PHYSICAL REVIEW B VOLUME 39, NUMBER 18 15 JUNE 1989-II

Temperature and concentration variation of the Hall coefficient in amorphous Y-Al alloys

M. L. Trudeau
Vice-Presidence de Recherche, Institut de Recherche d'Hydro-Québec (IREQ), 1800 Montée Sainte-Julie, Varennes, Québec, Canada J0L 2P0

R. W. Cochrane
Département de Physique, Université de Montréal, Case Postale 6128, Succursale A, Montréal, Québec, Canada H3C 3J7
(Received 3 November 1988)

We present the concentration and temperature variation of the Hall coefficient R_H in amorphous Y_xAl_{1-x} (with $0.60 \leq x \leq 0.80$) between 4.2 and 300 K. We find a positive R_H for all samples and discuss these results in view of recent models. Because of the difference in the temperature variation seen from alloy to alloy, we conclude that the dependence on temperature is not due to one particular process but can be ascribed to the sum of different effects, such as electron-electron interactions, spin-orbit interactions, and volume changes. We also discuss details of making small-area electrical contacts which reduce the possibility of sample recrystallization.

I. INTRODUCTION

A detailed understanding of the electronic conduction process in amorphous metals remains a significant problem today. This is especially true for the Hall conductivity in alloys where transition metals or rare earths are present. In those systems the Hall coefficient R_H, which takes the free-electron value $(-1/n|e|)$ in simple amorphous alloys, can be positive or negative, depending on the system studied.[1-10] To explain the Hall conductivity most models extend the Faber-Ziman theory by incorporating, in some way, the derivative of the density of states at the Fermi level.[11-14] Although this approach provides some qualitative understanding of the experimental data, it is almost impossible to make an unambiguous quantitative comparison.

Recently, Trudeau *et al.*,[4,5] have shown that in the *nonmagnetically ordered* amorphous systems Zr-Fe and Zr-Co a large part of the observed Hall conductivity comes from the presence of an extraordinary contribution due to Berger's side-jump mechanism.[15] This contribution comes from an interaction between the conduction-electron spin **S** and the ionic orbital moment **L**, and results from a spin-scattering displacement of the center of mass of the electron wave packet sideways by a value Δy at each collision. Because this interaction is proportional to the magnetization it has mainly been observed in magnetically ordered systems. However, by its proportionality to the square of the resistivity this mechanism is greatly enhanced in amorphous alloys where the resistivity is at least an order of magnitude greater than that found in crystalline alloys. Under these conditions an important extraordinary contribution should be observable even in paramagnetic amorphous alloys. Moreover, the temperature dependence of R_H should follow the magnetic susceptibility as the resistivity is only weakly temperature dependent. These characteristics are observed in the amorphous Zr-Fe and Zr-Co alloys.[4,5]

In this paper we present Hall data for the amorphous Y_xAl_{1-x} system for $0.60 \leq x \leq 0.80$ between 4.2 and 300 K. The measurement technique is summarized in Sec. II. Also presented in that section are several methods of making electrical contact to the narrow ribbons studied, with an attention to the geometrical form factor since these samples are not easily shaped in the usual Hall geometry. In Sec. III we present the variation of R_H for our Y-Al samples and in Sec. IV discuss both the absolute values and the temperature variations observed in the context of recent models.

II. EXPERIMENTAL DETAILS

Buttons of the appropriate alloy composition were formed by arc melting under a titanium-gettered argon atmosphere. The purity was 99.95% for Y and 99.999% for Al. The amorphous ribbons were melt spun on to a copper wheel (tangential velocity $\simeq 50$ m/s) under a helium atmosphere. Details of the ribbon fabrication and amorphicity analysis can be found in Richter *et al.*[16] The normal size of the ribbons was between 0.60 and 0.80 mm in width with a thickness around 15 μm.

A. Data acquisition

Several experimental difficulties are encountered when measuring Hall voltage in metallic glasses, principally, the small voltages to be detected and the relatively large sample resistivities. The large ρ value in conjunction with the unavoidable misalignment of the Hall contacts can result in resistive voltages up to 10^3 larger than the Hall signal. Furthermore, to avoid Joule heating, the sample currents must be limited to the milliampere region. To overcome these constraints, a sensitive ac bridge that operates near 150 Hz has been developed.[17] Alternating current eliminates the sensitivity to small thermoelectric voltages which plague most dc measure-

ments.[18] With this bridge a relative change of 5×10^{-7} in a 1-Ω resistance is detectable so that a Hall voltage of 10 nV can be detected to a precision of 0.5% even in the presence of 100 μV of resistive signal. However, the absolute precision in the Hall coefficient is dominated by the accuracy in the measurement of the sample dimensions.

