PHYSICAL REVIEW B VOLUME 39, NUMBER 17 15 JUNE 1989-I

Electron transport properties of amorphous $(\mathrm{Zr}_{0.64}\mathrm{Ni}_{0.36})_{1-x}\mathrm{Al}_x$ alloys

A. K. Bhatnagar,* R. Pan, and D. G. Naugle
Department of Physics, Texas A&M University, College Station, Texas 77843-4242

(Received 28 November 1988; revised manuscript received 16 March 1989)

Measurements of the electrical resistivity $\rho(T)$, thermopower $S(T)$, and Hall coefficient R_H for a series of rapidly quenched Zr-Ni-Al alloys are reported for concentrations from $x=0$ to 0.25. The resistivity is large ($\rho \approx 200\ \mu\Omega\,\mathrm{cm}$) and increases with Al content as does R_H, which is positive for all concentrations studied. The thermopower is positive but decreases in magnitude with Al concentration. A consistent qualitative explanation of the concentration dependence of ρ, R_H, and S is suggested.

I. INTRODUCTION

The electrical transport properties of amorphous transition-metal alloys have been reviewed by Mizutani[1] and by Naugle.[2] The behavior of the Hall coefficient in these highly disordered alloys has been one of the more interesting features. A positive sign for R_H is common for alloys comprised predominantly of the early transition metals.[1-6] For early-transition-metal–late-transition-metal and early-transition-metal–simple-metal or –metalloid amorphous alloys, the sign of R_H can change from positive to negative as the concentration of the early transition metal is decreased. This is particularly well illustrated by measurements on amorphous Zr-based alloys, Zr-Cu,[4,7,8] Zr-Ni,[8,9] Zr-Co,[8] and Zr-Fe.[8] Weir *et al.*[10,11] have proposed that the positive sign results from a negative dispersion for the *s* states produced by *s-d* hybridization. They explain the change in sign with increasing Cu concentration for Zr-Cu alloys in terms of a dilution of the early transition metal.[10] Yamada *et al.*[12] have recently examined the behavior of R_H for a series of $(\mathrm{Zr}_{0.67}\mathrm{Ni}_{0.33})_{1-x}\mathrm{Al}_x$ alloys for Al concentrations up to $x=0.30$. Although the value of the Zr concentration in this alloy series passes through the concentration for which R_H in the Zr-Ni alloys crosses over to a negative value, R_H remains positive and surprisingly becomes larger with increasing Al concentration (thus decreasing Zr and Ni concentration) for the Zr-Ni-Al alloys of this series.

The occurrence of a negative-temperature coefficient of resistivity and a positive thermopower which is almost linear in temperature are two other features in the electron-transport properties which have been frequently observed for amorphous transition-metal alloys and which have received considerable attention.[1,2] The thermopower of Zr-Ni alloys is positive for large Zr concentrations, but then decreases to a quite small, but not yet negative, value for smaller Zr concentrations.[13] Gallagher and Greig[14] have found that the Mott *s-d*–scattering model[15] can account for the sign and magnitude of the thermopower in amorphous Zr-Ni alloys. In this model the sign of the thermopower is determined primarily by the sign of the energy derivative of the *d*-band density of states at the Fermi surface; a large positive derivative of the *d*-band density of states is associated with a positive thermopower. It has also been suggested that positive values of R_H are associated with a positive derivative of the *d*-band density of states at the Fermi energy.[16] Nguyen-Manh *et al.*[17] have provided theoretical support for this observation based on the *s-d*–hybridization explanation of the positive Hall coefficient by Weir *et al.*[10,11] Thus, thermopower measurements may be helpful in sorting out the unexpected dependence of R_H on Al concentration reported by Yamada *et al.*[12] for amorphous $(\mathrm{Zr}_{0.67}\mathrm{Ni}_{0.33})_{1-x}\mathrm{Al}_x$ alloys.

We report measurements of the electrical resistivity ρ, thermopower S, and Hall coefficient R_H for a series of melt-spun amorphous $(\mathrm{Zr}_{0.64}\mathrm{Ni}_{0.36})_{1-x}\mathrm{Al}_x$ alloy ribbons with $x=0$, 0.05, 0.10, 0.15, 0.20, and 0.25. Values of R_H and $\rho(T)$ are in qualitative agreement with the results reported by Yamada *et al.*[12] for $(\mathrm{Zr}_{0.67}\mathrm{Ni}_{0.33})_{1-x}\mathrm{Al}_x$ alloys; however, we find systematic differences in the temperature dependence of ρ and the composition dependence of R_H. The thermopower measurements are interpreted in terms of the Mott *s-d*–scattering model together with a low-temperature enhancement due to the electron-phonon interaction.[18-20] A consistent qualitative explanation of the dependence of ρ, S, and R_H on Al concentration is offered.

II. EXPERIMENT

Master alloys of $(\mathrm{Zr}_{0.64}\mathrm{Ni}_{0.36})_{1-x}\mathrm{Al}_x$ with $x=0$, 0.05, 0.10, 0.15, 0.20, and 0.25 were prepared by melting 99.9%-pure Ni, 99.6%-pure Zr, and 99.999%-pure Al in an argon atmosphere using an arc furnace. Each alloy was melted several times to ensure homogeneous mixing of the constituent elements. The weight loss after melting was found to be less than 0.1% in each case. Metallic glass ribbons of $(\mathrm{Zr}_{0.64}\mathrm{Ni}_{0.36})_{1-x}\mathrm{Al}_x$ were prepared in an argon atmosphere by induction melting the alloy ingot in a quartz crucible and ejecting it onto a single-roller melt spinner. The surface speed of the wheel was approximately 27 m/s. The metallic glass ribbons were approximately 1–2 mm wide and 15–30 μm thick. The glassy state of the ribbons was confirmed by x-ray diffraction and differential scanning calorimetry.

The resistance was measured by the standard four-terminal dc method in the temperature interval 1.5–300 K. Room-temperature resistivities of the samples were determined from the room-temperature resistance and the geometrical factor of each sample determined from the mass, density, length, and width. The density of each sample was determined by the Archimedes method using toluene as the liquid. The maximum contribution to error in the resistivity measurements comes from the uncertainties in width and density measurements. The estimated absolute accuracy of resistivity is about 5%.

Thermoelectric power measurements were done using the standard differential technique in which a 99.999%-pure lead foil was used as the standard reference material. The voltage ΔV and temperature difference ΔT across two ends of the sample were measured using a Keithley model 148 nanovoltmeter together with a digital voltmeter on its output and a calibrated Au-Fe thermocouple with a Keithley model 181 nanovoltmeter. The temperature difference ΔT across the sample was as small as 0.2%, but never more than 4% of the average temperature of the sample. For each measurement ΔV and ΔT were averaged over 50–100 readings taken at an interval of 0.5–1 s to reduce the measurement error. Thermoelectric power data on lead by Roberts[21] was used to obtain absolute thermoelectric power (TEP) of the $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ alloys. The estimated absolute error in the measurement of TEP is about 5–8 % depending on the temperature interval. The apparatus was the same as used earlier in this laboratory for thermopower and resistivity measurements. Further details including experimental procedure and tests of the precision and accuracy can be found in those references.[16,20,22]

The crystallization temperatures of the samples were determined using a Perkin-Elmer differential scanning calorimeter (DSC-2), and the superconductive transition temperatures T_c were determined from four-terminal-resistance–versus–temperature measurements near T_c. A calibrated carbon-glass thermometer was used for the T_c measurements.

