

Ion-beam mixing of Al-V films: Structure and Hall effect

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Icosahedral and amorphous structures have been produced in multilayered Al-V by ion-beam mixing. In contrast to the possibilities with the Al-Mn alloy system, we find that the formation of "single-phase" icosahedral Al-V at higher temperatures is inhibited by a coexisting, as yet unreported, bcc phase ($a = 3.82 \text{ \AA}$). When the mixing is performed with 500-keV Xe^+ , transmission-electron-microscopy (TEM) -amorphous structures have been obtained at liquid-nitrogen temperature in an extended concentration regime (15–26 at. % V). Electrical resistivity data for all the alloys studied show a negative temperature dependence which cannot be explained quantitatively in the framework of current theories. The Hall coefficient in glassy Al-V is found to change sign and become positive above 16 at. % V. This fact is discussed in the context of existing theories for the sign of the Hall coefficient. As far as we know, this is the first time such a change of sign has been observed for a nonmagnetic glassy metallic system which is not of the "early-late" transition-metal type.

I. INTRODUCTION

Atomic-scale modification of the properties of thin multilayered films by high-energy bombardment is now a well-established method of producing novel materials.^{1,2} Ion-beam mixing (IM) and thermally assisted IM have been shown to be a powerful tool in producing glassy and icosahedral structures over extended compositional ranges that are significantly different from those which can be achieved with other techniques like rapid quenching, sputtering, or vapor codeposition. Recently, amorphization of Zr-(Fe,Ni,...) alloys with these different techniques has been compared and studied² in detail. The potential of the IM technique to develop, modify, and study new structures has been exemplified well in the Al-Mn system.^{3,4} The quenching rates available today, for example, in melt spinning have been shown to be inadequate⁵ to form "single-phase" icosahedral Al-Mn. However, glassy films seem possible to produce with vapor⁶ and sputter deposition⁷ at room temperature as well as elevated substrate temperatures. Using IM, on the other hand, both single-phase icosahedral and glassy $\text{Al}_{83}\text{Mn}_{17}$ have been successfully produced.^{3,4}

We have investigated the formation of glassy and icosahedral structures in Al-V by IM with 500-keV Xe^+ ions. We find that the icosahedral phase can be obtained, but not in the single-phase form, which is in contrast to the possibilities with Al-Mn. This, we find, is due to the formation of an accompanying new, previously unreported, metastable cubic phase of Al-V. However, with the substrate at liquid-nitrogen temperature we have been

able to amorphize the Al-V films. It is of interest to note that at compositions close to the stoichiometry for the icosahedral phase,⁸ Al-V can be amorphized rather easily with ion-beam mixing.

Since the first reports of positive Hall coefficients in nonmagnetic binary early-transition-metal-late-transition-metal (ETM-LTM) alloys,^{9–11} a basic understanding of this "sign" of the Hall coefficient remains one of the open questions, especially in disordered materials. Clearly, the explanations of the positive Hall effect in crystalline materials in terms of "holelike" parts of the Fermi surface are not applicable for materials lacking translational periodicity, especially because of the ambiguity in defining their properties in \mathbf{k} space.

In the later sections of this paper, we present Hall-effect and electrical resistivity studies on the ion-beam-mixed glassy Al-V. We find that the room-temperature Hall coefficient changes sign and becomes positive above 16 at. % V. This is the first time such a change in sign has been observed in a nonmagnetic binary alloy which is not of the ETM-LTM type. We discuss the origin of the sign of the Hall coefficient in the light of the existing theoretical models.

II. EXPERIMENT

A "sandwich" structure with Al and V layers was produced by e -beam evaporation onto substrates of sapphire or NaCl on sapphire (for TEM characterization). These films were ion-beam mixed with 500-keV Xe^+ ions and fluence of 2×10^{16} ions/cm². In order to ensure that virtually all bombarding ions penetrate through the film into

the substrate and complete atomic mixing of the layers occurs, the thickness of the multilayer was chosen to be only around 800 Å with a thickness of less than 100 Å for each layer. The mixing itself was performed in a vacuum better than 5×10^{-6} Pa, while controlling the temperature of the film substrates at 80, 298, 373, 423, or 473 K, respectively, to within a stability of ± 5 K.

The compositions of the ion-beam-mixed $\text{Al}_{100-x}\text{V}_x$ films, determined by Rutherford backscattering spectroscopy, were found to be $x=11, 15, 17, 20,$ and 26 (estimated error of less than 2 at. %). One film of $\text{Al}_{61}\text{V}_{39}$ was also prepared with vapor codeposition and confirmed to be x-ray amorphous. Structural characterization of the IM films (floated off from the NaCl) were performed with a 100-keV transmission electron microscope (TEM) and a Phillips PW 1051 standard x-ray diffractometer using a Cu anode.

Annealing treatments of the IM films were carried out in a separate furnace (in a vacuum better than 10^{-4} Pa) with the films laying strain free on TEM grids, which were eventually also used for TEM observations.

