PHYSICAL REVIEW B VOLUME 31, NUMBER 11 1 JUNE 1985

# Schottky-type specific heats in liquid Se-Te alloys

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(Received 27 December 1984)

The specific heats of liquid selenium-tellurium alloys have been measured as a function of temperature. The observed values show a large temperature dependence, and they are expressed in terms of the Schottky-type specific heats, in addition to the ordinal one which is known as the Dulong-Petit value.

The liquid Se-Te system is one of the most extensively investigated alloys[1,2] because of their anomalous temperature dependence on electronic properties, such as dc conductivity[3-5] and magnetic susceptibility,[6,7] and in thermodynamic properties such as molar volume,[8] adiabatic compressibility,[9] and atomic structure.[10-12]

In explaining these anomalous temperature dependences, it has been proposed by many workers that the gradual transition from the nonmetallic to metallic state occurs in the liquid state, accompanying the structural change from chain-like twofold coordination to pyramidal As-like threefold coordination with increasing temperature.[13,14] This change is caused by a recombination of bonding; that is, one of the lone pair electrons of an atom having twofold coordination is set free to the conduction band, and the remainder forms a new bond.[13,14] Recent optical investigations, such as the reflectivity,[15] Raman scattering,[16] and optical conductivity[17] for liquid $Se_xTe_{1-x}$ alloys, also suggest that the alloys have a structural transition from a twofold to a threefold coordination between $x = 0.2$ and 0.3 above the melting point, and these concentration scan effects can be in a sense reproduced by a temperature scan.[15]

In this Brief Report we present an anomalous temperature dependence in the specific heats of liquid Se-Te alloys. The experiments have, so far, been performed for the alloys of liquid $Se_xTe_{1-x}$ ($x = 0.1$ 0.2, 0.3, 0.4, and 0.5) up to the temperatures of about two-thirds of their boiling points. The experimental setup has been described before.[18]

The temperature dependences of the specific heats of the alloys are shown in Figs. 1(a) and 1(b). As is seen in these figures, there are several distinguished features: Large values of the specific heats of liquid Te and the alloys $Se_{0.1}Te_{0.9}$ at its melting point tend to decrease gradually with increasing temperature. There have been maxima in the specific-heat curves for the liquid alloys $Se_{0.2}Te_{0.8}$, $Se_{0.3}Te_{0.7}$, and $Se_{0.4}Te_{0.6}$. The specific heat of liquid $Se_{0.5}Te_{0.5}$ gradually increases, with increasing temperature, although its absolute value is not so large in comparison with those of other al-

