The thermodynamics of structural changes in the liquid sulphur-tellurium system:

compressibility and Ehrenfest's relations

The thermodynamics of structural changes in the liquid sulphur–tellurium system: compressibility and Ehrenfest's relations

Y Tsuchiya

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

Abstract. The velocity of sound in liquid sulphur–tellurium (S–Te) has been measured to investigate structural changes induced by raising the temperature. The sound velocity in a Te-rich alloy as a function of temperature shows a peaked minimum, which shifts to higher temperatures with increasing S content. The results have been used to deduce the isothermal compressibility. It has been shown that Ehrenfest's relations are satisfied among the temperature dependences of the isothermal compressibility, constant-pressure specific heat and volume expansion coefficient. The relations also explain the initial slope of the polymerization line in the pressure–temperature diagram for liquid S.

1. Introduction

The coordination number of liquid Te decreases upon cooling to about two in a deeply supercooled state, the structure of which is believed to be of a Se-like chain structure (hereafter referred to as the L-form) (Menelle *et al* 1988, 1989). The structural change proceeds quite rapidly around 353 °C where the specific heat, compressibility and volume expansion coefficient show marked extrema (Tsuchiya 1991a). Above the melting temperature (451 °C) the structural change is almost complete and liquid Te is essentially in a different form (the H-form), the coordination number of which is about three (Menelle *et al* 1988, 1989).

In a recent paper the author has reported that the L-form of Te is stabilized by adding S, which is manifested by the molar volume measurements which show that the peaked minimum in the volume expansion coefficient shifts to higher temperatures with increasing S content (Tsuchiya 1992). This inference has been confirmed by recent specific heat measurement by Kakinuma *et al* (1993). These thermodynamic characteristics of S–Te alloys are quite similar to those found for the liquid Se–Te system.

In this paper, the velocity of sound has been measured to evaluate the compressibility, for a better understanding of the structural changes occurring in the liquid S–Te system. The overall temperature and composition dependence of the sound velocity is found to be much the same as the one reported for the liquid Se–Te system. In addition the results confirm a two-melt phase bounded by a looped boundary (Tsuchiya 1992) that is located in the composition–temperature diagram well above the equilibrium liquidus temperature.

2. Experiment

The velocity of sound was measured using a standard pulse-echo, single-ended technique. Since sulphur has a very high vapour pressure, a sample sealed in a fused silica cell was used to keep the preferential evaporation of sulphur as small as possible. The details of cell assembly were the same as reported elsewhere (Tsuchiya 1988a). The velocity of sound was determined by measuring the time delay for water in the same sample cell kept at 0 °C. The sound velocity in the water at 0 °C was taken as 1402.71 m s^{-1} (Greenspan and Tschiegg 1957).

The resolution of the time interval on the oscilloscope display was better than 0.5×10^{-8} s, which corresponds to about 1 m s^{-1} in the velocity of sound. The time delay was digitally read our with a digital voltmeter. If we take into account the results obtained for different specimens having the same composition, the overall uncertainty is estimated to be within 0.2%.

The temperature was measured using a Pt–Pt (13 at.% Rh) thermocouple and stabilized with a digital temperature controller within ±0.5 °C.

3. Results

Figure 1 shows the velocity of sound, v_s, in the liquid S–Te alloy as a function of temperature, T. The results for Te are in reasonable agreement with those reported by Gitis and Mikhailov (1966) in the overlapping temperature region. For alloys with less than 50 at.% S, a minimum in v_s is observed in the present temperature range. The position of the minimum shifts to higher temperatures with increasing S content. For an alloy containing more than 50 at.% S, only the low-temperature portion of the whole v_s–T curve is observed and the sound velocity almost linearly decreases with temperature, although it is inferred from the results for Te-rich alloys that the sound velocity in a S-rich alloy would also take a minimum and then increase at much higher temperatures. In an alloy with 40 at.% S, a clear anomalous break of the v_s–T curve occurs between 690 and 750 °C. The results conform to the two-melt phase separation bounded by a looped boundary that has been found using a high-energy γ-ray attenuation technique (Tsuchiya 1992). The results for pure S at the lower temperature is plotted in the inset of figure 1. The sound velocity almost linearly decreases with increasing temperature, however at the polymerization temperature ($T_p = 159$ °C) its temperature coefficient changes almost discontinuously and a distinct inflection appears. The deviations from a linear relation around T_p have been reported by a few groups, but they have been ascribed to the systematic error (Poulis and Massen 1965) and seem not to be confirmed up to date.

