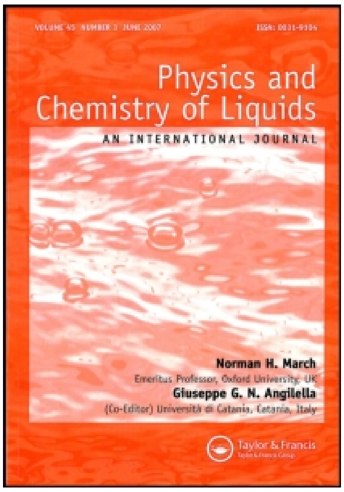

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Osamu Uemura[a]; Tsuneo Satow[a]; Tetsuo Yagihashi[a]
[a] Department of Chemistry, Faculty of Science, Yamagata University, Yamagata, Japan

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The Magnetic Susceptibilities of Liquid Na-Tl, Na-Cd, Cu-Ga and Cu-Ge Systems

OSAMU UEMURA, TSUNEO SATOW, and TETSUO YAGIHASHI
Department of Chemistry, Faculty of Science, Yamagata University, Yamagata, Japan

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The magnetic susceptibilities of liquid Na-Tl, Na-Cd, Cu-Ga and Cu-Ge systems were measured by the Faraday method over the whole range of composition. In the Na-Tl alloys, a pronounced maximum of diamagnetism around the concentration of the NaTl phase (50 at% Tl) found in the solid state almost disappeared on melting. These liquid alloys, however, showed a slight diamagnetic deviation from values interpolated using those of constituent elements. The magnetic susceptibilities of liquid Na-Cd alloys changed linearly with composition. In the liquid Cu-Ga and Cu-Ge alloys the diamagnetic peak was observed in the Cu rich region in the composition dependence of magnetic susceptibilities. It is considered that such a diamagnetic anomaly in liquid Cu alloys is caused by the formation of clusters with some ionic character.

1 INTRODUCTION

As is well known, noble metals form various Hume–Rothery type electron compounds on alloying with polyvalent metals. In the liquid state, the magnetic susceptibilities of these alloy systems indicate a large diamagnetic deviation from linearly interpolated values between the constituent atoms.[1] This suggests that liquid noble metal systems tend to have a short range order, although the electronic transport properties of these systems can often be explained by a nearly free electron model appropriate to a random mixture.[2] Thermodynamic data have supported the formation of some clusters. For example, these liquid systems show a negative heat of mixing[3–5] and a rapid increase of density[6] in the composition where electron compounds are found in the solid state. Recently, Steinleitner and Freyland[7] have found similar and more drastic anomalies in the magnetic and electronic properties of liquid Au-Cs alloys near the equi-atomic composition AuCs.

The alkali metals which have the same valence as noble metals also form various intermetallic compounds by alloying with other metals.

The liquid Na-Tl, Na-Cd, Cu-Ga and Cu-Ge alloys have been reported to have a considerable exothermic heat of mixing around the concentration of intermetallic compounds.[3,4] In this paper, we will measure magnetic susceptibilities of these systems in order to investigate whether the clustering occurs or not in the liquid state.

2 EXPERIMENTAL DETAILS

The purity of metals used was 99.999% for Cu, Ga, Ge, Tl and Cd, and 99.9% for Na, respectively. Appropriate amounts of the components were melted together in a fused quartz (for Cu alloys) or a pyrex glass (for Na alloys) ampoule which was evacuated up to 10^{-4} Torr. The molten alloy was water-quenched and then annealed sufficiently at higher temperatures under a vacuum of 10^{-4} Torr.

The Faraday method was chosen for the measurement of magnetic susceptibility. The feedback current required to cancel out the horizontal force acting on a sample in a magnetic field was recorded using a Curie–Chenevean type torsion balance. The sample was enclosed in an evacuated fused quartz or pyrex cell. Magnetic fields up to 12 kOe with a pole gap of 6 cm were applied. The sample was heated by a PID–SCR controlled silicon carbide furnace. Purified Ti metal was used as a standard sample. The temperature of the sample was measured using a PR thermocouple located near the sample.

