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The velocity of sound and compressibility in the melts of Hg-Te system

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Abstract. Liquid Hg-Te system has been investigated as a function of composition and temperature by measuring the velocity of sound. A minimum in the sound velocity as a function of temperature observed for Te persists up to 50 at.% Hg, of which the position increases rather steeply between 20 and 30 at.% Hg. This suggests that the molten HgTe and alloys in the Te-rich side undergo structural changes involving the change in coordination number with increasing temperature, and the crossover of the nature of the chemical bond from p-p σ to sp^3 covalent bond takes place with changing composition. It is concluded that the structural change in liquid HgTe is due to intrinsic nature of bonding of HgTe as a compound.

PACS. 62.60.+v Acoustical properties of liquids – 65.50.+m Thermodynamic properties and entropy – 65.70.+y Thermal expansion and density changes; thermomechanical effects

1 Introduction

There are many compounds especially containing chalcogenide elements as one component which show rapid structural changes in the liquid state [1]. General acceptance seems to be that the structural change is caused by dissociation of chemical clusters which persist in the melt. In the solid state, these types of compounds are generally covalent bonded semiconductors with low coordination number. Their coordination number is given by the 8-N rule where N is defined as the average number of sp electrons for the constituent elements [2]. Most of such structures are stabilized by the hybridization of atomic s and p states to form directed sp^3 covalent orbitals and their subsequent splitting into bonding and antibonding states with an energy gap at the Fermi level. For the elements typically in the Vb and VIb column of the periodic table, the formation of p-p σ bonds is dominated and the Peierls distortion mechanism on a simple cubic lattice stabilizes their deformed structures with low coordination number by opening an energy gap at the Fermi level [2]. Upon melting, the entropy term (temperature effects) exceeds the energy gain due to the formation of covalent bond, and a more isotropic and denser structure having metallic character is established for most of compounds [1,3].

Gaspard *et al.* have recently shown that the periodic condition is not a necessary condition for the Peierls distortion mechanism [3,4]. According to them, if the energy gain due to the Peierls distortion is large enough, a deformed structure in the solid state can be retained even after melting. They suggest that in the liquid state of the light elements in the Vb and VIb column of the periodic table the Peierls distortion mechanism dominates the stability of their local structures with low coordination number. Liquid Se is a typical case, for example [3]. Following this line, the structural change in liquid Te can be interpreted as being due to crossover between the energy gain by the distortion and temperature effects, and, hence, it is dominated by the Peierls distortion mechanism [5]. They have presented similar arguments for the stability of local structure in molten IIb-VIb narrow gap semiconductors in relation to their newly obtained neutron diffraction experiments that ZnTe and CdTe keep essential features of their crystal structures through melting while HgTe melts to an almost isotropic compact liquid [6]. They suggest that, (1) the sp^3 hybrid bond persists in the melts of lighter compounds, (2) the heaviest HgTe undergoes a major structural change upon melting, (3) this structural change can be interpreted as being due to the change from a sp^3 resonance to a non-hybridized p-p bond, (4) the lighter IIb-VIb compounds would also undergo similar structural changes at much higher temperatures due to the entropy effect. Physico-chemical properties so far reported conform to their conjecture [1]. On the other hand, density measurements indicate that the volume of HgTe takes a minimum just above the melting point and then increases while the volume of CdTe increases linearly with temperature as a normal behaviour of a liquid [7,8]. As inferred from liquid Te and Se cases [1,9], the density data suggest that the structural change of HgTe has

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not finished upon melting and its structure continuously changes with increasing temperature.

In the liquid Hg-Te system, the nature of the chemical bond changes from the p-p σ bond in Te to the sp^3 covalent bond in HgTe compound, and to the metallic binding in Hg [1,4]. The aim of this paper is to obtain information on the structural change in the molten HgTe in more detail and to investigate how the crossover in the bonding character is reflected in the structural changes in the molten state. Ultrasonic studies as a tool to investigate liquid semiconductors/alloys is now well established. In this paper, sound velocities studied for full composition range of the molten Hg-Te alloy have been reported. We discuss the results in the light of the previous reported studies including the mechanism of structural change in the molten HgTe.

