Low-field Hall coefficient of α-phase CuAl and dilute magnetic CuAl(Fe) alloys

G. Apostolopoulos and C. Papastaikoudis

Institute for Material Science, National Centre for Scientific Research "Democritos," GR-153 10 Agia Paraskevi, Athens, Greece

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The low-field Hall coefficient of a number of dilute α-phase CuAl alloys and CuAl containing 110-ppm Fe has been measured at 4.2 K as a function of the magnetic field. The difference in the values of the Hall coefficient between the two systems has been interpreted as arising from different anisotropies of the relaxation times of the host conduction electrons. By use of a two-group model for the conduction electrons of copper, it has been found that the relaxation time ratios τ_B/τ_N for the CuAl and CuAl 110-ppm Fe systems amount to 0.63 and 0.82, respectively. The difference in τ_B/τ_N between these two alloys has been attributed to the scattering of the conduction electrons by the localized magnetic moments of the Fe atoms.

I. INTRODUCTION

The significance of the anisotropic electron-impurity scattering in metals has been well recognized and investigated over the last two decades. The electronic transport properties of metals are most conveniently described in terms of an anisotropic relaxation time τ_k which may vary over the Fermi surface. From the measurement of the transport properties and especially from the Hall effect one can obtain information about this anisotropy of the relaxation time.

Most of the experimental and theoretical work concerning anisotropic scattering has been done so far on the noble metals and especially on copper. Ziman[1] was the first, to our knowledge, to realize that the anisotropy of τ_k should originate physically from the different character of the electron wave functions $\psi_k(r)$ in the different regions of the Fermi surface. The electrons in the region of the necks have mainly p-character. They, therefore, move with preference between the ion cores and will be mainly scattered by interstitial defects. On the other hand, electrons from the belly regions have s-character. Hence their density is largest at lattice sites and they will be mostly affected by a scattering potential localized at a lattice site.

According to Ziman's two-band model, the Tsuji[2] expression for the low-field Hall coefficient can be given by

$$R_H = -\frac{12\pi^3}{e}\left| \frac{\tau_B^2 \int_B \left[\frac{1}{\kappa}\right] v^2 dS + \tau_N^2 \int_N \left[\frac{1}{\kappa}\right] v^2 dS}{\left[\tau_B \int_B v\, dS + \tau_N \int_N v\, dS\right]^2} \right|,$$

(1)

where $(1/\kappa) = \frac{1}{2}(1/\kappa_1 + 1/\kappa_2)$ is the mean curvature of the Fermi surface at k and κ_1 and κ_2 are the local principal radii of curvature. τ_B and τ_N are the average relaxation times for the belly and neck areas, respectively, and v the velocity at the point considered.[3]

If the conduction electrons are scattered simultaneously by two types of scatterers, then the total scattering rate

is given by the sum of the scattering rates due to the two different impurities. The scattering mechanisms become more complicated if one of the centers is magnetic.

De Haas–van Alphen (dHvA) Dingle-temperature measurement[4,5] and magnetic-field-induced surface-state resonance studies (SSR) (Ref. 6) in CuAl alloys have shown that the scattering rate τ_k^{-1} is largest for electron states near the $\langle 111 \rangle$ neck and $\langle 100 \rangle$ regions, and it is smallest for the $\langle 100 \rangle$ direction and for regions within an angle of 20° to 30° from the $\langle 100 \rangle$ direction. From Dingle-temperature data it appears that the anisotropy ratio τ_B/τ_N at $\langle 111 \rangle$ direction takes values between 1.20 and 1.29,[5,7] while the ratio τ_{100}/τ_N is 1.04.[7]

On the other hand, measurements of the electrical resistivity on the CuAl alloys with additional Fe impurities show that the $Cu_{1-x}Al_x$ 110-ppm Fe alloy is a Kondo system and that the Kondo temperature T_K increases with Al concentration.[8]

The aim of the present investigation is to find out by measurements of the Hall coefficients as much as possible about the anisotropy of the relaxation time of the conduction electrons in copper under the influence of different scattering centers and to compare with other experimental methods.