3 EXPERIMENTAL RESULTS

In the Na-Tl system the existence of four intermetallic compounds has been confirmed, that is, Na_6Tl, Na_2Tl, NaTl and $NaTl_2$.[8] Among these phases the NaTl phase has a very high melting point and a large diamagnetic susceptibility, -55.5×10^{-6} emu/g-atom at room temperature because of a strong ionic bonding between unlike atoms. An obvious diamagnetic peak is seen at 50 at%Tl in the plots of magnetic susceptibility versus composition at room temperature as shown in Figure 1. The temperature dependence of magnetic susceptibility of the $Na_{0.505}\,Tl_{0.495}$ is described in Figure 2. The diamagnetic susceptibility of this alloy decreases rapidly when melting. This indicates that strong ionic bondings remarkably weaken and valence electrons bound around each ion become delocalized. Figure 3 shows the temperature dependences of magnetic susceptibility of the Na-Tl systems in the liquid state. The magnetic susceptibility changes little with temperature,

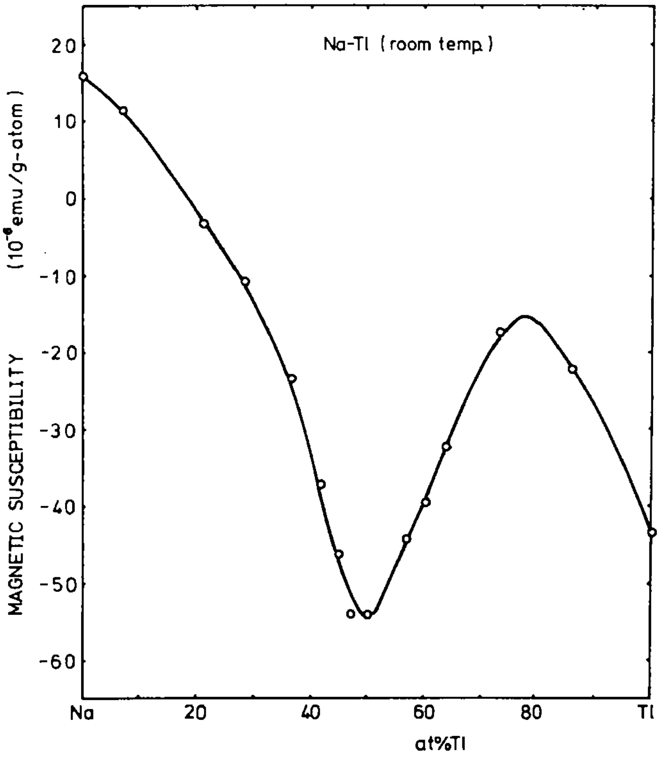

FIGURE 1 The magnetic susceptibilities of the Na-Tl system at room temperature for various compositions.

that is, liquid Na-Tl alloys take the Pauli paramagnetic behaviour over the whole range of composition.

Figure 4 shows the magnetic susceptibilities of liquid Na-Tl system just above the melting point for various compositions. An apparent peak of diamagnetism observed in the solid phase is no longer detectable in the liquid alloys. The susceptibilities, however, show a little diamagnetic deviation from linearly interpolated values represented by the broken line.

Figure 5 shows the composition dependence of magnetic susceptibility in the liquid Na-Cd alloys. When adding Cd to liquid Na the diamagnetic susceptibility gradually increases owing to the diamagnetic contribution of Cd ion cores. No anomaly can be seen in the liquid alloys in the relation between susceptibility and composition within experimental errors, although two intermediate phases, $NaCd_6$ and $NaCd_2$, exist in the solid state.[8] The magnetic susceptibilities of these liquid alloys are almost independent of temperature over the temperature range covered in this study (100–450°C).

