

Hall's coefficient for Cu-Zr alloys with amorphous and crystalline structure

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The resistance and Hall's coefficient R_H for Cu-Zr alloys in the amorphous and crystalline states are measured. As the temperature is increased up to room temperature, the quantity R_H^c for the crystalline alloys approaches the values of R_H^{am} characteristic for amorphous alloys, which, as is well known, have an anomalous sign: $R_H^{am} > 0$. To interpret the results a two-band (s - and d -) model with strong scattering in the d -band is proposed.

In recent years, the results of measurements of the Hall coefficient R_H of a large number of metallic alloys with an amorphous structure¹⁻⁵ and of liquid metals⁶ have been published. According to these data, in strongly disordered systems, consisting of atoms of simple metals, the classical expression

$$R_H = (nec)^{-1} \quad (1)$$

is valid even when the mean-free path length of electrons l is comparable to the interatomic distance a , when the resistivity of the alloy exceeds $100 \mu\Omega \cdot \text{cm}$.^{4,5} At the same time a number of liquid metals and amorphous alloys containing a large concentration of transition metal atoms with an unfilled d shell exhibit a positive Hall coefficient, as if most of the carriers were holes.^{1-3,6}

The amorphous alloys with positive R_H include the alloy Cu-Zr.^{1,2} Zirconium is a

transition element with four electrons in the outer $4d$ and $5s$ shells: two electrons in the s state and two in the d state. For purpose of further studying the problem of the positive R_H , we performed measurements on four alloys $\text{Cu}_x\text{Zr}_{1-x}$ with different composition ($x = 0.4, 0.5, 0.6,$ and 0.65) in the amorphous and crystalline states.

EXPERIMENT

An amorphous strip with a width of about 10 mm and a thickness of of 25–30 μm was obtained by rapid cooling of the alloy on the surface of a rotating copper drum. The absence of crystalline inclusions was checked by x-ray diffraction analysis and the composition was checked by a chemical analysis. The specimens had an area of 3.5×24 mm, and their thickness was determined from the dimensions, weight, and specific weight to within 5%. The electrical measurements were performed with dc current by the potentiometric method. The specimens were mounted in such a way as to eliminate mechanical stress in them during cooling. To prepare crystalline specimens the starting plates were annealed in a vacuum of 3×10^{-6} torr for 30 min. In different cases the annealing temperature varied from 550 to 750 $^\circ\text{C}$. The absence of residues of the amorphous material after annealing was checked by x-ray diffraction analysis.

RESULTS

Figure 1 shows the results of measurements of R_H and the specific resistivity ρ . For convenience, the points corresponding to measurements of a single type on alloys with different compositions are connected by the dashed curves. The shaded band indicates values of R_H which should appear, according to (1), in alloys with the corresponding composition. The lower edge of the band corresponds to the assumption that

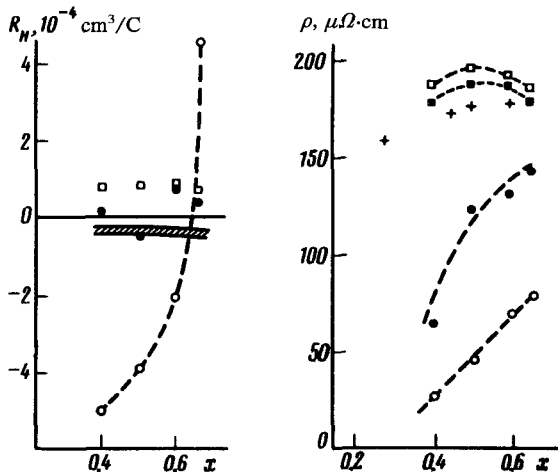


FIG. 1. Hall's coefficient R_H and the resistance ρ of alloys Cu-Zr. The squares are for the amorphous alloys and the circles are for the crystalline alloys. The light-colored signs are for $T = 4.2 \text{ K}$, and the black circles are for $T = 300 \text{ K}$. The cross marks are the data in Ref. 7.

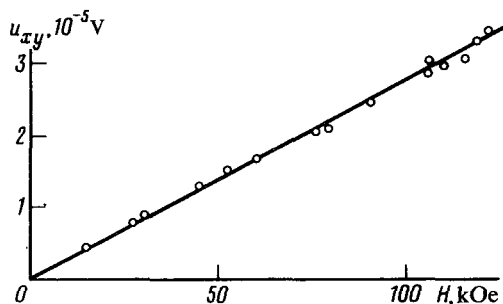


FIG. 2. Field dependence of the Hall voltage on an amorphous specimen of the alloy $\text{Cu}_{0.6}\text{Zr}_{0.4}$ at $T = 2$ K.

the zirconium atom gives up two electrons and the upper edge corresponds to the case of four electrons.

The absolute values of ρ and R_H for amorphous alloys coincide within the limits of error with the measurements performed by others.^{1,2,7} The basic experimental fact to which we would like to draw attention is the presence of a correlation between the quantity R_H and the scattering intensity, which is characterized numerically by the quantity ρ . As the temperature of the crystalline specimens is increased, ρ approximately doubles and R_H^{cr} approaches the values of R_H^{am} of the amorphous material.

