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Abstract. The velocity of sound in liquid Tl–Te alloys has been measured in order to investigate the composition dependence of the compressibility. The isothermal compressibility deduced from the velocity of sound, density and specific heat shows a characteristic cusp at Tl_2Te, which supports stable Tl_2Te association persisting in the liquid.

In addition a logarithmic singularity in the adiabatic compressibility has been found at the critical point of the two-melt phase separation between Tl and Tl_2Te.

1. Introduction

It has been shown that the concentration and temperature variations in the compressibility are sensitive to the bonding character of a binary liquid alloy and especially of a compound forming alloy containing Te as one component (McAlister and Crozier 1976, Glazov *et al* 1984, Tsuchiya 1991a). Among such alloys, the Tl–Te system is one of the most extensively studied (Cutler 1977). In spite of the fact that various properties show unusual behaviour at the composition Tl_2Te, the velocity and attenuation of ultrasound reported previously show no large anomaly (Turner 1974).

The velocity of sound was therefore remeasured over the whole concentration range to investigate the composition dependence of the compressibility. As will be seen, the previous conclusion was derived because, for the alloys chosen, the product of the adiabatic compressibility and the volume happened to fall on an apparently linear composition dependence. The compressibility of the liquid Tl–Te alloy shows a definite cusp at Tl_2Te as well as at other compound-forming alloys.

2. Experimental details

The velocity of sound was measured with a standard pulse method. As the experimental details have been reported elsewhere (Tsuchiya 1988a), only essential points are described in the following. A closed-cell assembly using a fused quartz ampoule was employed to keep the preferential evaporation of Te as small as possible. The time required for sound to travel between a delay-line end and reflector was measured with the time function of a Sony–Tektronix 465B oscilloscope, the output of which was monitored with a digital voltmeter. The time difference between two pulses could be

easily resolved on the oscilloscope screen down to 5×10^{-10} s. The velocity of sound was determined with reference to the velocity in the water at 0 °C measured in the same cell. The latter was taken as 1402.71 m s^{-1} (Greenspan and Tschiegg 1957). If we take into account the results obtained for two different specimens having the same composition, the overall uncertainty is estimated to be within 0.2%.

The molar volume was also measured using a high-energy γ-ray attenuation method (Tsuchiya 1988b) to complement the data previously reported. The mass absorption coefficients of Te and Tl were determined using a powder specimen of Te or Tl$_2$Te compressed into a brass tube. They were respectively $0.071\,82 \pm 0.000\,05$ cm^2 g^{-1} and 0.1029 ± 0.0001 cm^2 g^{-1}.

The temperature was measured with a Pt–Pt (–13 at.% Rh) thermocouple and controlled with a digital temperature controller. Although the absolute temperature uncertainty was ± 3 °C, the relative temperatures were accurate to better than 1 °C and the stability at a temperature was better than ± 0.5 °C.

3. Results and analysis

The temperature dependence of the sound velocity v_s is plotted in figure 1. In the supercooled region the sound velocity in liquid Te decreases very steeply and has a peaked minimum at around 353 °C as previously reported (Tsuchiya 1991b). With an addition of small amount of Tl (20 at.%), the unusual temperature variation in sound velocity in liquid Te at low temperatures has almost faded out and the sound velocity shows normal behaviour as in a liquid metal; it decreases almost monotonically with increasing temperature. The velocity of sound in Tl at the melting point (303 °C) and its temperature derivative, which have been obtained by fitting all the data to a linear temperature dependence, are 1663.4 ± 0.3 m s^{-1} and -0.254 ± 0.001 m s^{-1} K^{-1}. These values are in reasonable agreement with those found in a reference book (Iida and Guthrie 1988). The sound velocities in alloys with 66.67, 50 and 30 at.% Tl are in good agreement with those reported previously (Turner 1974).

