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Effect of pressure on the resistivity and Hall coefficient of amorphous metallic alloys

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Measurements have been made of the resistivity as a function of hydrostatic pressure in the range 0—5 kbar in the temperature interval 180—330 K for the amorphous alloys $Fe_{80}B_{20}$ (Metglas 2605), $Fe_{19}Ni_{61}P_{14}B_6$, $Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$ (Metglas 2826A), $Pd_{82}Si_{18}$, and $Cu_{42}Zr_{58}$. Measurements of the Hall coefficient were also made in $Fe_{19}Ni_{61}P_{14}B_6$ and Metglas 2826A. The pressure coefficients of resistivity were uniformly negative and, with the exception of $Fe_{80}B_{20}$, insensitive to temperature. The contributions of thermal and magnetic scattering to the resistivity are negligible. The simple formulation of the Ziman theory is found to be inadequate to account for the observed pressure dependence of the resistivity.

I. INTRODUCTION

In recent years amorphous metallic alloys have aroused a great deal of interest, and much attention has been focused on their mechanical, electrical, and magnetic properties in an effort to discover in what ways they resemble or differ from analogous crystalline materials.

Mechanically, amorphous metallic alloys appear to be similar to their crystalline counterparts. Their densities are in the range of 7—8 g/cm^3 (Refs. 1 and 2) and their compressibilities are very close to the values found in hard crystalline metals such as Fe and Ni.[3-5] In their thermal expansion a few of the amorphous metals more directly resemble oxide glasses[6] and Invar alloys[7] than common metals, but in general these materials behave mechanically much as do their crystalline counterparts.

The resistivity of amorphous metallic alloys has received a great deal of attention in recent years. In the past five years large quantities of FeNi-based alloys have been made available by Allied Chemical Corporation of Morristown, NJ, under the name Metglas (a registered trademark of Allied Corporation), and thorough studies of these materials have been made.[8-11] Similar alloys have been produced by individual researchers, permitting the study of the resistivity and its temperature coefficient as continuous functions of concentration.[12-25] There has also been some interest in the mostly nonmagnetic alloys based on PdSi,[26,27] and in alloys composed of two metallic species such as CuZr.[17,27]

The resistivity of all these materials shows several general features as a function of temperature. At room temperature the resistivity lies in the range of 120—200 $\mu\Omega$ cm, indicating a high degree of disorder scattering and an electron mean free path no longer than a few atomic spacings. The resistivity changes only slightly with temperature, varying linearly with T in the high-temperature region (typically above 100 K) and quadratically at low temperatures. In the linear region the temperature coefficient may be either positive or negative and is typically about 10^{-4} K^{-1}, ten times smaller than the value for most crystalline metals.

Some (but not all) of the magnetic alloys have distinct anomalies in the resistivity at the Curie transition,[10,11,17] indicating that a contribution from spin-disorder scattering is present.

The materials used in the present study were examined only in the high-temperature region, where the resistivity varies linearly with temperature. The one exception was Metglas 2826A ($Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$), which has a resistance minimum within the temperature range considered.

The resistivities have been interpreted primarily in terms of the model developed by J. M. Ziman and his collaborators[28-30] for liquid metals. This theory relates the resistivity to the single-ion pseudopotentials of the constituent atoms and to the scattering structure factor of the bulk material. It has been extended and applied to amorphous alloys,[31-34] and will be discussed in Sec. IV.

The Hall coefficients of amorphous alloys have sometimes been studied along with the ohmic resistivity. In magnetic materials such as the Metglasses[9-11,35,36] and similar alloys[11,17,37-40] the behavior of the Hall resistivity is found to conform quite closely to that of crystalline materials which are magnetically "soft." In these materials the Hall resistivity ρ_H varies with the applied field B_a and the magnetization M, as

$$\rho_H = R_0 B_a + 4\pi M R_s ,$$

where R_0 and R_s are the ordinary and spontaneous Hall coefficients, respectively, and $R_s \gg R_0$. This empirical relation describes a sharp linear rise in ρ_H at low fields with a slope of $R_H = R_0 + R_s$, and then at higher fields a "bending over" to a much smaller slope as saturation is reached. This is precisely the behavior observed in amorphous magnetic alloys below the Curie point. Above the Curie point the initial slope of ρ_H vs B_a drops precipitously, and this sharp drop can be used to determine the Curie temperature. In the ferromagnetic region the Hall coefficient R_H has a weaker temperature dependence than is observed in crystalline metals such as Ni, and at the Curie transition the drop in R_H is somewhat less sharp. The curves for amorphous and crystalline materials are otherwise extremely similar.

