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# Sign reversal of the Hall coefficient in amorphous Ni-Zr alloys

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We present a systematic study of the temperature and composition dependence of the Hall coefficient $R_H$ in amorphous $Ni_{1-x}Zr_x$ alloys. The weak temperature variation between 4 and 300 K is indicative of isotropic scattering in these alloys. There is, however, an abrupt but continuous crossover from negative to positive $R_H$ values with increasing $x$ near $x=0.6$. Comparison with the Hall coefficients found for CuZr alloys leads to the conclusion that the position and width of the 3$d$ component density of states plays a central role in the crossover behavior.

## I. INTRODUCTION

In view of the fact that several transport parameters, such as the resistivity and the thermoelectric power, have been extensively studied in amorphous metallic systems, it is surprising to note that the Hall effect has not been systematically researched in the nonmagnetic alloys. This situation arises from two factors which have tended to discourage such studies: the presence of considerable experimental difficulties and the absence of a consistent theoretical framework. Experimentally, the Hall coefficient of amorphous nonmagnetic alloys is small, characteristic of metals, but the relatively large resistivity often places considerable constraints on the stability of the measuring instrumentation. Theoretically, the interpretation of those Hall coefficients which have been reported is clouded by the fact that many alloys show positive values and that information on their temperature dependence has been unavailable.

Very recently Gallagher *et al.*[1] have addressed these problems in a study of the Hall coefficients in a series of amorphous CuZr, CuTi, and CuHf alloys. They show for these systems that there is no significant temperature dependence of $R_H$ and that the data indicate a crossover from negative $R_H$ at high Cu concentrations to positive values as the Zr content is increased beyond 20 at. %. Similar behavior has been found by Kunzi and Güntherodt[2] in noble-metal—rare-earth liquid metals. The $s$-$d$ hybridization interaction was considered[1] to be at the origin of the positive Hall coefficients.

In this paper we present measurements of the Hall coefficient for a series of $Ni_{1-x}Zr_x$ alloys with $30 \leq x \leq 80$ in the temperature range from 4 to 300 K. Resistivity and thermopower data for these same alloys have been determined by Altounian *et al.*[3,4] Across the entire phase diagram the Hall coefficient exhibits only a weak temperature dependence. More strikingly, there is a crossover from negative to positive $R_H$ values near $x=0.6$; Ni-rich alloys have negative $R_H$ while the Zr-rich ones have a positive $R_H$. When compared with the CuZr results cited above, these characteristics lead to the conclusion that the form and nature of the $d$ bands play a direct role in this sign reversal. It is implied that the partially filled Zr $d$ band which dominates the density of states at $E_F$ gives rise to the positive contribution to $R_H$. This term is systematically suppressed by the substitution of late transition-metal elements as their more tightly bound $d$ bands move closer to $E_F$.

## II. EXPERIMENTAL

The alloys were prepared by melt spinning under helium atmosphere[5] and stored under liquid nitrogen until mounted for measurement. The thickness of the samples was determined from the density and measurements of the two major dimensions. Because most of the ribbons are quite narrow ($\sim 1$ mm) the samples were not cut into the standard tabbed form. For the most part, fine copper wires were spot welded to the samples as close as possible to the outer edges; several contacts were made with conducting epoxy cement. In this configuration there is the possibility that the effective distance between contacts is less than the sample width, giving rise to an uncertainty in the value of the form factor. The consistency of measurements between samples from the same ribbon as well as those of different composition suggests an upper bound of 20% on the uncertainty of the absolute values. There is,

