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GROWTH OF SINGLE CRYSTALS BY VAPOR TRANSPORT

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ABSTRACT

The primary objectives of this research program were to establish basic vapor transport and crystal growth properties and to determine thermodynamic, kinetic and structural parameters relevant to chemical vapor transport systems for different classes of materials. An important aspect of these studies was the observation of the effects of gravity-caused convection on the mass transport rate and crystal morphology. These objectives have been accomplished through extensive vapor transport, thermochemical and structural studies on selected Mn-chalcogenides, II-VI and IV-VI compounds.

This research program established the existence of three different transport modes which control the mass flux in different pressure regimes of the vapor transport system. In addition, the negative effects of convective mass transport on crystal morphology were demonstrated. The thermochemical studies revealed the importance of a mobile surface layer and of surface defects on the sublimation mechanism and stability of single crystals. The crystallographic studies on IV-VI compounds demonstrated the existence of solid phase transformations, of considerable lattice expansions and rearrangements at temperatures employed in typical vapor transport reactions. These results are of immediate relevance for the degree of crystal perfection and for the growth of alloy-type crystals. The combined ground-based studies led to the definition of experimental conditions for crystal growth experiments in micro-gravity environment. The results of vapor transport experiments on IV-VI compounds performed during the Skylab and Apollo-Soyuz Missions demonstrated unambiguously a considerable improvement in crystal quality and greater mass transport rates than expected for diffusion controlled vapor transport. These results are of basic scientific and technological significance.

The combined vapor transport, crystal growth, thermochemical and structural data produced to date under this program and the information obtained from our space experiments provide a quantitative basis for definitive fluid dynamic studies on these and related systems. These experiments have been initiated under a separate project. The results of the present program led to the successful performance of previous space experiments. The results of continued research on the fluid dynamics of vapor transport systems are of importance for the design of critical future flight experiments and for space processing applications.

I. INTRODUCTION

The usefulness of chemical vapor deposition and transport reactions is demonstrated by the application of this technique for the growth of epitaxial layer and bulk single crystalline materials ranging from insulators via semiconductors to metals. One of the major advantages of chemical vapor transport reactions is the possibility to grow crystals at considerably lower temperatures than required for melt growth or for sublimation-condensation processes. This basic fact has several practical consequences including the thermodynamic stability of the growing crystal, reduced container and contamination problems and in general lower dislocation densities. It is for these reasons that a complete understanding and control of chemical vapor transport reactions is of far reaching technological significance.

The basic scientific and technical principles of vapor transport have been discussed earlier by Schäfer [1]. The chemical transport process is based on at least one reversible heterogeneous reaction and on mass and heat transfer in a temperature gradient. In this process, a gaseous transport agent reacts with the solid source material to form exclusively gaseous products. The gas phase species migrate from the source to the condensation zone of the reaction container where the reverse reaction occurs with formation of single crystals. The necessary concentration gradient is achieved by means of a temperature gradient. In view of the above, the transport and crystal growth properties are dependent upon the thermochemical, structural and fluid dynamic properties of the system.

From the beginning of this research program, the complex nature of vapor transport reactions was recognized and it determined the scope and experimental approach of this work. A meaningful interpretation of chemical transport processes requires a detailed understanding of thermodynamic and kinetic properties of solid-gas phase reactions, of crystallographic properties of the material to be transported and their dependence upon temperature. In addition, homogeneity ranges and phase transformations of the solid as well as compositional variations of the gas phase can affect crystal morphology or mass transport rates. The above properties must be well understood in order to quantitatively characterize the effects of convection on transport rates and crystal growth.

The primary objectives of this research program were to investigate the thermodynamic, kinetic and structural properties of materials in relation to vapor phase crystal growth and to establish the basic chemical transport properties of selected systems. This approach led to the observation of three different mass transport rate controlling steps in closed transport systems and to the elucidation of the sublimation mechanism of layer-type compounds. The combined studies provided the necessary data base for the reliable observation of the effects of gravity-driven convection on mass transport and crystal morphology. Supported by thermochemical and structural considerations, the above observations led to the definition and performance of our Skylab and Apollo-Soyuz experiments. The results of these space experiments on binary and mixed Ge-chalcogenides demonstrated distinctly improved crystal quality and greater mass transport rates in microgravity than expected for a diffusion controlled vapor transport process. As a result of the ground and space experiments performed to date, continued research activities in our laboratory are focused on the investigation of fluid dynamic properties of chemical vapor transport systems. These studies have been initiated in recent years under a separate project.