The isothermal compressibility, κ_T, may be obtained from the following thermodynamic relation:

$$\kappa_T = \rho^{-1} v_s^{-2} + T V \alpha_P^2 C_P^{-1}$$

where ρ is the mass density, T the temperature, V the molar volume, α_P the volume expansion coefficient, and C_P the constant-pressure specific heat. The thermodynamic data required for the evaluation of κ_T were taken from Tsuchiya (1992) and Kakinuma *et al* (1993). The results are plotted in figure 2, in which the temperature range is limited by the available specific heat data. Corresponding to a minimum in the v_s–T curve, κ_T for Te and Te-rich alloys has a peaked maximum, the position of which shifts to higher temperatures with increasing S content, with an accompanying broadening of the peak width.
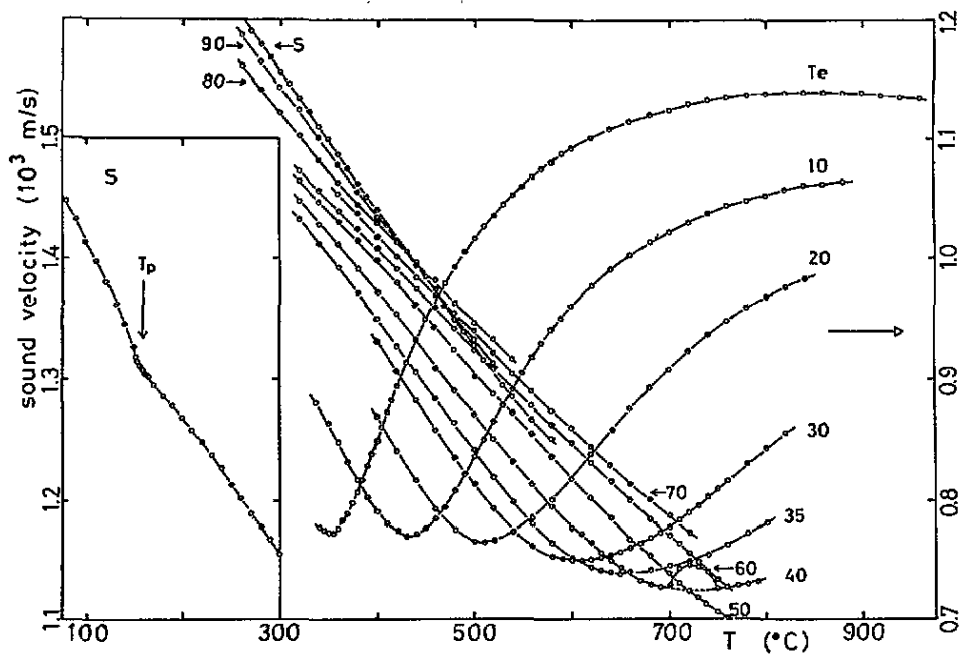
Figure 1. The dependence on temperature of the velocity of sound in the liquid S–Te system. The numbers indicate the atomic percentages of S. A clear break between 690 °C and 750 °C from the smooth variation (dotted curve) for 40 at.% S corresponds to a two-melt phase separation bounded by a looped boundary (Tsuchiya 1992). The inset shows the results for S around the polymerization temperature, $T_p = 159$ °C.
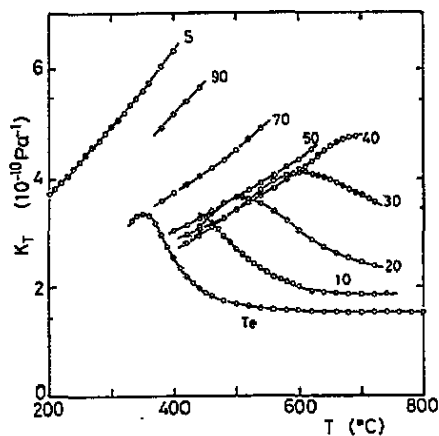

