Thermodynamic Properties and Defect Structure of Semiconducting Compound Phases: Tin Telluride

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Defect equilibria for binary semiconducting compound phases which exhibit ionized native donor and acceptor defects were considered, and equations describing the pressure-temperature-composition relationships for these compound phases were derived. These equations were used to analyze experimental data from the literature for tin telluride. Excellent agreement was obtained between calculated thermodynamic and phase boundary values and experimental data. The approach presented is readily extended to obtain equations for the thermodynamic properties of ternary and higher order semiconducting compound phases.

I. INTRODUCTION

THE IV-VI semiconducting compounds have narrow band gaps and may be used for infrared detectors and tunable lasers. These compounds have appreciable ranges of homogeneity and their semiconducting properties depend strongly on the extent of deviation from the stoichiometric composition. In order to optimize the conditions for growing crystals, it is essential to have a knowledge of the pressure-temperature-composition relationship within the homogeneous range. Using a statistical thermodynamic approach, Brebrick[1] has derived equations for the chemical potentials of the component elements as a function of deviation from the stoichiometric ratio. Because of his definition of the partial Gibbs energy of the component elements in terms of the defect concentrations, however, extension of his approach to ternary phases is difficult. Brebrick[2] subsequently applied these equations to analyze the pressure-temperature-composition data of SnTe and PbTe. One of the parameters of the model is the intrinsic carrier concentration at the stoichiometric composition. To treat the temperature dependence of the intrinsic carrier concentration, Brebrick[2] assumed that $\ln n_i = A + B/T$, with n_i being the intrinsic carrier concentration. This cannot be correct, because we know from theoretical considerations that $\ln n_i$ must have a $3/2 \ln T$ term.[3] This point is treated later.

By considering the chemical equilibrium of defects, Harman and Strauss[4] derived equations to represent the pressure-temperature-composition dependence of semiconducting compounds which exhibit singly ionized native donor and acceptor defects. Extension of their approach to semiconducting compounds which exhibit doubly ionized native donor and acceptor defects yields equations which are mathematically complex. Application of these equations to describe the thermodynamic properties of semiconducting compound phases is cumbersome. The data for PbS were analyzed by Harman and Strauss[4] using the equations derived by them for singly ionized native donor and acceptor defects.

The objectives of the present study are (1) to derive thermodynamic equations for binary, ternary, and higher order semiconducting compounds which have native donor and acceptor defects and (2) to analyze the pertinent data for SnTe in terms of the derived equations.

II. DERIVATION OF THE THERMODYNAMIC EQUATIONS

A. *Binary Semiconducting Compound Phases*

Let us consider a semiconducting compound phase MX exhibiting predominant Schottky defects. These defects are completely ionized vacancies on the metal and metalloid sublattices, respectively. For native donor defects, we have the following defect equilibrium:

$$M(\mathrm{g}) = M_M + \square_X^{+Z} + Z_{e-} \qquad [1]$$

where $M(\mathrm{g})$ represents pure metal in the gas phase, M_M represents the metal atoms on the metal sublattice, $\square_X^{+Z}$ is the vacancy on the metalloid sublattice with a Z degree of ionization, and e^- is an electron. Similarly, for native acceptor defects, we have the following equilibrium:

$$\frac{1}{2}X_2(\mathrm{g}) = X_X + \square_M^{-Z} + Zh^+ \qquad [2]$$

where X_2 is pure gaseous X_2, X_X is the metalloid atom on the metalloid sublattice, $\square_M^{-Z}$ is the vacancy on the metal sublattice with a Z degree of ionization, and h^+ is a hole. The equilibrium between the component elements and the compound phase is

$$M(\mathrm{g}) + \frac{1}{2}X_2(\mathrm{g}) = MX\,(c) \qquad [3]$$

When the defect concentrations are small, we may obtain the following relations:

$$n = \left[\frac{K_1 p_M}{\square_X^{+Z}}\right]^{1/Z} \qquad [4]$$

$$p = \left[\frac{K_2 p_{X_2}^{1/2}}{\square_M^{-Z}}\right]^{1/Z} \qquad [5]$$

and

$$p_M = \left[\frac{K_3}{p_{X_2}^{1/2}}\right] \qquad [6]$$

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Manuscript submitted March 25, 1985.

