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On the Anomalous Physical Properties of Liquid Copper Alloys*

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Synopsis

Magnetic susceptibilities and electrical resistivities of the liquid copper alloys, Cu-Bi, Cu-Sn and Cu-In have been measured as functions of chemical compositions at temperatures in the neighbourhood of 1000°C.

In the liquid Cu-Bi alloy, observed magnetic susceptibility and electrical resistivity are well explained in terms of a model which assumes random distribution of Cu and Bi ions in a free electron gas atmosphere.

In the liquid Cu-Sn and Cu-In alloys, anomalous behaviours are observed in their magnetic susceptibility and electrical resistivity. It is shown that the observed deep valleys of diamagnetism in the magnetic susceptibility curves of both liquid alloys correspond to the peaks in the curves of the heat of mixing for the respective alloys observed in our previous report. The observed values of magnetic susceptibility are compared with theoretical curves calculated by taking account of a contribution from n_R pseudo-molecules which are formed by association of Cu ions with Sn or In ion. It is found that about two electrons are localized in a pseudo-molecule for both liquid alloys near 1100°C and that the observed deep diamagnetism originates from the existence of pseudo-molecules.

Electrical resistivities for both kinds of liquid alloys are given as the sum of contributions from scattering of conduction electrons by randomly distributed free ions and by pseudo-molecules. The contribution ρ_1 caused by the former mechanism can be estimated in terms of a hard sphere model for the Ashcroft potential, and the latter contribution ρ_2 can be assumed to be in proportion with the distribution function n_R of the pseudo-molecule in the liquid alloy on the bases of its flexible structure.

For both kinds of alloys such a proportional relationship is regarded as a reasonable assumption because the n_R curve behaves similarly to that of $\rho_2 = \rho - \rho_1$ versus alloying compositions, where ρ is the observed total resistivity.

I. Introduction

The heat of mixing of liquid copper alloys Cu-Sb, Cu-Ge, Cu-Bi, Cu-Sn and Cu-In has been measured in the previous reports.⁽¹⁾ In the liquid Cu-Bi alloy heat absorption has been observed on mixing and the amount of heat absorbed varies parabolically with alloying compositions. The curve of the heat of mixing calculated under the assumption of random mixing of Cu and Bi atoms agrees with the

* The 1611th report of the Research Institute for Iron, Steel and Other Metals.

(1) S. Takeuchi, O. Uemura and S. Ikeda, Proceedings of 2nd International Conference on the Properties of Liquid Metals, (1973), p. 489; J. Japan Inst. Metals, **37** (1973), 834; Sci. Rep. RITU, **A 25** (1974), 41.

experimental values. On the other hand in the case of the other copper alloys a peak of heat evolution has been observed in the composition range of 75 to 80% Cu.

In these liquid alloys, some atoms are distributed randomly and the others associate into clusters like molecules of a type A_mB , which are in thermal equilibrium with dissociated free atoms in random distribution. These molecules are considered to have a flexible structure which is so different from a real molecule of a rigid structure that the distance between dissimilar atoms is nearly fixed but the bond angles are variable to some extent. Thus, they are referred to as pseudo-molecules.

The distribution function n_R for these pseudo-molecules in the case of liquid Cu-Sn and Cu-In alloys has been estimated⁽¹⁾ under the above assumption. The curve of the heat of mixing for such liquid alloys calculated with this estimation of n_R are in good agreement with observed results as shown in the previous reports.⁽¹⁾

In this paper the above mentioned model for the pseudo-molecule will be applied to the explanation of magnetic susceptibility and electrical resistivity of the liquid Cu-Sn and Cu-In alloys. The detailed structure⁽²⁾ of this pseudo-molecule is discussed in addition to the previous analysis.

II. Magnetic susceptibilities of liquid copper alloys Cu-Bi, Cu-Sn and Cu-In

Mass magnetic susceptibilities for these liquid alloys are measured by the torsion balance method.⁽²⁾

The magnetic susceptibility χ^g per unit mass versus the alloying composition of the liquid Cu-Bi alloy at 1100°C is shown in the curve of Fig. 1, where the observed values are noted by open circles and the full line shows a theoretical susceptibility calculated under the assumption of random mixing of ions Cu^{+1} and Bi^{+5} . The influence by temperature variation is found to be negligible. Figures 2 and 3 show the observed magnetic susceptibilities at 1100°C and 900°C for the liquid Cu-Sn and Cu-In alloys, respectively. A deep valley of diamagnetism is found near 20% Sn in the case of the Cu-Sn alloy and near 25% In in the Cu-In alloy. These peaks of diamagnetism correspond to those of heat evolution in the curves of the heat of mixing⁽¹⁾ observed in the same alloys. Temperature variations, however, of the magnetic susceptibility for these alloys exhibit the behavior contrary to the case of the Cu-Bi alloy. If n_R and n_B are the respective numbers of A and B atoms distributed randomly, and n_R the number of pseudo-molecules A_mB composed of one B atom and m A atoms in a liquid alloy consisting of N_A atoms of A and N_B atoms of B in its volume V° , the following relations are obtained,

(2) S. Takeuchi, K. Suzuki, M. Misawa, F. Ito and K. Murakami, J. Japan Inst. Metals, **37** (1973), 1011; Proceedings of 2nd International Conference on the Properties of Liquid Metals, (1973), p. 68.

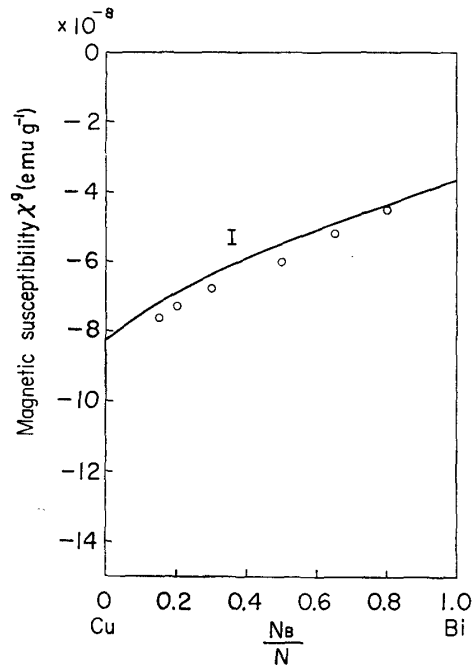


Fig. 1. Observed magnetic susceptibility for liquid Cu-Bi alloy at 1100°C.