Figure 2. The dependence on temperature of the isothermal compressibility, κ_T, for the liquid S–Te system. The numbers are the same as in figure 1.
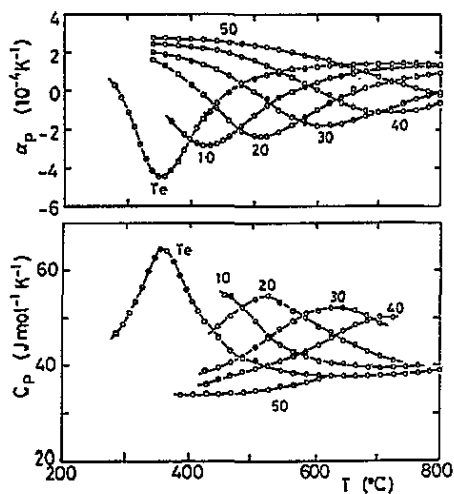
Figure 3. The dependence on temperature of the expansion coefficient, α_P (Tsuchiya 1992), and the constant-pressure specific heat, C_P (Kakinuma *et al* 1993), for the liquid S–Te system. The numbers are the same as in figure 1.

4. Discussion

4.1. Ehrenfest's relations in Te and Te-rich alloys

As plotted in figure 3, the volume expansion coefficient and the constant pressure specific heat as a function of temperature have peaked extrema where the isothermal compressibility takes a maximum. The peak width of these thermodynamic functions becomes broadened with increasing S content, which may be interpreted as being due to the concentration fluctuations caused by alloying. Taking into account the similar behaviour of these thermodynamic functions for the liquid Se–Te system (Thurn and Ruska 1976, Tsuchiya 1988b, Kakinuma and Ohno 1987, Tsuchiya 1991b), one may suppose that the low-temperature form of Te is stabilized by adding S and the unusual temperature dependence of the thermodynamic functions are caused by rapid structural changes from the L- to the H-form in the alloy.

In the following effects of the structural changes on the thermodynamic functions are considered. To begin with let us suppose that there exists a single variable besides the temperature, T, and the pressure, P, which specifies the equilibrium state of a S–Te alloy, and consider a Gibbs' free energy having the functional form $G(T, P, C)$. Here C denotes the fraction of atoms in the high-temperature (H-) form and is a function of T and P. The necessary and sufficient condition for thermal equilibrium is $(\partial G/\partial C)_{T,P} = 0$. It is a straightforward calculation to show that κ_T, α_P and C_P take the following forms, respectively:

$$\kappa_T = -(1/V)(\partial V/\partial P)_{T,C} - (1/V)(\partial V/\partial C)_{T,P}(\partial C/\partial P)_T \equiv \kappa_T^0 + \delta\kappa_T \quad (1)$$

$$\alpha_P = (1/V)(\partial V/\partial T)_{P,C} + (1/V)(\partial V/\partial C)_{T,P}(\partial C/\partial T)_P \equiv \alpha_P^0 + \delta\alpha_P \quad (2)$$

$$C_P = (\partial H/\partial T)_{P,C} + (\partial H/\partial C)_{T,P}(\partial C/\partial T)_P \equiv C_P^0 + \delta C_P \quad (3)$$

where H is the enthalpy and other symbols have their usual meanings. The first term on the RHS is the normal thermodynamic function expected if there were no structural changes, and the second an excess contribution caused by the change of the fraction of H-form atoms with temperature or pressure.

