PHYSICAL REVIEW B VOLUME 40, NUMBER 2 15 JULY 1989-I

Electronic properties of a new class of aluminum-based metallic glasses: $Al_{100-x-y}(T)_x(La,Y)_y$ with T = Fe, Co, Ni, and Cu

M. Pont, J. Gonzalo, and K. V. Rao
Department of Solid State Physics, Royal Institute of Technology, S-100 44 Stockholm, Sweden

A. Inoue
Department of Solid State Physics, Royal Institute of Technology, S-100 44 Stockholm, Sweden and Institute for Materials Research, Tohoku University, Sendai, Miyagi 980, Japan

(Received 16 March 1989)

Electrical and Hall resistivity studies have been carried out on a new class of melt-spun Al-T-R, Al-rich (above 75 at.%) ternary amorphous alloys in order to study the possible correlation between their electronic and enhanced mechanical properties. We find for all these alloys (over 26 of them) the room-temperature Hall coefficient has a *negative* sign and increases significantly in magnitude with the (T-R) content, which indicates a decrease in the effective carrier concentration. This is consistent with the suggestion that the observed remarkable mechanical properties in these alloys are due to the enhanced strength of the additional local Al−T and Al−R bonds. In these alloys the electrical resistivity at room temperature increases from about 65 $\mu\Omega$ cm for the binary $Al_{90}(R)_{10}$ amorphous alloys to over 250 $\mu\Omega$ cm on further substitution of Al with less than 15 at.% of T elements. From a systematic study the importance of the s-d scattering mechanism and a crossover in the electronic properties from s- to d-band amorphous metal with T substitution are discussed.

INTRODUCTION

Recently, by melt spinning a new class of ductile Al-rich binary and ternary amorphous alloys, $Al_{100-x-y}(T)_x(R)_y$ have been reported[1] in a rather wide composition range with $0 \leq x \leq 15$ and $2 \leq y \leq 15$, where T = Fe, Co, Ni, or Cu and R = Y or La. Some of the remarkable physical parameters of these new alloys are: enhanced tensile fracture strengths $\sigma_f > 1000$ MPa, and Vickers hardness ranging from 260 to 350 DPN (diamond pyramid hardness number). These properties are significantly higher than those known for crystalline Al-based alloys. The possibilities to form amorphous "single-phase" Al-based material with good ductility was demonstrated for the first time only last year when Al-Ni-Si amorphous alloys containing above 80 at.% Al were produced by melt spinning.[1] It has also been found that these alloys can be warm extruded to form bulk amorphous materials, and rods as large in diameter as 2–3 cm have been obtained[2] without losing the properties of the glassy state. The discovery of this new class of high-strength low-density materials is thus expected to be of significant technological importance. The enhanced mechanical properties as well as the high thermal stability of these alloys have been thought to be mainly due to the strong attractive interaction between the constituent elements, especially through the formation of Al−T and Al−R covalent bonds. In this Rapid Communication we report measurements of the electrical resistivity and the Hall effect at room temperature in order to find possible correlations between the mechanical and electronic properties of these industrially important materials. Our data suggest that change in the s-d electronic structure, brought about on substitution with the transition elements, possibly plays a role in enhancing the bonding structure suggested by Inoue *et al.*[1]

EXPERIMENT

Al-T-Y and Al-T-La, T = Fe, Co, Ni, or Cu ternary alloys in the nominal composition range below 15 at.% R and 15 at.% T were produced by melt spinning on a single roller. These ribbons of thickness in the range 8–20 μm were ductile and had a highly reflective surface. The amorphicity of the structure of the melt-spun ribbons was confirmed by x-ray-diffraction measurements. The room-temperature electrical and Hall resistivities were measured simultaneously for each sample using the "double ac technique."[3] Electrical contacts were made using conducting silver epoxy glue to avoid any local heating or crystallization close to the contact areas. The thickness of the ribbons, necessary to calculate absolute values of the transport coefficients, was estimated from a density-length-weight method. The absolute error in our measurements is estimated to be of the order of 15%.

