

The velocity of sound in liquid arsenic: evidence for rapid structural changes with temperature

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1997 J. Phys.: Condens. Matter 9 10087

(<http://iopscience.iop.org/0953-8984/9/46/006>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.209

The article was downloaded on 14/05/2010 at 11:05

Please note that [terms and conditions apply](#).

The velocity of sound in liquid arsenic: evidence for rapid structural changes with temperature

Y Tsuchiya

Department of Physics, Faculty of Science, Niigata University, Ikarashi 2-8050, Niigata 950-21, Japan

Received 11 July 1997

Abstract. The velocity of sound in liquid arsenic has been measured as a function of temperature, and shows an unusually large positive dependence on temperature. The results provide the first evidence that the structure of liquid arsenic around the melting temperature changes very rapidly with temperature as found in liquid tellurium.

1. Introduction

The elemental group VIA chalcogenide (S, Se, and Te) liquids show systematic behaviour in their structural changes with rising temperature. The coordination number, Z , of molten Te is about 2.7 at the melting point ($T_m = 450^\circ\text{C}$) and increases to about three with rising temperature (Menelle *et al* 1987). As the supercooling proceeds the coordination number decreases and a twofold-coordinated structure is approached, which is manifested by peaked extrema occurring around $T = 353^\circ\text{C}$ in the thermodynamic response functions (specific heat, compressibility and volume expansion coefficient) (Tsuchiya 1991). Accompanying the structural change liquid Te transforms from a poor metallic to a semiconducting state with falling temperature. Molten Se has a chain structure at the melting point ($T_m = 219^\circ\text{C}$), which is persistent even above 1000°C and transforms around 1500°C to a denser structure under moderate pressures (Tamura 1996). The transition is believed to be of an allotropic type found in liquid Te. In the corresponding temperature–pressure region, the semiconductor–metal transition has been found. Molten S at the melting point ($T_m = 113^\circ\text{C}$) consists of ring molecules as in the solid and shows the lambda transition from a ring to a polymeric chain structure at 159°C . The coordination number remains about $Z = 2$ in the experimentally accessible temperature region and liquid S is essentially an insulator (Winter *et al* 1990). It has been suggested that the systematic trend in the stability of the twofold-coordinated structure is in consequence of a Peierls distortion in the p-bonding mechanism (Gaspard *et al* 1987).

The structure and electrical properties of the group Va pnictide liquids (As, Sb, and Bi) have been interpreted along the same lines (Gaspard *et al* 1987). At the melting, the entropic term exceeds the energy gain due to a Peierls distortion for the latter two elements. Consequently, the coordination number increases to $Z = 6$ for Sb and $Z = 8.8$ for Bi upon melting, while it remains as $Z = 3$ as in the solid for As (Bellissent *et al* 1987). The dependences on temperature of the electrical properties appear to conform to this picture: molten Sb and Bi have metallic characters with small temperature dependence while liquid As is semiconducting (Glazov *et al* 1969). The recent calculations based on the MD

simulation are not in contradiction with these experimental results (Bichara *et al* 1993). It seems, therefore, to be generally accepted that in the pnictide column of the periodic table molten As and Sb behave much more like molten Se and Te, respectively.

The behaviour of the thermodynamic response functions of Sb and Bi also supports the above conjecture. Their dependences on temperature are much the same as those of a metallic liquid except for liquid Sb around the melting point ($T_m = 630.5^\circ\text{C}$). In the accessible supercooled region ($580^\circ\text{C} < T$), the compressibility, volume expansion coefficient and specific heat behave like those in liquid Te just above T_m , although the extent is small (Tsuchiya 1997). The results have been interpreted as an indication of structural changes of liquid Sb with decreasing temperature. In contrast the thermodynamic data for molten As are as yet insufficient to infer whether or not structural changes take place. Rather old data on the specific heat show a definite peak just above the melting point ($T_m = 817^\circ\text{C}$), suggesting rapid structural changes, while the density decreases monotonically with increasing temperature, corresponding to the normal thermal behaviour (Klemm *et al* 1960, McGonigal and Grosse 1962).