Now we can show that $\delta\kappa_T$, $\delta\alpha_P$ and δC_P are not all independent. Bearing in mind that the molar volume takes the form $V = V(T, P, C)$, we have

$$dV = (\partial V/\partial T)_{P,C}\, dT + (\partial V/\partial P)_{T,C}\, dP + (\partial V/\partial C)_{T,P}\, dC. \quad (4)$$

Dividing by dT and assuming constant C we get

$$(\partial V/\partial T)_C = (\partial V/\partial T)_{P,C} + (\partial V/\partial P)_{T,C}(\partial P/\partial T)_C. \quad (5)$$

Using a theorem on partial differentiation, $(\partial w/\partial y)_x = (\partial w/\partial y)_z + (\partial w/\partial z)_y(\partial z/\partial y)_x$, the LHS is rewritten as

$$(\partial V/\partial T)_C = (\partial V/\partial T)_P + (\partial V/\partial P)_T(\partial P/\partial T)_C. \quad (6)$$

Equating the RHS of equations (5) and (6), and using equations (1) and (2):

$$\delta\kappa_T(T)/\delta\alpha_P(T) = (\partial T/\partial P)_C. \quad (7)$$

The same argument may be applied to the entropy $S(T, P, C)$ to yield the relation between δC_P and $\delta\alpha_P$ (Tsuchiya 1991b):

$$\delta C_P(T)/\delta\alpha_P(T) = TV(\partial P/\partial T)_C. \quad (8)$$

Combining equations (7) and (8), we get

$$\partial C_P(T)\delta\kappa_T(T)/\delta\alpha_P(T)^2 = TV. \tag{9}$$

Here $(\partial T/\partial P)_C$ refers to the slope of constant C on the P–T diagram. These relations are formally equivalent to Ehrenfest's relations for the second kind of phase transition.

It would be of interest to mention the sign of the excess thermodynamic functions. Since $(\partial V/\partial C)_{T,P}$ is the volume change associated with the structural change, the structural change proceeds with an applied pressure if the sign of $(\partial V/\partial V)_{T,P}$ is negative, and vice versa. Then the sign of $(\partial V/\partial C)_{T,P}(\partial C/\partial P)_T$ is always negative. This shows immediately why $\delta\kappa_T$ should be positive. By virtue of equation (9) δC_P is also positive while $\delta\alpha_P$ is of undetermined sign, depending on the sign of $(\partial V/\partial C)_{T,P}$. These requirements on the excess thermodynamic parameters are independent of a specific model for the Gibbs' free energy in so far as it takes the form $G(T, P, C)$ (Davies and Jones 1953). For the S–Te system, the molar volume in the transitional region contracts with increasing temperature (Tsuchiya 1992). Thus $(\partial V/\partial C)_{T,P}$ is negative and $\delta\alpha_P$ becomes negative.

