Hall Effect in Liquid Copper Alloys

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(Received Feb. 28, 1974; revised manuscript
received Sept. 10, 1974)

Synopsis

Hall coefficients of liquid copper alloys Cu-Bi, Cu-Sb, Cu-Sn and Cu-In have been measured by means of the double-alternating current method in a wide temperature range from 500° to 950°C.

No temperature dependence of the Hall coefficient is observed in the liquid state of these alloys. The observed composition dependence of the Hall coefficient for 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 and of free electron approximation. In the other copper alloys, however, deviations from the free electron values R_0 calculated under the above simple situation are observed. It is considered that some of the constitutent atoms are randomly distributed and others are associated into clusters consisting of several atoms. Such a cluster is referred to as a pseudo-molecule. A theoretical formula for the Hall coefficients of these liquid alloys is derived as a function of the quantities n_R/N, $2p$ and $\alpha\Omega_0$ where n_R/N is the concentration of the pseudo-molecules, $2p$ is the number of localized electrons contributing to the bonding of the pseudo-molecule and $\alpha\Omega_0$ an effective volume of pseudo-molecule seen by conduction electrons. Using experimental values of these parameters obtained from the observation of the heat of mixing, magnetic susceptibility and the electrical resistivity, composition dependence of the Hall coefficients of the liquid Cu-In and Cu-Sn alloys are calculated in good agreement with the observed ones. The temperature dependence of the Hall coefficients estimated from the above formula is found too small to be observed with the present technique of experiment.

I. Introduction

If the conduction electrons in a metal behave as a free electron gas, the Hall coefficient of the metal is given by,

$$R_0 = \frac{1}{ne}, \tag{1}$$

where n denotes the density of the electrons and e the charge of an electron. It is generally assumed that in a molten state of the metal positive ions are randomly distributed in an atmosphere of a conduction electron gas. The observed value of the Hall coefficient, R, for various pure metals such as Ag, Au, Cu, Na, K, Cd, In, and Sn etc. in their liquid state has been known to be very close to R_0.

However, in the case where the electrical resistivity is so high that the mean

* The **1612th** report of the Research Institute for Iron, Steel and Other Metals.

free path of the conduction electron is of the order of magnitude comparable to the average interatomic distance, the value of R deviates from R_0 as observed in liquid Pb and Sb. In many of the liquid alloys, their Hall coefficients often deviate appreciably from the free electron value R_0.

Here the Hall coefficient for liquid copper alloys, Cu-Bi, Cu-Sb, Cu-Sn[1] and Cu-In are measured with high sensitivity provided by the AC modulation technique. For these liquid alloys, measurements of heat of mixing, magnetic susceptibility and electrical resistivity have been performed as reported in the previous papers.[2],[3] In the case of the liquid Cu-Bi alloy the above physical properties can be understood in terms of a simplified model that Cu and Bi ions randomly distributed in the atmosphere of the electron gas. In the cases of the other copper alloys, however, anomalous physical properties, such as, a peak of heat evolution in the neighbourhood of 70=80%Cu in the heat of mixing curves, a diamagnetic valley in the magnetic susceptibility curve and a maximum of electrical resistance near the similar compositions have been observed and they become more prominent as the temperature of alloys decreases. The assumption of random distribution of all ions, therefore, can not be applied for these copper alloys. The above anomalous behaviors of the liquid alloys Cu-Sb, Cu-Sn and Cu-In can be explained by an assumption[3] that some of atoms composing of liquid alloys are in random distribution, but others associate into a number of clusters in which atoms are bound with each other by a sort of covalent bond. For example, such a cluster in the liquid Cu-Sn alloy is something like a molecule of a composition Cu_4Sn, and the number of electrons localized in a cluster is considered to be only about two according to our previous study on the magnetic susceptibility.[3] Therefore such a molecule differs from a real molecule with a fixed atomic configuration, and as expected from the observed structure factor a(k) of the liquid Cu-Sn alloy the interatomic distance between Cu and Sn ions in these molecules is nearly fixed, but the bond angle is variable. Therefore they are referred to as pseudo-molecules in the previous reports.[2] Upon these assumptions the distribution of pseudo-molecules n_R/N in the liquid Cu-Sn and Cu-In alloys has been estimated as a function of composition.[2] Using the estimated value of n_R the heat of mixing for the liquid Cu-Sn and Cu-In alloys are found to be in good agreement with the observed value. The electrical resistivities of these copper alloys are estimated with the approximation that free ions and pseudo-molecules are randomly distributed, and they form

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(3) S. Takeuchi, K. Suzuki, F. Itoh, K. Kai, M. Misawa and K. Murakami, Proc. 2nd Internat. Conf. on the Properties of Liquid Metals (1972), p. 69; J. Japan Inst. Metals, **37** (1973), 1011 (in Japanese); Sci. Rep. RITU, **A 25** (1974), 56.

scattering centers to contribute to the resistivity. In this case there are insufficient numbers of electrons for complete covalent bonding in the pseudo-molecule and only about two electrons are localized in it, so it can not be an insulator. Conduction electrons can to some extent pass through its volume and are scattered there. It is, therefore, considered that an effective volume of the pseudo-molecule seen by conduction electrons is smaller than its molecular volume Ω_0, (which is given approximately by $4\Omega_{Cu}+\Omega_{Sn}$ in the case of the liquid Cu-Sn alloy), and hence, it is given by $\alpha\Omega_0(\alpha<1)$. A parameter α is selected to make the calculated resistivity best fit with the experimental value. The numerical value of α has been taken as 0.4 for the liquid Cu-Sn alloy and 0.45 for the liquid Cu-In alloy. The density of conduction electrons and, hence, the Fermi energy are influenced greatly by the value of the parameter α. Thus α is closely related to the electrical resistivity of liquid alloys containing pseudo-molecules.