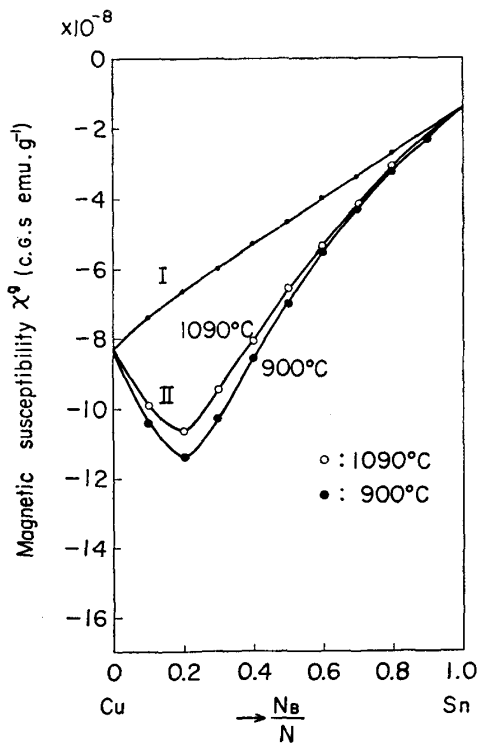


Fig. 2. Observed magnetic susceptibility for liquid Cu-Sn alloy at 900°C and 1100°C given by curves II and random mixing approximation in the curve I.

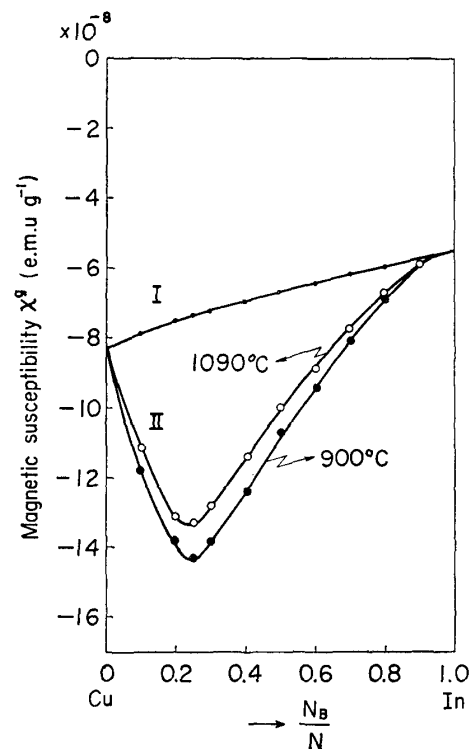


Fig. 3. Observed magnetic susceptibility curves II at 900°C and 1100°C and curve I by random mixing approximation for liquid Cu-In alloy.

$$\begin{aligned}
 mn_R + n_A &= N_A \\
 n_R + n_B &= N_B \\
 N_A + N_B &= N.
 \end{aligned}
 \tag{1}$$

Some valence electrons of these N atoms are localized in the pseudo-molecules and contribute to their bondings, and others form a dense electron gas through which n_A of ion A, n_B of ion B and n_R of pseudo-molecules are randomly distributed. Hence, the total magnetic susceptibility per the volume V° is given by

$$\chi = \chi_e + n_A \chi_i^A + n_B \chi_i^B + n_R \chi_R,
 \tag{2}$$

where χ_e denotes the paramagnetic susceptibility of the electron gas, χ_i^A , χ_i^B the diamagnetic susceptibilities of ions A and B, and n_R the diamagnetic susceptibility of the pseudo-molecule.

If N atoms are randomly mixed and $n_R=0$, the total magnetic susceptibility χ reduces to χ° ,

$$\chi^\circ = \chi_e^\circ + N_A \chi_i^A + N_B \chi_i^B.
 \tag{3}$$

Then, it follows:

$$\begin{aligned}
 \Delta\chi &= \chi^\circ - \chi \\
 &= (\chi_e^\circ - \chi_e) + n_R (m\chi_i^A + \chi_i^B - \chi_R).
 \end{aligned}
 \tag{4}$$

If we put

$$\Delta\chi_e = \chi_e^\circ - \chi_e,$$

then, we have

$$\Delta\chi - \Delta\chi_e = n_R (m\chi_i^A + \chi_i^B - \chi_R).
 \tag{5}$$

Thus, a proportional relationship is expected between $\Delta\chi - \Delta\chi_e$ and n_R if $\Delta\chi - \Delta\chi_e$ could be estimated numerically. χ_i^A and χ_i^B for elementary components A and B measured by different authors fluctuate over a wide range, so the diamagnetic susceptibilities of ions A and B are given by those obtained by subtracting the calculated susceptibility of electron gas from the observed total magnetic susceptibility of pure liquids. Then, using χ_i^A and χ_i^B mentioned above, one may calculate the total magnetic susceptibility χ° for the case where the total atoms are randomly mixed, as shown by the curves I in Figs. 1, 2 and 3.

χ or χ° used in the above formulas is the total magnetic susceptibility for $N(=N_A+N_B)$ atoms in the volume V° and χ_i is the molar magnetic susceptibility of ions. The observed susceptibility is, however, given by the term of the susceptibility per unit mass χ^g , therefore χ in the above equations must be changed into χ^g by the following relations,

$$\chi_i^A = M_A \chi_i^g{}_A, \quad \chi_i^B = M_B \chi_i^g{}_B \quad \text{and} \quad \frac{\chi}{N} = \bar{A} \chi^g,$$

where M_A and M_B are atomic weights of atom A and B respectively, and \bar{A} is mean

atomic weight. Then, it follows,

$$\frac{\Delta\chi}{N} = \frac{\chi^0 - \chi}{N} = \bar{A}\Delta\chi^g \quad (6)$$

$$\frac{\Delta\chi_e}{N} = \frac{\chi_e^0 - \chi_e}{N} = \bar{A}\Delta\chi_e^g \quad (7)$$

and

$$\frac{1}{N} (\Delta\chi - \Delta\chi_e) = \bar{A} (\Delta\chi^g - \Delta\chi_e^g). \quad (8)$$

If N atoms in a liquid alloy are randomly mixed, χ_i and χ_e in eq. (3) are written as follows,

$$\begin{aligned} \chi_i^g &= \frac{\chi_i}{V^0} \frac{1}{\rho} = \frac{\chi_i}{N\bar{A}} \\ &= \frac{N_A M_A \chi_{i,A}^g + N_B M_B \chi_{i,B}^g}{N\bar{A}} \\ &= \frac{\rho_A V_A \chi_{i,A}^g + \rho_B V_B \chi_{i,B}^g}{V^0 \rho} \end{aligned} \quad (9)$$

where V_A and V_B are volumes occupied by N_A atoms of A and N_B of B respectively, and also ρ_A and ρ_B are densities of respective pure liquids A and B, and mean density ρ and mean atomic weight \bar{A} are written as

$$\rho = (1-x)\rho_A + x\rho_B$$

and

$$\bar{A} = (1-x)M_A + xM_B.$$

If it follows

$$\frac{\rho_A}{\rho} = \frac{M_A}{\bar{A}} \quad \text{and} \quad \frac{\rho_B}{\rho} = \frac{M_B}{\bar{A}},$$

then we have

$$\frac{V_A}{V^0} = 1-x \quad \text{and} \quad \frac{V_B}{V^0} = x,$$

and

$$\begin{aligned} \frac{\chi_i}{N} &= \bar{A}\chi_i^g \\ &= \bar{A} \left[\frac{(1-x)\rho_A \chi_{i,A}^g + x\rho_B \chi_{i,B}^g}{\rho} \right]. \end{aligned} \quad (9')$$