As shown in a series of papers, the excess thermodynamic functions caused by the rapid structural changes in a liquid are dependent on each other and the Prigogine–Defay ratio becomes unity (Tsuchiya 1991). Therefore the measurement of the velocity of sound can be a very sensitive probe to possible structural changes in a liquid. In this paper, we present for the first time thermodynamic evidence that a Peierls-type distortion in liquid As is quite temperature dependent as in liquid Te, contrary to the supposition that As has a very stable structure in the liquid state.

2. Experimental details

The difficulty in measuring the sound velocity in liquid As arises from its very high vapour pressure. At the triple point, $T = 817^\circ\text{C}$, the vapour pressure is 35.8 atm (Horiba 1922). A delay-line-closed cell assembly made of fused silica with 1.8 mm thickness has been used to overcome such a high vapour pressure (Tsuchiya 1988). The sound velocity was determined with reference to the value in distilled water in the cell at 0°C . It was taken to be 1402.71 m s^{-1} (Greenspan and Tschiegg 1958). Piezoelectric ceramics operated at about 8 MHz were used to produce and detect the sound pulse. The time interval required for sound to travel between the delay-line end and reflector was measured with the time function of a Sony-Tektronix 460B oscilloscope, the output of which was read out digitally. The time resolution was $5 \times 10^{-8}\text{ s}$, which corresponded to the uncertainty in the sound velocity of about 0.3 m s^{-1} for the present experimental condition. Although the absolute temperature uncertainty was $\pm 2^\circ\text{C}$, the relative temperatures were accurate to better than 0.2°C and the stability at a temperature was better than $\pm 0.05^\circ\text{C}$. Since As is extensively toxic and has very high vapour pressure, the measurements were restricted in the region below $T = 850^\circ\text{C}$ and in the supercooled region to avoid a burst of the cell.

3. Results and discussion

The velocity of sound, v_s , in liquid As is plotted as a function of temperature in figure 1: it increases quite rapidly with rising temperature in contrast to the behaviour in typical liquid metals where in general the sound velocity decreases almost linearly over a wide range of temperature (Gitis and Mikhailov 1966). In all the molten elements such unusual behaviour of v_s has been found only in molten Te so far. The magnitude of dv_s/dT is as large as that

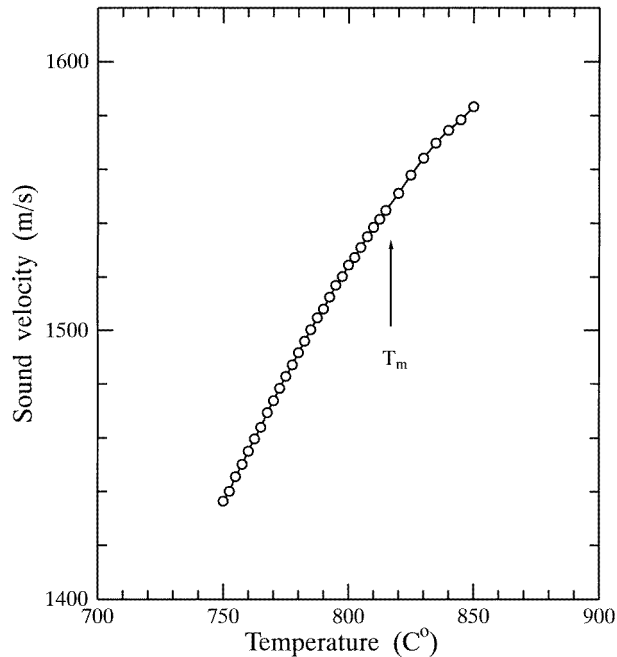


Figure 1. Velocity of sound in liquid As. T_m denotes the melting point, 817 °C. The line through the data is drawn as a guide for the eye.

