# Hall coefficient and resistivity of amorphous $Ti_{1-x}Al_x$ films

K. D. D. Rathnayaka, B. D. Hennings,* and D. G. Naugle

*Texas A&M University, College Station, Texas 77843-4242*

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The resistivity of codeposited amorphous $Ti_{1-x}Al_x$ films has been measured from 1.5 to 300 K over the composition range $0.4 \leq x \leq 0.92$, and the Hall coefficient has been measured at 4 K. The resistivity exhibits a relatively small temperature dependence. The magnitude of the room-temperature resistivity varies appreciably with composition, with a broad maximum around 250 $\mu\Omega$ cm near $x \approx 0.5$. The Hall coefficient is positive at $x = 0.4$ and increases to a maximum at $x \approx 0.6$. It becomes negative at $x \approx 0.85$ with a value comparable to that of liquid Al at the highest value of $x$. The positive values of the Hall coefficient and their dramatic increase with $x$ below $x \approx 0.5$ are discussed in terms of current theories for a positive Hall coefficient.

## I. INTRODUCTION

The Hall coefficients of amorphous metals are generally positive when the alloy is dominated by an early-transition-metal component. (See reviews by Howson and Gallager,[1] Mizutani,[2] Naugle,[3] and Naugle and Rhie.[4]) This has been thoroughly investigated for early-transition-metal–late-transition-metal (ETM-LTM) alloys. The Zr-based amorphous alloys [Zr-Cu,[5,6] Zr-Ni[7–9], Zr-Co,[8,10] Zr-Fe (Refs. 8 and 11)] compose one of the most completely studied ETM-LTM alloy system. As the composition of the late-transition-metal component is increased, the sign of $R_H$ changes from positive to negative at a critical composition $x_c$ that increases with the column number of the late-transition-metal component. Rathnayaka et al.[12] have shown that for a fixed late-transition-metal component Ni the value of $x_c$ does not vary strongly with the ETM row (Hf-5d, Zr-4d, Ti-3d).

Positive values of the Hall coefficient for certain early transition-metal–simple-metal (ETM-SM) alloys [La-Ga,[13,14] La-Al,[15] Y-Al,[16] V-Al (Ref. 17)] have also been reported. With the exception of certain Ba-Ca alloy quench-condensed thin films,[18] values of $R_H$ for most amorphous alloys consisting entirely of simple metals are negative[2,19] with values close to the free-electron model. Due to the limited composition ranges available in the previously reported studies of the Hall coefficient in amorphous ETM-SM alloys,[13–17] no systematic study of the variation of $R_H$ with simple metal composition for a fixed early-transition metal has been reported. Our laboratory[20] has demonstrated that amorphous Ti-Al alloy films can be prepared with crystallization temperatures well above room temperature over a very wide composition range. We report here measurements of the resistivity and Hall coefficient for codeposited amorphous $Ti_{1-x}Al_x$ alloy film as a function of Al composition $x$.

## II. EXPERIMENT

Amorphous Ti-Al alloy films were codeposited from separate e-guns onto predeposited silver contact pads on sapphire substrates held at liquid-nitrogen temperature in an ultrahigh vacuum chamber. The source materials in the e-guns were 99.99% pure Ti and 99.999% pure Al ingots. Alloy composition was controlled with two Inficon electron-impact emission spectrometry rate monitors, each shielded so that it looked only at one of the sources. Parameters of deposition were adjusted so that the film thickness of each film was about 1000 Å. The deposition rate was approximately 1–2 Å/sec. The use of a movable mask allowed a series of three independent films to be deposited without breaking the vacuum. The base pressure of the deposition chamber was approximately $10^{-10}$ Torr, and the pressure during deposition rose to approximately $10^{-9}$ Torr.

