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Velocity of sound and high-energy γ -ray attenuation in liquid Ag–Se alloys

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Abstract. The velocity of sound and high-energy γ -ray attenuation in Ag–Se alloys have been measured as functions of temperature over the whole composition range. The sound velocity in an alloy with a miscibility gap shows an unusual temperature dependence which is characteristic of the critical behaviour associated with the two-melt phase separation. Using these quantities, the molar volume, volume expansion coefficient and adiabatic compressibility have been deduced, which show a distinct cusp at Ag_2Se . The results suggest the existence of stable ionic Ag_2Se association in the liquid. No indication in the temperature dependences of these thermodynamic functions was found which would correlate with the unusual temperature dependence of the electrical conductivity.

1. Introduction

The liquid Ag–Se system shows highly unusual behaviour of electrical properties near the stoichiometric compound Ag_2Se (Grazov *et al* 1986, Ohno *et al* 1994). The electrical conductivity shows a sharp local maximum at Ag_2Se around which it increases with increasing temperature in contrast with the observation for most liquid semiconductors (Enderby and Barns 1990). To investigate the possible structural reasons for the unusual electrical properties, neutron diffraction measurements have been performed (Price *et al* 1993). Their results are summarized as firstly that the local structure of liquid Ag_2Se is similar to that of the high-temperature form of the solid and secondly that evident structural characteristics have not been found which could be connected with the anomalous dependence on temperature of the electrical conductivity. Of further interest is that the coordination number of Ag rises significantly with small increase in the Se fraction around the composition Ag_2Se . In the analysis of the diffraction data, the density of the alloy was adjusted and thus the radial distribution function becomes zero at small distances. The tabulated data indicate that the number density decreases by 40% while the fraction of Se changes by only 6%. In that case, the structure would change radically in contradiction to the experimental result that the structure factor shows no visible changes around Ag_2Se , for which no explanation has been given, however.

In this paper we present the sound velocity measured over the whole composition range. Since the sound velocity is related to the second derivative of the free energy, useful information would be obtained if there were any thermodynamic anomaly around Ag_2Se relating to the unusual behaviour of the electrical conductivity. Further, to resolve the apparent inconsistency of the density estimation in the structural investigations, the molar volume of the Ag–Se system has been deduced from the linear absorption coefficient of

high-energy γ -rays. The results are discussed in conjunction with the critical phenomena associated with the two-melt phase separation occurring on either side of the composition Ag_2Se and with the recent structural investigations by neutron diffraction experiments.

2. Experimental details

Since the experimental details were the same as reported elsewhere (Tsuchiya 1988a, b), only essential points are described in the following.

The velocity of sound was measured with a conventional pulse method using a piezoelectric ceramic as a transducer. To study an alloy having a critical temperature as high as 1000°C , a sealed specimen in a small fused silica crucible was used in spite of the somewhat larger uncertainty in determining the absolute magnitude of the velocity of sound. The crucible had parallel side walls, one of which was the end surface of a buffer rod about 10 cm long (Tsuchiya 1988a). For an alloy in the two-melt phase, the sound velocity along the phase boundary could be measured by adjusting the position of the meniscus with respect to the buffer end. The sound velocity was determined with reference to the velocity of sound in distilled water at 0°C . It was taken as 1402.71 m s^{-1} (Greenspan and Tschiegg 1957). The frequency of the sound was $8 \times 10^6 \text{ Hz}$. In the present cell arrangement, it was not possible to change the path length and to keep the temperature-independent interface between fused silica and the molten alloy, so that the sound attenuation could not be measured. As the phase boundary was passed, however, it was observed that the echo signal on the oscilloscope screen went through a minimum in a very small temperature interval, suggesting critical sound attenuation.

The linear absorption coefficient of high-energy γ -rays was measured using ^{137}Cs at about 110 MBq as a γ -ray source of 661.6 keV. From the linear absorption coefficient μ_{alloy} of an alloy, the molar volume V may be deduced using the following relation under the assumption that the mass absorption coefficient μ_i for each constituent is independent of alloying as well as temperature:

$$V = (x_1 A_1 \mu_1 + x_2 A_2 \mu_2) / \mu_{\text{alloy}} \quad (1)$$

where x_i and A_i are the fraction and atomic mass, respectively, of element i . The mass absorption coefficient was $0.07382 \pm 0.00007 \text{ cm}^2 \text{ g}^{-1}$ for Ag and $0.06820 \pm 0.00006 \text{ cm}^2 \text{ g}^{-1}$ for Se. They were measured with the present experimental apparatus using a polycrystalline specimen for Ag and a powder specimen compressed into a steel tube for Se.