Between Tl and Tl$_2$Te, the two-melt phase appears. The sound velocity in this region above the upper critical solution temperature decreases with decreasing temperature towards the phase boundary. The phase boundary indicated by an inflection point in the v_s-temperature curve is in reasonable agreement with the previous results (Hoshino *et al* 1978).

The isotherms of v_s at several temperatures are plotted in figure 2. At high temperatures above about 700 °C, alloying Te with Tl causes only a small change in v_s up to the composition Tl$_2$Te while, at low temperatures where v_s in liquid Te has a large positive temperature coefficient, v_s increases quite steeply on adding a small amount of Tl. Between Tl and Tl$_2$Te, v_s increases towards the value in liquid Tl. Consequently a characteristic inflection appears in the v_s-composition curve at Tl$_2$Te. As the temperature is lowered, the inflection point appears to move slightly to the Te-rich region and to occur at the composition corresponding to the solid compound Tl$_5$Te$_3$ which has a congruent melting point (Elliott 1965).

The molar volume V of Te has a minimum slightly above the melting point and increases with decreasing temperature in the accessible supercooled region as well as with increasing temperature (Thurn and Ruska 1976). For alloys with 10 and 20 at.% Tl, V increases linearly with temperature except at around the liquidus temperature where the rate of increase in V decreases as the equilibrium liquidus temperature is
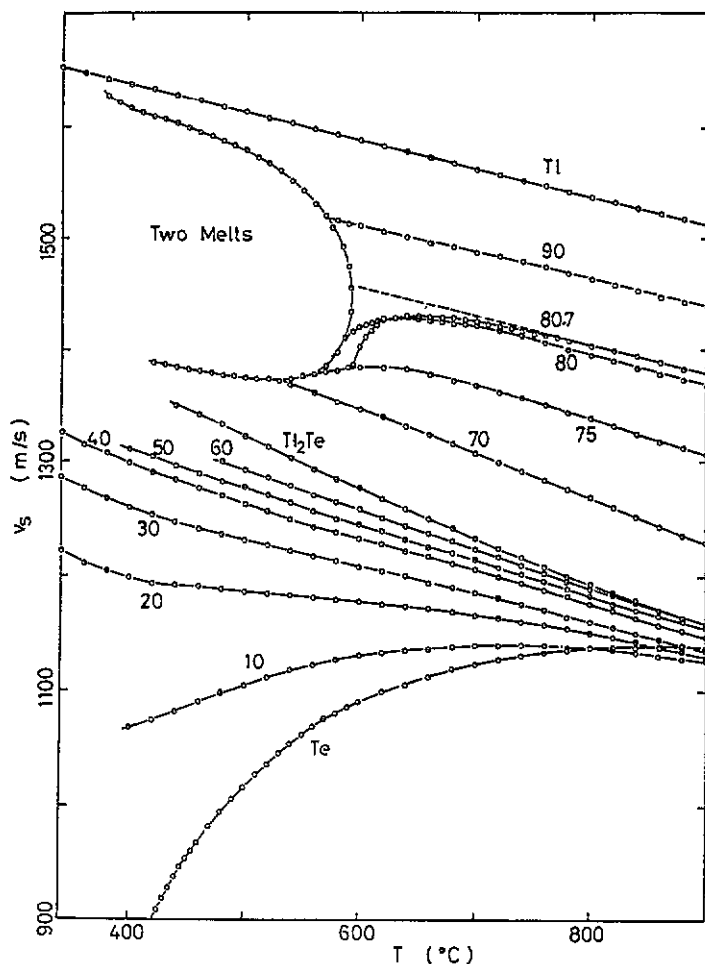
Figure 1. Velocity v_s of sound in the liquid Tl–Te alloys. The numbers on the curves indicate the atomic percentages of Tl. The results reported by Turner (1974) for Tl_2Te, 50 at.% and 30 at.% Tl coincide with the present results on this scale.