A three-terminal technique[3] was used for the room-temperature Hall measurements. The Hall leads were spot welded to the sample. The Hall voltage as a function of field up to 1 T was measured with a Keithley model 147 nanovoltmeter. Typical measuring currents of 200 mA were used. The principal contribution to the uncertainties in values of R_H arises from the uncertainties in measurements of foil thicknesses and the width between the probes. Measurements with thin Au and Pt foils indicate an accuracy of better than ±10%.

III. RESULTS

The density measurements were done in order to calculate the thickness of a sample accurately. The room-temperature density variation of a-$(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ alloys as a function of aluminum concentration x is shown in Fig. 1 and values are given in Table I. The room-temperature density value of the $Zr_{0.64}Ni_{0.36}$ glassy alloy is 7.254 ± 0.12 g/cm^3 and agrees reasonably well with the density value 7.10 g/cm^3 for a $Zr_{0.635}Ni_{0.365}$ glassy alloy as reported by Altounian and Strom-Olsen.[23] The density of $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ glassy alloys decreases linearly as a function of x. Similar behavior has been observed in other amorphous alloys.[24] This result is indicative of the linear dependence of x on the packing fraction of aluminum in these alloys. A further analysis of this result will be presented elsewhere.

The room-temperature resistivity of $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ amorphous alloys versus x is shown in Fig. 2, and the values are listed in Table I. A comparison of resistivities of a-$(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ with those of a-$(Zr_{0.67}Ni_{0.33})_{1-x}Al_x$ alloys reported by Yamada *et al.* (also shown in Fig. 2) shows that there is good agreement between the two. Our data as well as those of Yamada *et al.* demonstrate that the addition of aluminum to Zr-Ni amorphous alloys, at least for the compositions studied, increases the room-temperature resistivity.

The temperature dependence of $\rho(T)/\rho(300\text{ K})$ for all amorphous $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ alloys is shown in Fig. 3. All samples showed a negative temperature coefficient of resistance. The concentration dependence of $\rho(T)$ reported here is significantly different from that reported by Yamada *et al.*[12] for $(Zr_{0.67}Ni_{0.33})_{1-x}Al_x$ alloys. Although the shape of their normalized resistivity curves are somewhat similar, they find that the temperature dependence of the normalized resistivity is greatest for $x=0$ and decreases as x increases. In contrast, as shown in Fig. 3, the temperature dependence of the normalized resistivity for our samples is smallest for $x=0$ and reaches a maximum for $x=0.15$. To check our results, the resistance measurements were repeated on three different sets of samples made at different times. No significant changes were observed. The inclusion of a small crystalline fraction

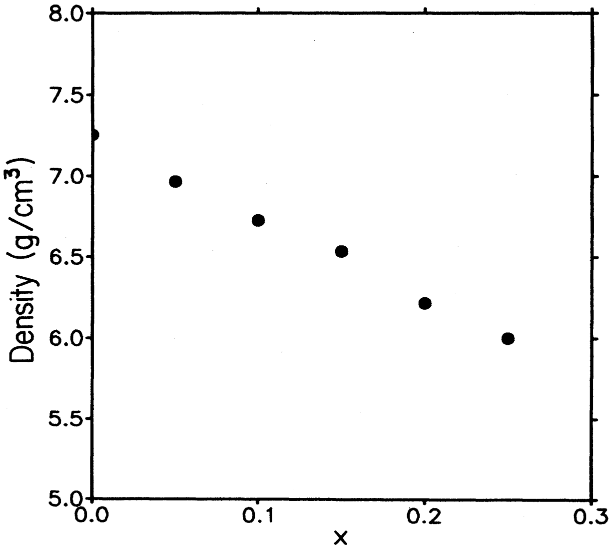

FIG. 1. Density as a function of Al concentration x for amorphous $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ alloys.

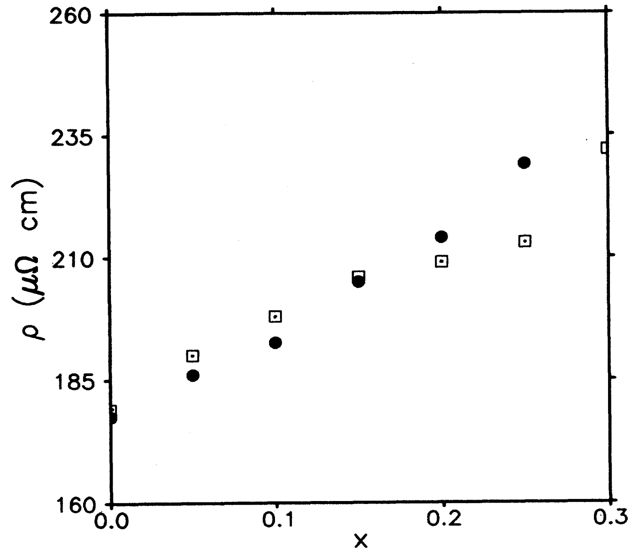

FIG. 2. Room-temperature (300-K) resistivity ρ as a function of Al concentration x for amorphous $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ alloys. ●—this work. □—from Yamada *et al.* for amorphous $(Zr_{0.67}Ni_{0.33})_{1-x}Al_x$ alloys, Ref. 12.

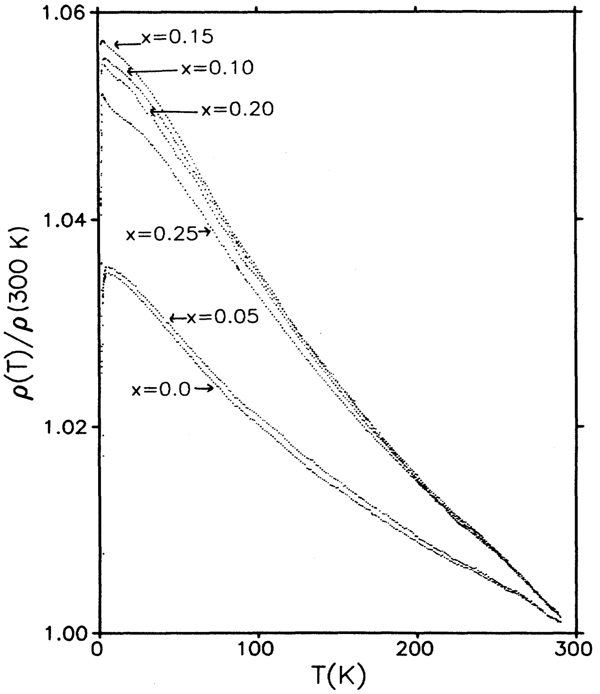

FIG. 3. Normalized temperature dependence of resistivity, $\rho(T)/\rho(300\text{ K})$ for amorphous $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$ alloys.