In the transitional region the change in C dominates the temperature dependence of the thermodynamic parameters because C changes from zero to unity while κ_T^0, α_P^0, and C_P^0, as well as the temperature, would change at most by 20% as inferred from figures 2 and 3. Then one expects that κ_T and C_P would vary linearly when plotted against α_P unless $(\partial T/\partial P)_C$ has a large temperature dependence. The constant-pressure specific heat (Kakinuma *et al* 1993) and the isothermal compressibility for Te and alloys with an S content of up to 40 at.% have been plotted against α_P in figures 4 and 5, respectively, where the temperature is a hidden parameter. The C_P–α_P plot falls almost on a common straight line, irrespective of S content. This would imply that C_P^0 is not really dependent on the alloy composition, corresponding to the fact that C_P takes almost the same value for all specimens if there are no structural changes. The slope of these plots gives $TV(\partial P/\partial T)_C$. In contrast κ_T as a function of α_P has duplex values, a reason for which may be mainly due to the temperature dependence of κ_T^0. Since the analysis for respective alloys brings about a fairly large scatter in the composition dependence of $(\partial T/\partial P)_C$, we have just shown in figure 5 lines having slopes corresponding to the straight line in figure 4. The latter has been determined by fitting all the data in the C_P–α_P plot to a linear relation. The results appear to bear out the Ehrenfest relations shown by equations (7) to (9), and they predict that an applied pressure lowers the transitional region of structural change at a rate of $(\partial T/\partial P)_C = -2.8$ (Te), -3.6 (10 at.% S), -3.9 (20 at.% S), -4.4 (30 at.% S), or 4.8 (40 at.% S) $\times 10^{-7}$ K Pa^{-1}. Using the thermodynamic relation $(\partial C_P/\partial P)_T = -TV[\alpha_P^2 + (\partial\alpha_P/\partial T)_P]$ or $(\partial\alpha_P/\partial P)_T = -(\partial\kappa_T/\partial T)_P$, one can estimate C_P or α_P under an applied pressure. As calculated for Te (Tsuchiya 1991a), with an applied pressure the peak position in C_P shifts to lower temperatures by the amount just predicted.

4.2. Thermodynamic anomaly around the polymerization temperature of S

As depicted in figure 6, at the polymerization temperature $T_p = 159\,°C$, C_P (Braune and Möller 1954) and α_P (Kellas 1912, Tsuchiya 1992) for S change somewhat discontinuously and with increasing temperature approach the values extrapolated from those below T_p, and thus they show peaked extrema around T_p. These very sharp changes at T_p may be related to the fact that the polymerization proceeds in a very small temperature interval at T_p (Tobolsky and Eisenberg 1959). The plot of C_P against α_P is shown in figure 7, the slope of which gives the pressure dependence of the polymerization temperature as seen from equation (8). The straight line in the figure predicts that the polymerization temperature would be lowered
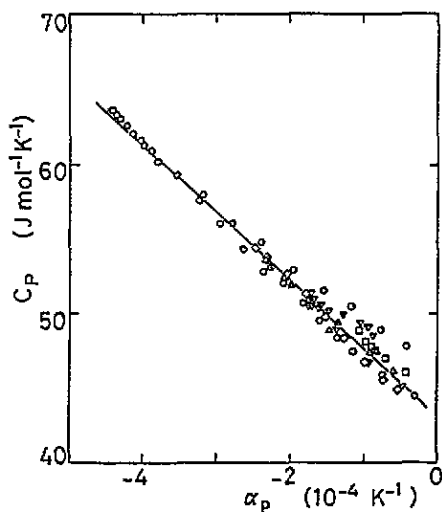
Figure 4. The dependence on the expansion coefficient, α_P, of the constant-pressure specific heat, C_P: Te (O), 10 at.% S (◇), 20 at.% S (△), 30 at.% S (▽), and 40 at.% S (□). A straight line indicates the prediction of equation (8).

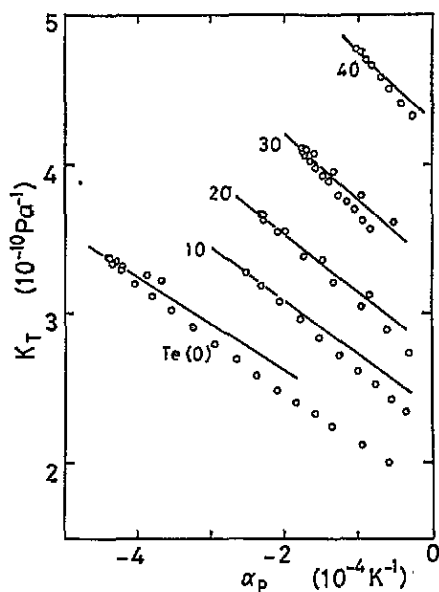**Figure 5.** The dependence on the expansion coefficient, α_P, of the isothermal compressibility, κ_T. The numbers are the same as in figure 1. A straight line through the respective data is the prediction of equation (7) where $(\partial T / \partial P)_C$ is evaluated from the C_P–α_P plot in figure 4, and the TV value at the maximum for the respective alloys.

at a rate of -1.7×10^{-7} K Pa^{-1}, which is in good agreement with experimental results (Bröllos and Schneider 1974).