2 Experimental method

Hg-Te system has very high vapour pressure which rises with the rise in content of Hg and temperature. Fused silica crucibles of 1.8 mm wall thickness with parallel faces were used to avoid the selective evaporation of its constituents [10]. Measurements were restricted below the partial vapour pressure of Hg of the order of approximately 40 atm to avoid the burst of the cell. Sound velocity measurements were carried out using standard pulse echo overlap technique. Measurements were carried out with reference to sound velocity in distilled water at 0 °C. It was taken to be 1 402.71 m/s [11]. A piezoelectric ceramics transducer operated at about 8 MHz was used to produce and detect the sound pulse. Time interval required for sound to travel between delay line end and reflector was measured with the help of Sony-Tektronix 465B oscilloscope. Time resolution of oscilloscope is of the order of 5×10^{-8} s which corresponds to velocity measurements resolvable up to 0.3 m/s for the present experimental setup. Temperature was measured with calibrated Pt-Rh (13% Pt) thermocouple attached to the specimen and uncertainty was estimated to be within ±3 °C. Temperature was controlled with a digital temperature controller which could keep a temperature within to ±0.2 °C during a measurement. Relative temperatures were accurate to better than 0.5 °C.

3 Results

Figure 1 shows the variation of sound velocity (ν_s) with temperature in the Hg-Te alloy measured at every 10 at.%. A minimum in sound velocity from Te rich side persists up to 50 at.% of Hg. This behaviour of the sound velocity is quite contrast to the one in most of liquid metals that the sound velocity almost linearly decreases with increasing temperature as plotted for pure Hg. It can be observed that the ν_s-T curve for Te becomes shallower by adding Hg up to 20 at.% and it again becomes deeper beyond 30 at.%.

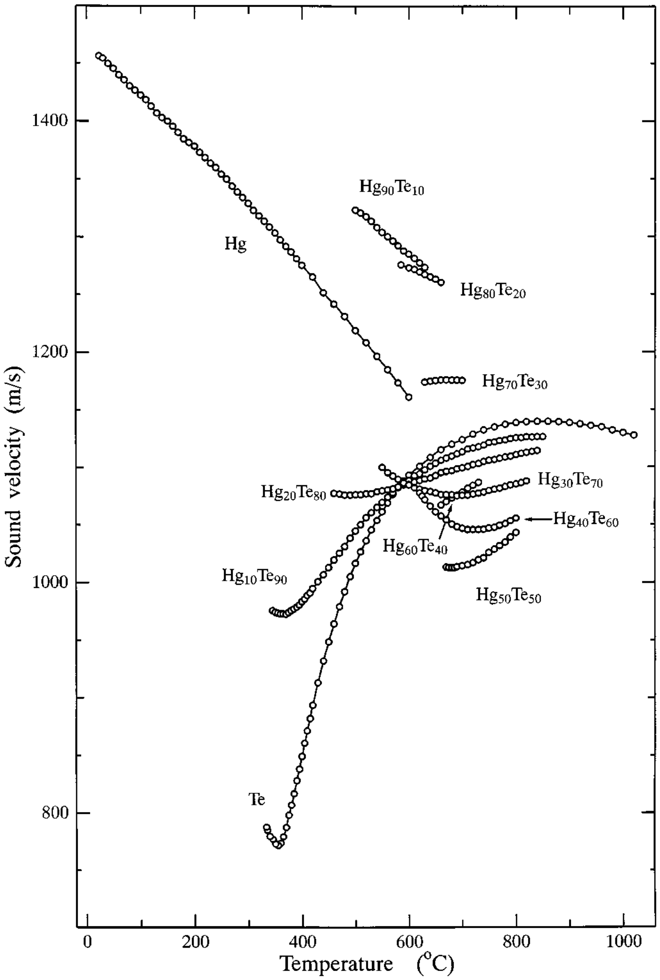

Fig. 1. Sound velocity as a function of temperature for different compositions of the Hg-Te system.