found for liquid Te in the supercooled region. The logarithmic derivative of v_s with respect to temperature, $v_s^{-1}dv_s/dT$, is shown in figure 2 as a function of temperature together with the results for molten Te. The logarithmic derivative of the sound velocity may be given by

$$v_s^{-1} dv_s/dT = 1/2\{\alpha_p - \kappa_S^{-1}(d\kappa_S/dT) + v_s^{-1} dv_s/dp(dp/dT)\} \quad (1)$$

where α_p and κ_S are the volume expansion coefficient and adiabatic compressibility, respectively. The third term on the RHS formally takes into account the fact that liquid As is in equilibrium with a very high vapour pressure which increases at the rate of about 0.3 atm K⁻¹ with increasing temperature (Horiba 1922). Substituting the known values it is seen immediately that $\kappa_S^{-1}(d\kappa_S/dT)$ is dominant and the other two terms are smaller by about two orders of magnitude.

To obtain the adiabatic compressibility, $\kappa_S = \rho^{-1}v_s^{-2}$, the mass density in the supercooled region was evaluated by the linear extrapolation of the data by McGonigal and Grosse (1962) to a first approximation. The results are plotted in figure 3 together with those for Sb and Bi (Tsuchiya 1997, Kakinuma *et al* 1996). The isothermal compressibility, $\kappa_T = \kappa_S + TV\alpha_p^2C_p^{-1}$, may be more appropriate to discuss the structural change. However, since the dilatation term is about 5% of the total and κ_S dominates the temperature dependence of κ_T , we will make no distinction between κ_T and κ_S in the following arguments.

Apart from the dependence on temperature, the compressibility of As is about twice those of Sb and Bi while it is much the same for the three elements in the solid. The results may correspond to the fact that molten As has a very open structure and its bonding mechanism is quite different from the one in the latter two liquids, that show almost metallic behaviour

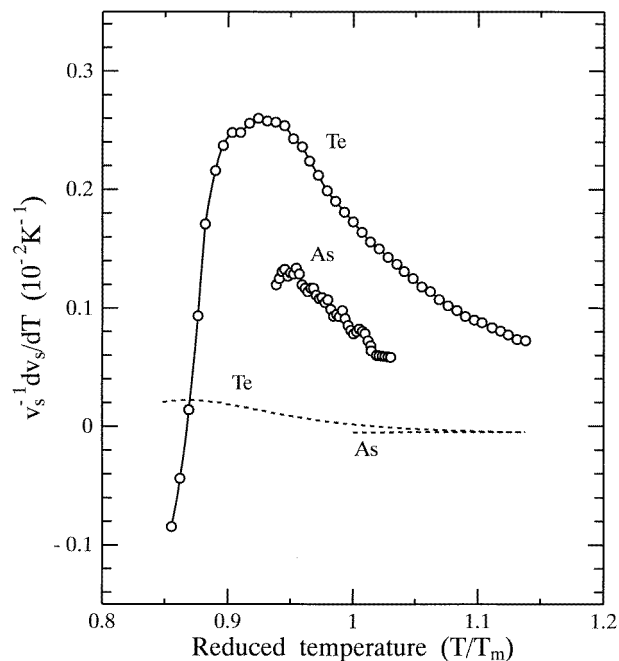


Figure 2. Logarithmic derivative of the sound velocity in As and Te as a function of reduced temperature, where T_m is the melting point. The line through Te results is drawn as a guide for the eye.

(Bichara *et al* 1993). The isothermal compressibility is related to the density fluctuations in terms of the radial distribution function $g(r)$ by a familiar equation,

$$nk_B T \kappa_T = 1 + 4\pi n \int [g(r) - 1] r^2 dr \quad (2)$$

where n and k_B are the number density and the Boltzmann constant. Thus the very large dependence on temperature of κ_T by itself implies that $g(r)$ and hence the structure of As changes very rapidly around the melting temperature. As shown in a previous paper (Tsuchiya 1991), in such circumstances the compressibility is enhanced as well as the specific heat and their dependence on temperature satisfies the Ehrenfest relation in an extended form. A peak in κ_S against temperature corresponding to a peak in C_p reported in a review (Klemm *et al* 1960) could not be found in the corresponding temperature region. Rather the temperature derivative of the sound velocity in figure 2 suggests that the compressibility would have a maximum at a temperature a little lower than the accessible supercooled temperature as observed for liquid Te. Taking into account the results on the volume expansion coefficient (McGonigal and Grosse 1962), it is, therefore, supposed that a peak in C_p just above the melting point would be an artifact as often appears in C_p measurements by the drop-calorimetry method.