If free ions and pseudo-molecules are randomly distributed in an atmosphere of conduction electrons of liquid copper alloys, the Hall coefficient is in inverse proportion to the density of conduction electrons of the alloys. Thus, we can determine the value of the parameter α directly from the observed Hall coefficient.

In this investigation values of α for the liquid alloys Cu-Sb, Cu-Sn and Cu-In are estimated from measurement of the Hall coefficients and are compared with the above values of α obtained from the electrical resistivity.

II. Experimental method and preparation of specimens

There are several methods to measure the Hall effect of metals, but for liquid metals the double alternating current method is considered to be better to improve signal to noise ratio in the measured Hall voltages at higher temperatures.

The Hall voltage V_H is given by

$$V_H = \frac{I_s \cdot H_z}{d} R, \tag{2}$$

where I_S denotes the electrical current in the specimen, H_Z the magnetic field applied perpendicular to the direction of the electrical current, d thickness of the specimen and, R, the Hall coefficient. If I_s and H_Z change sinusoidally with the frequencies f_1 and f_2, respectively, so that,

$$I_s = I_0 \cos 2\pi f_1 t \quad \text{and} \quad H_z = H_0 \cos 2\pi f_2 t, \tag{3}$$

the Hall voltage, V_H, is given by the following,

$$V_H = \frac{I_0 H_0}{d} R \{\cos 2\pi (f_1 - f_2) t + \cos 2\pi (f_1 + f_2) t\}. \tag{4}$$

Then, if signals with only a frequency (f_1-f_2) or (f_1+f_2) are amplified, noises which may be included in current I_S and in magnetic field H_Z can be separated out from

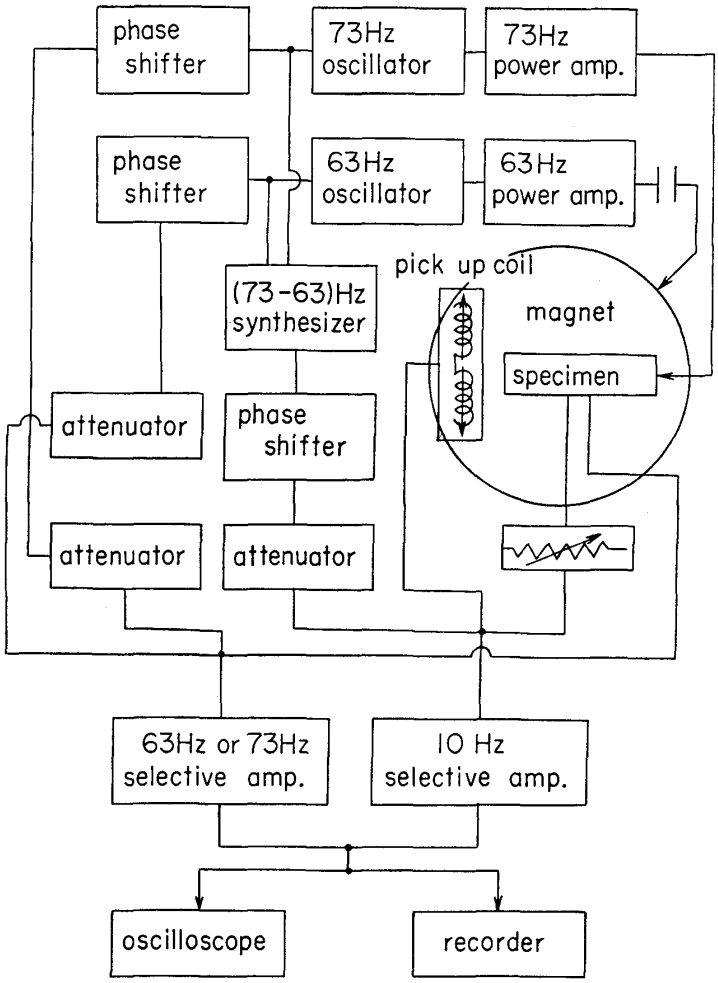

Fig. 1. Block diagram of two-alternating current method for measuring the Hall voltage.

the Hall voltage. The Nernst-Ettinghousen effect associated with symmetry of the Hall terminals and with inhomogeneity of magnetic field and temperature distribution are completely removed out from the pick up voltage by using alternating current and magnetic field. A block diagram of experimental apparatus is shown in Fig. 1. In our experiments, alternating current with f_1=73 Herz and alternating magnetic field with f_2=63 Herz are used and only a signal of f_1-f_2=10 Herz in the Hall voltage is selectively amplified for detection. The Hall voltage V_H is potentiometrically measured by using a standard voltage of 10 Herz and its sign is determined by comparing with that of a standard specimen of pure copper of 23.0μ. thick. If the spurious signal of 63 or 73 Herz is found in the pick up voltage of 10 Herz, it is eliminated by the adjustment of a phase shifter and an attenuator.

