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DARK CONDUCTIVITY OF CdS AS A FUNCTION OF S-VAPOR PRESSURE DURING HEAT TREATMENT BETWEEN 500° and 700°C*

by

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Abstract

The dark conductivity of CdS as a function of the sulfur vapor pressure is investigated during heat treatment in a temperature range $500^\circ < T < 700^\circ C$. The pressure dependence follows $j \sim p_S^{-1/m}$ with $m = \ell x$, ℓ being the average number of sulfur atoms per molecule. For $500^\circ < T < 525^\circ C$, $x = 3$, for $525^\circ < T < 630^\circ C$, $x = 1$ and for $630^\circ < T < 700^\circ C$, $x = 1$. These results are explained by thermodynamic disorder and a Cd-rich nonstoichiometric equilibrium below 525°C. Schottky-Wagner disorder most probably is dominant above 525°C. The energy of doubly ionizing a sulfur vacancy is $E_c - E_{V_S} = 0.48$ ev.

Es wurde die Dunkelleitfähigkeit von CdS als Funktion des Schwefeldampfdruckes während der Temperung zwischen 500° und

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700°C untersucht. Der Dunkelstrom genügt $j \sim p_S^{-1/m}$ mit $m = \ell x$, wobei ℓ die mittlere Anzahl von Schwefelatomen per Molekül ist. Es wurde gefunden, dass $x = 3$ für $500^0 < T < 525^0$, $x = 1$ für $525^0 < T < 630^0$C und $x = 3$ für $630^0 < T < 700^0$C ist. Die Ergebnisse wurden durch Thermodynamische Fehlordnung und durch Cd - Überschuss-nichtstöchiometrisches Gleichgewicht unterhalb 525°C erklärt. Schottky-Wagner Fehlordnung ist höchstwahrscheinlich oberhalb 525°C vorherrschend. Die Energie zur zweifachen Ionisierung einer Schwefellücke $E_c - E_{V_S}$ ist 0.48 eV.

1. Introduction

For obtaining contributions to the understanding of the intrinsic defect structure of CdS, heat treatments of these crystals in Cd- or S- vapor have been performed and connected changes in the dark-conductivity, photo-conductivity and luminescence have been studied.

Objections were made to earlier experiments, in which the treatments were conducted at relatively high temperatures ($T > 800^0$C) and the crystals cooled very rapidly, in an attempt to freeze-in the presumably equilibrium-state at high temperatures[1]. Most objectionable is the fact that different defect-

chemical reactions have a different freezing-in temperature, and during cooling there will be a separation of these freezing-in temperatures. Therefore, to the frozen-in state, one cannot assign one equilibrium temperature for processes activated at the treatment temperature, - besides the fact that freezing-in temperatures will be, possibly considerably, below the treatment temperature and are unknown.

In order to investigate the problem of shifting the stoichiometry under different conditions, more recently electrical measurements and vapor treatments have been performed simultaneously[2,3]. The difficulties here lie in the fact that - intentionally - one has to work with a system which is not in complete thermodynamic equilibrium. The electrode-CdS system has to stay frozen-in, while, hopefully, the vapor-CdS system is at equilibrium.

Unfortunately no electrode material is presently known which does not diffuse into the CdS or is attacked by the corrosive Cd- or S- vapor at temperatures at which one can be reasonably sure that otherwise equilibrium can be achieved within a "laboratory time span", e.g. one hour. From treatment experiments without electrodes it is known that one has to go above 800°C in order to obtain certain changes in electrical or optical properties of CdS after one hour treatment and rapid cooling. On the other hand electrical measurements

during S- treatments have been made only up to 572°C due to electrode problems.

These experiments were encouraged by the fact that at these temperatures rapid changes in electrical conductance had been observed. A quantitative analysis of the time dependence of the current after rapid changes of the vapor pressure[2] indicated that the observed effect cannot be explained only by a change at the surface, but that some diffusion through the entire crystal must take place. A time constant for this diffusion of less than an hour has been reported[2].