The structure of liquid As has been investigated by neutron diffraction experiments. The coordination number remains three as in the crystal, which shows that a Peierls-type distortion persists in a liquid As. The change toward a structure with a sixfold coordination expected for its absence has not been detected at least at the accessible experimental temperature region ($T < 1250^\circ\text{C}$) (Bergman *et al* 1989). From those results it has been

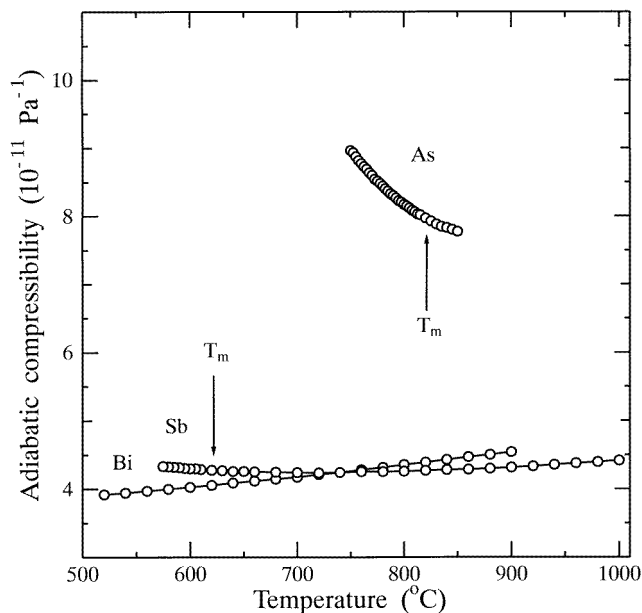


Figure 3. Adiabatic compressibility for pnictide (As, Sb and Bi) liquid. T_m denotes the melting point, 817 °C for As and 630 °C for Sb. The lines are drawn as a guide for the eye.

concluded that the Peierls distortion mechanism in molten As is firm enough to keep the low coordination number. Solid Te undergoes successive phase transitions with an increasing pressure: Te changes its structure from a hexagonal to a puckered layer around 5 GPa, and then to a β -ponium structure around 9 GPa. The structural change realized in the supercooled liquid Te is now considered to be a transition corresponding to the first pressure sequence in the solid (Bichara *et al* 1996). To the author's knowledge, however, the allotropic transition to a simple cubic structure with an applied pressure has not been reported up to 20 GPa for As. Thus the structural change suggested by the present experiments may not be of a type predicted by a naive Peierls distortion mechanism. The recent numerical tight-binding simulations have shown that molten As consists of threefold- and fourfold-coordinated atoms and a considerable fraction of As atoms already have fourfold coordination upon melting (Bichara *et al* 1993). Assuming the calculations, therefore, the change with temperature in the fraction of those atoms having different coordination could be a plausible explanation for the rapid structural changes in molten As.

Table 1. Melting entropy of Va and VIa elements ($\text{J mol}^{-1} \text{K}^{-1}$).

As	23.1	Se	12.7
Sb	22.0	Te	24.2
Bi	20.8		

As listed in table 1, the melting entropy for Va elements is very large and does not change from element to element except for a big difference between those for Se and Te. Taking it for granted that molten As is in a fully distorted state as well as molten Se, the results are quite puzzling (Bellissent *et al* 1987). For VIa elements, the difference between for Se

and Te has been interpreted as being due to the structural changes in liquid Te (Tsuchiya 1986). An anomalously high melting entropy of Te consists of two contributions. One is the entropy required to melt to a chainlike liquid Te which is a value close to the one for Se to a first approximation. The other corresponds to a fraction (about 0.7 for Te) of the difference in entropy between a low-temperature (a chainlike fully Peierls-distorted Te liquid) and a high-temperature form. As mentioned in the preceding paragraph, the compressibility of As would take a maximum slightly below the accessible supercooled temperature as found in liquid Te. This implies that the molten As at melting point is already at the high-temperature side of an assumed structural change and not in a fully Peierls-distorted liquid. Then the transition entropy from a hypothetical fully distorted liquid with threefold coordination to a liquid with fourfold coordination could take part in an anomalously high melting entropy of As as in the Te case.

