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Electron transport properties of Cu-based alloy films

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The resistivity (ρ), Hall coefficient (R_H), temperature coefficient of resistance (TCR), and mobility (μ) of Cu-based alloy films containing 1, 2, and 5 at.% of Al, Ge, and Sn, in the temperature range 80–600 K, have been investigated. The resistivity increases linearly (and the TCR decreases correspondingly) with concentration of the impurities in accordance with Matthiessen's rule. The magnitude as well as the temperature dependence of R_H and μ decrease on addition of impurities. At a concentration of 5-at.% Ge and Sn, the temperature dependence of R_H is reversed. The addition of 5-at.% Al makes R_H independent of temperature. The observed electron transport properties have been explained in terms of scattering behavior of electron and hole states in a mixed conduction mechanism, and distortions in the Fermi surface.

I. INTRODUCTION

We have established[1-3] that large contributions of structural defects to such electron-transport properties as ρ, R_H, and thermoelectric power (TEP) of Cu films have to be understood in terms of marked changes in the number of carrier states (n), the energy dependence of the relaxation time (τ), mean free path (l), and the effective mass (m^*) produced by distortions in the nonspherical Fermi surface of Cu. Progressive distortions of the Fermi surface[4-8] and enhanced anisotropic scattering[7-11] are also known to occur in noble metals by addition of impurities. From the point of view of both understanding fundamental aspects of the physics of metals as well as technical applications of thin metal films in microelectronics, a natural question arises as to how the Fermi surface and consequently the electron-transport properties of a metal film are modified by the presence of defects and impurities. In particular, one would like to know the influence of defects and impurities on the transport properties and hence such parameters as n, m^*, τ, and μ. This can be achieved by a systematic and simultaneous study of ρ, R_H, and TEP on the same specimens of a typical noble metal such as copper. The convenience of preparing alloys of various compositions and that of transport measurements make thin films ideally suited for electron-transport studies. No such studies have, however, been reported in the literature on any metal system.

A few limited studies on R_H[4-11] and TEP[12-15] of α-phase alloys of bulk metals have revealed considerable difficulties in understanding the observed results. Taking the particular case of bulk α-phase alloys of copper, the resistivity obeys[16-19] Matthiessen's rule (generally above 80 K) so that scattering from impurities is simply additive to the ideal phonon scattering of the solvent metal. However, studies of Hall coefficients[8] present a bewildering confusion. The typical behavior[8,11] is a steep drop in $n^* = 1/|R_H| Nec$ with increasing number of available conduction electrons ($n = \mathfrak{z}$, number of available conduction electrons per atom) followed by a steady rise displaced from the corresponding free-electron value. These observations cannot be reasonably explained[4,8] in terms of distortions of the shape of the Fermi surface alone; the scattering mechanisms must also be considered. It has been further suggested[8] that the initial rapid changes in n^* occur as the resistivity due to the impurity scattering (ρ_I) becomes dominant over the ideal resistivity due to phonon scattering (ρ_p). Thereafter, there is a steady rise in n^* corresponding to the new form of $\tau(\vec{k})$ resulting from the swelling of the Fermi surface as more electrons are added to the solvent metal. For some series of α-phase alloys, the two contributions have been separated[20-23] empirically with the scattering contribution being dependent on concentration and temperature while the other contribution depends only upon the $\mathfrak{z}$ value. The latter contribution is in accordance with Ziman's[8] predictions for reasonable values of the energy-gap parameter u.

The scattering contribution to R_H requires[14] anisotropy [$A_I = (\tau_N/\tau_B)_I$, the ratio of relaxation times at neck and belly regions of the Fermi surface] of scattering by impurities to be less than one. The same has also been predicted theoretically.[9] However, the results on the temperature dependence of R_H of several alloys cannot be explained[11] unless we assume A_I greater than one. The existence of anisotropic scattering for phonons as well as impurities is also evident from ultrasonic attenuation,[24] de Haas–van Alphen effect,[25] deviations from Matthiessen's rule,[26,27] electronic specific heat,[28] and infrared absorption[29] measurements on Cu and its alloys. Unfortunately, these results show[30] that different values of A_I are required to explain different properties of the same

systems. Also, different values of A_I derived from the experimental data cannot be understood or reconciled. The conclusions are hampered by the fact that data on the temperature dependence of R_H of various alloys are lacking. These data are expected to give most valuable information on the role of the scattering mechanisms. A similar situation exists for the thermoelectric-power[12–15] data on dilute Cu-based alloys.

The preceding discussion makes it clear that the behavior of R_H (and TEP) of bulk α-phase alloys of copper (and also other noble metals) is hardly understood, largely as a result of lack of appropriate data. This calls for a comprehensive study of transport properties in one or more of the alloy systems. We have thus undertaken a study of the electron-transport properties of Cu alloys with Ge, Sn, and Al in thin-film form. These alloying impurities have been chosen because they dissolve substitutionally[31] in Cu and have a large scattering potential due to their valency being different from that of Cu by 2 and 3. Germanium and tin, which are expected to provide the same number of electrons (=3), have been chosen to delineate the effect of scattering on R_H by two different solute atoms. This paper reports results on resistivity, temperature coefficient of resistance (TCR), R_H, and μ of Cu-based alloy films. The results on TEP are discussed elsewhere.[32]