In the present experiment measurements have been made of the effect of hydrostatic pressure in the range of 0–5 kbar on the resistance and Hall voltage of several prototypical amorphous metallic alloys. Measurements of the resistivity as a function of pressure at constant temperature provide a sensitive test of presumed scattering mechanisms, and, particularly when combined with measurements at atmospheric pressure, can be used to distinguish simple volumetric effects from more complex mechanisms.

Very little work has been reported to date on the behavior of amorphous alloys under pressure. Ast and Krenitsky[41] examined the material Metglas 2826 ($Fe_{40}Ni_{40}P_{14}B_6$) under hydrostatic pressure and uniaxial tensile stress and found that the resistance decreased under pressure but increased under tension, to a greater degree than would be predicted from volumetric effects alone. Lazarus[42] studied the $Pd_{82-x}V_xSi_{18}$ series, and, upon finding no change in the resistance with pressure, concluded that the resistivity scaled precisely with the linear compressibility. Cochrane and collaborators[43] looked at several Metglas alloys under pressure between room and nitrogen temperatures and found that in all cases the resistance decreased with increasing pressure at room temperature. The value of the pressure coefficient of resistance at nitrogen temperature generally differed from that at room temperature by no more than 20%, except in the case of Metglas 2605 ($Fe_{80}B_{20}$) where the coefficient changed sign. They found no relationship between the pressure and temperature coefficients in these materials. Cote and Meisel[44] did a similar experiment at room temperature, examining the pressure coefficient of resistance of several amorphous and crystallized alloys. They found that the pressure coefficient increased markedly in absolute value upon crystallization, except in the case of Metglas 2826A which crystallized in at least two stages and in its final form had a positive coefficient. In all of these experiments the pressure coefficients of the amorphous materials were found to be four or five times smaller than the values observed in typical crystalline metals such as Fe or Ni.

A number of researchers have studied the effect of pressure on other properties of amorphous alloys, notably the Curie temperature[45–49] the crystallization temperature,[50,51] and the superconducting transition temperature,[52] but none of these investigations have shed much light upon the behavior of the resistivity under pressure.

That behavior is the subject of the present study. The available data do not provide much help in separating the possible contributions to the resistivity: volumetric effects, disorder scattering, scattering from thermal vibrations, magnetic scattering, and any other effects which may be present. By studying the resistance of several amorphous alloys as a function of pressure and temperature it is hoped that at least some idea of the relative importance of these effects might be obtained. Combining measurements at varying pressure and constant temperature with those at varying temperature and constant pressure allows an evaluation of the magnitude of the thermal scattering, which is the dominant contribution in crytalline metals. In two materials measurements were made of resistance and Hall coefficient above and below the Curie point in an effort to examine the behavior under pressure of any contribution from magnetic scattering which may be present.

Out of the large number of materials available for study, five materials were chosen as prototypes which could fairly be taken as representative of larger sets. $Fe_{80}B_{20}$ (Metglas 2605) was chosen because it is a simple binary material with a Curie point well above the highest temperature at which measurements were made. $Fe_{19}Ni_{61}P_{14}B_6$ has its Curie point within the temperature range studied, so that measurements could be taken in both the ferromagnetic and paramagnetic regimes, to look for magnetic contributions to the resistivity and Hall coefficient. Metglas 2826A has a resistivity minimum within the available temperature range, and an examination could thus be made of the pressure coefficients above and below both the resistance minimum and the Curie point. $Pd_{82}Si_{18}$ was chosen as representative of the nonmagnetic metal-metalloid systems, and $Cu_{42}Zr_{58}$ of the metal-metal alloys. $Cu_{42}Zr_{58}$ also has a negative temperature coefficient of resistivity over the entire temperature range considered, and an attempt could therefore be made to relate this behavior to the properties of the material under pressure.

II. EXPERIMENTAL METHOD

The high-pressure experiments were carried out in a vessel of the conventional Bridgman type. The vessel was machined from René 41, a high-strength nonmagnetic alloy. This material was used with the expectation that the measurements would be extended to very high and very low temperatures. It later became apparent, however, that the temperature dependence of the pressure coefficients was small and of limited interest, and the measurements were restricted to the range 180—330 K. The René 41 stock was purchased in the fully hardened condition, and great care was required in the machining process to ensure that the cutting tools remained sharp. The sample chamber, which was $1\frac{5}{8}$ in. deep and $\frac{1}{2}$ in. in diameter, proved to be too deep and too narrow to be cut with conventional machining techniques, and so electrical discharge machining was used.