And also χ_e^0 is calculated by the following relation,

$$\begin{aligned}\frac{\chi_e^0}{N} &= 2 \times 0.623 \times 10^{-6} \left(\frac{n_0}{V^0} \right)^{1/3} \frac{V^0}{N} \\ &= 1.246 \times 10^{-6} (\bar{A})^{2/3} \rho^{-2/3} (\bar{Z})^{1/3},\end{aligned}\quad (10)$$

where \bar{Z} denotes mean valence electrons per atom.

In the liquid Cu-Bi alloy, the composition dependence of $\chi^0 N / \bar{A}$ is calculated from eqs. (9) and (10). It is shown by a full line in Fig. 1 and is in good agreement with experimental results so that in this liquid alloy, Cu^{+1} and Bi^{+5} ions are approximated to be randomly mixed. In the cases of the liquid Cu-Sn and Cu-In alloys, however, the observed curves II in Figs. 2 and 3 are remarkably different from the curves I of $\chi^0 N / \bar{A}$. $\Delta \chi N / \bar{A}$ is given by the difference between curves I and II in the same figures.

The volume of a pseudo-molecule is given by

$$\Omega_R^0 = m\Omega_A + \Omega_B \quad (11)$$

And if electrons of $2m$ in number were localized in a pseudo-molecule of the type $A_m B$ and were necessary and sufficient to form the covalent bonding in it, it would be a complete insulator and conduction electrons could not pass freely through the volume Ω_R^0 . In a case where the number of localized electrons is less than $2m$, the effective volume of a pseudo-molecule seen by conduction electrons should be given by $\alpha \Omega_R^0$ ($\alpha < 1$). Therefore, if n_R pseudo-molecules exist in the total volume V^0 of liquid alloy, the volume V , in which the conduction electron gas can travel, is given by

$$V = V^0 - n_R \alpha \Omega_R^0 \quad (12)$$

and the number of conduction electrons moving in the effective volume V is given by

$$n = Z_A N_A + Z_B N_B - 2p n_R, \quad (13)$$

where $2p$ denotes the number of electrons localized in a pseudo-molecule, and Z_A and Z_B the number of valence electrons of A and B atoms, respectively.

Thus, the magnetic susceptibility χ_e of electron gas in the liquid alloy containing N atoms in the volume V^0 is written as

$$\begin{aligned}\frac{\chi_e}{N} &= 2 \times 0.623 \times 10^{-6} \left(\frac{n}{V} \right)^{1/3} \frac{V}{V^0} \frac{V^0}{N} \\ &= 1.246 \times 10^{-6} \left(\frac{\bar{Z} - 2p \frac{n_R}{N}}{\bar{\Omega} - \frac{n_R}{N} \alpha \Omega_R^0} \right)^{1/3} \left(\bar{\Omega} - \frac{n_R}{N} \alpha \Omega_R^0 \right) \\ &= 1.246 \times 10^{-6} (\bar{A})^{2/3} \rho^{-2/3} \left(\bar{Z} - 2p \frac{n_R}{N} \right)^{1/3} \left(1 - \alpha \frac{n_R}{N} \frac{\Omega_R^0}{\bar{\Omega}} \right)^{2/3},\end{aligned}\quad (14)$$

where $\bar{\Omega}$ is the mean atomic volume.

If we put

$$q(n_R) = \left(1 - \alpha \frac{n_R}{N} \frac{\Omega_R^0}{\bar{\Omega}}\right)^{2/3} \quad (15)$$

we have then,

$$\begin{aligned} \frac{\Delta\chi_e}{N} &= \frac{\chi_e^0 - \chi_e}{N} \\ &= 1.246 \times 10^{-6} \rho^{-2/3} \left[(\bar{Z})^{1/3} - \left(\bar{Z} - 2p \frac{n_R}{N} \right)^{1/3} q_1(n_R) \right]. \end{aligned} \quad (16)$$

The composition dependence of n_R/N in both liquid alloys is shown in Fig. 4, and then $\Delta\chi_e/N$ can be obtained from eq. (16) if numerical values of p and α are given. p is considered less than or equal to 4 in the liquid Cu-Sn alloy and $p \leq 3$ in the liquid Cu-In alloy. According to eq. (5), $1/N (\Delta\chi - \Delta\chi_e)$ is proportional to n_R/N . Then, if $\Delta\chi/N\bar{A} = \Delta\chi^s$ is given by the difference between the curves I and II in Figs. 2 and 3, in each of the cases where $\alpha = 0, 0.40$ and 0.45 $1/N (\Delta\chi - \Delta\chi_e)$ is calculated as a function of composition N_B/N for $p = 4, 3, 2$ and 1 for both liquid alloys, respectively. Figure 5 shows $1/N (\Delta\chi - \Delta\chi_e)$ curves for the liquid Cu-Sn alloy

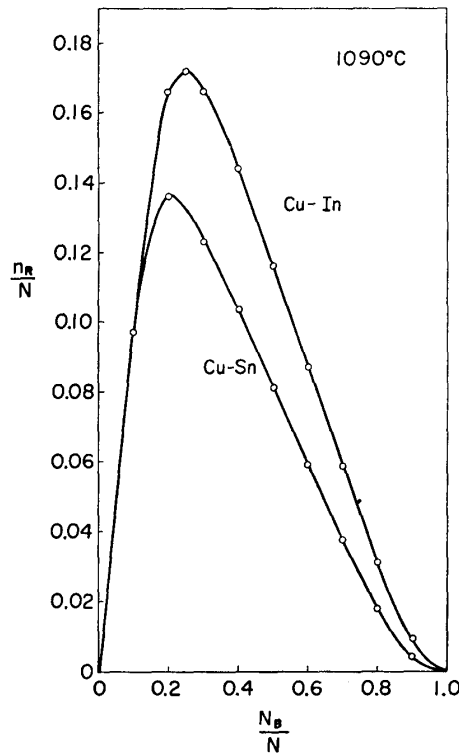


Fig. 4. Distribution curves of pseudo-molecules n_R/N in liquid Cu-Sn and Cu-In alloys at 11.00°C