II. EXPERIMENTAL DETAILS

Alloys of copper with Sn, Al, and Ge of 1-, 2-, and 5-at.% concentrations were prepared by mixing respective materials of 99.999% purity in proper proportions and heating them in a graphite boat in vacuum for about an hour. The temperature of the boat was so adjusted that no evaporation of the constituents could take place as indicated by a quartz-crystal monitor placed near the boat. Films of dilute copper alloys were obtained by thermal evaporation of the bulk alloy from a tungsten basket, in a vacuum ~10^{-6} Torr. Deposition was carried out through a mask onto suitably cleaned glass substrates (with predeposited thick-Cu-film contacts) held at temperatures ranging from 80 to 600 K. The rate of evaporation and film thickness were controlled by a quartz-crystal monitor precalibrated against thicknesses measured (to an accuracy of 20 Å) by Talystep. The films were subsequently annealed *in situ* and measurements of ρ and R_H, at 80 to 600 K, were performed[33,34] simultaneously using Van der Pauw's technique. The fact that the results of measurements on these films could be reproduced by deposition in different sequences from the same melt shows that the film composition was maintained throughout. The composition of some alloy films was checked by mass-spectrometer analysis. The microstructure of the films deposited on mica substrates was investigated by transmission electron microscopy and electron-diffraction techniques.

III. RESULTS

The diffraction pattern of the alloy films showed the existence of a single homogeneous polycrystalline phase having fcc structure. There was no segregation of the constituents in any of these as-deposited films, nor on annealing and deposition at elevated temperatures. The grain size estimated from the transmission electron micrographs was found to be same as that of similarly prepared pure-Cu films.[2] No significant difference was found from the corresponding Cu films[2] even on annealing.

The thicknesses of the alloy films used in our studies are in the range from 800 to 1100 Å. The choice of thickness for measurements of transport properties is determined by the fact that, in this range of thickness, the size effects arising from the limitation of the mean free path are found to be negligible, as expected.[33]

The large number of structural defects (mainly vacancies) frozen in during the formation of a vapor-deposited film contribute significantly to the electron-transport properties. On annealing these films, the defects migrate/annihilate and bring about changes in these properties. A typical annealing curve showing changes in resistivity of some alloy films is shown in Fig. 1. The effect of both annealing temperature and deposition temperature on ρ and R_H of some alloy films is shown in Figs. 2 and 3. Note that R_H is plotted deleting its negative sign. For reasons associated with the nucleation and the growth kinetics[33–35] of a vapor-deposited film, deposition at an elevated temperature has a larger effect on transport properties than annealing of a low-temperature deposited film at the same elevated temperature. From Figs. 1–3, it is clear that the defects anneal out completely at ~500 K so that no further irreversible changes in ρ and R_H occur on raising the temperature beyond 500 K. Thus, from the measured data on ρ and R_H of as-deposited and annealed copper and copper-based alloy films, the contributions due to structural defects and impurities can be separated. The results on resistivity, so obtained, are shown in Fig. 4. The impurity contribution ($\Delta\rho$) to the resistivity increases linearly with impurity concentration and its value of 1.50, 3.75, and 2.75 $\mu\Omega$ cm/at.% for Al, Ge, and Sn, respectively, is nearly the same as that observed[16]

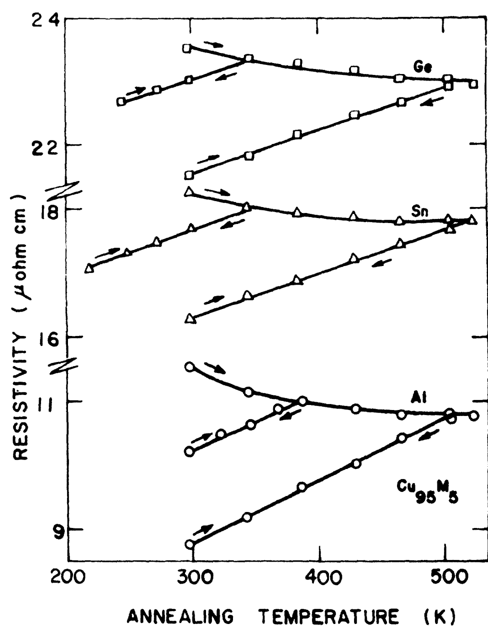

FIG. 1. Variation of resistivity of Cu-based alloy films deposited at 300 K with cyclic annealing at higher temperatures, indicating reversible and irreversible changes.

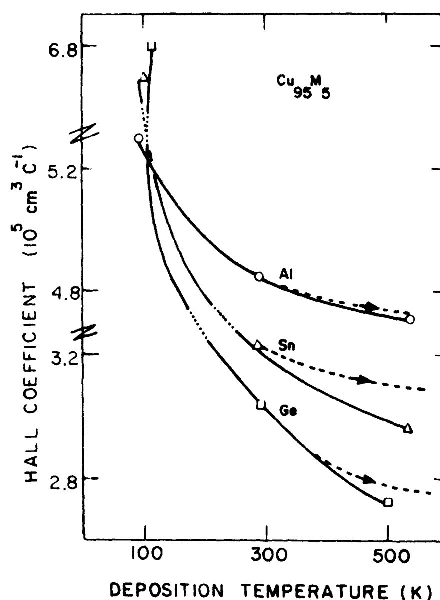

FIG. 3. Variation of negative Hall coefficient (at 300 K) of Cu-based alloy films with temperature of deposition. The dotted curve represents the variation of R_H of films deposited at 300 K with annealing temperature. Note that the negative sign of R_H is deleted in this and all other figures.