In both experiments the temperature was measured with a Pt–Pt(13 at.% Rh) thermocouple and controlled to within $\pm 0.5^\circ\text{C}$ with a digital temperature controller. The vertical temperature gradient over a specimen was less than 1°C . No special effort was made to determine the absolute temperature very accurately.

The correction due to the thermal expansion of vitreous silica was not taken into account, because it is very small compared with the intrinsic temperature dependence of the volume and the sound velocity. Including all sources of errors, the uncertainty was estimated to be 0.5% for the volume and 0.3% for the sound velocity. The relative change in the velocity could be resolved down to 0.5 m s^{-1} .

3. Results

Figure 1 shows the velocity v_s of sound in Ag–Se alloys as a function of temperature. The sound velocity in liquid Ag linearly decreases with increasing temperature. At the

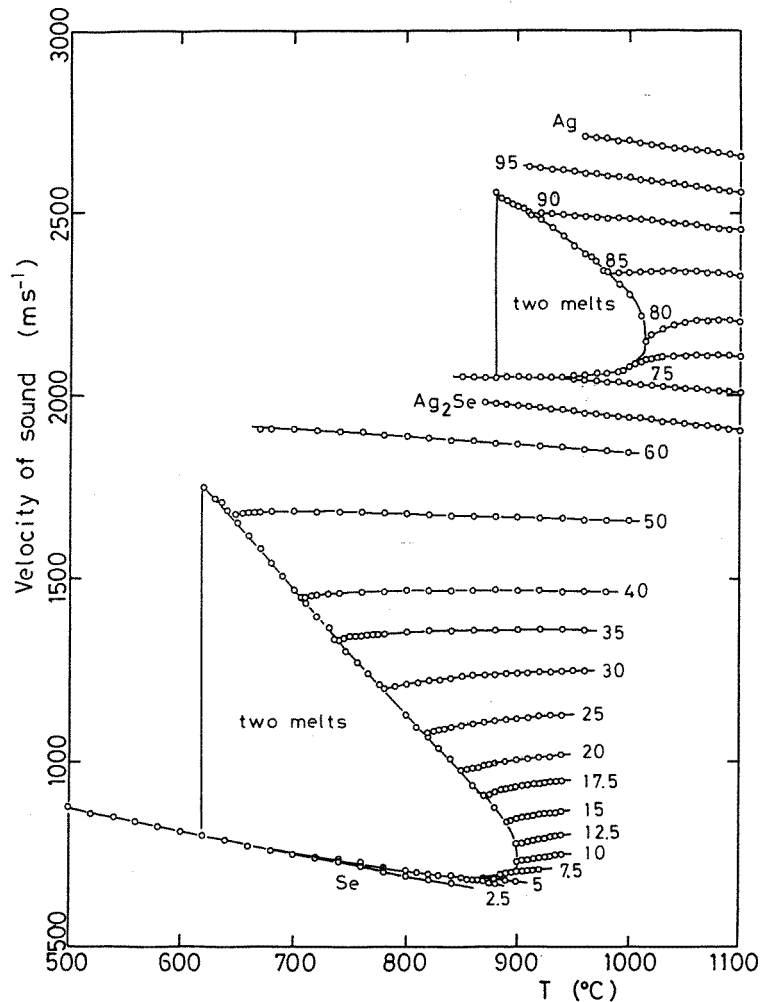


Figure 1. Sound velocity in Ag–Se alloys as a function of temperature. The numbers on the curves indicate the atomic percentage of Ag.

melting point ($961\text{ }^{\circ}\text{C}$), v_s and its temperature coefficient dv/dT are $2714.8 \pm 0.6\text{ m s}^{-1}$ and $-0.385 \pm 0.007\text{ ms}^{-1}\text{ K}^{-1}$, respectively. These values are in reasonable agreement with those in a standard reference book (Iida and Guthrie 1988). On the other hand, in an alloy with a miscibility gap the velocity of sound decreases more rapidly as the phase boundary is approached while it decreases linearly with temperature in molten Ag_2Se . In most Se-rich alloys, the sound velocity just above the phase boundary increases with increasing temperature, going through a maximum at much higher temperatures, as it does in a Ag-rich alloy with a miscibility gap. Because of the very high vapour pressure of Se, measurements at much higher temperatures were not possible, however.