Most low-temperature measurements of R_H were performed in a field up to 20 kOe. We also always checked that the Hall voltage u_{xy} increases linearly with increasing field. For the amorphous alloy $\text{Cu}_{0.6}\text{Zr}_{0.4}$ the linearity of the dependence $u_{xy}(H)$ was checked in fields up to 125 kOe (see Fig. 2). The linearity of $u_{xy}(H)$ as well as the absence of a temperature dependence $R_H^{\text{am}}(T)$ in amorphous alloys virtually exclude the possibility of explaining the observed anomalies by phenomena such as oblique scattering.⁸

DISCUSSION

We assume that the anomalies of the Hall coefficient in amorphous alloys containing transition metals can be explained with a two-band model.^{9,10} It is natural to suppose that the collectivized s and d states in the alloy are not completely hybridized but form two separate isotropic energy bands. According to experimental data on the photoemission spectra,¹¹ the peak in the density of states near the Fermi level in the alloys Cu-Zr is due to d -electrons, belonging initially to zirconium. In the alloy they form a quite narrow band.

The carriers in the narrow band are usually scattered more strongly, so that the criterion of strong scattering

$$W \cong \hbar / \tau \tag{2}$$

(W is the width of the band), which is equivalent to the relation $l \simeq a$, can be attained in the d band under conditions such that for the remaining carriers the inequality $l > a$ is still satisfied. Under conditions (2) the kinetic equation is obviously inapplicable. The conduction in such a d band is more reminiscent of hopping conductivity in semiconductors. As is well known, under the conditions of hopping conductivity the

sign of the Hall effect for carriers of a given sign can be different: It depends on the amount and arrangement of the nearest neighbors of the atoms, i.e., on the short-range order in the material.^{12,13}

There is one other analogy to the physics of semiconductors. It is known that relations (1) are not satisfied in some very narrow-band organic semiconductors and oxides of transition metals. The explanation of this¹⁴ is based on the fact that with a bandwidth

$$W < kT \quad (3)$$

carriers with all possible masses, both positive and negative, participate in the conduction process. Here the sign of R_H depends on the symmetry of the crystal. Criterion (2) is in some respects similar to criterion (3). In the case of (3) all states of the band contribute to the kinetic coefficients due to the Boltzmann factor $\exp(-W/kT)$. In the case of (2) they become mixed due to the uncertainty relation, which has the form $\Delta\epsilon \simeq W$.

Thus we arrive at the following picture. In the crystalline state the electronic spectra of different intermetallic phases are described with the help of electronic and hole Fermi surfaces. At helium temperatures, scattering by numerous defects probably smoothes the anisotropy in the dispersion law, but the hole and electronic natures of the bands remains. The partial compensation of electronic and hole volumes leads to absolute values of R_H greatly exceeding (1). In this case R_H can have any sign, depending on the band structure of the corresponding intermetallide. Both the transition to the amorphous structure and the increase in the temperature of the crystalline specimen are accompanied by an intensification of scattering. In both cases criterion (2) is realized in the narrow d band. The metallic nature of the alloy in this case remains due to the presence of the s band, where $l > a$. Because of the high density of the d states, however, the scattering of s electrons in most cases is accompanied by their transition to the d band. For this reason, the quantity R_H is probably attributable to the properties of both bands.

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¹B. L. Gallagher, D. Greig, M. A. Howson, and A. M. Croxon, *J. Phys. F* **13**, 119 (1983).

²H. J. Guntherodt *et al.*, *J. Phys. (Paris)* **41**, Colloque No. 8, CB-381 (1980).

³P. J. Colter, T. W. Adair III, and D. G. Naygle, *Phys. Rev. B* **20**, 2959 (1979).

⁴T. Matsuda and U. Mizutani, *Solid State Commun.* **44**, 145 (1982), *J. Phys. F* **12**, 1877 (1982).

⁵U. Mizutani and T. Yashida, *J. Phys. F* **12**, 2331 (1982).

⁶H. U. Kunzi and H. J. Guntherodt, *The Hall Effect and Its Applications*, edited by C. L. Chien and C. R. Westgate, Plenum, New York, 1980 p. 215.

⁷B. L. Gallagher and D. Greig, *J. Phys. F* **12**, 1721 (1982).

⁸A. Fert and A. Hamzic, *Ref. 6*, p. 77.

⁹R. Evans, D. A. Greenwood, and P. Lloyd, *Phys. Lett A* **35**, 57 (1971).

¹⁰N. F. Mott, *Phil. Mag.* **26**, 1249 (1972).

¹¹P. Oelhafen, E. Hauser, and H. J. Guntherodt, *Solid State Commun.* **35**, 1017 (1980).

¹²L. L. Friedman, *Phil. Mag. B* **38**, 467 (1978).

¹³D. Emin, *Ref. 6*, p. 281.

¹⁴L. L. Friedman, *Phys. Rev.* **131**, 2445 (1963), *Phys. Rev. A* **133**, 1668 (1964).

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