The adiabatic compressibility ($\kappa_\mathrm{s} = \rho^{-1}\nu_\mathrm{s}^{-2}$: ρ, mass density) and thermal expansion coefficient (α_P) as a function of temperature for Te, Hg and HgTe are shown in Figures 2 and 3, respectively in which the density data were taken from references [8,9,12].

The adiabatic compressibility as a function of temperature shows a continuous increase for Hg while it has a peak at about 355 °C and at about 680 °C, respectively for Te and HgTe. Negative thermal expansion coefficients have been found for Te and HgTe near liquidus temperatures indicating the volume contraction with increasing temperature. It should be noted that there exists close correlation between κ_s and α_P as a function of temperature. The logarithmic derivative of ν_s with respect to the temperature,

$$\nu_\mathrm{s}^{-1}\mathrm{d}\nu_\mathrm{s}/\mathrm{d}T = -2\left(\kappa_\mathrm{s}^{-1}\mathrm{d}\kappa_\mathrm{s}/\mathrm{d}T - \alpha_P\right), \qquad (1)$$

has been plotted for all compositions in Figure 4. As compared with the thermal expansion coefficient plotted in Figure 3, it can be seen that the contribution from α_P to the right hand side of equation (1) is very small. Then zero and a maximum in $\nu_\mathrm{s}^{-1}\mathrm{d}\nu_\mathrm{s}/\mathrm{d}T$ correspond, respectively, to a maximum and an inflexion point in the κ_s-T

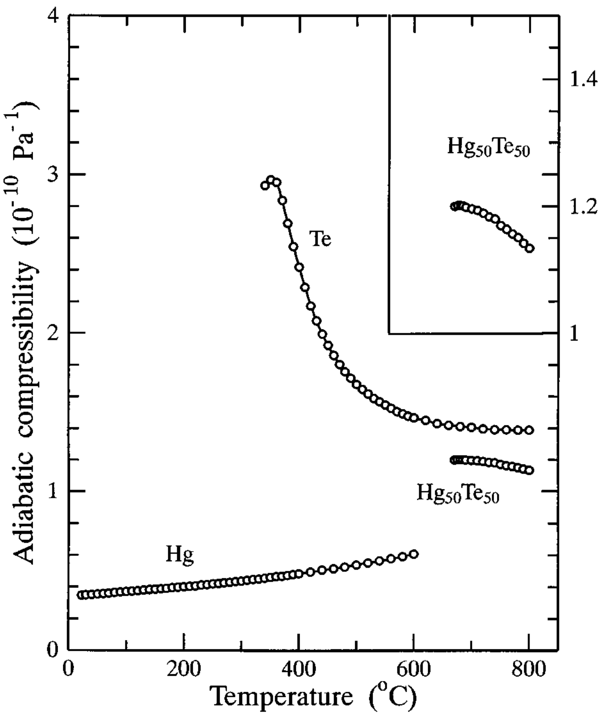

Fig. 2. Variation of adiabatic compressibility with respect to temperature for Te, HgTe and Hg. Note that the vertical scale in the inset has been enlarged.

curve. The temperature, T^*, corresponding to a minimum in the sound velocity (or a maximum in the adiabatic compressibility) obtained in this way is plotted as a function of composition in Figure 5. The vertical bar on the data indicate the interval between T^* and an inflexion point in the ν_s-T (or κ_s-T curve). T^* decreases steeply between 20 and 30 at.% Hg. The isotherms at 670 °C of the adiabatic compressibility and sound velocity are given in Figure 6. In the calculations, for lack of full experimental data, we assumed that molar volume changes linearly between pure Hg and HgTe, and between HgTe and Te. Corresponding to a dip in the sound velocity, a cusp-like inflection appears for the adiabatic compressibility at 50 at.% of Te.