Figure 2 shows the temperature dependence of the molar volume, as found from the γ -ray attenuation experiment. Except for the alloy with 5 at.% Ag, the molar volume increases linearly with increasing temperature. The onset of the two-melt phase was detected by a sharp break in the volume as a function of temperature. To evaluate the volume

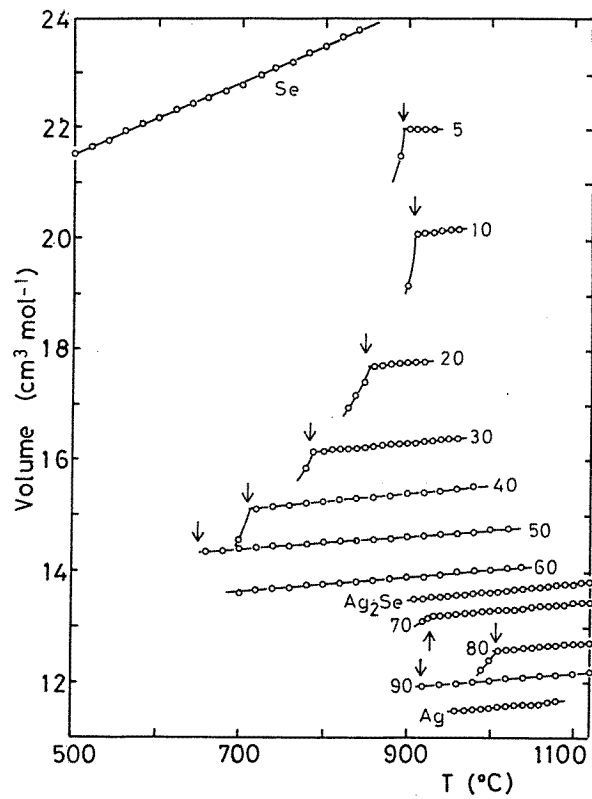


Figure 2. Molar volumes of Ag–Se alloys as functions of temperature. The numbers on the curves indicate the atomic percentage of Ag and the arrows indicate the two-melt phase boundary.

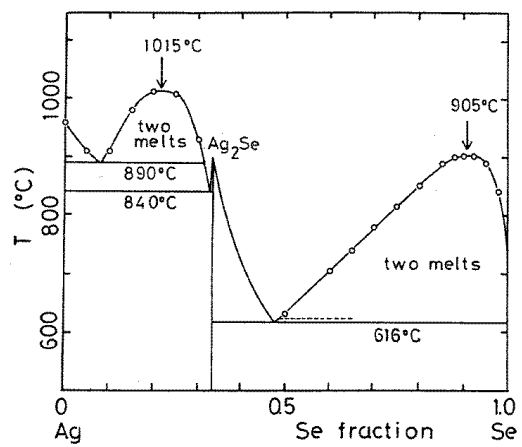


Figure 3. Phase diagram for Ag–Se system taken from Hansen and Anderko (1958) superimposed by the two-melt phase boundary.

expansion coefficient $\alpha_P = V^{-1}(\partial V/\partial T)_P$, all the data for the respective alloys were fitted to $V = V(T_0) + (dV/dT)(T - T_0)$. These parameters are listed in table 1. The results for Ag and Se are in reasonable agreement with those reported previously (Crawly 1974, Thurn and Ruska 1976).