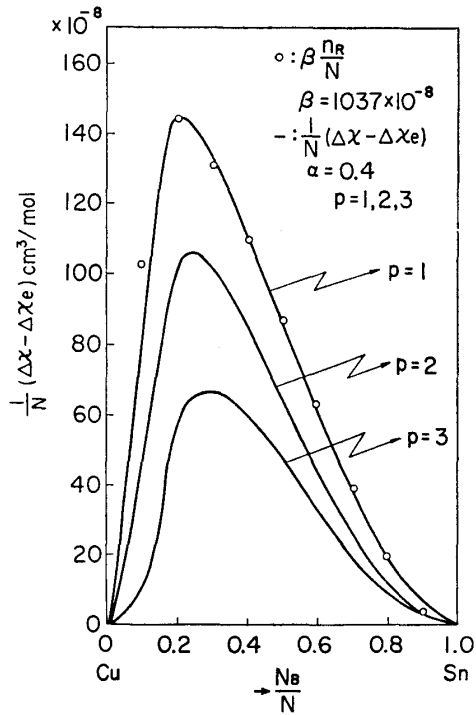


Fig. 5. $1/N (\Delta\chi - \Delta\chi_e)$ curves calculated for various values of p and n_R/N in liquid Cu-Sn alloy at 1100°C.

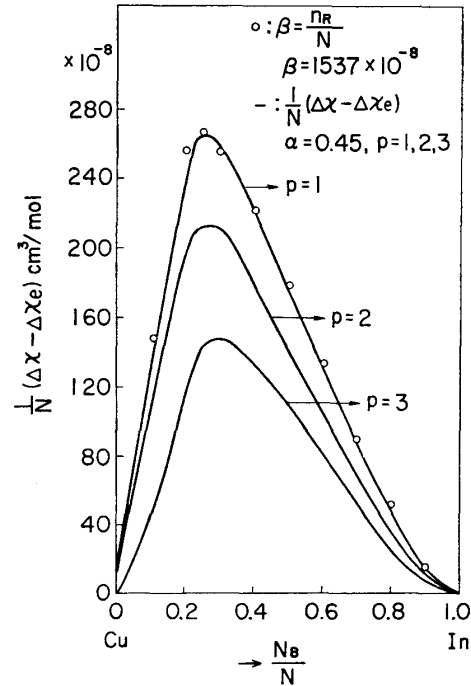


Fig. 6. $1/N (\Delta\chi - \Delta\chi_e)$ curves calculated for various values of p and n_R/N in liquid Cu-In alloy at 1100°C.

at 1100°C, which were calculated for various values of p in the case of $\alpha=0.4$. Figure 6 shows $1/N (\Delta\chi - \Delta\chi_e)$ curves of the liquid Cu-In alloy calculated for $p=1, 2$ and 3 at $\alpha=0.45$. Open circles in these figures show the values of n_R/N at 1090°C multiplied by a factor β . β is taken as $10.63 \cdot 10^{-6}$ in the liquid Cu-Sn alloy and as $15.37 \cdot 10^{-6}$ in the liquid Cu-In alloy. It is found that the position of the peak and the shape of the $1/N (\Delta\chi - \Delta\chi_e)$ curve for $p=1$ correspond extremely well with those of the $\beta \cdot n_R/N$ curve, and are nearly independent of values of α in both liquid alloys. The peak of the $1/N (\Delta\chi - \Delta\chi_e)$ curve for $p=1$ is found at 20%Sn in the liquid Cu-Sn alloy and at 25%In in the liquid Cu-In alloy, and the shape of the curve is remarkably similar with that of the n_R/N curve in both alloys. But the curves for $p \geq 2$ deviate from that of n_R/N in the shape and in the position of the peak.

Since $\chi_i^{\text{Cu}} = -10.16 \cdot 10^{-6}$ per mole, $\chi_i^{\text{Sn}} = -15.66 \cdot 10^{-6}$ per mole and $\chi_i^{\text{In}} = -17.91 \cdot 10^{-6}$ per mole, it follows from eq. (5) that $\chi_R = -67 \cdot 10^{-6}$ per mole in the liquid Cu-Sn alloy and $-64 \cdot 10^{-6}$ per mole in the liquid Cu-In alloy at 1090°C.

The values of α used in the above calculations are chosen to fit well with the Hall coefficient and the electrical resistivity of both liquid alloys.

Thus, we can suppose that in both liquid alloys the average number of electrons localized in a pseudo-molecule at 1090°C is only about 2. As suggested in the previous report⁽²⁾, this number of localized electrons is less than $2m$ neces-

sary for formation of a rigid molecule with covalent bond, and, therefore, the pseudo-molecule differs from a real molecule with a rigid structure and it is considered to have a flexible structure such that the distance between unlike ions is nearly fixed, but the bond angle is variable.

Based upon the above discussions, we consider, now, the configuration of Cu and Sn ions in the liquid Cu-Sn alloy which contains n_R pseudo-molecules of the type Cu_4Sn . It is possible for Cu ions bound to a Sn ion in a pseudo-molecule to take various configurations, and therefore, the configuration of Cu and Sn ions in n_R pseudo-molecules randomly distributed in the liquid alloy may be considered to be not so much different from that of free Cu and Sn ions surrounding pseudo-molecules over a wide range of the value of n_R . Similar circumstances are found in the liquid Cu-In alloy.

If all Cu and Sn atoms are randomly distributed in the liquid Cu-Sn alloy, the position of the 1st peak in the structure factor $a(K)$, which could be measured by means of X-ray or neutron scattering, should shift with the variation of alloy composition because of different diameters of Cu and Sn atoms; further, if pseudo-molecules in the liquid alloy has a definite configuration of constituent atoms, an extra peak due to their mutual interference should be observed at a position in the range of K closer to zero than that of the 1st peak. It is, however, known that the position of the 1st peak in the structure factor of liquid Cu-Sn alloy is kept nearly constant in a wide range of composition and no additional peak has been observed. This fact means that due to various configurations of constituent atoms in pseudo-molecules as described above, the atomic configuration in this liquid alloy seen by X-ray or neutrons resembles that in an assembly of Cu and Sn atoms randomly mixed with the mean distance between neighbouring unlike atoms which is nearly equal to that between neighbouring Cu atoms.

On the other hand from the standpoint of electron scattering, a pseudo-molecule behaves as a different type of scattering center than free Cu and Sn ions, and the presence of pseudo-molecules, therefore, would greatly influence its electrical resistivity.