approached; a minimum has not been observed, however. The temperature variation in V for Tl and Tl-rich alloys appears almost linear. To evaluate the thermal expansion coefficient α_P, the data were fitted to a linear temperature dependence except for a few data for Te-rich alloys near the liquidus line. Linear fitting for all the data for Tl gives the volume at the melting point ($T_m = 303\,°C$) as $18.245 \pm 0.006\,cm^3\,mol^{-1}$ and $dV/dT = 0.246 \pm 0.002\,cm^3\,mol^{-1}\,K^{-1}$). These values are in good agreement with those compiled in a review paper (Crawley 1974). The parameters for all the alloy and the temperature range for linear fitting are listed in table 1. The isotherms of V and the excess mixing volume at 700 and 900 °C are shown in figure 3. The volume is not so dependent on Tl composition up to 66.7 at.% Tl but has an inflection point at Tl_2Te and decreases to Tl very steeply. Consequently the excess mixing volume has a cusp-like maximum at Tl_2Te. On the Tl-rich side it is concave upwards while on the Te-rich side it is convex downwards. The isotherm for Te-rich alloys agrees well with that reported by Nakamura and Shimoji (1973).
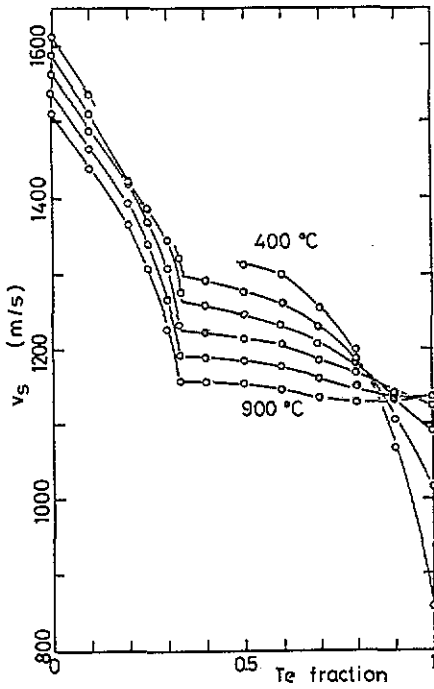
Figure 2. The velocity of sound as a function of composition. The temperatures from top to bottom are 400 °C, 500 °C, 600 °C, 700 °C, 800 °C and 900 °C, respectively.
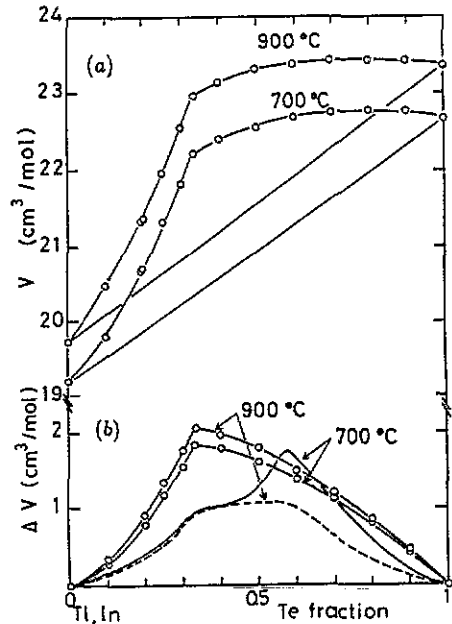
Figure 3. (a) Molar volume V as a function of Te concentration. (b) Excess volume of mixing (———) compared with that for the liquid In–Te system (————) taken from Thurn and Ruska (1976).