Table 1. List of parameters for the molar volume $V = V(T_0) + (dV/dT)(T - T_0)$.

| Se (at.%) | T_0 (°C) | $V(T_0)$ (cm ³ mol ⁻¹) | dV/dT (10 ⁻² cm ³ mol ⁻¹ K ⁻¹) |
|--------------------|---------------|--|--|
| Ag | 1130 | 11.593 ± 0.004 | 0.135 ± 0.014 |
| 10 | 1020 | 12.052 ± 0.004 | 0.133 ± 0.007 |
| 20 | 1060 | 12.638 ± 0.002 | 0.117 ± 0.006 |
| 30 | 1000 | 13.264 ± 0.004 | 0.127 ± 0.007 |
| Ag ₂ Se | 1010 | 13.649 ± 0.003 | 0.145 ± 0.005 |
| 40 | 860 | 13.839 ± 0.004 | 0.131 ± 0.004 |
| 50 | 840 | 14.548 ± 0.004 | 0.115 ± 0.004 |
| 60 | 840 | 15.292 ± 0.005 | 0.130 ± 0.007 |
| 70 | 880 | 16.290 ± 0.003 | 0.141 ± 0.007 |
| 80 | 880 | 17.744 ± 0.001 | 0.094 ± 0.008 |
| 90 | 930 | 20.152 ± 0.008 | 0.214 ± 0.09 |
| 95 | 900 | 22.042 ± 0.015 | -0.16 ± 0.2 |
| Se | 540 | 21.797 ± 0.009 | 0.667 ± 0.007 |

The phase boundary determined from the data in figures 1 and 2 is plotted in figure 3. The rectilinear law for the extended diameter of the binodal is obeyed. From this law the critical points were determined, and they are $1015 \pm 5^\circ\text{C}$ at 21 ± 1 at.% Se and $905 \pm 5^\circ\text{C}$ at 91 ± 1 at.% Se. The former is lower by about 50°C than that reported recently (Ohno *et al* 1994). Owing to the lack of details on their furnace arrangement, a discussion on this discrepancy is unable to be given except for the fact that a rather long specimen was used for resistivity measurements and the temperature gradient over the specimen could be very large at high temperatures.

The adiabatic compressibility may be obtained from the thermodynamic relation $K_s = \rho^{-1}v_s^{-2}$, where ρ is the mass density. The results are plotted as a function of temperature in figures 4 and 5.

4. Discussion

4.1. Critical behaviour of the sound velocity

As shown in figure 2, the velocity of sound in an Ag-rich alloy in a range of about 50 K above the critical temperature deviates from a linear temperature dependence and decreases as the critical temperature is approached. The anomalous temperature dependence becomes weaker as the composition of alloy becomes further away from the critical composition and disappears in a miscible alloy. Similar behaviour is also seen in the figure for Se-rich alloys as well although it was not possible to demonstrate clearly because of the very high vapour pressure of Se. As plotted in the inset of figure 4, the adiabatic compressibility of Ag₈₀Se₂₀ increases as $\ln(T - T_c)$ towards the phase boundary in accord with the formal theory (Chase *et al* 1964). Thus it is reasonable to assume that the anomalous temperature dependence of the sound velocity above the phase boundary is a critical phenomenon associated with the two-melt phase separation.

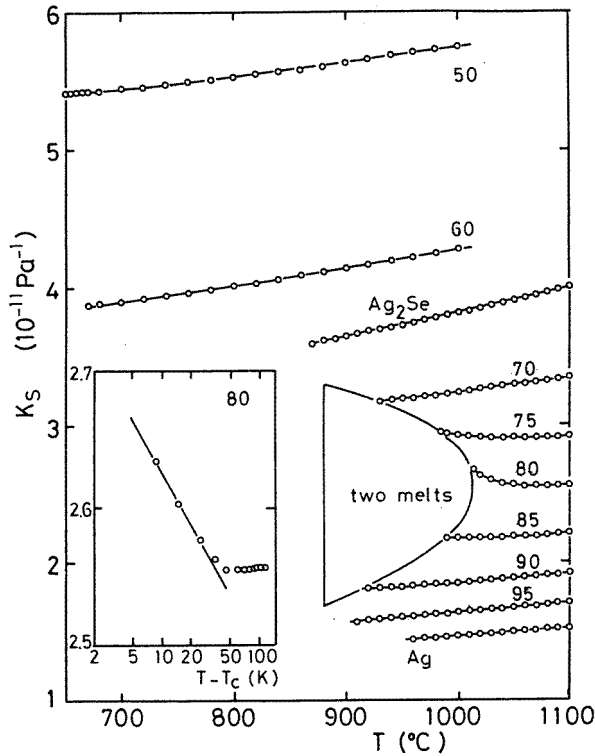


Figure 4. Adiabatic compressibility for Ag-rich alloys as a function of temperature. The symbols are the same as in figure 1. The inset shows the results for $\text{Ag}_{80}\text{Se}_{20}$ plotted against $\ln(T - T_c)$.