III. Resistivities of liquid Cu-Bi, Cu-Sn and Cu-In alloy

Since all of Cu and Bi atoms in the liquid Cu-Bi alloy near 1000°C are considered as randomly mixed, the structure factor $a(K)$ can be calculated from a model of a binary mixture of hard spheres with different sizes. If the Ashcroft potentials are used as the scattering potentials for Cu and Bi ions, the electrical resistivity for this liquid alloy can be estimated and compared with observed results. The electrical resistivity of a liquid binary alloy is given by the Ziman-Faber formula as follows:

$$\rho = \frac{3\pi}{he^2} \frac{1}{v_F^2} \frac{N}{V} \langle x_1 U_1^2 + x_2 U_2^2 + x_1^2 U_1^2 [a_{11}(K) - 1] \rangle$$

$$+x_2^2 U_2^2 [a_{22}(K) - 1] + 2x_1 x_2 U_1 U_2 [a_{12}(K) - 1] \rangle ,$$

where

$$\langle F(K) \rangle \equiv \frac{1}{4k_F^4} \int_0^{2k_F} F(K) K^3 dK$$

and

$$x_1 = \frac{N_A}{N} , \quad x_2 = \frac{N_B}{N} .$$

U_1 and U_2 denote the scattering potentials of ions A and B, respectively, and $a_{11}(K)$, $a_{22}(K)$ and $a_{12}(K)$ are the partial structure factors, which can be obtained by using the following packing parameter η

$$\eta = \frac{\pi}{6} \frac{(N_A \sigma_A^3 + N_B \sigma_B^3)}{V^0} \quad (17)$$

with diameters of hard spheres $\sigma_A = 2.26 \text{ \AA} (\text{Cu})$ and $\sigma_B = 2.290 \text{ \AA} (\text{Bi})$. The Ashcroft model potential is given by the following formula,

$$U(y) = - \frac{\lambda^2 \cos sy}{y^2 + \lambda^2 f(y)}$$

where

$$y = \frac{K}{2k_F} , \quad \lambda^2 = \frac{1}{\pi a_0 k_F} \quad \text{and} \quad s = 2k_F R_c .$$

a_0 denotes the Bohr radius, $f(y)$ the screening function of Lindhard and R_c a constant. The electrical resistivity—composition curve for the liquid Cu-Bi alloy calculated by the above method is in fair agreement with the observed resistivity curve at 1100°C as shown in Fig. 7.

Next, we consider the electrical resistivity of the liquid Cu-Sn alloy. The resistivity in the region of 20% Sn has a negative temperature coefficient by which it decreases with increase in temperature as shown in Fig. 8. If all Cu and Sn atoms in this alloy are also randomly mixed, the structure factor $a(K)$ can be estimated under the assumption of a binary mixture of hard spheres with diameters $\sigma_A = 2.26 \text{ \AA} (\text{Cu})$ and $\sigma_B = 2.28 \text{ \AA} (\text{Sn})$ and with packing fractions $\eta_A = 0.449$ and $\eta_B = 0.384$ for the pure liquids of Cu and Sn, respectively. The electrical resistivity versus composition curve calculated by using $a(K)$, as given above, and the Ashcroft model potentials with $R_c^A = 0.410 \text{ \AA}$ and $R_c^B = 0.7255 \text{ \AA}$ is also shown by ρ_{HS} in Fig. 8. In this case the calculated curve deviates markedly from the observed one. These large deviations from the observed curve must be considered to have originated through neglecting the scattering from pseudo-molecules. Therefore, three sorts of scattering centers, A and B ions and pseudo-molecules, must be considered in the liquid Cu-Sn alloy.

When n_R pseudo-molecules, n_A A-ions and n_B B-ions are distributed randomly

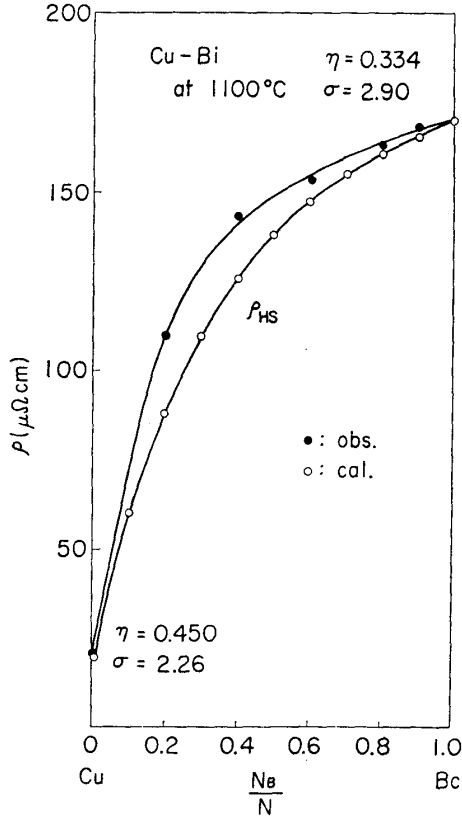


Fig. 7. Observed electrical resistivity and random mixing approximation for liquid Cu-Bi alloy at 1100°C.

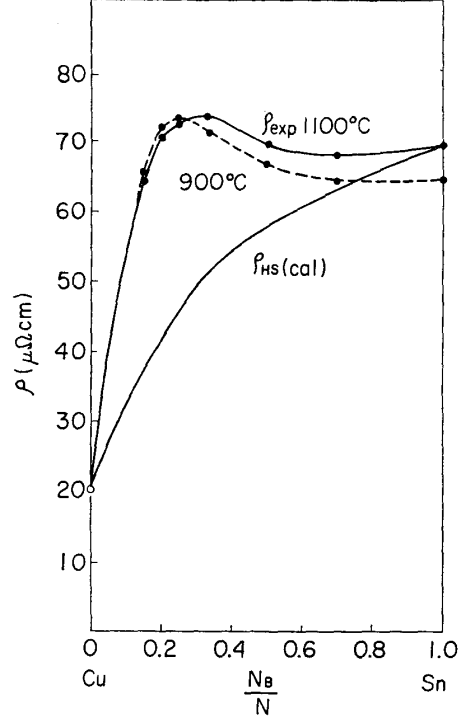


Fig. 8. Observed electrical resistivities at 900°C and 1100°C and random mixing approximation for liquid Cu-Sn alloy.

in the volume V of the liquid alloy, the total resistivity of this alloy can be written as follows:

$$\begin{aligned} \rho = \frac{3\pi}{\hbar e^2} \frac{1}{v_F^2} \frac{N_S}{V^0} \langle & x_1 U_1^2 + x_2 U_2^2 + x_1^2 U_1^2 (a_{11} - 1) \\ & + x_2^2 U_2^2 (a_{22} - 1) + 2x_1 x_2 U_1 U_2 (a_{12} - 1) \\ & + x_3 U_3^2 + 2x_1 x_3 U_1 U_3 (a_{31} - 1) + 2x_2 x_3 U_2 U_3 (a_{32} - 1) \\ & + x_3^2 U_3^2 (a_{33} - 1) \rangle, \end{aligned} \quad (18)$$

where N_S denotes the total number of scattering centers,

$$N_S = n_A + n_B + n_R$$

and x_1 , x_2 and x_3 are fractions of scattering centers,

$$x_1 = \frac{n_A}{N_S}, \quad x_2 = \frac{n_B}{N_S} \quad \text{and} \quad x_3 = \frac{n_R}{N_S}.$$