4 Discussion

It has been shown for liquid Te that the unusual dependence on temperature of ν_s is brought about by the rapid structural changes accompanying the increase in coordination number and the volume contraction with raising temperature [12]. If the structure changes rapidly with increasing temperature and/or an applied pressure, the constant pressure specific heat, C_P, thermal expansion coefficient, α_P, and isothermal compressibility, κ_T, involve the contribution associated with the rate of the structural change. Then they take the forms, $C_P = C_P^0 + \delta C_P$, $\alpha_P = \alpha_P^0 + \delta\alpha_P$, and $\kappa_T = \kappa_T^0 + \delta\kappa_T$, in which the first term is a thermodynamic response function expected assuming no structural change. The excess terms are not all independent of one another, but satisfy the Ehrenfest's relations in an extended form. Since apart from the sign δC_P, $\delta\alpha_P$ and $\delta\kappa_T$ have an extremum around the same temperature, C_P, α_P and κ_T have an extremum as well unless the first terms have large temperature dependence as compared with the second. The extremum occurs around a temperature at which the structural change proceeds about half way [12], and thus of which the position gives

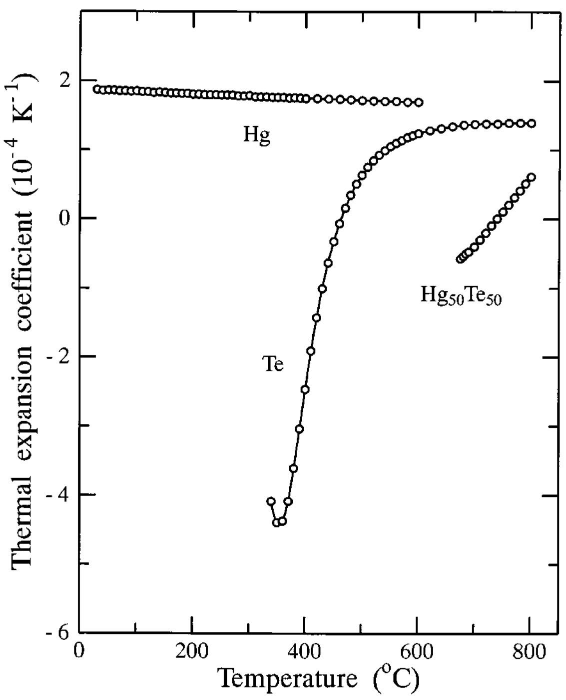

Fig. 3. Plot of thermal expansion coefficient with respect to temperature for Te, HgTe and Hg.

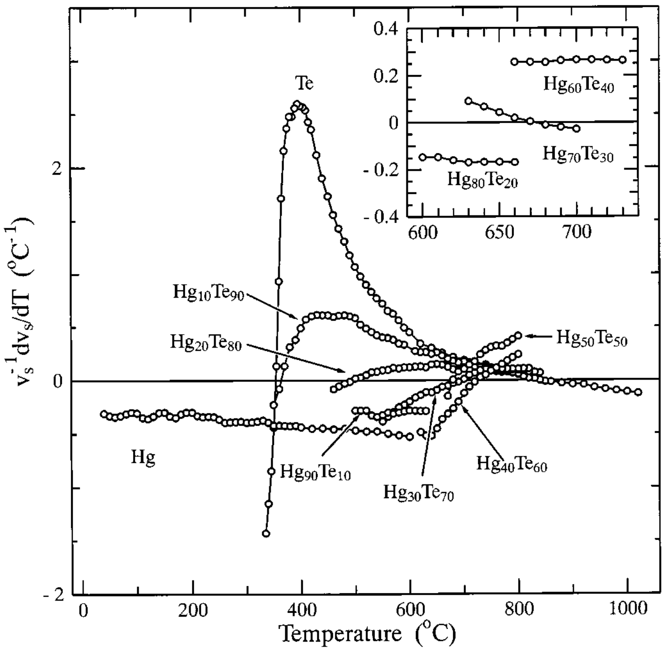

Fig. 4. Temperature dependence of $\nu_s^{-1}\mathrm{d}\nu_s/\mathrm{d}T$ for different compositions.