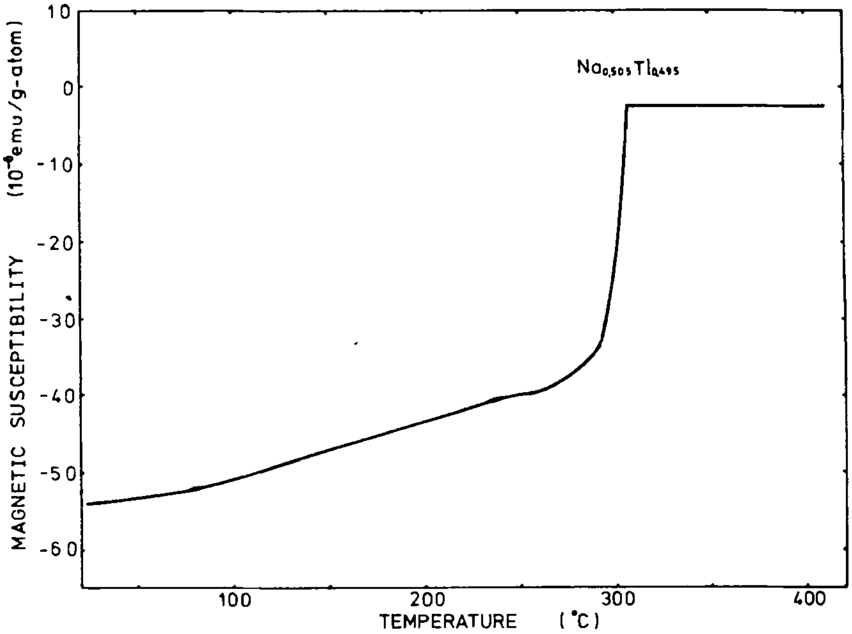

FIGURE 2 The temperature dependence of the susceptibilities of the NaTl phase in the solid and liquid states.

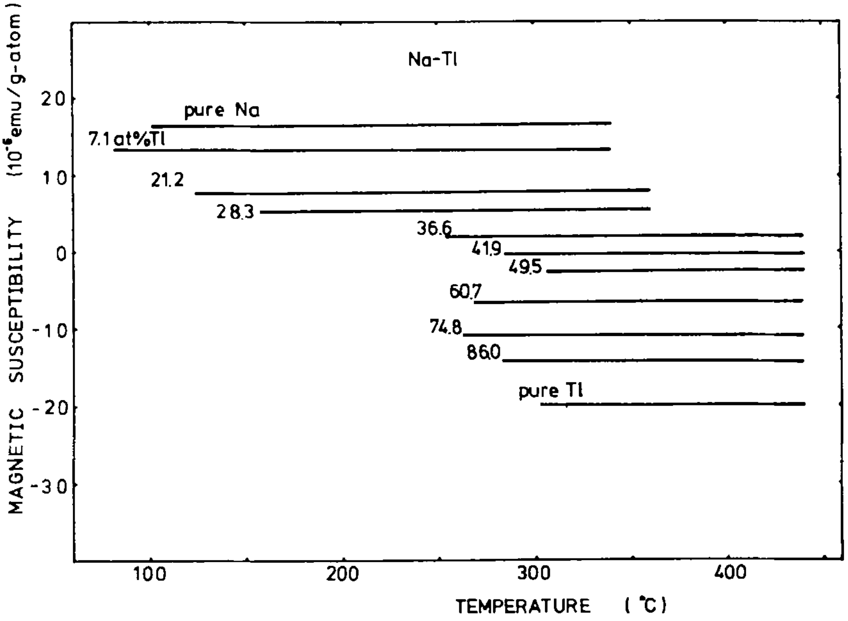

FIGURE 3 The temperature dependences of the susceptibilities in the liquid Na-Tl system.