Table 1. Molar volumes of Tl–Te alloys. Data are fitted to $V = a + b(T - 800\,°C)$.

| Tl (at.%)	Volume at 800 °C (cm^3 mol^{-1})	dV/dT (10^{-2} cm^3 mol^{-1} K^{-1})	Range of linear fitting (°C)
0 (Te)	22.98 ± 0.01	0.340 ± 0.005	760–920
10	23.10 ± 0.01	0.323 ± 0.004	560–900
20	23.11 ± 0.01	0.325 ± 0.003	480–900
30	23.09 ± 0.01	0.340 ± 0.003	240–900
40	23.02 ± 0.01	0.352 ± 0.002	280–900
50	22.93 ± 0.01	0.358 ± 0.002	360–900
60	22.78 ± 0.01	0.363 ± 0.003	440–900
66.7	22.59 ± 0.01	0.374 ± 0.004	560–900
70	22.19 ± 0.01	0.366 ± 0.002	480–900
75	21.63 ± 0.01	0.345 ± 0.004	560–900
80	21.03 ± 0.01	0.322 ± 0.003	600–900
80.7	21.01 ± 0.01	0.325 ± 0.003	600–900
90	20.14 ± 0.01	0.297 ± 0.004	540–900
100 (Tl)	19.47 ± 0.01	0.246 ± 0.002	320–900
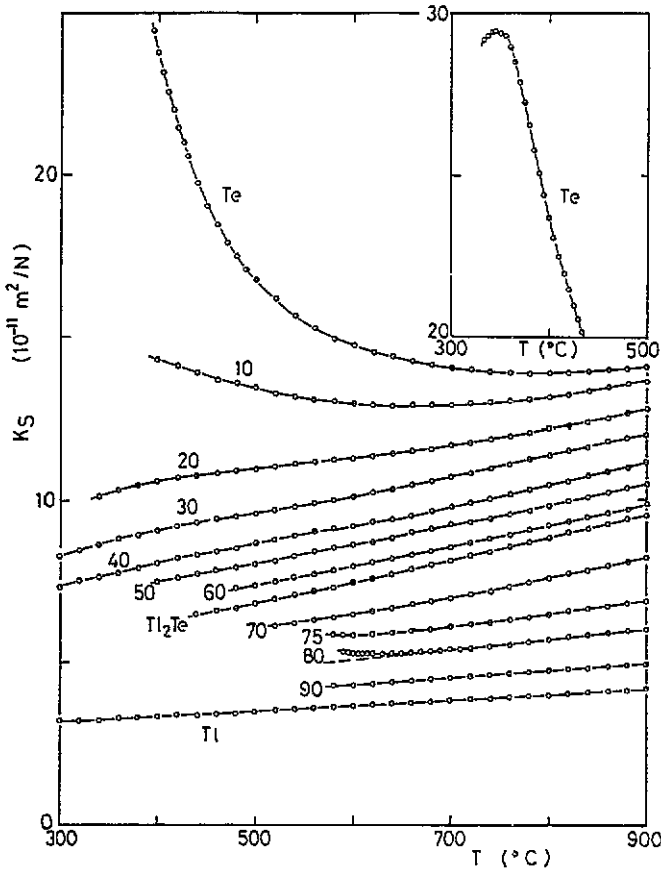
Figure 4. Adiabatic compressibility κ_S of liquid Tl–Te alloys. The numbers on the curves indicate the atomic percentages of Tl. The inset shows the results for Te at low temperatures.

The adiabatic compressibility κ_S may be obtained from

$$\kappa_S = 1/\rho v_s^2 \tag{1}$$

where ρ is the mass density. The adiabatic compressibility is shown in figure 4. Except for Te and $Tl_{10}Te_{90}$, the adiabatic compressibility increases with increasing temperature rather linearly. Using the thermodynamic relation between the adiabatic and isothermal compressibility, i.e. $\kappa_T = \kappa_S + TV\alpha_P^2/C_P$, the isothermal compressibility at 800 °C has been evaluated, where the constant-pressure specific heat C_P has been taken from the work of Kakinuma *et al* (1991). Figure 5 shows the results on κ_T as a function of composition. The compressibility has a definite cusp at Tl_2Te.