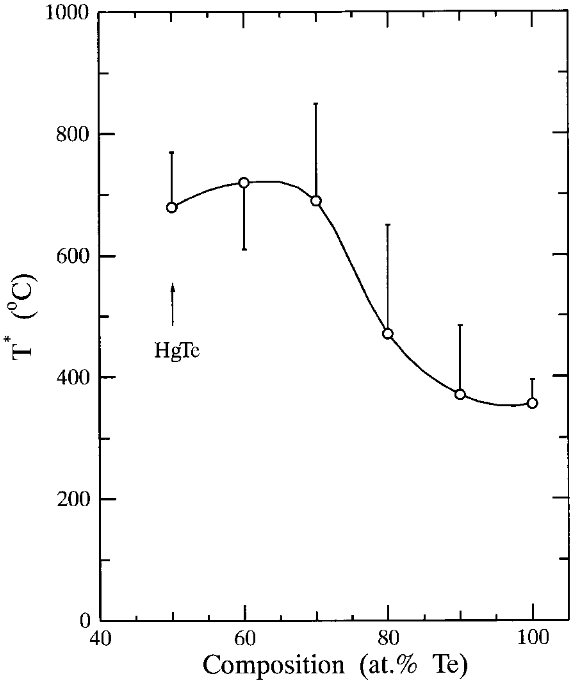

Fig. 5. The position of a minimum in the sound velocity, T^*, as a function of composition. Error bar on the data represents the interval between T^* and the position of inflexion point in the ν_s-T curve.

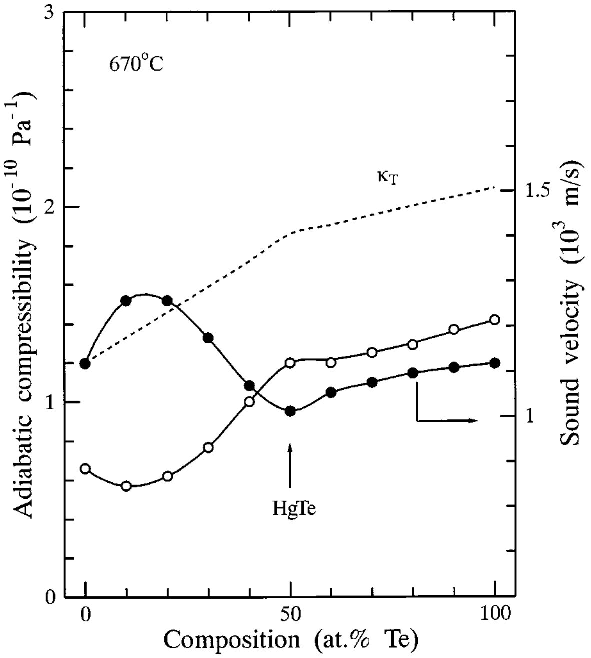

Fig. 6. Sound velocity and adiabatic compressibility *vs.* composition at 670 °C. Broken curve is the isothermal compressibility, κ_T, calculated with a model of binary hard sphere.

a measure of transition point analogue to the phase transition in the solid state. Since the temperature dependence of κ_T dominates the temperature dependence of ν_s, the sound velocity takes a minimum around the same temperature for a negative peaked minimum in the α_P-T curve. This temperature corresponds to T^* plotted in Figure 5. Close correlation between the temperature dependences of the sound velocity and thermal expansion coefficient for liquid HgTe plotted in Figures 1 and 3 thus suggests that the local structure of liquid HgTe changes fairly rapidly with raising temperature as does in liquid Te. Furthermore the persistence of a ν_s-T curve with a minimum for the Te-side alloys implies that structural changes also take place in these alloys.

In conjunction with the volume contraction with raising temperature observed in the molten HgTe just above the melting point, Chandra assumed [13] that liquid HgTe consists of two types of domains as proposed for molten Te by one of present authors and Seymour [14], one with high coordination number and stable at high temperature and other with low coordination number and progressively more stable at low temperature.