Room-temperature Hall effect and electrical resistivity were measured using the double ac technique at low fields (0–0.5 T). Conducting silver paint contacts were used to avoid any accidental crystallization from other contact techniques which involve heating. In addition, we have extended the electrical resistivity measurements, using the same four-probe contacts, down to helium temperature.

The maximal error in the absolute value of the Hall coefficient and the electrical resistivity, arising mainly from uncertainties in determination of the film thickness and the contact positions, is estimated to be 10%. Note that as far as the sign of the Hall coefficient and the relative temperature dependence of the electrical resistivity are concerned, these sources of error are unimportant, and the maximal error is considerably lower.

III. RESULTS

A. Structure

Figure 1(a) is a typical TEM diffraction pattern obtained for the Al-V films in the amorphous state upon ion mixing at liquid-nitrogen temperature. The amorphous state was identified from featureless micrographs (indicating the absence of grain boundaries) and broad diffraction “halos” in TEM. In Fig. 1(b), a TEM diffraction pattern of the $\text{Al}_{85}\text{V}_{15}$ -film IM at 473 K is shown. Four diffraction rings belonging to the four most intense icosahedral reflections, the $I(100\ 000)$, $I(110\ 000)$, $I(110\ 001)$, and $I(101\ 000)$, with the indexing of Ref. 12, are observed. We are unaware of any crystalline phases in the Al-V binary phase diagram which have any Bragg reflections close to the $I(110\ 001)$. For this reason, the four observed rings seem sufficient to establish that the binary icosahedral Al-V can be formed with IM.

We also observe [Fig. 1(b)] five reflections which could not be identified with any known equilibrium or non-equilibrium binary Al-V phases. These reflections can be described as belonging to a cubic structure, hereafter

called the “ x phase,” with $a=3.82$ Å. The observed Bragg planes would accordingly be indexed as (110), (200), (211), (220), and (310), consistent with a bcc structure ($h+k+l=2n$).

Figure 2 shows the compositional ranges in which amorphous (open squares), partly amorphous (half-filled squares), and crystalline (solid squares) Al-V were formed after IM at various substrate temperatures. The $\text{Al}_{85}\text{V}_{15}$ and $\text{Al}_{80}\text{V}_{20}$ mixed at room temperature showed very weak diffraction rings belonging to fcc Al and the metastable x phase, respectively. None of these very weak reflections observed in TEM could be detected by standard x-ray diffractometry. These samples can thus be described to be “x-ray amorphous,” but not “TEM amorphous.”

In Fig. 3 we show schematically the compositions where the various phases formed under thermally assisted IM of Al-V at 373, 423, and 473 K appear. Two crystalline phases (fcc Al and the x phase) and the icosahedral phase could be identified in addition to an amorphous phase. With increasing mixing temperature, the amounts of both the x phase and the icosahedral phase increase at the expense of smaller amounts of the amorphous component. Single-phase icosahedral Al-V could not be produced by IM. We always observed it in coexistence with either the x phase or fcc Al (V).

Heat treatments of TEM-amorphous $\text{Al}_{85}\text{V}_{15}$ and $\text{Al}_{80}\text{V}_{20}$ were performed for 1 h at 513, 553, 593, 633, 683, and 733 K, respectively. The films were found to remain amorphous below 683 K for $\text{Al}_{85}\text{V}_{15}$ and below 633 K for $\text{Al}_{80}\text{V}_{20}$. At these temperatures they were found to crystallize into the tetragonal Al_3V phase and fcc Al (V). No indication of amorphous-to-icosahedral transitions were observed.

B. Hall and electrical resistivity data

A selection of the films described above were made and these were prepared in larger quantities for Hall-effect and electrical resistivity studies. Specifically, films mixed at liquid-nitrogen and room temperature, i.e., TEM-amorphous films, or those with only traces of crystallinity, were selected.

The Hall resistivity of all studied samples is found to be strictly linear in magnetic field, and thus the Hall coefficient is well defined. In Fig. 4 we show the Hall coefficients measured at room temperature of the IM films of $\text{Al}_{100-x}\text{V}_x$ (these films are either amorphous or have only slight traces of crystallinity), along with that for the codeposited $\text{Al}_{61}\text{V}_{39}$ (open circle). Also, the Hall coefficient of liquid Al is shown (solid circle). The Hall coefficient increases monotonically from -0.22×10^{-10} m³/As for $x=11$, changes its sign at $x=16$, and then increases to $+0.60 \times 10^{-10}$ m³/As for the $x=39$ alloy.