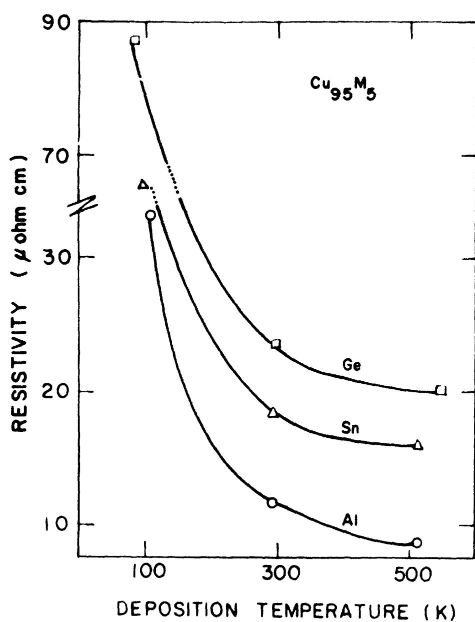

FIG. 2. Variation in resistivity (at 300 K) of Cu-based alloy films with temperature of deposition.

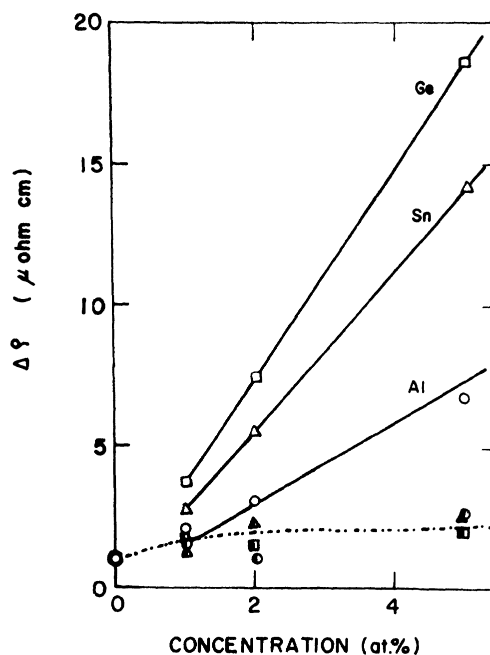

FIG. 4. Contributions to the resistivity of Cu films by (1) impurities (——) and (2) structural defects (–·–·) in films of different compositions. The half-filled symbols in the dashed curve refer to the alloy systems represented by the corresponding open symbols.

in corresponding bulk systems. The contribution of the structural defects to the resistivity (shown by dash-dotted line in Fig. 4) is almost the same in the three alloy systems. Its value is, however, larger than that found in pure-Cu films[2] deposited under the same conditions. This point is discussed later. The temperature dependence of the resistivity of the alloy films is essentially linear (see Fig. 1). The corresponding values of the TCR of annealed films are shown in Fig. 5.

Figure 6 shows the contributions of impurities and structural defects to the Hall coefficient of copper films. The Hall coefficient decreases smoothly with Al concentration. On the other hand, for Cu-Sn and Cu-Ge systems, it decreases rapidly first and then very slowly beyond 2-at.% concentration. The corresponding mobility of these alloy films, obtained from the relation $\mu = R_H/\rho$, is shown in Fig. 7.

The temperature dependence of R_H of various as-deposited (at 300 and 500 K) and annealed (at 500 K) alloy films is shown in Figs. 8–10. By normalizing the data with respect to the room-temperature values of R_H, the variation of R_H with temperature for various alloy systems has been replotted, as shown in Fig. 11. Clearly, all the three impurities tend to reduce the temperature dependence of R_H at low temperatures with increasing concentration. A reverse temperature dependence is observed at 5-at.% Ge, 2-at.% Sn, and 5-at.% Sn concentrations.

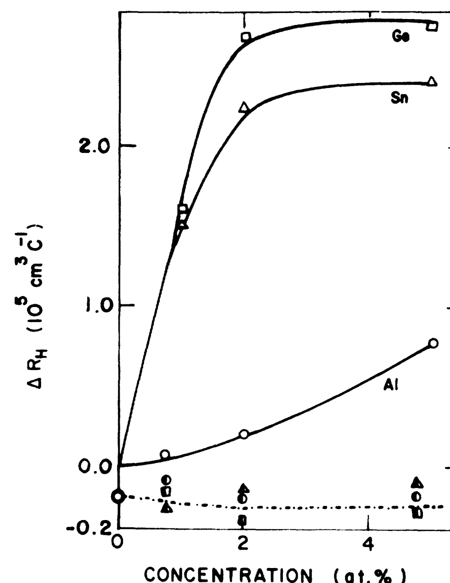

FIG. 6. Contributions to the negative Hall coefficient of Cu films by (1) impurities (——) and (2) structural defects (–•–•) in films of different compositions. The half-filled symbols in the dashed curve refer to the alloy systems represented by the corresponding open symbols.

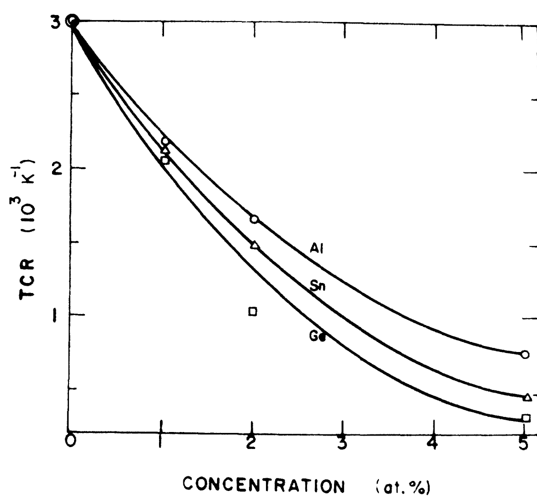

FIG. 5. Variation of temperature coefficient of resistivity (TCR) at 300 K with concentration of various impurities in annealed Cu films.