II. EXPERIMENTAL PROCEDURE

The dilute CuAl and CuAl(Fe) alloys were prepared from 99.999% pure copper (ASARCO), 99.9997% pure aluminum (VAW, Bonn) and 99.995% pure iron (JMC) by induction melting under an argon gas pressure and then rolled into foils of about 80-μm thickness. The samples were stamped out from these foils with a special steel tool in rectangular shapes (20×2 mm²) with two similar extensions for Hall contacts. For final homogenization, the alloys were annealed at 840 °C for 24 h in a vacuum of about 10^{-6} mbar.

The Hall voltage measurements were carried out in a conventional stainless steel helium cryostat that contained a superconducting solenoid. The resistivity and Hall voltage were measured by the standard four termi-

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nal technique. The dc signals were amplified by a gal-vanometric photocell amplifier (Sefram "Amplispot"). The sample current was reversed in order to eliminate thermovoltage drifts. The final resolution was of the order of 1×10^{-9} V.

III. RESULTS

Figure 1 shows the Hall coefficient R_H of pure poly-crystalline Cu with residual resistivity ratio (RRR) of 1800 and of seven CuAl alloys at 4.2 K in Kohler representation, i.e., plotted as a function of the "effective" magnetic field H/ρ_0, where ρ_0 is the residual resistivity at zero magnetic field. The figure shows that (i) the magnetic field is not high enough in order for the Hall coefficient of pure polycrystalline Cu to reach the high-field value $R_\infty = -14.5 \times 10^{-11}$ m^{3}C^{-1} of a single crystal for $H \| [100]$,[9] (ii) in the low-field region the Hall coefficient R_H is constant and takes values between -5×10^{-11} and -4.2×10^{-11} m^{3}C^{-1}, and (iii) the low-field Hall-coefficient values are higher than the free-electron value $R_{FE} = -7.45 \times 10^{-11}$ m^{3}C^{-1} of copper.

Figure 2 shows the Hall coefficient R_H of pure Cu and six CuAl 110-ppm Fe alloys also in Kohler representation. The figure shows that (i) the low-field Hall coefficient R_H^0 of the CuAl(Fe) system is lower than the R_H^0 of pure Cu, (ii) remains constant at a value of about -5×10^{-11} m^{3}C^{-1}, which means that the Kohler rule is valid, and (iii) its value is smaller than the R_H^0 values of the CuAl alloys.

In Fig. 3 the residual resistivity of the CuAl system and the low-field Hall coefficients R_H^0 of CuAl and CuAl(Fe) alloys, taken at a constant value of $H/\rho_0 = 5 \times 10^6$ T/Ω cm, are plotted as a function of aluminum concentration c at 4.2 K. It can be seen that there is a linear relationship between the residual resis-

tivity of CuAl and the impurity concentration, which means that the Al atoms are distributed statistically in the Cu lattice. The resistivity per atomic percent Al is about 105×10^{-8} Ω cm, in agreement with previous data that lie between 110 and 122×10^{-8} Ω cm.[6,7] This figure shows also that the low-field Hall coefficient of the CuAl system increases rapidly and then saturates to the constant value -4.2×10^{-11} m^{3}C^{-1}, which is more or less independent of the concentration. On the contrary, the respective Hall coefficient of the CuAl(Fe) system saturates very soon to the constant value -4.80×10^{-11} m^{3}C^{-1}. In these regions, the Kohler rule is valid for both systems. The initial increase of the low-field Hall coefficient in the CuAl alloy system is due to the residual impurities, grain boundaries, or dislocations that were produced during the mounting and cooling of the samples.