TABLE I. Values of the crystallization temperature T_{cryst} and the superconducting transition temperature T_c together with room-temperature (300-K) values of the mass density ρ_m, resistivity ρ, temperature coefficient of resistivity α, thermopower divided by temperature S/T, and Hall coefficient R_H for amorphous $(Zr_{0.64}Ni_{0.36})_{1-x}Al_x$.

x	T_{cryst} (K)	T_c (K)	ρ_m (g/cm^3)	ρ ($\mu\Omega$ cm)	α (10^{-4} K^{-1})	S/T (nv/K^2)	R_H (m^3/C)
0	679^a	2.54^a	7.25^a	178±9^a	−0.96±0.08^a	+8.3±0.4^a	+0.94±0.2^a
	747^{a,i}	2.560^c	7.10^c	173^c	−1.15^c	+7.1^f	
		2.68^g		179±6^b	−1.3^e	+7.8^h	+2.0 ±0.1^b
				171^d			+1.03^d
0.05	718^{a,i}	2.05^a	6.96^a	186±9^a	−0.96±0.10^a	+7.7±0.4^a	+1.2 ±0.15^a
	785^{a,i}	2.33^g		190±5^b			
0.10	764^a	1.62^a	6.73^a	193±10^a	−1.50±0.05^a	+6.7±0.3^a	+2.5 ±0.2^a
		1.81^g		198±5^b			+5.4 ±0.3^b
0.15	792^a		6.53^a	205±10^a	−1.5 ±0.1^a	+6.4±0.3^a	
				206±5^b			+4.2 ±0.7^b
0.20	800^a		6.21^a	214±11^a	−1.4 ±0.1^a	+6.2±0.3^a	+6.7 ±0.4^a
				209±4^b			+7.0 ±0.7^b
0.25			6.00^a	229±11^a	−1.50±0.05^a	+5.7±0.3^a	+8.4 ±0.4^a
				213±6^b			
0.30				232±7^b			+8.9 ±0.5^b

[a] This work.
[b] Yamada *et al.* Ref. 12, for $(Zr_{0.67}Ni_{0.33})_{1-x}Al_x$.
[c] Altounian and Strom-Olsen, Ref. 23 for $Zr_{0.635}Ni_{0.365}$.
[d] Cochrane *et al.*, Ref. 9, interpolated.
[e] Pekala and Trykozko, Ref. 25.
[f] Altounian *et al.*, Ref. 13, for $Zr_{0.67}Ni_{0.33}$.
[g] Yamada *et al.*, Ref. 38, for $(Zr_{0.67}Ni_{0.33})_{1-x}Al_x$.
[h] Gallagher and Hickey, Ref. 19.
[i] Second of two exothermic peaks observed in DSC scans.

can significantly alter the temperature coefficient of resistance, but within the accuracy of the x-ray-diffraction data there was no indication of crystallinity. We believe that our reported temperature dependence is a real behavior of the amorphous phase and not due to small crystalline inclusions.

From Fig. 3 it is seen that the normalized resistivity is not linear in the temperature over the range 1.5–300 K. There is a slight positive curvature in the data from 290 to 200 K. At lower temperatures ($T=20$ K) the curvature becomes negative. We believe that $T=20$ K is too far from the superconducting transition temperatures for superconducting fluctuations to be important. This behavior is also seen in the data of Yamada *et al.* not only on $(\mathrm{Zr}_{0.67}\mathrm{Ni}_{0.33})_{1-x}\mathrm{Al}_x$ alloys, but also for other $(\mathrm{Zr}_{0.67}\mathrm{Ni}_{0.33})_{1-x}M_x$ ($M=$B,Si,H) alloys as well.

The temperature coefficient of resistance (TCR) at room temperature, α, is plotted against x for our results in Fig. 4. The value of α for $\mathrm{Zr}_{0.64}\mathrm{Ni}_{0.36}$ is -0.96×10^{-4} K^{-1}. This values agrees well with the value -1.1×10^{-4} K^{-1} of a $\mathrm{Zr}_{0.67}\mathrm{Ni}_{0.33}$ amorphous alloy indicated by Yamada *et al.*[12] and the values -1.15×10^{-4} and -1.3×10^{-4} K^{-1} for $\mathrm{Zr}_{0.64}\mathrm{Ni}_{0.36}$ reported by Altounian and Strom-Olsen[23] and Pekala and Trykozko,[25] respectively. The magnitudes of α for our $(\mathrm{Zr}_{0.64}\mathrm{Ni}_{0.36})_{1-x}\mathrm{Al}_x$ at higher Al concentrations alloys are appreciably larger in magnitude, however, than those for $(\mathrm{Zr}_{0.67}\mathrm{Ni}_{0.33})_{1-x}\mathrm{Al}_x$ indicated by Yamada *et al.*

The superconducting transition temperature of samples with $x=0$, 0.05, and 0.10 are listed in Table I. The T_c of 2.52 K for $\mathrm{Zr}_{0.64}\mathrm{Ni}_{0.36}$ agrees well with the T_c of 2.54 K for $\mathrm{Ni}_{0.365}\mathrm{Zr}_{0.635}$ as reported by Altounian and Strom-Olsen.[23] The change in T_c is almost linear between $x=0$ and 0.10 with a slope of $dT_c/dx=-0.092$ K/at. %. T_c for alloys with higher Al concentrations were below the limits of this cryostat, 1.5 K.

Thermoelectric powers of $(\mathrm{Zr}_{0.64}\mathrm{Ni}_{0.36})_{1-x}\mathrm{Al}_x$ alloys are shown as a function of temperature from 1.5 to 300 K in Fig. 5. The thermopower for all samples is positive over the entire temperature range and its magnitude decreases with increasing aluminum concentration. At temperatures higher than 100 K, the thermopower is approximately linear in temperature, and there is a change in slope near 75 K. The temperature dependence of the

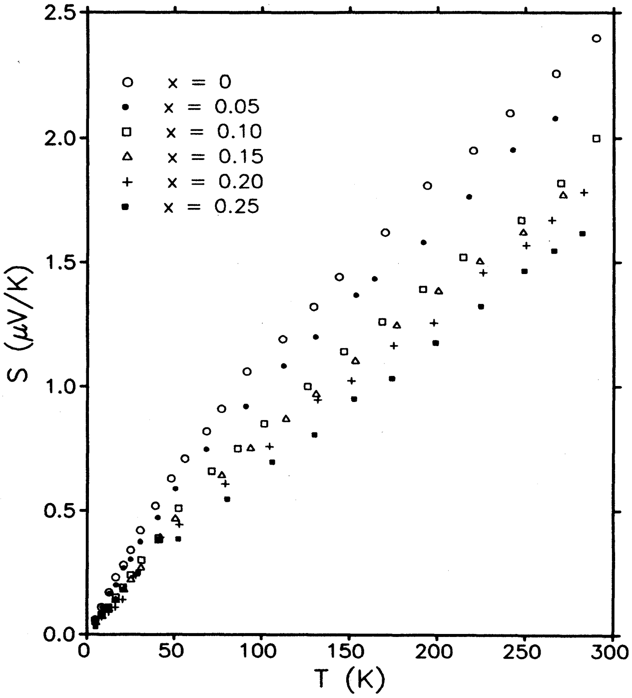

FIG. 5. Thermopower S as a function of temperature for amorphous $(\mathrm{Zr}_{0.64}\mathrm{Ni}_{0.36})_{1-x}\mathrm{Al}_x$ alloys. ○—$x=0$, ●—$x=0.05$, □—$x=0.10$, △—$x=0.15$, +—$x=0.20$, and ■—$x=0.25$.