$a_{11}(K)$ is a partial structure factor denoting a correlation between free A ions in random distribution and $a_{22}(K)$ a correlation function between free B ions. It

is known that generally $a_{11}(K) \neq 1$ and also $a_{22}(K) \neq 1$. a_{31} or a_{32} denotes a correlation function between pseudo-molecules and free A ions or B ions and a_{33} a correlation function between pseudo-molecules under the assumption that a pseudo-molecule can be treated as a particle such as on A or B ion. However, the pseudo-molecule has a large volume Ω_R^0 and a flexible structure with variable configurations of atoms in it. Therefore, it can not be approximated in terms of a hard sphere. On the average, there seems no correlation between phases of scattered waves from any pair of neighbouring pseudo-molecules because of various configurations of constituent atoms in them so that we can approximate as

$$a_{33} = 1, \quad (19)$$

and also

$$a_{31} = a_{32} = 1 \quad (20)$$

Then, eq. (18) can be rewritten with two terms as follows:

$$\rho = \rho_1 + \rho_2,$$

where

$$\begin{aligned} \rho_1 = \frac{3\pi}{\hbar e^2} \frac{1}{v_F^2} \frac{N_S}{V^0} \langle x_1 U_1^2 + x_2 U_2^2 + x_1^2 U_{11}^2 (a_{11} - 1) \\ + x_2^2 U_2^2 (a_{22} - 1) + 2x_1 x_2 U_1 U_2 (a_{12} - 1) \rangle \end{aligned} \quad (21)$$

and

$$\rho_2 = \frac{3\pi}{\hbar e^2} \frac{1}{v_F^2} \frac{N_S}{V^0} \langle x_3 U_3^2 \rangle. \quad (22)$$

ρ_1 is considered to correspond to the contribution to the total resistivity from n_A ions of A and n_B ions of B distributed randomly in the volume $V^0 - n_R \Omega_R^0$. The partial structure factors a_{11} , a_{22} and a_{12} in eq. (21) can be approximated by those in a binary mixture of hard spheres with diameters σ_A and σ_B and a packing fraction

$$\eta = \frac{\frac{\pi}{6} (n_A \sigma_A^3 + n_B \sigma_B^3)}{V^0 - n_R \Omega_R^0}. \quad (23)$$

On the other hand, the number of localized electrons contributing to the bonding in a pseudo-molecule is less than the maximum value $2m$ for the bonding, so that it is not an insulator and conduction electrons can to some extent pass through its volume and are scattered there. Then, if the effective volume of a pseudo-molecule seen by conduction electrons is denoted by $\alpha \Omega_R^0$ ($\alpha < 1$), the electron density can be given by

$$\frac{Z_A N_A + Z_B N_B - 2p n_R}{V^0 - n_R \alpha \Omega_R^0}$$

in which we can insert $p=1$ as described above. Thus k_F is written as

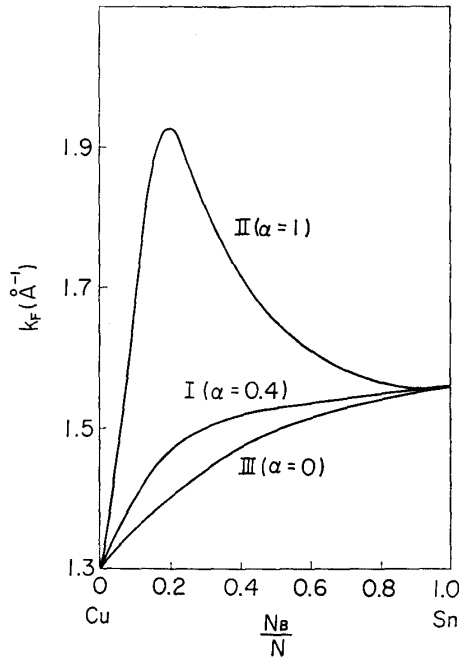


Fig. 9. Composition dependences of k_F for $\alpha=1, 0.4$ and 0 in liquid Cu-Sn alloy.

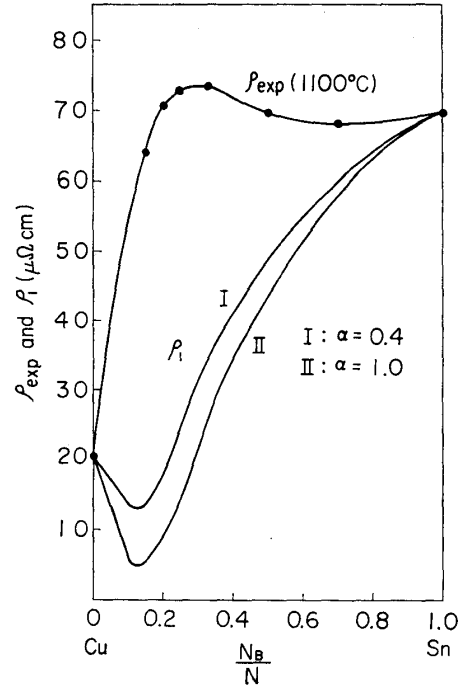


Fig. 10. Observed electrical resistivity ρ_{exp} of liquid Cu-Sn alloy and contribution from free ions ρ_1 calculated for $\alpha=0.4$ and 1 .

$$k_F = \left\{ 3\pi^2 \left(\frac{Z_A N_A + Z_B N_B - 2n_R}{V^0 - n_R \alpha \Omega_R^0} \right) \right\}^{1/3} \quad (24)$$

and k_F depends upon n_R and α . The composition dependence of k_F in the liquid Cu-Sn alloy for $\alpha=1, 0.4$ and 0 is shown in Fig. 9.

With the above consideration ρ_1 in the liquid Cu-Sn alloy is calculated using the Ashcroft model potentials for Cu and Sn ions. Curves I and II in Fig. 10 show ρ_1 calculated for $\alpha=0.4$ and $\alpha=1.0$ respectively.