Figure 4 shows the resistivity of a series of CuAl 110-ppm Fe alloys as a function of ln$T$. From the data it is immediately apparent that the spin-scattering curve, the Kondon step heights $\rho(2$ K$)-\rho(T_{min})$, and the slopes $|d\rho_{spin}/d\ln T|$ are independent of the Al concentration. This indicates that the Kondo temperature T_K of the present alloys remains unshifted. This behavior is not in agreement with previous results in the Cu$_{1-x}$Al$_x$ 110-ppm Fe alloys with Al concentrations between 0 and 11.6 at. %,[8] which show that T_K increases with increasing Al content. The cause of this discrepancy can be referred to the small Al concentration of the present alloys.

IV. DISCUSSION

The present experimental result of the CuAl and CuAl 110-ppm Fe systems show that the low-field Hall coefficient R_H^0 is larger than the isotropic free-electron value R_{FE} and that it depends on the kind of the impuri-
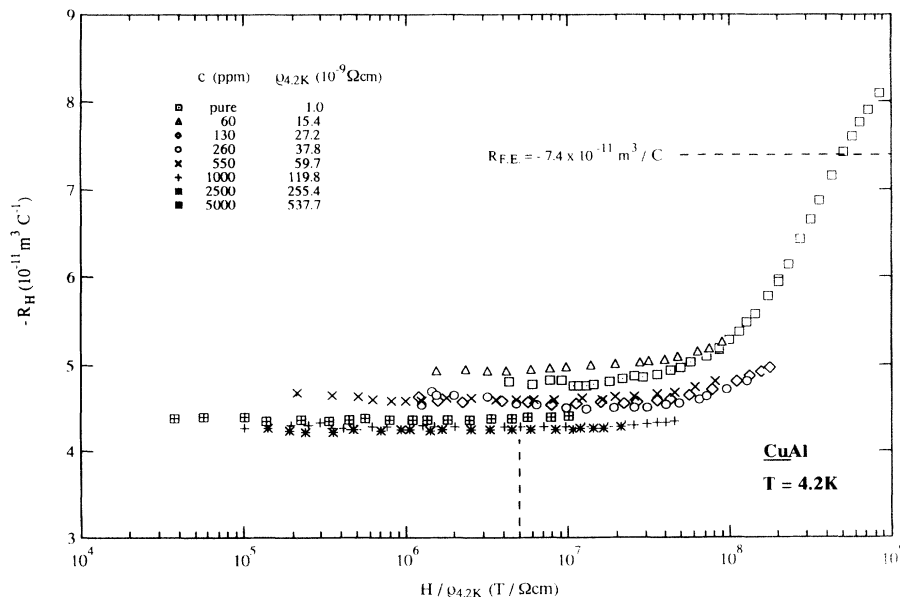

FIG. 1. The Hall coefficient R_H of CuAl alloys as a function of effective magnetic field in the Kohler representation.
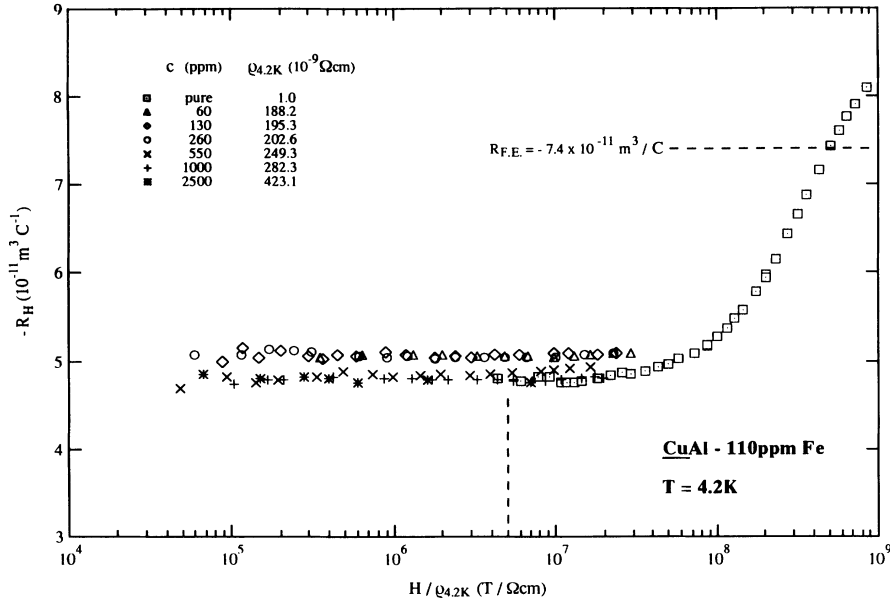
FIG. 2. The Hall coefficient R_H of <u>Cu</u>Al 110-ppm Fe alloys as a function of effective magnetic field in the Kohler representation.

