

## Anomalous volume expansion in $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$ melts: An analysis employing the inhomogeneous structure model

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(Received 8 January 1985)

New insights into anomalous volume expansion observed earlier in liquid HgTe are made possible if we assume that the liquid consists of a mixture of two kinds of domains and that the anomalous behavior arises from a continuous transformation of one kind into the other with increasing temperature. The analysis is consistent with some of the conclusions of the inhomogeneous structure model of Cohen and Jortner and is along the line of similar analyses carried out on liquid Te,  $\text{In}_2\text{Te}_3$ , and  $\text{Ga}_2\text{Te}_3$  by various workers. Following a thermodynamic approach, we have used this model to interpret the negative thermal expansion below  $750^\circ\text{C}$ , indicating that the transformation of the liquid with heating to a structure of higher coordination number is for the most part completed when the minimum volume point is reached (at  $\sim 750^\circ\text{C}$ ), even though appreciable heterogeneity persists above  $800^\circ\text{C}$ . The expansion at higher temperatures arises from normal volume expansion of the high-temperature phase. This description of a progressive transformation of the HgTe liquid into a high-coordination-number domain which may be more metallic is consistent with the rapid increase in the magnitude of experimental thermal diffusivity values of HgTe melts reported recently, though no direct determination of the liquid structure is available at this time. The analysis has been extended to pseudobinary  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  melts, containing 5, 10, and 20 mol % solutions of CdTe in HgTe, respectively. For these melts, the volumes, which have been measured earlier, can be closely approximated as sums of volumes of two separate liquids—one HgTe and the other CdTe. The CdTe in the pseudobinary melt undergoes normal volume expansion consistent with the behavior reported for a pure CdTe melt by other workers.

### I. INTRODUCTION

Recently the densities of several  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  liquid pseudobinary alloys were measured.<sup>1</sup> When the liquidus temperature of the system was lower than  $750^\circ\text{C}$ , an anomalous increase in density with temperature or negative thermal expansion was observed. For pure HgTe ( $x=0$ ), this effect is very strong, with the temperature range over which this anomalous behavior is observed extending from  $670^\circ\text{C}$ , the melting point, to  $750^\circ\text{C}$ . The return to normal behavior, that is, the resumption of volume expansion as a linear function of increasing temperature, is not complete even at  $800^\circ\text{C}$ . A similar strong effect is observed for both liquid  $\text{In}_2\text{Te}_3$  and  $\text{Ga}_2\text{Te}_3$ .<sup>2</sup> For these three compounds, the temperature range over which the negative thermal expansion is observed and the magnitude of the volume contraction itself are among the highest when compared with the corresponding values for any other compounds or elements at elevated temperatures.

Interestingly, the solid-to-liquid volume changes of these three compounds do not follow a similar pattern. Pure HgTe decreases in volume on melting,<sup>1</sup> whereas  $\text{In}_2\text{Te}_3$  and  $\text{Ga}_2\text{Te}_3$  display the "normal" behavior, namely, an increase in volume upon melting. In this respect, HgTe is similar to Si, Ge, and a host of other semiconducting III-V compounds.<sup>1,2</sup> For these latter materials contraction upon melting has been explained to be due to an increase in the atomic coordination number.<sup>2-4</sup> These materials also exhibit metallic conductivity ( $\sigma > 10^4$

$\Omega^{-1}\text{cm}^{-1}$ ) immediately above the melting point ( $T_m$ ).<sup>5</sup> It is postulated that a similar increase in the average atomic coordination number must also accompany melting of HgTe. But unlike Si, Ge, and InSb, the continuing increase of the HgTe melt density upon increase of the temperature also indicates a *continuing* increase in local coordination.

In this paper, we analyze the anomalous dependence of molar volume on temperature for pure HgTe by assuming the liquid to consist of two kinds of domains and the anomalous behavior to arise from a progressive transformation of one kind of domain into another. We use a model based on an extension of the inhomogeneous structure model developed by Cohen and Jortner (Refs. 6 and 7) who applied it to pure Te (Ref. 8) and similar to the description of the molar volume, electrical conductivity, magnetic susceptibility, and thermoelectric power of liquid selenium-tellurium,  $\text{In}_2\text{Te}_3$  and  $\text{Ga}_2\text{Te}_3$  systems employed by Tsuchiya and co-workers.<sup>9-11</sup> We subsequently demonstrate that a relatively straightforward extension of the model can explain the molar volumes of 5, 10, and 20 mol % solutions of CdTe in the melt. Implications of this analysis will be discussed in light of the thermal data available for  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  melts.