where n is the concentration of the electrons and p that of the holes. Eliminating p_M from Eqs. [4] and [6] yields

$$n = \left[\frac{K_1K_3}{\square_X^{+Z} p_{X_2}^{1/2}}\right]^{1/Z} \qquad [7]$$

At the stoichiometric composition, Eqs. [7] and [5] become

$$n_i = \left[\frac{K_1K_3}{\square_X^{+Z,0} p_{X_2}^{\circ\ 1/2}}\right]^{1/Z} \qquad [8]$$

and

$$p_i = \left[\frac{K_2(p_{X_2}^{\circ})^{1/2}}{\square_M^{-Z,0}}\right]^{1/Z} \qquad [9]$$

From Eqs. [7], [8] and [5] and [9], we obtain

$$n = n_i\left\{\left[\frac{\square_X^{+Z,0}}{\square_X^{+Z}}\right]\left[\frac{p_{X_2}^{\circ}}{p_{X_2}}\right]^{1/2}\right\}^{1/Z} \qquad [10]$$

$$p = p_i\left\{\left[\frac{\square_M^{-Z,0}}{\square_M^{-Z}}\right]\left[\frac{p_{X_2}}{p_{X_2}^{\circ}}\right]^{1/2}\right\}^{1/Z} \qquad [11]$$

Since $n_i = p_i$, Eq. [11] becomes

$$p = n_i\left\{\left[\frac{\square_M^{-Z,0}}{\square_M^{-Z}}\right]\left[\frac{p_{X_2}}{p_{X_2}^{\circ}}\right]^{1/2}\right\}^{1/Z} \qquad [12]$$

Subtracting Eq. [10] from Eq. [12] yields

$$\frac{p-n}{n_i} = \left\{\left[\frac{\square_M^{-Z,0}}{\square_M^{-Z}}\right]\left[\frac{p_{X_2}}{p_{X_2}^{\circ}}\right]^{1/2}\right\}^{1/Z} - \left\{\left[\frac{\square_X^{+Z}}{\square_X^{+Z,0}}\right]\left[\frac{p_{X_2}}{p_{X_2}^{\circ}}\right]^{1/2}\right\}^{-1/Z} \qquad [13]$$

The above equation may be simplified for a nondegenerate semiconductor as given below. For a nondegenerate semiconductor,

$$np = n_i^2 = p_i^2 \qquad [14]$$

$$(\square_X^{+Z})(\square_M^{-Z}) = K_s = (\square_X^{+Z,0})(\square_M^{-Z,0}) = (\square_X^{+Z,0})^2 = (\square_M^{-Z,0})^2 \qquad [15]$$

In order to maintain electrical neutrality, we have

$$(n-p) + Z(\square_M^{-Z} - \square_X^{+Z}) = 0 \qquad [16]$$

From Eqs. [13] and [15], we obtain

$$\frac{p-n}{n_i} = \left\{\left[\frac{K_s^{1/2}}{\square_M^{-Z}}\right]\left[\frac{p_{X_2}}{p_{X_2}^{\circ}}\right]^{1/2}\right\}^{1/Z} - \left\{\left[\frac{K_s^{1/2}}{\square_M^{-Z}}\right]\left[\frac{p_{X_2}}{p_{X_2}^{\circ}}\right]^{1/2}\right\}^{1/Z} \qquad [17]$$

Using a hyperbolic sine function to represent the RHS of Eq. [17], we have

$$\frac{p-n}{n_i} = 2\sinh\left[\ln\left\{\left[\frac{K_s^{1/2}}{\square_M^{-Z}}\right]\left[\frac{p_{X_2}}{p_{X_2}^{\circ}}\right]^{1/2}\right\}^{1/Z}\right] \qquad [18]$$

Alternatively, the above equation may be represented as

$$Z\sinh^{-1}\left(\frac{p-n}{2_{n_i}}\right) = \ln\left[\frac{K_s^{1/2}}{\square_M^{-Z}}\right] + \frac{1}{2}\ln\left[\frac{p_{X_2}}{p_{X_2}^{\circ}}\right] \qquad [18A]$$