The vessel was sealed with a Bridgman unsupported area seal, using a copper expansion ring supplemented with a small amount of indium wire or common solder to improve the initial seal. Two beveled stainless-steel rings prevented the copper from extruding.

The electrical leads were brought out of the vessel via a swaged tube which was vacuum-brazed to the end seal. Attempts were made to use helium and argon gas as pressure media and a few successful runs were made, but a reliable seal to prevent the gas from leaking down the swaged tube proved impossible to obtain. A 4:1 methanol-ethanol mixture was ultimately used as the pressure medium. This liquid did not leak out, but it did vitrify at approximately 170 K, limiting measurements to temperatures above about 180 K. At temperatures below about 200 K the viscosity of the fluid became quite high, and it was necessary to allow a long time for the medium to relax after the ballast pressure had been changed.

A resistance heater consisting of 15 feet of 24-gauge Chromel A wire sleeved in fiberglass was wound noninductively directly onto the vessel and cemented in place with Sauereisen cement.

The alcohol-filled sample chamber was pressurized with argon gas by means of a liquid-gas separator and a two-stage Aminco air-driven compressor and an oil-driven Harwood piston intensifier.

The measuring apparatus was quite simple. The resistance measurement was made using the conventional four-wire technique. The dc current was supplied with a Keithley model 227 constant-current source with a range of 1 μA—1 A. The voltage was measured with a Keithley model 191 5-$\frac{1}{2}$ digit multimeter with a range of 1 μV—1 kV.

The Hall voltage measurements were made with a three-point geometry, the two wires on the same side of the sample being connected by a 10-Ω 10-turn variable resistor. This resistance was adjusted to zero the Hall voltage in the absence of the magnetic field. The Hall voltage was measured with another Keithley 191 multimeter.

The magnetic field was generated by a Varian superconducting solenoid with a 2 in. bore and a maximum field of 40 kG. The field was read out as a voltage, to an accuracy of ± 50 G.

The temperature was monitored and controlled with a Lake Shore Cryotronics model DRC-84C digital controller. This instrument can be used over a range of 0—800 K with a resolution of 0.1 K and an accuracy of ± 1 K, depending on the sensor used. For most measurements a 100-Ω platinum resistance thermometer, also provided by Lake Shore, was used. For some low-temperature measurements a silicon diode sensor was substituted. The sensor was slipped into a small hole in the wall at the top of the pressure vessel. The vessel was heated with the resistance wire heater and cooled by heat exchange with the liquid nitrogen or helium in the magnet well.

All data runs were taken with decreasing pressure to allow more efficient use of the pressure generating equipment and to make the temperature stabilization less time consuming. To begin a resistance run the chamber was pressurized to 5.0—5.5 kbar and allowed to equilibrate to the desired temperature, overnight when possible. The constant current source was adjusted to give a current of 50—200 mA. The current passed through a 1-Ω standard resistor before continuing on to the sample, and the voltage across this resistor was monitored with a 1-μV resolution digital voltmeter to give the current to a precision of $\pm 10\,\mu$A.

The resistance of the samples varied from about 100—600 mΩ, so with a 200-mA current the ohmic voltages obtained were typically 20—120 mV. Sample-to-sample resistance variations were dominated by variations in the spacing of the potential leads welded to the sample.

A run involving Hall measurements proceeded in a similar manner except that at each pressure the magnetic field was ramped up and down. After the pressure and temperature had equilibrated, the Hall voltage reading was zeroed. The ohmic voltage and the pressure were then recorded, and the magnetic field was turned on. When the desired maximum field had been reached, the magnet ramp was halted and then reversed, and readings were taken at the same spacing for decreasing field. The maximum field used varied from sample to sample and run to run, dependent on the field at which the sample saturated.

Each magnetic field run took 25—30 min, and during that time the zero of the Hall voltage tended to drift. This offset was apparent when the field was returned to zero and the Hall voltage did not return to its previous zero-field value. The discrepancy usually did not amount to more than ±2—3 μV, but on occasion it was as large as 20 μV. The slopes of V_H vs B were computed separately for the increasing and decreasing field ramps, to minimize the effect of this drift.

The values of the Hall voltages observed at maximum field varied with the composition, the width, and the magnetic state of the sample. For most samples at currents of 100 and 200 mA and fields of less than 20 kG the maximum values recorded were in the range 20—200 μV.

All the samples used in this experiment were either purchased from Allied Chemical Corporation or obtained from various investigators, as noted below. For this reason exact details about the manufacture of these materials are unavailable. All the materials used in this experiment were prepared by melt spinning.