### II. PREVIOUS WORK

#### A. Liquid tellurium

A few of the compounds containing tellurium are among the materials displaying the most persistent nega-

tive thermal-expansion coefficients in the melt and have been mentioned above. Liquid tellurium itself also displays similar behavior slightly above the melting point or when undercooled<sup>5,9</sup> and has been extensively analyzed by many workers. It is appropriate here to review briefly the electronic and structural properties of liquid tellurium and subsequently to indicate the relevance of the behavior of the molar volume for this and related systems.

Liquid tellurium is very important among electronically conducting liquids since it exhibits some features of both metallic and semiconducting behavior. For example, a relatively large weakly temperature-dependent electrical conductivity<sup>12-17</sup> ( $\sigma$ ) and a Knight-shift value<sup>17,18</sup> characteristic of metals suggest that it is essentially a poor liquid metal. On the other hand, the conductivity and Knight shift increase with increasing temperature,<sup>17</sup> the Hall coefficient<sup>13,15,17,19</sup> exceeds the free-electron value by a factor of 2 and decreases with increasing temperature, and the thermoelectric power is positive;<sup>12-14,16,20</sup> these properties are qualitatively similar to those of so-called "liquid semiconductors" in which both electron concentrations and mobilities are found to be strongly dependent on temperature.<sup>17</sup>

Cabane and Friedel,<sup>21</sup> employing elastic and quasielastic neutron scattering experiments, interpreted this behavior as arising from a continuous random network of Te atoms which are either twofold or threefold coordinated. The twofold (binary) coordination is a remnant of the helical chain structure of solid Te and is dominant near the melting point. At higher temperatures, there is increasing incidence of threefold (ternary) coordination with covalent bonding similar to that of the arsenic (A7) crystal structure. This latter bonding is responsible for its nearly metallic properties.

Two very different models have been proposed to explain the nonmetal-to-metal transition in this system. The first one is mainly due to Mott<sup>22</sup> and is the so-called pseudogap model in which the electrons see a uniform liquid. It is also known as the "metallic" model. Mott argues that a conductivity value of about  $3000 \Omega^{-1} \text{cm}^{-1}$  represents a lower bound for the conductivity of a normal liquid metal whose properties are describable by a nearly-free electron model; this minimum occurring when the electron mean free path becomes comparable with the average interatomic spacing and the predicted value agrees reasonably well with the observed conductivity of liquid Te (Refs. 17 and 22) ( $\sigma \sim 2000 \Omega^{-1} \text{cm}^{-1}$ ). The binary bonding discussed above was held responsible for a minimum or pseudogap in the density of states apparently explaining the low number of electrons per atom ( $\sim 2.5$  from Hall-coefficient measurements).<sup>17,22,23</sup> As the concentration of ternary sites increases at higher temperatures, free electrons are generated according to this model, and these additional carriers are responsible for the increasingly metallic character of the liquid at higher temperatures.

A second model has been proposed recently by Cohen and Jortner<sup>6-8</sup> to explain the continuous nonmetal-metal transition, as indicated here. Both the local electronic structure and the transport properties were described as a consequence of inhomogeneities (microscopic or submacro-

scopic) in the liquid. The metal-nonmetal change in expanded liquid mercury<sup>6</sup> and metal-ammonia solutions<sup>7</sup> involved a distribution of density fluctuations and concentration fluctuations, respectively. The model was extended to tellurium<sup>8</sup> where the medium was considered as submacroscopically inhomogeneous. Two well-characterized types of domains are assumed, the sizes of which are large enough to allow definition of *separate* electronic properties within the respective domains. One kind of domain has a twofold Te configuration and is nonmetallic, and the other has threefold coordination and is metallic. Changes of electronic properties are induced by relative changes of the fractions of two domains. The inhomogeneous transport model appears to be able to explain experimental results on physical and electronic properties, yielding considerably better agreement with the transport data than was possible with any kind of homogeneous transport theories.<sup>6-8</sup> This seems particularly true for systems where, like tellurium, the observed nonmetal-to-metal transition or the transformation of a structure with lower coordination to one with higher coordination is gradual and continuous, as is apparent from a recent series of extensive studies<sup>9-11,24,25</sup> on liquid  $\text{In}_2\text{Te}_3$ ,  $\text{Ga}_2\text{Te}_3$ , and the Se-Te systems. Note that all of these were either compounds or alloys of tellurium.