RESULTS

In order to systematically investigate in the amorphous state the consequence of substitution of T and R elements in Al on the electronic properties we present data on melt-spun amorphous Al-T-R, in which (a) for a fixed R element (10 at.% La, Y in the present study), the T element (Fe, Co, and Ni—in that order as presented here) concentration is changed, and (b) for a chosen concentration (10 at.%) of the T element, the R element content is varied. To simplify the above-mentioned points only

TABLE I. Experimental data for electrical resistivity and the Hall effect in the alloys studied.

Alloy	R	x	$\mu\Omega$ cm	$-R_H$ (10^{-12} m^3/As)
$Al_{90}(R)_{10}$	Y		62	22
	La		64	23
$Al_{90-x}Fe_x(R)_{10}$	Y	5	96	25
		10	214	...
	La	2	63	...
		5	78	...
		15	129	...
$Al_{90-x}Co_x(R)_{10}$	Y	5	94	22
		15	230	26
	La	2	102	23
		5	96	...
		10	144	33
		15	337	42
$Al_{90-x}Ni_x(R)_{10}$	Y	3	66	22
		7	84	23
	La	2	66	...
		4	65	...
		8	82	25
		10	90	22
		15	160	34
$Al_{90-x}Cu_x(R)_{10}$	Y	3	80	...
		10	84	26
$Al_{90-x}Co_{10}(R)_x$	Y	2	91	32
		15	220	62
	La	5	116	37
		10	144	33

room-temperature data are presented. This approach enables us to identify at least qualitatively the *s-d* interaction effects in the electronic properties. To clarify the importance of this scattering mechanism we consider the Hall effect and electrical resistivity of $Al_{90-x}(T)_xY_{10}$. These results are qualitatively similar for the $Al_{90-x}(T)_xLa_{10}$ system as well, and hence, for simplicity in this Rapid Communication we only discuss data for the Y system. We shall then discuss the electronic properties of this new class of amorphous Al-rich, Al-*T*-*R* alloys. The experimental data for electrical resistivity and Hall effect in the alloys studied herein are summarized in Table I.

$Al_{90-x}Fe_x(R)_{10}$

Figure 1 shows the electrical resistivity as a function of the Fe content. It is observed that the electrical resistivity increases rapidly in the Al-Fe-Y system with Fe content; from 63 $\mu\Omega$ cm for the alloy with a 2 at.% of Fe to 214 $\mu\Omega$ cm for the alloy with 10 at.% of Fe. The increase in the Al-Fe-La system is not as pronounced as in the Y system. Therefore a marked difference which depends on the two *R* species, Y and La, is observed. The Al-Fe-La ribbons studied in this batch were rather narrow (<0.5 mm). In addition, the Hall resistivity in the normal state is quite small for these alloys. Hence, at present we do not report the Hall data for the ribbons containing Fe.

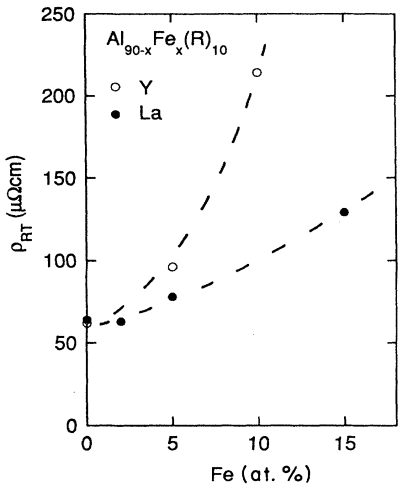

FIG. 1. Fe concentration dependence of the electrical resistivity for melt-spun amorphous $Al_{90-x}Fe_x(R)_{10}$.

$Al_{90-x}Co_x(R)_{10}$, R=Y,La

The effect of substituting Co for Al while keeping the same concentration of *R* (10 at.%) is shown in Figs. 2(a) and 2(b). The electrical resistivity increases with the concentration of *T* as we have already seen in Fig. 1, but in this case it is *independent* of the nature of the *R* element. In contrast to the similarity in the resistivity behavior, the Hall coefficient, which is found to be negative for all the alloys studied here, is found to depend on the alloyed rare-earth element. However, the general feature that emerges is that as the (Co+*R*) content increases the magnitude of the Hall coefficient also increases.