After deposition of three films, each with a different composition, the substrate was warmed to room temperature and removed from the vacuum. The edges of the films were trimmed to eliminate regions of compositional inhomogeneity due to differences in shadowing of the two sources, and the films were then mounted in the sample chamber of a variable-temperature cryostat. The sample chamber was evacuated and then filled with low-pressure He exchange gas to insure that the samples and the thermometer remained at the same temperature during the measurements. After completion of the resistivity and Hall measurements, the samples were removed and their compositions were determined by wavelength dispersive spectroscopy in an electron-beam microprobe. The composition was checked at several points along the film to determine the sample homogeneity. The variation was within the overall accuracy of the method, approximately 2 at. %. After completion of the compositional analysis, a silver coating was deposited over the films, and the thickness was determined by optical interference with a Varian Å-Scope. The uncertainty in this film thickness determination was approximately 10%. Values of thickness were not corrected for the thin oxide layer formed on the surface during the time the films were exposed to air.

Four terminal dc resistance measurements with forward and reversed current were made as a function of temperature from 1.7 to 300 K. A calibrated platinum resistance thermometer was used for temperature measurements above 50 K while a calibrated carbon-glass thermometer was used at lower temperatures. Three ter-

minal dc Hall measurements were made at 4 K in fields up to 6 T which were provided by a superconducting solenoid. The field was varied in steps of approximately 0.1–0.5 T. The sample was mechanically flipped at each field value in order to measure the field reversed Hall voltage, and the current was reversed at each value (and direction) of the field.

Values of the Hall coefficient were determined from the Hall voltage measurements, the current, and the measurements of film thickness. Values of resistivity were determined from measurements of the longitudinal voltage, the current, and measurements of the film width, film thickness, and separation between the longitudinal voltage probes. For temperature dependence, the relative accuracy of the measured data points is better than $\pm 1\%$ for resistivity. The absolute accuracy for the film composition is $\pm 2\%$, and that for the resistivity and Hall coefficient is $\pm 10$ and $\pm 15\%$, respectively. The principal uncertainty is $R_H$ and $\rho$ arises from the uncertainty in film thickness.

## III. EXPERIMENTAL RESULTS

Values of the room-temperature resistivity of the $Ti_{1-x}Al_x$ alloy films as a function of Al composition $x$ are shown in Fig. 1. For comparison, values of resistivity as a function of simple metal composition for amorphous La-Al,[15] Y-Al,[16] V-Al,[17] and $(Ti_{0.76}Ni_{0.24})_{1-x}Al_x$ (Ref. 21) alloys are also shown. A broad maximum in the resistivity is located in the range $0.45 < x < 0.65$. At higher Al concentrations the resistivity decreases rapidly with $x$. For $x = 0.92$ the room-temperature resistivity drops to the order of 64 $\mu\Omega$ cm, typical of an amorphous simple metal. The temperature dependence of the resistivity of selected $Ti_{1-x}Al_x$ alloys is shown in Fig. 2. For high-Ti concentration the temperature coefficient is negative, with the typical temperature dependence of a nonmagnetic transition-metal alloy.[2] At much higher Al concentra-
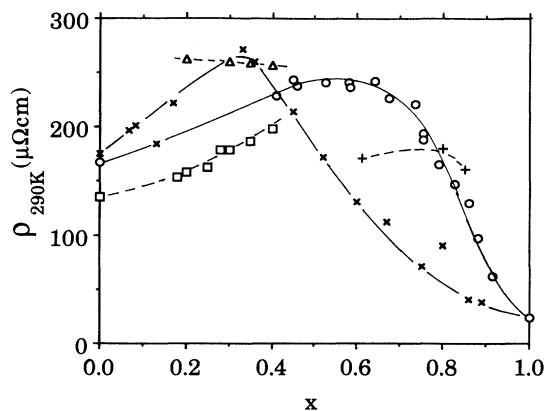
tions the temperature coefficient is positive, typical of many amorphous simple metals.[2,19] In the intermediate composition range there is a resistivity minimum at low temperature which Gallagher and Howson[1] argue is related to electron-electron interaction effects.

Values of $R_H$ of $Ti_{1-x}Al_x$ alloy films measured at 4K as a function of Al composition $x$ are shown in Fig. 3. Room-temperature values of $R_H$ as a function of simple metal composition for amorphous La-Al,[15] Y-Al,[16] V-Al,[17] Zr-Cu,[5,6] and Ti-Cu,[1] and 4 K values for $(Ti_{0.76}Ni_{0.24})_{1-x}Al_x$ (Ref. 21) are shown for comparison. The temperature dependence of the Hall coefficient of these ETM-LTM and ETM-SM alloys is relatively weak.