### B. Behavior of molar volume

The temperature dependence of the molar volume is very important in an understanding of all these systems.<sup>8-11</sup> These materials show a nonlinear temperature dependence of the molar volume, similar to  $\text{HgTe}$ . An approach consistent with the basic conclusions of the inhomogeneous structure model is employed to describe the molar volume.<sup>8-11,24,25</sup> The mole fraction of the metallic domains is obtained from the Knight-shift measurements, where the contribution from nonmetallic domains, being very small, is neglected. At sufficiently high temperatures, all nonmetallic domains disappear and the Knight shift becomes almost independent of temperature. The temperature dependence of the Knight shift arises almost completely as a linear function of the mole fraction of the metallic domains.<sup>8-11</sup> The molar volume of the melt is now expressed as

$$V(T,P) = C(T,P)V_0(T,P) + [1 - C(T,P)]V_1(T,P), \quad (1)$$

where  $C(T,P)$  is the mole fraction of the metallic domains, the subscripts 0 and 1 referring to the metallic and nonmetallic domains, respectively, and the temperature and pressure dependence being explicitly shown by  $T$  and  $P$ . When the pressure dependence is ignored, the respective domain molar volumes are expressed as

$$V_i(T) = V_i(T_m)[1 + \alpha_i(T - T_m)],$$

where  $T_m$  is the melting point,  $\alpha_i$  the coefficient of volume expansion, and  $i=0$  or  $1$ .

### III. MOLAR VOLUME OF LIQUID $\text{HgTe}$

The temperature dependence of the molar volume of the  $\text{HgTe}$  melt mentioned above and reported previously<sup>1</sup>

cannot be satisfactorily explained from the decomposition reactions of HgTe alone.<sup>26</sup> During the present investigation this temperature dependence is analyzed employing the inhomogeneous structure model. Here, as in the study on liquid Te, In<sub>2</sub>Te<sub>3</sub>, Ga<sub>2</sub>Te<sub>3</sub>, and Se-Te systems, only two types of domains are assumed, one with a higher coordination number and stable at high temperatures and the other with a lower coordination number and progressively more stable at lower temperatures. As in these other systems, the higher-coordination-number structure may be more metallic, which implies a continuous transformation of the melt into a metallic liquid with heating. This observation is consistent with the rapid rise with increasing temperature in experimental thermal-diffusivity values of liquid HgTe reported recently.<sup>27</sup> This will be discussed in more detail in later sections. However, no other experimental data, such as Knight-shift values or measurements of physical, electronic, or structural properties of liquid HgTe, are available in the literature, due at least in part to experimental difficulties. Some limited thermochemical data exist.<sup>28-30</sup> Therefore a direct (experimental) estimation of the mole fraction of the "high-temperature" phase is impossible. A chemical approach can be employed to overcome this problem. We describe the progressive transformation of liquid HgTe from a structure with a lower coordination number to one with a higher coordination number with increasing temperature by writing an expression for the free energy of mixing for a mixture of domains:

$$G_M = C \Delta G + RT[C \ln C + (1-C) \ln(1-C)], \quad (2)$$

where  $\Delta G$  is the difference in bulk molar free energy between the two domain types and the second term is absolute temperature multiplied by the entropy of mixing (unmixing) of the domains. Here the average dimension of a domain was assumed large enough so that the interaction terms among clusters were neglected. The equilibrium value of  $C$  at a given temperature is given by

$$\left( \frac{\partial G_M}{\partial C} \right)_{T,P} = 0,$$

which leads to

$$\frac{C}{1-C} = \exp \left[ - \frac{\Delta G}{RT} \right]. \quad (3)$$

Now  $\Delta G$  can be written as

$$\Delta G = \Delta H - T \Delta S, \quad (4)$$

where  $\Delta H$  represents the change in molar enthalpy in moving from one type of domain to another and  $\Delta S$  is the difference in internal entropy between the two kinds of domains per mole. Combining Eqs. (3) and (4) yields

$$\frac{C}{1-C} = \exp \left[ - \frac{\Delta H}{RT} + \frac{\Delta S}{R} \right], \quad (5)$$

where  $\Delta H$  and  $\Delta S$  can be assumed to be independent of temperature over the temperature range of interest. This approach then predicts a linear relation between  $\ln[C/(1-C)]$  and  $1/T$ .