The observation of "diffusion-time constants" of the same order of magnitude (recently supplemented by direct tracer analysis[4,5]) at temperatures between 550° and about 900°C indicates that obviously different processes for diffusion must be involved which are activated at different threshold temperatures.

In order to contribute information to this question S- vapor treatments and simultaneous electrical measurements were extended over a larger temperature range.

2. Experimental Metnod

"Undoped" CdS single crystal platelets, obtained by sublimation of CdS powder in an N_2 - H_2S atmosphere at about 1000°C, were used. For lower temperature treatments, evaporated Au and Au covered with Pt electrodes were employed. Two small electrodes between the current electrodes were applied for potential probing (elimination of barrier layers). At temperatures above 600°C the electrodes started to diffuse rapidly into the crystal. Here Au-wire point contacts were used which gave useful results up to treatment temperatures of 700°C after "formation" with a current pulse (10 ma) at about 500°C. Again four point probing was used. The results with Au-point contacts agree reasonably well with the results obtained with evaporated Au-layers at lower temperatures as long as the crystal was not subjected to a treatment above 650°C for an extended period of time.

For the treatment a two vessel, two oven arrangement in vertical alignment as given in Figure 1 was used. In the lower oven the temperature and consequently the vapor pressure of the sulfur was adjusted. The upper vessel contained the CdS platelet and was connected by a 2mm diameter capillary with the lower vessel. Both quartz vessels were thermally shielded with fibrofax from each other. The temperature was measured

inside both vessels with two Pt/Pt-Rh thermocouples, enclosed in quartz capillaries. The crystal was mounted on a quartz plate with the aid of quartz springs and Au-wire. The wire feedthrough was initially sealed with torrseal and during the measurements permanently sealed with distilled sulfur, having in equilibrium, automatically, a surface temperature T_s equal to the temperature in the sulfur vessel.

The sulfur used was 99.999% pure and carbonydrate-free, vacuum-distilled in the vessel. Before sealing the vessel, it was outgassed and evacuated to 10^{-6} torr.

The current through the crystal and both probe potentials were continuously recorded.

Due to difficulties with electrodes only a few treatments could be made per crystal. As soon as lower temperature conductivities became not reproducible or the potential probes indicated excessive barriers, the crystal was discarded and the measurement continued with a new crystal. Ten crystals were used for the measurements reported here; all of them showed a surprisingly similar behavior.

3. Experimental Results

The CdS crystal was heated to the desired treatment temperature T_{CdS} and the sulfur vapor pressure p_S adjusted to about 10 torr by choosing the proper T_S.* After reaching a stationary dark current, T_S was increased to provide the next sulfur vapor pressure point etc. After reaching the highest S- vapor pressure (always $T_S < T_{CdS}$), T_S was lowered again and the dark current measured with decreasing p_S. A slight hysteresis was sometimes observed and gave an indication as to how far stationarity was reached during measurements. If lower temperature currents did not agree well enough with previously obtained values, this indicated electrode difficulties and the crystal was discarded.

Figure 2 shows a typical set of current vs. sulfur vapor pressure curves obtained at different crystal temperatures. At low crystal temperatures in many crystals the current does not change with sulfur vapor pressure below about 10^2 torr. Very probably defects already present in the crystal, e.g. impurities, mask the influences of the sulfur vapor treatment. At sulfur vapor pressures above 10^2 torr a decrease of the dark current j with increasing p_S according to

$$j \sim p_S^{-1/m} \qquad (1)$$

has always been observed.

* For S-sealing, as described above, a short initial "treatment" at high S-pressure (about 1 atom) was done.

At low treatment temperatures tne slope 1/m was in general quite small, at intermediate temperatures much larger and at nign temperatures again very small. Figure 3 summarizes tne experimentally obtained m-values of different crystals and runs as a function of tne CdS treatment temperature.