III. Observed results of Hall coefficients for liquid copper alloys

The Hall coefficients of the liquid alloys Cu-Bi, Cu-Sb, Cu-Sn and Cu-In are

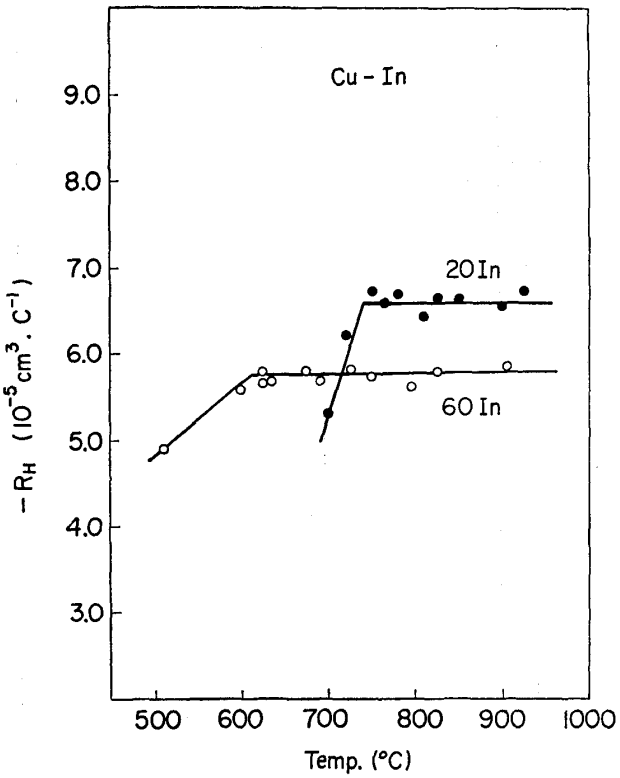

Fig. 2. The Hall coefficient of Cu-In alloys of 20%In and 60%In plotted against temperature.

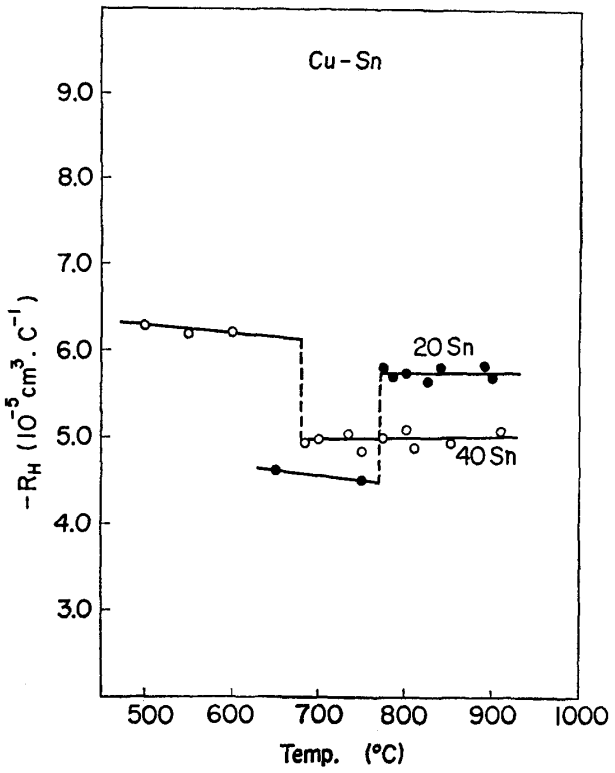

Fig. 3. The Hall coefficient of Cu-Sn alloys of 20%Sn and 40%Sn plotted against temperature.

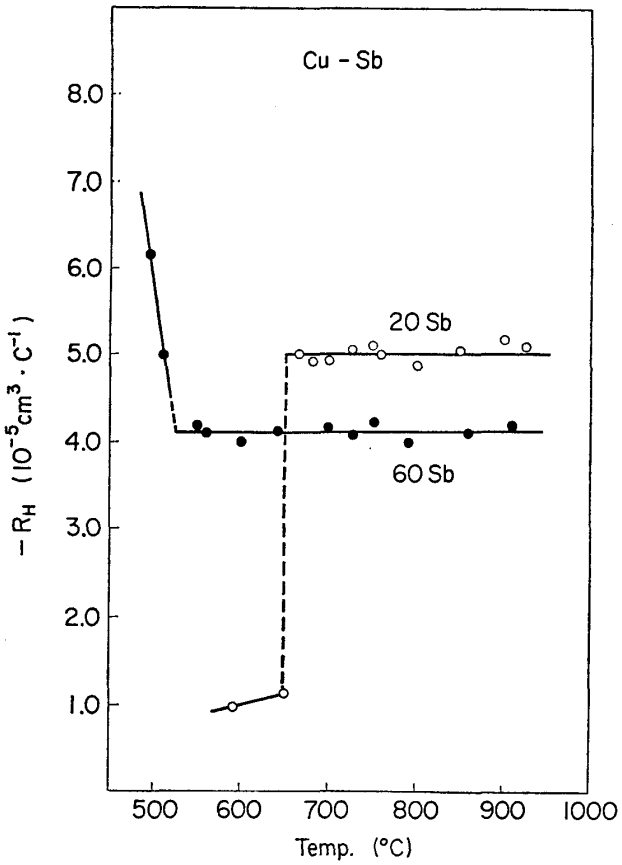

Fig. 4. The Hall coefficient of Cu-Sb alloys of 20%Sb and 60%Sb plotted against temperature.