4. Discussion

The thermodynamic functions of pure liquid Te have been extensively studied by one of the present authors (Tsuchiya 1991b). It has been shown that the unusual temperature
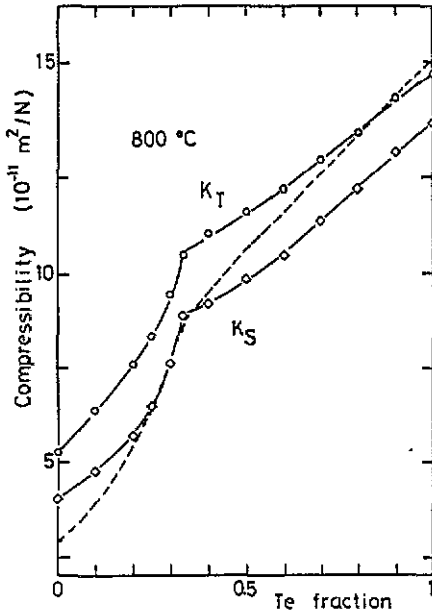
Figure 5. Isothermal compressibility κ_T and adiabatic compressibility κ_S at 800 °C as a function of Te. Concentration: ———, isothermal compressibility calculated with a binary hard-sphere model.
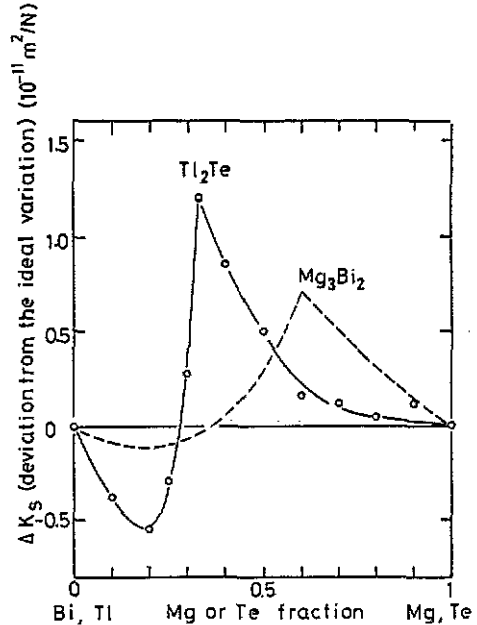
Figure 6. Deviation from the ideal variation in κ_S at 800 °C compared with the results for the liquid Mg–Bi alloy at 832 °C (McAlister *et al* 1973).

variation in the thermodynamic functions of Te in the supercooled region is a manifestation of the structural change towards a low-temperature form characterized by the two-fold coordination. Even above the melting temperature, the structural change has not finished as yet and the structure slowly changes with temperature to a high-temperature form, which is reflected in the anomalous behaviour of v_s (figure 1) and V above the melting point (Tsuchiya 1991b).

On addition of Tl, the anomalous behaviours of the v_s and V quickly fade, which may indicate that a Tl–Te alloy has a rather isotropic structure like that of Te in the high-temperature form. Similar alloying behaviour has been observed for most polyvalent elements except Si and Ge (Tsuchiya and Takahashi 1990, Tsuchiya 1991a). If the '8-N' rule is obeyed for Tl in liquid Te where N is the number of outermost electrons, Tl would have five-fold coordination to a rough approximation (Phillips 1979), and then a small amount of Tl would suffice to destroy the low-temperature form of Te. Therefore, the present results may rule out the structural model for a Te-rich Tl–Te alloy proposed by Cutler (1977) where a mixture of Te chains terminated by a onefold Tl ion at the end is assumed. The following discussion will be concentrated on the composition dependence of the compressibility at high temperatures where the effects due to the structural changes in the liquid Te are neglected.