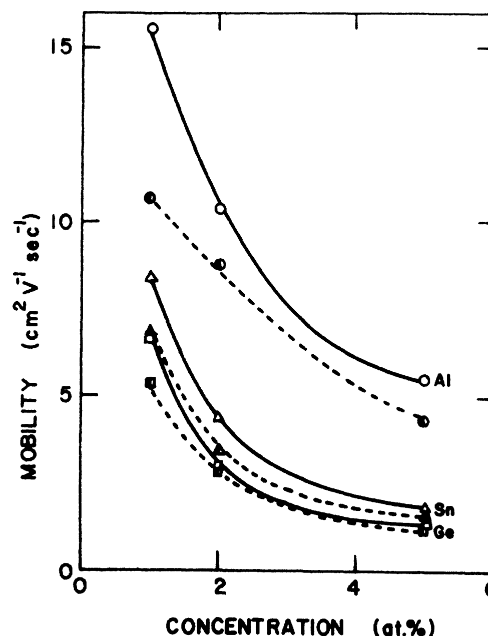

FIG. 7. Variation of mobility with concentration of Al, Ge, and Sn in (1) as-deposited (at 300 K) Cu films (---) and (2) annealed (at 500 K) Cu films (——).

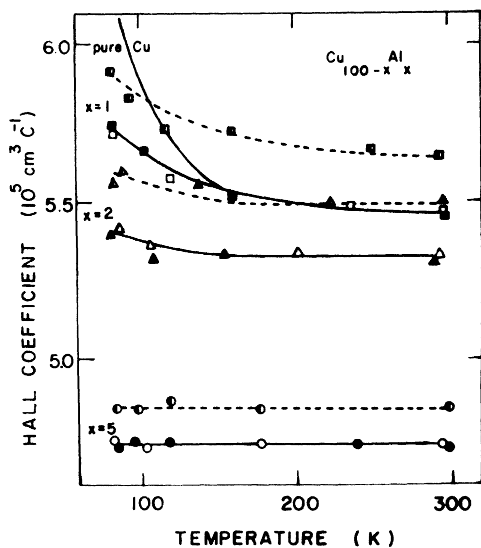

FIG. 8. Temperature dependence of negative Hall coefficient of Cu-Al alloy films. Half-filled symbols—as-deposited (at 300 K) films; open symbols—films deposited at 300 K and annealed at 500 K; and completely filled symbols—films deposited at 500 K.

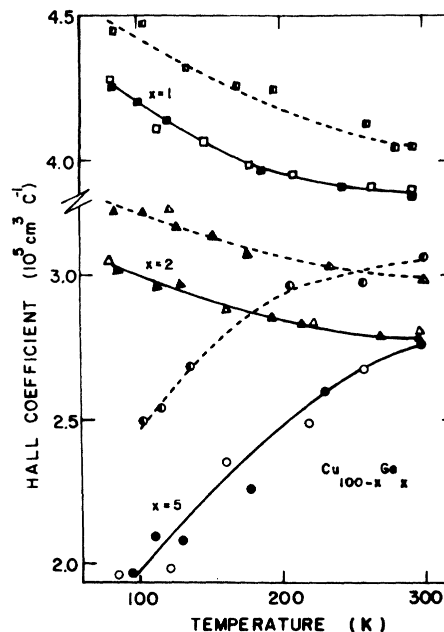

FIG. 10. Temperature dependence of negative Hall coefficient of Cu-Ge alloy films. The description of symbols is same as that in Fig. 8.

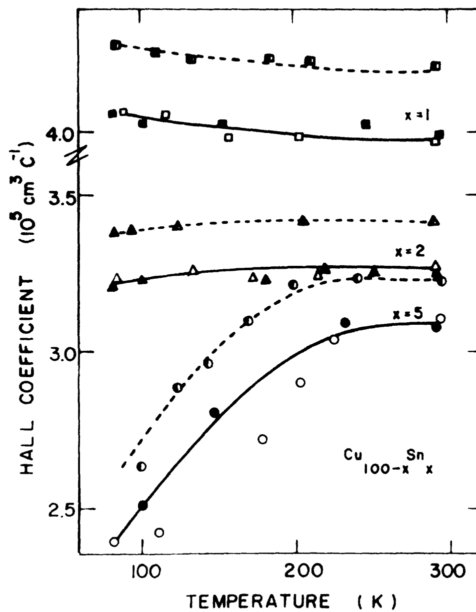

FIG. 9. Temperature dependence of negative Hall coefficient of Cu-Sn alloy films. The description of symbols is same as that in Fig. 8.

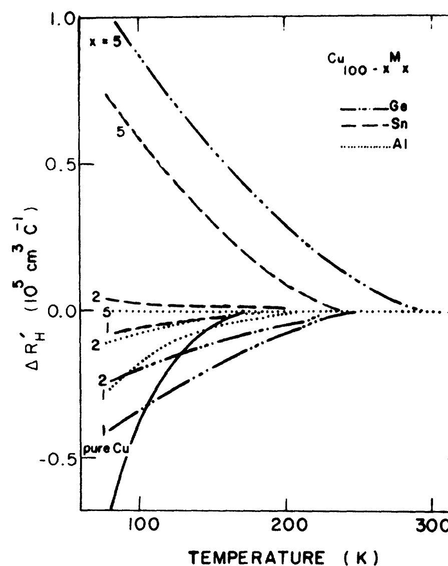

FIG. 11. Temperature dependence of negative R_H of a series of Cu-based alloy films normalized to the corresponding room-temperature values.