The materials designated by a number as well as a chemical formula are Metglas alloys purchased from Allied Chemical Corporation, Morristown, NJ. The compositions of these alloys, as of all the others, are nominal.

The $Fe_{19}Ni_{61}P_{14}B_6$ alloy was obtained from Dr. K. V. Rao (currently at the 3M Corporation, Minniapolis, MN) who had in turn obtained it from Dr. Egami at the University of Pennsylvania. The PdSi samples were obtained from Mr. K. Kelton of Harvard University. The CuZr sample was prepared by Mr. Eric Cotts of the University of Illinois.

All the samples came in the form of thin ribbons ranging in length from a few centimeters to 30 m. The sample thicknesses ranged from about 20 μm to about 50 μm. The widths of the samples varied quite widely from as much as 25 mm for one material from Allied Chemical to as little as 0.5 mm for some of the "homemade" samples. To each sample were spot-welded seven 0.005-in.-diam Pt wires to serve as electrical leads: four wires for the resistance measurement and three for the Hall measurement. These wires were in turn welded to brass binding posts mounted on a Lavite disk which had been cut so that the samples were free standing, thus insuring strictly hydrostatic conditions. The binding posts were pressed against spring contacts soldered to the copper wires which emerged from the swaged tube. A common difficulty was that of welding the Hall leads to very narrow samples. Attempts to weld them on the very edge of the ribbon frequently damaged the sample, and yet it was necessary that the leads on the two sides be widely enough separated that the Hall voltage would be of appreciable magnitude. For the narrowest samples it proved impossible to make Hall measurements, although Hall leads were attached to give mechanical support. All samples were checked by x-ray analysis to ensure that the transient heating during welding did not result in crystallization of the samples.

III. RESULTS

When the measured resistance was plotted against pressure, the result was a strictly linear relationship in all runs for all materials at all temperatures. In every case the slope was negative, i.e., the resistance decreased as the pressure was increased.

The change in resistance under pressure results in part from a simple change in sample dimensions due to the compressibility of the substance. In order to separate this effect from the more fundamental effect of the pressure on the resistivity, the logarithmic derivative of the resistance with pressure was converted to the corresponding quantity for the resistivity through the expression $d\ln\rho/dP = d\ln R/dP - \beta$, where β is the linear compressibility. The values used for β were derived from the work of Davis *et al.*[3–5] and in some cases they represent approximations from data for similar materials where actual measurements on the material in question were not available. These values are also strictly valid only for room temperature and atmospheric pressure, since no information is available about the variation of the compressibility with temperature and pressure. Such variations can be presumed small, by comparison to crystalline materials of comparable compressibility.

It is convenient to introduce here the abbreviations for the specimen names used henceforth: FeB represents $Fe_{80}B_{20}$ (Metglas 2605); FNPB represents $Fe_{19}Ni_{61}P_{14}B_6$; 2826A is the Metglas designation for $Fe_{32}Ni_{36}Cr_{14}P_{12}B_6$; PdSi stands for $Pd_{82}Si_{18}$ and CuZr represents $Cu_{42}Zr_{58}$.

In addition to the effect of compression, the effect of thermal expansion should also be taken into account. In the present case this correction is so small that the only values affected by it were the atmospheric pressure measurements on 2826A, which show an extremely shallow minimum in the resistivity as a function of temperature. The minimum in the resistance falls near 270 K but when thermal expansion is taken into account (using the value given by Shelby[6]) the minimum in the resistivity falls near 230 K.

The values of $-d\ln\rho/dP$ and $\rho(0,T)/\rho(0,290)$ for FeB are displayed in Fig. 1. The data represent three sets of runs on two different samples. The

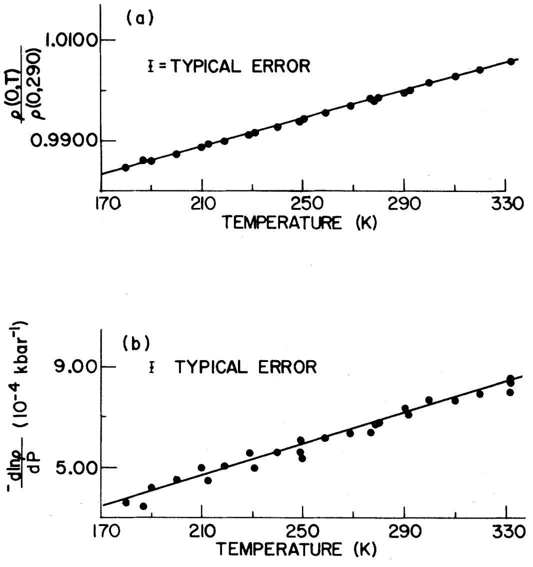

FIG. 1. Relative resistivity and pressure coefficient as a function of temperature for FeB.

variation of the resistivity at atmospheric pressure gives a temperature coefficient which is positive and equal to 1.41×10^{-4} K^{-1}.