Turner (1974) reported that the compressibility did not show the appreciable anomaly at Tl_2Te where the resistivity has a sharp pronounced peak. The results are in contrast with those for the liquid Mg–Bi alloy, the compressibility of which shows a sharp maximum at the Mg_3Bi_2 (McAlister *et al* 1973) and also with those recently obtained for the Sn–Te and Pb–Te alloys. The compressibilities for the last two systems also show a

definite cusp at 50 at.% Te where an anomaly in electrical properties has been found (Tsuchiya and Takahashi 1990, Tsuchiya 1991a). In figure 6 the present results are compared with those for the Mg–Bi system where the deviation from the ideal variation in the following adiabatic compressibility is plotted:

$$\kappa_S(\text{ideal}) = [xV_1\kappa_S^1 + (1 - x)V_2\kappa_S^2]/[xV_1 + (1 - x)V_2]. \tag{2}$$

V_1 and V_2 are the molar volumes of the two species, and x and $1 - x$ the respective atomic fractions. As seen in the figure, the compressibility of the Tl–Te system has a sharp peak at Tl_2Te, similar to the behaviour of the compressibility of the Mg–Bi alloy.

One of the basic problems in the physics of liquid semiconductors is whether or not the rapid temperature dependence of electronic properties is associated with the structural changes. A typical example of the former case is the liquid In–Te system. The marked semiconductive character around In_2Te_3 is associated with rapid structural modifications with increasing temperature (Tsuchiya 1988a, b). An experimental clue to this question may be obtained from the temperature variation in the thermodynamic parameters. As an example, the profile of excess mixing volume of the In–Te system is plotted in figure 3 which is very sensitive to the temperature variation (Thurn and Ruska 1976). On the contrary for the Tl–Te alloy the increasing temperature has no greater effect on the excess mixing volume than it does on the volume expansion.

Besides the isothermal compressibility χ_T, the specific heat C_P and the thermal expansion coefficient α_P have a characteristic cusp-like maximum at Tl_2Te as plotted in figure 7. If these anomalies were brought about by rapid structural changes associated with dissociation of the chemical complex Tl_2Te in the liquid, Ehrenfest's relations would be obeyed between the excess parts of χ_T, C_P and α_P (hereafter designated by the symbol δ) (Tsuchiya 1991b). The Prigogine–Defay ratio ($R = \delta C_P \delta \chi_T / \delta \alpha_P^2 TV$) is a convenient measure for the criterion. The deviation from Kopp's law may be taken as δC_P. In an ideal alloy system, χ_T and α_P are linear functions of the volume fractions of Tl and Te (cf equation (6)), then the deviations of these may be taken as $\delta \chi_T$ and $\delta \alpha_P$. The excess quantities estimated in this way give a value of 4.5 for the Prigogine–Defay ratio in contrast with the value of unity expected for the case when the rapid structural changes cause enhancement of these thermodynamic functions. It is, therefore, difficult to explain the significant peak in these thermodynamic parameters at around Tl_2Te in terms of rapid structural changes with increasing temperature.

In figure 5, a binary hard-sphere model (see, e.g., Shimoji 1977) with the following assumptions is plotted for comparison. The hard-sphere diameter is equal to the distance of closest approach obtained from $g(r)$ for the pure metal and is independent of the composition. The respective hard-sphere diameters (2.97 Å for Te and 3.04 Å for Tl) have been taken from Waseda *et al* (1979). The mean packing fraction of an alloy has been estimated from the actual volume with these hard-sphere diameters. The calculated compressibility appears to reproduce the characteristic inflection at Tl_2Te of the compressibility–composition curve. The results may suggest that packing effects associated with development of ionic bonding (Enderby and Barnes 1990) dominate the characteristic cusp at Tl_2Te. Certainly a decrease in the electron gas density around Tl_2Te would also play an important role as discussed by McAlister *et al* (1973); full understanding of the origin of the cusp on a microscopic basis is not possible at the moment, however.

