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Two melts phase separation in the liquid Sb-Sb_2S_3 system: critical sound wave propagation and metal-non-metal transition

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Abstract. The sound velocity and magnetic susceptibility as a function of temperature and composition were measured to investigate critical sound wave propagation and metal-non-metal transition in the liquid Sb-Sb_2S_3 system. The sound velocity in a homogeneous alloy around 60 at.% of Sb decreases very rapidly and the rate of decrease increases as the two melts phase is approached, which is the typical temperature dependence of the sound velocity in a liquid with a miscibility gap. Below the critical point, the sound velocity was measured along the phase boundary. Using those data, the phase boundary was precisely determined. The critical point is located at 901±2 °C and 41.5 ±0.5 at.% S, and the critical exponent of the phase boundary is about 1/3. On the other hand, the magnetic susceptibility as a function of temperature and composition indicates that the electronic state is metallic in liquid Sb and non-metallic in molten Sb_2Se_3, and crossover form the metallic to non-metallic state occurs around the critical composition.

1 Introduction

There reported many binary elemental systems which have miscibility gaps in the liquid state. Most of their phase boundaries are, however, qualitative especially for systems having high critical temperature [1]. The critical indices of the concentration differences between the coexisting two liquids for most of those systems have been undetermined and it is not known whether or not other thermodynamic quantities exhibit critical behavior along the phase boundary as well.

In the previous investigations, we studied, for example, the sound velocity in the Ag-Se system by measuring sound velocity [2]. This system has two immiscible regions between Ag-Ag_2Se and Ag_2Se-Se. For both immiscible regions, the critical sound propagation in alloy close to a critical composition has been observed as the temperature is approached to the two-melt critical point from above. The sound velocity along the phase boundary has not been determined, however, because such measurements are time-consuming and it is not known the characteristics of the sound velocity along the phase boundary so far.

Recently, we have developed a new sound velocity measuring system which enables to determine the sound velocity almost continuously with changing temperature once the initial setup of a specimen has been made [3]. In this paper, we report the results of Sb-Sb_2S_3 system. In addition, very detailed magnetic susceptibility measurements have been made. From the latter we have obtained information on changes in the electronic structure with increasing S.

2 Experimental procedure

The present system for the sound velocity measurements consists of LeCroy LT262 (350MHz) oscilloscope, Panametric 5077 pulsar-receiver, and Okura EC5500 or Yamatake-Honeywell SDC40 digital temperature controller, which are controlled by PC. The program is a home-made program on Visual Basic.

Ultra-sonic transducer was PZT operating at about 9 MHz. A cell was made of fused quartz, of which the thickness of sample reservoir was determined by measuring the sound velocity in distilled water as a function of temperature in the temperature interval from room temperature to 96°C. The sound velocity could be fitted to the reference data [4] within to less than 0.1% over the above mentioned temperature interval by taking the thickness of sample reservoir as a single disposable parameter. In the actual measurements, the thermal expansion of a cell was neglected because it is very small as compared with changes in the sound velocity in a specimen. The time interval that the sound propagates in a sample was measured using the time function of the LeCroy oscilloscope, the resolution of which is approximately 0.32 ns. The sound velocity in a quartz buffer rod has a temperature dependence, however the change does not affect the results because the reflection method was used, in which the time required for the sound pulse to propagate in the rod is automatically cancelled. In the measurements we changed temperature by 1 K step, and checked whether the temperature was equal to the setting temperature or not. The check was made 3 times at every 0.5 min, and then measurements were made after few minutes waiting time

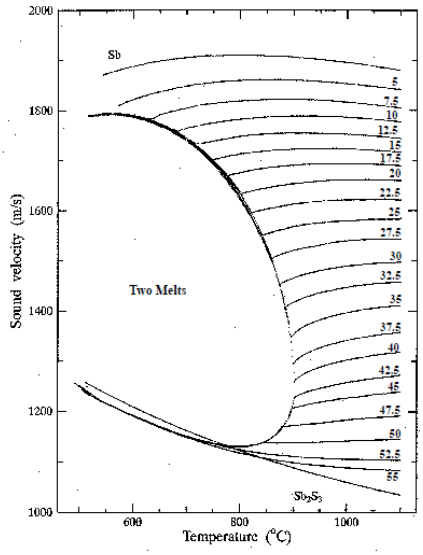

Fig. 1 Sound velocity in the Sb-Sb_2S_3 system. The number on the curve indicates at.% S.