Tne long relaxation time in tne T_S furnace prevented a reliable determination of tne time-dependent current after "abrupt" cnanges in tne sulfur vapor pressure.

4. Discussion

A simple mass reaction analysis, assuming thermodynamic equilibrium between tne sulfur vapor and a certain type of electrically active defect in tne bulk of tne crystal, e.g. a sulfur vacancy, acting as a donor and being progressively annihilated with increasing p_S yields a relationship

$$n \sim p_{S_\ell}^{\,1/\ell x} \qquad (2)$$

between tne electron density n and tne average length ℓ of a sulfur molecule, x being 1, 3/2, 2 or 3 for relatively simple processes and reflecting tne type of reaction kinetic equilibrium.

Assuming $j/\Delta V \sim n$ (no major influence of sulfur treat-

ment on the mobility) the results shown in Figure 3 suggest that the treatment temperature be divided into three ranges:

$$500^{\circ} < T_{CdS_1} < 525^{\circ}C,\ 525^{\circ} < T_{CdS_2} < 630^{\circ}C \text{ and } 630^{\circ} < T_{CdS_3} < 700^{\circ}C,$$

with a respective change of x in these three ranges from $x = 3$ to $x = 1$ to $x = 3$. This indicates a change in the average length of a sulfur molecule from about 8 at 500°C to about 5 at 700°C, values, which are slightly higher than given for the superheated sulfur vapor[6-8]. Nearby liquid sulfur surfaces at T_S at the electric feedthrough seals may account for this discrepancy.

For further discussions, out of many, more complicated models, the most economical one will be chosen which can account for the observed effects. For this it will be assumed, that only single point defects contribute to the observed sulfur pressure dependence of the dark current, an assumption which seems reasonable in the light of a supposed bulk effect, since diffusion of defect associates should be negligible at these relatively low temperatures. Moreover, only interaction with intrinsic defects will be assumed since the investigated crystals were "undoped", for undoped crystals the dark conductivity is determined already at somewhat lower temperatures by self-activated semiconductivity only[9,10], and, the observed behavior was practically the same for all investigated crystals.

A sulfur vapor treatment can, under the given assumptions, a) reduce the density of sulfur vacancies V_S, or, b) reduce the density of cadmium interstitials Cd_i (The introduction of a sulfur interstitial at the treatment temperatures is neglected* in agreement with the observations of Hall and Woodbury[4,5]). These reactions can be written as

$$\frac{1}{\ell} S_\ell \text{ (gas)} + V_S^x \rightleftarrows S_S \qquad (3)$$

or

$$\frac{1}{\ell} S_\ell \text{ (gas)} + Cd_i^x \rightleftarrows CdS \text{ (surface)} \qquad (4)$$

The intrinsic defects can be supplied by Schottky-Wagner disorder

$$V_S^x + V_{Cd}^x \rightleftarrows CdS \text{ (surface)} \qquad (5)$$

or by Frenkel disorder

$$Cd_{Cd}^x \rightleftarrows V_{Cd}^x + Cd_i^x. \qquad (6)$$

The vacancies and interstitials can become singly or doubly ionized

---

* Moreover, only neutral sulfur interstitials can be accommodated on interstitial sites and would not be observable with electrical measurements reported here.

$$V_S^x \rightleftarrows V_S^{\bullet} + \ominus \tag{7}$$

$$V_S^{\bullet} \rightleftarrows V_S^{\bullet\bullet} + \ominus \tag{8}$$

$$Cd_i^x \rightleftarrows Cd_i^{\bullet} + \ominus \tag{9}$$

$$Cd_i^{\bullet} \rightleftarrows Cd_i^{\bullet\bullet} + \ominus \tag{10}$$

$$V_{Cd_1}^x \rightleftarrows V_{Cd}^{'} + \oplus \tag{11}$$

$$V_{Cd} \rightleftarrows V_{Cd}^{''} + \oplus \tag{12}$$

These equations are connected by the quasi neutrality condition

$$n + [V_{Cd}^{'}] + 2[V_{Cd}^{''}] = [V_S^{\bullet}] + 2[V_S^{\bullet\bullet}] + [Cd_i^{\bullet}] + 2[Cd_i^{\bullet\bullet}] \tag{13}$$