Analysis of experimental results available in the literature<sup>9-11</sup> provides considerable evidence that this description is accurate. In liquid tellurium, the difference in bulk molar free energy ( $\Delta G$ ) was deemed to be the main factor in determining the ratio of numbers of two domains while the surface energy, not considered above, was mainly concerned with the domain sizes, from an analysis of the temperature dependence of the molar fraction of the metallic domains determined experimentally.<sup>9</sup> For liquid In<sub>2</sub>Te<sub>3</sub>, the experimental temperature dependence of the volume fraction of the metallic domains  $C$  appears to conform to this model very closely<sup>10</sup> and similar conclusions can be drawn for liquid Ga<sub>2</sub>Te<sub>3</sub>.<sup>11</sup> Note, as indicated above, the experimental determination of  $C$  for these three systems refers essentially to Knight-shift measurements.<sup>9-11</sup>

Equation (5) now describes the temperature dependence of the mole fractions of respective domains required in Eq. (1). We rewrite

$$C = \frac{Be^{-A/T}}{1 + Be^{-A/T}}, \quad (6)$$

where

$$B = \exp \left[ \frac{\Delta S}{R} \right]$$

and

$$A = \frac{\Delta H}{R}.$$

Combining Eqs. (1) and (6) gives

$$V(T) = \frac{Be^{-A/T}}{1 + Be^{-A/T}} V_0(T) + \frac{1}{1 + Be^{-A/T}} V_1(T), \quad (7)$$

where

$$V_0(T) = V_m^0 [1 + \alpha_{V_m} (T - T_m)] \quad (8)$$

and

$$V_1(T) = V_{sm}^0 [1 + \alpha_{V_{sm}} (T - T_m)]. \quad (9)$$

Here  $T_m$  is the melting point,  $V_m^0$ ,  $V_{sm}^0$ , the molar volumes of the high- and low-temperature phases, respectively, at the melting point with  $\alpha_{V_m}$  and  $\alpha_{V_{sm}}$  representing the respective coefficients of volume thermal expansion.

Equation (7) contains six adjustable parameters. The volume data for pure HgTe melt were fitted to Eq. (7) by a method for the estimation of nonlinear parameters due to Marquardt.<sup>31</sup> This program for least-squares estimation yielded values of all six parameters, given in Table I. Figure 1 shows the experimental data and the curve predicted from these parameters. From the nature of multiparameter nonlinear least-squares analysis programs, a degree of correlation between some sets of parameters is unavoidable. Some idea about this can be obtained from an analysis of 95% confidence intervals around each parameter estimated for simultaneous changes of all the parameters. The only relatively large fractional span is associated with coefficients of volume expansion (Table I). The general effect of correlation between parameters on the best-fit values reported in the second column of Table

TABLE I. Values of parameters obtained by fitting Eqs. (7)–(9) to experimental volume data of a  $\text{HgTe}$  melt.

| Parameters        | Magnitude of best fits | 95% Confidence intervals on parameters |             | Units                             |
|-------------------|------------------------|--|-------------|-----------------------------------|
|                   |                        | Upper limit                            | Lower limit |                                   |
| $\Delta H$        | 47.5                   | 47.9                                   | 47.0        | kcal/mole                         |
| $\Delta S$        | 49.6                   | 50.0                                   | 49.1        | e.u.                              |
| $V_m^0$           | 40.0                   | 40.1                                   | 40.0        | $\text{cm}^3/\text{mole}$         |
| $V_{sm}^0$        | 41.9                   | 42.1                                   | 41.7        | $\text{cm}^3/\text{mole}$         |
| $\alpha_{V_m}$    | 1.4                    | 2.1                                    | 1.2         | $10^4\text{ }^\circ\text{C}^{-1}$ |
| $\alpha_{V_{sm}}$ | 3.0                    | 10.0                                   | 1.0         | $10^5\text{ }^\circ\text{C}^{-1}$ |

I is insignificant.