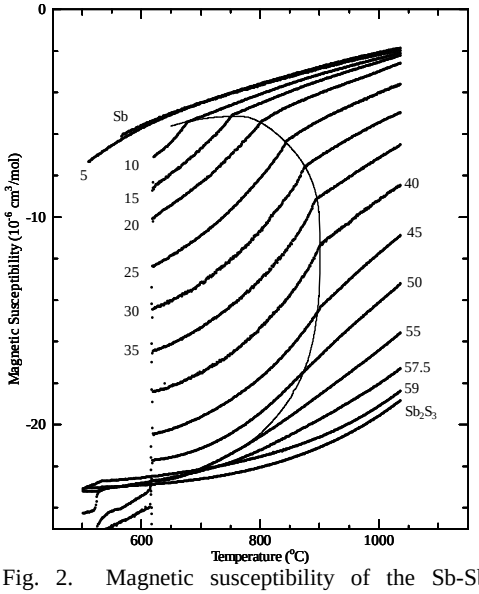

Fig. 2. Magnetic susceptibility of the Sb-Sb_2S_3 system. Smooth curve is the magnetic susceptibility along the phase boundary explained in the text. Numbers indicate at.% S.

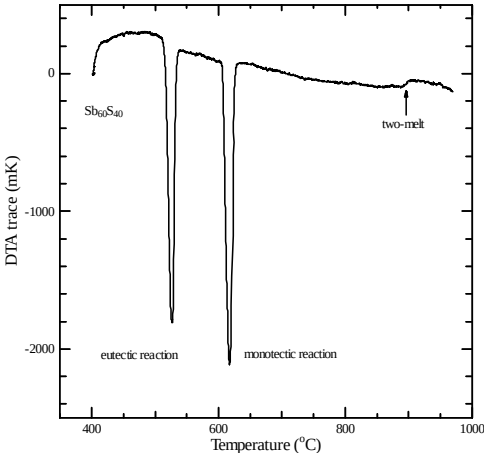

Fig. 3. DTA trace of $Sb_{60}S_{40}$

for thermal equilibrium. The total time required for the measurements of one specimen for 300 K interval, for example, was about 10 hours.

The magnetic susceptibility was measured using a torsion balance with 0.65 T magnetic fields. The 5 nine grades of Ag metal was used as a reference, of which the magnetic susceptibility is 0.175 cm^3/g. The measuring procedure was the same as in the sound velocity measurements. At each step, the magnetic field was changed from zero to 0.65 T. The net output at a temperature was obtained from the outputs for these two field strengths. A sample was sealed in a fused silica glass and its amount was 0.012 mol.

The temperature was detected by a Pt-Pt(13at.%Rh) thermocouple. The difference between the indication of temperature controller and the temperature of a sample was corrected by measuring the magnetic susceptibility of a few elements so as to the change in the magnetic susceptibility upon melting occurs at their compiled melting points.

The magnetic susceptibility measured in this way was in reasonable agreement with those reported previously.

3 Results and discussion

Fig. 1 shows the sound velocity in the S-Sb_2S_3 measured at every 1 K. The numbers in the figure represent the at.%S. The sound velocity in pure Sb increases with increasing temperature, and takes a broad maximum around 800°C and then decreases with temperature as in the case of most simple liquid metals. The decrease in the sound velocity with lowering temperature is called "the softening" in the solid state physics, because the decrease in the sound velocity indicates that the solid actually becomes soft. The softening is unusual even in the liquid and now it is generally accepted that the softening is an indication of crossover transition in the liquid. The case of Sb has been discussed in the reference [5].

The phase boundary in the Sb-rich alloy could be easily detected by observing an inflexion in the sound velocity as a function of temperature. In the two-melt region, the sound velocity changes along either an Sb-rich or S rich boundary. Thus one obtains a unique duplex curve along the phase boundary. In the homogeneous liquid region, the softening develops up to about 40 at.% S.