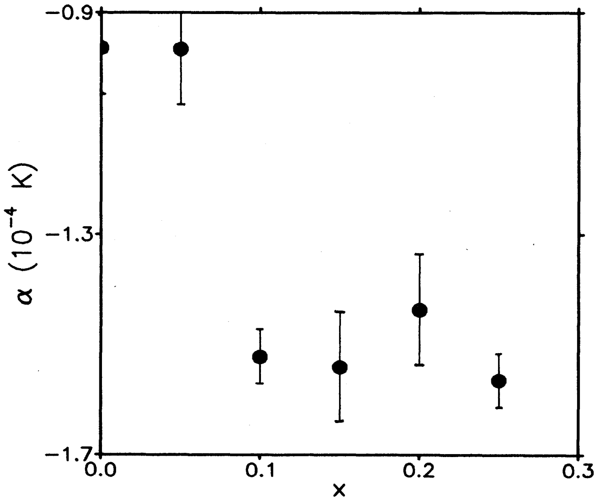

FIG. 4. Room-temperature (300-K) temperature coefficient of resistance $\alpha=R^{-1}dR/dT$ for amorphous $(\mathrm{Zr}_{0.64}\mathrm{Ni}_{0.36})1_{1-x}\mathrm{Al}_x$ alloys as a function of Al concentration x.

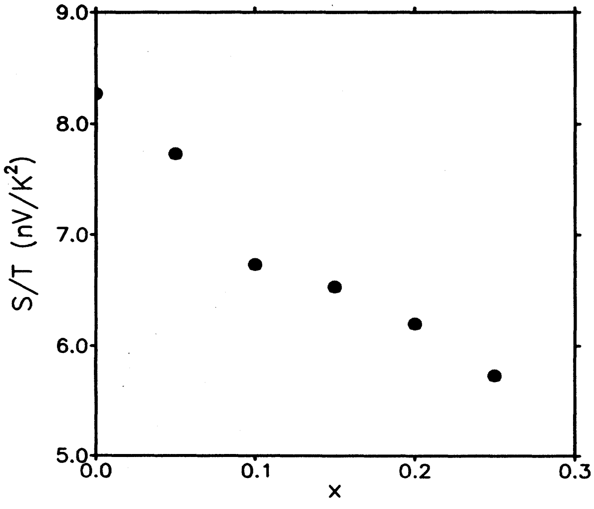

FIG. 6. Room-temperature (300-K) values of thermopower divided by temperature S/T for amorphous $(\mathrm{Zr}_{0.64}\mathrm{Ni}_{0.36})_{1-x}\mathrm{Al}_x$ alloys as a function of x.

magnitude of the thermopower for Zr-Ni-Al alloys is similar to that observed for amorphous La-Al (Ref. 16) and Ca-Al (Ref. 22) alloys. The room-temperature values of S/T as a function of aluminum concentration x are shown in Fig. 6 and also listed in Table I.

The room-temperature (300-K) values of the Hall coefficient R_H of amorphous $(\mathrm{Zr}_{0.64}\mathrm{Ni}_{0.36})_{1-x}\mathrm{Al}_x$ alloys are listed in Table I and shown as a function of x in Fig. 7. Values of R_H for amorphous $(\mathrm{Zr}_{0.67}\mathrm{Ni}_{0.33})_{1-x}\mathrm{Al}_x$ alloys reported by Yamada *et al.*[12] are also shown together with the value for amorphous $\mathrm{Zr}_{0.64}\mathrm{Ni}_{0.36}$ interpolated from data reported by Cochrane *et al.*[9] Our result for $x=0$, 0.94×10^{-11} m^3/C, is in excellent agreement with the interpolated value from data of Cochrane *et al.*,[9] 1.07×10^{-11} m^3/C, but it is approximately a factor of 2 smaller than the value reported by Yamada *et al.*[12] Although the general trend of R_H with composition x of our measurements is in agreement with those of Yamada *et al.*, the magnitudes of R_H which we measure are appreciably smaller than those reported by Yamada *et al.* at low Al concentrations and somewhat larger at higher Al concentrations. This is somewhat surprising since the agreement between the room-temperature values of ρ for the two sets of data is quite reasonable. The Hall coefficient of amorphous Zr-Ni alloys changes appreciably with the [Zr]/[Ni] ratio in this composition range,[9] but not so rapidly as to explain the relatively large differences between these two series of Al alloys with almost the same [Zr]/[Ni] ratio. It is conceivable that the compositional dependence of R_H for the ternary alloy system is more sensitive to the [Zr]/[Ni] ratio than for the binary Zr-Ni alloy system due to subtle interplay between the Al *s-p* states and the Zr and Ni *d* states.

The crystallization temperatures T_x of amorphous $(\mathrm{Zr}_{0.64}\mathrm{Ni}_{0.36})_{1-x}\mathrm{Al}_x$ alloys are listed in Table I. The crystallization temperature of these alloys increases sharply as aluminum is added initially, but eventually the increase in T_x with x flattens out.

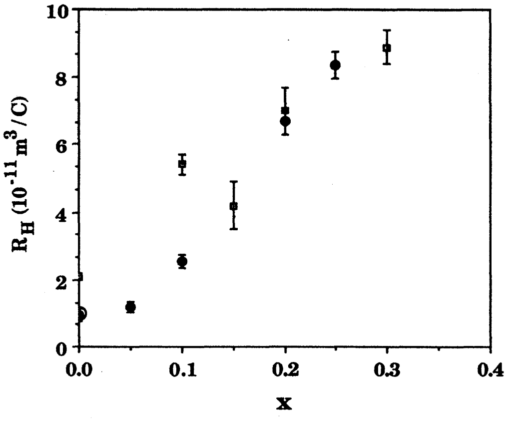

FIG. 7. Room-temperature (300-K) values of the Hall coefficient R_H for amorphous $(\mathrm{Zr}_{0.64}\mathrm{Ni}_{0.36})_{1-x}\mathrm{Al}_x$ alloys as a function of Al concentration of x. ●—this work. □—from Yamada *et al.*, Ref. 12, for amorphous $(\mathrm{Zr}_{0.67}\mathrm{Ni}_{0.33})_{1-x}\mathrm{Al}_x$ alloys. ○—value interpolated from data by Cochrane *et al.*, Ref. 9, for $(\mathrm{Zr}_{0.64}\mathrm{Ni}_{0.36})$.