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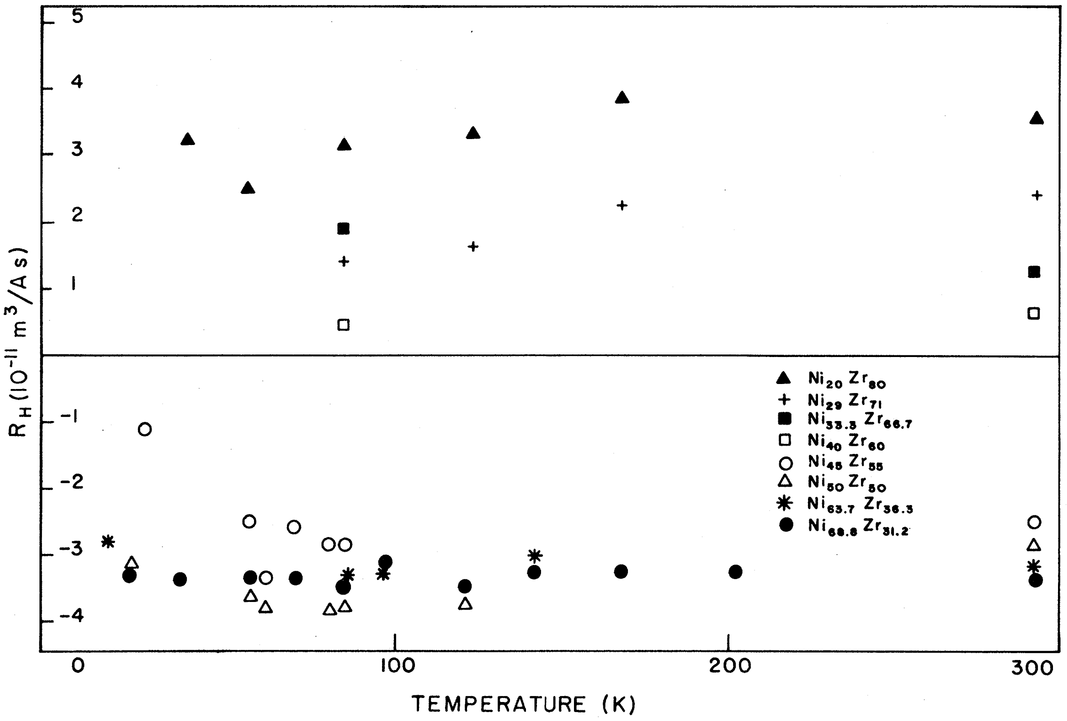

FIG. 1. Hall coefficient $R_H$ as a function of temperature for the NiZr alloys.

however, no such uncertainty on the sign of $R_H$ nor on the crossover composition.

The measurements were taken with the use of a low-frequency ( ~200-Hz) current and lock-in detection based on the high-resolution differential ohmmeter circuit described by Cochrane *et al.*[6] This circuit has been modified to permit direct feedback control during the field sweeps. All field and temperature changes as well as the bridge balance have been adapted for microcomputer control and will be described in a forthcoming paper.[7]

## III. RESULTS

The Hall coefficients for the NiZr alloys are shown in Fig. 1 as a function of temperature between 4 and 300 K. Table I lists the room-temperature $R_H$ values as well as their resistivities and densities.[4]

The weak temperature dependence (with the possible exception of the alloy with $x = 0.71$) is consistent with the assumption of very little aging in these samples. This conclusion is reinforced by the excellent agreement with the value of $R_H(300\text{ K})$ for $Ni_{24}Zr_{76}$ taken from Güntherodt *et al.*[8] Indeed, crystallization studies[5] indicate that the NiZr system is not subject to the same oxidation crystallization that plagues the CuZr system.

The principal feature of these data is clearly the rapid change in sign of $R_H$ near $x = 0.6$ as indicated in Fig. 2 which plots $R_H(300\text{ K})$ vs $x$. The near

TABLE I. Room-temperature density, resistivity, and Hall coefficients for the NiZr alloys.

| Zr content (at. %) | Density[a] (g/cm$^3$) | Resistivity[a] ($\mu\Omega$ cm) | Hall coefficient ($10^{-11}$ m$^3$/A s) |
|---|---|---|---|
| 31.2 | 8.20 | | $-3.17\pm0.13$ |
| 36.3 | 7.97 | 172 | $-3.3\ \pm0.13$ |
| 50 | 7.49 | 183.5 | $-2.80\pm0.25$ |
| 55 | 7.34 | 185 | $-2.48\pm0.07$ |
| 60 | 7.21 | 176 | $+0.67\pm0.06$ |
| 66.7 | 7.05 | 168 | $+1.27\pm0.07$ |
| 71 | 6.96 | 164 | $+2.39\pm0.09$ |
| 80 | 6.78 | 160 | $+3.51\pm0.13$ |

[a] From Ref. 4.