The adiabatic compressibility, in contrast, has no such singularity and just shows an inflection at T_p, as plotted in figure 8. Since the sharp depression of α_P makes the dilatation term, $TV\alpha_P^2/C_P$, very small just above T_p, the isothermal compressibility decreases rather discontinuously at T_p. The results confirm the data reported previously (Poulis and Massen 1965) and the change in κ_T at the polymerization temperature is definitely negative. The 'negative' $\delta\kappa_T$ at T_p is not reconciled with the general arguments in the preceding section that both δC_P and $\delta\kappa_T$ have to be positive. On the other hand, theoretical calculations predict that an applied pressure stimulates the polymerization process and the polymerization rate with pressure has a very sharp peak at T_p (Eisenberg 1963). This implies that $(\partial C/\partial P)_T$ has a peaked maximum around T_p. As shown from equation (1), therefore, κ_T should have a peak at T_p as well as C_P and α_P. A possible explanation for the inconsistency found for the behaviour of κ_T deduced from the sound velocity may be as follows. According to Klement (1974) the relaxation time for the polymerization could be as long as 300 s at T_p and decreases to 20 s at 200 °C. It is thus impossible for the sound wave $\sim$ 10 MHz to stimulate the pressure-induced polymerization with such a long relaxation time: i.e. $(1/V)(\partial V/\partial C)_{T,P}(\partial C/\partial P)_T$ in equation (1) cannot be probed by ultrasonic measurements and the inflextion in κ_S would reflect a change in κ_S^0 associated with the polymerization. In this respect it would be of great interest to measure static compressibilities for a thorough understanding of the thermodynamics of polymerization in liquid sulphur.

At the very vicinity of the polymerization temperature ($|T - T_p| < 0.1$ K), the temperature dependence of the molar volume has a logarithmic singularity (Patel and Borst
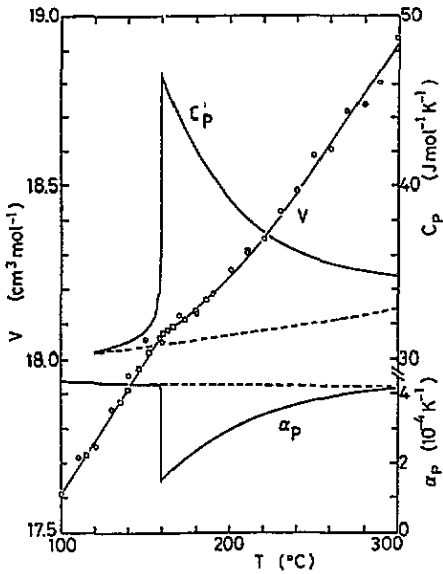
Figure 6. The dependences on temperature of C_P (Braune and Möller 1954), molar volume, V (Kellas 1912, Tsuchiya 1992), and volume expansion coefficient, α_P, calculated from the line through the volume data. The broken lines are smooth interpolations between the data below T_p and above 380 °C, indicating C_P^0 and α_P^0, respectively.
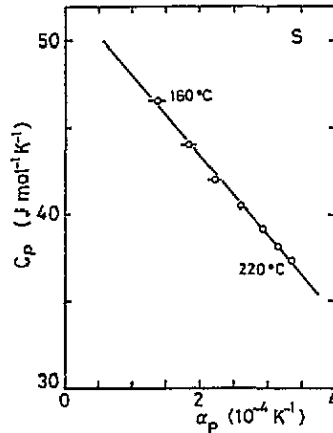
Figure 7. The dependence of C_P on α_P. Data are taken every 10 °C. The prediction of equation (7) is apparently borne out for the polymerization transition in liquid S as well.
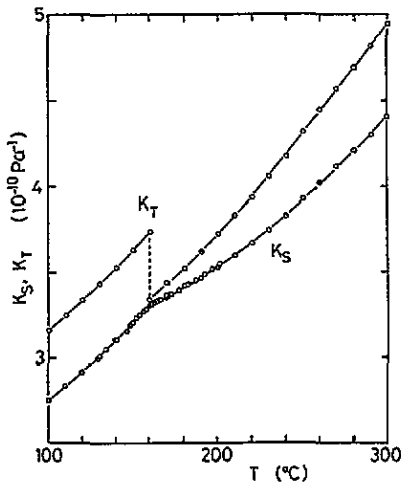