Figure 5 shows the temperature dependencies of the normalized resistivity of two TEM-amorphous Al-V films which have negative and positive Hall coefficients. In addition, in the figure, data for the codeposited $x=39$ film are also presented. Note that no significant change is observed among the temperature dependencies of the resistivities. The magnitude of the electrical resistivity at

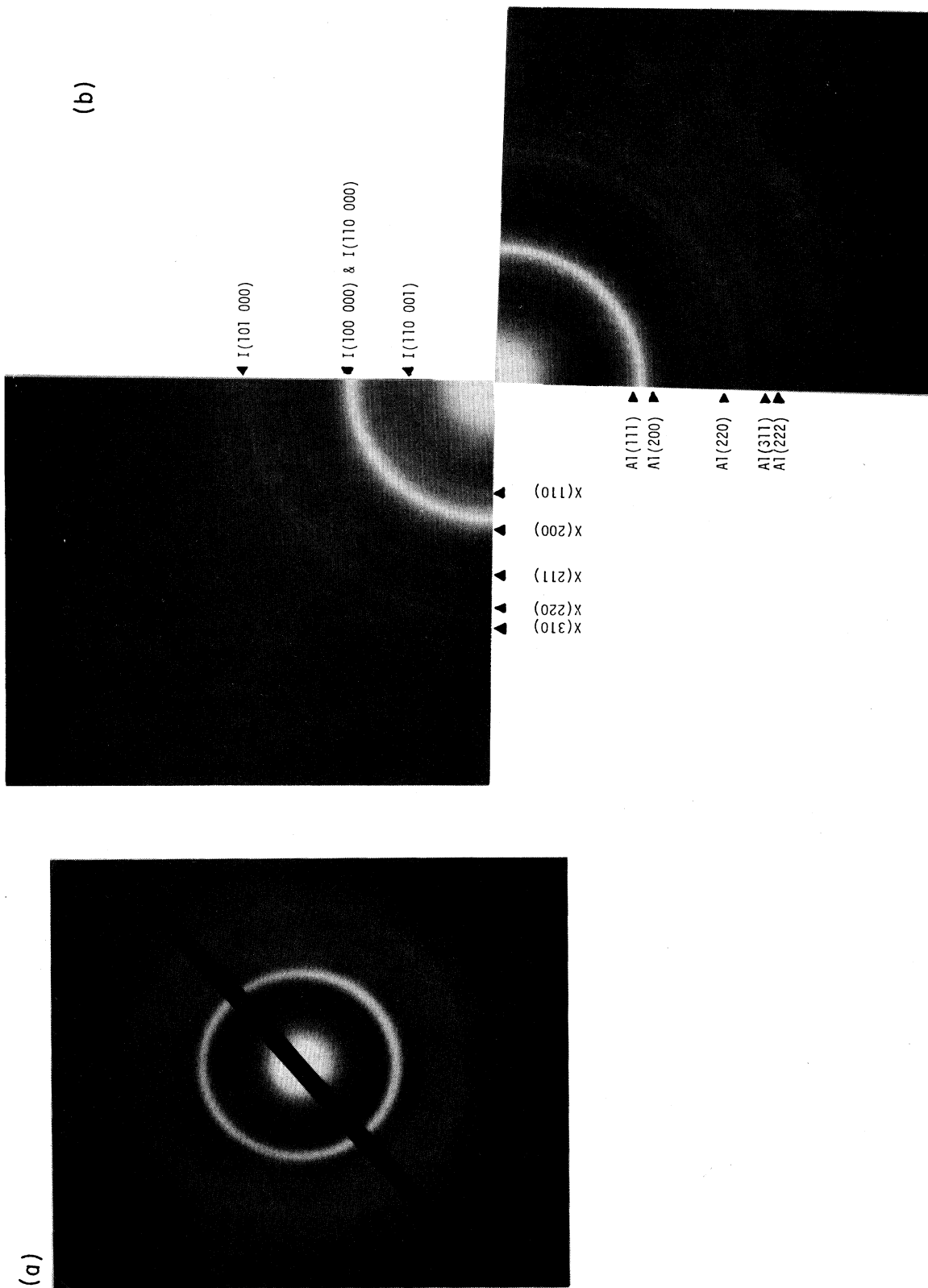


FIG. 1. (a) TEM-diffraction pattern of Al-V amorphized by IM at liquid-nitrogen temperature. (b) Diffraction pattern of Al₈₅V₁₅ ion-beam mixed at 473 K. Lines corresponding to the icosahedral phase, the x phase, and fcc Al (V) are indicated.

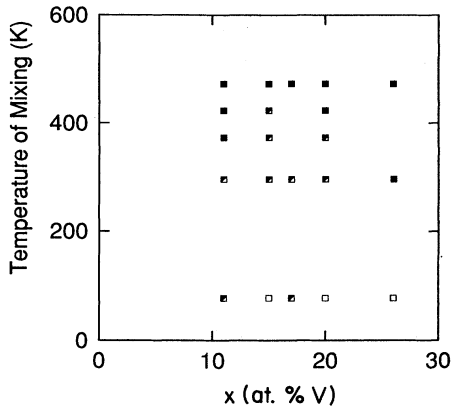


FIG. 2. The observed phases as a function of irradiation temperature and composition. \square , amorphous; \blacksquare , amorphous with crystalline material embedded; \blacksquare , crystalline phases.