IV. DISCUSSION

A. Composition dependence of ρ, S, R_H

Experimental results presented in the preceding section show the following changes in the electron-transport properties of amorphous $(\mathrm{Zr}_{0.64}\mathrm{Ni}_{0.36})_{1-x}\mathrm{Al}_x$ alloys as a function of aluminum concentration which one would like to explain.

(1) The room-temperature resistivity for all samples is high (greater than 175 $\mu\Omega$ cm) and increases with the aluminum concentration.

(2) The temperature coefficient of resistivity at 300 K is negative for all the samples studied. It becomes more negative as small amounts of aluminum are added to the parent alloy.

(3) The room-temperature thermopower of all the samples studied is positive and decreases with the aluminum concentration.

(4) The Hall coefficient is positive and increases with the addition of aluminum.

In addition, earlier work of Yamada *et al.*[12] on an amorphous alloy system, $(\mathrm{Zr}_{0.67}\mathrm{Ni}_{0.33})_{1-x}\mathrm{Al}_x$, with a similar composition reported similar behavior for ρ and R_H, but they also reported that (a) the density of states at the Fermi level $N(\varepsilon_F)$ decreases linearly with x, and (b) the magnetic susceptibility χ decreases with x. Although measurements of $N(\varepsilon_F)$ (specific heat) and χ have not been made on $(\mathrm{Zr}_{0.64}\mathrm{Ni}_{0.36})_{1-x}\mathrm{Al}_x$ alloys of the present work, nor are they available in literature, it can be safely assumed that a similar variation with x would be found.

Theoretical works which are frequently used to interpret or explain experimental data on the transport properties, especially electrical resistivity, of metallic glasses are (a) Ziman's theory, (b) Mott's *s-d*–scattering model, (c) scattering from a structural two-level system, and (d) localization and electron-electron correlations. A discussion of these is given in the review article by Naugle.[2] Recently Delgado *et al.*[16] demonstrated that the *d*-band contribution was the dominant factor for electron transport in amorphous La-based alloys. A major *d*-band contribution appears, however, to be relatively uncommon. A difference in sign between the thermopower and the Hall coefficient across the alloy series appears to be one indication of a significant *d*-band contribution, but that is clearly not the case for the Zr-Ni or the Zr-Ni-Al alloy series. Scattering from two-level defects and localization and correlation effects may play a roll in the small temperature dependence of the resistivity, but they are not important for the thermopower, the Hall coefficient, or the magnitude of the resistivity. Thus, we expect the composition dependence of ρ and S to be at least qualitatively understandable in terms of the Ziman-Faber model as extended by Evans *et al.*[26] for transition metals or the Mott *s-d*–scattering model. Gallagher and Greig[14] have pointed out the similarity between the expression for the resistivity given by Evans *et al.* for the extended Ziman-Faber model and that given by Brown *et al.*[27] for Mott *s-d* scattering. They also found that the experimental transport coefficients for a wide range of amorphous alloys including amorphous $\mathrm{Zr}_{1-y}\mathrm{Ni}_y$ alloys were in better agreement with the Mott *s-d* model. Consequently, we expect the Mott *s-d*–scattering model to be the preferred simple model as well as somewhat easier to use.

The most satisfactory explanation of the positive Hall coefficient which is routinely found for amorphous transition-metal alloys dominated by an early-transition-metal component is that based on the anomalous dispersion of *s*-like states due to *s-d* hybridization.[10,11] Nguyen-Manh *et al.*[17] have used a linear-response formula derived by Morgan and Howson[28] to show that the contribution to the Hall coefficient from each band in a simple approximation is proportional to the derivative of the density of states of that band at the Fermi surface. They find that the hybridization between the *s-p* and the *d* bands leads to the anomalous dispersion for the *s-p* band which, in turn, produces the negative energy derivative of the density of states for this band. They also demonstrate for $\mathrm{Zr}_{1-x}\mathrm{Cu}_x$ alloys that, if good electronic-structure calculations are available, the linear-response formalism permits calculations of both ρ and R_H as a function of composition x that are in reasonable agreement with experiment. Unfortunately, electronic-structure calculations for Zr-Ni-Al alloys are not available, and it is doubtful that reasonable calculations for such a complicated alloy system (two different transition metals and a simple-metal component) can be performed at this time. Although Nguyen-Manh *et al.* stressed that their simple expression for R_H was not valid, in general, that the contribution due to the hybridized *d* states (for σ, S, and R_H) should not be negligible over the complete composition range for amorphous Zr-based alloys and that the Mott *s-d* model greatly underestimates the conductivity contribution from the hybridized *s* states, we wish to see if the simplest models capable of qualitatively explaining transport in amorphous Zr-Ni transition-metal alloys can provide a qualitative understanding of the unusual effects of adding Al to these $(\mathrm{Zr}_{1-y}\mathrm{Ni}_y)_{1-x}\mathrm{Al}_x$ alloys. To date, experiments have been reported only for Zr-rich alloys ($y=0.33$ and 0.36). For those alloys the significant experimental effects to be understood are (a) the increase of ρ with x, (b) the dramatic increase of R_H (positive) with x, and (c) the decrease of S/T or S (also positive) with x.

In this admittedly naive approach, we will ignore any possible contribution to R_H, σ, or S from the *d* band. We will use the simplest result for R_H from Nguyen-Manh *et al.*[17] which relates R_H to the energy derivative of the hybridized *s*-band density of states,

$$R_H = \frac{-\alpha}{2|e|N_s^2(\varepsilon_F)} \left. \frac{dN_s(\varepsilon)}{d\varepsilon} \right|_{\varepsilon=\varepsilon_F} , \tag{1}$$

where α is a constant of order unity and $N_s(\varepsilon)$ is the density of states of the hybridized *s* states. The *s-d* hybridization leads to negative values of $dN_s/d\varepsilon$ and thus a positive Hall coefficient when ε_F lies roughly in the lower half of the *d* band. In the simplest form, that for free-electron rather than hybridized states, the expression for ρ in the Mott *s-d*–scattering model is[17]

$$\rho \simeq \frac{24\pi^4 \hbar \Gamma N_d(\varepsilon_F)}{e^2 K_0 k_F^3} , \tag{2}$$

where $N_d(\varepsilon)$ is the *d*-band density of states, k_F the Fermi wave number, Γ and $E_0=\hbar^2 K_0^2/2m$ are the width and energy of the *d* resonance, and m is the electron mass. The thermopower in this model is then

$$\begin{aligned} S &= \frac{\pi^2 k_B^2}{3|e|} T \left. \frac{\partial \ln \rho}{\partial \varepsilon} \right|_{\varepsilon=\varepsilon_F} \\ &= \frac{\pi^2 k_B^2}{3|e|} \left[-\frac{3}{2\varepsilon_F} + \left. \frac{\partial \ln N_d}{\partial \varepsilon} \right|_{\varepsilon=\varepsilon_F} \right] T , \end{aligned} \tag{3}$$

where e is the charge of the electron, k_B is the Boltzmann constant, and $\varepsilon_F = h^2 k_F^2/2m$ is the Fermi energy. A problem with this model, as with the Ziman-Faber model, is the determination of the appropriate value of k_F. To determine the variation with x, we primarily need to consider the relative variation of the quantities k_F, ε_F, $N_s(\varepsilon_F)$, $N_d(\varepsilon_F)$, $dN_s/d\varepsilon$, and $dN_d/d\varepsilon$.