FIG. 2. Temperature dependence of the resistivity, $R(T)/R(290)$, for selected $Ti_{1-x}Al_x$ alloys.



FIG. 1. Room-temperature values of resistivity $\rho$ as a function of simple metal composition $x$ for $ETM_{1-x}Al_x$ alloys; ($\bigcirc$) Ti-Al (this work), ($\square$) La-Al (Ref. 15); ($\triangle$) Y-Al (Ref. 16), ($+$) V-Al (Ref. 17), ($x$) for the pseudobinary $(Tl_{0.76}Ni_{0.24})_{1-x}Al_x$ (Ref. 21). Values at $x = 0$ and $x = 1$ are for the pure liquid metal at its melting point (Ref. 1). Lines indicate trends for a given series.
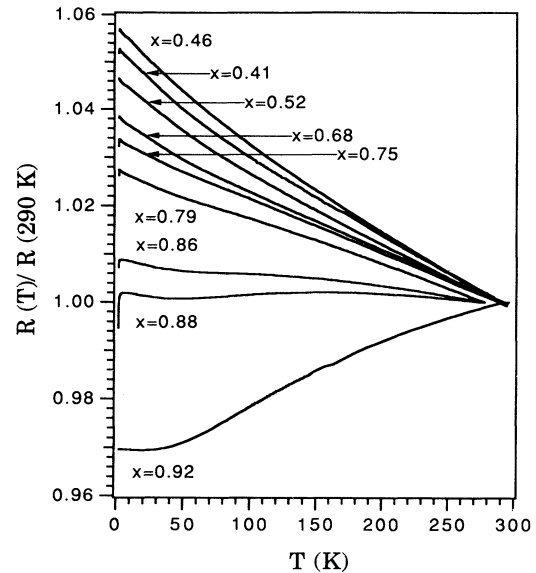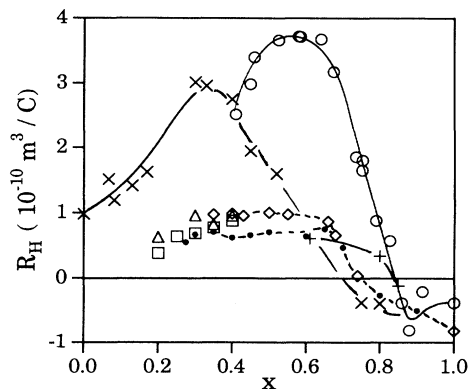


FIG. 3. Composition dependence of the Hall coefficient $R_H$ for $ETM_{1-x}SM_x$ alloys. ($\bigcirc$) Ti-Al (this work), ($\square$) La-Al (Ref. 15), ($\triangle$) Y-Al (Ref. 16), ($+$) V-Al (Ref. 17), ($x$) $(Ti_{0.76}Ni_{0.24})_{1-x}Al_x$ (Ref. 21), ($\bullet$) Zr-Cu (Ref. 5 and 6) ($\Diamond$) Ti-Cu (Ref. 1). Values of $R_H$ for the alloys are for 300 K except for the Ti-Al and Ti-Ni-Al alloys which were taken at 4 K. Values $x = 0$ and $x = 1$ are for the pure liquid metal at its melting point (Ref. 1). The lines indicate trends for a given series.

Consequently, use of the 4 K values of $R_H$ for comparison with the room-temperature values of the other ETM-SM amorphous alloys is acceptable. Between values of $x \approx 0.4$ and 0.5, $R_H$ increases rapidly with $x$ for the $Ti_{1-x}Al_x$ alloy family. $R_H$ reaches a maximum at approximately $x = 0.6$ and then decreases rapidly for larger values of $x$ to become negative at $x \approx 0.85$.