Figure 8. The adiabatic compressibility, κ_S, and isothermal compressibility, κ_T, of liquid S. The latter decreases discontinuously at the polymerization temperature, $T_P = 159$ °C, which is caused by the dilatation term, $TV\alpha_P^2/C_P$.

1971). Since it was not possible to do such detailed experiments on the sound velocity in the corresponding temperature region, it is uncertain whether or not the above arguments may apply to this temperature range.

5. Summary

The sound velocity in liquid S–Te alloys has been measured as a function of temperature. A

clear break in the sound velocity versus temperature curve for 40 at.% S confirm a two-melt phase separation having a looped boundary. The sound velocity has been used to deduce the isothermal compressibility, which has been found to have a peaked maximum where an extremum appears in the volume expansion coefficient and constant-pressure specific heat as a function of temperature. It has been proved that Ehrenfest's relations are obeyed in the structural changes in the liquid S–Te alloys as well as in the Se–Te system. In pure liquid S, the adiabatic compressibility only shows an inflection at the polymerization temperature. The absence of the effects due to the polymerization may be a reflection of the very slow polymerization rate.

Acknowledgment

References

Braune H and Möller O 1954 *Z. Naturf.* **99** 210
Bröllos K and Schneider G M 1974 *Ber. Bunsenges. Phys. Chem.* **78** 296
Davies R O and Jones G O 1953 *Adv. Phys.* **2** 370
Eisenberg A 1963 *J. Chem. Phys.* **39** 1852
Gitis M B and Mikhailov I G 1966 *Sov. Phys.–Acoust.* **12** 14
Greenspan M and Tschiegg C E 1957 *J. Res. N.* **59** 249
Kakinuma F and Ohno 1987 *J. Phys. Soc. Japan* **56** 619
Kakinuma F, Ohno S and Suzuki K 1993 *J. Non-Cryst. Solids* **156–8** 691
Kellas A M 1918 *J. Chem. Soc.* **113** 903
Klement W Jr 1974 *J. Polym. Sci.* **12** 815
Menelle A, Bellissent R and Flank A M 1988 *Europhys. Lett.* **4** 707
—— 1989 *Physica* B **156 & 157** 174
Patel H and Borst L B 1971 *J. Chem. Phys.* **54** 822
Poulis J A and Massen C H 1965 *Elemental Sulphur* ed B Meyer (New York: Interscience) p 109
Thurn H and Ruska J 1976 *J. Non-Cryst. Solids* **22** 331
Tobolsky A V and Eisenberg A 1959 *J. Am. Chem. Soc.* **81** 780
Tsuchiya Y 1988a *J. Phys. C: Solid State Phys.* **21** 5473
—— 1988b *J. Phys. Soc. Japan* **57** 3851
—— 1991a *J. Phys.: Condens. Matter* **3** 3163
—— 1991b *J. Phys. Soc. Japan* **60** 960
—— 1992 *J. Phys.: Condens. Matter* **4** 4335