It is of interest to compare the values given in Table I with similar values for the liquid tellurium,  $\text{In}_2\text{Te}_3$ , and  $\text{Ga}_2\text{Te}_3$  systems. The activation enthalpy for liquid tellurium is 17.4 kcal/mole (Ref. 9) whereas for  $\text{In}_2\text{Te}_3$  and  $\text{Ga}_2\text{Te}_3$  the values are 27.4 and 30 kcal/mole, respectively (Refs. 10 and 11). Figure 2 shows the mole fraction  $C$  versus temperature. At the melting point,  $670^\circ\text{C}$ , the amount of the high-temperature phase is  $\sim 40\%$ . The transformation is for the most part completed ( $C=83.2\%$ ) at  $\sim 750^\circ\text{C}$ , the temperature where the molar volume reaches the minimum value (Fig. 1). Nevertheless, appreciable heterogeneity persists above  $800^\circ\text{C}$ . At higher temperatures, the volume change is almost exclusively due to simple thermal expansion of the high-temperature phase.

The thermochemical analysis outlined above can be compared with the description of Glazov<sup>5</sup> for the systems  $\text{In}_2\text{Te}_3$  and  $\text{Ga}_2\text{Te}_3$ : Two competing processes take place in the molten state consisting of a change in the short-range order and the usual increase in the interatomic spacings, the appearance of local vacancies, etc., which make the structure looser. The change in the short-range order above the melting point results in an increase in the packing density. Therefore, according to Glazov, the liquids change progressively from a structure reminiscent of the solid to a high-temperature structure with denser packing and a higher coordination number.

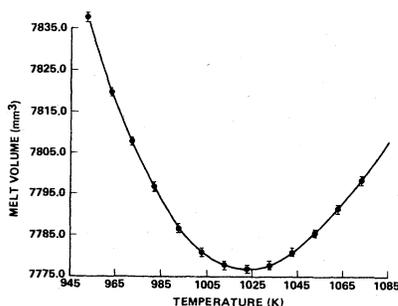


FIG. 1. Experimental data (●) reported previously (Ref. 1) for a pure  $\text{HgTe}$  melt (Ref. 1) fitted to Eqs. (7)–(9) (solid line), as described in the text.

It is of interest to observe that the molar volume of the low-temperature phase at the melting point ( $V_{sm}^0$  in Table I) is higher by about 1.8% than the corresponding solid molar volume just below the melting point ( $41.17\text{ cm}^3/\text{mole}$ ). This latter value was determined by us experimentally and referred to in the previous publication.<sup>1</sup> A slightly different value of 2.1% is obtained when the solid molar volume at the melting point is obtained from the known solid density at room temperature<sup>32</sup> and the low-temperature thermal-expansion coefficients reported by Caporaletti and Graham.<sup>33</sup> Hence normal volume expansion upon melting with a magnitude within a factor of  $\sim 2$  of values determined for metals<sup>34</sup> (4–5%) occurs so far as this phase is concerned.

#### IV. MOLAR VOLUMES OF LIQUID $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$

Densities have been measured for 5%, 10%, and 20 mol % solutions of  $\text{CdTe}$  in  $\text{HgTe}$ .<sup>1</sup> The molar volumes appear to increase with increasing  $\text{CdTe}$  mole fraction and within the appropriate temperature range display negative thermal expansions closely similar to the behavior shown by pure  $\text{HgTe}$ . The dependence of molar volume on temperature is dominated by the  $\text{HgTe}$  portion of the melt, with  $\text{CdTe}$  acting only as a diluent with no contribution to the negative expansion. This is consistent with the behavior of the pure  $\text{CdTe}$  melt itself, the volume of which appears to increase linearly with increasing temperature<sup>2</sup> with no indication of negative expansion.<sup>2</sup> The pseudobinary melt volume was therefore expressed as a

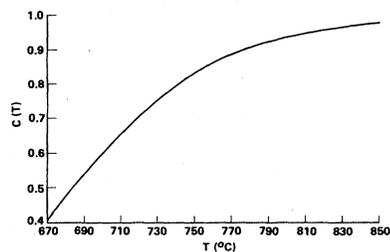


FIG. 2. Variation of the mole fraction  $C(T)$  of the high-temperature phase in a pure  $\text{HgTe}$  melt with temperature.