In comparison with the other ETM-SM and ETM-Cu alloys it is interesting to note that the magnitude of $R_H$ in the ETM-rich composition range is generally much greater for Ti-Al. Nevertheless, the change in sign from positive to negative with increasing simple metal composition occurs at almost the same value of $x$ for $Ti_{1-x}Al_x$ and $V_{1-x}Al_x$. Similarly, in the ETM-rich region, values of $R_H^{-1}dR_H/dx$ for $Y_{1-x}Al_x$ and for $La_{1-x}Al_x$ are comparable to those for the $Ti_{1-x}Al_x$ alloys. The overall compositional dependence for Ti-Al alloys resembles somewhat that of the (Ti-Ni)-Al pseudobinary, but the maximum in $R_H$ is at higher Al composition for the binary, and the magnitude at this maximum is larger for the binary.

## IV. DISCUSSION

Discussion of resistivity and its temperature dependence will be postponed until magnetoresistance measurements are available since there is good reason[1] to believe that weak localization and electron interaction contributions will be important. Consequently, the discussion will focus on the Hall coefficient. Two entirely different explanations for the existence of a positive Hall coefficient in amorphous alloys containing early-transition metals have been offered, (a) $s$-$d$ hybridization leading to a negative dispersion curve (see Ref. 1 for an excellent review of the ideas) and (b) the side jump induced by spin-orbit scattering (see Ref. 4 for a recent review of the theory and the most current summary of the experimental evidence supporting this mechanism).

The Ti-Al system is ideally suited for detailed calculations of the contribution of $s$-$d$ hybridization, but there are none to date. The only ETM-SM system for which such calculations have been made is Zr-Cu,[22] and here the $d$ states of Cu, unlike Al, could play some role. The Hall coefficient for several liquid TM-Cu alloys and amorphous TM-Cu alloys appears to scale with Cu concentration when normalized to the free-electron Lorentz contribution, $R_H^0$.[23] Figure 4 shows $R_H/R_H^0$ as a function of $x$ for the $Ti_{1-x}Al_x, Zr_{1-x}Cu_x$,[5,6] $Ti_{1-x}Cu_x$,[1] and the calculated results for $Zr_{1-x}Cu_x$.[22] We note that, although the behavior of Ti-Cu and Zr-Cu is similar to the calculations for Zr-Cu, the behavior for Ti-Al is quite different. To a first approximation, one might expect the behavior for Ti-Cu and Ti-Al to be the same if $s$-$d$ hybridization was the determining factor. Unfortunately, there is no simple dependence in the $s$-$d$ theory, and very detailed calculations are required for the comparison of theory with experiment.

The side-jump contribution $R_H^{SJ}$, on the other hand, is an anomalous contribution to $R_H$. Trudeau and co-workers[11] have expressed $R_H$ in terms of this contribu-
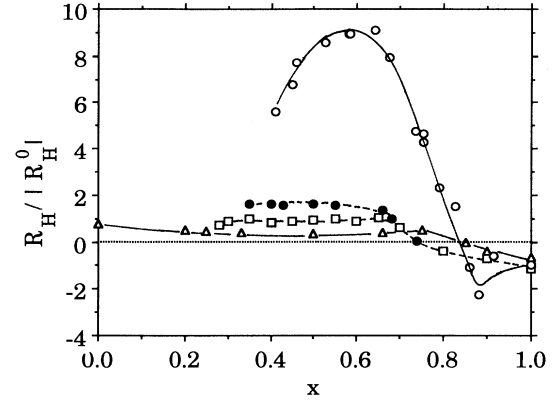


FIG. 4. $R_H/R_H^0$ as a function of $x$ for $Ti_{1-x}Al_x$, ($\bigcirc$) (this work), $Zr_{1-x}Cu_x$ ($\square$) (Refs. 5,6), $Ti_{1-x}Cu_x$ ($\bullet$) (Ref. 1); calculations based on $s$-$d$ hybridization for $Zr_{1-x}Cu_x$ ($\triangle$) (Ref. 22). The lines indicate trends for a given series.