ρ_2 corresponds to the resistivity due to scattering from pseudo-molecules and is rewritten as

$$\begin{aligned} \rho_2 &= \frac{3\pi}{\hbar e^2} \frac{1}{v_F^2} \frac{N_S}{V^0} \langle x_3 U_3^2 \rangle \\ &= \frac{3\pi}{\hbar^3} \frac{m^2}{e^2} \frac{\bar{n}_0}{k_F^2} \frac{n_R}{N} \langle U_3^2 \rangle, \end{aligned} \quad (25)$$

where \bar{n}_0 denotes the mean number density of the liquid alloy N/V^0 . But, ρ_2 cannot be calculated directly from eq. (25), because the scattering potential $U_3(K)$ for the pseudo-molecule is unknown. However, ρ_2 is obtained by subtracting ρ_1 from the measured electrical resistivity ρ .

$$\rho_2 = \rho - \rho_1.$$

The factor $\langle |U_3(K)|^2 \rangle$ in the right hand side of eq. (25) is rewritten as follows:

$$\left\langle \left| U_3 \left(\frac{K}{2k_F} \right) \right|^2 \right\rangle = \int_0^1 \left| U_3 \left(\frac{K}{2k_F} \right) \right|^2 4 \left(\frac{K}{2k_F} \right)^3 d \left(\frac{K}{2k_F} \right).$$

This integration is mainly determined by the value of $|U_3(K/2k_F)|^2$ in the region of $K \approx 2k_F$, so it may be assumed that

$$\left\langle \left| U_3 \left(\frac{K}{2k_F} \right) \right|^2 \right\rangle \approx \left| U_3 \left(\frac{K}{2k_F} \right) \right|_{K=2k_F}^2.$$

Thus we have the following relation from eq. (23)

$$\frac{k_F^2}{\bar{n}_0} (\rho - \rho_1) \propto \frac{n_R}{N} \left| U_3 \left(\frac{K}{2k_F} \right) \right|_{K=2k_F}^2. \quad (26)$$

Since the scattering potential $U_3(K)$ depends upon k_F , which varies generally with alloy compositions, $|U_3(K/2k_F)|_{K=2k_F}^2$ depends upon the alloy composition. The composition dependence of k_F is influenced greatly by the value of the parameter α as shown in Figs. 9 and 13. The parameter α can be determined directly from the measurement of the Hall coefficient and in the following report it will be shown that $\alpha=0.4$ for the liquid Cu-Sn alloy and $\alpha=0.45$ for the liquid Cu-In alloy can explain satisfactorily the measured Hall coefficients of the liquid alloys.

In the liquid Cu-Sn alloy k_F for $\alpha=0.4$ changes very slowly with the alloy composition over 20%Sn, then $|U_3(K/2k_F)|_{K=2k_F}^2$ is expected to be nearly independent of the composition in the concentration range higher than 20%Sn. Under the above circumstances the relationship of eq. (26) is examined in the case of liquid Cu-Sn alloy.

The calculated curves of $k_F^2/\bar{n}_0(\rho - \rho_1)$, of which $\rho - \rho_1$ is determined from the measured resistivity ρ_{exp} and curve I ($\alpha=0.4$) or curve II ($\alpha=1.0$) in Fig. 10, have a peak at 20%Sn; also the n_R/N curve, which is given in Fig. 4, shows a peak for the same composition. These curves are shown in Fig. 11 where each values of the curves at 20%Sn is normalized to 1 and the values of n_R/N are shown by open circles. Figure 11 shows that curve II for $\alpha=1.0$ deviates from the n_R/N curve in its shape, but curve I for $\alpha=0.4$ has a little deviation from n_R/N but is in excellent agreement with the n_R/N curve as a whole. $|U_3(K/2k_F)|_{K=2k_F}^2$ is estimated from eqs. (25) and (26) using n_R/N and $k_F^2/\bar{n}_0(\rho - \rho_1)$ for $\alpha=0.4$ as shown by curve I in Fig. 12. It is nearly constant in the concentration range over 20%Sn and corresponds with the k_F curve for $\alpha=0.4$ in Fig. 9. The magnitude of $|U_3(K/2k_F)|_{K=2k_F}^2$ is taken as about 11.4 Ryd² from curve I in Fig. 12 and is considered to be reasonable compared with

$$\left\langle \left| U_2 \left(\frac{K}{2k_F} \right) \right|^2 \right\rangle + 4 \left\langle \left| U_1 \left(\frac{K}{2k_F} \right) \right|^2 \right\rangle = 5.8 \text{ Ryd}^2$$

at 20% Sn.

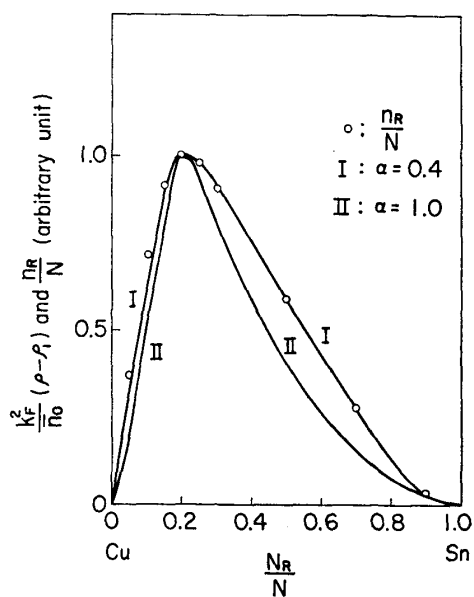


Fig. 11. Relation between $k_F^2/\bar{n}_0(\rho-\rho_1)$, and n_R/N in liquid Cu-Sn alloy.

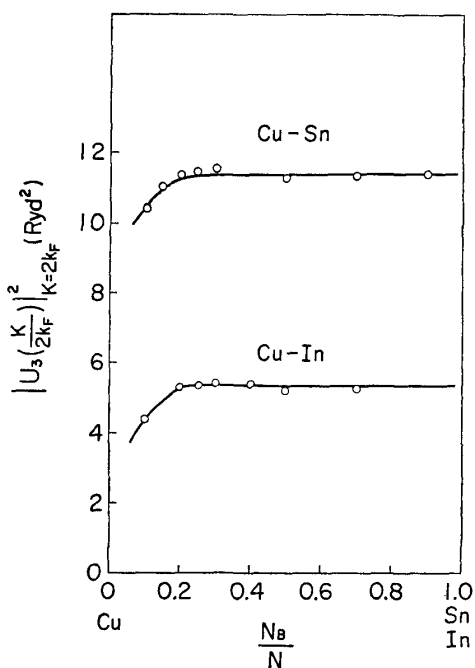


Fig. 12. Composition dependences of $|U_3(K/2k_F)|^2_{K=2k_F}$ in liquid Cu-Sn and Cu-In alloys.