IV. DISCUSSION

A comparison of the annealing behavior (dependence on deposition and annealing temperature) of ρ and R_H of Cu-based alloy films with that of pure-Cu films[1,2] shows that their annealing kinetics are similar. Since the grain sizes of corresponding Cu and Cu-based alloy films are nearly the same, it follows that the defect structure associated with the grain boundaries in the two cases is nearly alike. Thus, as in pure-Cu films, the excess resistivity in alloy films may be attributed to the presence of vacancies. As seen from Fig. 4, the contribution of defects to resistivity increases with concentration of impurities to reach a constant value of 2 $\mu\Omega$ cm at 1-at.% composition. This corresponds to a vacancy concentration of 1.54 at.% in alloy films as compared to a vacancy concentration of 0.77 at.% found in similarly deposited pure-Cu films. Furthermore, in the case of Cu films,[1,2] we have shown that it is the defects associated with the grain boundaries and not the grain boundaries themselves that are responsible for the additional scattering of current carriers. The observed magnitude of the defect contribution in alloy films suggests that either the vacancy concentration associated per grain boundary is increased on alloying or the scattering power of vacancies has increased.

As already mentioned, the impurity contributions to the resistivity are in accordance with the corresponding bulk values[17-19] and follow Matthiessen's rule. The corresponding TCR $[=1/\rho(d\rho/dT)]$ is found to be proportional to $1/\rho$ ($d\rho/dT$ is constant, see Fig. 1). This result further emphasizes that the contributions of various impurities to ρ are primarily due to additional scattering from these impurities.

The defect contribution to R_H (ΔR_H) increases with concentration of Al, Ge, and Sn from a value of -0.20 units for pure-Cu films to a value of -0.26 units for 1-at.% compositions. It is constant for concentrations greater than 1-at.%. Following arguments advanced elsewhere[2] in the case of resistivity, this contribution can be attributed to a vacancy concentration of ~0.7 at.%. Since mobility is derived from R_H and ρ, the changes in μ on annealing are understandable.

Although the resistivity increases linearly with impurity concentration, the magnitude of R_H (and hence μ) first decreases rapidly on addition of 1-at.% Al, Ge, and Sn and thereafter gradually. It appears that changes in R_H and μ occur as impurity scattering becomes comparable to that by phonons (that is, $\rho_p \sim \rho_I$). Thus, when impurity conduction dominates, changes in R_H and μ are small. In sharp contrast to the variation of the magnitude of R_H, its temperature dependence shows gradual changes with increasing concentration of alloying impurities (Fig. 11). The magnitude and temperature dependence of R_H of alloy films can be understood by the following analysis.

In a mixed-conduction mechanism due to electron and hole states, the Hall coefficient is given[36] by

$$R_H = \frac{n_h \mu_h^2 - n_e \mu_e^2}{(n_h \mu_h + n_e \mu_e)^2} \frac{1}{Nec} . \quad (1)$$

The temperature dependence of R_H follows from Eq. (1):

$$\frac{dR_H}{dT} = \left[\left(2n_h \mu_h \frac{d\mu_h}{dT} - 2n_e \mu_e \frac{d\mu_e}{dT}\right)(n_h \mu_h + n_e \mu_e)^{-2} - 2(n_h \mu_h^2 - n_e \mu_e^2)(n_h \mu_h + n_e \mu_e)^{-3}\left(n_h \frac{d\mu_h}{dT} + n_e \frac{d\mu_e}{dT}\right)\right] \frac{1}{Nec} . \quad (2)$$

Since $\mu = e\tau/m$, we have

$$\frac{dR_H}{dT} = \left[2e\left(\frac{n_h \mu_h}{m_h} \frac{d\tau_h}{dT} - \frac{n_e \mu_e}{m_e} \frac{d\tau_e}{dT}\right)(n_h \mu_h + n_e \mu_e)^{-2} - 2eR_H (n_h \mu_h + n_e \mu_e)^{-1}\left(\frac{n_h}{m_h} \frac{d\tau_h}{dT} + \frac{n_e}{m_e} \frac{d\tau_e}{dT}\right)\right] \frac{1}{Nec} . \quad (3)$$

It can be easily verified that the sign of dR_H/dT will be determined by the first term comprising of the differentiation of the numerator in Eq. (1) (which determines the effective balance of holes and electrons). The second term, which comprises the differentiation of the denominator of Eq. (1) is a second-order effect and is small in magnitude. Hence we may consider the first term only.

Identifying electron states to the states lying in the belly (subscript B) regions of the Fermi surface and hole states to those lying in the neck (subscript N) regions of the Fermi surface, we can rewrite Eq. (3) as

$$\frac{dR_H}{dT} = \frac{1}{Nec} 2e\left(\frac{n_N \mu_N}{m_N} \frac{d\tau_N}{dT} - \frac{n_B \mu_B}{m_B} \frac{d\tau_B}{dT}\right) \times (n_N \mu_N + n_B \mu_B)^{-2} + \cdots . \quad (4)$$

The magnitude and temperature dependence of R_H of Cu on addition of various concentrations of

impurities can be understood in terms of Eqs. (1) and (4) as follows.

A. Temperature dependence of R_H of pure Cu

It is well known[9] that the probability of umklapp processes to occur for electron states at belly regions decreases at low temperatures until a cutoff is reached at a particular temperature where these processes are completely frozen. However, for hole states (that is electron states at necks), all scattering processes are allowed. Consequently, the increase of relaxation time with decreasing temperature is larger[9,11,36] for belly states than that for neck states. Thus,

$$\left|\frac{d\tau_B}{dT}\right| > \left|\frac{d\tau_N}{dT}\right|$$

or (5)

$$\frac{d\tau_B}{dT} < \frac{d\tau_N}{dT}$$

since $d\tau/dT$ is negative in both cases. From Eqs. (5) and (6), one finds that dR_H/dT is positive, so that R_H will decrease at low temperatures. Since R_H is negative in pure Cu, R_H will therefore become increasingly negative, in accordance with the experiment results.