The electrical conductivity of As decreases upon melting and then increases with temperature. The apparent electrical gap is found to be about 0.5 eV while the theory predicts a gap of 0.15 eV (Li *et al* 1990). This is a situation observed only for liquid Te where the apparent electrical gap in the supercooled state is 0.5 eV while no real gap is predicted by optical measurements. The discrepancy can be explained by noting that the electrical conductivity reflects the activation process of the rapid structural changes (Cutler 1977).

4. Conclusion

The velocity of sound in molten As has been found to have very large positive temperature dependence, which provides the first evidence that a Peierls distortion in molten As depends quite strongly on temperature and the structure of liquid As changes very rapidly with temperature. This is, however, not in contradiction with the neutron diffraction experiments in which no appreciable changes of the structure have not been detected, because it is not easy to determine the first coordination number and its temperature variation very precisely, especially for liquid As, because of experimental difficulty. Then from the experimental side detailed density and specific heat measurements, and from the theoretical side MD calculations focused on the temperature dependence, would be important to shed further light on the structural changes and the Peierls distortion in molten As.

Acknowledgment

The author thanks Dr C Bergman at CNRS, Marseille for fruitful discussions on the structure of molten As.

References

- Bellissent R, Bergman C, Ceolin R, and Gaspard J-P 1987 *Phys. Rev. Lett.* **59** 661
- Bergman C, Pellegatti A, Bellissent R, Mennelle A, Ceolin R and Gaspard J-P 1989 *Physica B* **156/57** 158
- Bichara C, Pellegatti A and Gaspard J-P 1993 *Phys. Rev. B* **47** 5002
- Bichara C, Raty J-Y and Gaspard J-P 1996 *Phys. Rev. B* **53** 206
- Cutler M 1977 *Liquid Semiconductors* (New York: Academic)
- Gaspard J-P, Marinell F and Pellegatti A 1987 *Europhys. Lett.* **3** 1095
- Gitis M B and Mikhailov I G 1966 *Sov. Phys.-Acoust.* **12** 131
- Glazov V M, Chizhevskaya S N and Glogaleva N N 1969 *Liquid Semiconductors* (New York: Plenum)
- Greenspan M and Tschiegg 1958 *J. Res. Natl Bur. Stand.* **59** 5473
- Horiba S 1922 *Z. Phys. Chem.* **105** 295

- Kakinuma F, Tsuchiya Y and Suzuki K 1996 *J. Phys. Soc. Japan* **65** 2129
Klemm W, Spitzer H and Nierman 1960 *Angew. Chem.* **72** 985
Li X-P, Allen P B, Car R, Parrinello M and Broughton J Q 1990 *Phys. Rev. B* **41** 3260
McGonigal P J and Grosse A V 1962 *J. Chem. Phys.* **36** 469
Menelle A, Bellssent R and Frank A M 1987 *Europhys. Lett.* **4** 703
Tamura K 1996 *J. Noncryst. Solids* **205-207** 239
Tsuchiya Y 1986 *J. Phys. C: Solid State Phys.* **19** 2865
———1988 *J. Phys. C: Solid State Phys.* **21** 5473
———1991 *J. Phys.: Condens. Matter* **3** 3163
———1997 *J. Phys. Soc. Japan* **66** 120
Winter R, Szornel C, Pilgrim W-C, Howells W S, Egelstaff P A and Bodensteiner T 1990 *J. Phys.: Condens. Matter* **2** 8427