We will next use the electrical neutrality equation to express $\square_M^{-Z}$ in terms of K_s. Dividing, Eq. [16] and rearranging of terms yields

$$\frac{p-n}{ZK_s^{1/2}} = \left[\frac{\square_M^{-Z}}{K_s^{1/2}}\right] - \left[\frac{\square_X^{+Z}}{K_s^{1/2}}\right] \qquad [19]$$

Eliminating ${}_X^{+Z}$ from Eqs. [15] and [19] yields

$$\frac{p-n}{ZK_s^{1/2}} = \left[\frac{\square_M^{-Z}}{K_s^{1/2}}\right] - \left[\frac{\square_M^{-Z}}{K_s^{1/2}}\right]^{-1} \qquad [20]$$

Again using a hyperbolic sine function to represent the RHS term of Eq. [20], we obtain

$$\sinh^{-1}\left[\frac{p-n}{2ZK_s^{1/2}}\right] = \ln\left[\frac{\square_M^{-Z}}{K_s^{1/2}}\right] \qquad [21]$$

Eliminating the term $\ln[\square_M^{-Z}/K_s^{1/2}]$ from Eqs. [18A] and [21] and rearranging of terms yields

$$\ln p_{X_2} = \ln p_{X_2}^{\circ} + 2Z\sinh^{-1}\left[\frac{p-n}{2n_i}\right] + 2\sinh^{-1}\left[\frac{p-n}{2ZK_s^{1/2}}\right] \qquad [22]$$

From Eqs. [6] and [22], we obtain the corresponding equation for the chemical potential of the metal component as

$$\ln p_M = \ln p_M^{\circ} - 2Z\sinh^{-1}\left[\frac{p-n}{2_{n_i}}\right] - 2\sinh^{-1}\left[\frac{p-n}{2ZK_s^{1/2}}\right] \qquad [23]$$

If values of p_M° and $p_{X_2}^{\circ}$ are known at the stoichiometric composition, these equations contain two parameters, n_i and K_s. Values of n_i and K_s may be obtained by optimization from experimental data as a function of composition and temperature. In addition, the value of $p_{X_2}^{\circ}$ may be obtained by optimization from experimental data since the phase may not be stable at the stoichiometric composition. In fact, even when the phase exists at the stoichiometric composition, the experimental value of $p_{X_2}^{\circ}$ may not be available and the second approach may be the preferred way for obtaining the best values of $p_{X_2}^{\circ}$, n_i, and K_s.

Equations [22] and [23] are the same as those obtained by Brebrick[1,2] from statistical thermodynamics. Since Brebrick defined the chemical potential of the component elements in terms of the number of moles of the vacancies formed, it is difficult to extend the treatment to ternary phases. As will be shown in the next section, the present approach may be extended readily to ternary and even quaternary phases. If Z is set equal to 1, Eqs. [22] and [23] reduce to the same equations obtained by Harman and Strauss.[4] As mentioned earlier, application of their equations for compound phases with doubly ionized donor and accepter defects is cumbersome.

B. *Ternary Semiconducting Compound Phases*

For a ternary compound phase, $(M_1, M_2)X$, we may have the following equilibria:

$$M_1(g) = (M_1)_M + \square_X^{+Z} + Z_{e^-} \qquad [24]$$

$$M_2(g) = (M_2)_M + \Box_X^{+Z} + Z_{e^-} \quad [25]$$

$$\frac{1}{2}X_2(g) = X_X + \Box_M^{-Z} + Z_{h^+} \quad [26]$$

$$M_1(g) + \frac{1}{2}X_2(g) = M_1X(\text{sol'n}) \quad [27]$$

$$M_2(g) + \frac{1}{2}X_2(g) = M_2X(\text{sol'n}) \quad [28]$$

where (sol'n) stands for the solid solutions between M_1X and M_2X. These may be represented as $(M_1)_{1-y}(M_2)_yX$, with y being the mole fraction of M_2X in $(M_1,M_2)X$. From Eqs. [24] through [28], we have the following relations:

$$n = \left[\frac{K_{24}p_{M_1}}{\Box_X^{+Z}}\right]^{1/Z} \quad [29]$$

$$n = \left[\frac{K_{25}p_{M_2}}{\Box_X^{+Z}}\right]^{1/Z} \quad [30]$$

$$p = \left[\frac{K_{26}p_{X_2}^{1/2}}{\Box_M^{-Z}}\right]^{1/Z} \quad [31]$$

$$K_{27}^{-1} = p_{M_1}p_{X_2}^{1/2} \quad [32]$$

$$K_{28}^{-1} = p_{M_2}p_{X_2}^{1/2} \quad [33]$$

Following the procedure used for binary compound phase MX from Eq. [7] to Eqs. [22,23], we obtain the following three equations for the partial pressures of X_2, M_1, and M_2 as

$$\ln p_{X_2}(y) = \ln p_{X_2}^{\circ}(y) + 2Z\sinh^{-1}\left[\frac{p-n}{2n_i}\right] + 2\sinh^{-1}\left[\frac{p-n}{2ZK_s^{1/2}}\right] \quad [34]$$

$$\ln p_{M_1}(y) = \ln p_{M_1}^{\circ}(y) - 2Z\sinh^{-1}\left[\frac{p-n}{2n_i}\right] - 2\sinh^{-1}\left[\frac{p-n}{2ZK_s^{1/2}}\right] \quad [35]$$

$$\ln p_{M_2}(y) = \ln p_{M_2}^{\circ}(y) - 2Z\sinh^{-1}\left[\frac{p-n}{2n_i}\right] - 2\sinh^{-1}\left[\frac{p-n}{2ZK_s^{1/2}}\right] \quad [36]$$

where y specifies the mole fraction of M_2X in the solid solution $(M_1)_{1-y}(M_2)_y$. These three equations describe the composition dependence of the chemical potentials of X_2, M_1, and M_2 as a function of the metalloid composition at a specified value of y. Values of $\ln p_{X_2}^{\circ}$, $\ln p_{M_1}^{\circ}$, and $\ln p_{M_2}^{\circ}$ may be obtained directly from experimental data. Alternatively, we may have a thermodynamic solution model to describe $(M_1,M_2)X$ as a quasibinary using a quasi-regular or quasi-subregular model. The model parameters may be obtained from direct thermochemical data or estimated from other pertinent data. With this approach, Eqs. [24] through [26] may be rewritten in terms of the chemical potentials of M_1,X_2 and M_2,X_2 for M_1X and M_2X.

For a quaternary phase, we may follow the same approach by writing the appropriate defect equilibria and then derive the pertinent equations for the partial Gibbs energy of the component elements.

III. THE TIN TELLURIDE

The thermodynamic behavior and phase relationships of the Sn-Te binary system, including the semiconducting compound phase, SnTe, have been investigated more thoroughly than those of the other IV-VI binaries. The thermodynamic properties of the liquid phase were measured by Nakamura, Himuro, and Shimoji,[5] Rakotomavo, Baron, and Petot,[6] and Blachnik and Gather;[7] those of solid SnTe were measured by McAteer and Seltz,[8] Ravindar, Mehrotra, and Tare,[9] Pool,[10] Robinson and Bever,[11] Pool, Spencer, and Guadagno,[12] Shamsuddin and Misra,[13] Nesterova, Pashinkin, and Novoselova,[14] Hirayam, Ichikawa, and DeRou,[15] Brebrick and Strauss,[16] Colin and Drowart,[17] Lyubimov and Bespal'teseva,[18] and Sokolov, Pashchinkin, Novoselova, Ryazantsev, Dolgikh, and Klinchikova.[19] The liquidus of the binary was determined by Biltz and Mecklenburg,[20] Kobayashi,[21] LeBouteiller, Martre, Farhi, and Petot,[22] Rakotomavo *et al.*,[6] Pool *et al.*,[10] Harris, Longo, Gertner, and Clarke,[23] and Rakotomavo *et al.*[6] The range of stability of SnTe is appreciable and was determined by Krebs, Grun, Kallen, and Lippert,[24] Umeda, Jeong, and Okada,[25] Brebrick,[26] Brebrick and Strauss,[16] and Shelimova and Abrikosov.[28] The thermodynamic and phase equilibrium data were assessed by Hsieh, Wei, and Chang[29] using an associated solution model for the liquid phase. The SnTe compound phase was taken by Hsieh *et al.*[29] to be a line compound. They obtained excellent correlation between the calculated thermodynamic properties, the phase diagram of the system, and the experimental data available in the literature. More recently, Sharma and Chang[30] made a review of the system which included all pertinent data and the model of Hsieh *et al.*[29] In the present study, the pressure-temperature-composition relationships of SnTe were obtained using the model of Hsieh *et al.*[29] along the phase boundary of SnTe and the measured values within the solid phase field.