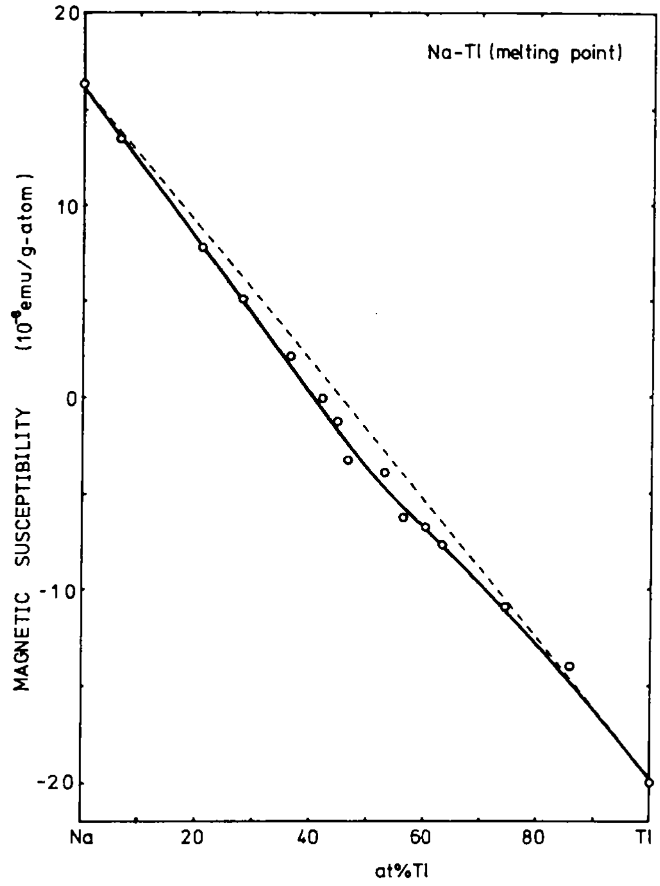

FIGURE 4 The magnetic susceptibilities of the Na-Tl system just above the liquidus temperature for various compositions.

It can be assumed therefore that constituting atoms in the Na-Cd alloys mix at random in the liquid state.

Figure 6 shows the temperature dependence of magnetic susceptibility in the liquid Cu-Ga system except for the Cu rich region. The diamagnetic susceptibility decreases slightly with increasing temperature. The degree of its temperature change becomes rather large as increasing Cu concentration. Figure 7 illustrates the composition dependence of magnetic susceptibility in the liquid state, which has a diamagnetic maximum around 27 at %Ga. This result suggests that in the liquid Cu-Ga alloys the formation of some clusters is involved around the concentration of $GaCu_3$.

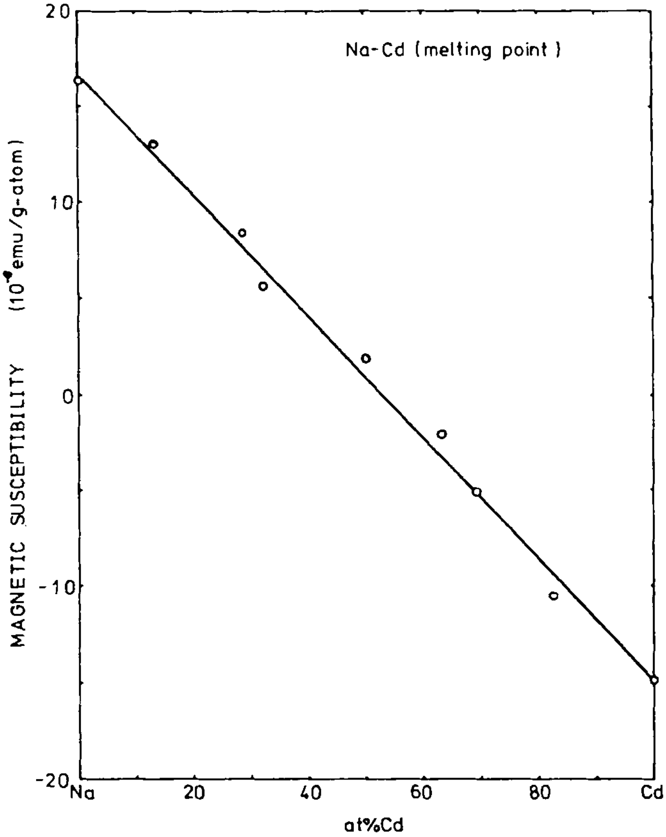

FIGURE 5 The magnetic susceptibilities of the Na-Cd system just above the liquidus temperature for various compositions.

The magnetic susceptibilities of the liquid Cu-Ge system are plotted against temperature and composition in Figures 8 and 9, respectively. These alloys show the temperature and the composition dependences of susceptibility similar to the liquid Cu-Ga system. The diamagnetic susceptibility has a maximum around 20 at %Ge.