So far very few experimental results have been available that were aimed at investigating the critical sound wave propagation in a metallic alloy with a miscibility gap. Extensive and accurate data on the Bi-Ga system were reported by Puls and Kirkaldy (1971). Their experimental results on the attenuation of the sound wave were quantitatively in agreement with the theory proposed by Fixman (1962). No apparent critical effects upon the velocity were reported, however.

The Fixman (1962) theory predicts that the velocity of sound is affected by the presence of fluctuations associated with the two-melt phase separation and follows the equation

$$(v_s - v_s^0)/v_s^0 = -1/2HR(d) \quad (2)$$

where v_s^0 is the sound velocity expected if there were no effects due to phase separation. H is a constant depending on the frequency $\omega/2\pi$ of the sound and a critical temperature T_c . $R(d)$ is the real part of the definite integral which is known analytically. The corresponding expression for the absorption coefficient is given in terms of the imaginary part of that integral. The critical behaviour of the temperature dependence arises through the argument d in $R(d)$ as follows:

$$d = K^2(h/\omega)^{1/2} \quad (3)$$

where h is a constant involving the parameters α and K which characterize the long-range correlation function:

$$g(r) \sim (\alpha/r) \exp(-Kr). \quad (4)$$

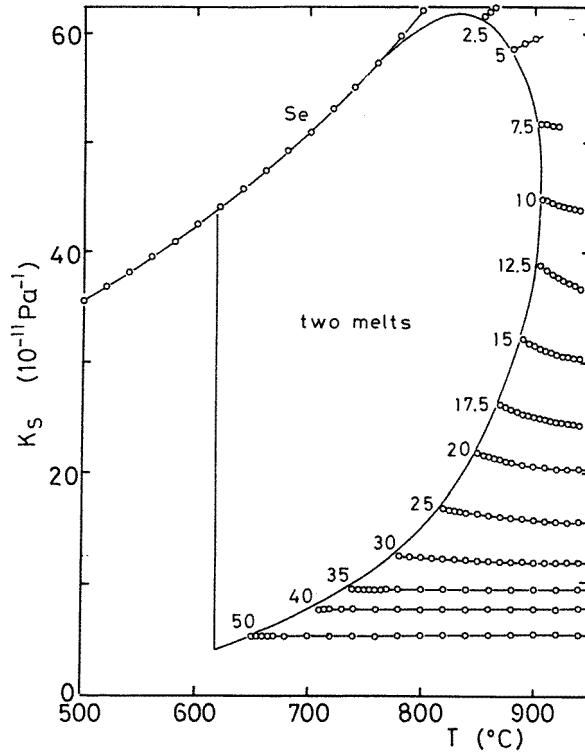


Figure 5. Adiabatic compressibility for Ag-rich alloys as a function of temperature. The symbols are the same as in figure 1.

The Debye relation is usually assumed for K^2 :

$$K^2 = (6/l^2)[(T - T_c)/T_c] \quad (5)$$

where l is the Debye short-range correlation length between atoms. Then the temperature dependence of d varies simply as $d_0(T - T_c)$. The parameters H and d_0 defined in this way satisfy the following relation (Fixman 1962):