The most striking thing about the results for FeB is the strong increase in the absolute value of the pressure coefficient with temperature, a phenomenon seen in none of the other materials examined in this study. The variation is linear over the entire temperature range measured, with a slope of -3.07×10^{-6} $(\mathrm{kbar\,K})^{-1}$. If this behavior continues to lower temperatures the pressure coefficient would vanish at approximately 60 K and become positive below.

The values of $-d\ln\rho/dP$ and $\rho(0,T)/\rho(0,290)$ for FNPB are shown in Fig. 2. The resistivity at atmospheric pressure varies with the temperature as $d\ln\rho/dT=2.56\times10^{-4}$ K^{-1}. The Curie temperature of this material is 260 K, and the resistivity shows no anomaly whatsoever at this temperature. The pressure coefficient, $d\ln\rho/dP$, shows essentially no change with temperature, with the values all falling within $\pm0.38\times10^{-4}$ kbar^{-1} of the mean value of -3.73×10^{-4} kbar^{-1}. There is no detectable change at the Curie temperature.

2826A has a very shallow minimum near 230 K in the resistivity at atmospheric pressure. This minimum seems to have no connection with the Curie transition, which occurs at 255 K. The pressure coefficient in this material is even less sensitive to temperature than that of FNPB, with a maximum deviation of $\pm0.24\times10^{-4}$ kbar^{-1} from a mean value of -5.65×10^{-4} kbar^{-1}. There is no anomaly to be seen at the Curie transition.

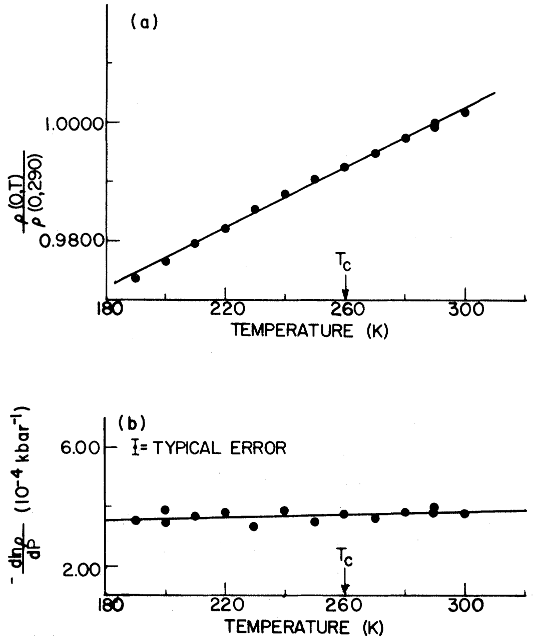

FIG. 2. Relative resistivity and pressure coefficient as a function of temperature for FNPB.

In PdSi the resistivity at atmospheric pressure is strictly linear with a slope $d\ln\rho/dT=1.43\times10^{-4}$ K^{-1}. The resistivity as a function of pressure has a slope that varies little over the temperature range investigated, deviating at most $\pm0.56\times10^{-4}$ kbar^{-1} from the mean value of -2.91×10^{-4} kbar^{-1}. In this material the effect measured in the resistance is quite small, usually less than half of the compressibility. There is some tendency for the pressure coefficients at lower temperatures to be smaller in absolute value than those at higher temperatures, and a line of slope $(d/dT)(d\ln\rho/dP)=-1.26\times10^{-6}$ $(\mathrm{kbar\,K})^{-1}$ can be fitted to the data, with a standard deviation of 0.50×10^{-6} $(\mathrm{kbar\,K})^{-1}$, but the data are too few to make this particularly meaningful.

CuZr is the only material in this study to display a negative temperature coefficient of resistivity over the entire temperature range considered. The slope is given by $d\ln\rho/dT=-1.19\times10^{-4}$ K^{-1}. Once again, the pressure coefficient is remarkably constant with temperature, deviating no more than $\pm0.87\times10^{-4}$ kbar^{-1} from the mean value of -10.05×10^{-4} kbar^{-1}. CuZr has the strongest variation with pressure of all the materials studied.