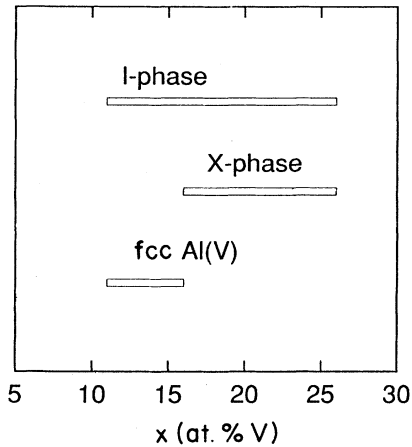


FIG. 3. The composition ranges where the various phases are observed on thermally assisted ion-beam mixing of Al-V at and above room temperature.

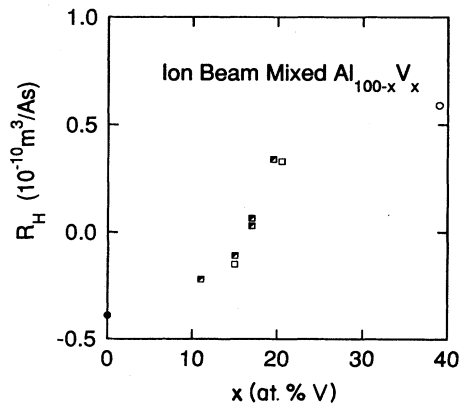


FIG. 4. The room-temperature Hall coefficient as a function of composition for ion-beam-mixed Al-V films. The symbols are in Fig. 2. For details, see text.

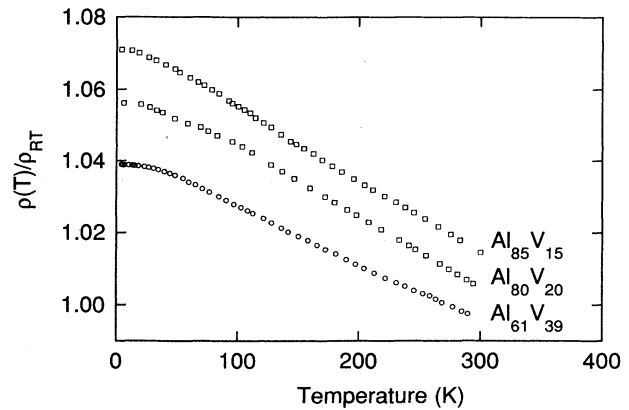


FIG. 5. Temperature dependence of the resistivity (normalized to room-temperature values) for amorphous $\text{Al}_{85}\text{V}_{15}$, $\text{Al}_{80}\text{V}_{20}$, and $\text{Al}_{61}\text{V}_{39}$.

room temperature is also found to be of the same order (160, 180, and $170 \mu\Omega \text{ cm}$ for $x=15, 20$, and 39 , respectively), suggesting that these films are either glassy or amorphous, with no significant crystalline phase in them.

In Fig. 6 we show the temperature dependence of the resistivity (normalized) for the two $\text{Al}_{85}\text{V}_{15}$ films, ion mixed at liquid-nitrogen and room temperature, respectively. The influence of a small fraction of fcc Al (V) in the x-ray amorphous film is clearly noticeable, especially at low temperatures, as a change in the temperature coefficient as well as in the magnitude of the resistivity.

In Table I we summarize the room-temperature Hall and electrical resistivity data for the glassy ion-beam-mixed Al-V films. We have also included data for glassy and icosahedral Al-Mn. Notice that the respective resistivity values for Al-Mn are roughly twice those of Al-V.

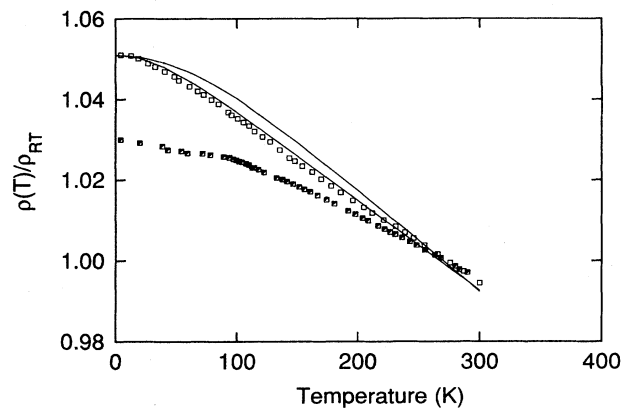


FIG. 6. Temperature dependence of the resistivity (normalized to its value at room temperature) for $\text{Al}_{85}\text{V}_{15}$. The solid lines are calculated from the extended Ziman-Faber model. The top line is the result for chosen reasonable k_F and Θ . The line which seemingly gives a better fit to the data results from unphysical values for k_F and Θ , when treated as fitting parameters. The symbols are as in Fig. 2.