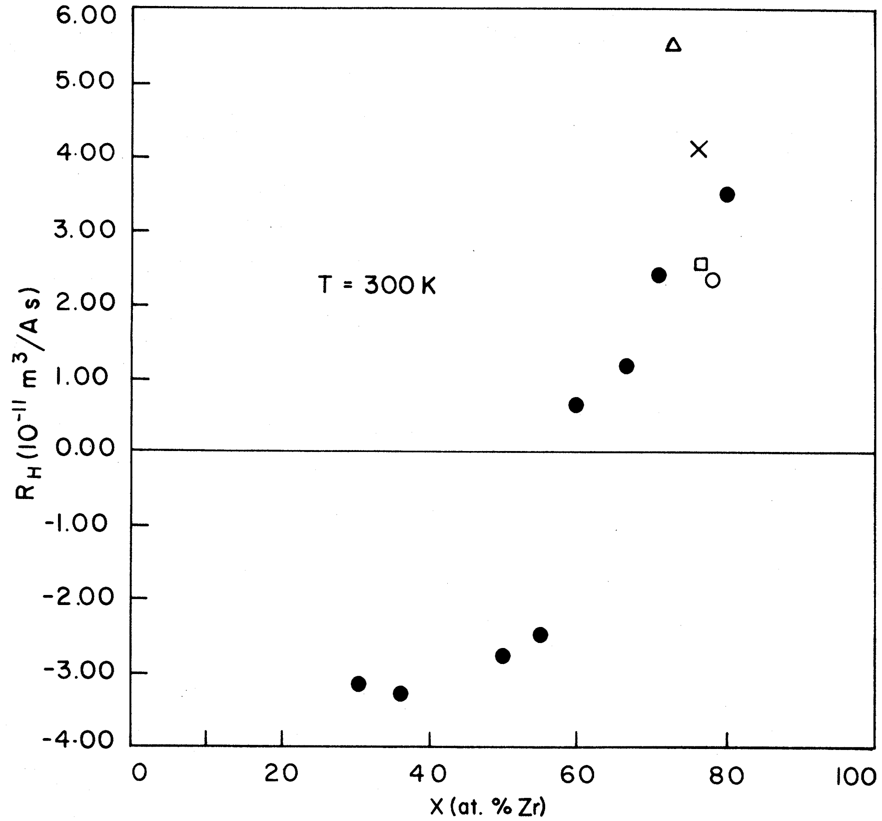

FIG. 2. Hall coefficient $R_H$ as a function of composition for our NiZr alloys (●). Also shown is data on $Cu_{27.5}Zr_{72.5}$ (Ref. 1) (△), $Ni_{24}Zr_{76}$ (Ref. 8) (□), $Co_{22}Zr_{78}$ (Ref. 8) (○), and $Fe_{24}Zr_{76}$ (Ref. 8) (×). ($x$ = at. % Zr.)

zero value at $x = 0.6$ (see Table I) confirms that the crossover is a smooth one. Also shown in this figure are the data for the late Zr 3$d$ alloys near $x = 0.75$: $Cu_{27.5}Zr_{72.5}$,[1] $Ni_{24}Zr_{76}$,[8] $Co_{22}Zr_{78}$,[8] and $Fe_{24}Zr_{76}$.[8]

## IV. DISCUSSION

Before treating the sign reversal of $R_H$, a comment on the weak temperature dependence can be made. Gallagher *et al.*[1] have concluded that the absence of an appreciable temperature dependence in the amorphous CuZr, CuTi, and CuHf alloys arises from the inherent isotropy of the scattering processes. We are lead to the same conclusion for the NiZr alloys. Moreover, given that only very small resistivity temperature derivatives are observed, it would be unreasonable to expect strong temperature variations in the Hall constant.