Apart from Te and a few Te-rich alloys, an unusual dependence of v_s on temperature is seen for the alloys which undergo two-melt phase separation. A similar temperature variation in v_s has been found for In–Te alloys above the upper critical solution temperature (Tsuchiya 1988a). The anomaly appears to increase as the critical concentration
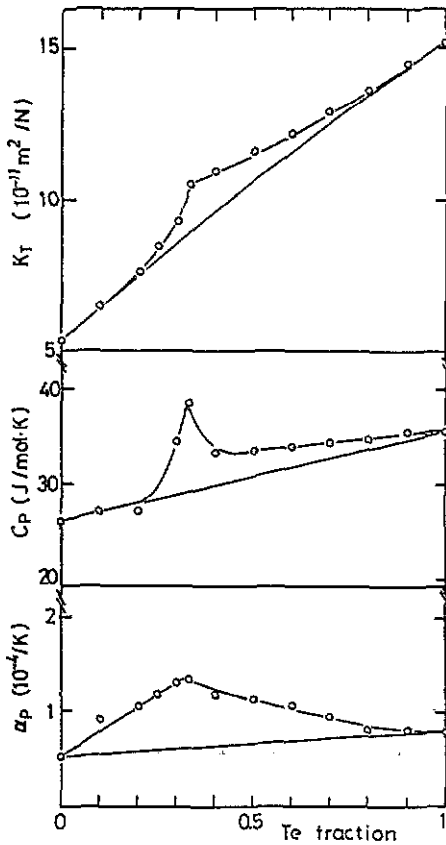
Figure 7. Isothermal compressibility κ_T, constant-pressure specific heat C_P (Kakinuma *et al* 1991) and thermal expansion coefficient α_P at 800 °C.

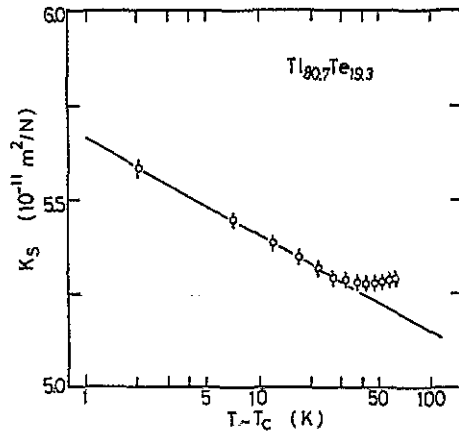**Figure 8.** Adiabatic compressibility of $Tl_{80.7}Te_{19.3}$ (the alloy having the critical composition) as a function of $\ln(T - T_c)$ in the critical region.

of Tl (80.7 at.%) (Hoshino *et al* 1978) is approached. A theory of the dispersion of sound in a critical mixture was developed by Fixman (1962). The present results are qualitatively in accord with the prediction. However, an analysis based on his theory is not possible because a number of parameters to be evaluated from other experiments are involved. On the other hand, formal theory predicts that the adiabatic compressibility increases as $-\ln(T - T_c)$ when the critical temperature T_c is approached from above (Chase *et al* 1964, Fisher 1967). In figure 8, the adiabatic compressibility is plotted against $\ln(T - T_c)$ where $T_c = 593$ °C. The presence of a logarithmic singularity is clearly indicated. We therefore conclude that the unusual temperature variation in the sound velocity in an alloy undergoing two-melt phase separation is due to a critical phenomenon associated with the phase separation. In principle, the thermal expansion coefficient α_P should show a similar temperature variation; however, the present measurements on the volume are not accurate enough to show such a singularity in α_P.

In summary, we have measured the sound velocity and the molar volume of the liquid Tl–Te system. Both the sound velocity and the molar volume as functions of composition show a characteristic inflection at Tl_2Te at which the electrical resistivity has a cusp-like maximum. The compressibility deduced from the sound velocity and the

volume shows a cusp at Tl_2Te, the magnitude of which is much larger than that reported for the liquid Mg–Bi system when the deviation from an ideal composition dependence is compared. In the composition range showing the two-melt phase separation, the critical behaviour of the sound velocity is observed as the critical temperature is approached from above.

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