From the experimental (and theoretical) data[30,37] for bulk Cu, we know that the effective mass of hole states at necks is 0.46 (in free-electron mass units) while that at belly is 1.37. Since $\mu = e\tau/m$ and $\tau_N = \tau_B$ at 300 K, $\mu_h/\mu_e = m_e/m_h = 1.37/0.46$. On the basis of Eq. (1), the ratio of the number of hole states to that of electron states required to explain the observed R_H [$= -5.5$ units, R_H (free electron) $= -7.45$ units] of Cu at 300 K is $\frac{2}{98}$. At 80 K, the scattering at necks and bellies is such that $\tau_N = 0.8\tau_B$. Since the number of carrier states is not expected to change, $\mu_h/\mu_e = \tau_h m_e/\tau_e m_h \simeq (0.8\times 1.37)/0.46$ and $n_h/n_e = \frac{2}{98}$. Substituting these values in Eq. (1), we get, R_H at 80 K $= -6.1$ units which is close to the experimental value. Thus the temperature dependence of R_H of pure Cu can be understood in terms of a mixed-conduction mechanism by taking the relative scattering at neck and belly regions into account and assuming that the number of carrier states remains the same.

B. Effect of impurities

The belly regions of the Fermi surface of Cu correspond[38] to electron states (having s symmetry, with maximum amplitude at the ion sites). The neck regions correspond to holelike states (having p symmetry, with maximum amplitude in between the ion sites). The impurities Al, Ge, and Sn are known to go substitutionally[31] in copper. From symmetry considerations, it follows that electrons in belly states will be scattered more severely than holes in the neck states, implying thereby that $\tau_N > \tau_B$. Consequently, on addition of these substitutional impurities, R_H will become more positive in agreement with the observed experimental results on alloy films. Note that since these impurities have large perturbation potentials extending to few atomic dimensions, the holes in the neck states are also scattered by these impurities but to a much lesser extent than electrons in the belly states.

Since $\rho_I \gg \rho_p$, especially for 5-at.% impurities, a large part of τ_B consists of τ_{BI} while a large part of τ_N is due to τ_{Np} which is temperature dependent. Thus,

$$\left|\frac{d\tau_N}{dT}\right| > \left|\frac{d\tau_B}{dT}\right| . \tag{6}$$

Since $d\tau/dT$ is negative for both the bands, $d\tau_N/dT < d\tau_B/dT$. According to Eq. (4) $|n_N\mu_N(d\tau_N/dT)| > |n_B\mu_B(d\tau_B/dT)|$, that is, dR_H/dT will become negative so that R_H will increase as the temperature is reduced. Since R_H is still negative for alloy systems and the majority carriers are still electronlike, the magnitude of R_H decreases with decrease in temperature. This agrees with the results for 5-at.% Ge and Sn alloys. Thus, we have shown that without actually changing the number of electron and/or hole states, the differential scattering by impurities at the two regions of the Fermi surface reverses the temperature dependence of R_H of Cu. The same arguments also explain the observed temperature dependence of R_H in Al, In, and Pb,[38] which have dominant states available for conduction as those lying in the hole zone (second Brillouin zone) and for which dR_H/dT is negative irrespective of the sign of R_H. Thus, whereas the magnitude of R_H is determined by electrons, its temperature dependence is dominated by hole conduction.

We can now calculate from Eq. (1) the ratio of μ_e/μ_h for various values of R_H. Taking n_h/n_e to be the same ($= \frac{2}{98}$) as that for pure Cu and further assuming that the effective masses of electrons and holes remain unchanged in dilute alloys, the ratio μ_e/μ_h ($\equiv \mu_B/\mu_N$) yields directly τ_N/τ_B. The results so obtained are shown in Fig. 12. For comparison, we have also shown the theoretical plots obtained by Matsuda[11] and Dugdale and Firth[10] on the basis of a two-band model. The three curves differ from each other appreciably. Matsuda's calculations are made by dividing the Fermi surface of copper into eight similar cones[8] having $n = 1$ and $u = 0.40$. The value of u taken is questionable as it is quite different from that observed in bulk Cu ($u = 0.20$).[8] Our calculations are based

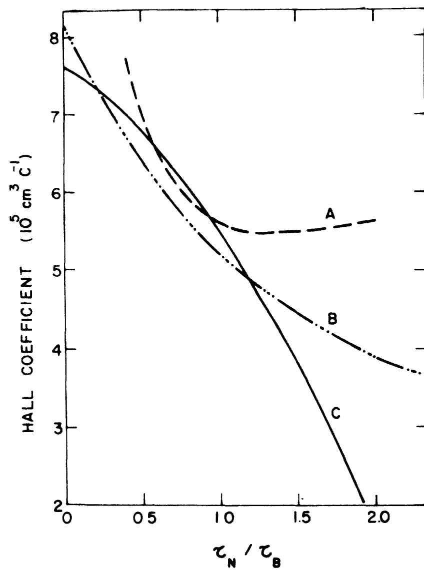

FIG. 12. The calculated dependence of negative Hall coefficient on anisotropy (τ_N/τ_B) of relaxation time. A—Matsuda; B—Dugdale and Firth; and C—present work.

on a simplified two-band model in which n_e/n_h and m_e/m_h are assumed to be constant and same as that in pure Cu. The calculations of Dugdale and Firth, based on Tsuji's[39] generalized expression of R_H, also consider only scattering at neck and belly regions to be different, with the other transport parameters being constant. Their results differ from ours probably because their method of integration involves a different value of m_e/m_h and n_e/n_h. This is supported by the fact that the limiting value of R_H for $\tau_N/\tau_B \to 0$, which is a function of n_e only, is different for the two cases (see curves B and C in Fig. 12). It is important to note that, in a two-band model, R_H can be increased to a maximum value of -7.6 units by changing the ratio of τ's or m's. This value is close to the free-electron value[36] of -7.45 units, the difference of 0.15 units is obviously due to the existence of a small number (2%) of hole states. Physically speaking, $\tau_N/\tau_B \to 0$ implies that the necks do not contribute to the process of conduction and R_H approaches the free-electron value.