measured as functions of temperature and compositions. Figures 2, 3 and 4 show temperature dependences of the Hall coefficient observed for several choices of composition of the liquid copper alloys. As shown in these figures the Hall coefficients in the liquid state are nearly independent of temperature within experimental errors. Figures 5, 6, 7 and 8 show composition dependences of the observed Hall coefficients in these alloys and of those calculated under the free electron approximation in which all of valence electrons in constituent atoms of the alloys behave as conduction electrons. The observed Hall coefficients in the liquid state of pure Cu, Sn and In agree with the respective free electron values R_0 and those of pure Bi and Sb somewhat disagree with R_0 as seen in Figs. 7 and 8. However, those of the liquid alloys Cu-Sn, Cu-In and Cu-Sb are clearly smaller than $|R_0|$. The Hall coefficient curve for the liquid Cu-Bi alloy may be regarded very close to the R_0 curve. This result implies that Cu^{+1} and Bi^{+5} ions are randomly distributed in the gas atmosphere of conduction electrons. Figure 9 shows the electrical resistivities of these four alloys measured at 800°C and 1000°C. Figure 10 shows the Hall mobilities of these alloys $\mu_H = |R|\sigma$ estimated from the above electrical resistivity and the Hall coefficient. The value of μ_H in the Cu-Bi alloy decreases rapidly with increase in Bi concentration up to about 30% and then it does gradually up to 60%Bi. However, the mobility of the other alloys

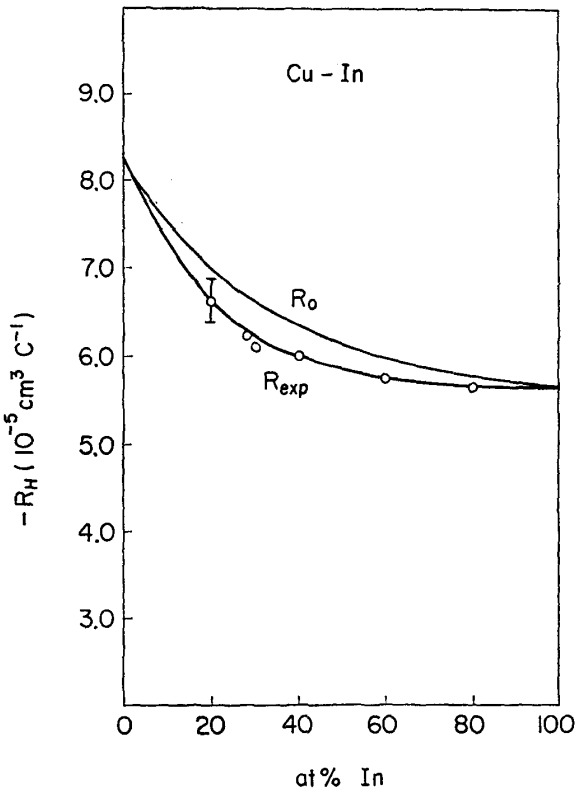

Fig. 5. The composition dependence of the observed Hall coefficient of liquid Cu-In alloys at 1000°C and R_0 curve calculated by free electron approximation.

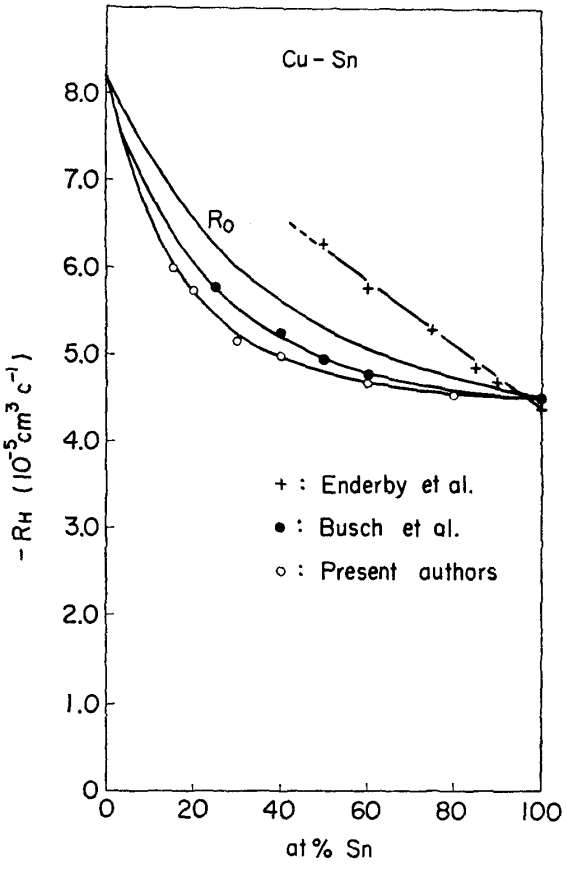

Fig. 6. The composition dependence of the observed Hall coefficient of liquid Cu-Sn alloys at 1000°C and R_0 curve. Open circle: present authors, closed circle: Bush[1], and +: Enderby[1].