The behavior of the resistivity of all of these materials with pressure and temperature is displayed in Sec. IV, with the behavior of crystalline Fe included for comparison.

The determination of the Hall resistivity from the voltage and current recorded requires a knowledge of the dimensions of the sample, which in this case are quite uncertain. The Hall resistivity is given by $\rho_H = E_H / J_x$, where E_H is the Hall electric field and J_x is the current density. In this case the spacing between the Hall leads, w, is not equal to the width of the sample, W, so $\rho_H = (V_H / w)/(I / Wt)$, where V_H is the Hall voltage, I is the current, and t is the sample thickness. The experimentally accessible quantity, V_H / I, is thus equal to ρ_H / g, where $g = (Wt)/w$. The slope of ρ_H / g as a function of magnetic field (at low fields) gives R_H / g, R_H being the Hall coefficient.

When measurements of ρ_H / g were taken as a function of magnetic field, B, there was often a marked difference in the values of the slope at increasing and decreasing field within a single run. There did not seem to be any tendency for one to be consistently larger than the other, however. These differences determined the error bars shown in later figures. The error in the measurements on FNPB is larger than that for 2826A because the FNPB samples were smaller and lower currents were used to reduce resistance heating, so the values of V_H were smaller.

Figure 3 shows two representative curves of ρ_H / g vs B for 2826A, one below the Curie transition and one above. The scatter is rather large, especially at the higher temperature, but the general shapes of the curves are clearly visible. The initial slope in the ferromagnetic regime is about 2.5 times larger than in the paramagnetic regime.

The slopes of the ρ_H / g vs B curves are plotted as a function of pressure in Fig. 4, for the ferromagnetic and paramagnetic regimes. There is no clear trend with pressure in either case, aside from a slight tendency for R_H / g to increase with pressure in the ferromagnetic regime.

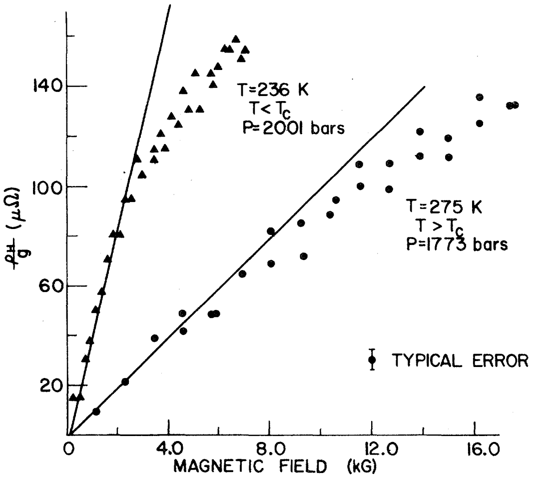

FIG. 3. Hall resistivity as a function of magnetic field for 2826A.

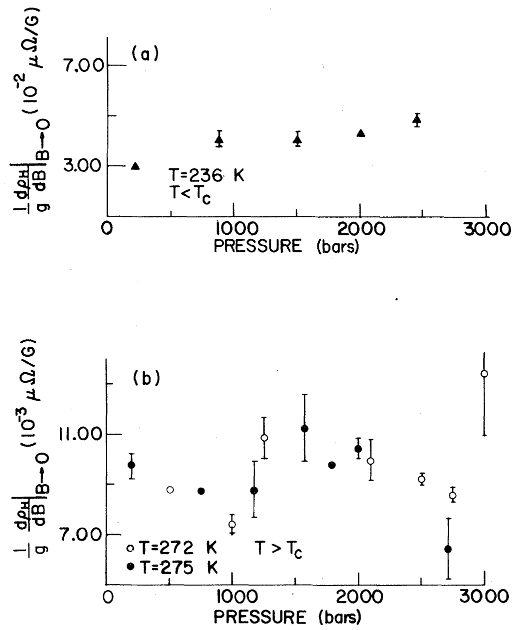

FIG. 4. Initial slope of the Hall resistivity with magnetic field as a function of pressure for 2826A.