With the help of curve C of Fig. 12, values of τ_N/τ_B can be calculated from the corresponding values of R_H for alloys of different compositions. Some typical values of τ_N/τ_B as a function of concentration and temperature are shown in Figs. 13–15. The corresponding values of μ_e/μ_h are also shown. By substituting these values of μ_e/μ_h, we have verified that dR_H/dT is indeed negative for 5-at.% Sn, 5-at.% Ge and 2-at.% Sn alloys and is

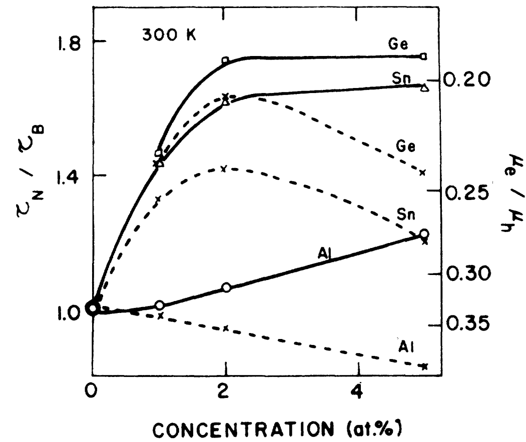

FIG. 13. Variation in anisotropy τ_N/τ_B (and the corresponding μ_e/μ_h) at 300 K (——) with concentration of alloying impurities in Cu films. The cross (✕) symbols show the corresponding variation when the distortions are also taken into account.

positive for all other alloy films as also for pure Cu. This is obviously a cross check and indicates that though

$$|n_h \mu_h^2| < |n_e \mu_e^2|, \qquad \left| n_h \mu_h \frac{d\mu_h}{dT} \right| > \left| n_e \mu_e \frac{d\mu_e}{dT} \right| \tag{7}$$

holds for reasonable values of μ_e/μ_h. A close examination of Eq. (1) reveals that this is due to the fact that μ_h is greater than μ_e by a factor of

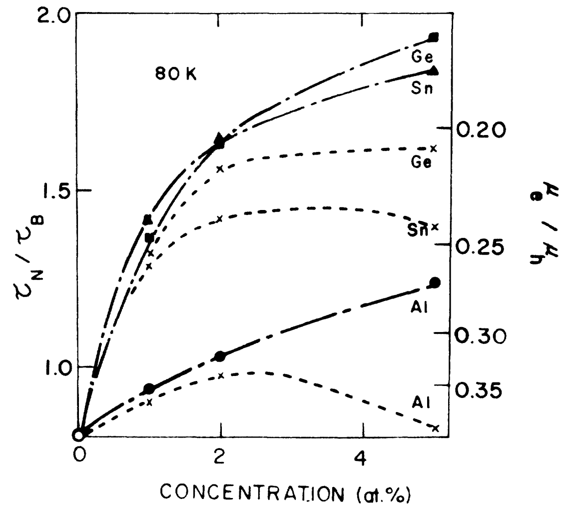

FIG. 14. Variation in anisotropy τ_N/τ_B (and the corresponding μ_e/μ_h) at 80 K (–·–·) with concentration of alloying impurities in Cu films. The cross (✕) symbols show the corresponding variation when the distortions are also taken into account.

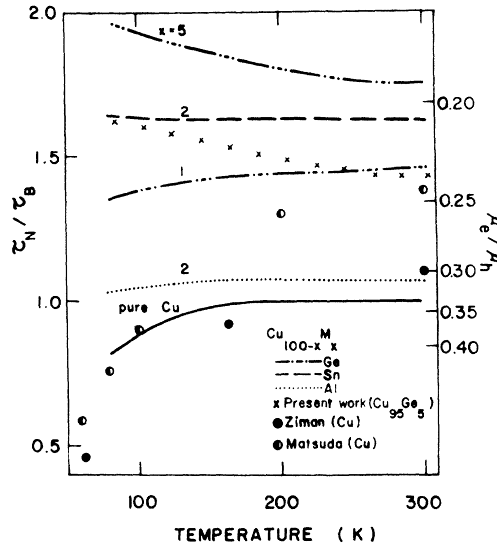

FIG. 15. Variation of τ_N/τ_B with temperature for Cu and some Cu-based alloy films. The values calculated by Matsuda and Ziman, for pure Cu, are also drawn. The cross symbols indicate the variation of τ_N/τ_B when distortions are taken into account.

nearly three in pure Cu. Any further decrease in the electron mobility would bring about a considerable change in R_H and a still larger change in dR_H/dT.

It is important to emphasize here that the above treatment of the Hall coefficient of Cu in terms of changes in μ_e does not affect the corresponding resistivity values of the alloy films.