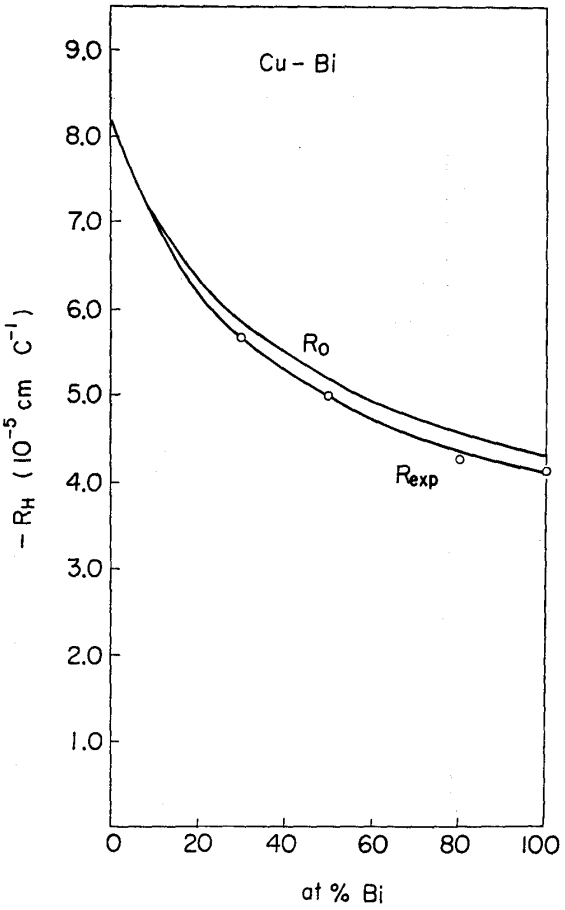

Fig. 7. The composition dependence of the observed Hall coefficient of liquid Cu-Bi alloys at 1000°C and R_0 curve.

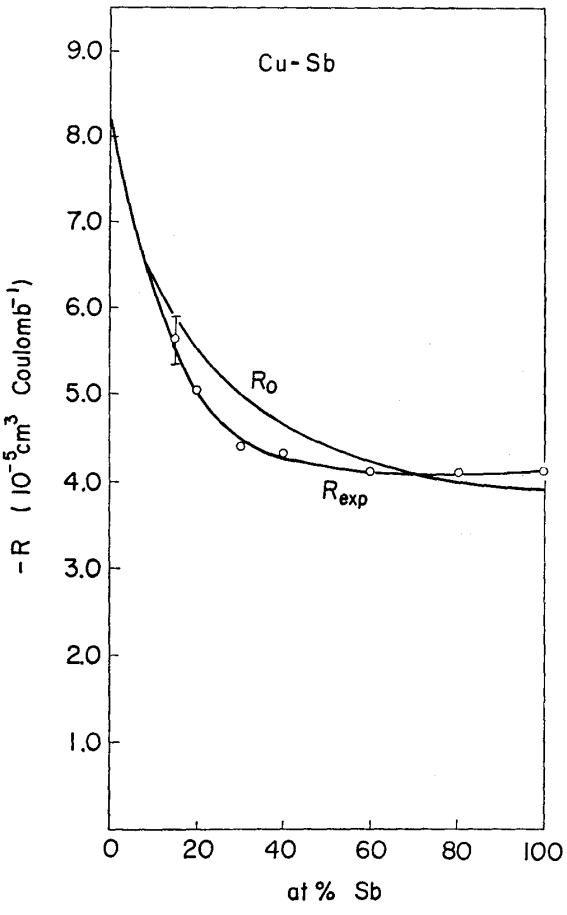

Fig. 8. The composition dependence of the observed Hall coefficient of liquid Cu-Sb alloys at 1000°C and R_0 curve.

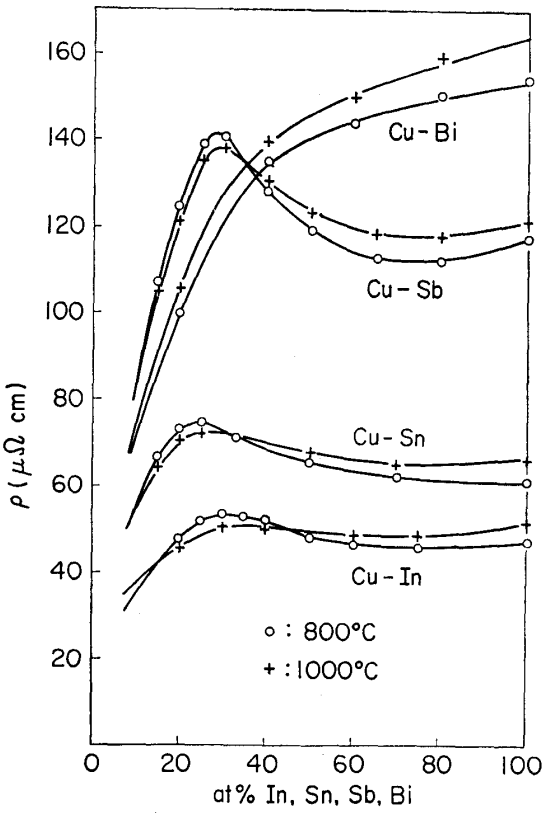

Fig. 9. The electrical resistivities of liquid Cu-In, Cu-Sn, Cu-Bi and Cu-Sb alloys at 800°C and 1000°C.