The results obtained under the present contract include the establishment of basic chemical transport properties and the determination of quantitative thermodynamic, kinetic and crystallographic parameters of selected systems. The combined data in connection with those of continued ground-based studies are of practical importance for the definition of future flight experiments.

II. SUMMARY OF RESULTS

II.1. Materials and Techniques

The materials and transport systems investigated under this contract include Mn-chalcogenides, selected II-VI compounds, mixtures of Mn-II-VI systems and representative IV-VI compounds. These materials were selected for ground-based studies because of their interesting structural and electronic properties. In addition, these compounds cover a wide range of crystallographic structures from highly symmetric cubic systems to anisotropic layer structures. Their thermodynamic and kinetic properties are significantly different. Developments in device oriented applications indicate the potential use of some of these systems as components in alloy-type semiconductors.

In order to reduce the complexity of the transport process and to observe the effects of natural convection on transport rates and crystal morphology, chemical vapor transport experiments were performed in evacuated, closed ampoules of fused silica. For the determination of thermodynamic and kinetic properties, high temperature mass spectrometric and vacuum microbalance techniques were employed. For the investigation of structural parameters, room and high temperature X-ray diffraction methods were used. The above studies were supported by morphological investigations on single crystals employing various optical and electron microscopic techniques.

In view of the broad scope of this research program, the pertinent results obtained are summarized below for the different classes of materials.

II.2. Manganese Chalcogenide Systems

In previous phase studies [2] it was shown that MnS and MnSe (both NaCl-type structure) form a continuous series of solid solutions. Prior to this research program, these isotropic materials were employed to investigate the effects of various experimental parameters on crystal growth. Mass transport rate studies in the multi-component, multi-reaction system MnS-MnSe-iodine were performed on atomic mixtures of high purity elements in the temperature gradient 945 → 850°C and with iodine pressures ranging from about 0.5 - 7.8 atm [3]. The results in terms of flux ($mol/cm^2 \cdot sec$) as a function of pressure show that the mass transfer process is predominantly by convection within the applied pressure range. Growth studies of single crystals of MnS, MnSe and of solid solutions by vapor transport of the elements with iodine yielded crystals of several mm edge length (octahedra and platelets) using iodine concentrations of 1-3 mg/cm^3 tube volume and temperature gradients $\Delta T < 50°C$. The as-grown surfaces of the platelets are (111) planes. Thermoelectric measurements revealed p-type conductivity of the single crystals. The effects of different iodine concentrations (pressures), temperature gradients and pretreatment of the transport ampoules on crystal morphology were observed. It is worthwhile noting that the crystal habit (platelet or octahedra) was measurably affected by the duration of etching of the transport ampoule during the cleaning procedure of the ampoules. This revealed the effects of nucleation sites of the substrate on crystal habit. These studies [3] showed the necessity to maintain reproducible conditions for systematic transport and morphology studies.

As a result of the above transport studies on MnSe [3], it was desirable to determine the actual lattice parameters and thermal expansion of MnSe at elevated temperatures. Similar data for MnS were available in the literature. For this purpose, the thermal expansion of MnSe and $MnSe_2$ (NaCl- and pyrite-type structure, respectively) were studied above room temperature up to 710° and 522°C by X-ray diffraction techniques using a 190 mm Unicam high temperature camera [4]. The thermal expansion coefficients, β, obtained from a linear least-squares analysis of the data are for MnSe: $\beta = 24.5 \cdot 10^{-6} {}^\circ C^{-1}$ (94 to 450°C) and $\beta = 14.3 \cdot 10^{-6} {}^\circ C^{-1}$ (450 to 710°C). The expansion of $MnSe_2$ is linear up to the temperature range of decomposition. A least-squares analysis yields a value for β of $20.0 \cdot 10^{-6} {}^\circ C^{-1}$ (73 to 522°C). These studies confirmed the composition of mixed MnS-MnSe single crystals obtained by chemical transport [3] and showed that $MnSe_2$ is not stable under transport conditions.

In connection with phase studies of the MnTe-CdTe system, the formation of $MnTe_2$ single crystals was observed [5]. In view of the low stabilities of the Mn- dichalcogenides relative to the monochalcogenides, this interesting observation was difficult to understand. In order to explain the growth of $MnTe_2$ crystals under annealing conditions, the stability and heat of formation of $MnTe_2$ were determined by quantitative Knudsen effusion studies in the temperature range 551 - 685 K [6]. The results demonstrate, that $MnTe_2$ decomposes according to the reaction

$$MnTe_2(s) = MnTe(s) + \tfrac{1}{2}\, Te_2(g).$$

The observed heat of reaction is 20.0±1.0 kcal/mol at 298 K. This yielded the standard heat of formation of $MnTe_2(s)$ to be -26.4 kcal/mol. For the above calculations, the heat capacity of $MnTe_2(s)$,

$$C_p^\circ = 17.83 + 1.23\times10^{-3}\ T\ (eu),$$

was determined in this work [6] between 328 and 573 K.