B. Electrical contacts

One major problem in the study of the electrical properties in amorphous metals is the electrical contact to the sample. This problem is particularly severe for Hall effect measurements in narrow samples because of the proximity of the voltage contacts. Two major contacts categories can be distinguished: pressure and permanent. The first does not damage to relatively thick amorphous samples but can give some major difficulties by being electrically noisy or by being mechanically unstable to differential thermal contractions between the leads and the sample.[19] For the Hall effect this is an important factor since it can produce significant errors in the sample form factor leading to systematic errors in relative as well as absolute values of R_H. The other contact category has the leads fixed permanently to the sample. In this group at least three major methods exist. A first uses conductive epoxy or paint. We have found that these contacts can present three major difficulties. Firstly, a high electrical noise level due principally to small fluctuations in the contact resistance. Best results are achieved only after careful curing of the conductive cement. Another problem is the high resistance and relatively large area of such contacts so that a non-negligible part of the current flows in parallel to the sample current. Finally, such contacts are not very resistant to thermal cycling between 300 and 4.2 K.

A second method of electrical contact consists of direct soldering using tin-lead solders, indium or other alloys. Difficulties arise because proper bonding is sometimes impossible on account of surface quality or chemistry. However, the major problem arises from recrystallization of the amorphous matrix around the contact point.

The third method is the spot-welding technique, where a small wire (normally copper) is melted onto the sample surface by a high-voltage discharge. This technique normally makes very stable and solid contacts but suffers one major flaw. Because of the high power used, recrystallization of the amorphous alloy around the point of contact or at least formation of large structural defects often occurs. For samples having a typical length of 3–4 cm this recrystallization around the current or resistive leads is normally negligible, when considering the ratio of the damaged area to the total area between the contacts. However, for the two Hall contacts, where the typical separation is around 0.5 mm, this ratio is much more important. When the recrystallization can be as high as 30–50 % of the total area it is certain that the transport properties will be affected dramatically. Even if only large structural defects are produced, they will alter the current flow pattern which will increase the misalignment voltage and also cause some systemtic errors.[20] In Fig. 1

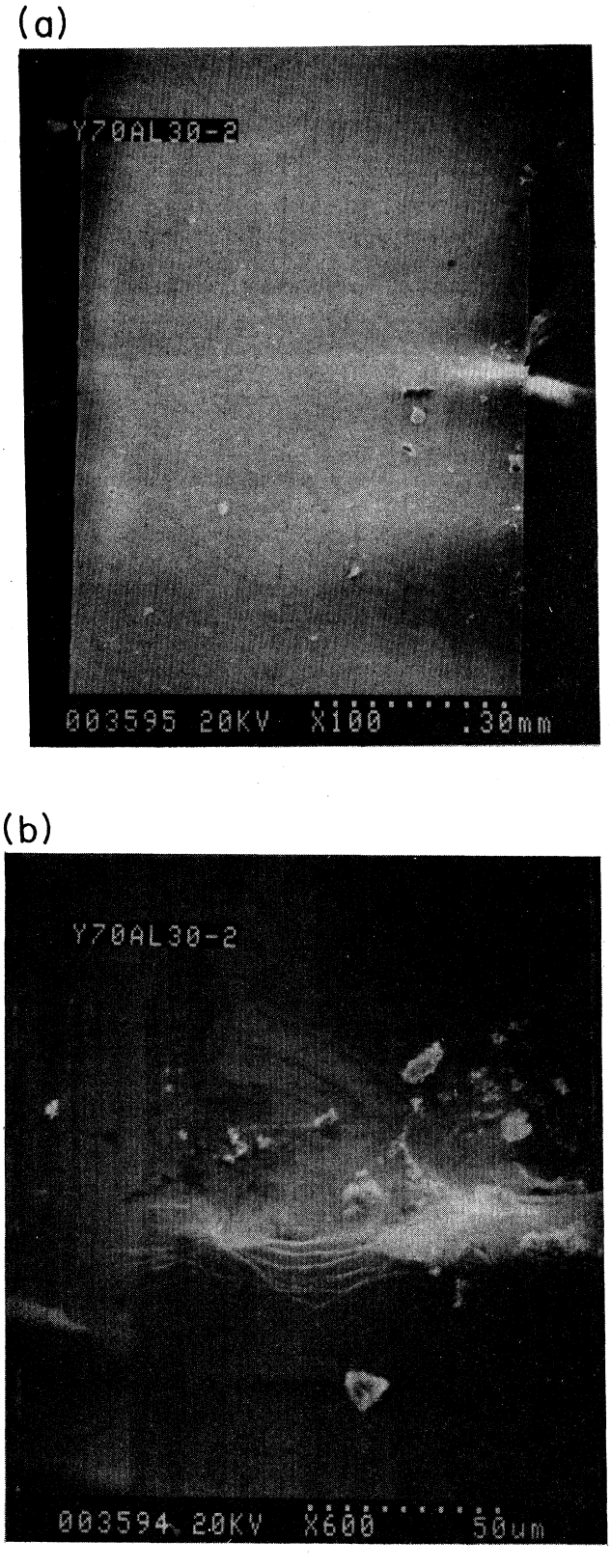


FIG. 1. (a) Sample of $Y_{70}Al_{30}$ showing damaged area due to the spot-welding of a 0.09-mm-diam copper wire; (b) enlargement of the same area.

is a photograph of $Y_{70}Al_{30}$ with a spot-welded 0.09-mm-diam copper wire. The damaged length covers $\simeq 100\ \mu$m of the width of the sample. Two similar contacts would easily modify 33% of the width between the Hall contacts. Furthermore, x-ray diffraction of this section of the sample shows that a partial recrystallization has occurred. Under these circumstances it is impossible to be confident about the final result. Normally, one way to minimize most of the effects of this recrystallization is to cut the sample in the form of a cross, where the contacts are placed on each of the sidearms away from the current flow. However, for very small or brittle samples it is often not possible to cut them into this geometry so that the contacts must be placed as close as possible to the sides of the sample.