Before carrying out the evaluation, let us first discuss the temperature dependence of the intrinsic carrier concentration n_i. As mentioned in the introduction, Brebrick[2] expressed $\ln n_i$ as a linear function of reciprocal temperature. According to the theory of nondegenerate semiconductors,[3]

$$n_i = 2\left[\frac{2\pi kT}{h^2}\right]^{3/2}(m_e m_h)^{3/4}\exp\left(-\frac{E_g}{2kT}\right) \quad [37]$$

where k is the Boltzmann constant, T the absolute temperature, and h Planck's constant; m_e and m_h are the effective masses of an electron and a hole; and E_g is the energy band gap. If we assume m_e and m_h to be temperature-independent and E_g to be a linear fraction of temperature, Eq. [37] may be reduced to

$$\ln n_i = A' + \frac{B'}{T} + 1.5\ln T \quad [38]$$

where $A' = \ln[2(2\pi k/h^2)^{3/2}(m_e m_h)^{3/4}] - (\partial E_g/\partial T)1/2k$ and $B' = (-E_{g0}/2k)$ with E_{g0} being the energy band gap at absolute zero. In the present study, the value of B' is calculated from E_{g0} and only A' is treated as an adjustable parameter. The temperature dependence of $\ln n_i$ expressed in Eq. [38] differs from that used by Brebrick.

Let us next examine Eqs. [22, 23]. In addition to n_i, the other model parameter is K_s. We must also treat $p^{\circ}_{X_2}$ as a parameter, since SnTe does not exist at the stoichiometric composition. Values of $\ln p^{\circ}_{M}$ may be obtained from those of $\ln p^{\circ}_{X_2}$ and the integral Gibbs energy of formation of SnTe. In the present study both $\ln K_s$ and $\ln p^{\circ}_{X_2}$ are assumed to vary linearly with the reciprocal temperature as given below:

$$\ln K_s = C + \frac{D}{T} \qquad [39]$$

$$\ln p^{\circ}_{X_2} = E + \frac{F}{T} \qquad [40]$$

We now have a total of 5 parameters, A', C, D, E, and F, whose values must be obtained from pressure-temperature-composition data for SnTe.

Solid SnTe exists only with an excess of Te atoms; accordingly, it is a p-type semiconductor. The relationship between $(p - n)$ and the deviation from stoichiometry is

$$(x_{\mathrm{Te}} - 0.5) = \frac{(p - n)M_{\mathrm{SnTe}}}{4Z\rho \mathrm{N}} \qquad [41]$$

where M_{SnTe} is the molecular weight of SnTe, ρ is the density, and N is Avogadro's number. The density of SnTe, obtained from Brebrick,[31] is given in Table I; since SnTe is known to exhibit doubly ionized vacancies,[31,32] $Z = 2$. The band gap at 0 K, E_{g0}, is 0.36 eV, according to Burke and Riedl.[33] Knowing the values of Z, ρ, and E_{g0}, values of A', C, D, E, and F were obtained by optimization from the pressure-temperature-composition data available in the literature.[16,30] These parameter values are given in Table I. Figure 1 shows a comparison between the calculated and experimental values of $\log p_{\mathrm{Te}_2}$ within the field of SnTe. Agreement is within the uncertainty of the data. Figures 2(a) and (b) show comparisons between the calculated phase boundary of SnTe and the experimental boundary reported in the literature.[16,26,28,31,32,34,35] Again, excellent agreement is obtained between the calculated and experimental data. It is noteworthy to point out that we have used the same approach to analyze several other IV-VI semiconducting phases with equal success.

APPENDIX

In the present study, we have derived equations for the thermodynamic properties of components of binary semiconducting phases which exhibit native defects. We have used the same approach to obtain equations for the properties of other types of defects, such as metal and metalloid interstitials. For instance, for the case of interstitial defects we may have the following equilibria:

$$M(\mathrm{g}) = M_i^{+Z} + Z_{e^-} \qquad [\mathrm{A1}]$$

$$\frac{1}{2}X_2(\mathrm{g}) = X_i^{-Z} + Z_{h^+} \qquad [\mathrm{A2}]$$

Following the procedure presented in Section II, we can obtain the desired thermodynamic equations. In fact, for the defect equilibria given by Eqs. [A1, A2], we obtain equations identical to Eqs. [22, 23].