IV. DISCUSSION

A. Structure

In this work we have demonstrated that binary Al-V can be amorphized. In many respects the phases formed after IM of Al-V show similarities with the rather-well-studied Al-Mn system. Both systems can be amorphized with IM, and after thermally assisted mixing, the icosahedral phase has been observed. It is informative to note that alloys which can be formed into the icosahedral phase by melt spinning or thermally assisted IM over certain composition ranges, as in Al-Mn and Al-V, also can be amorphized with IM in the same stoichiometric range appropriate for the icosahedral phase.⁸ This observation can be important, since the possible existence of local icosahedral order in glassy metals has been frequently discussed from a theoretical point of view.¹³⁻¹⁵ Icosahedral short-range order, shown to be the energetically most favorable arrangement of 12 atoms interacting with Lennard-Jones potentials, was early suggested by Frank¹³ to be relevant in liquids. The relative positions of the three first peaks in the static structure factor $S(q)$ of several glassy metals have been found to be in close agreement with the theoretical predictions¹⁴ for local icosahedral ordering. On the other hand, cautions against this reasoning have been expressed¹⁵ based on the simple observation that several rather different geometrical arrangements also can reproduce the experimentally obtained $S(q)$ equally well.

In both Al-V and Al-Mn, metastable bcc phases (the x phase reported here and the F phase,¹⁶ respectively) are found to coexist with the icosahedral phase after thermally assisted IM. It is found that the x phase starts to form already at 15 at. % V and the F phase at 20 at. % Mn. The formation range of the competing x phase overlaps with the icosahedral composition range of the Al-V,⁸ and thus no single-phase icosahedral structure can be formed with IM, contrary to the case with Al-Mn.

With heat treatment, glassy IM films of Al-Mn (Ref. 17) and melt-spun glassy ribbons of Al-V-Cu (Ref. 18) have been shown to transform into the icosahedral phase and, upon further annealing, into equilibrium phases. Our study on glassy Al-V shows that it transforms directly into the tetragonal Al_3V phase and the fcc Al (V) phase. This is rather surprising because several equilibrium phases with local icosahedral arrangements (such arrangements do not exist in the tetragonal phases) are compositionally closer to the amorphous Al-V studied here.

B. Electrical resistivity

At least four major theoretical models have been proposed to explain quantitatively the observed temperature dependence of the electrical resistance of amorphous materials: the natural extension of the Ziman theory for simple liquid metals,¹⁹ the structural analogue of the Kondo phenomenon,²⁰ the coherent scattering exchange model,²¹ and the Mott s - d scattering model.²² In addition, possible localization effects have also been invoked.

In a recent detailed review,²³ Naugle rightly points out that "to date no single mechanism has been established, and with the wide variety of behavior observed when all the transport properties are considered, there is no universal explanation as yet" for the electronic transport properties of even nonmagnetic amorphous metals.

One important problem in comparing different experiments, we believe, is the lack of information regarding proper characterization of the samples: e.g., errors in alloy concentration, impurities (magnetic and/or otherwise), partial crystallization, or phase separation on an atomic scale not easily observable in x-ray analyses, etc. To illustrate this, we consider the resistivity of two samples of $\text{Al}_{85}\text{V}_{15}$ ion-beam mixed at room temperature and at liquid-nitrogen temperatures, respectively. The temperature dependence of the resistivity for these samples is shown in Fig. 6. Note that while both samples were found to be x-ray amorphous, TEM pictures reveal nucleated short-range-order effects or nanocrystallinity in the sample ion mixed at room temperature. Qualitatively, both resistivities have a negative temperature coefficient not significantly different from each other, even in magnitude.

It is thus useful to analyze these data, because for the first time we have an example of and evidence for a material of the same overall composition yet different microstructure on an atomic scale. Since these Al-V alloys are nonmagnetic, it is reasonable to consider the extended Ziman-Faber free-electron model in which the temperature dependence of the Debye-Waller factor and the relative position of the Fermi-energy with respect to the peak in the structure factor determines the resistivity behavior. As we shall discuss later, the extended Ziman-Faber model naturally predicts the expected overall change in the magnitude and the negative temperature coefficient for the resistivity. There are, however, significant discrepancies with the details of the experimentally observed temperature dependence and the theoretical expectations.

We will analyze the temperature dependence of IM $\text{Al}_{85}\text{V}_{15}$ within the framework of the extended Ziman-Faber model following the work of Cote and Meisel,²⁴ who obtained

$$\rho(T) = (1 - \gamma)\rho_i + \rho_0 \exp\{-2[W^*(T) - W(0)]\}, \quad (1)$$

where ρ_i is the ideal electron-phonon resistivity and γ is close to 1. The Debye-Waller factor is given by

$$2W^*(T) = \frac{12\hbar^2 k_F^2}{Mk_B\Theta} \left[\frac{T}{\Theta} \right]^2 \int_0^{\Theta/T} x \left[\frac{1}{e^x - 1} + \frac{1}{2} \right] dx. \quad (2)$$

Because $\rho_i \ll \rho_0$ and $1 - \gamma$ is close to zero, we neglect the first term in Eq. (1) and rewrite the second using Eq. (2). This gives

$$\frac{\rho(T)}{\rho_0} = \exp \left[- \frac{12\hbar^2 k_F^2}{Mk_B\Theta} \left[\frac{T}{\Theta} \right]^2 \int_0^{\Theta/T} \frac{x dx}{e^x - 1} \right]. \quad (3)$$

This equation contains only two unknown physical parameters, the Debye temperature Θ and k_F (M , the atomic mass, is taken to be the average atomic mass of

$\text{Al}_{85}\text{V}_{15}$, i.e., 30.6 u).