Because of all these constraints and the need for a high precision in the relative as well as in the absolute value of R_H, we have used small aluminum wires (0.025 mm in diameter) ultrasonically bonded to the sample. With the right setting of power, contact time, and pressure, very stable contacts can be made on most alloys, including Zr-Fe, Zr-Co, Zr-Ni, Mg-Cu, and Y-Al amorphous alloys. However, because of their very small diameter the wires are very fragile and cannot be attached directly to the sample holder terminal. For each contact, a bond was made between the sample and a small copper pad to which a copper wire had been soldered. To ensure intimate thermal contact the sample and copper pads are mounted on a small copper block covered with a thin electrically insulating sheet. In Fig. 2(a) the contact area is seen in detail. A high magnification of one contact point [Fig. 2(b)] shows less damage than seen in Fig. 1 and x-ray diffraction of the area confirms the absence of noticeable crystallization.

Finally, it should be noted that when contacts are made to the sample without sidearms not all the current flows between the contacts. As a result, the form factor used in the calculation of the absolute Hall coefficient has to include a term equal to the ratio of the contact separation divided by the sample width. Figure 2(a) confirms that there is considerable advantage in determining the correct form factor when using the microcontacts described above. Measurements on different samples of the same alloy, with different thickness and form factors, allow us to put an upper bound of 5% on the absolute error of R_H.

III. RESULTS

Table I gives values for R_H at 300, 77 and 4.2 K for the four Y-Al samples studied, along with the room-temperature resistivities and densities. The temperature variation for the samples is presented in Fig. 3 and in greater detail for the $Y_{60}Al_{40}$ system in Fig. 4.

From these results we note that the overall temperature variation of R_H is very small, with an average temperature coefficient, $\kappa = |R_H(300\text{ K}) - R_H(4.2\text{ K})| / R_H(4.2\text{ K}) \simeq 6\%$. However, the shape of the variation is itself interesting. On the one hand, a general increase between 30 and 4.2 K is noted. On the other hand, the behavior between 300 and 77 K varies from sample to sample.