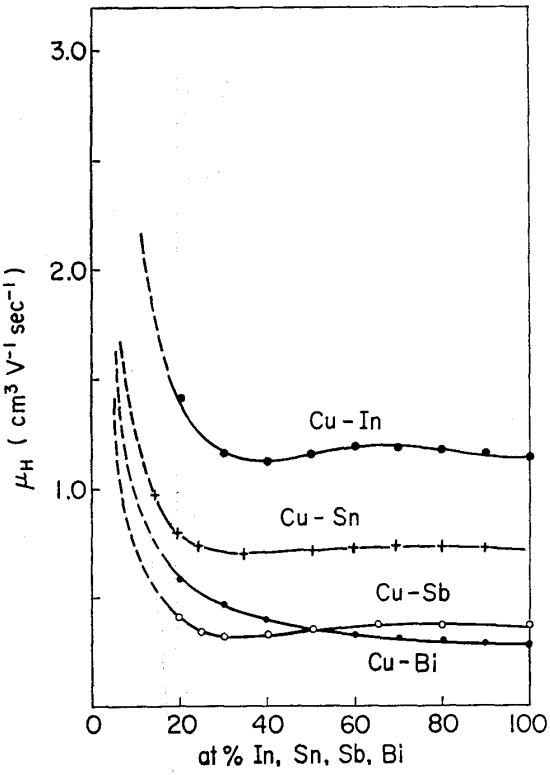

Fig. 10. The mobility $\mu_H+R_H|\sigma|$ of liquid copper alloys at 1000°C as a function of alloying composition.

has a minimum in ranges of 70 to 80%Cu and shows a different behavior from that of the Cu-Bi alloy.

IV. Discussions

In the liquid Cu-Bi alloy, the measured value of Hall coefficient is very close to the free electron value R_0, and hence Cu and Bi ions in this alloy are considered to be randomly distributed in the electron gas atmosphere consisting of their valency electrons. In the other liquid copper alloys the composition dependence of the Hall coefficient differs markedly from the R_0 curve. As explained in the previous reports,[3] the anomalous behaviors in physical properties such as heat of mixing, magnetic susceptibility and electrical resistivity for the liquid copper alloys Cu-Sb, Cu-Sn and Cu-In is reasonably explained by the introduction of the concept of pseudo-molecules. Therefore, the above deviation of the observed Hall coefficient, R, for these alloys from the free electron value, R_0, can be interpreted in terms of the coexistence of the pseudo-molecules with free ions of random distribution.

Now, if a liquid alloy, consisting of N_A and N_B of atoms A and B respectively contains n_R pseudo-molecules of composition A_mB, together with n_A and n_B free

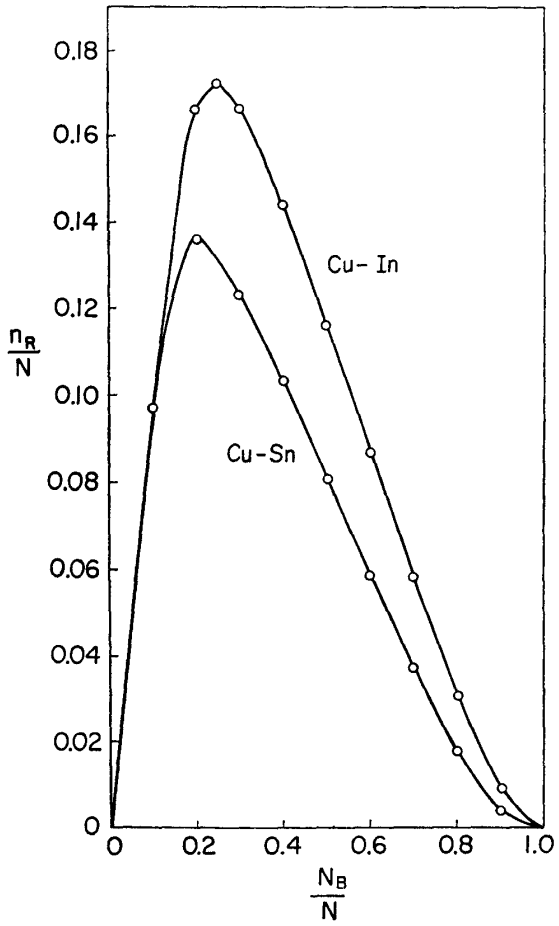

Fig. 11. The distribution curve of pseudo-molecules n_R/N in liquid Cu-In and Cu-Sn alloys at 1100°C.

ions, respectively for each element, it follows that

$$\left.\begin{aligned} mn_A+n_R &= N_A \\ n_B+n_R &= N_B \\ N_A+N_B &= N \end{aligned}\right\} \tag{5}$$

Figure 11 shows the composition dependences of the pseudo-molecules n_R in the liquid Cu-Sn and Cu-In alloys at 1100°C. In these alloys free ions and pseudo-molecules are randomly distributed and are expected to play a role as scattering centers to conduction electrons. Whereas, in this case, a band structure of these conduction electrons can be considered to be approximated by that of a free electron gas, so that, the Hall coefficient is independent of the scattering power of the pseudo-molecule and hence, depends mainly upon the density of conduction electrons. The number of conduction electrons in the liquid alloy is given by

$$Z_AN_A+Z_BN_B-2pn_R\,, \tag{6}$$

where $2p$ denotes numbers of electrons localized in a pseudo-molecule, Z_A and Z_B

are the number of valence electrons of atoms A and B, respectively. If atomic volumes of A and B are denoted by Ω_A and Ω_B, respectively, and the volume of pseudo-molecule by $\Omega_R{}^0=m\Omega_A+\Omega_B$, the total volume of the liquid alloy V^0 is written as