Based on the above measured decomposition pressures [6] of $MnTe_2(s)$, the reproducible growth of $MnTe_2$ single crystals by chemical vapor transport with iodine in the presence of excess Te was accomplished [7]. Through systematic studies of the mass transport rate as a function of iodine and tellurium pressure, the transport mode and mechanism could be determined. The results of this work are of practical importance for the growth of single crystals of materials which are not stable under conventional transport conditions.

II.3. Manganese-Cadmium Chalcogenide Systems

In order to provide a basis for subsequent studies of the variation of the energy gap with composition and of the transport properties of MnSe-CdSe solid solutions, the temperature-composition phase diagram for the solid region of the MnSe-CdSe system was investigated by X-ray diffraction techniques over the temperature range 500 - 1100°C [8]. The small degree of solid solution on the MnSe-rich side compared to the wide CdSe-rich one-phase region can be explained by the differences in structural and bonding properties of the components. The electronic structure of manganese permits both octahedral (NaCl-type) and tetrahedral (wurtzite) configurations with s-p-d and s-p orbitals, respectively. For cadmium to form octahedral bonds in the MnSe-rich (NaCl-type) solid solutions, higher d-orbitals have to be used which is energetically unfavorable. The lattice parameters of compositions in the one-phase regions can be expressed for the MnSe-rich cubic phase by the equation

$$a_0 = 5.462 + 0.202 \cdot N,$$

and for the CdSe-rich hexagonal phase by the equations

$$a_0 = 4.173 + 0.124 \cdot N$$

and

$$c_0 = 6.822 + 0.193 \cdot N,$$

where N is the mole fraction of CdSe.

The phase boundary of the cubic region changes from about 3 mol % at 500°C to about 20 mol % CdSe at 1100°C. The boundary of the wurtzite phase is at approximately 50 mol % CdSe and practically temperature independent [8].

Based on the above phase studies, the variation of the optical energy gap with composition in MnSe-CdSe solid solutions was determined by reflectance measurements on microcrystalline powders and by transmittance measurements on single crystal platelets for the cubic and hexagonal one-phase regions of the system [9]. For this purpose, a Beckman DU and a Cary model 14R spectrophotometer, respectively, were used. The results show, that the energy gap varies linearly with composition. For the CdSe-rich hexagonal one-phase region (50 - 100 mol % CdSe), this relationship can be expressed by the equation

$$E_G = 2.78 - 1.08 \cdot N,$$

where N is the mol fraction of CdSe and E_G is given in eV. Since CdSe has a direct band transition, the linear variation of the band gap suggests that the solid solutions might also have direct gaps. Thermoelectric measurements on CdSe single crystal platelets revealed n-type conductivity due to the selenium deficiency of CdSe. Measurements on solid solution single crystals with 50 and 60 mol % CdSe, respectively, also indicated n-type conductivity [9].

The single crystal specimens required for the above optical studies [9] were grown by chemical transport techniques in connection with the investigation of the crystal growth and transport properties of the mixed system MnSe-CdSe [10]. A temperature gradient of 875 → 840°C and elemental iodine were used as a transport agent. Studies of the growth morphology of MnSe and CdSe crystals revealed that the MnSe habit changes from platelet to octahedron with increased chemical etching of the tube walls during the cleaning procedures of the transport ampule. This is attributed to the geometry of the growth sites on the silica surface. The morphology of CdSe crystals is affected by the transport mode. Diffusion controlled transport yields elongated needles, under convection conditions hexagonal platelets are predominant. The growth of mixed crystals of the MnSe-CdSe system was studied by vapor transport of the elements, of binary compounds, and of solid solutions as a function of composition of the source material, and by direct sublimation of solid solutions as a function of composition and temperature range. Experimental results in terms of composition and crystalline quality of the transport and sublimation products are explained by the thermodynamic properties (vapor pressures and activities) of the individual components of the system. These studies [10] demonstrated again the effects of transport mode and of thermochemical properties of the materials on the morphology and composition of single crystals.