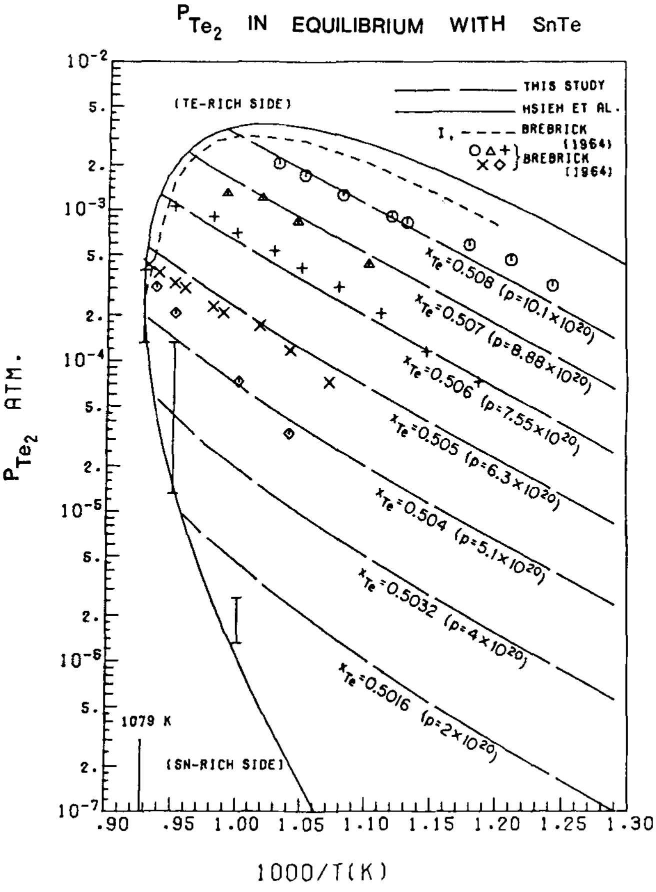
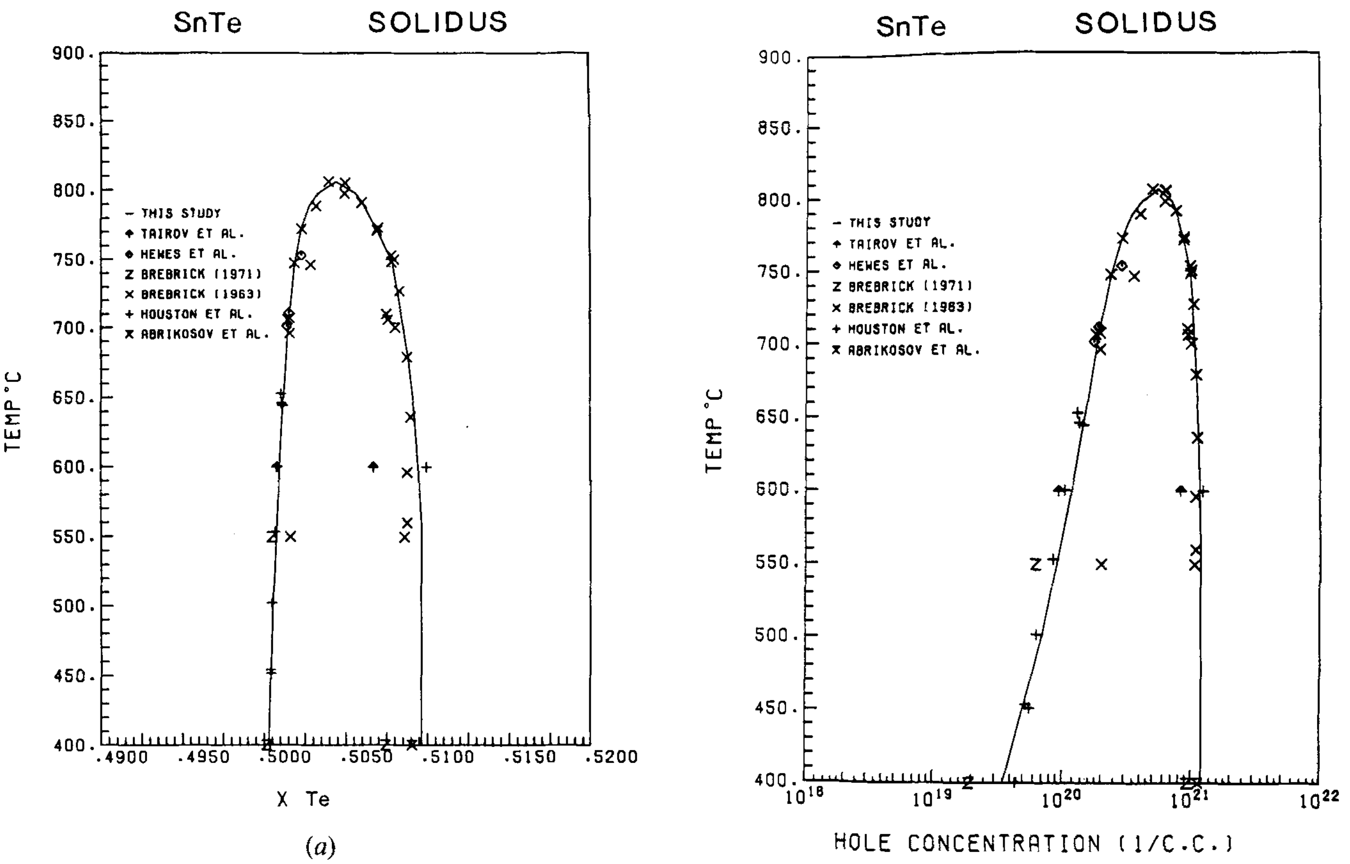