TABLE II. Values of parameters obtained by fitting Eq. (11) to experimental volume data of  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  melts.

| Parameters                 | Best fit values |          |          | Mean value | Maximum deviation from mean value ( $\pm$ ) | Units                     |
|----------------------------|-----------------|----------|----------|------------|---|---------------------------|
|                            | $x=0.05$        | $x=0.10$ | $x=0.20$ |            |   |                           |
| $\Delta S$                 | 49.3            | 48.9     | 48.9     | 49.0       | 0.3   | e.u.                      |
| $(V_m^0)_{\text{CdTe}}$    | 41.7            | 41.8     | 41.7     | 41.7       | <0.1  | $\text{cm}^3/\text{mole}$ |
| $(\alpha_V)_{\text{CdTe}}$ | 3.0             | 3.1      | 3.0      | 3.0        | <0.1  | $10^5\text{C}^{-1}$       |

sum of three separate liquid volumes—two arising from the HgTe portion and the third from CdTe:

$$V(T) = X(V_m^0)_{\text{CdTe}}[1 + (\alpha_V)_{\text{CdTe}}(T - T_m)] + (1-X)\{C(T)V_0(T) + [1 - C(T)]V_1(T)\}, \quad (10)$$

where  $X$  is the mole fraction of CdTe in the melt,  $(V_m^0)_{\text{CdTe}}$  is the molar volume of CdTe liquid at the melting point of HgTe, conveniently used as the base-line temperature for pseudobinary melts of all compositions, and  $(\alpha_V)_{\text{CdTe}}$  is the volume thermal-expansion coefficient of liquid CdTe.  $C(T)$ ,  $V_0(T)$ , and  $V_1(T)$  have been defined earlier [Eqs. (7)–(9)] and refer to the HgTe portion of the melt only. Presence of CdTe has a barely detectable effect, limited to a shift of the location of the minimum volume point.<sup>1</sup> This was accounted for by considering the entropy term [ $B = \exp(\Delta S/R)$ ] in Eq. (6) as a variable also. We rewrite (10):

$$V(T) = X(V_m^0)_{\text{CdTe}}[1 + (\alpha_V)_{\text{CdTe}}(T - T_m)] + (1-X) \left[ \frac{Be^{-A/T}}{1 + Be^{-A/T}} V_0(T) + \frac{1}{1 + Be^{-A/T}} V_1(T) \right], \quad (11)$$

where  $A$ ,  $V_0(T)$ , and  $V_1(T)$  were obtained from fitting Eq. (7) to the pure HgTe data, as discussed above (Fig. 1 and Table I). These three parameters are now treated as invariants. The volume data for the pseudobinary  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  melts are fitted to Eq. (11) by employing a least-squares analysis program to determine the values of  $(V_m^0)_{\text{CdTe}}$ ,  $(\alpha_V)_{\text{CdTe}}$ , and  $\Delta S (= R \ln B)$ , respectively. These values are shown in Table II. The experimental data and the curves predicted from these parameters are shown in Fig. 3.

The entropy values obtained from this analysis are very close to corresponding values obtained from fitting Eq. (7) to pure HgTe volume data (Table I), with the mean value falling almost within the range given in Table I. The molar volume of CdTe obtained appears to be independent of the CdTe concentration in the melt. It falls between the molar volumes of the high-temperature ( $V_m^0$ ) and the low-temperature ( $V_{sm}^0$ ) structures of pure HgTe melt given in Table I, being closer in magnitude to the molar volume of the low-temperature phase. The molar volume of CdTe in the pseudobinary melt, if extrapolated to the melting point of pure CdTe at 1092°C ( $42.3 \text{ cm}^3/\text{mole}$ ) employing

the thermal-expansion coefficients obtained, agrees very well with the experimentally determined molar volume of pure CdTe immediately upon melting ( $42.3 \text{ cm}^3/\text{mole}$ ) as reported by Glazov *et al.*<sup>2</sup>

