus behaves amphoterically acting as a donor on Hg lattice sites and as an acceptor interstitially on Te lattice sites. A majority of the phosphorus is found to be present as neutral species formed from the pairing reaction between phosphorus on Hg lattice sites and phosphorus in interstitial sites. Equilibrium constants for the intrinsic excitation reaction as well as for the incorporation of the different dopants and the native acceptor defects have all been established. These constants satisfactorily explain all the experimental results in the undoped as well as the doped crystals.

As a result of the work performed on this program, it is possible to predict the nature and concentration of defects obtained in $Hg_{1-x}Cd_xTe$

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compounds as a function of the annealing temperature, partial pressure of Hg and dopant concentration. It is now possible to vary the concentration of defects controllably as a function of the crystal preparation conditions and in turn correlate the physical characteristics such as carrier lifetime and carrier concentrations with defect centers in the crystals.