$Al_{90-x}Ni_x(R)_{10}$

In Figs. 3(a) and 3(b) we present the concentration dependence of room-temperature electrical resistivity and Hall coefficient for amorphous Al-Ni-*R* alloys with 10 at.% *R* (La and Y, respectively). The observed dependencies on Ni concentration are quite similar to those on Co

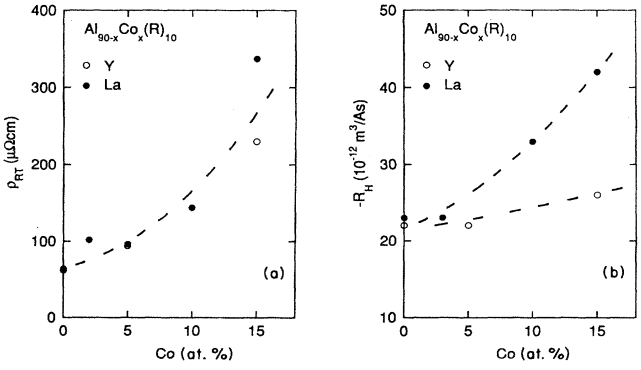

FIG. 2. (a) Co concentration dependence of the electrical resistivity for melt-spun amorphous $Al_{90-x}Co_x(R)_{10}$. (b) Hall coefficient vs Co content for the samples in (a).

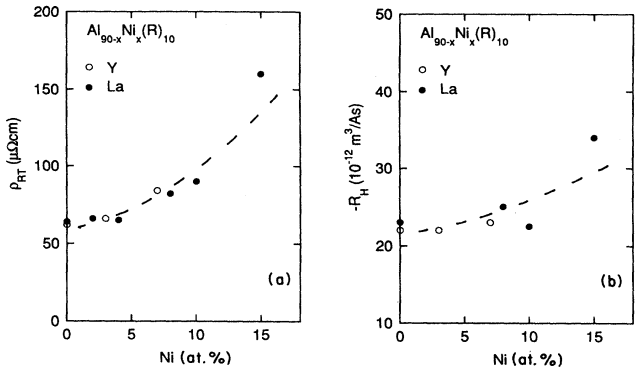

FIG. 3. (a) Ni concentration dependence of the electrical resistivity for melt-spun amorphous $Al_{90-x}Ni_x(R)_{10}$. (b) Hall coefficient vs Ni content for the samples in (a).

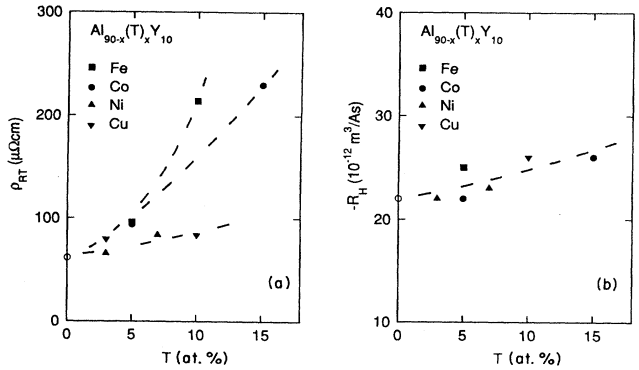

FIG. 5. (a) Electrical resistivity for melt-spun amorphous $Al_{90-x}(T)_xY_{10}$ with T=Fe, Co, Ni, and Cu. (b) Hall coefficient for the same alloy systems.

substitution except that in the present alloys both Hall coefficient and electrical resistivity *do not seem to depend* on Y or La.

$$Al_{90-x}Co_{10}(R)_x,\ R=Y,La$$

Figures 4(a) and 4(b) show the electrical resistivity and the Hall coefficient as a function of the R content. In this case it is observed that the electrical resistivity increases rapidly from about 90 to 220 $\mu\Omega$ cm with 13 at.% substitution of R, almost parabolically with the concentration of R but it is independent of the substituted R elements La and Y. The magnitude of the Hall coefficient is also found to increase rapidly (in the present case it almost doubles in magnitude for a substitution of about 13 at.% R) with the content of R independent of whether La or Y is substituted.

$$Al_{90-x}(T)_xY_{10}$$

Finally, we present in Figs. 5(a) and 5(b) the room-temperature electrical resistivity and Hall-effect data for $Al_{90-x}(T)_xY_{10}$ with T=Fe, Co, Ni, and Cu. Qualitatively, the data for the Al-T-La alloys are quite similar to those of the Al-T-Y alloys, hence for brevity we do not show this data although it is given in Table I. It is easily seen from Figs. 5(a) and 5(b) that the resistivity increases with T concentration, in a manner already noted before. This increase is more pronounced in the alloys containing Fe and Co (in that order), while for Ni and Cu substitution the electrical resistivity is almost a constant. However, the increase in the magnitude of the Hall coefficient appears *not to* depend on the nature of the T element.