We will now evaluate Eq. (3) in two different ways. First, physically realistic values for Θ and k_F will be chosen and using these Eq. (3) will be compared with our experimental data. This is achieved by setting $k_F = 1.5 \text{ \AA}^{-1}$, which corresponds to $K_p/2$ (K_p , the wave vector of the first peak in the structure factor, was found to be 3.0 \AA^{-1} for $\text{Al}_{85}\text{V}_{15}$). The Debye temperature is set to 400 K (that of crystalline Al is 428 K and that of crystalline V is 380 K). With this choice, the upper of the two lines in Fig. 6, the magnitude of the temperature dependence of glassy $\text{Al}_{85}\text{V}_{15}$ seems to be rather well described by the extended Ziman-Faber model.

Finally, k_F and Θ can be treated as two free-fitting parameters, and a much improved agreement can then be obtained. The lower line in Fig. 6 shows this result with $k_F = 0.70 \text{ \AA}^{-1}$ and $\Theta = 200 \text{ K}$.

In conclusion, this analysis shows that the Ziman-Faber model can account for the magnitude of the negative temperature dependence of the resistivity if physically realistic values for k_F and Θ are assumed. On the other hand, the detailed temperature behavior of resistivity of Al-V can only be described within the theory at the expense of "unphysical" values for k_F and Θ ($k_F = 0.23K_p$ and $\Theta = 200 \text{ K}$).

The significant influence of the existence of micro-(nano-) crystallinity in an otherwise glassy metallic film on the electrical resistivity is exemplified in Fig. 6. The overall change in the temperature dependence of the electrical resistivity can be directly linked to the existence of and reflected by the very weak fcc Al lines observed in TEM (but not with x rays) for one of the films. For the $\text{Al}_{85}\text{V}_{15}$ -film IM at room-temperature with small traces of crystallinity, the temperature dependence could also be influenced by the positive temperature dependence of the small crystalline fraction. To calculate this influence in detail, information on the resistivity of the crystalline fraction, its volume fraction, and its geometrical distribution are necessary. It is seen that, being x-ray amorphous is not always a sufficient criterion to characterize thin films for electrical property studies of glassy metals.

Notice that the consequence of the change of sign of the Hall coefficient is not reflected in any obvious way in the electrical resistivity data. This will be further discussed below. The observed change in the Hall coefficient towards a positive value strongly suggests that a simple band free-electron model is not an adequate picture to describe the electronic properties of these Al-V alloys. This, of course, strongly limits the applicability of the Ziman model to explain the resistivity behavior.

C. Hall effect

We first discuss briefly various mechanisms that may explain the positive Hall coefficients in metals. Ever since the first reports of positive Hall coefficients⁸⁻¹⁰ and later of sign changes in the Hall coefficient with changing composition²⁵⁻³⁰ for nonmagnetic glassy metals, this issue has puzzled both theorists and experimentalists. In crystalline materials, a positive Hall coefficient is explained in terms of "holelike" parts of the Fermi surface,

but in disordered materials, which lack translation periodicity, concepts based on k-space considerations break down.

Based on the Ziman-Faber model, Harris³¹ recently evaluated the Hall coefficient using the Kubo-Greenwood formalism. His result shows the possibility of positive Hall coefficients in liquid and amorphous metals. The final result for the Hall coefficient from this analysis is expressed as

$$R = -\frac{1}{ne} \left[1 + \frac{2}{5} \frac{\partial \ln \tau}{\partial \ln E} \right]_{E=E_F}, \quad (4)$$

where $-1/ne$ is the well-known free-electron expression reflecting the actual number of conduction electrons, E is the electron self-energy, and τ is the lifetime of an electronic state. In systems where the lifetime of the conduction electrons changes rapidly with their energy, strong deviations from a free-electron-like behavior of the Hall effect can occur, and thus eventually a positive sign for the Hall coefficient can be expected. This elegant result does not, however, shed much light on the possible physical mechanisms that give a positive Hall coefficient in disordered materials (also pointed out by Harris).

Three additional models for a positive Hall coefficient have been attempted. In studying the question of positive Hall coefficients, several authors^{27,28,30} observe that the position of the early-transition-metal (ETM) d band seems to play a crucial role. Photoemission experiments and calculations indicate that the d states dominate at the Fermi level for ETM-LTM (late TM) binary glassy metals in which positive Hall coefficients are experimentally observed. Using such observations, the compositions for sign change have been predicted^{27,28} correctly for several ETM-LTM alloy systems.

Besides this empirical observation of common features in the electronic states for different glassy alloys, the two other direct physical mechanisms, giving a positive Hall coefficient, that have been proposed are the s - d -hybridization model³² and the asymmetric scattering of magnetic origin.^{33,34} Despite their different physical origin, both mechanisms can, in principle, be described within the Harris model, i.e., by Eq. (4). Furthermore, the two above-mentioned mechanisms also require d -electron states to be close to the Fermi level.