Fig. 1 — Pressure-temperature-composition diagram for SnTe: comparison between calculated and experimental values.

Table I. Thermodynamic and Other Properties of SnTe

			References
$\log n_i$, $(\mathrm{cc})^{-1}$	$-906.19/T + 1.5 \log T + 16.18$	673 to 1079 K	this study
$\log K_s^{1/2}$	$-2922.9/T + 22.98$	673 to 1079 K	this study
$\log p^{\circ}_{\mathrm{Te}_2}$, atm	$-16{,}294.79/T + 7.54$	673 to 1079 K	this study
$^{\circ}G_{\mathrm{SnTe}} - 1/2(^{\circ}G^{l}_{\mathrm{Sn}} + {}^{\circ}G^{l}_{\mathrm{Te}})$ kJ/gatom	$-85\,098 + 37.99\,T$	533 to 1030 K	29, 30
ρ, g/cc	6.461		31
Z	2	—	31, 32
E_{g0}, eV	0.36	0 K	33



(*a*)

(*b*)

Fig. 2—(*a*) The phase boundary of SnTe in equilibrium with the liquid phase: comparison between the calculated and experimental values. (*b*) The phase boundary of SnTe in equilibrium with the liquid phase in terms of hole concentrations: comparison between the calculated and experimental values.

ACKNOWLEDGMENT

The authors wish to thank the National Science Foundation for financial support through grants No. NSF-DMR-83-10529 and NSF-DMR-85-14421.