$$H/d_0^{1/2} = 54^{1/2}(\gamma - 1)R/(2\pi^2 C_p^0 n l^3) T_c^{1/2} \quad (6)$$

where γ is the specific heat ratio, R the gas constant, C_p^0 the non-critical constant-pressure specific heat and n the number density. Thus the Debye short-range correlation distance l can be estimated from the temperature dependence of the sound velocity. The data for $\text{Ag}_{80}\text{Se}_{20}$ were fitted to equation (1) to obtain H and d_0 where a linear temperature dependence of v_s^0 was assumed phenomenologically. They are, respectively, v_s^0 (m s^{-1}) = $2571.1 - 0.293T$ K, $H = 0.117$ and $d_0 = 0.0599 \text{ K}^{-1}$. The reduced sound velocity $R(d) = -2(v_s - v_s^0)/(v_s^0 H)^{-1}$, is compared with the Fixman theory in figure 6 where the concomitant function for the sound attenuation is also plotted. The theory can adequately explain the anomalous temperature dependence of the sound velocity above the two-melt phase boundary. It should be noted that the effects of the two-melt phase separation on the sound velocity persist in a very wide temperature interval. Since $C_p^0 \sim 3R\gamma$ and $\gamma \sim 1.1$ to a rough approximation, equation (6) is reduced to $H/d_0^{1/2} \simeq 0.034l'^{-3}T_c^{1/2}$ where l' is l scaled up by an average interatomic distance, from which we obtain l as 3.8 \AA .

This estimation of l compares well with $l = 4.5 \text{ \AA}$ for the Bi-Ga system deduced from the critical sound attenuation (Puls and Kirkaldy 1971) and with other l values obtained from light scattering experiments on monatomic liquid-gas systems (Brumberger 1966).

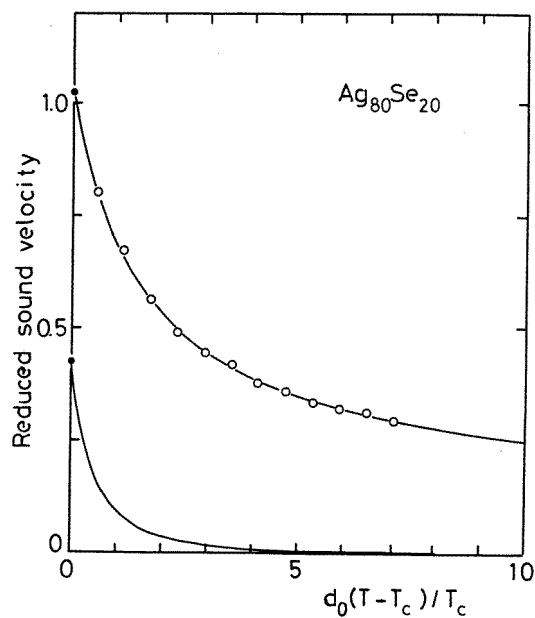


Figure 6. Reduced sound velocity $-2(v-v_0)(v_0H)^{-1}$ for $\text{Ag}_{80}\text{Se}_{20}$ as a function of $d_0(T-T_c)$. The Fixman theory is represented by a smooth curve through the data. The lower curve is the concomitant function describing the sound wave attenuation.

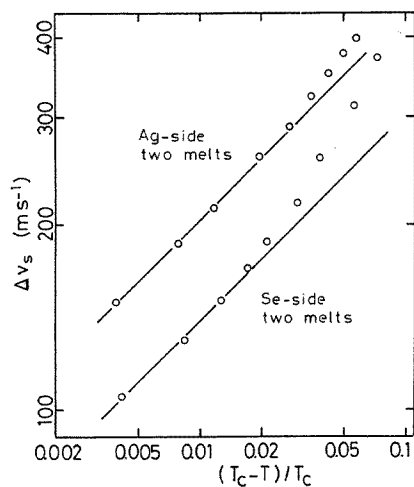


Figure 7. The log-log plot of the difference Δv_s in the sound velocity, along the phase boundary and the reduced temperature $(T_c - T)/T_c$. The straight lines correspond to a critical index of about $1/3$.

Figure 7 shows the logarithmic plot of the difference in the sound velocity along the phase boundary against $\ln(1 - T/T_c)$. The slope appears to approach 1/3 as T approaches T_c for both phase boundaries. Those results would be expected if the sound velocity along the phase boundary changes in proportion to the binodal composition in the temperature interval near the critical temperature and if the binodal line has the non-classical value of the critical exponent (Fisher 1967).