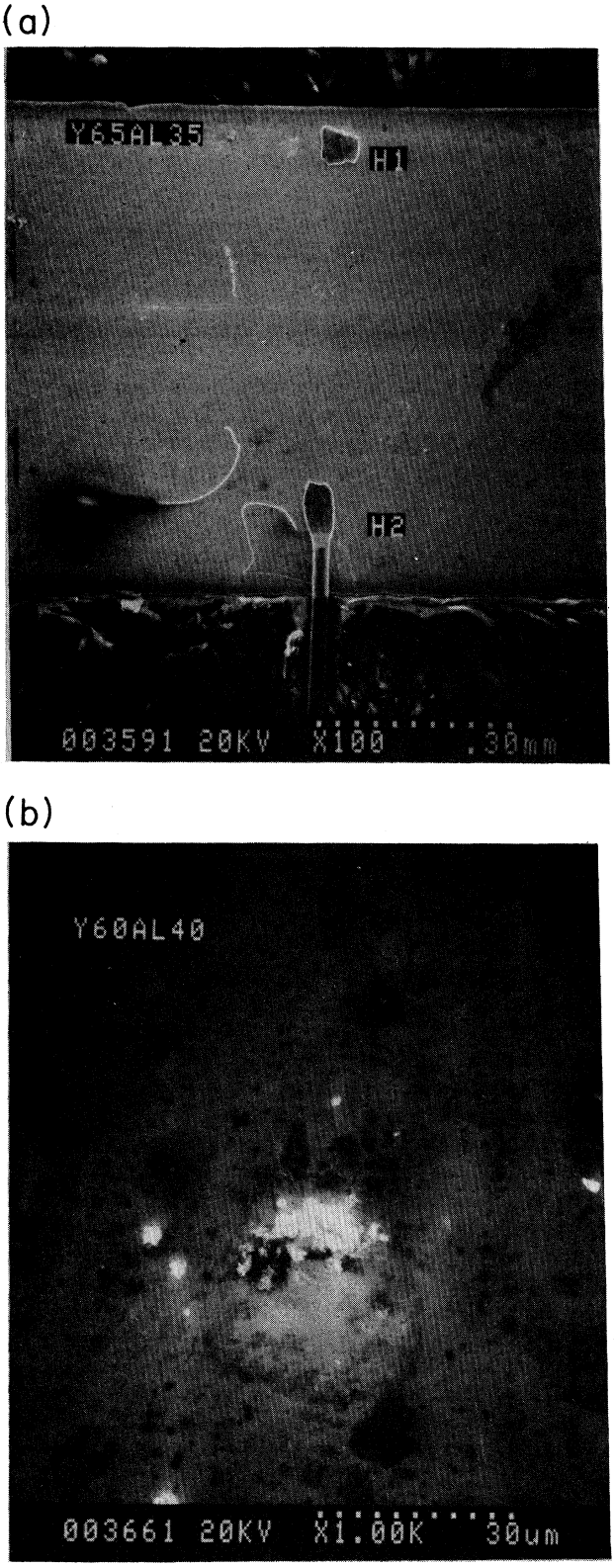


FIG. 2. (a) Detail of the area between the two Hall contacts made by bonding ultrasonically very small aluminum wires; (b) enlargement of the similar contact area with the aluminum wire removed.

TABLE I. Room-temperature density (Ref. 16), resistivity (Ref. 16), and Hall coefficient at 300, 77, and 4.2 K.

Alloy system	Room-temperature density ($g\,cm^{-3}$)	resistivity ($\mu\Omega\,cm$)	R_H(300 K) ($10^{-11}\,m^3A^{-1}s^{-1}$)	R_H(77 K) ($10^{-11}\,m^3A^{-1}s^{-1}$)	R_H(4.2 K) ($10^{-11}\,m^3A^{-1}s^{-1}$)
$Y_{80}Al_{20}$	4.27±0.06	2.62±0.09	6.73±0.04	6.14±0.04	6.21±0.04
$Y_{70}Al_{30}$	4.16±0.06	2.60±0.09	9.26±0.04	9.3±0.04	9.52±0.04
$Y_{65}Al_{35}$	4.06±0.06	2.59±0.09	8.59±0.04	7.86±0.04	8.15±0.04
$Y_{60}Al_{40}$	3.99±0.06	2.57±0.09	8.81±0.04	9.05±0.04	9.49±0.04

$Y_{80}Al_{20}$ and $Y_{65}Al_{35}$ show a decrease, $Y_{60}Al_{40}$ shows an increase, and $Y_{70}Al_{30}$ is a practically stable value. This already suggests that at least two different mechanisms could be responsible for the overall temperature variation.

The absolute value of R_H is also unusual in that R_H is positive and shows a small increase with the aluminum content. Yamada *et al.*[9] and Mizutani *et al.*[10] have observed a similar increase with Al content in $Cu_{50}Zr_{50-x}Al_x$ and $Ni_{50}Zr_{50-x}Al_x$ alloys. It would seem that these metallic systems with effective spherical Fermi surfaces exhibit positive Hall coefficient which increases on adding electrons (Al). Cu-Ti (Ref. 19) and La-Al (Ref. 6) alloys are also characterized by positive R_H values which increase with resistivity.

IV. DISCUSSION

A. Absolute value of R_H

As mentioned in the Introduction the positive Hall coefficient of disordered alloys remains controversial in origin. The situation is further complicated by the presence of an extraordinary Hall term even for paramagnetic amorphous alloys. Recently,[5] the presence of this nonclassical extraordinary Hall conductivity has been conclusively shown in the case of the Zr-Fe paramagnetic alloys and was explained easily through the side-jump mechanism proposed by Berger.[15] The total Hall coefficient in an amorphous metal (where transition metals or rare earths are present) should then be written

$$R_H = R_0 + R_s\chi = R_0 + \frac{2e^2}{\mu_0\hbar\mu_B g}\rho^2\lambda_{\text{s.o.}}\,, \tag{1}$$

where R_0 is the ordinary (Lorentz) Hall contribution and the second term, which is proportional to the valence (Pauli) susceptibility χ, is the side-jump term. In this equation ρ represents the electrical resistivity and $\lambda_{\text{s.o.}}$ the orbital matrix element which has a form related to the Van Vleck susceptibility χ_{VV}.

Using the R_s value ($4\times10^{-7}\,m^3/A\,s$) found for the Zr-Fe alloys[5] as an estimate and scaling for the larger Y-Al resistivity, we estimate an R_s of $10^{-6}\,m^3/A\,s$ in these al-