Morgan and Weir³² have argued that s - d hybridization can lead to positive values for the Hall coefficient through a negative slope in the electronic dispersion relation $E(k)$. Their results have, however, been questioned by Bose *et al.*,³³ who, in a computer simulation of liquid and amorphous Fe, could not find any evidence of a negative slope in $E(k)$ arising from s - d hybridization.

Asymmetric scattering in metals originating from magnetic moments is a well-accepted effect.³⁴ The large Hall effect found in ferromagnetic glassy metals^{35,36} has inspired the idea that a positive Hall effect found in paramagnetic early-TM-based alloys also could be of the same origin.^{37,38} This is in spite of the fact that it is not obvious that early-TM-based alloys have free magnetic moments in them. Theoretically, two different kinds of asymmetric scattering, the "side-jump" and the "skew

TABLE I. Hall coefficients and electrical resistivities of glassy and icosahedral films. RT denotes room temperature.

Films	Hall coefficient (RT) ($10^{-10} \text{ m}^3/\text{A s}$)	Resistivity (RT) ($\mu\Omega \text{ cm}$)
$\text{Al}_{85}\text{V}_{15}$ (glassy, IM)	-0.12	160
$\text{Al}_{80}\text{V}_{20}$ (glassy, IM)	+0.33	180
$\text{Al}_{61}\text{V}_{39}$ (glassy, codep.)	+0.60	170
$\text{Al}_{83}\text{Mn}_{17}$ (glassy, IM) ^a	-0.7	330
$\text{Al}_{83}\text{Mn}_{17}$ (icosahedral, IM) ^a	-1.4	300

^aReference 4.

scattering,³⁶ have been considered. In particular, the side-jump mechanism has been attributed the ability to give a positive Hall coefficient for paramagnetic Fe-Zr,³⁸ while the skew scattering has been considered but rejected³⁹ as a sufficient explanation for deviations from the free-electron picture for the Hall effect in glassy and liquid metals based on early TM's.

We now discuss the relevance of the above possibilities to explain the resulting positive Hall coefficient observed in this work for amorphous Al-V. Positive Hall coefficients have been reported for nonmagnetic glassy metals with the main component of Zr (Refs. 10, 11, and 25-28), Hf (Ref. 25), Ti (Refs. 25 and 40), La (Ref. 9), or V (Ref. 40), and sign changes have been observed in binary ETM-LTM glassy metals. We have here for the first time observed a sign change in a non-TM-based glassy metal of Al-V at a V content of $x_c = 16$ at. %. The Hall coefficient is found to change monotonically around x_c , exhibiting some of the smallest values of the Hall coefficient ever reported in literature. From Eq. (4), however, it is clear that the actual number of carriers, n , in this equation, does not necessarily have to diverge at x_c when the Hall coefficient changes sign ($R=0$). The composition of $R=0$ can instead be determined by the strength of the second term in Eq. (4), and from this point of view the absence of any dramatic changes in the behavior of the electrical resistivity can be understood.

Based on studies of x-ray-induced photoemission spectroscopy (XPS) on Al-TM films,⁴¹ the electronic structure of glassy Al-V can be assumed to be similar to that of the ETM-LTM glassy metals. Thus, the d -electron contribution from vanadium at the Fermi level is expected to increase with vanadium content and a change in the sign of the Hall coefficient is observed. The idea of s - d hybridization thus cannot be ruled out for glassy Al-V.

We now consider possible contributions arising from asymmetric scattering, which could be side-jump and/or skew-scattering mechanisms. In this approach the sign of

the Hall coefficient depends as a rule of thumb on the filling of the d band³⁶ in a given material, especially if it is magnetic. For a more-than-half-filled d band and a less-than-half-filled d band, the sign of the Hall coefficient is expected to be negative and positive, respectively. On this basis, since the Hall coefficient for liquid Al has a negative sign (Fig. 4) and V has only three d electrons, upon alloying with V the sign of the Hall coefficient would eventually become positive.

This picture of d -band occupation seems to explain well the sign of the Hall coefficient (Table I) for the amorphous and icosahedral states of Al-Mn as well. The Mn d band is more than half-filled, as shown from XPS studies,⁴¹ and so with increasing Mn the negative Hall coefficient is enhanced.

In conclusion, a sign change observed in the Hall coefficient of glassy Al-V indicates that this phenomenon is not only restricted to the ETM-LTM type of metallic glasses. Such a sign change appears to occur in any glassy metal with a content of early TM larger than a critical value x_c . For the amorphized Al-V system we find $x_c = 16$ at. % V. In light of the above discussion on the possible mechanisms, asymmetric scattering, in terms of d -state occupation, appears to consistently explain the data on amorphized Al-Mn and Al-V systems.