The behavior of ρ_H / g vs B for FNPB was very similar to that displayed by 2826A in Fig. 3. The slopes obtained for various temperatures and pressures are given in Fig. 5. As the error bars indicate, the slopes for increasing and decreasing field tended

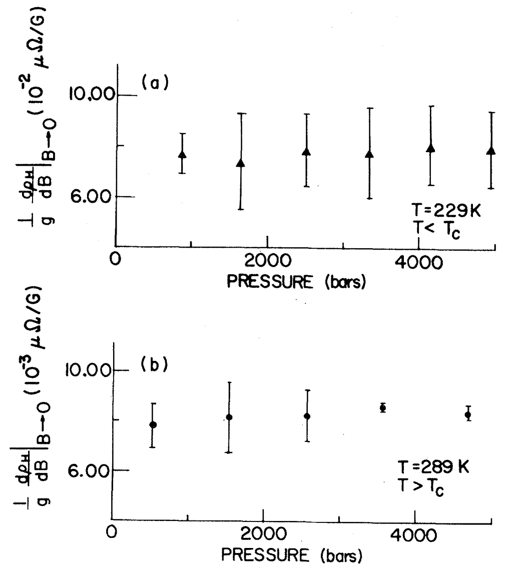

FIG. 5. Initial slope of the Hall resistivity with magnetic field as a function of pressure for FNPB.

on the whole to be more disparate in FNPB than in 2826A. This may or may not be due to the greater resolution obtained in 2826A due to the greater signal magnitude. No trend in the data is apparent either above or below the Curie point.

The random errors in the experiment consist of variations in the voltages and currents measured and in the temperature and pressure. At a given temperature and pressure, the ohmic voltage had a ± 1 μV resolution and the current a ± 10 μA resolution, so for a voltage of 56.75 mV and a current of 200 mA (typical for FNPB), random error in resistance would be approximately 0.02 mΩ, out of a total of about 283 mΩ. Calculations for other materials yield similar results.

The temperature variation within a given run should not have been larger than ± 0.2 K, and the temperature setting was accurate to ± 1.0 K. The pressure was known to ± 4 bars, so these errors are small enough to introduce only negligible errors in the quoted results.

Taking the resistance versus pressure data for representative runs of each material allows the calculation of the standard deviations associated with the least-squares fit; these are given in Table I. S_R is the standard deviation associated with the variation of the resistance ΔR_i about the line of best fit, and S_M and S_B are the standard deviations of the slope dR/dP and intercept $R(0,T)$, respectively. Also in the table are the expected deviation in the relative slope $\Delta(d\ln R/dP)$ and the resistance at atmospheric pressure $\Delta[R(0,T)/R(0,290)]$. $\Delta(d\ln R/dP)$ is found by dividing S_M by the best-fit value of $R(0,T)$ for that run (the error in that value does not have a significant effect), and $\Delta[R(0,T)/R(0,290)]$ is determined in the same way by dividing S_B by $R(0,290)$ for that run. The values of the corresponding errors for resistivity would be identical in this case, as the resistance and resistivity derivatives differ by a fixed constant, β.

As can be seen in Table I, the standard deviations are approximately 1% of the slope and considerably less for the intercept. Confidence can therefore be placed in the slopes and intercept calculated for each run. Errors in the determination of the temperature and pressure presumably contribute to the uncertainty of the results, but the strict linearity of the curves obtained for $R(P,T)/(0,T)$ and $R(0,T)/R(0,290)$ indicates that these errors are likely to be small.

IV. DISCUSSION

The results are in reasonable agreement with the small body of previously published data. Cochrane *et al.*[43] obtained a value of -4.50×10^{-4} kbar^{-1} for the pressure coefficient of resistance of FeB at 290 K, quite close to the average value of -4.77×10^{-4} kbar^{-1} presented here. These investigators also found a strong variation of the pressure coefficient with temperature, and the two points they report imply a slope of $d\ln R/dP=-3.52\times10^{-6}$ (kbar K)$^{-1}$, whereas the present data are fitted to a line of slope -3.07×10^{-6} (kbar K)$^{-1}$.

The agreement is less good for 2826A. This material was studied both by Cochrane *et al.* and by Cote and Meisel,[44] who reported the pressure coefficient of resistance at room temperature as -5.80×10^{-4} kbar^{-1} and -5.00×10^{-4} kbar^{-1}, respectively, whereas the value obtained in this study was -3.76×10^{-4} kbar^{-1}. However, the negligible temperature sensitivity of the pressure coefficient in this material was also reported by Cochrane *et al.*

For PdSi Lazarus[42] found no change in the resistance with pressure at room temperature to one part in 10^{-4}, and although a nonzero value was measured in this study, it was quite near Lazarus's resolution limit, with an average value of -1.13×10^{-4} kbar^{-1}.

No measurements have been previously reported on the remaining materials examined in this study, but their behavior and the behavior of the materials considered by other investigators show the same general characteristics: negative pressure coefficient of resistivity at room temperature independent of the temperature coefficient of resistivity, magnitude of the pressure coefficient small compared to values for crystalline metals, and pressure coefficient rela-

TABLE I. Standard deviations.