Applying the mass action law to the reactions (3) - (12) one obtains the following set of equations:

$$[V_S^x] = K_1 \, p_{S_\ell}^{-1/\ell} \tag{3a}$$

or

$$[Cd_i^x] = K_1^* \, p_{S_\ell}^{-1/\ell} \tag{4a}$$

$$[V_S^x] \; [V_{Cd}^x] = K_2 \tag{5a}$$

$$[Cd_i^x]\ [V_{Cd}^x] = K_3 \tag{6a}$$

$$n\,[V_S^{\bullet}] = K_4\,[V_S^x] \tag{7a}$$

$$n\,[V_S^{\bullet\bullet}] = K_5\,[V_S^{\bullet}] \tag{8a}$$

$$n\,[Cd_i^{\bullet}] = K_6\,[Cd_i^x] \tag{9a}$$

$$n\,[Cd_i^{\bullet\bullet}] = K_7\,[Cd_i^{\bullet}] \tag{10a}$$

$$n\,[V_{Cd}^x] = K_8\,[V_{Cd}^{'}] \tag{11a}$$

$$n\,[V_{Cd}^{'}] = K_9\,[V_{Cd}^{''}] \tag{12a}$$

Since the activity coefficients K_i are exponential functions of temperature, $K_i = K_{io} \exp - (E_i/kT)$ with quite different K_{io} for the different reactions and with different slopes E_i/k it is reasonable to assume that, at certain temperatures, only one density is dominant on both sides of the quasi-neutrality equation (13). This dominance will not change with p_S, since herewith only relatively small changes in densities will be induced. Then one can equate these major densities and can solve (3a) or 4a) and (5a) - (12a) for $n = n(p_S)$.

Although the K_i's are not known and therefore it

is not possible to draw a Brouwer diagram[11], one can, by physical reasoning, easily discard all but one temperature sequence for each model (3) or (4) out of the 12 possible, simplified neutrality conditions.

To see this let us give the complete set of solutions

$$n = \varkappa \, p_S^{-1/\ell x} \qquad (14)$$

The values of $\varkappa$ and x are given in Table 1 for model (3) and for model (4).

For both models an x sequence 3, 1, 3 requires predominant $Cd_i^{\bullet\bullet}$ and $V_S^{\bullet\bullet}$ for x = 3 and the neutrality condition No. 5 or No. 7 for x = 1.

For model (4) it seems reasonable to assume neutrality condition No. 5 since here cadmium interstitials are assumed to interact predominantly with the sulfur vapor. With increasing temperature one would therefore expect that V_S'', $Cd_i^{\bullet}$ and Cd_i'' are the most important defects in the three temperature ranges indicating a predominant Frenkel-disorder, directly observable at higher temperatures and, at lower temperatures the known nonstoichiometry (Cd surplus) located as vacancies in the sulfur sublattice.

For the model of equation (3) neutrality condition No. 7 would apply and the temperature sequence of predominant defects must be written as Cd_i'', $V_S^{\bullet}$, and V_S''. This indicates

predominant Schottky-Wagner disorder, observable at higher temperatures and the low temperature nonstoichiometry located in the Cd-sublattice as Cd-interstitials.

Although the later possibility seems to be more probable on the grounds of ease of diffusion (Cd_i vs V_S) and of the energy of double ionization (E_5 vs E_7), with the experimental results described here, the first explanation cannot be completely ruled out.