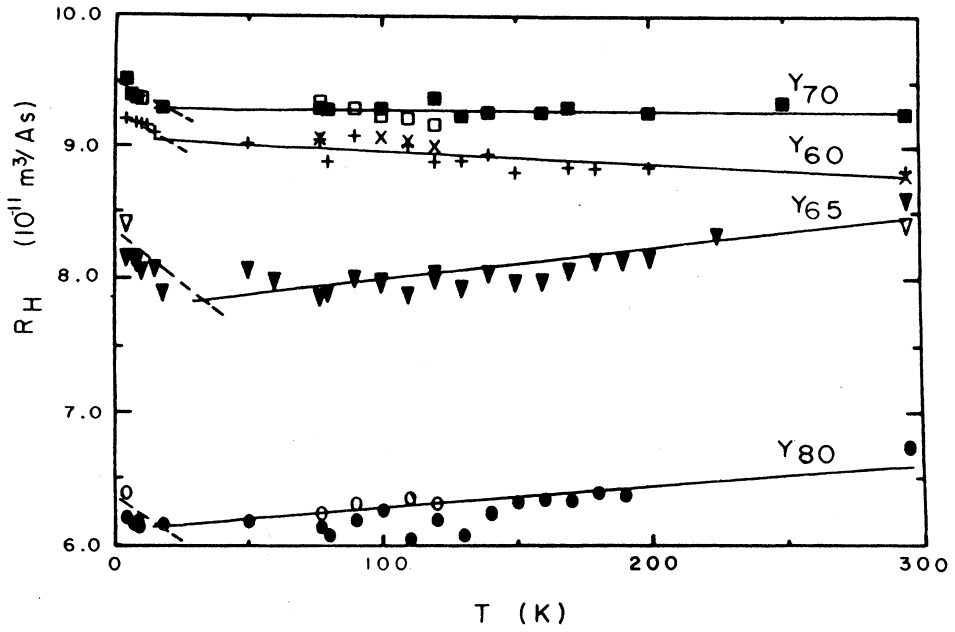


FIG. 3. Hall coefficient R_H as a function of the temperature for the Y-Al alloys: ●,○, $Y_{80}Al_{20}$; ■,□, $Y_{70}Al_{30}$; ▼,▽, $Y_{65}Al_{35}$; +,×, $Y_{60}Al_{40}$.

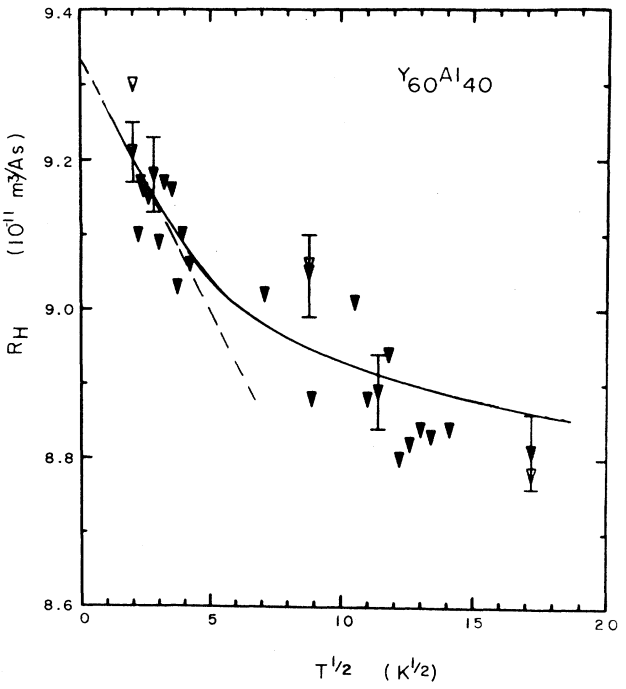


FIG. 4. Details of the temperature variation of R_H in $Y_{60}Al_{40}$ (the solid line is a guide for the eye; the dotted line is the $\sqrt{T}$ variation).

loys. From (1) the value of R_s depends on the resistivity which is ~ 1.5 times greater in the Y-Al system (giving an increase of ~ 2.3). Furthermore, if we look at the weak-localization study of the same samples[21] we find that the spin-orbit characteristic time (which depends mostly on the Y atoms) is very close to the one found in Zr alloys, giving basis to the fact that the spin-orbit coupling constant (even if smaller in the Y alloys) is probably not that different. It should be emphasized that both these R_s values are very large when compared to the ones found in crystalline ferromagnets, underlining the enhancement brought about by the strong scattering, i.e., the high resistivity. Taking a value for the Pauli susceptibility,[22] $\chi \approx 3.7 \times 10^{-5}$, leads to an estimated side-jump component $R_s \chi \approx 4 \times 10^{-11}$ m³/A s. This term is thus of the same order as the measured R_H supporting its importance for the present alloys.

To reemphasize, the extraordinary contribution does not require the presence of a long-range, ordered magnetic state but rather arises from the spin-orbit interaction between the spin of the moving electron and the orbital moment of the atom shell. Also, this process does not depend on the carrier mobility and for that reason is dominated by d electrons because of their high density of states. A complete understanding of the Hall effect in amorphous transition-metal alloys clearly has to include the presence of this term. Unfortunately, there is to date no detailed theory that can give the value of the effective number of conduction electrons in transition metals in order to calculate precisely the Lorentz term R_0.

B. Temperature variation of R_H

Several mechanisms will contribute to the temperature dependence of R_H. A first is the relative volume change due to thermal expansion which gives rise to a positive temperature coefficient[23] $\kappa_v = (1/R_H)(dR_H/dT) \approx 7 \times 10^{-5}$ K^{-1}. This contribution can then give a total change $\Delta R_H \simeq 10^{-12}$ m³/A s, which is about an order of magnitude smaller than the one observed.