Ultraviolet-photoelectron-spectroscopy (UPS) measurements for amorphous Zr-Ni alloys[29] show that the peak of the Zr *d* band lies somewhat above the Fermi energy while that for the Ni *d* band lies further below the Fermi energy. Recent UPS measurements on $\mathrm{Zr}_{0.67}\mathrm{Ni}_{0.33}$ and $(\mathrm{Zr}_{0.67}\mathrm{Ni})_{0.85}\mathrm{Al}_{0.15}$ alloys[30] show that as Al is added both the Zr and the Ni *d*-band contributions to the spectra are reduced equally in intensity. While it is difficult to make an accurate estimate in decrease of $N_d(\varepsilon_F)$ and $dN_d(\varepsilon)/d\varepsilon$, from these measurements a rough estimate has been made. Based on Cp data[31] $N_d(\varepsilon_F)$ decreases by 19% with addition of 15 at. % Al. The UPS data show that the apparent decrease in $N_d(\varepsilon)$ is only about 9%. An estimate of $N_d^{-1}\, dN_d/d\varepsilon$ can be made from the UPS data. If the UPS data are adjusted to give the same decrease in N_d on addition of 15 at. % Al as given by C_p measurements, it is found that this addition of Al decreases $N_d^{-1}\, dN_d/d\varepsilon$ at the Fermi energy by roughly 3%. If we do not make that adjustment, we estimate a decrease of 14%. A *worst*-possible-case estimate would be a 35% decrease. Thus, at least for the [Zr]/[Ni] ratio of these experiments and those of Ref. 12 one can assume that the relative shape of $N_d(\varepsilon)$ remains essentially unchanged even though $N_d(\varepsilon_F)$ is reduced when Al is added. The derivative of the *s*-band density of states $dN_s/d\varepsilon$ is determined by *s-d* hybridization. We cannot know its behavior except by detailed electronic-state calculations. Instead, we argue that, since the change in R_H with y in $\mathrm{Zr}_{1-y}\mathrm{Ni}_y$ alloys for $y=0.36$ is one-half the change with Al in $(\mathrm{Zr}_{0.64}\mathrm{Ni}_{0.36})_{1-x}\mathrm{Al}_x$ alloys, the effect should be related, at least in the low-Al-concentration range, to changes in the *s* density of states, i.e., when the [Zr]/[Ni] ratio is held fixed, addition of small amounts of Al should not affect *s-d* hybridization as strongly as it affects $N_s(\varepsilon_F)$. Thus, the sharp increase in R_H suggests a sharp decrease in $N_s(\varepsilon_F)$ or equivalently k_F as the Al concentration x is increased. Although $N_d(\varepsilon_F)$ is reduced also as x is increased, this simple model suggests that the k_F^3 term in Eq. (2) will lead to an increase in ρ as observed.

For the thermopower the variation would come from the free-electron term which is negative and would become larger in magnitude, whereas the positive contribution from the d-band density of states would be relatively unaffected. Thus, the model, with the assumption that the dominant effect from the addition of Al is the reduction of the s-state density of states, provides a qualitative description of the experimental observations of the changes in R_H, ρ, and S when Al is added to this Zr-Ni amorphous alloy. Clearly the model is far too naive to provide a quantitative estimate of the transport properties.

The model can be carried further, however, to make a qualitative prediction of the compositional variation of the transport properties of Ni-rich amorphous $(\mathrm{Zr}_{1-y}\mathrm{Ni}_y)_{1-x}\mathrm{Al}_x$ alloys. For the Ni-rich alloys R_H is negative[8] and S is small but positive.[13] Similar arguments to those above for Zr-rich alloys indicate that the addition of Al to the Ni-rich alloys would lead to a large increase in the magnitude of R_H which should remain negative, an increase in ρ and a decrease in S which should become negative. Although experimental values of the transport coefficients of Ni-rich Zr-Ni-Al alloys are not presently available, these alloys probably can be prepared in the amorphous state by standard rapid quenching techniques.

B. Temperature dependence of ρ and S

Recently, Mizutani[32] has given a short review of electron-transport properties of metallic glasses. He has concluded that the temperature dependence of resistivity ρ of group-V metallic glasses, simple-metal glasses like Ca-Mg-Al (for the definition of group-I–V metallic glasses, see Mizutani[1]), can be explained using the generalized Faber-Ziman theory in which the Debye-Waller factor predominantly determines the temperature variation of ρ. On the other hand, metallic glasses in group-IV, nonmagnetic transition-metal glasses like Cu-Zr, Ti-Cu, Y-Al, Ti-Ni, and Zr-Ni-Al, show a temperature-dependent resistivity which cannot be explained within this theory. Mizutani has used extensive experimental data on group-IV metallic glasses to show that the temperature dependence of these metallic glasses is well represented by the empirical relation

$$\frac{\rho}{\rho_0}=A+B\exp\left[-\frac{T}{\Delta}\right], \tag{4}$$

where A, B, and Δ are fitting parameters and ρ_0 is the resistivity at 300 K. Mizutani has found that the parameter Δ is strongly correlated to the Debye temperature Θ_D, and an increase in Θ_D leads to an increase in Δ.

We initially tried to fit our data (Fig. 3) to this expression for the resistivity ratio given above. However, it was found that not only was the fit not good, but it was not possible to find unique values of parameters A, B, and Δ. One could find different values of these parameters without affecting the fit tremendously. We, therefore, looked into other possible explanations for the results.

Recently, many workers have analyzed resistivity data on metallic glasses in terms of weak-localization and electron-interaction effects. Howson[33] and Howson and Greig[34,35] have discussed the importance of quantum corrections on the resistivity of metallic glasses. These corrections become important in the regime when a significant interference between scattered partial waves takes place as electrons propagate between two scattering events. There are two major corrections to the Boltzmann equation in this regime: (1) the localization effect, and (2) modification of electron-electron interaction. Howson[33] gives the expression for the temperature-dependent part of the conductivity due to the effect of localization,

$$\sigma_L(T)=\frac{e^2}{\pi^2\hbar L_i(T)}, \tag{5}$$

where $L_i^2(T)=l_e l_i/2$, l_e is the elastic mean free path, and l_i is the inelastic mean free path. This expression leads to the temperature dependence of σ_L as

$$\sigma_L \propto \begin{cases} T & \text{for } T<\Theta_D/3\ , \\ T^{1/2} & \text{for } T>\Theta_D/3\ . \end{cases}$$

This different temperature dependence of σ_L in different regimes arises due to the T^{-2} dependence of the inelastic mean free path below $\Theta_D/3$, instead of the usual T^{-3} dependence because the requirement for momentum conservation is relaxed in amorphous metals. Above $\Theta_D/3$, l_i should vary as T^{-1} as usual with σ_L proportional to $T^{1/2}$.