The central feature of our data is the sharp but continuous sign reversal of the Hall coefficient near $x = 0.6$ over a concentration interval of approximately 10 at. %. To put this variation in perspective we note a similar reversal for the CuZr alloys at a much smaller Zr concentration ($x \sim 0.2$). Furthermore, the thermoelectric power[3] undergoes a sign reversal in NiZr, but on the Ni-rich side of the phase diagram ($x = 0.32$), and the temperature derivative of the resistivity extrapolates to zero in the same neighborhood. These latter variations have been extensively discussed[1,3] within the Faber-Ziman and Mott models which can, in principle, accommodate such reversals. There exists, however, no such framework for formulating an analysis of the Hall coefficient.

In attempting to delineate the important parameters which control the positive contributions to $R_H$ our attention focuses on the $d$ density of states in the alloy series (Cu, Ni, Co, Fe)-Zr. Ultraviolet-photoemission–spectroscopy (UPS) measurements[9] show a two-peaked structure where the peak at higher binding energies broadens and approaches the second one in a systematic fashion from Cu to Co to Fe. Several recent calculations[10–12] reproduce this structure while indicating that the Zr subband around $E_F$ is practically unchanged as the high-$d$ element varies along this series. The rapid increase in the crossover composition moving from Cu to Ni suggests that the broader Zr 4*d* band at $E_F$ is principally responsible for the positive contribution to $R_H$ and that the interaction with the transition-metal 3*d* band reduces this anomalous term.

This suggestion is consistent with the characteristics mentioned by Gallagher *et al.*[1] who point out the following.

(i) $R_H$ is very similar in the liquid, amorphous, and (for *d* metals) crystalline states.

(ii) Liquid Cu, Ni, and Co have $R_H < 0$ while liquid Fe, Mn, and La have $R_H > 0$.

The general features depend not on structure but on the form of the *d*-band density of states.

Theoretically, there is reason to believe that $R_H$, for both a tight-binding *s* band[13] and a tight-binding *d* band,[14] are negative. This led to the hypothesis that *s*-*d* hybridization is at the origin of the positive contribution to $R_H$. Weir and Morgan[14] maintain that $E(k)$ curves are a valid representation of the electron dynamics even in these strongly disordered environments and that *s*-*d* hybridization gives negative group velocities in the middle of the *d* band and hence a positive $R_H$.

In disordered systems, where the wave vector *k* is not necessarily a good quantum number, an alternative approach to an analysis of electronic transport phenomena is afforded by the use of the Kubo formalism, as has been proposed by Datta.[15] This author has shown that the conductivity is characterized by an effective mass $m^*$, given by

$$\frac{1}{m^*} = 2\sum_{\beta} \frac{|(v_x)_{\alpha\beta}|^2}{E_\beta - E_\alpha} ,$$

where $v_x$ is the velocity operator and the $\beta$ summation extends over all states to which an electron can make transitions from $\alpha(E_F)$. It is to be noted that the mass above is the *longitudinal* effective mass, i.e., that mass defined by calculating the response of the charge to a static electric field, whereas, in a Hall experiment, it is the *tangential* component that is of relevance (Ballentine[16]). The approach described by Datta is a reasonable one; however, the calculations have to be modified, when discussing the Hall effect, to reflect the behavior of the expectation value of the acceleration operator for a charged particle in motion, subject to a magnetic field, rather than the response of a charged particle to a static electric field. We expect that the new result for $m^*$ will depend on a combination of factors: (i) the density of states, (ii) the position of the Fermi level $E_F$, and (iii) the magnitude and energy dependence of specific matrix elements. Such an approach highlights the characteristics which appear to be important to an understanding of the systematic variations found experimentally; further, it avoids a recourse to the concept of *E*-*k* surfaces, which cannot easily be extended to disordered systems.

A number of further Hall experiments suggest themselves at this point, experiments related to the various issues raised above, and we are currently engaged in such measurements. A first series involves the adjacent CoZr and FeZr sequences, where the crossover concentration is expected to continue to increase until swamped by magnetic interactions. On this point, Güntherodt *et al.*[8] report a positive $R_H$ for both $Co_{22}Zr_{78}$ and $Fe_{24}Zr_{76}$, so that in neither system has the crossover been eliminated. A second series involves varying the early bandwidth by going from Ti to Zr to Hf. In this latter case there is an indication that the Hall coefficients increase in the same order.[1]

## ACKNOWLEDGMENTS

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