The deduced values of τ_N/τ_B ($\equiv A_I$) are large, particularly for 5% alloys, primarily because we have so far neglected contributions due to distortions in the Fermi surface. Taking these contributions into account, more reasonable values of τ_N/τ_B are required to explain the observed results. The effect of distortions in alloy films can be calculated by using the published data[22] on similar bulk alloys. For series of bulk Cu-based alloys, the Hall coefficient may be separated[23,36] empirically into two terms, one associated with the band structure (and hence the distortions in the Fermi surface) and the other associated with the scattering mechanism. Assuming the values of distortion contribution to R_H in alloy films to be same as that in bulk, we have deduced the values of τ_N/τ_B from the observed values of R_H of alloy films. The results are shown in Figs. 13–15. As seen, these values of τ_N/τ_B are physically more meaningful.

The distortions in the Fermi surface are expected to change the ratio of the effective masses of electrons and holes in the two bands as well as the ratio of the number of corresponding states. The distortion contribution due to these factors can also be calculated by using Eq. (1), that is, from mixed-conduction mechanism. Some of the typical parameters so calculated from curve C of Fig. 12 are shown in Table I. For comparison, the values of n, τ, m^*, and μ for electrons and holes in pure Cu are also shown. It may be noted that R_H becomes very sensitive to the choice of n_e/n_h and hence τ_N/τ_B because of the large weightage of the first term in Eq. (1). Further, the values of τ_N/τ_B required to explain the observed results on R_H of alloy films are reduced by increasing the ratio of n_h/n_e or m_e/m_h.

We have shown that changes in R_H of Cu on alloying can be understood in terms of scattering behavior of electrons and holes in a mixed-conduction mechanism. The difference in the behavior of Ge and Sn impurities is primarily due to the known[16–19] different scattering power of these impurities.

Our interpretation of the results is based on simplifying assumptions and average values of the transport parameters. A more rigorous analysis of the results should consider the variation of all the transport parameters within each band.

Finally, a comparison of our results with those on the TEP behavior of alloy films is of interest.

TABLE I. Values of R_H given below are in units of -10^5 cm^{3}C^{-1}, those of m^* are in free-electron mass units, and n_e and n_h denote the percentage of electrons and holes.

	R_H at 300 K	R_H at 80 K	n_e	n_h	m_e^*	m_h^*	μ_e/μ_h at 300 K	τ_N/τ_B at 300 K	μ_e/μ_h at 80 K	τ_N/τ_B at 80 K
Pure Cu	5.5	6.1	98	2	1.37	0.46	0.3357	1.0	0.420	0.8
$Cu_{95}Sn_5$	3.1	2.4	98	2	1.37	0.46	0.201	1.67	0.183	1.84
$Cu_{95}Sn_5$	3.1	2.4	95	5	1.37	0.46	0.3357	1.0	0.280	1.2
$Cu_{95}Sn_5$	3.1	2.4	98	2	2.29	0.46	0.201	1.0	0.183	~1.2

Whereas the addition of impurities tends to make R_H of Cu more holelike, the TEP tends towards a more electronlike character. Vacancies tend to make R_H as well as TEP more electronlike. On the other hand, dislocations tend to make the thermopower of Cu films more holelike while R_H remains unaffected. Further, we have shown[2,3] that the effect of vacancies and dislocations on TEP (as also R_H[2]) can be understood only in terms of distortions of the Fermi surface and hence energy dependence of τ, mfp, or m^*. In the preceding discussion, we have shown that the understanding of R_H of alloy films requires both the Fermi-surface distortions and the scattering mechanisms to be taken into account. On the basis of Matthiessen's rule, TEP may be rewritten[40] as

$$S = \sum_i S_i \rho_i \Big/ \sum_i \rho_i = \frac{S_p \rho_p}{\rho} + \frac{S_I \rho_I}{\rho} + \frac{S_d \rho_d}{\rho} + \frac{S_v \rho_v}{\rho} , \quad (8)$$

where subscripts p, I, d, and v refer to phonons, impurities, dislocations, and vacancies, respectively. In well-annealed films, the latter two contributions are expected[2] to be negligible. Further, since ρ_I is significantly larger than ρ_p (typically, for 5-at.% Sn alloy, $\rho_I = 14.45$ $\mu\Omega$ cm as compared to $\rho_p = 1.8$ $\mu\Omega$ cm), the impurity contribution is the dominant factor. For example, the impurity contribution is 0.645 μV/K as compared to the phonon contribution of 0.155 μV/K in $Cu_{95}Sn_5$ films at 300 K. As analyzed elsewhere,[32] two-thirds of the change in TEP on alloying is due to enhanced scattering from impurities and the rest is due to additional distortions of the Fermi surface of Cu. Thus, the behavior of both R_H and TEP can be understood by similar physical mechanisms.

V. CONCLUSIONS

(i) Whereas vacancies make R_H of Cu films more electronlike (magnitude increases), the substitutional impurities Al, Ge, and Sn make it more holelike (magnitude decreases).

(ii) The observed contributions of various impurities to R_H of Cu have to be understood in terms of both, the distortions of the Fermi surface of Cu as well as the differential scattering from neck and belly regions of the Fermi surface and hence anisotropy of $\tau(\vec{k})$. On the other hand, the contribution of vacancies (dislocations do not contribute significantly) to R_H is primarily due to the distortions of the Fermi surface.

(iii) Although the magnitude of R_H of pure-Cu and alloy films is determined by electrons, its temperature dependence is determined by holes and at 5-at.% concentration of the alloys, it is dominated by hole conduction.

(iv) For better quantitative understanding, a more rigorous theoretical analysis which will incorporate actual variation of all transport parameters within a band itself instead of taking average values into consideration is required.

(v) The enhanced anisotropic scattering and distortions of the Fermi surface in alloy films need independent verification by such studies as de Haas–van Alphen and cyclotron resonance on thin films of several alloy systems.

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