Fig. 2 shows the magnetic susceptibility as a function of temperature measured at every 1 K. The concentration was

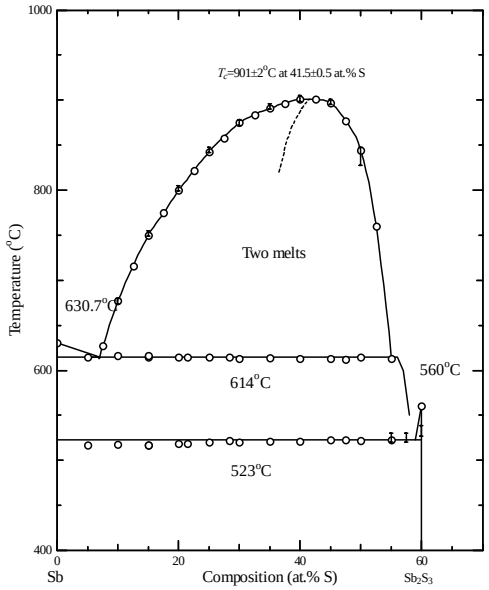

Fig. 4. Phase diagram of Sb-Sb2S3. A small bar is the boundary obtained from the magnetic susceptibility measurements.

changed by 5 at.% of S. At the phase boundary, the magnetic susceptibility shows an inflection. In the two-melt region, the value in the figures is the magnetic susceptibility for a mixture of two melts. The smooth curve connecting inflection points in the Fig. 2 is obtained with a standard curve fitting program and it represents the magnetic susceptibility along the phase boundary.

Fig. 3 represents a TDA trace of $Sb_{60}S0_{40}$, in which two endothermic peaks and a small step around 900°C can be seen. The former two peaks correspond to the eutectic and monotectic reactions in the alloy, respectively. The latter small signal is indicative of the phase separation.

Combining the above mentioned three measurements, we have made the phase diagram of Sb-Sb_2S_3 as shown in Fig. 4. The immiscibility gap opens at about 7 at.% S and extends to about 55 at.% S. The dotted curve in the figure is a locus connecting the centers of diameters of phase boundary. The crossing point between the phase boundary and the locus is the critical point, which is located at 901.5±2 °C and 41.5 ±0.5 at.% S.

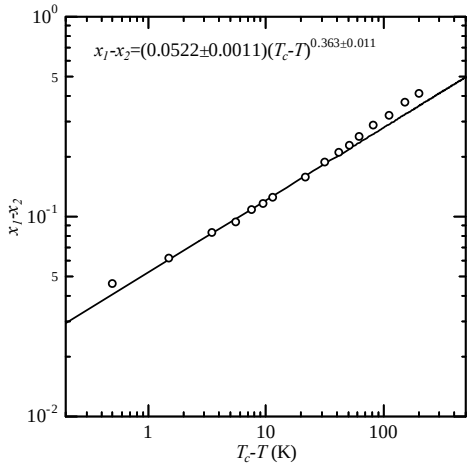

Fig. 5. Log-log plot of the difference x_1-x_2 in the concentration along the phase boundary.

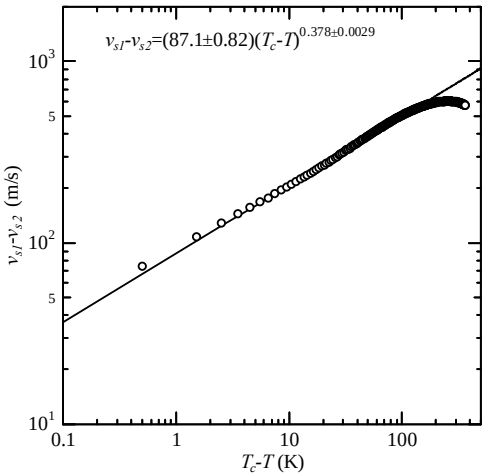

Fig. 6. Log-log plot of the difference v_1-v_2 in the sound velocity along the phase boundary.

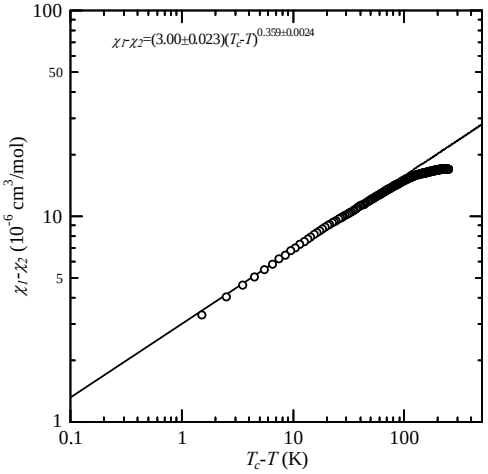

Fig. 7. Log-log plot of the difference v_1-v_2 in the sound velocity along the phase boundary.