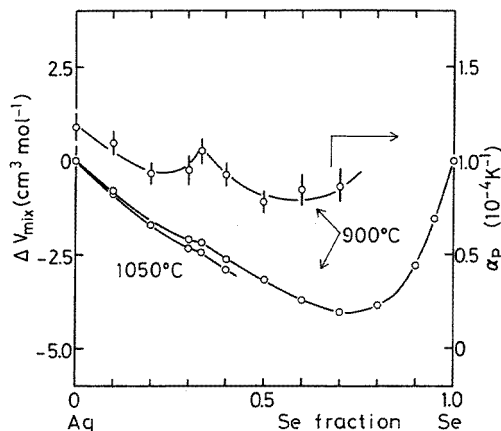


Figure 8. Dependences on composition of the excess mixing volume and the volume expansion coefficient.

4.2. Compound forming effects

Figure 8 shows the isotherms of the excess mixing volume $\Delta V_{mix} = V - \bar{V}$, and the volume expansion coefficient α_p where \bar{V} is a composition average of the quantities for Ag and Se, and the value for Se is that extrapolated from low temperatures. Very large volume contraction on the Se side and a small cusp at Ag_2Se are apparent. The volume expansion coefficient also shows a cusp at the same composition. Reflecting the cusp in ΔV_{mix} , the partial volumes jump discontinuously at the composition Ag_2Se , as plotted in figure 9. Note that the results on either side of the composition Ag_2Se are for different temperatures. As can be inferred from figure 2, however, the characteristic profile would not be altered if the calculations are made at a common temperature using extrapolated values. Such behaviour is characteristic of ionically ordered alloys, in which each ionic species surrounds itself as much as possible with ions of the opposite sign. So the coordination number increases away from stoichiometry while the bond length remains almost unchanged, causing an increase in density on either side of the stoichiometric composition (Robertson 1979).

Figure 10 shows the deviations of the adiabatic compressibility from an ideal behaviour defined by $\Delta = (K_s - K_{ideal})/K_{ideal}$, where K_{ideal} is given by a weighted sum of K_s for Ag and Se with their volume fractions as weighting factors. The characteristic feature of Δ is a small but distinct cusp at the composition Ag_2Se superimposed on a concave composition dependence, which is very similar to that of the excess mixing volume. As already reported for a number of binary systems containing Se or Te as one constituent, a close correlation exists between the composition dependences of the molar volume and of the compressibility (Tsuchiya 1991, 1993). It has been shown that the packing effect due to the change in the molar volume dominates the gross feature of the composition dependence

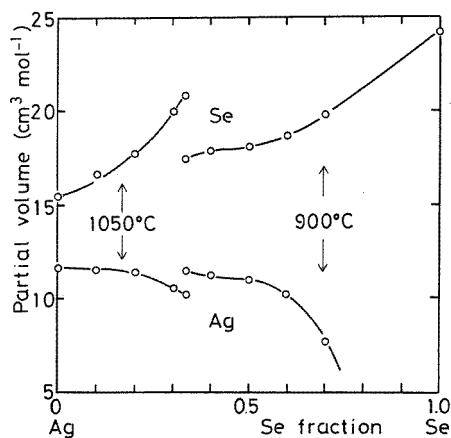


Figure 9. Dependence on composition of the partial volume.

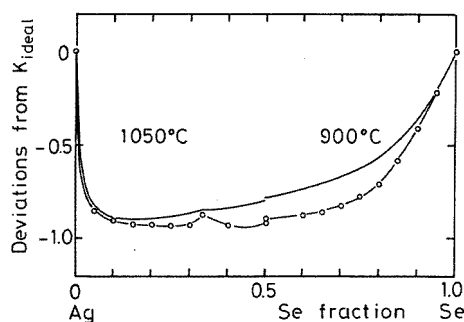


Figure 10. Deviations of the adiabatic compressibility from an ideal behaviour defined by $\Delta = (K_s - K_{ideal})/K_{ideal}$.

of the compressibility. In figure 10, Δ estimated with the binary hard-sphere model is compared with experimental results. In the calculations, the hard-sphere diameters of Ag and Se were chosen to fit their compressibility and the effects due to the change in the molar volume were taken into account by the packing fraction. Although the experimental Δ is for K_s , the results will not be very different if the values of the isothermal compressibility were evaluated, because the specific heat ratios in the numerator and denominator of Δ would almost cancel. As seen in figure 10, the essential feature of the compressibility is well reproduced. In figure 11, the volume converted for 1 mol of a pseudo-binary mixture, $(\text{Ag or Se})_{1-y}(\text{Ag}_2\text{Se})_y$ is plotted against the mole fraction of Ag_2Se clusters. It changes linearly except for Se-rich alloys. These results may also suggest that an Ag–Se alloy consists of Ag_2Se clusters and excess Ag or Se atoms to a rough approximation.