Anomalous behaviour for the thermal expansion coefficient has been explained by the continuous transformation with temperature of one kind into the other due to intrinsic nature of bonding of HgTe as a compound. Recently Glazov *et al.* confirmed the previous results [5], although small discrepancy exists in the respective density values [8]. They have made an attempt to explain the temperature dependence by assuming dissociation of HgTe and Hg_2Te_3 associates coexisting in the molten HgTe. It may be noted that there exists essential difference in the way of explaining by both of them.

Our sound velocity data offer a clue to this point. As summarized in the preceeding section, the ν_s-T curve becomes shallower by adding Hg into Te up to 20 at.% and then gets deeper as more Hg is added and meantime the width of a ν_s-T curve appears to become largest for alloys with 20 and 30 at.% Hg. Figure 5 shows the interval between a position of a minimum, T^*, and an inflexion point in the ν_s-T curve, which have been obtained from a $\nu_s^{-1}\mathrm{d}\nu_s/\mathrm{d}T$-$T$ curve plotted in Figure 3. The interval represents a measure of the width of ν_s-T curve and hence the sharpness of structural changes. It can be observed from Figure 4 that structural changes become continuously blurred with addition of Hg in Te up to 20 at.%. After that, it again starts becoming sharper when the content of Hg is raised from 30 to 50 at.%. The Hg-Te system forms a single congruent HgTe compound at 50 at.% Hg and at either side of 50 at.% its phase diagram is of an eutectic type [15]. To a first approximation, it may be considered from the phase diagram that a melt consists of HgTe chemical association and excess Te at the Te-side and of HgTe association and excess Hg at the Hg-side. Therefore the observed behaviour of the structural changes with composition could be interpreted as being due to fluctuations in the transition temperature, T^*, caused by fluctuations in the concentration if HgTe changes its structure as a compound HgTe. This conjecture is also consistent with the adiabatic compressibility as a function of composition plotted in Figure 6: a clear inflexion appears only at 50 at.% and no apparent structure appears at 40 at.% Hg corresponding to Hg_2Te_3 association.

As already shown for a number of Te based binary alloys, a cusp-like inflexion in the compressibility at the compound forming composition is related to the change in the composition dependence of the packing factor caused by the change in the bonding character with alloying [16,17]. The isothermal compressibility calculated with a model of binary hard sphere [20] has been plotted in Figure 4 for comparison. In the calculations, the hard sphere diameter for Hg has been chosen to give the packing fraction at 20 ℃ as 0.45 [18] and for Te the intra-chain distance [19] has been taken as the hard sphere diameter. They were assumed to be independent of temperature and composition. At 670 ℃, the packing fraction was 0.367 for Hg, 0.338 for HgTe, and 0.337 for Te. Rather small change in the compressibility with composition in the Te-side alloy, therefore, correlates with the small change in the packing fraction and thus suggests the persistence of covalent open structure. The much steeper composition dependence of the compressibility in the Hg-rich side corresponds to the increase of the packing fraction reflecting the change in the bonding character from covalent to metallic bonding. As the pure Hg is approached, the metallic bonding becomes dominant and the contribution of the electron gas further stimulates the decrease in the compressibility [21]. Correspondingly, the positive temperature dependence of ν_s diminishes and the normal behaviour of ν_s, or monotonous decrease with increasing temperature, is observed for 80 and 90 at.% Hg.