The solid-gas phase equilibria and thermodynamic properties of CdSe were investigated by quantitative Knudsen effusion studies [11]. The results show that at about 400°C CdSe sublimes initially by losing selenium to form nonstoiciometric $CdSe_{1-x}$, where $x \approx 0.002$; the resulting compound $CdSe_{1-x}$ sublimes congruently. With the heat capacity function of CdSe(s),

$$C_p^\circ = 12.36 + 1.45 \cdot 10^{-3}\ T\ (\mathrm{eu}),$$

measured for the first time in this work, the vapor pressure measurements were evaluated in terms of the standard heat of formation, $\Delta H^\circ_{298} = -35.7$ kcal/mol, and the absolute entropy, S°_{298} = 19.8 eu, of CdSe(s). These data [11] were used for the interpretation of the above transport studies [10] and for subsequent activity measurements on solid solutions.

The Knudsen effusion technique was employed to derive the activities of CdSe and of MnSe in MnSe-CdSe solid solutions as a function of composition and temperature [12]. In the CdSe-rich hexagonal phase the system shows ideal behavior. In the MnSe-rich cubic phase the activities of CdSe show positive deviations and the activities of MnSe negative deviations from Raoult's law. Partial molar Gibbs free energies, enthalpies, and entropies were calculated from which the Gibbs free energy, enthalpy, and entropy of mixing were derived. The experimentally determined entropies are close to the ideal values, suggesting that no preferential ordering of Mn and Cd ions in cation sites occurs.

The combined thermochemical information obtained from the Knudsen measurements [11,12] was used to explain the compositional variations of solid solution single crystals [10] grown under different experimental conditions.

Systematic mass transport rate studies on the systems CdS, CdSe and CdTe using elemental iodine or CdI_2 as initial transport agents confirmed the effects of pressure on transport mode and crystal morphology [13]. At lower pressures the transport is diffusion controlled and at higher total pressures convective transport is predominant. The crystal morphology varies with the change in transport mode and reveals decreasing quality with increasing convective motion.

II.4. Germanium Chalcogenide Systems

Because of their interesting structural and bonding properties, the germanium chalcogenides were selected for systematic crystal growth, thermodynamic, kinetic and structural investigations.

Vapor transport experiments with iodine were performed on the systems GeSe, $GeSe_2$ and GeTe to define optimum growth conditions in terms of crystal size and surface perfection [14]. Mass transport rate studies on the GeTe-iodine system were carried out in the temperature gradients 560 → 445°C and 420 → 350°C with iodine pressures ranging from 0 to about 2 atm (based on diatomic iodine and assuming a perfect gas). Evaluation of experimental data in terms of flux ($mol/cm^2 \cdot sec$) as a function of iodine pressure revealed the predominant transport mode in different pressure ranges. Comparison of experimental results with calculated material fluxes based on a diffusion model was used to substantiate the predominant transport mechanism given by the reaction

$$GeTe(s) + GeI_4(g) = 2\ GeI_2(g) + \tfrac{1}{2}\ Te_2(g).$$

At low pressures, the transport rate is controlled by the rate of the heterogeneous solid-gas phase reaction; at intermediate pressures, diffusion controls the mass transport; at higher pressures, convective transport is predominant. Diffusion controlled transport yields predominantly octahedral type crystals of GeTe and convective flow causes mainly platelet type crystals. The as-grown surfaces of the platelets are (111) planes. Surface imperfections increase with increasing predominance of the convectional contribution to the transport.

The above studies [14] represent the first systematic investigation of the interrelation of pressure, transport mode and crystal morphology in chemical vapor transport systems. In addition, the observations demonstrated the negative effects of gravity-caused convective interference with the transport process on crystal perfection. In view of the technological importance of these results for crystal growth on earth and in a microgravity environment, these studies were extended to the GeSe system.

Mass transport rate studies on the system GeSe-GeI_4 were performed [15] in closed ampules of fused silica in the temperature gradients 520 → 420°C, 420 → 350°C and 380 → 300°C with GeI_4 pressures ranging from 0 to about 2 atm. The experimental results in terms of material flux versus GeI_4 pressure reveal the different transport modes in agreement with the above observations on the GeTe system [14]. Comparison of observed and computed material fluxes [15] based on a diffusion model confirmed the dominant transport reaction

$$GeSe(s) + GeI_4(g) = 2\ GeI_2(g) + \tfrac{1}{2}\ Se_2(g).$$

Diffusion controlled chemical transport yields GeSe single crystal platelets of high surface and bulk quality. The (001) orientation of the as-grown surfaces is in accordance with the structural properties of GeSe. With increasing dominance of the convective transport mode, the crystal habit changes from well developed platelets to dendrites.

The combined morphological studies on the Mn- and Cd-chalcogenide systems and, in particular, on GeSe and GeTe performed in our laboratory under this program demonstrated unambiguously the negative effects of gravity-caused convection on the perfection of crystals grown by chemical transport techniques.