4 DISCUSSION

The total magnetic susceptibility χ_{total} of simple metals is written as follows;

$$\chi_{\text{total}} = \chi_i + \chi_e \qquad (1)$$

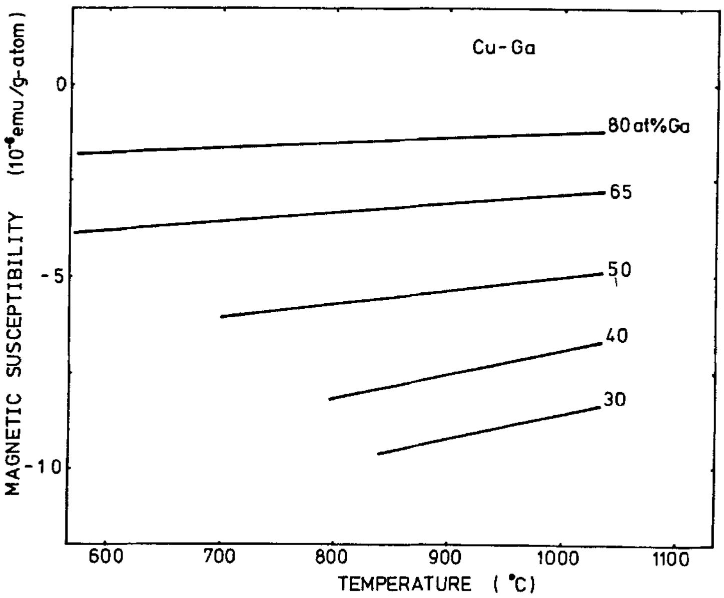

FIGURE 6 The temperature dependences of the susceptibilities in the liquid Cu-Ga system.

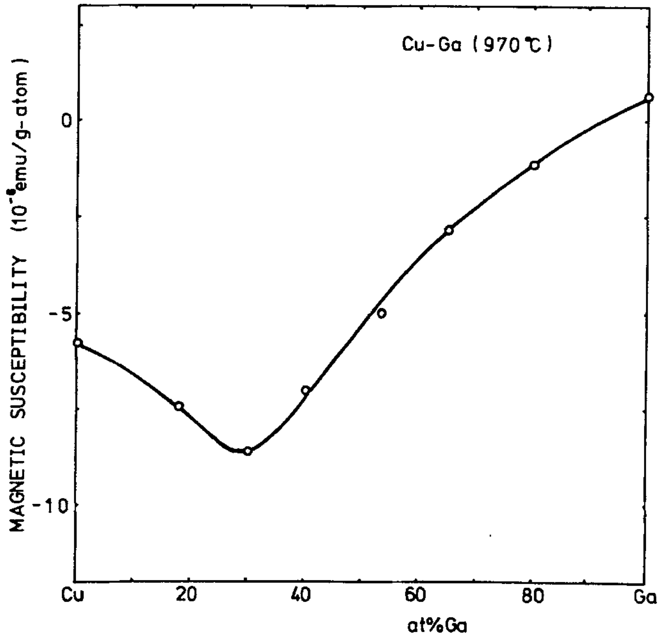

FIGURE 7 The composition dependence of the susceptibilities in the liquid Cu-Ga system at 970°C. The value of pure copper is cited from Gardner and Flynn (1100°C).[9]

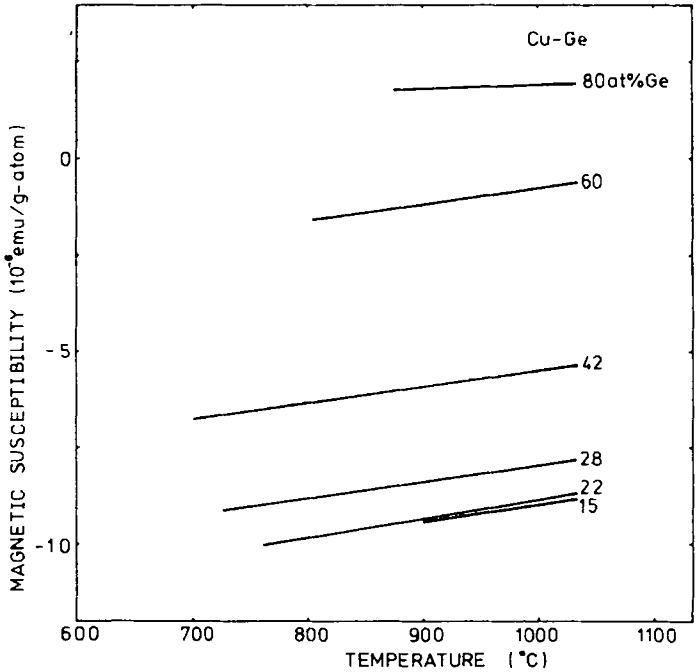

FIGURE 8 The temperature dependences of the susceptibilities in the liquid Cu-Ge system.