Another possible contribution to the temperature variation comes from the structural disorder present in amorphous systems; this disorder increases the electron wave-function localization and enhances the electron-electron interaction. However, Fukuyama[24] has shown that there is no change to the value of R_H associated with weak-localization. On the other hand, Al'tshuler *et al.*[25] demonstrated that the increase in the electronic interactions due to the diffusive motion, which is partly responsible for the decrease in the conductivity at low temperature,[21] has a direct effect on the Hall constant. They showed that the relative change in R_H is related to the conductivity variation by

$$\frac{\Delta R_H(T)}{R_H(0\ \mathrm{K})} = -2\frac{\Delta\sigma_I(T)}{\sigma(0\ \mathrm{K})} . \tag{2}$$

Olivier *et al.*[21] have shown that in the same series of Y-Al alloys the correction to the conductivity due to electron-electron interaction results in an increase in the conductivity of about 0.2% from 4.2 to 20 K. For this temperature interval a decrease in $R_H \approx 0.4\%$ is then expected. Furthermore, since the dominant process in the electron-electron interaction (for these systems) is the enhanced interaction between electrons and holes (interactions in the so-called "diffusion channel") due to spin splitting, the variation of R_H could be written as[25]

$$\frac{\Delta R_H(T)}{R_H(0\ \mathrm{K})} = -\frac{2.6\rho(0\ \mathrm{K})}{\sqrt{2}}\left[\frac{e^2}{4\pi^2\hbar}\right]\left[\frac{k_B T}{\hbar D}\right]^{1/2} \times\left[\frac{4}{3}-\lambda_\sigma^{J=1}(F)\left[\frac{3}{2}+\frac{g_3(\delta)}{1.3}\right]\right], \tag{3}$$

where $g_3(x)$ is a field-dependent function with $\delta = g\mu_B B/k_B T$. In this equation $\lambda_\sigma^{J=1}(F)$ is a conductivity-renormalized value of the effective Coulomb interaction constant, F, for the case of the triplet state of spin $J=1$. The function $g_3(x)$ was defined by Lee and Ramakrishnan[26] and an analytical approximation can be found in Ousset *et al.*[27] Finally, in this equation D is the electronic diffusion coefficient and $\rho(0)$ the $T=0$ resisitvity.

Neglecting any magnetic enhancement (the magnetic susceptibility is small and the magnetoresistivity data show no presence of such effect[25]) and restricting the analysis to temperature above 4.2 K we find then for $Y_{60}Al_{40}$ (Fig. 4)

$$R_H(T) \approx 9.33\times10^{-11} - 6.76\times10^{-13}T^{1/2}\ \mathrm{m^3/A}\ . \quad (4)$$

This value for the $T^{1/2}$ slope is three times greater than the *maximum* predicted value that can be expected from (3) using $D=5\times10^{-5}$ m^2/s (see Ref. 21) and taking $\lambda_\sigma^{J=1}(F)=0$. Even if part of this temperature variation arises from this mechanism, it is clear that it cannot be used to explain the entire temperature variation from 4.2 to 300 K, as proposed by Gallagher *et al.*[28] Bergmann[29] and Fukyama[30] have clearly demonstrated that the electron-electron interaction is very dependent on the phase coherence between the two interacting electrons, which is rapidly destroyed by inelastic scattering as the temperature is increased.

Finally, a third possible contribution to the temperature variation of R_H arises from the extraordinary term proposed in the previous section for the change of sign of R_H. The temperature-dependent part is given by the product $\rho^2\chi$; the small decrease in ρ with T is then consistent with the variation shown for the $Y_{60}Al_{40}$ system. However, a complete picture will have to wait for the direct measurement of the small temperature variation of the susceptibility in these materials.

V. CONCLUSION

We have reported on the temperature and concentration variation of the Hall constant in the amorphous Y-Al alloys, between 60 and 80 at. % of yttrium. We have shown that the positive Hall coefficient observed in all alloys is consistent with an important extraordinary Hall contribution. The temperature variation of R_H is still unaccounted for completely. The predicted *e-e* term at low temperatures is much smaller than the variation observed. Moreover, it is not possible to evaluate the temperature dependence of the proposed extraordinary term for lack of susceptibility data. It seems evident, however, that the final explanation will have to include a complete analysis of all these mechanisms and that complete susceptibility, resistivity, and magnetoresistivity as well as thermal expansion data will have to be included in the analysis.

It would also be of interest to expand the range of alloys to follow the crossover in sign of the Hall effect from the Al-rich to the Y-rich regions. We are currently attempting to sputter such alloys to extend the range of stable amorphous alloys in this system.

ACKNOWLEDGMENTS

We would like to thank Professor John Strom-Olsen and Dr. Reinhart Richter for providing the Y-Al samples.