However, taking the results of Boyn, Goede and Kuschnerus[3] into consideration, the second explanation seems even more probable: With Cd-treatment more Cd interstitials are introduced and the temperature range T_{CdS}, is widened. The conductivity is increased, the Fermi-level shifted towards the conduction band and the crossover for $Cd_i^{\bullet}$ to $Cd_i^{\bullet\bullet}$ to become the most important defect* in the neutrality condition is also shifted towards slightly higher temperatures ($\sim 500^{\circ}C$ in[3] to $< 500^{\circ}C$ for S-treatments). Cd-interstitials determine the "low temperature range" of Cd-surplus. Sulfur vacancies must predominate at higher temperatures, -as shown above. Therefore, in the untreated -or slightly sulfur treated crystal Schottky-Wagner disorder is predominant above about $530^{\circ}C$. For the Cd-treated crystal (dependent on the Cd-vapor pressure) Cd-surplus

* For the different conclusion in[3] a too simplified model ($V_{Cd}'' + Cd_i^{\bullet\bullet} \rightleftarrows Cd_{Cd}$) is used.

is increased and the Schottky-Wagner disorder range starts at slightly higher temperatures.

From the transition temperature between temperature range 2 and 3, $T_{2,3} = 630^{\circ}C$, one can estimate the energy of doubly ionizing the sulfur vacancy. Here must $[V_S^{\cdot}(T_{2,3})] = [V_S^{\cdot\cdot}(T_{2,3})]$. This requires[12] that $n = K_5$ or $E(V_S^{\cdot}) = E_F + kT\ell n2$, with E_F the Fermi-level at $630^{\circ}C$. Using the measured j ($630^{\circ}C$), $\mu = 50$ (cm^2/Vs) and $m_{eff} = 0.2\ m_o$ one obtains $E_c - E(V_S^{\cdot}) = 0.48$ eV. This energy is relatively small. Moreover, all other ionization energies for intrinsic donors must, according to the previous discussion lie at even smaller values. This indicates that deeper trap levels observed in CdS and connected with intrinsic defects must belong to defect associates, e.g. divacancies.

It certainly needs further experimental evidence to substantiate this model, however it is remarkable that in recent years more and more results for CdS seem to indicate that single defects, such as vacancies or interstitials have already at relatively low temperatures a high mobility and diffuse markedly. Defect associates probably are one cause of a lower than expected diffusion above $700^{\circ}C$ and Cd-divacancies are one example of such associates which are expected to be relatively stable at these temperatures (the binding energy should be at around 4 eV as obtained from an S_2 molecule).

TABLE 1

No.	Neutrality	$\varkappa$ (3)	x(3)	$\varkappa$ (4)	x(4)
1	$n=[Cd_i^{\bullet}]$	$(K_1K_3K_6/K_2)^{1/2}$	2	$(K^*_1K_6)^{1/2}$	2
2	$n=2[Cd_i^{\bullet\bullet}]$	$(2K_1K_3K_6K_7/K_2)^{1/3}$	3	$(2K^*_1K_6K_7)^{1/3}$	3
3	$n=[V_S^{\bullet}]$	$(K_1K_4)^{1/2}$	2	$(K^*_1K_2K_4/K_3)^{1/2}$	2
4	$n=2[V_S^{\bullet\bullet}]$	$(2K_1K_4K_5)^{1/3}$	3	$(2K^*_1K_2K_4K_5/K_3)^{1/3}$	3
5	$[V'_{Cd}]=[Cd^{\bullet}_i]$	$(K_1^2K_4K_8/K_2)^{1/2}$	1	$(K^{*2}_1K_6K_8/K_3)^{1/2}$	1
6	$[V'_{Cd}]=2[Cd_i^{\bullet\bullet}]$	$(2K_1^2K_3K_6K_7K_8/K_2^2)^{1/3}$	3/2	$(2K^{*2}_1K_6K_7K_8/K_3)^{1/3}$	3/2
7	$[V'_{Cd}]=[V_S^{\bullet}]$	$(K_1^2K_4K_8/K_2)^{1/2}$	1	$(K^*_1K_2K_4K_8/K_3^2)^{1/2}$	1
8	$[V'_{Cd}]=2[V_S^{\bullet\bullet}]$	$(2K_1^2K_4K_5K_8/K_2)^{1/3}$	3/2	$(2K^{*2}_1K_2K_4K_5K_8/K_3^2)^{1/3}$	3/2
9	$2[V''_{Cd}]=[Cd_i^{\bullet}]$	$(K_1^2K_3K_6K_8K_9/2K_2^2)^{1/3}$	3/2	$(K^{*2}_1K_6K_8K_9/2K_3)^{1/3}$	3/2
10	$[V_{Cd}'']=[Cd_i^{\bullet\bullet}]$	$(K_1^2K_3K_6K_7K_8K_9/K_2^2)^{1/4}$	2	$(K^{*2}_1K_6K_7K_8K_9/K_3)^{1/4}$	2
11	$2[V''_{Cd}]=[V_S^{\bullet}]$	$(K_1^2K_4K_8K_9/2K_2)^{1/3}$	3/2	$(K^{*2}_1K_2K_4K_8K_9/2K_3^2)^{1/3}$	3/2
12	$[V''_{Cd}]=[V_S^{\bullet\bullet}]$	$(K_1^2K_4K_5K_8K_9/K_2)^{1/4}$	2	$(K^{*2}_1K_2K_4K_5K_8K_9/K_3^2)^{1/4}$	2