The pseudobinary melt, therefore, can be closely approximated by an ideal solution of CdTe in HgTe or

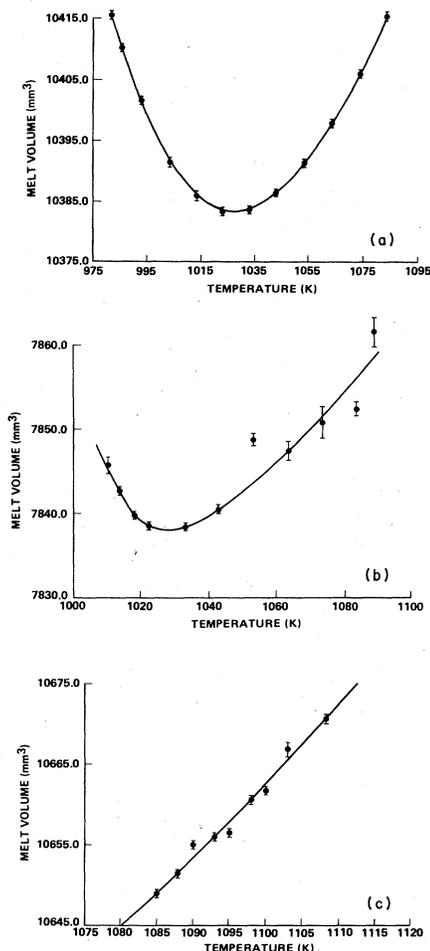


FIG. 3. (a) Experimental data (●) reported previously (Ref. 1) for a  $\text{Hg}_{0.95}\text{Cd}_{0.05}\text{Te}$  melt fitted to Eq. (11) (solid line), as described in the text. (b) Experimental data (●) reported previously (Ref. 1) for a  $\text{Hg}_{0.9}\text{Cd}_{0.1}\text{Te}$  melt fitted to Eq. (11) (solid line), as described in the text. (c) Experimental data (●) reported previously (Ref. 1) for a  $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$  melt fitted to Eq. (11) (solid line), as described in the text.

equivalently, it obeys the laws of mixtures. The molar volume of CdTe in the pseudobinary melt (Table II) is higher by about 0.6% than the molar volume of solid CdTe at the same temperature calculated from the solid density at room temperature<sup>32</sup> and the thermal-expansion coefficient reported.<sup>35</sup> The expansion of pure CdTe upon melting is approximately the same.<sup>2</sup>

The change in molar volume of the melt with progressive addition of CdTe (Ref. 1) is higher than the corresponding changes in solid  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  molar volume (Ref. 32). CdTe is a much more strongly associated compound than HgTe,<sup>29,30</sup> hence, the activity of Te in the melt will be dominated by HgTe decomposition, which will lead to a suppression of CdTe decomposition. CdTe will therefore remain a compound molecule. From the present studies and the work of Glazov *et al.*,<sup>2</sup> it appears that the structure of CdTe in the melt does not suffer modification with heating either when dissolved in HgTe or when it is pure. This may be consistent with the virtual absence of decomposition as discussed above, since structural change has been implicitly suggested to be equivalent to decomposition.<sup>24,25</sup>

## V. GENERAL DISCUSSION

The decrease in molar volume with increasing temperature up to  $\sim 750^\circ\text{C}$  for liquid HgTe has been modeled as arising from a continuous transformation of a low-coordination-number structure to one with a denser packing and higher coordination number, the liquid being always a mixture of these two. The high-coordination-number structure is postulated to be present as domains with the same total number of Hg and Te atoms in the ratio of 1:1 as is present in the lower-coordination-number structure. Analogous to liquid  $\text{In}_2\text{Te}_3$ ,  $\text{Ga}_2\text{Te}_3$ , and elemental Te,<sup>8-11</sup> the high-temperature structure is presumably more metallic. This description is supported by the very large increase in experimental thermal-diffusivity values of HgTe between  $670^\circ\text{C}$  and  $840^\circ\text{C}$  reported recently.<sup>27</sup> At the highest temperatures studied ( $\sim 840^\circ\text{C}$ ), the thermal-diffusivity approaches that of metals.<sup>36</sup>