ty. The first fact must be due to an anisotropy of the scattering time τ_k on the Fermi surface.

According to the two-group model of conduction electrons of copper, Barnard[10] has reduced the Tsuji expression (1) to a more simple form which is given by

$$R_H = -7.65 \left[\frac{1+0.054(\tau_N/\tau_B)^2}{[1+0.257(\tau_N/\tau_B)]^2} \right] \times 10^{-11} \text{ m}^3 \text{C}^{-1} .$$

(2)

This formula allows one to obtain the ratio τ_B/τ_N from the low-field Hall-coefficient data. It also allows one to show the influence of the scattering potential on the τ_B/τ_N ratio.

From an extrapolation of the data of Fig. 3 one obtains

for the low-field Hall coefficient of <u>Cu</u>Al and <u>Cu</u>Al 110-ppm Fe systems the values -4.20×10^{-11} m^{3}C^{-1} and -4.80×10^{-11} m^{3}C^{-1}, respectively. In combination with Eq. (2) these values give the relaxation time ratios $\tau_B/\tau_N=0.63$ for the <u>Cu</u>Al alloy and $\tau_B/\tau_N=0.82$ for the <u>Cu</u>Al 110-ppm Fe system. A comparison between these two values shows that the aluminum impurities scatter belly electrons more than neck electrons. On the other hand, the introduction of Fe in the <u>Cu</u>Al alloys as a type of controlled "residual" impurity, seems to cause a reduction of τ_N as will be discussed below. In other words the coexistence of Al and Fe scattering centers in copper behave competitively.

It must be noted that the anisotropy ratio τ_B/τ_N for <u>Cu</u>Al alloys is inconsistent with the Dingle-temperature
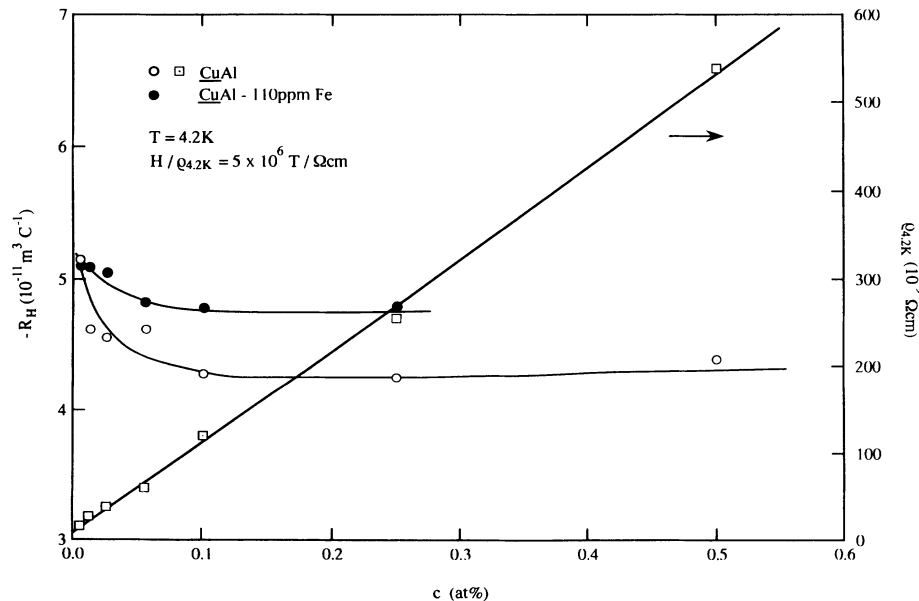