tion as follows:

$$R_H = R_H^0 + R_H^{SJ}\chi_v = R_H^0 + 2e^2\lambda_{so}^{SJ}\chi_v\rho^2/\hbar\mu_0 g_L\mu_B , \quad (1)$$

where $\chi_v$ is the Stoner enhanced Pauli susceptibility for paramagnetic alloys, $g_L$ the Landé $g$ factor, and $\mu_B$ the Bohr magneton. The effective spin-orbit parameter is

$$\lambda_{so}^{SJ} = \sum_n \frac{|\langle n|\overline{L}|0\rangle|^2}{\varepsilon_n - \varepsilon_F}Id^2A_{so} , \quad (2)$$

where the sum is over both filled and unfilled states, $I$ the overlap integral at the scatterer, $d$ the distance between scatterers and $A_{so}$ the atomic spin-orbit parameter. According to this result $R_H - R_H^0 = \chi_v R_H^{SJ}$ should vary linearly as $\rho^2\chi_v$ provided $\lambda_{so}^{SJ}$ is not changing dramatically. There are no susceptibility data for the Ti-Al alloys, but Fig. 5 shows $R_H - R_H^0$ as a function of $\rho^2$ for Al composition $x < 0.85$. The values scatter but do vary approximately linearly with $\rho^2$. We clearly would not expect, however, that $\lambda_{so}^{SJ}$ given by Eq. (2) would be constant over so broad a composition range, and we would expect that $\chi_v$ would also vary appreciably with $x$. Consequently, a
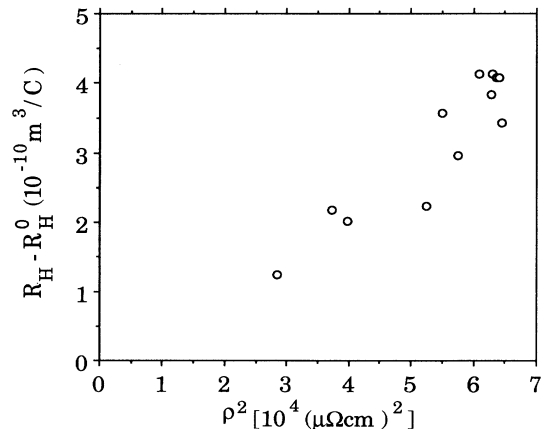


FIG. 5. $R_H$-$R_H^0$ as a function of $\rho^2$ for $Ti_{1-x}Al_x$.

quantitative comparison with this theory cannot be made, but we do note that the behavior of $R_H$ for the Ti-Al alloys is very similar to that for Ti-Ni-Al (Ref. 21) and the Zr-LTM-Al pseudobinaries, Zr-Cu-Al (Ref. 24) and Zr-Ni-Al alloys.[4] Naugle and Rhie[4,24] have explained how the composition dependence for small Al compositions of these pseudobinary alloys and that for the Zr-LTM, over a larger composition range, can be understood in terms of Eqs. (1) and (2).

We note that Movaghar and Cochrane[25,26] have raised objections to the derivation of the side-jump contribution. In tight-binding calculations using the Kubo formula[25] they did not find a term similar to Eq. (1), but in a more elegant calculation[26] they did find a term that reduces to Eqs. (1) and (2) without having to introduce the idea of a side jump as originally proposed by Berger. We have used the original term "side jump" without regard to the controversy regarding its actual origin.

## V. CONCLUSIONS

Resistivity and Hall-coefficient measurements have been reported over a wide composition range for an ETM-SM amorphous alloy. No definitive conclusions as to the source of the positive Hall coefficient, $s$-$d$ hybridi-

zation, or side-jump effect can be made although the similarity to Zr-LTM-SM pseudobinary alloys seems to favor the side jump. This alloy system would be ideal for theoretical calculations based on the $s$-$d$ hybridization. Further measurements, including a determination of the susceptibility, at much lower Al compositions might provide a better test of the side jump contribution. We have been unable to prepare the amorphous phase by cocondensation at room temperature or liquid-nitrogen temperature for values of $x < 0.4$. Cocondensation onto liquid-He-cooled substrates may extend the composition at which the amorphous phase can be formed. If formed, we would expect them to remain amorphous at or above room temperature, based on the trends in crystallization temperatures with composition previously reported.

*Present address: NAVSEA 08, James K. Polk Building (NC2), 2521 Jefferson Davis Highway, Arlington, VA 22202.

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