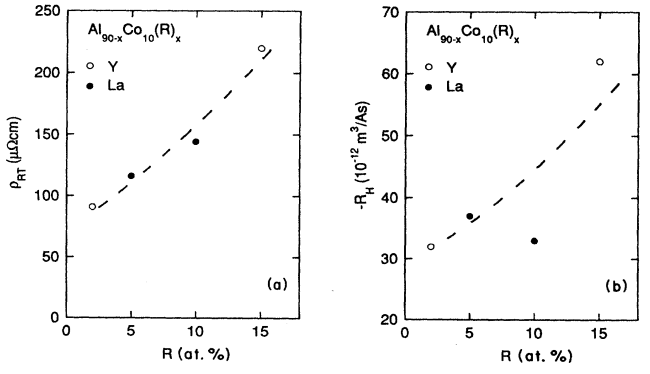

FIG. 4. (a) Concentration dependence of the electrical resistivity for melt-spun amorphous $Al_{90-x}Co_{10}(R)_x$ with R=Y and La. (b) Hall coefficient vs rare-earth content for the samples in (a).

DISCUSSION

The electronic properties of simple metal amorphous alloys are expected to behave according to the free-electron model since the spatial isotropy that should exist in homogeneous amorphous alloys would lead to a spherical Fermi surface. However, substitution of Al by R and/or T species raises the fundamental question as to how the free-electron-like behavior expected for a-Al will be altered by the presence of other atoms with a very different electronic structure and atomic size. The two R species examined in this work, Y and La, have a very similar atomic radius and the same outer electronic structure, namely (d^1s^2), thus substitution of 10 at.% of Al by any R element should essentially produce similar changes in the electronic properties. Indeed this is what we observe experimentally: For example, within the limits of experimental error both $Al_{90}La_{10}$ and $Al_{90}Y_{10}$ present an electrical resistivity of 66 $\mu\Omega$ cm and an ordinary Hall coefficient of $R_H \approx -22.5\times10^{-12}$ m^3/As. In a free-electron model it will be expected that the Hall coefficient of these two alloys shows an almost free-electron value, given by

$$R_H = -1/(Nne)\,, \tag{1}$$

where N is the atomic denstiy and n is the number of electrons per atom. Assuming three conduction electrons per Al and Y (or La) atom, Eq. (1) gives a Hall coefficient, $R_H = -38\times10^{-12}$ m^3/As. This is almost twice the experimental value. On the other hand, it has been shown[4] that La-based amorphous alloys have positive Hall coefficients and for liquid La the value of $R_H = +61.5\times10^{-12}$ m^3/As has been reported.[5] We now discuss the effects of transi-

tion elements on partial substitution of aluminum.

The Hall-effect data [Fig. 5(b)] indicate that there is a decrease in the carrier density when increasing the T content probably because of the formation of additional Al$-T$ bonds in addition to those existent of Al$-R$. Thus, while the progressive formation of local Al$-T$ covalent bonds seems to result in a decrease in the effective free-electron concentration irrespective of the nature of the transition element, the electrical resistivity strongly suggests that s-d scattering contribution decreases with Fe, Co, and Ni—in that order—as expected from the d-state occupation in these elements. The Cu atom has its $3d$ band filled and thus no (s,p)-d scattering is expected to contribute to the electrical resistivity which will be determined by (s,p) electrons. On the other hand, the Fe and Co atoms with an incomplete $3d$ band offer a more complex situation. In this case both the formation of covalent bonds and a larger probability for the conduction electrons of Al to be scattered into d states of the T atoms contribute to an increase of the electrical resistivity. An x-ray photoemission spectroscopy study of late transition metals dissolved in Al (Ref. 6) indicates that there is an hybridization of the $3d$ electrons of the T with the conduction electrons (s,p) of Al which lead to a density of states in the Fermi level characterized by (s,p) electrons, the $3d$ band of the T atoms lying well below the Fermi level. The hybridization will enhance (s,p)-d scattering in agreement with our measurements. This would explain, in part, the additional contribution and different rates of increase of the electrical resistivity as being due to s-d scattering from Fe, Co, Ni, and Cu. However, it is necessary to point out that the total change in the magnitude of the electrical resistivity from about 65 $\mu\Omega$ cm to as high as 250 $\mu\Omega$ cm or more in the amorphous state for a change in concentration of the additional elements by about 15 at.% is unusual. Such large changes in resistivity are not observed with compositional changes of the order of 20 at.% in d-band amorphous materials rich in transition metal components.[7]