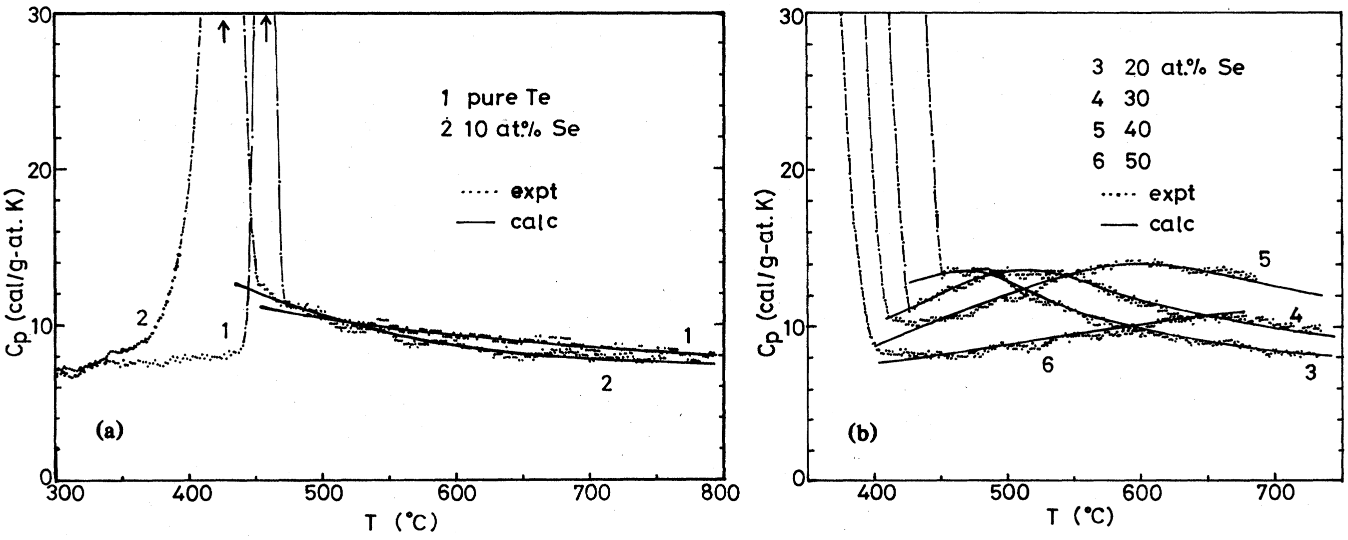

FIG. 1. (a) The observed specific heat of pure Te and 10 at. % Se alloy as a function of temperature. Arrows indicate each melting temperature. Solid curves: calculated specific heat curves based on our model. (b) The observed specific heat of liquid Se-Te alloys as a function of temperature. Solid curves: calculated specific heat curves based on our model.

loys. The maximum of the specific heat moves toward higher temperature, and this Lorentzian-type curve is broadened, with increasing concentration of Se. These temperature dependences may be related to the defect formation associating with either a network structural change[13,14] or an increasing of interchain disorder.[16]

The specific-heat measurment cannot specify what kind of defect occurs in these alloys with increasing temperatrue; however, it may be possible to consider the two extreme cases as the alloy with zero defect and that with fully saturated defects. Hereafter we will refer to the former as $N$ and the latter as $M$.

In the temperature range, where the present measurements were carried out, the alloy is, in such a sense, in the intermediate state of the above two extreme cases. This intermediate state in chemical equilibrium can be expressed as follows:

$$(\mathrm{Se}_x\mathrm{Te}_{1-x})^N \rightleftarrows (\mathrm{Se}_x\mathrm{Te}_{1-x})^M .$$

Therefore, the equilibrium condition should be determined by the temperature and composition $x$. The atomic fraction of $N$ and $M$ at a given equilibrium state are written as $c_N$ and $c_M$ $(=1-c_N)$, respectively. Based on the above idea and law of mass action, we have

$$\frac{c_N}{1-c_N} = e^{\Delta g/RT} , \qquad \Delta g = G_M^{(0)} - G_N^{(0)} , \tag{1}$$

where $G_i^{(0)}$ means the molar Gibbs free energy of the above extreme case $i$ $(=N$ or $M)$. The atomic fraction $c_N$ is immediately obtained from Eq. (1) and is expressed as follows:

$$c_N = e^{\Delta g/RT}/(1+e^{\Delta g/RT}), \quad c_M = 1/(1+e^{\Delta g/RT}) . \tag{2}$$

Equation (2) is equivalent to the case of defect formation in the solid state. It is emphasized that $\Delta g$ is a function of temperature and varies its sign at the temperature $T_c$, which satisfies the condition $c_N = c_M = 1/2$, since $M$ is more predominant than $N$ in the temperature range $T > T_c$ and vice versa. In this sense $T_c$ is a kind of transition temperature. Therefore, $\Delta g$ is, in the following form, expanded as a function of $T - T_c$,

$$\Delta g = \begin{cases} \alpha(T-T_c)+\beta_N(T-T_c)^2+\gamma_N(T-T_c)^3 & \text{for } T < T_c , \\ \alpha(T-T_c)+\beta_M(T-T_c)^2+\gamma_M(T-T_c)^3 & \text{for } T > T_c , \end{cases} \tag{3}$$

where $\alpha$, $\beta_N$, $\beta_M$, $\gamma_N$, and $\gamma_M$ are independent of the temperature.