$$V^0 = n_A\Omega_A+n_B\Omega_B+n_R\Omega_R{}^0 . \tag{7}$$

Since $2p$ valence electrons are localized in a pseudo-molecule, conduction electrons are excluded not from the whole volume of the pseudo-molecule $\Omega_R{}^0$ but from only a part of the volume, $\alpha\Omega_R{}^0(\alpha<1)$. Accordingly an effective volume of a pseudo-molecule seen by the conduction electron is considered to be given by $\alpha\Omega_R{}^0$. Thus, a volume in which conduction electrons may occupy in the liquid is given by

$$V^0-n_R\alpha\Omega_R{}^0 = N_A\Omega_A+N_B\Omega_B-n_R\alpha\Omega_R{}^0 , \tag{8}$$

and the density of the conduction electrons is written as

$$n = \frac{Z_AN_A+Z_BN_B-2pn_R}{V^0-n_R\alpha\Omega_R{}^0} . \tag{9}$$

Therefore, the Hall coefficient R can be expressed by

$$\begin{aligned} R &= \frac{1}{e}\frac{V^0-n_R\alpha\Omega_R{}^0}{Z_AN_A+Z_BN_B-2pn_R} \\ &= \frac{1}{e}\frac{\dfrac{V^0}{N}-\alpha\Omega_R{}^0\dfrac{n_R}{N}}{Z_A(1-x)+Z_Bx-2p\dfrac{n_R}{N}} , \end{aligned} \tag{10}$$

where

$$x = \frac{N_B}{N} \quad \text{and} \quad p = 1 . \tag{11}$$

n_R/N in Eq. (10) is given in Fig. 11.

Thus, the Hall coefficients for the liquid Cu-Sn and Cu-In alloys can be calculated from Eq. (10) and are shown in Figs. 12 and 13. Curves I, II and III in Fig. 12 for the Cu-In alloy are the results calculated for $\alpha=0$, 0.3 and 0.45, respectively. Curves I, II and III in Fig. 13 for the Cu-Sn alloy are given for $\alpha=0$, 0.3 and 0.4, respectively. The broken curves in both figures show the free electron values R_0 for both alloys and the measured values denoted by the closed circles give their best fit with $\alpha=0.45$ for Cu-In alloy and $\alpha=0.4$ for Cu-Sn, respectively. These values of parameter α give also good agreement between the calculated values of electrical resistivity and that of the observed ones.[3] The Hall coefficient for the liquid Cu-Sb alloy is also explained by Eq. (10) if a curve of N_R/N versus composition may be obtained.

Thus, the Hall effect in liquid copper alloys can be explained by only the

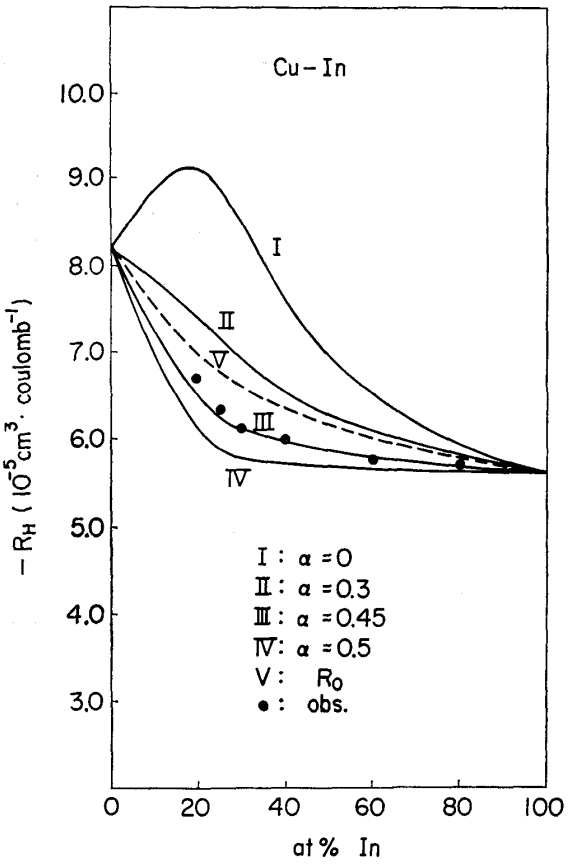

Fig. 12. The comparison of the observed Hall coefficient of liquid Cu-In alloys with curves calculated by Eq. (10) for $\alpha=0$, 0.3, 0.4 and 0.5.

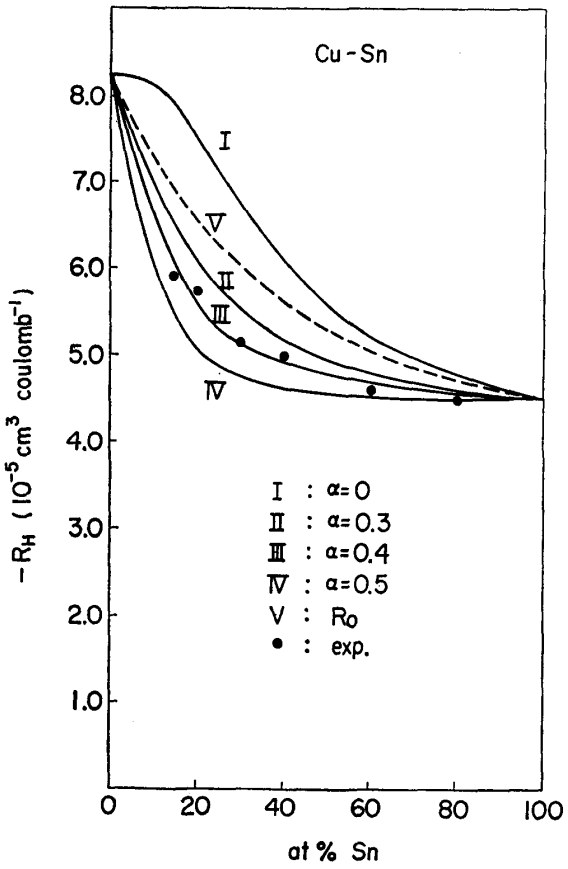

Fig. 13. The comparison of the observed Hall coefficient of liquid Cu-Sn alloys with curves calculated by Eq. (10) for $\alpha=0$, 0.3, 0.4 and 0.5.