REFERENCES

1. R. F. Brebrick: *J. Solid State Chem.*, 1969, vol. 1, pp. 88-97.
2. R. F. Brebrick: *J. Electron. Mater.*, 1977, vol. 6, pp. 659-92.
3. C. Kittel: *Introduction to Solid State Physics*, 5th ed., John Wiley & Sons, Inc., New York, NY, 1976.
4. T. C. Harman and A. J. Strauss: *J. Electron. Mater.*, 1976, vol. 5, pp. 621-44.
5. Y. Nakamura, S. Himuro, and M. Shimoji: *Ber. Bunsenges. Phys. Chem.*, 1980, vol. 84, pp. 240-44.
6. J. Rakotomavo, M-C Baron, and C. Petot: *Metall. Trans. B*, 1981, vol. 12B, pp. 461-67.
7. R. Blachnik and B. Gather: *Z. Metallkd.*, 1983, vol. 74, pp. 172-76.
8. J. H. McAteer and H. Seltz: *J. Am. Chem. Soc.*, 1936, vol. 58, pp. 2081-84.
9. P. Ravindar, G. M. Mehrotra, and V. B. Tare: *Metall. Trans. B*, 1979, vol. 10B, pp. 117-18.
10. M. J. Pool: *Trans. TMS-AIME*, 1965, vol. 233, pp. 1711-15.
11. P. M. Robinson and M. B. Bever: *Trans. TMS-AIME*, 1966, vol. 236, pp. 814-17.
12. M. J. Pool, P. J. Spencer, and J. R. Guadagno: *Trans. TMS-AIME*, 1968, vol. 242, pp. 1481-82.
13. Shamsuddin and S. Misra: *J. Therm. Anal.*, 1975, vol. 7, pp. 309-16.
14. Y. M. Nesterova, A. S. Pashinkin, and A. V. Novoselova: *Russ. J. Inorg. Chem.*, 1961, vol. 6, pp. 1031-33.
15. C. Hirayam, Y. Ichikawa, and A. M. DeRou: *J. Phys. Chem.*, 1963, vol. 67, pp. 1039-42.
16. R. F. Brebrick and A. J. Strauss: *J. Chem. Phys.*, 1964, vol. 11, pp. 197-205.
17. R. Colin and J. Drowart: *Trans. Faraday Soc.*, 1964, vol. 60, pp. 673-83.
18. A. P. Lyubimov and I. I. Bespal'teseva: *Inorg. Mater.* (Engl. Transl.), 1969, vol. 5, pp. 1097-98.
19. V. V. Sokolov, A. S. Pashchinkin, A. V. Novoselova, A. A. Ryazantsev, V. A. Dolgikh, and S. A. Klinchikova: *Inorg. Mater.* (Engl. Transl.), 1969, vol. 5, pp. 12-15.
20. W. Biltz and W. Mecklenburg: *Z. Anorg. Chem.*, 1909, vol. 64, pp. 226-35.
21. M. Kobayashi: *Z. Anorg. Chem.*, 1911, vol. 69, pp. 6-9.
22. M. LeBouteiller, A. M. Martre, R. Farhi, and C. Petot: *Metall. Trans. B*, 1977, vol. 8B, pp. 339-44.
23. J. S. Harris, J. T. Longo, E. R. Gertner, and J. E. Clarke: *J. Cryst. Growth*, 1975, vol. 28, pp. 334-42.
24. H. Krebs, K. Grun, D. Kallen, and W. Lippert: *Z. Anorg. Allg. Chem.*, 1961, vol. 308, pp. 200-11.
25. J. Umeda, M. Jeong, and T. Okada: *Jpn. J. Appl. Phys.*, 1962, vol. 1, pp. 277-82.
26. R. F. Brebrick: *J. Phys. Chem. Solids*, 1963, vol. 24, pp. 27-36.
27. L. E. Glukhikh and N. K. Abrikosov: *Russ. J. Inorg. Chem.*, 1963, vol. 8, pp. 930-31.
28. L. E. Shelimova and N. K. Abrikosov: *Russ. J. Inorg. Chem.*, 1964, vol. 9, pp. 1017-20.
29. K.-C. Hsieh, M. S. Wei, and Y. A. Chang: *Z. Metallkd.*, 1983, vol. 74, pp. 330-37.
30. R. C. Sharma and Y. A. Chang: Univ. of Wisconsin-Madison, Madison, WI, 1984, unpublished research.
31. R. F. Brebrick: *J. Phys. Chem. Solids*, 1971, vol. 32, pp. 551-62.
32. B. B. Houston, R. S. Allgaier, R. S. Babiskin, and P. G. Sieberman: *Bull. Am. Phys. Soc.*, 1964, vol. 9, p. 60.
33. J. R. Burke and H. R. Riedl: *Phys. Rev.*, 1969, vol. 184, pp. 830-36.
34. S. M. Tairov, B. F. Ormont, and N. O. Skostak: *Inorg. Mater.* (Engl. Transl.), 1970, vol. 6, pp. 1399-1402.
35. C. R. Hewes, M. S. Adler, and S. D. Senturia: *J. Appl. Phys.*, 1973, vol. 44, pp. 1327-32.