[1]B. L. Gallagher, D. Greig, M. A. Howson, and A. A. M. Croxon, J. Phys. F **13**, 119 (1983).
[2]A. Shulte and G. Fritsch, J. Phys. F **16**, L55 (1986).
[3]R. W. Cochrane, J. Destry, and M. Trudeau, Phys. Rev. B **27**, 5955 (1983).
[4]M. L. Trudeau, R. W. Cochrane, and J. Destry, in *Proceedings of the 6th International Conference on Rapidly Quenched Metals, Montréal, 1987* [Mater. Sci. Eng. **99**, 187 (1988)].
[5]M. L. Trudeau, R. W. Cochrane, D. V. Baxter, J. O. Strom-Olsen, and W. B. Muïr, Phys. Rev. B **37**, 4499 (1988).
[6]C. L. Tsai and F. C. Lu, J. Appl. Phys. **55**, 1945 (1984).
[7]U. Mizutani, Prog. Mater. Sci. **28**, 98 (1983).
[8]D. G. Naugle, J. Phys. Chem. Solids **45**, 367 (1984).
[9]Y. Yamada, Y. Itoh, T. Matsuda, and U. Mizutani, J. Phys. F **17**, 2313 (1987).
[10]U. Mizutani, Y. Yamada, C. Mishima, and T. Matsuda, Solid State Commun. **62**, 641 (1987).
[11]G. J. Morgan and M. A. Howson, J. Phys. C **18**, 4327 (1985).
[12]B. Movaghar, in *Physics of Disordered Materials,* edited by D. Adler (Plenum, New York, 1987), p. 999.
[13]D. Nguyen-Manh, D. Mayou, G. J. Morgan, and A. Pasturel, J. Phys. F **17**, 999 (1987).
[14]R. Harris, J. Phys. F **16**, 53 (1986).
[15]L. Berger, Phys. Rev. B **2**, 4559 (1970).
[16]R. Richter, Z. Altounian, and J. O. Strom-Olsen, J. Mater. Sci. Lett. **4**, 1005 (1985).
[17]R. W. Cochrane and M. L. Trudeau (unpublished).
[18]H. L. McKinzie and D. S. Tannhauser, J. Appl. Phys. **40**, 4954 (1969).
[19]A. Schulte, A. Roithmayer, G. Fristsch, and E. Lüscher, in *Amorphous and Liquid Materials,* edited by E. Lüscher, G. Fritsch, and G. Jaccuci (Plenum, New York, 1987), p. 408.
[20]C. Hurd, *The Hall Effect in Metals and Alloys* (Plenum, New York, 1972).
[21]M. Olivier, J. O. Strom-Olsen, Z. Altounian, R. W. Cochrane, and M. Trudeau, Phys. Rev. B **33**, 2799 (1986).
[22]Since no susceptibility data are available for the Y-Al system we have used an approximation based on the Cu-Zr alloy in E. Batalla, Z. Altounian, and J. O. Strom-Olsen, Phys. Rev. B **31**, 577 (1985).
[23]A. Shulte, A. Eckert, G. Fritsch, and E. Lüscher, J. Phys. F **14**, 1877 (1984).
[24]H. J. Fukuyama, in *Electron-Electron Interaction in Disordered Systems,* Vol. 10 of *Modern Problems in Condensed Matter Science,* edited by A. L. Efros and M. Pollak (Elsevier, Amsterdam, 1985), pp. 155–230.
[25]B. L. Al'tshuler and A. G. Aronov, in Ref. 24, pp. 1–154.
[26]P. A. Lee and T. V. Ramakrishanan, Phys. Rev. B **26**, 4009 (1982).
[27]J. C. Ousset, S. Askenazy, H. Rakoto, and J. M. Broto, J. Phys. **46**, 2145 (1985).
[28]B. L. Gallagher, D. Greig, and M. A. Howson, J. Phys. F **14**, L225 (1984).
[29]G. Bergmann, in *Localization and Interaction,* edited by D. M. Finlayson (SUSSP, St. Andrews, 1986), pp. 149–171.
[30]H. J. Fukuyama, in Ref. 29, pp. 117–148.