density of conduction electrons, independent of mechanisms of electron scattering. This fact means that conduction electrons in the liquid copper alloys behave as free electrons.

V. Temperature variation of Hall coefficient

Our previous reports[3] show a considerable temperature dependence of the electrical resistivity or magnetic susceptibility for the copper liquid alloys. It can be considered that these temperature dependences are caused by the change in n_R/N with temperature. On the other hand we can find no temperature variation for the observed Hall coefficients as shown in Figs. 2, 3 and 4. An explanation for this phenomenon may be given as follows: The density of conduction electrons in liquid alloy is,

$$n=\frac{\bar{Z}-2py}{\bar{\Omega}-a\Omega_R{}^0 y} \tag{12}$$

where

$$\bar{Z}=Z_A(1-x)+Z_Bx\,, \tag{13}$$

$$\bar{\Omega}=\Omega_A(1-x)+\Omega_Bx \tag{14}$$

and

$$y=\frac{n_R}{N}<1\,. \tag{15}$$

n in Eq. (5) can be expressed in a power series expansion of y, so that

$$n=\frac{\bar{Z}}{\bar{\Omega}}+\frac{a\bar{Z}\Omega_R{}^0-2p\bar{\Omega}}{\bar{\Omega}^2}y-\frac{(a\bar{Z}\Omega_R{}^0-2p\bar{\Omega})a\Omega_R{}^0}{\bar{\Omega}^3}y^2+\cdots\,. \tag{16}$$

In the case of the liquid Cu-Sn alloy, we may use the approximation,

$$\Omega_R{}^0\fallingdotseq 5\bar{\Omega}\,. \tag{17}$$

Accordingly, it follows that,

$$n=\frac{\bar{Z}}{\bar{\Omega}}\left[1+\left(5a-\frac{2p}{\bar{Z}}\right)y-5a\left(5a-\frac{2p}{\bar{Z}}\right)y^2+\cdots\right] \tag{18}$$

For the case of $x=0.2$ where concentration of the pseudo-molecule n_R/N takes the maximum value, we have $y=0.136$, $a=0.4$ and $p=1$ at 1100°C. Therefore it follows

$$n=\frac{\bar{Z}}{\bar{\Omega}}(1+0.75y-1.5y^2)=\frac{\bar{Z}}{\bar{\Omega}}\times 1.073 \tag{19}$$

It is calculated that $(n_R/N)_{\max}$ at $x=0.2$ increases by about 10% if temperature decreases from 1100° to 900°C without any change in p. When y increases to 0.17 by the decrese in temperature from 1100°C to a temperature lower than 900°C, n becomes

$$n=\frac{\bar{Z}}{\bar{\Omega}}\times 1.099\,. \tag{20}$$

Hence, n increases by only about 2%. Even in a case where p increases to 1.5 from 1 and α increases to 0.6 from 0.4 in addition to the above increase in y, the increase in n is only about 2%. Therefore, these increases in density of conduction electrons can not contribute to any appreciable change in the Hall coefficient.

Summary

(1) The Hall coefficient of liquid alloys Cu-Bi, Cu-Sb, Cu-Sn and Cu-In has been measured by means of the alternating current and alternating magnetic field method over the temperature range from 500°C to 950°C. Alternating current of frequency f_1=73 Herz and alternating magnetic field of f_2=63 Herz are used and only the signal of f_1-f_2=10 Herz in the Hall voltage is selectively amplified for measurement.

(2) No temperature variation of the Hall coefficient is observed for various compositions of the liquid alloys.

(3) In the case of the liquid Cu-Bi alloy the observed composition dependence of the Hall coefficient is in good agreement with the curve R_0 calculated with the free electron approximation, but those for the liquid alloys Cu-Sb, Cu-Sn and Cu-In are found to be different from their R_0 values.

(4) The electrical properties of the latter group of liquid alloys are characterized by the existence of pseudo-molecules, which consist of several ions bound together, in addition to free ions in random distribution. Their conduction electrons, therefore, are scattered by the above pseudo-molecules and free ions.

As the Hall coefficient depends only upon the density of conduction electrons, it is a function of the number of pseudo-molecules n_R, the number of electrons localized in pseudo-molecules $2p$ and an effective volume of pseudo-molecule $\alpha\Omega_R{}^0$.

(5) The calculated Hall coefficients with α=0.4 for the liquid Cu-Sn alloy and α=0.45 for the liquid Cu-In alloy, which have been estimated from our previous data on the electrical resistivity, are found to be in good agreement with the measured value of the coefficients.

(6) The temperature variation of the Hall coefficients calculated from the above consideration is found negligibly small to be measured experimentally.