The infinitesimal enthalpy of the system, $\delta H$, between the temperature $T$ and $T+\delta T$ is written in the following form:

$$\delta H = c_M C_p^{(M)}\delta T + \left(\frac{\partial c_M}{\partial T}\right)_p H_M^{(0)}\delta T + c_N C_p^{(N)}\delta T - \left(\frac{\partial c_M}{\partial T}\right)_p H_N^{(0)}\delta T . \tag{4}$$

The specific heat at constant pressure $C_p$ is then given by

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = c_M C_p^{(M)} + c_N C_p^{(N)} + \Delta h \left(\frac{\partial c_M}{\partial T}\right)_p , \qquad \Delta h \equiv H_M^{(0)} - H_N^{(0)} , \tag{5}$$

where $H_i^{(0)}$ is the molar enthalpy of the pure state $i$ $(=M$ or $N)$. Using the thermodynamic relation

$$\Delta h = -T^2\left[\frac{\partial}{\partial T}\left(\frac{\Delta g}{T}\right)\right]$$

and Eq. (3), $\Delta h$ at the temperature around $T_c$ is equal to

$$\Delta h = -\alpha T_c - \beta_{N \text{ or } M}(T^2 - T_c^2) - \gamma_{N \text{ or } M}(2T+T_c)(T-T_c)^2 . \tag{6}$$

Differentiating Eq. (6) with temperature, we have

$$\frac{\partial \Delta h}{\partial T} \equiv C_p^{(M)} - C_p^{(N)} = -2\beta_{N \text{ or } M} T - 6\gamma_{N \text{ or } M} T(T-T_c) . \tag{7}$$

Since the quantity $C_p^{(M)} - C_p^{(N)}$ should be continuous at the temperature $T_c$, $\beta_N$ is equal to $\beta_M$. Hereafter we will write it as $\beta$.

Using Eq. (7), Eq. (5) is converted to

$$C_p = C_p^{(M)} + 2c_N\beta T + 6\gamma_{N \text{ or } M} c_N T(T-T_c) + \frac{\Delta h^2}{RT^2}\frac{e^{\Delta g/RT}}{(1+e^{\Delta g/RT})^2} , \tag{8}$$

where $\gamma_{N \text{ or } M}$ means $\gamma_N$ for $T < T_c$ and $\gamma_M$ for $T > T_c$. The last term is a kind of Schottky-type specific heat.

At higher temperatures beyond $T_c$, the values of the last three terms in Eq. (8) tend to be smaller, and $C_p^{(M)}$ is obtained from the saturated value of the experimental specific heat at high temperature. As is seen in Figs. 1(a) and 1(b), the observed $C_p$'s of the alloys, except for $\mathrm{Se}_{0.5}\mathrm{Te}_{0.5}$, tend to be saturated. In the case of alloys of 10 and 20 at.% Se concentrations, the saturated values of $C_p$'s may be close to about 7.5 cal/g-at. K (31.5 J/g-at. K) as seen in Fig. 1(a).

TABLE I. Several estimated values of $\alpha$, $\beta$, $\gamma_N$, $\gamma_M$, and $T_c$ by fitting the observed specific heat.

| | $T_c$ (K) | $\alpha$ (cal $\mathrm{K}^{-1}$) | $\beta$ ($10^{-3}$ cal$\mathrm{K}^{-2}$) | $\gamma_N$ ($10^{-5}$ cal$\mathrm{K}^{-3}$) | $\gamma_M$ ($10^{-6}$ cal$\mathrm{K}^{-3}$) | $-\alpha T_c[=\Delta h(T_c)]$ ($10^3$ cal) |
|---|---|---|---|---|---|---|
| Pure Te | 620 | −6.8 | 0.5 | · · · | −1.0 | 4.22 |
| $\mathrm{Se}_{0.1}\mathrm{Te}_{0.9}$ | 675 | −6.8 | 1.3 | · · · | −7.0 | 4.59 |
| $\mathrm{Se}_{0.2}\mathrm{Te}_{0.8}$ | 740 | −6.7 | 1.5 | 1.7 | −5.5 | 4.96 |
| $\mathrm{Se}_{0.3}\mathrm{Te}_{0.7}$ | 790 | −6.7 | 1.7 | 1.6 | −3.5 | 5.29 |
| $\mathrm{Se}_{0.4}\mathrm{Te}_{0.6}$ | 885 | −6.7 | 1.7 | 1.0 | −0.1 | 5.93 |
| $\mathrm{Se}_{0.5}\mathrm{Te}_{0.5}$ | 960 | −4.5 | 1.6 | 0.6 | · · · | 4.32 |