where, χ_i is the diamagnetic susceptibility of ion cores and χ_e the contribution from conduction electrons. Silverstein[10] has expressed the electron spin paramagnetism χ_s by the following equation;

$$\chi_s = \chi_p \times [1 - (1 - \alpha)\chi_p/\chi_{p_0}]^{-1}, \tag{2}$$

where α is the effective mass ratio m/m*, χ_{p_0} the electron spin paramagnetic susceptibility of free non-interacting electrons and χ_p is that of free interacting electrons with $\alpha = 1$. Hence, the complete conduction electron susceptibility χ_e, including diamagnetism, is represented as[11]

$$\chi_e = \chi_p \times \left[\frac{1 - \alpha^2/3}{1 - (1 - \alpha)\chi_p/\chi_{p_0}}\right]. \tag{3}$$

χ_{p_0} and χ_p were given graphically by Silverstein[10] as functions of the radius of electronic sphere $r_s = 1.388(A/Z\rho)^{1/3}$ Bohr units, where A, Z and ρ are atomic weight, valence and density, respectively. χ_i for pure metals can be estimated by subtracting χ_e calculated with $\alpha = 1$ from the experimental values χ_{exp}. If χ_i for constituent atoms keeps unchanged on alloying, we can determine the composition dependence of α using χ_{exp} for various compo-

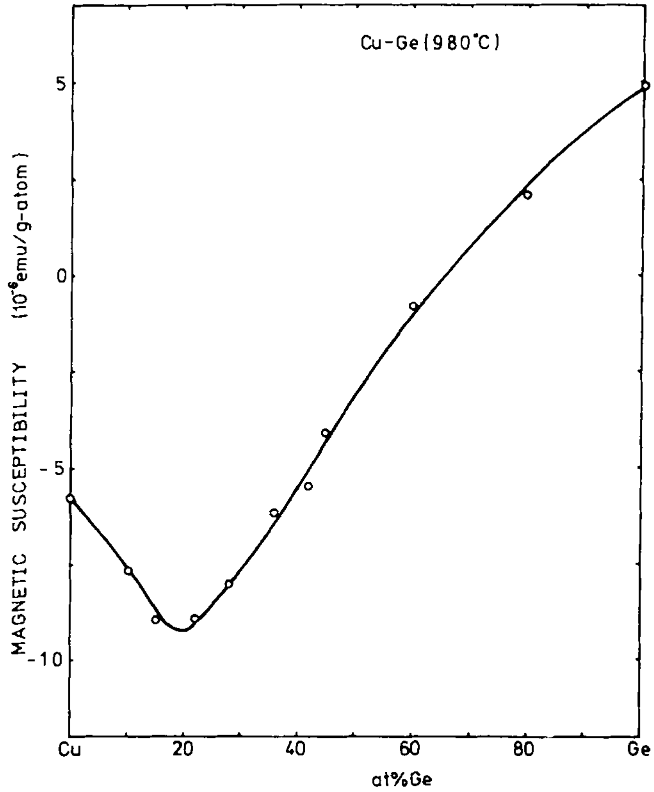

FIGURE 9 The composition dependence of the susceptibilities in the liquid Cu-Ge system at 980°C. The value of pure copper is cited from Gardner and Flynn (1100°C).[9]

sitions. The result of the liquid Na-Tl system is shown in Figure 10. A considerable deviation from free electron values is found around 50 at % Tl in the relation between α and composition.

By the free electron model, α relates to the ratio of free and real electron densities of states, $N(E_{F_0})/N(E_F)$. Therefore, the increase in α near 50 at % Tl can be attributed to decrease in the electron density of states at the Fermi level.