The structures of molten Ag_2Se and off-stoichiometric alloys have been discussed using the radial distribution function obtained from neutron diffraction experiments (Enderby and Barns 1990, Price *et al* 1993). The total structure factor has a small but clear pre-peak at 1.7 \AA^{-1} , indicating charge ordering. It was concluded that the local structure is similar to that of the high-temperature form of the solid. The first coordination numbers are 4.6, 3.7 and 3.9, respectively, for 30 at.% Se, Ag_2Se and 36 at.% Se after correcting the

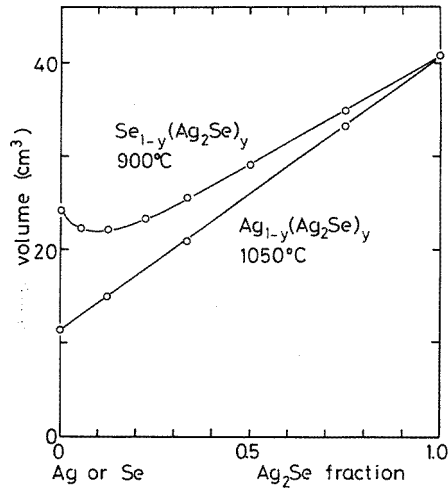


Figure 11. Dependence on excess Ag or Se fraction of the volume for a pseudo-binary mixture $(\text{Ag or Se})_{1-y}(\text{Ag}_2\text{Se})_y$.

number density using the present molar volume data. Since the near-neighbour distance is almost independent of the composition, the results of diffraction experiments suggest that the density must increase on either side of the composition Ag_2Se . This is consistent with a cusp-like local maximum of the molar volume at the composition Ag_2Se . It is interesting to note that the composition dependence of ionic correlations somewhat differs on either side of the stoichiometric composition. Roughly the coordination number increases on the Ag side while it remains constant on the Se side. Such a difference would be expected if the excess Ag ions and Ag_2Se form a random mixture with ionic bonds whereas the excess Se ions form predominantly covalent bonds with Ag_2Se (Robertson 1979). Starting from a stoichiometric structure at low temperatures, both increasing the temperature and adding an excess constituent would cause further increase in potential and topological disorder and hence decrease the carrier mobilities, both of which in turn would increase the carrier density either by excitation across the mobility gap or by changing the position of the Fermi level (Robertson 1979). If the former effect dominates, the electrical conductivity could decrease with increasing temperature or away from stoichiometry. The anomalous behaviour of the electrical conductivity of liquid Ag_2Se along these lines has been extensively discussed by Ohno *et al* (1994).

5. Conclusion

The sound velocity and molar volume of the Ag–Se system were measured over the whole composition range. The boundaries of two-melt phase separation occurring on either side of the composition Ag_2Se were determined. It was found that the sound velocity above the critical temperature decreases markedly from a linear extrapolation from the higher temperatures. The extent of the deviation becomes more appreciable as the critical point is approached. The Fixman theory can satisfactorily explain the critical sound wave propagation in an alloy with a miscibility gap. Below the critical point, the sound velocity has been measured along the phase boundary, which shows critical behaviour where the critical exponent approaches the non-classical value of $1/3$ as the critical point is approached.

A cusp in the isotherms of the molar volume, compressibility and volume expansion coefficient together with information from neutron diffraction suggests that liquid Ag_2Se has an ordered structure having predominantly ionic character. An unusually marked dependence on composition of the first coordination number around the composition Ag_2Se deduced from neutron diffraction experiments has now been corrected using the results of the present study.

Acknowledgment

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