As mentioned in the introduction Gaspard *et al.* have found that ZnTe and CdTe keep essential features of their crystal structures through melting while HgTe melts to an almost isotropic compact liquid [6]. Upon melting the coordination number of HgTe increase from 4 to 6.3. They have concluded that the bonding mechanism in the compound HgTe has almost completely changed upon melting from a sp^3 resonance to a non hybridized p-p bond in terms of the molecular orbital theory. As seen in Figure 1, however, we observed the high temperature wing of the whole ν_s-T curve at 50 at.% Hg. This may imply that structural change has not finished for the molten HgTe at the melting point and its energy state around the melting point is rather resemble to that of Te. For Te the entropy term increases with raising temperature to exceed to an energy gain due to the Peierls distortion , which causes continuous structural changes [5]. This may be also what happens in the molten HgTe and alloys in the Te-side. As mentioned before T^* plotted in Figure 6 can be regarded as a temperature at which the structural change has proceeded about half way to a high temperature form, and thus it gives a measure of the energy gain due to the formation of sp^3 covalent bond for HgTe or the Peierls distortion for Te. It is noted that increase in T^* takes place in a rather stepwise between 20 and 30 at.% Hg accompanied, which is quite contrast to the case of Se-Te and As-Te systems in which the bonding nature is mainly p-p σ over the whole composition range [2,4] and T^* changes monotonously with composition [22,23]. Since in the Hg-Te system the stability of sp^3 orbitals decreases while the possibility of the forming of p-p σ bonds increases as the Te-side is approached, the different dependence on composition of T^* among these systems would be originated in the difference in the composition dependence of the bonding nature.

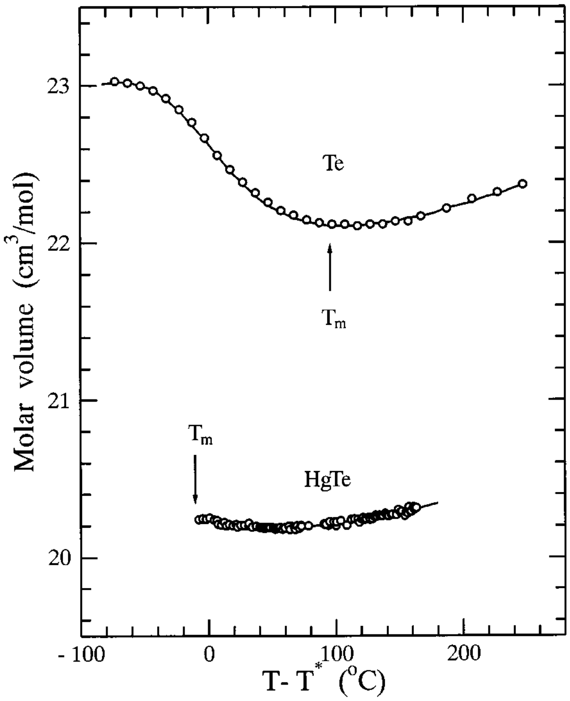

Fig. 7. Temperature dependence of the molar volume for molten Te and Hg-Te around T^*. T_m denotes the melting temperature.

It should be finally added the following points. Solid Te undergoes successive phase transitions with an increasing pressure. Around 5 GPa it changes from an hexagonal to a puckered layer, and then to a β-polonium structure around 9 GPa. The structural changes realized in the supercooled liquid Te is considered to be a transition corresponding to the first pressure sequence in the solid [5]. The compound HgTe also undergoes successive phase transitions with an applied pressure. The zincblende phase of HgTe transforms into the cinnabar structure around 1.4 GPa and then to the β-tin structure around 12 GPa ([24], and references therein). The coordination number of these structures are 4, $4 + 2$ and 6, respectively. The volume contraction in molten HgTe around T^* with increasing temperature is very small as compared with Te case as plotted in Figure 7 [8,12], which suggests that the change in dimensions of structure in molten HgTe is not very large. Taking into account the fact that the coordination number at melting point is already approximately 6 [6], a plausible explanation is, therefore, that HgTe would melt to a liquid having a structure analogue to the cinnabar structure and then approach a more isotropic structure similar to the rocksalt structure with raising temperature as realized in the successive structural transition with an applied pressure.

5 Conclusions

In summary, the sound velocity measurements supply evidence for rapid structural changes in the HgTe and Te-rich Hg-Te alloys in the liquid state. Steep increase in the transition temperature, T^*, has been observed between 20 and 30 at.% Hg, which is accompanied with large fluctuations in transition temperature. This behaviour may indicate that the structural change in liquid HgTe is due to the intrinsic nature of bonding of HgTe as a compound, which is related to the stability of sp^3 covalent bonds in the topologically disordered state with increasing temperature.

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