Timbie and White[12] have calculated electron susceptibilities of liquid metals on a basis of nearly free electron approximation. They have shown that α in Eq. (3) corresponds to the term arising from the electron-ion interaction in the pseudo-potential formalism. This term depends largely on the structure factor $S(q)$ in q-space. Therefore, a deviation of α from free electron values is considered to indicate that in the liquid Na-Tl system atoms do not distribute randomly near the equiatomic composition.

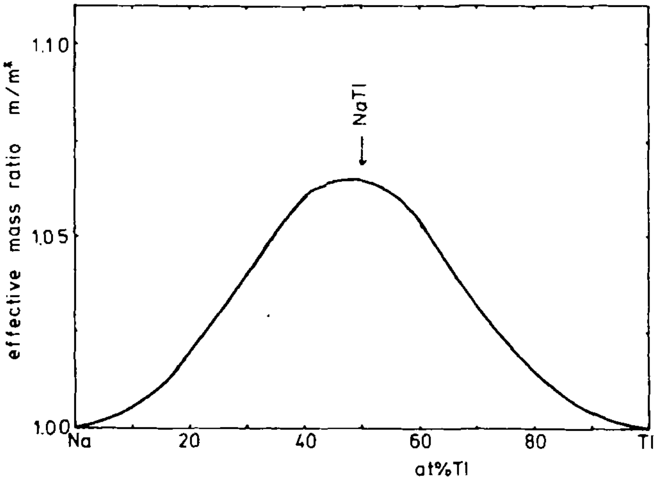

FIGURE 10 The effective mass ratios in the liquid Na-Tl system.

Solid Na-Tl and Na-Cd alloys form some intermetallic compounds with rather stronger ionic characters such as NaTl. Nevertheless, these alloys do not show a pronounced maximum of the diamagnetism in the liquid state. On the other hand, such a maximum can be observed in the liquid Cu-Ga and Cu-Ge alloys as shown in Figures 7 and 9. It may be understood that the diamagnetic maximum in the susceptibility versus composition curves is caused by forming some clusters in the liquid noble metal systems. This maximum appears near the concentration where Hume-Rothery type electron compounds exist in the solid phase. However, it is not clear whether bondings of such clusters are related to those of solid electron compounds. For example, the liquid Ag-Ge system shows similar anomalies in the composition dependence of both electronic and thermodynamic properties[13] in spite of the fact that no intermetallic compounds exist in the solid phase. In the case of liquid Se which has chain and ring structures similar to the solid state, the structural properties (e.g. coordination number and interatomic distance)[14] and the electronic properties (e.g. magnetic susceptibility)[15] change little on melting. In the noble metal alloys, however, a difference in the above quantities is found between solid and liquid phases.

In liquid substances the influence of the size factor on compound formation weakens, while the electronegativity and the valence factors become more important. Generally the electronegativity x of elements is quite well expressed by Gordy's relation,[16]

$$x = 0.31 \times \left(\frac{n+1}{r}\right) + 0.50,$$

where *n* and *r* denote the number of valence electrons and the single-bond covalent radius, respectively. However, noble metal group does not obey the above equation because of their large electronegativity. This suggests that liquid noble metal alloys have a tendency to form clusters in which outer-shell electrons are localized around electronegative noble metal ions. In fact the liquid Au-Cs system is known as a typical ionic semiconductor.[17,18] Therefore, the diamagnetic anomalies seen in Figures 7 and 9 are considered to indicate that clusters with ionic bondings of unlike atoms are present in liquid Cu-Ga and Cu-Ge systems, and the electron paramagnetic susceptibility decreases due to the formation of such bonding.

It has often been found that the electron susceptibility in liquid semiconductors has a negative value[19] since the number of localized electrons is very large and the orbital susceptibility of valence electrons dominates the spin paramagnetism of conduction electrons at the Fermi level. Using susceptibilities of Cu^{1+}, Ga^{3+} and Ge^{4+} ion cores calculated by Hurd and Coodin,[20] the electron susceptibilities of liquid $Cu_{0.70}Ga_{0.30}$ and $Cu_{0.78}Ge_{0.22}$ are estimated as $+4.3 \times 10^{-6}$ emu/g-atom and $+4.1 \times 10^{-6}$ emu/g-atom, respectively. This result demonstrates that both liquid Cu alloys remain good electronic conductors and the degree of the electron localization is considerably less than for the case of liquid semiconductors.

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