Fig. 5 shows a log-log plot of the difference x_1-x_2 in the concentration along the phase boundary as a function of temperature measured from the critical temperature, T_c=901.5°C. The straight in the figure shows a critical behavior,

$$x_1\text{-}x_2=(0.0522\pm0.01)\times(T_c\text{-}T)^{0.363\pm0.011},$$

where fitting was made for T_c-T<40K. A critical index is close to the value of a modern theory, 1/3 [6].

Similar critical behavior in the sound velocity and the magnetic susceptibility has been observed as shown in Figs 6 and 7, respectively. The critical index is 0.378±0.0029

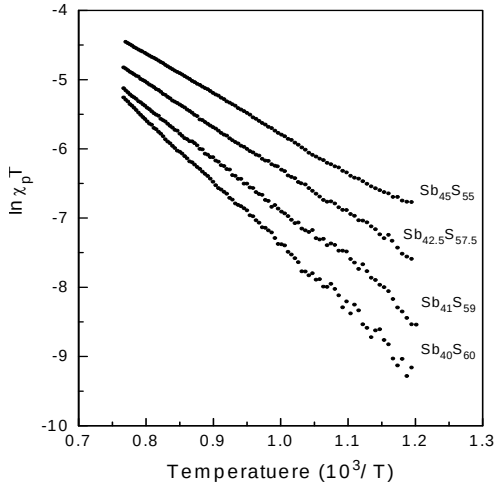

Fig. 8. Linear relation in $\ln\chi_p T$-T^{-1} plot suggests a Curie type temperature dependence of the magnetic susceptibility.

and 0.359±0.0024, respectively for the difference v_1-v_2 in the sound velocity and the difference χ_1-χ_2 in the magnetic susceptibility along the phase boundary. They are both very close to the critical index of the concentration difference.

It is not easy to clarify the origin of the phase separation in this system. On one hand, there exists systematic trend for two-melt phase separation in the Sb-Sb_2S_3, Sb-Sb_2Se_3 and Sb-Sb_2Te_3 systems. The phase separation tendency decreases in this order: an immiscible region in the Sb-Sb_2Se_3 system is very small and localizes very close to Sb_2Se_3 [7] and the Sb-Sb_2Te_3 is fully miscible [1]. On the other hand, liquid Sb_2Te_3 is metallic, liquid Sb_2Se_3 is semiconductor and Sb_2S_3 is of a molecular type as suggested by the present magnetic susceptibility measurements. Fig. 8 shows $\ln\chi_p T - T^{-1}$ plot, which obeys to a linear relation or a Curie type temperature dependence. The results suggest the electron state changes from extended to localized state in this concentration range. The much weaker temperature dependence of χ in more S rich liquids in Fig. 2 may be a reflection of molecular nature of Sb_2S_3. The rapid changes in the electronic structure or metal-non-metal transition together with formation of stable molecular Sb_2S_3 association in the melt could be its origin in the large immiscibility gap in this system.

4 Summary

By qausi-continuous measurements of sound velocity and magnetic susceptibility as a function of temperature, we have determined the two-melt phase boundary in the Sb-Sb_2S_3 system, the sound velocity and the magnetic susceptibility along the phase boundary. The critical point is located at 901 ± 2 °C and 41.5 ± 0.5 at.% S. The differences in the concentrations, sound velocities and magnetic susceptibilities along the two branches of the boundary show critical behavior as the critical temperature is approached. Their critical indices are close to 1/3.

References

1. T. B. Massalski (ed.), *Binary Alloy Phase Diagrams* (AMS, Metals Park OH, 2nd edn 1990)
2. Y. Tsuchiya, J. Phys.: Condens. Matter **8**, 1897 (1996)
3. Y. Tsuchiya and M. Hisakabe, J. Non-Cryst. Solids **353**, 3000 (2007)
4. M. Greenspan and C. E. Tsciegge, J. Res. NBS **59**, 249 (1957)
5. Y. Tsuchiya, Int. Mat. Res. (formerly Z. Metallkd.) **97**, 4 (2006)
6. M. E. Fisher, Rep. Prog. Phys. **30**, 615 (1967)
7. F. Kakinuma, Y. Tsuchiya and K. Suzuki, J. Non-Cryst. Solids **160**, 228 (1993)