To analyze our resistivity data within the framework of localization effects, we have plotted $\rho(300\ \mathrm{K})/\rho(T)$, which is proportional to $\sigma(T)$ versus T/Θ_D and $(T/\Theta_D)^{1/2}$ for various samples as shown in Figs. 8 and 9. Values of Θ_D are taken from Yamada *et al.*[12] for $(\mathrm{Zr}_{0.67}\mathrm{Ni}_{0.33})_{1-x}\mathrm{Al}_x$, alloys. From these figures it can be seen that the temperature dependence of σ is in good agreement with the predictions of Eq. (5), i.e., it varies as

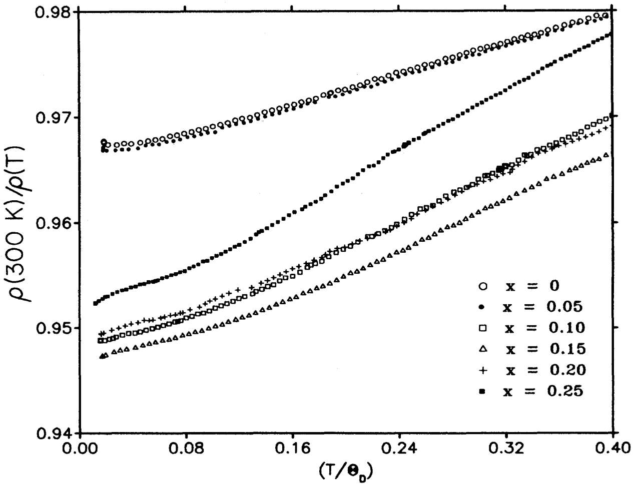

FIG. 8. $\rho(300\ \mathrm{K})/\rho(T)$ vs T/Θ_D for amorphous $(\mathrm{Zr}_{0.64}\mathrm{Ni}_{0.36})_{1-x}\mathrm{Al}_x$ alloys. Symbols are defined in Fig. 5.

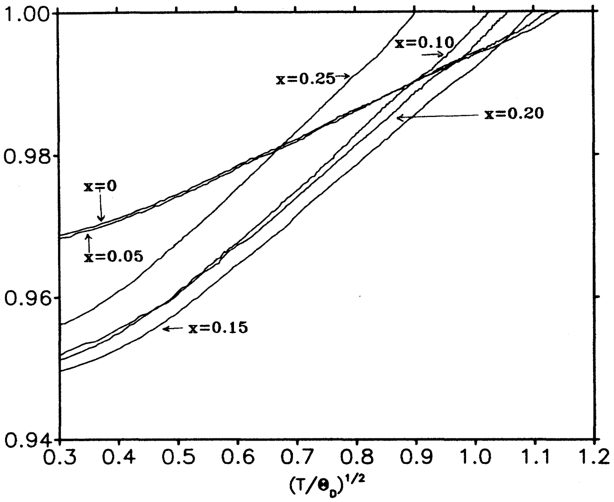

FIG. 9. $\rho(300\text{ K})/\rho(T)$ vs $(T/\Theta_D)^{1/2}$ for amorphous $(\mathrm{Zr}_{0.64}\mathrm{Ni}_{0.36})_{1-x}\mathrm{Al}_x$ alloys.

$T^{1/2}$ from approximately $\Theta_D/3$ to Θ_D and as T below $\Theta_D/3$ to about $\Theta_D/10$. Above Θ_D there is a significant departure from a linear dependence on $T^{1/2}$ or T. Although we have data for only a small temperature range above Θ_D, the conductivity appears to vary approximately as T^2. We note that a T^2 dependence would be expected from the Mott *s-d*-scattering model. The temperature dependence of σ for these alloys is consistent with a contribution from localization effects plus a term from Mott *s-d* scattering. Delgado *et al.*[16] observed a temperature dependence of σ for melt-spun La-Al alloys that was in good agreement with localization predictions also, but the temperature dependence of splat-quenched alloys of the same concentration was very different even though the other transport properties (ρ and S) were almost identical. They argued that crystalline inclusions corresponding to a few percent of the sample were probably present in the splat-quenched samples. They also observed small structure in the thermopower measurements with samples containing very small amounts of crystalline inclusions. No such structure was observed for the samples of this report. Some caution must be exercised in the interpretation of the temperature dependence of σ since the effect is very small and there are many effects that can contribute, some fundamental and some artifacts of the particular samples.

The temperature variation of the thermopower is shown in Fig. 5. Above about 75 K the thermopower varies linearly with temperature, but below 75 K a gradual change of slope to a larger value takes place producing a "knee" in the data near this temperature. Similar data have been reported for a number of nonmagnetic metallic glasses[16,19,20,22] and interpreted in terms of electron-phonon energy renormalization, velocity and relaxation-time renormalization, and the Nielsen-Taylor higher-order effects. For the simplest case, values of the electron-phonon–interaction parameter λ may be determined from the ratio of $S(T \gg \Theta_D)/T$ to the low-temperature limit of $S(T)/T$. Estimated values of λ determined in this fashion are 0.63, 0.55, and 0.51 for comparison with estimates of λ from the superconducting transition temperature T_c based on the McMillan formula[36] of 0.58, 0.54, and 0.49 for alloys with $x=0$, 0.05, and 0.10, respectively. The values are in reasonable agreement for the three samples for which we could measure T_c. The principal effect on superconductivity due to the addition of Al to amorphous Zr-Ni alloys appears to result from the reduction of the electron-phonon coupling. This is somewhat peculiar since amorphous simple metals generally are very strong-coupling superconductors[37] with $\lambda \approx 2.0-2.6$, whereas the amorphous transition-metal alloys generally have intermediate coupling[38] with values of $\lambda \approx 1.7-1.9$. This raises the interesting question of how and why the electron-phonon coupling changes from strong to intermediate in going from an amorphous predominantly simple-metal alloy to an amorphous predominantly transition-metal alloy. Unfortunately, Al can be incorporated only up to 25–30 at. % in these alloys. A more complete analysis of the electron-phonon renormalization contribution to the thermopower along with T_c measurements for the amorphous alloys with higher Al concentrations ($x=0.15$, 0.20, and 0.25) will be presented elsewhere.

V. SUMMARY AND CONCLUSIONS

The addition of Al to amorphous Zr-Ni alloys strongly influences the electron-transport properties. For Zr-rich alloys the addition of Al greatly increases R_H, increases ρ, decreases S, and decreases the superconducting transition temperature T_c. The assumption that the addition of Al to the alloy reduces the *s*-state density of states, together with the simplest version of the Mott *s*-*d*-scattering model for the thermopower and electrical conductivity and with a simplified expression based on the *s-d*-hybridization model to explain the positive Hall coefficient, is in qualitative agreement with the experimental observations of the transport coefficients. This model is clearly too naive, but perhaps the general ideas are correct. More detailed calculations are required.