Note that this trend is in contradiction to the normal behavior of liquids.<sup>37</sup> The mole fraction of the high-temperature phase increases from a value of 0.4 to more than 0.95 within this temperature range (Fig. 2). The change in thermal-conductivity values may even be higher than the thermal-diffusivity values reported<sup>27</sup> since the specific heat of the melt may be much greater than the classical value due to structural transformations and chemical change. Similar rapid rise in thermal conductivity has also been reported for both liquid  $\text{In}_2\text{Te}_3$  and  $\text{Ga}_2\text{Te}_3$  with increasing temperature.<sup>38</sup> This behavior, therefore, appears to be present for systems where the metallization is progressive and continuous over a relatively wide temperature range. Note that the behavior will, in general, differ for molten metals or systems which become fully metallic immediately upon melting. The latter include silicon and germanium.<sup>5</sup> For these systems, the electrical conductivity usually decreases with tempera-

ture and the Wiedemann-Franz law is approximately obeyed.<sup>23,38,39</sup> Consequently, the thermal conductivity will be independent of or weakly dependent on temperature.<sup>38,39</sup>

Solid-to-liquid volume changes can also now be interpreted consistently employing this model. For Si, Ge, and III-V compounds AlSb, InSb, GaAs, and InAs, the transition from mainly covalent bonding in the solid state to mainly metallic bonding in the liquid state is complete or nearly complete immediately upon melting<sup>2,5</sup> leading to an increase in the coordination number<sup>2</sup> (contraction in volume). Further heating only introduces normal thermal expansion but it does not introduce any additional structural changes, the liquid being homogeneous with the maximum realizable coordination already attained. Materials which are already fully metallic in the solid state remain metallic on melting<sup>34</sup> and experience a normal volume expansion of a few percent.<sup>34</sup> Similarly materials like CdTe and ZnTe which are semiconductors in the solid state and melt according to the "semiconductor-to-semiconductor" scheme, also expand upon melting.<sup>2,5</sup> Covalent bonds (in reality, ionic-covalent bonds)<sup>40</sup> in the solid state are retained in the melt (the three-dimensional system of covalent bonds of the solid may be replaced by a chainlike, or a molecular structure<sup>5</sup>) for these compounds. For HgTe,  $\text{In}_2\text{Te}_3$ ,  $\text{Ga}_2\text{Te}_3$ , and Te, the picture is different. Solid-to-liquid volume changes for these compounds will depend on an involved interaction between the degree of transformation upon melting into a mixture of domains with different coordination numbers and their respective molar volumes. These changes, therefore, could either be an expansion or a contraction.

For the pseudobinary  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  melts, the present results would be in agreement with the presence of CdTe either as (1) separate "domains" coexisting with HgTe domains or (2) as dissolved in HgTe forming an ideal solution. The former (separate domains) appears to be more in agreement with the vapor pressure data of Steinger.<sup>28</sup> He concluded that the vapor pressure of mercury over liquid  $\text{Hg}_{1-x}\text{Cd}_x\text{Te}$  (and the total pressure, since the vapor consisted almost exclusively of mercury) appeared to be unaffected by CdTe addition up to the mole fraction of CdTe studied ( $X=0.6$ ). In addition, the average  $P_{\text{Hg}}$  value over the pseudobinary melts is approximately 35% of that over the element at the same temperature and this ratio seemed independent of temperature. He inferred that mercury maintains an approximately constant activity of 35% over cadmium-mercury-telluride melts. He took the constancy of mercury activity rather than the activity coefficient over these melts as an indication that the melt should be considered as a binary mercury-tellurium solution, rather than a ternary cadmium-mercury-tellurium one. The HgTe domains may not interact or interact very little with the CdTe domains.

## ACKNOWLEDGMENTS

The work was supported in part by the Materials Processing in Space Program of the U.S. National Aeronau-

tics and Space Administration and by the Universities Space Research Association (U.S.R.A.) through its sponsorship of the author as a U.S.R.A. Scientist. The author would like to thank Professor L. R. Holland of the Alabama A&M University for constant encouragement during

the course of this investigation and for a critical review of the manuscript. The author would also like to thank Dr. S. L. Lehoczky for several helpful discussions and Ms. E. Cothyan for assistance with the computer programs employed.

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