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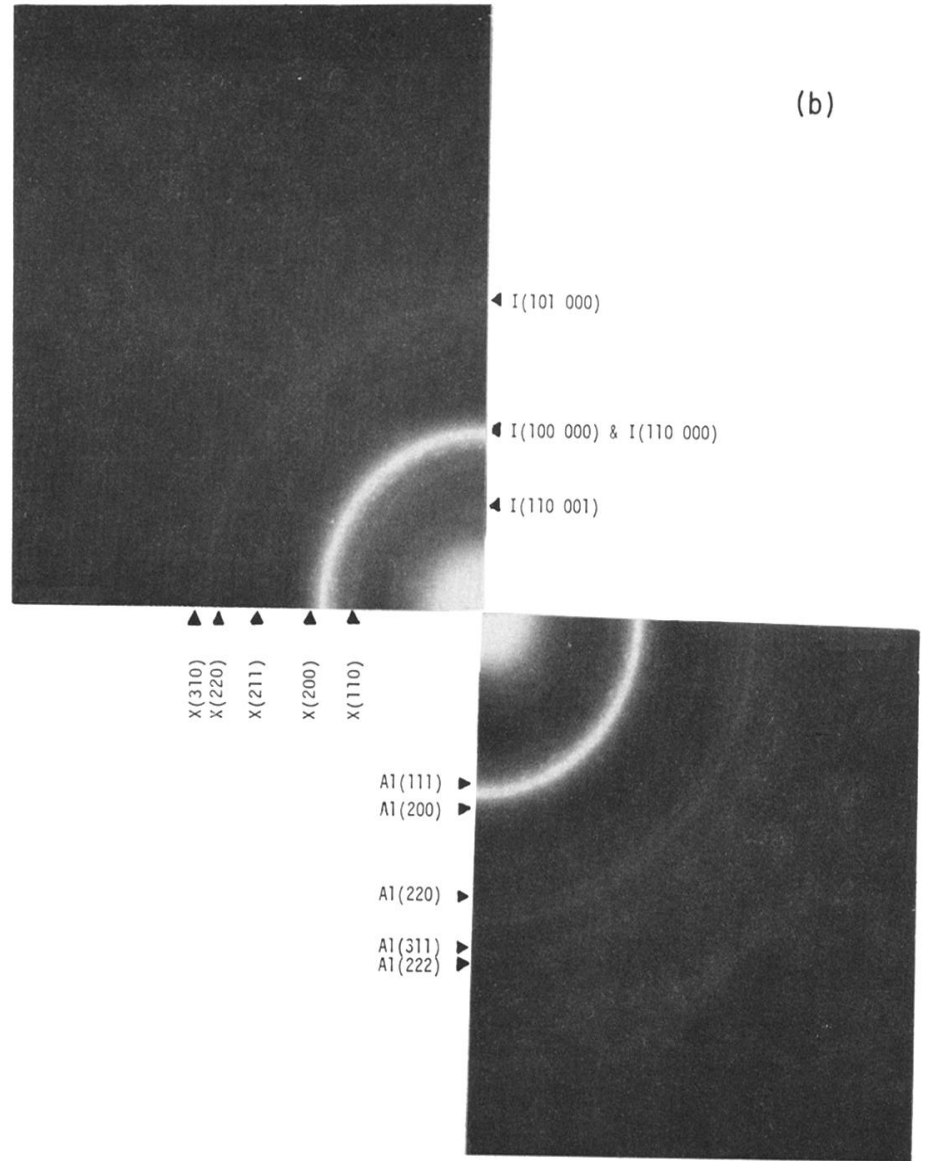
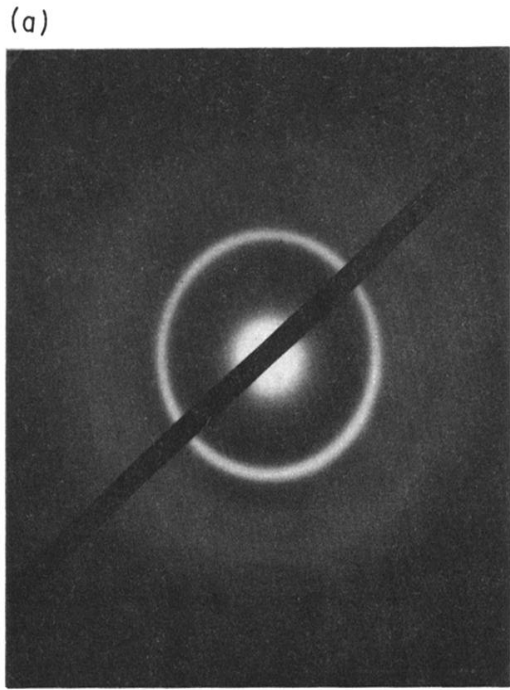


FIG. 1. (a) TEM-diffraction pattern of Al-V amorphized by IM at liquid-nitrogen temperature. (b) Diffraction pattern of $\text{Al}_{85}\text{V}_{15}$ ion-beam mixed at 473 K. Lines corresponding to the icosahedral phase, the x phase, and fcc Al (V) are indicated.