ELECTRONIC PROPERTIES OF LIQUID Tl-Se MIXTURES
M. Misonou, T. Goto, H. Endo, H. Hoshino

To cite this version:

HAL Id: jpa-00220234
https://hal.archives-ouvertes.fr/jpa-00220234
Submitted on 1 Jan 1980

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
ELECTRONIC PROPERTIES OF LIQUID TI-Se MIXTURES

M. Misonou, T. Goto*, H. Endo and H. Hoshino**

Department of Physics, Faculty of Science, Kyoto University, Kyoto 606, Japan.
*Physics Laboratory, College of General Education, Kyoto University, Kyoto 606, Japan.
**Faculty of Education, Hirosaki University, Hirosaki 036, Japan.

Abstract.—The measurements of magnetic susceptibility \( \chi \) and NMR were carried out for liquid TI-Se mixtures in Se-rich side. The paramagnetic susceptibility increases with temperature and TI concentration, which is attributed to the increase of paramagnetic centers at dangling bonds. Knight shift at 500°C is not detectable up to 6 at.% TI and increases considerably with further addition of TI.

Introduction.—From the measurements of various properties[1], liquid Se is known to be a typical liquid semiconductor in which the chemical bonding is purely covalent. When TI atoms are added to liquid Se, the Se-Se covalent bond is broken and as the result, a transition from semiconductor to metal is expected to occur. In the TI-Se mixtures the liquid-liquid two-phase region exists in the TI-rich and Se-rich sides[2]. The existence of the two-phase region may be associated with the difference in the atomic configuration and the bonding nature at each sides across the two-phase region.

It is interesting to investigate the aspects and mechanism of the semiconductor to metal transition in liquid Se-rich TI-Se mixtures from the microscopic point of view. In this paper, we report the results of magnetic susceptibility \( \chi \) and NMR measurements for liquid TI-Se mixtures in the Se-rich side.

Experimental Procedure.—The magnetic susceptibility was measured by a standard Faraday method. Sample was sealed in thin quartz capsules (i.d. 3mm, length 20mm). Sample was heated up to 700°C for 5 hours for the mixture to become homogeneous. The error of \( \chi \) was within \( \pm 0.5 \times 10^{-6} \) emu/mole. For NMR measurements sample was sealed in quartz capsule (i.d. 8mm, length 35mm). Sample was shaken by hands to improve homogeneity. Measurements were performed using pulsed NMR technique at a frequency of 7.4 MHz. The resonance shift of \( ^{77}\text{Se} \) was defined to be zero for the liquid Se at the melting point and the shifts were measured relative to this value. The spin-lattice relaxation time \( T_1 \) was measured with a standard \( \pi - \pi/2 \) sequence and the spin-spin relaxation time \( T_2 \) was determined from analysis of the free induction decay following a single \( \pi/2 \) pulse.

Results and Discussion.—Figure 1 shows the temperature variation of molar susceptibility \( \chi_{\text{tot}} \) for liquid TI-Se mixtures in the Se-rich side. The susceptibility becomes nearly temperature-independent at lower temperature. The value of \( \chi_{\text{tot}} \) are negative and increase considerably with temperature at higher temperature.
The ion core contribution $\chi_i$ is deduced by free-hand extrapolation to low temperature limit. At higher temperatures the differential susceptibility $\chi_p$, which is given by $\chi_{\text{tot}} = \chi_i$, must be due to paramagnetic defects for Se-rich mixtures ($\geq 12$ at.% Tl). We expect

$$\chi_p = N\mu^2/k_BT,$$

where $\mu = g\mu_B[J(J+1)]^{1/2}$ is the magnetic moment of the defect and $N$ is the number of defects per mole. Figure 2 shows the logarithmic plots of $N$ deduced from the equation (1) as a function of reciprocal temperature for liquid Tl-Se mixtures. Such plots show good linearity in all these mixtures. One sees that $N$ increases with addition of Tl to liquid Se. Assuming random bonding of Tl and Se atoms, the number of defects per mole $N$ can be given by

$$N = N_A \exp \left(\frac{S_X}{k_BT} - \frac{E_X}{k_BT}\right),$$

where $N_A$ is the Avogadro's number and $S_X$ and $E_X$ represent the activation entropy and energy of formation of a dangling bond atom from a two-fold bonded atom, respectively. In Fig. 3, the concentration variations of $S_X$ and $E_X$ are shown. The values of $E_X$ decrease remarkably by addition of small amount of Tl to liquid Se and by further addition of Tl the rate $c$ concentration variation of $E_X$ becomes small (see Table I). The values of $S_X$ drop by addition of small amount of Tl to liquid Se. The substantial decrease of $S_X$ by addition of small amount of Tl is attributed to the breaking up of liquid Se polymeric complexes by Tl chain stoppers.
The decrease of \( E_X \) probably reflects a homogeneous weakening of Se-Se bond strength by addition of small amount of Tl.

Figure 4 shows the temperature variation of \( T_1 \) and \( T_2 \) of \( ^{77}\text{Se} \) for liquid Se and 12 at.% Tl mixture. At higher temperatures their temperature variations become small and the difference between \( T_1 \) and \( T_2 \) decreases by addition of Tl to liquid Se. Since the natural abundance of \( ^{77}\text{Se} \) nucleus is extremely small (7.5%), the nuclear dipole-dipole coupling is negligible\[^3\]. Therefore, the relaxation process is mainly considered to be a contact interaction with unpaired electron at Se chain ends. The concentration of unpaired electron \( p \) in Se-rich mixtures can be deduced from the data of \( T_1 \) and \( T_2 \) using the formulae developed by Bloembergen\[^4\]. If the temperature dependence of \( p \) is described by the activation process, we obtain the activation energy \( E_p \) for respective Tl concentration as indicated in Table I. As seen in Table I, the values of \( E_p \) are reasonably close to those of \( E_X \) deduced from the magnetic susceptibility data.

Figure 5 shows the temperature variations of \( ^{77}\text{Se} \) Knight shift \( \Delta K \) for Tl-Se mixtures. The values of \( \Delta K \) increase with temperature. It is a reasonable assumption that the resonance shift due to paramagnetic dangling bonds\[^5\] becomes small with Tl content. Figure 6 shows the concentration variation of \( ^{77}\text{Se} \) \( \Delta K \) at 500°C. The Knight shift is not detectable up to 6 at.% Tl and it increases considerably with further addition of Tl. This evidence indicates that the transition from semiconductor to metal onsets around 10 at.% Tl, which is reflected on the con-
Fig. 6. Concentration variation of $^{77}$Se Knight shift at 500°C for liquid Tl-Se mixtures.

Concentration variation of the conductivity [6]. In Fig. 7, we plot the locus at which the transition from semiconductor to metal onsets on the concentration-temperature plane. This locus is determined from the results of the temperature variation of $\Delta K$. The transition from semiconductor to metal may be related to the structural change. The measurements of X-ray diffraction and Raman spectra are helpful to understanding these phenomena.

Acknowledgements. — The authors are grateful to Professor K. Hayashi and Mr. K. Matsumoto for technical assistance. They are grateful to Professor T. Kawai for his continuous encouragement.

References.

Fig. 7. Locus at which the transition from semiconductor to metal onsets is plotted on the concentration-Temperature plane, including the liquid-liquid two-phase region for liquid Tl-Se mixture in the Se-rich side. Hatched part represents the region where $\Delta K=0$. 