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FIGURE CAPTIONS

Figure 1. Treatment vessels and furnace.
1: stainless steel tube, 2: asbestos disk,
3: Mullite tube with Kantal winding,
4: asbestos board with Kantal winding, 5: Fibrofax insulation, 6: asbestos box, 7: CdS, 8: SiO_2-spring, 9: thermocouples, 10: sulfur, 11: electrical feedthrough, 12: O-ring seal.

Figure 2. Current at treatment temperatures T_{CdS} as function of the sulfur vapor pressure.

Figure 3. m (see equation 1) as function of treatment temperature.

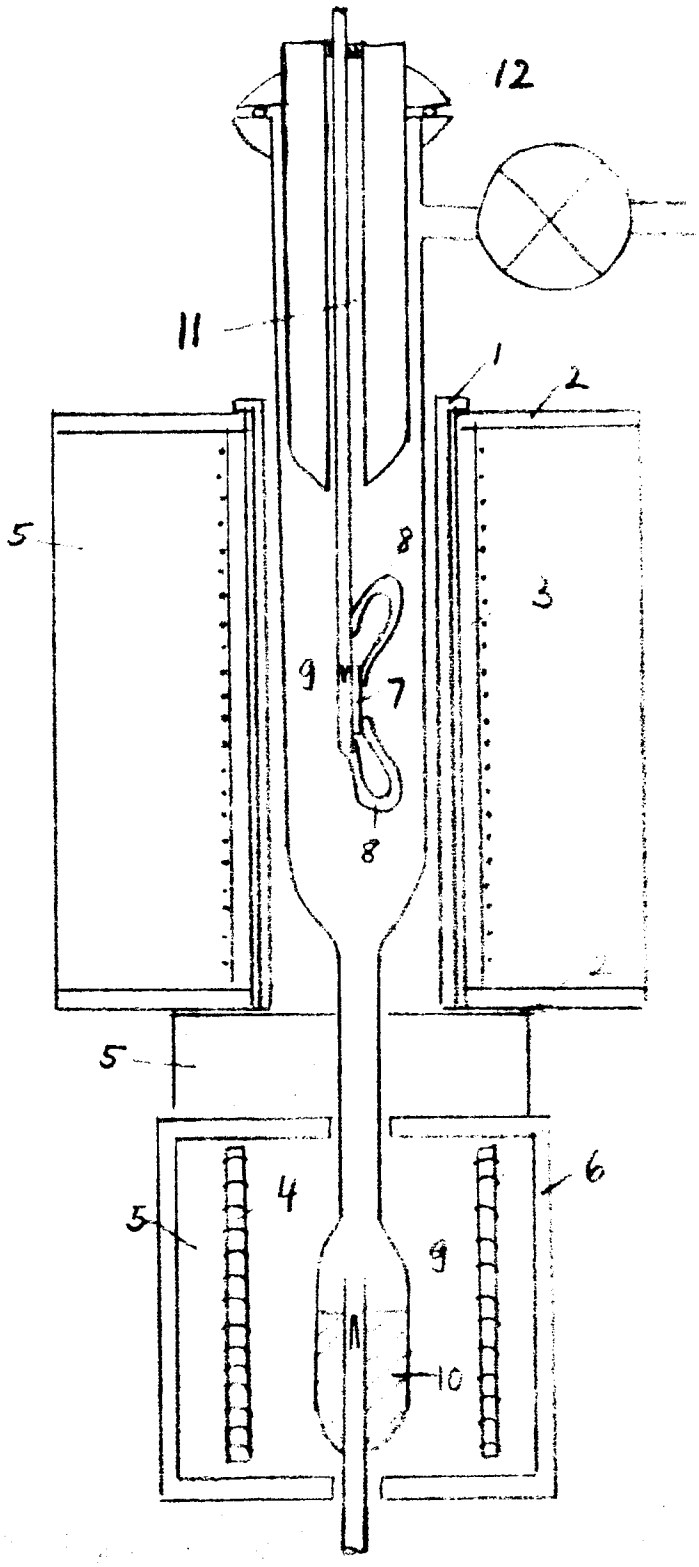

Figure 1

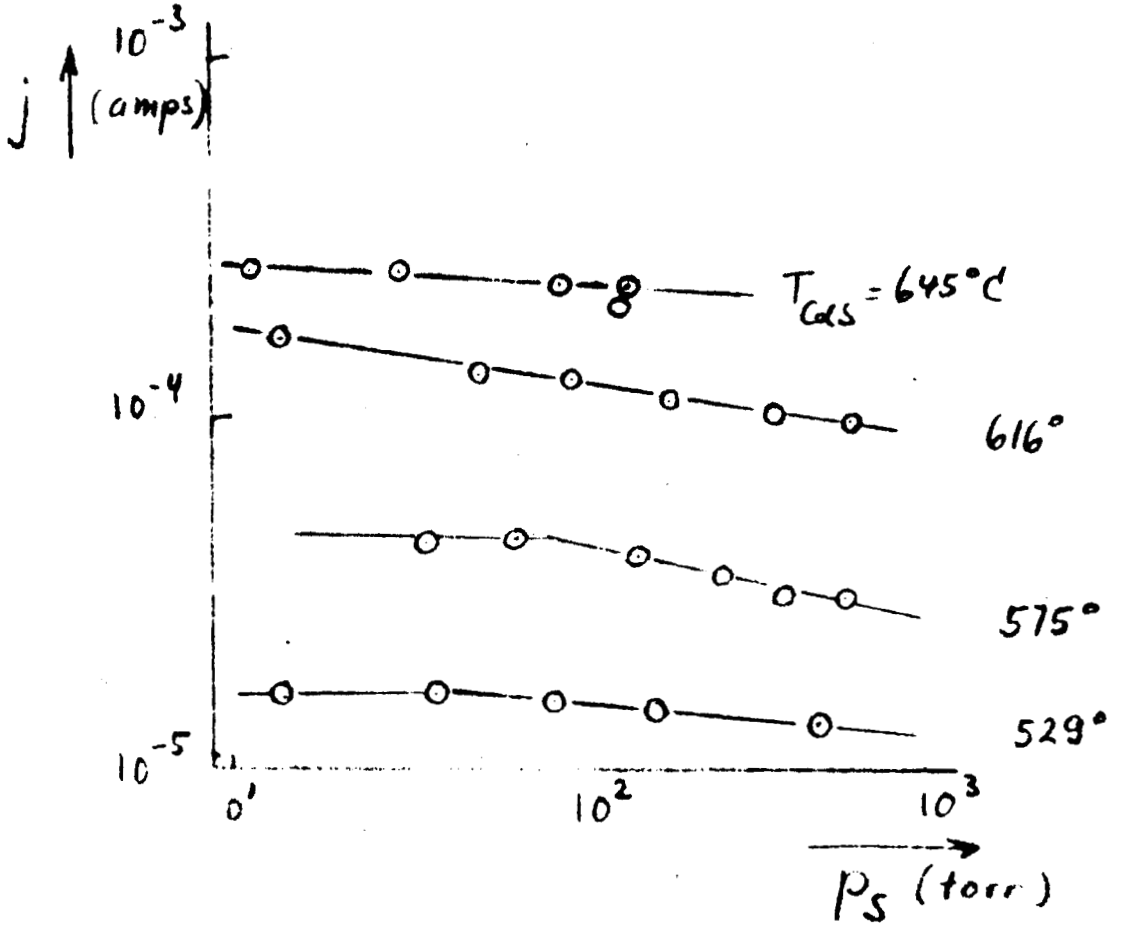

Figure 2

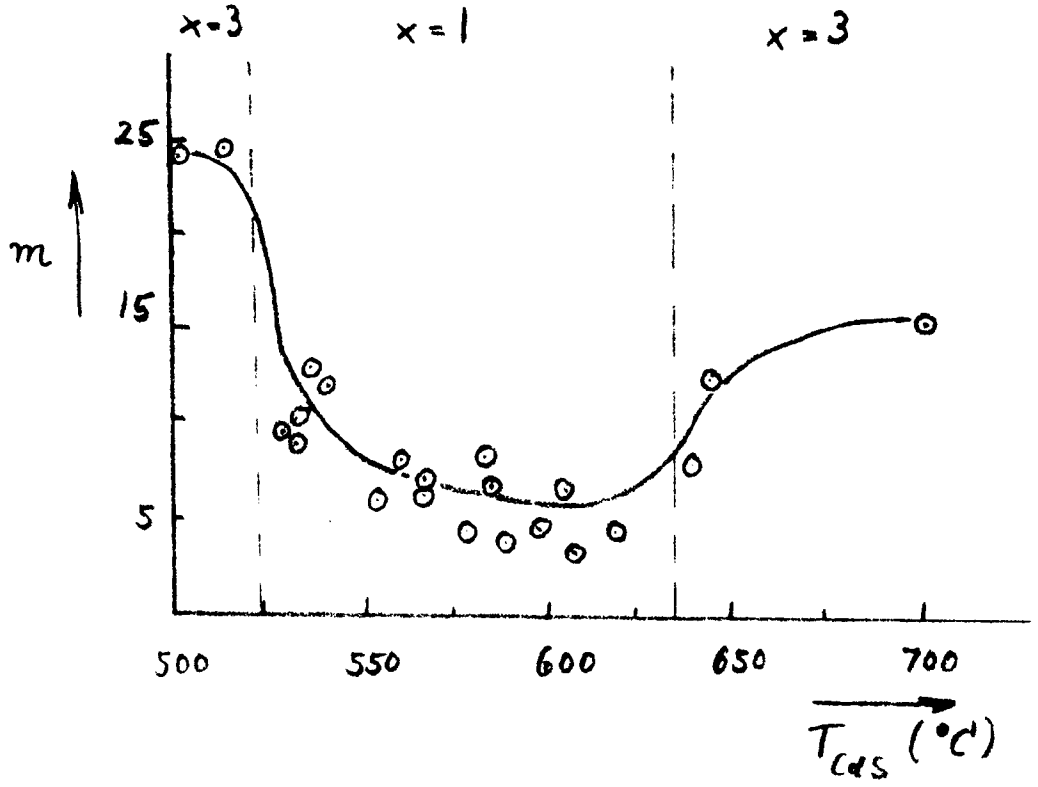

Figure 3