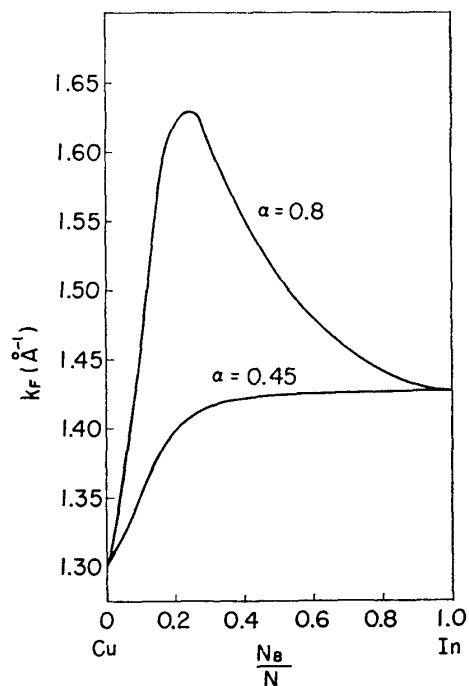


Fig. 13. Composition dependences of k_F for $\alpha=0.45$ and 0.8 in liquid Cu-In alloy.

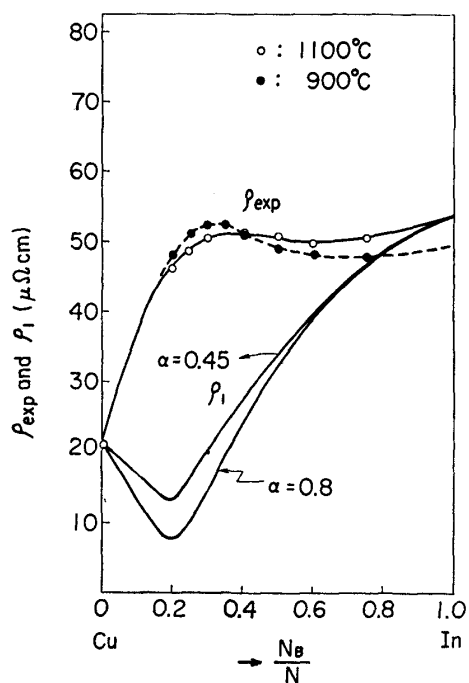


Fig. 14. Observed electrical resistivity ρ_{exp} of liquid Cu-In alloy and contribution from free ions ρ_1 calculated for $\alpha=0.45$ and 0.8 .

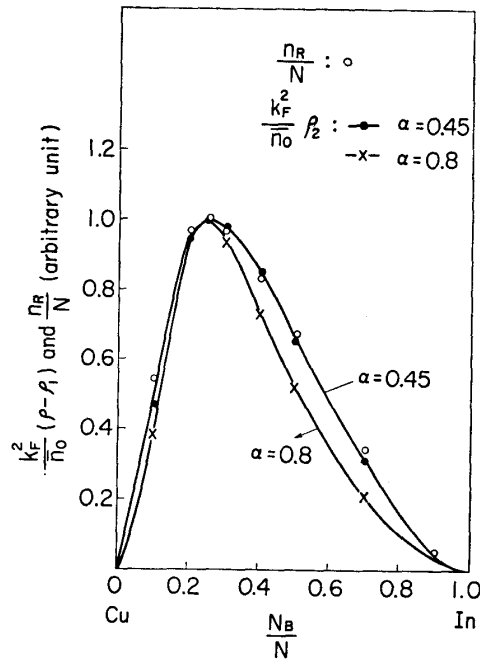


Fig. 15. Relation between $k_F^2/\bar{n}_0(\rho-\rho_1)$ and n_R/N in liquid Cu-In alloy.

The relationship (26) is also examined for the case of the liquid Cu-In alloy which has an anomalous feature in the electrical resistivity curve. Figure 13 shows the composition dependences of k_F for $\alpha=0.45$ and 0.8. k_F for $\alpha=0.45$ is nearly independent of the alloy composition in the higher concentration range than 25%In. Figure 14 shows the observed resistivity ρ and ρ_1 for $\alpha=0.45$ and 0.8, respectively. ρ_1 corresponds to the resistivities by scattering from free ions Cu^{+1} and In^{+3} in the volume $V^0-n_R\Omega_R^0$. Curves of $k_F^2/\bar{n}_0(\rho-\rho_1)$ estimated for $\alpha=0.45$ and 0.8 respectively are shown in Fig. 15. The curve for $\alpha=0.45$ is in good agreement with the n_R/N curve of the liquid Cu-In alloy given in Fig. 4. $|U_3(K/2k_F)|_{K=2k_F}^2$ for the liquid Cu-In alloy is shown by curve II in Fig. 12. It is nearly constant over a wide range of compositions corresponding to the curve of k_F for $\alpha=0.45$.

These facts as mentioned above mean that the assumptions of eqs. (19) and (20) are practically valid and the effective volume of the pseudo-molecule seen by conduction electrons is about $0.4\Omega_R^0$ in the liquid Cu-Sn alloy and about $0.45\Omega_R^0$ in the liquid Cu-In alloy.

Thus it is clear that the anomalous behaviours of the electrical resistivity of the liquid Cu-Sn and Cu-In alloys are caused mainly by scattering from the pseudo-molecules having a flexible structure.

Summary

(1) The magnetic susceptibilities and the electrical resistivities of the liquid alloys, Cu-Bi, Cu-Sn and Cu-In, have been measured at temperatures near 1100°C.

(2) The composition dependence of the magnetic susceptibility in the liquid Cu-Bi alloy is in good agreement with that calculated under the assumption of random mixing of Cu^{+1} and Bi^{+5} ions in an electron gas consisting of conduction electrons.

(3) In the liquid Cu-Sn and Cu-In alloy, the magnetic susceptibility curves exhibit deep valleys of diamagnetism at 20% Sn for the Cu-Sn alloy and at 25% In for the Cu-In alloy, respectively. These diamagnetic valleys become deeper with decreasing temperature. These features are explained by assuming the existence of pseudo-molecules in addition to free ions in an atmosphere of electrons with their density depending upon the concentration of the pseudo-molecules n_R/N and the number of localized electrons in them. The observed magnetic susceptibility curves indicate that in both liquid copper alloys only about two electrons per pseudo-molecule are localized at temperatures close to 1100°C.

(4) The electrical resistivity of the liquid Cu-Bi alloy has been calculated with structure factors estimated under the assumption of a binary mixture of hard spheres having different diameters and the Ashcroft potentials, and the result is in fair agreement with observed resistivity.

(5) The anomalous features of the resistivity curves for the liquid Cu-Sn and Cu-In alloys are explained under the assumption that the resistivities of these alloys are given by the sum of the contributions from scattering by free ions in randomly mixed state, ρ_1 , and from scattering by pseudo-molecules, ρ_2 .

It is shown that ρ_2 obtained by subtracting ρ_1 , which is calculated from a hard sphere model, from the observed resistivity ρ is proportional to $\bar{n}_0/k_F^2 \cdot n_R/N$ for both alloys.