These results led to the prediction that crystals of improved quality could be obtained under conditions of reduced convective interference in a micro-gravity environment. In order to optimize the conditions of space experiments and to facilitate their reliable interpretation, additional thermodynamic and structural studies were performed on the Ge-chalcogenides selected for crystal growth experiments in microgravity.

In order to calculate the contribution of sublimation to the mass flux under chemical transport conditions, the absolute partial pressure and stability of GeSe were determined [16]. For this purpose, Knudsen effusion studies of the sublimation of polycrystalline GeSe were performed employing mass spectrometry in a temperature range of about 530 - 730 K and vacuum microbalance techniques in the temperature range 601 - 796 K and at pressures ranging from about 10^{-6} - 10^{-4} atm. The results are concordant and demonstrate that GeSe vaporizes congruently under present experimental conditions according to the reaction GeSe(s) = GeSe(g).

The mean values for the third law heat and second law entropy of reaction based on direct mass-loss data are ΔH°_{298} = 42.0±1.5 kcal/mol and ΔS°_{298} = 42.3± 1.6 eu. From these data the standard heat of formation and absolute entropy of GeSe(s) were calculated to be -10.1 kcal/mol and 16.9 eu, respectively [16].

The above equilibrium thermochemical studies [16] provided the necessary reference data for the detailed investigation of the vaporization mechanism of this system [17]. The sublimation kinetics of (001) oriented GeSe single crystal platelets was studied by means of high temperature mass spectroscopy, quantitative vacuum microbalance techniques and hot stage optical microscopy. Solid GeSe sublimes under non-equilibrium conditions according to the reaction GeSe(s) → GeSe(g).

The activational enthalpy and entropy for the mean experimental temperature 563 K are ΔH^*_{563} = 32.3 kcal/mol and ΔS^*_{563} = 19.1 eu. The vaporization coefficient α is less than unity for the temperature range studied and α decreases with increasing temperature. The combined experimental data could be correlated through the application of the reverse Langmuir-Hinshelwood mechanism. The results demonstrate the importance of a mobile surface layer in the sublimation mechanism of GeSe [17]. These studies also showed that sublimation is initiated at surface defects leading to a complete coverage of the crystal surface by intersecting thermal etch pits under steady-state conditions. Because of the reversibility principle, the result of these investigations are of immediate importance for the elucidation of the growth mechanism of GeSe single crystals.

In connection with the synthesis of GeSe, the formation of trace amounts of $GeSe_2$ was sometimes observed. For this reason, the determination of the stability and decomposition of $GeSe_2$ was desirable. This was accomplished by Knudsen effusion studies of $GeSe_2$ employing high temperature mass spectrometric and vacuum microbalance techniques in the temperature range 610 - 800 K [18]. The results demonstrate that $GeSe_2$ vaporizes congruently under present experimental conditions according to the predominant reaction (1) $GeSe_2(s) = GeSe(g) + \frac{1}{2} Se_2(g)$ and a minor reaction (2) $GeSe_2(s) = GeSe_2(g)$. The mean values for the third law heat and second law entropy of reaction (1) based on direct mass-loss data are $\Delta H^\circ_{298} = 70.4 \pm 2$ kcal/mol and $\Delta S^\circ_{298} = 64.7 \pm 2$ eu. From these the standard heat of formation and absolute entropy of $GeSe_2(s)$ were calculated to be -21.7 kcal/mol and 24.6 eu, respectively, [18]. Based on these results, the relative stabilities of GeSe and $GeSe_2$ can be determined under actual transport and crystal growth conditions.

Because of questionable literature data concerning the high temperature crystal structure of GeSe, the thermal expansion of GeSe was studied between room temperature and the melting point of 670±5°C by X-ray diffraction techniques using a 190 mm Unicam high temperature camera [19]. The thermal expansion of the crystallographic axes is linear with a distinct change of the expansion coefficients for all axes above 400°C. The relative changes of the axes indicate a rearrangement of the structure towards cubic symmetry with increasing temperature. The transformation of GeSe from the orthorhombic to a normal NaCl-type structure is observed at 651±5°C. The lattice parameter of the cubic form of GeSe is $a_0 = 5.730 \pm 0.003$ Å at 656°C. The GeSe lattice remains cubic up to the melting point. These studies [19] demonstrated that the orthorhombic modification of GeSe is stable within the temperature ranges employed for chemical vapor transport studies and that the reported transformation to a hexagonal structure at higher temperatures is incorrect.