Despite the negative values observed for the Hall coefficient in all the studied alloys and the increase in magnitude when Al is substituted by T and R indicating a decrease in the density of carriers we have shown that a free-electron model is not quantitatively applicable even though the large concentration of Al might suggest it. This fact suggests that s-d scattering which is assumed to contribute to the electrical resistivity may also be important in order to understand quantitatively the Hall coefficient for these alloys.

The different behavior observed between alloys containing Y or La remains at the moment unexplained, especially because preliminary magnetic measurements on these alloys indicate that they are weakly paramagnetic with a susceptibility of the order of 10^{-6} at $T=4$ K. This fact rules out the possibility to explain the observed differences between the Y and La series as being due to different types of magnetic interactions.[8]

In any case, we have in melt-spun Al-T-R alloys a unique opportunity to test quantitatively the consequences of transition from an s- to d-band type amorphous material. For a quantitative estimate of the above points, measurements of the electrical resistivity as well as the Hall coefficient in an extended temperature range for these alloys are in progress.

CONCLUSIONS

The observed decrease in the effective electron concentration, as inferred from the negative Hall-coefficient data, suggests that substitution of Al by T and/or R atoms results in changes in local chemical short-range order such that the formation of Al$-T$ and Al$-R$ bonds are promoted. The presence of many intermetallic compounds in the equilibrium phase diagram of Al-based binary systems[9] probably favors the formation of bonds. The above observations are consistent with the reported[1,2] enhancement in the mechanical properties for these new class of amorphous Al-based ternary alloys. The unusually large increase in the electrical resistivity from about 65 to above 250 $\mu\Omega$ cm with hardly 15 at.% substitution of T for Al, provides us with an opportunity to study more systematically the consequences of the transition from s- to d-band amorphous metallic alloys on their electronic properties. Studies of the temperature dependence of the transport properties in an extended range are in progress.

ACKNOWLEDGMENTS

It is our pleasure to acknowledge many valuable discussions with Professor Y. Makino during this work. We also acknowledge the keen interest and many comments on this work from Professor J. S. Muñoz, Autonoma University of Barcelona. One of us (M.P.) is thankful to the Spanish Government for support. Work in Sweden has been supported through a research grant from the Swedish Board for Technical Development, STU, under a "ram program" on rapid solidification technology.

[1] A. Inoue, K. Ohtera, A. Tsai, and T. Masumoto, Jpn. J. Appl. Phys. **27**, L280 (1988); **27**, L479 (1988); see also Y. Hei, S. J. Poon, and G. J. Shiflet (unpublished).

[2] A. Inoue *et al.* (unpublished).

[3] B. Lundberg and G. Bäckström, Rev. Sci. Instrum. **43**, 873 (1972).

[4] R. Delgado, H. Armbrüster, D. B. Naugle, C. L. Tsai, W. L. Johnson, and A. Williams, Phys. Rev. B **34**, 8288 (1986).

[5] G. Bush and H. J. Güntherodt, in *Solid State Physics,* edited by F. Seitz and D. Turnbull (Academic, New York, 1974), Vol. 29, p. 235.

[6] P. Steiner, H. Höchst, W. Steffen, and S. Hüfner, Z. Phys. B **38**, 191 (1980).

[7] P. J. Cote and L. V. Meisel, in *Glassy Metals I,* edited by H. J. Güntherodt and H. Beck, Topics in Applied Physics, Vol. 46 (Springer-Verlag, Berlin, 1981).

[8] N. Heiman and N. Kazama, Phys. Rev. B **19**, 1623 (1979).

[9] *Constitution of Binary Alloys,* edited by M. Hansen and K. Anderko (McGraw-Hill, New York, 1958).