FIG. 3. The low-field Hall coefficient R_H^0 and the residual resistivity as a function of Al concentration.
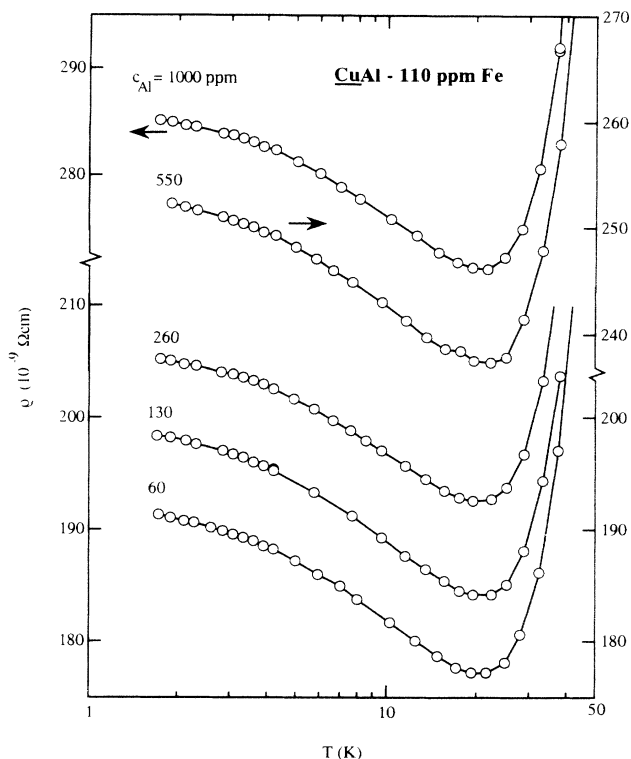
FIG. 4. The electrical resistivity of CuAl 110-ppm Fe as a function of the temperature.

and surface-state resonance data that predict both τ_B/τ_N ratios of about 1.20 to 1.29 (Refs. 5 and 7) and 1.58,[6] respectively, while the τ_B/τ_N ratio of the CuAl 110-ppm Fe system is in very good agreement with the value 0.87 in monocrystals of Cu containing 21-ppm Fe derived also from low-field Hall effect measurements.[11] The discrepancy with the dHvA and SSR methods may be due to the fact that the relaxation times that appear in Eqs. (1) and (2) and thus calculated from Hall-coefficient data, are by definition averages over certain regions of the Fermi surface. Another possible explanation for the discrepancy may arise from the fact that quantum phenomena (such as dHvA and probably SSR) are more sensitive to small-angle scattering of electrons than are semiclassical phenomena such as the Hall effect. Thus, the impurities may exert different influences on data taken by various methods.

The anisotropy of the relaxation time and the influence of the kind of impurities on the scattering can be understood if one considers the variations of the specific nature of the electron wave functions over the Fermi surface of copper. As was mentioned in the Introduction the probability density $|\psi_k(\mathbf{r})|^2$ for an electron to be found around $\mathbf{r}$ in real space depends on the wave vector $\mathbf{k}$ of the corresponding state. The probability density for the electrons occupying states at the necks has a node at the lattice sites and a maximum at the interstitial regions.[12] These states have for symmetry reasons a strong p character.[1]

On the other hand, the electrons at the belly regions of the Fermi surface have a maximum probability density at the lattice sites and have, therefore, predominantly s-like character. This means that a substitutional defect with a well localized scattering potential should scatter the belly electrons stronger than the neck electrons, i.e., $\tau_B < \tau_N$. On the other hand, a defect localized at an interstitial site should scatter the electrons on the neck stronger than those on the belly, i.e., $\tau_B > \tau_N$. Aluminum impurities as a solution take substitutional positions in copper, therefore, one expects that the belly electrons are strongly scattered by them. Under these considerations the ratio for aluminum impurities must be smaller than the isotropic value of 1, which agrees with the present results.