Similar thermal expansion studies on GeS were performed between room temperature and the melting point of 658±5°C by high temperature X-ray diffraction techniques [20]. The thermal expansion of the crystallographic axes is linear with distinct changes in the rate of expansion at about 250°C, 370°C and 510°C. These observations reveal an approach to cubic symmetry with increasing temperature. However, no first-order structural transformation of GeS was observed and the orthorhombic structure exists up to the melting. The results of thermal expansion studies on GeTe [20] confirmed the structural transformation of GeTe from rhombohedral to a normal NaCl-type modification at about 375°C. The transformation temperature changes slightly with composition within the homogeneity range of GeTe.

In addition to the observed phase transformations, the thermal expansion studies on GeS, GeSe and GeTe [19,20] provided quantitative expressions for the computation of actual lattice parameters at the temperatures of crystal growth. This is of practical importance for the growth of alloy-type single crystals of these materials. The GeTe phase transformation affects the degree of perfection of single crystals as a result of strain induced by the transformation during cooling of the crystals to room temperature. The observed trends in the thermal expansion behavior of the germanium monochalcogenide series can be explained by the degree of distortion from the NaCl-type structure and by the degree and type of hybridization of their bonding orbitals [20].

The combined information obtained from the above transport, thermodynamic and structural studies on the germanium chalcogenides provided the basis and reference data for space experiments performed on these systems during the Skylab and Apollo-Soyuz Missions. The results of these microgravity experiments are briefly summarized below.

Six vapor transport experiments on the systems GeSe-GeI_4 and GeTe-GeI_4 were performed on Skylab [21] to determine the effects of micro-gravity on crystal growth and transport rates. Based on a direct comparison of crystals and transport data obtained on earth and in space, employing X-ray diffraction, microscopic and etching techniques, the results demonstrate a considerable improvement of the space grown crystals in terms of growth morphology and bulk perfection. The observation of greater mass transport rates than expected in micro-gravity for diffusion-controlled transport could indicate the existence of other transport modes in a reactive solid-gas phase system. The combined results show that the interference of gravity-driven convection with the transport process causes negative effects on crystal growth as observed on earth for otherwise identical conditions. This points to the unique environment of weightlessness for the observation of basic transport phenomena.

In order to confirm the partially unexpected Skylab results [21], the micro-gravity studies were extended to mixed compounds of the above systems, employing different transport agents, pressures and temperature gradients.

The positive effects of micro-gravity on crystal growth and basic properties of the vapor transport reaction were established by analyzing the results of three transport experiments of multicomponent systems performed during the Apollo-

Soyuz mission [22]. The systems employed were $GeSe_{0.99}Te_{0.01}$-GeI_4, $GeS_{0.98}Se_{0.02}$-$GeCl_4$, and GeS-$GeCl_4$-Ar. The crystallographic analysis is based on a direct comparison of space- and earth-grown (prototype) crystals, employing X-ray diffraction, microprobe, microscopic, and chemical etching techniques. The results demonstrate a considerable improvement of the space-grown crystals in terms of chemical and crystalline homogeneity, surface morphology, and bulk perfection relative to earth specimens. The confirmation of greater mass transport rates than predicted for diffusion-controlled transport in micro-gravity suggests the existence of "thermochemically" induced convective motion in chemical vapor transport systems. The morphological observations indicate, that the presence of different convective components yields turbulence which adversely affects crystal quality as observed on earth. The internal consistency and agreement between our ASTP [22] and Skylab [21] results obtained for several compounds, transport agents, and temperature gradients strongly support the validity of these observations.

The combined Skylab [21] and ASTP [22] experiments represent the systematic investigation of the transport properties of an entire series of IV-VI compounds in micro-gravity. The results are of basic scientific and technological significance. They have demonstrated, that present theoretical vapor transport models are incomplete and that the vapor transport technique is suitable for future space processing applications. These space experiments also show, that extensive ground-based studies are required for the successful performance of micro-gravity studies. In order to further elucidate the unexpected transport phenomena observed in space, new fluid dynamic studies on these and related systems are in progress under a separate project.

II.5. Tin Chalcogenide Systems

In connection with vapor transport and crystal growth studies in the tin-sulfide systems, the occurrence of reverse transport was observed. Since this is a basic phenomenon which may occur in many other chemical transport systems, systematic investigations were performed on the SnS_2-SnI_4-I_2 system to determine the effects of temperature and pressure on the transport direction. The results are briefly summarized below.