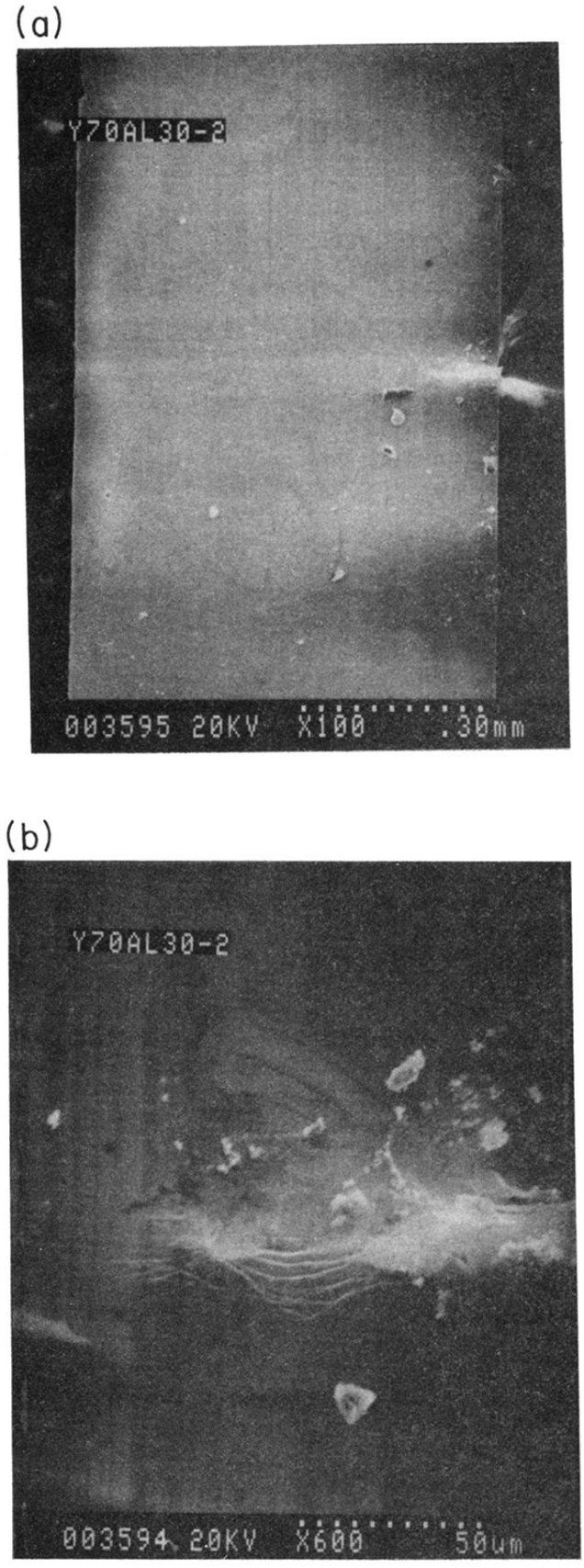
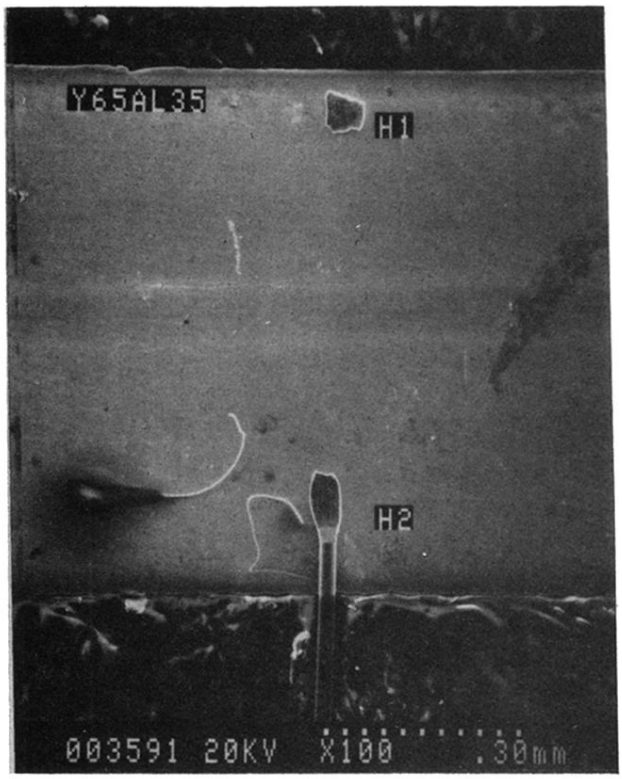


FIG. 1. (a) Sample of $Y_{70}Al_{30}$ showing damaged area due to the spot-welding of a 0.09-mm-diam copper wire; (b) enlargement of the same area.

(a)



(b)

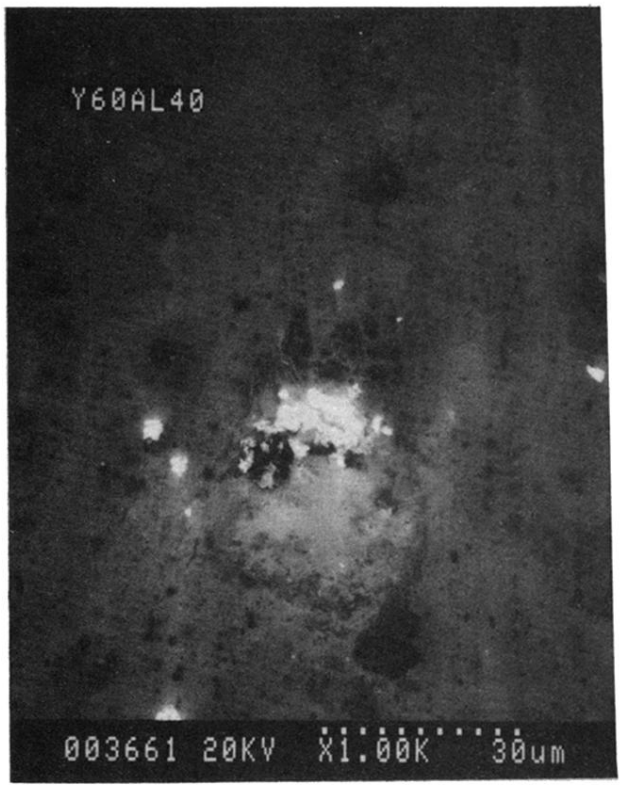


FIG. 2. (a) Detail of the area between the two Hall contacts made by bonding ultrasonically very small aluminum wires; (b) enlargement of the similar contact area with the aluminum wire removed.