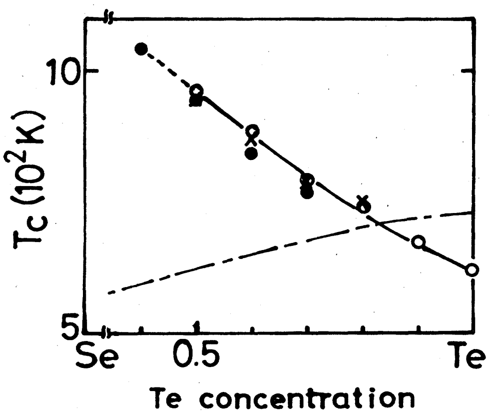

FIG. 2. Concentration dependences of the transition temperature, $T_c$, estimated from various measurements. ○, estimated from the specific heat measurements. ●, estimated from the adiabatic compressibility measurements (Ref. 9). ×, extimated from the temperature coefficient of the magnetic susceptibility (Ref. 6). – – –, liquidus temperature.

Hereafter we will assume that the saturated values of $C_p$'s of other Se-Te alloys lie around 7.5 cal/g-at. K for the simplicity.

Comparing the experimental results of $C_p$ to equations described above, the temperature $T_c$'s and all parameters as $\alpha$ $\beta$, $\gamma_N$, and $\gamma_M$ are obtained as listed in Table I, and $T_c$'s are plotted as a function of Se concentration in Fig. 2. The curves of $T_c$ are nearly located at the center of the transition area from nonmetallic to metallic states suggested by Endo.[14] Using these parameters, the reproduction of $C_p$'s are satisfactorily indicated as the solid curves in Figs. 1(a) and 1(b). The enthalpies at the temperature $T_c$ are equal to $\Delta h(T_c)$ $(=-\alpha T_c)$, and these are also plotted as a function of Se concentration in Fig. 3. It is remarkable that $\Delta h(T_c)$'s are approximately indicated by a quadratic function and deviate at the composition of $\mathrm{Se_{0.5}Te_{0.5}}$. These facts suggest that the mechanism of the transition from nonmetallic to metallic phases may, at least, be similar from pure Te to $\mathrm{Se_{0.4}Te_{0.6}}$ and that of Se-rich alloys including $\mathrm{Se_{0.5}Te_{0.5}}$ seem to be different.

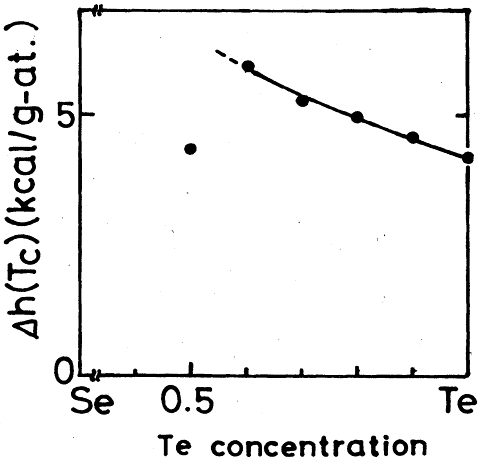

FIG. 3. The concentration dependences of the enthalpies at the temperature $T_c$.

According to Magaña and Lannin,[16] the Raman peaks of liquid $\mathrm{Se}_x\mathrm{Te}_{1-x}$ alloys have a drastic change in the concentration range $0.2 < x < 0.3$ near the melting points. They concluded that there exists a threshold of transition from three- to twofold bonding in that region and consequently indicates an increasing interchain disorder for the alloys at $x \geqslant 0.3$. Other optical results by Fainchtein and Thompson[15] suggest that there is a nonmetal to metal transition between $x = 0.3$ and 0.4 at 500 °C. Since the concentration range of the metal to nonmetal transition is considered to move to higher concentration of Se with increasing temperature, the transition temperatures, $T_c$, up to the concentration of $x \leqslant 0.4$ obtained by the present experiment, agree well with these optical results in view of the metal to nonmetal transition.

In conclusion the specific heats of liquid $\mathrm{Se}_x\mathrm{Te}_{1-x}$ alloys exhibit a Shottky-type temperature dependence in relating to a formation of defects with increasing temperature.

The authors express their thanks to Professor Melvin Cutler, Oregon State University, for his valuable comments on this work. One of the authors (S. Takeda) is grateful to the Ministry of Education, Science and Culture of Japan for financial support.

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