Mass transport rate studies on SnS_2 in the temperature gradient 648 - 723 K using SnI_4 as initial transport agent revealed the existence of forward (high → low temperature) and reverse (low → high temperature) transport [23]. The net transport direction was found to be pressure dependent. At higher temperatures, only forward transport was observed for the SnS_2-SnI_4 system. When elemental iodine is employed as initial transport agent in the above gradient, SnS_2 is transported from low to high temperature for pressures between about 0.3 and 150 kPa. Thermodynamic calculations for these systems yielded partial pressures of the major gaseous species SnI_4, SnI_2, I_2, I, S_2, S_3, S_4, S_5, S_6, S_7, and S_8 which led to the formulation of the dominant transport reactions consistent with the observed net transport direction. The major transport reactions are

$$SnS_2(s) + SnI_4(g) = 2\ SnI_2(g) + S_2(g),$$

$$SnS_2(s) + 2\ I_2(g) = SnI_4(g) + S_2(g)$$

and

$$SnS_2(s) + 2\ I_2(g) = SnI_4(g) + 2/i\ S_i(g),$$

where i = 3, 4, 5, 6, 7 and 8. It is important to note that all reactions occur simultaneously to some extent. The relative dominance of these reactions, in particular those involving higher molecular sulfur species, determine the net transport direction.

Based on the hypothetical pressure P* of SnS_2, defined as the "solubility" of SnS_2 in the gas phase, the quantity ΔP^* is given by the equation

$$\Delta P^* = P^*(SnS_2)_{T_2} - P^*(SnS_2)_{T_1},$$

where $T_2 > T_1$. The solubility of SnS_2 can be expressed in terms of the gaseous sulfur or Sn-iodide species, e.g., P* is the sum of the sulfur partial pressures in terms of S_2 molecules,

$$P^*(SnS_2) = P(S_2) + 3/2\ P(S_3) + 2P(S_4) + 5/2\ P(S_5) + 3\ P(S_6) + 7/2\ P(S_7) + 4\ P(S_8).$$

The partial pressures are calculated at T_2 and T_1 based on the above indicated transport reactions. The quantity ΔP^* is calculated for different temperature gradients as a function of total pressure of the system.

In the absence of kinetic limitations, for positive values of ΔP^* forward transport ($T_2 \rightarrow T_1$) is dominant. When ΔP^* is negative, net reverse transport will occur. The presence of both forward and reverse transport implies the existence of an inversion temperature at which the solubility of the solid is a minimum. Calculations of ΔP^* as a function of pressure reveal that the inversion pressure (change in transport direction) occurs at higher total pressures with increasing temperature. The results of these calculations are consistent with present investigations and previous studies on the SnS_2-SnI_4 and SnS_2-I_2 systems.

For the calculation of partial pressures in this truly multi-component multi-reaction system SnS_2-SnI_4-I_2 [23], a program was developed for the simultaneous solution of several chemical equilibria. The program is based on the minimization of the free energy for the entire system as a function of temperature and pressure. The results of the above studies are of general applicability and are of basic scientific and practical importance. Through the use of the hypothetical pressure (solubility) P^* of SnS_2, a relationship has been given which allows the unambiguous calculation of the net transport direction. This is of practical value for the optimization of crystal growth and transport conditions.

Before reliable transport experiments and thermodynamic calculations on the above systems could be performed, the stability range of SnS_2 had to be established [24]. Based on mass spectrometric studies, SnS_2 decomposes measurably at temperatures above about 350°C according to the reaction

$$2\ SnS_2(s) = Sn_2S_3(s) + \tfrac{1}{2}\ S_2(g)\ .$$

Higher molecular species were below the detection limits of the instrument. Quantitative Knudsen-type mass-loss measurements employing automatic vacuum microbalance techniques in the temperature range 350° - 500°C yielded absolute partial pressures of S_2 for the above reaction to be in the range 10^{-7} - 10^{-4} atm.

Similar mass spectrometric and microbalance mass-loss measurements [24] established the decomposition and absolute partial pressures for Sn_2S_3 according to the reaction

$$Sn_2S_3(s) = 2\ SnS(s) + \tfrac{1}{2}\ S_2(g)\ .$$

In the temperature interval 400°C - 525°C, the partial pressures of S_2 range from about 5×10^{-7} to 10^{-4} atm.

The final decomposition product sublimes congruently [24] according to the reaction

$$SnS(s) = SnS(g)\ .$$

The absolute partial pressures of SnS(g) at temperatures between about 475° and 650°C are in the range 10^{-8} to 10^{-4} atm.

The above studies [24] demonstrated that SnS_2 decomposes via

Sn_2S_3 to SnS. The extent of decomposition depends upon temperature and pressure. These studies also yielded the enthalpies and entropies of the above decomposition reactions from which the heats of formation and absolute entropies of $SnS_2(s)$, $Sn_2S_3(s)$ and SnS(s) were obtained. These results [24] were used for the thermodynamic calculations of the transport studies [23]. Under the conditions of the chemical vapor transport reactions of SnS_2 [23], the decomposition of SnS_2 [24] does not occur.