This experiment, together with those from Mizutani and co-workers,[12,30,31] indicates that the Zr-Ni-*M* (where *M* is a simple metal such as Al, Ga, or Sn) amorphous alloys would be well suited as a rigorous test for the more recent ideas concerning transport in amorphous transition-metal alloys, particularly for the effects of *s-d* hybridization.[10,11,17,28] These types of amorphous alloys[39] provide the opportunity to study the interplay between the simple-metal *s-p* states, the Ni *d* resonance which lies below ε_F and the Zr *d* resonance above ε_F. It is hoped that the development of new experimental data for these alloys and even the use of such a naive model in analysis of the experimental results will lead to efforts toward more realistic calculations for these admittedly electronically complex systems.

The analysis of the temperature dependence of the thermopower and the concentration dependence of the superconducting transition temperature indicates that the depression of T_c is due to a decrease in the electron-phonon–coupling constant λ. For simple-metal-rich amorphous alloys we expect λ to increase. It may be possible to find a simple-metal–transition-metal alloy where the evolution of λ could be studied from the simple-metal-rich side to the transition-metal-rich side. This evolution has not been documented experimentally, except on the extreme ends of the alloy system, and there is no coherent theoretical picture of why it changes. We find that the temperature dependence of the resistivity of these alloys is better described by weak-localization effects rather than the exponential form [Eq. (4)] given by Mizutani.[31] The addition of Al, which may behave as a metalloid in these alloys, enhances their stability against crystallization.

ACKNOWLEDGMENTS

This research was supported in part by grants from the U.S. National Science Foundation (Grant No. DMR-87-15433), the Robert A. Welch Foundation U.S. (Houston, TX), and the Texas Advanced Technology Program. We wish to thank U. Mizutani and R. Zehringer for providing data from UPS studies of amorphous $(\mathrm{Zr}_{0.67}\mathrm{Ni}_{0.33})1_{1-x}\mathrm{Al}_x$ alloys prior to submission for publication. We also acknowledge support in establishing the facilities for these experiments from the Texas A&M Board of Regents Materials Research Initiative. We gratefully acknowledge K.-W. Rhie for measurements of the Hall coefficient of these alloys and B.-H. Zhang and T. Stevens for help with differential-scanning-calorimetry and density measurements. One of us (A.K.B.) would like to thank the Physics Department of Texas A&M University for their support and hospitality during his stay.

---

[*] Permanent address: School of Physics, University of Hyderabad, Hyderabad 500 134, Andhra Pradesh, India.

[1] U. Mizutani, Prog. Mater. Sci. **28**, 97 (1983).

[2] D. G. Naugle, J. Phys. Chem. Solids **45**, 367 (1984).

[3] P. C. Colter, T. W. Adair, and D. G. Naugle, Phys. Rev. B **20**, 2959 (1979).

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

[5] B. Bandyopadhyay, P. Watson, B. Yin, D. G. Naugle, and V. M. Nicoli, Z. Phys. B **63**, 207 (1986).

[6] P. Watson, B. Bandyopadhyay, B. Yin, D. Rathnayaka, and D. G. Naugle, Mater. Sci. Eng. **99**, 175 (1988).

[7] G. V. Minnigerode and H. G. Bottjer, Z. Phys. B **60**, 351 (1985).

[8] J. Ivkov, E. Babic, and R. L. Jacobs, J. Phys. F **14**, L53 (1984).

[9] R. W. Cochrane, J. Destry, and M. Trudeau, Phys. Rev. B **27**, 5955 (1983).

[10] G. F. Weir, M. A. Howson, M. A. Gallagher, and G. J. Morgan, Philos. Mag. B **47**, 163 (1983).

[11] G. J. Morgan and G. F. Weir, Philos. Mag. B **47**, 177 (1983).

[12] Y. Yamada, Y. Itoh, T. Matsuda, and U. Mizutani, J. Phys. F **17**, 2313 (1987).

[13] Z. Altounian, C. L. Foiles, W. B. Muir, and J. O. Strom-Olsen, Phys. Rev. B **27**, 1955 (1983).

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

[15] N. F. Mott, Philos. Mag. **26**, 1249 (1972).

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

[17] D. Nguyen-Manh, D. Mayou, G. J. Morgan, and A. Pasturel, J. Phys. F **17**, 999 (1987).

[18] A. B. Kaiser, Phys. Rev. B **29**, 7088 (1984).

[19] B. L. Gallagher and B. J. Hickey, J. Phys. F **15**, 911 (1985).

[20] D. G. Naugle, R. Delgado, H. Armbruster, C. L. Tsai, W. L. Johnson, and A. R. Williams, J. Phys. F **15**, 2189 (1985).

[21] R. B. Roberts, Philos. Mag. **36**, 91 (1977).

[22] D. G. Naugle, R. Delgado, H. Armbruster, C. L. Tsai, T. O. Callaway, D. Reynolds, and V. L. Moruzzi, Phys. Rev. B **34**, 8279 (1986).

[23] Z. Altounian and J. O. Strom-Olsen, Phys. Rev. B **27**, 4149 (1983).

[24] W. L. Johnson and A. Williams, Phys. Rev. B **20**, 1640 (1979), and references therein.

[25] K. Pekala and R. Trykozko, Phys. Lett. **86A**, 176 (1981).

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

[27] D. Brown, S. Fairbairn, and G. J. Morgan, Phys. Status Solidi B **93**, 617 (1979).

[28] G. J. Morgan and M. A. Howson, J. Phys. C **18**, 4327 (1985).

[29] P. Oelhafen, E. Hauser, and H. J. Güntherodt, Solid State Commun. **35**, 1017 (1989).

[30] U. Mizutani and R. Zehringer (private communication).

[31] Y. Yamada, Y. Stoh, U. Mizutani, N. Shibagakli, and K. Tanaka, J. Phys. F **17**, 2303 (1987).

[32] U. Mizutani, Mater. Sci. Eng. **99**, 165 (1988).

[33] M. A. Howson, J. Phys. F **14**, L25 (1984).

[34] M. A. Howson and D. Greig, Phys. Rev. B **30**, 4805 (1984).

[35] M. A. Howson and D. Greig, J. Phys. F **16**, 989 (1986).

[36] W. L. McMillan, Phys. Rev. **167**, 331 (1968).

[37] G. Bergmann, Phys. Rep. **27C**, 159 (1976).

[38] W. H. Shull and D. G. Naugle, Phys. Rev. Lett. **39**, 1580 (1977).

[39] Subsequent to the initial submission of this article we have succeeded in preparing amorphous Zr-Ni-Ga alloys of the same [Zr]/[Ni] ratio and are presently measuring their transport properties. We have unsuccessfully attempted to make amorphous Zr-Ni-Sn alloys at this [Zr]/[Ni] ratio and Ni-rich amorphous Zr-Ni-Al alloys. We are continuing efforts to prepare these two alloys.