The additional 110-ppm Fe impurities in the dilute CuAl alloys take substitutional positions too, and thus the Coulomb potentials due to the Fe should also scatter the belly electrons according to the above assumptions. If one considers the additional Fe atoms as a kind of controlled residual impurities in the otherwise "pure" dilute CuAl alloy series, then these residual impurities would change only the rapid variation of the low-field Hall coefficient at the very small aluminum concentrations. If this assumption was correct, then as the aluminum concentration increased, the values of the low-field Hall coefficient and consequently the ratios τ_B/τ_N of CuAl and CuAl 110-ppm Fe systems would coincide. This is in contradiction to the experimental results which show that the low-field Hall coefficient of the two systems are not the same (Fig. 3). As was mentioned above, the Al impurities are the main source of scattering for the belly electrons and since it was found that the τ_B/τ_N ratio is higher in the CuAl 110-pm Fe alloy, the introduction of the Fe must cause a reduction of τ_N.

Since the value of the low-field Hall coefficient for the CuAl 110-ppm Fe system is in very good agreement with the one of the binary CuFe alloy,[11] and both systems show Kondo anomalies in their electrical resistivities, it can be concluded that the Kondo scattering of the conduction electrons by the localized magnetic moments of the Fe is strong, and that the neck electrons suffer a significant portion of that scattering.

The occurrence of local moments in noble metals such as copper, containing impurities from the $3d$ series, is usually discussed in the context of the Anderson model[13] or equivalently the Wolff model,[14] which are based on Friedel's virtual bound-state concept.[15] The scattering of the conduction electrons of copper by the localized magnetic moment of the Fe is, according to Kondo,[16] the reason of the appearance of the minimum in the electrical resistivity of CuAl 110-ppm Fe system and their logarithmic decrease with temperature.

Mertig and Mrosan[17] using an expansion of the vector mean-free path in sets of Fermi-surface harmonics have calculated the Hall coefficient of Cu containing $3d$ transition-metal impurities. In the low-field limit $(H/\rho_0 = 10^7 \text{ T}/\Omega \text{ cm})$ the calculation shows that the Hall coefficient has the trend of a minimum near the middle of the $3d$ series. They have explained the appearance of this minimum, according to the Friedel-Anderson model, to

the resonant scattering of the host conduction electrons at the virtual bound state caused by the $3d$ impurity states. In the middle of the $3d$ series the position of this virtual bound state is near to the Fermi energy of copper and causes a strong resonant scattering.

It must also be mentioned here that early investigations on Cu $4d$ alloys[18] have shown the general trend of the low-field Hall coefficient is a minimum, while the trend of the corresponding relaxation time ratios τ_B/τ_N seems to be a maximum near the middle of the $4d$ series. The appearance of this maximum has been attributed to the resonant scattering of the host conduction electrons at the virtual bound state caused by the $4d$ impurity states and it was concluded that the $4d$ electronic states

prefer to scatter the neck electrons more effectively than those of the belly.

V. CONCLUSION

The present measurements of the low-field Hall coefficients R_H^0 of <u>Cu</u>Al and <u>Cu</u>Al 110-ppm Fe alloys at 4.2 K are analyzed in terms of a two-group model and it is found that the relaxation time ratios τ_B/τ_N amount to 0.63 and 0.82, respectively. The difference of these ratios is attributed to the localized magnetic moments that form when Fe is diluted in Cu. The increase of the ratio τ_B/τ_N for <u>Cu</u>Al 110-ppm Fe, in comparison to binary alloy <u>Cu</u>Al, is due to the increased scattering of the neck electrons by the localized magnetic moments of the Fe.

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