Chemical vapor transport and crystal growth studies on the Sn-monosulfide and Sn-selenide systems are in progress. Emphasis in these studies is on the elucidation of the crystal growth mechanism of SnS and SnSe and on the reverse transport phenomena of SnSe and $SnSe_2$. The compounds SnS and SnSe have the orthorhombic structure. For crystal growth studies on these materials it is desirable to establish their crystallographic identity and possible phase transformations at elevated temperatures. The results of these studies are briefly summarized below.

The thermal expansion of SnS and SnSe was studied above room temperature up to the melting point of 1163 ± 5 K and 1135 ± 5 K, respectively, by X-ray diffraction techniques using a 190 mm Unicam high temperature camera [25]. The changes of the lattice parameters indicate that the atomic positions in the (010) plane approach a square planar arrangement with increasing temperature. The transformation of SnS and SnSe from orthorhombic to a pseudo-tetragonal orthorhombic modification with $a \simeq c < b$ is observed at 878 ± 5 K and 807 ± 5 K, respectively. The lattice parameters of the high temperature modifications are for SnS $\overline{a,c} = 4.162 \pm 0.006$ Å, $b = 11.517 \pm 0.015$ Å at 932 K and for SnSe $\overline{a,c} = 4.313 \pm 0.006$ Å, $b = 11.703 \pm 0.015$ Å at 820 K. Both compounds maintain this structure type up to the melting points.

The results of these studies [25] reveal that SnS and SnSe undergo considerable changes in lattice parameters with increasing temperature. This is of practical importance with respect to the degree of perfection of single crystals of these materials which could be measurably affected by the rate of cooling the crystals from growth to room temperature. This is of particular concern for Sn containing alloy-type single crystals where the rates of thermal expansion (contraction) are different for the individual components. The effects of coooling rate on crystal morphology will be considered in these on-going studies.

III. SUMMARY AND DIRECTION OF FUTURE RESEARCH

The primary objectives of this research program were to establish the basic vapor transport and crystal growth properties and to determine the thermodynamic, kinetic and structural properties of different classes of materials relevant to the conditions of chemical vapor transport reactions. An important aspect of this program was to observe and to measure the effects of transport parameters, in particular of gravity-driven convection, on the mass transport rate and crystal morphology. These goals have been accomplished through extensive studies on selected Mn-chalcogenides, II-VI and IV-VI compounds. Three different transport modes have been identified which control the mass transport rate in different pressure regimes of the transport system. The negative effects of convective mass transport on crystal morphology have been demonstrated. The thermodynamic and kinetic studies on IV-VI compounds revealed the importance of surface defects and of a mobile surface layer for the sublimation mechanism of single crystals. This is of immediate relevance for the condensation and growth mechanism of crystals. The structural studies on IV-VI compounds demonstrated the existence of solid phase transformations at elevated temperatures associated with considerable lattice expansions and rearrangements of lattice sites. These results have practical consequences for the degree of perfection of crystals and for the growth of alloy-type crystals of these and related materials.

The combined information obtained from these ground-based studies was used to define the systems and experimental conditions for crystal growth studies in micro-gravity environment which were performed during the Skylab and Apollo-Soyuz Missions. The results of these space experiments demonstrated unambiguously a considerable improvement in crystal quality for the space grown specimens relative to corresponding prototype samples obtained on earth. The second major result of the Skylab and Apollo-Soyuz experiments is the observation of greater mass transport rates than expected for a diffusion controlled vapor transport. The results obtained for different compounds, pressures and temperature gradients in micro-gravity are of basic scientific and technological significance.

The vapor transport and crystal growth data produced to date under this program on earth and in space determine the direction of continued research efforts in this area. These can be summarized as follows:

1) The application of rigorous thermodynamic calculations to chemical vapor transport systems to quantitatively characterize the vapor phase. This will lead to a priori determinations of the net transport direction, of the inversion temperature and of optimimum growth conditions of a system. 2) Continued investigations of fluid dynamic properties of vapor transport systems, including measurements of temperature fluctuations inside closed ampoules and of the effects of ampoule orientation and geometry on transport rates and crystal morphology. 3) Detailed growth rate studies of individual single crystals to differentiate between the effects of gas motion (convection) and growth mechanism on growth velocity and morphology of crystals.

The above indicated future studies have been initiated under a separate project. The results will be of practical importance for the design of future flight experiments and for the space processing of single crystals of preselected orientation and growth velocity.