Material	S_R (mΩ)	S_M (mΩ/bar)	S_B (mΩ)	$\Delta\dfrac{d\ln R}{dP}$ (kbar^{-1})	$\Delta\dfrac{R(0,T)}{R(0,290)}$
FeB	6.88×10^{-3}	1.55×10^{-6}	3.61×10^{-3}	7.20×10^{-6}	1.67×10^{-5}
FNPB	7.36×10^{-3}	1.17×10^{-6}	3.55×10^{-3}	4.10×10^{-6}	1.25×10^{-5}
2826A	5.18×10^{-3}	6.02×10^{-7}	1.77×10^{-3}	3.98×10^{-6}	1.17×10^{-5}
PdSi	1.76×10^{-2}	3.56×10^{-6}	1.10×10^{-2}	7.90×10^{-6}	2.44×10^{-5}
CuZr	1.66×10^{-2}	2.06×10^{-6}	3.08×10^{-3}	3.78×10^{-6}	5.68×10^{-6}

tively insensitive to temperature.

In an attempt to explain these experimental results, one might turn first to the simplest model of metallic conduction—the nearly-free-electron model, in which the conduction electrons move freely about the metal, with occasional scattering from the fixed defects, giving rise to a resistivity $\rho=(ne\mu)^{-1}$, where n is the charge-carrier density, e is the electronic charge, and μ is the charge-carrier mobility. To determine the variation of the resistivity with pressure in this model, note first that n scales with volume as V^{-1}. The mobility in a disordered material can be assumed to be related to the mean free path, which is related to the interatomic spacing and therefore scales with volume as $V^{1/3}$. The logarithmic derivative of the resistivity with pressure in this simple model is therefore given by

$$\begin{aligned}(d\ln\rho/dP) &= -(d\ln n/dP)-(d\ln\mu/dP)\\ &= -3\beta+\beta=-2\beta\ ,\end{aligned}$$

where β is the linear compressibility. Comparing this simple result with the values of $d\ln\rho/dP$ obtained at room temperature, it can be seen in Table II that for the amorphous alloys the agreement is remarkably good for such a crude model. The largest deviation for the amorphous metals is for CuZr. In crystalline Fe the mean free path is limited not by the lattice spacing but by thermal scattering. The success of this model is surprising in view of the fact that for a typical resistivity of 150 $\mu\Omega$ cm the mean free path is of the order of a few atomic spacings, casting doubt upon the validity of a nearly-free-electron model, and indeed upon the concept of a mean free path.

In crystalline metals the dominant contribution to the resistivity in the high-temperature region derives from thermal scattering, and the primary effect of compression is the reduction of the amplitude of the thermal vibrations of the positive ions, resulting in a reduction in electron-phonon scattering and therefore in the resistivity. This decrease in the phonon spectrum under pressure parallels the decrease that occurs upon cooling the solid, and so compression and cooling are said to be corresponding states. In these materials the pressure and temperature coefficients of resistivity are thus of opposite sign.

TABLE II. Nearly-free-electron model.

Material	$-\dfrac{d\ln\rho}{dP}\Big/2\beta$
FeB	1.53
FNPB	0.94
2826A	1.52
PdSi	0.77
CuZr	2.28
Crystalline Fe	5.85[a]

[a] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 81, 167 (1952).

In amorphous alloys it is clear from the very small temperature coefficients that thermal scattering is not the dominant contribution to the resistivity. The temperature coefficients of resistivity are approximately ten times smaller in these materials than in crystalline metals. The pressure measurements, however, give a much more telling demonstration of the unimportance of thermal scattering. In FeB, FNPB, and PdSi the pressure and temperature coefficients have opposite sign, while in CuZr both the pressure and temperature coefficients are negative. Similarly, the resistivity of 2826A is nearly constant as a function of temperature, but the pressure coefficient is negative and of intermediate size. There is no difference whatsoever between the behavior with pressure below the resistance minimum and the behavior above it. The model of corresponding states therefore clearly does not apply to these materials.

This argument is illustrated in Figs. 6 and 7. Figure 6 shows the relative resistivity as a function of pressure at 290 K for the materials studied, as well as for crystalline Fe. Figure 7 shows the relative resistivity as a function of temperature at atmospheric pressure. In the model of corresponding states these drawings would have been approximate mirror images of one another, but the differences between them are quite striking. The magnitudes of the slopes of the two lines ought to be at least roughly related, particularly since the compressibilities of the materials are all similar, but in the case of FeB and PdSi the temperature coefficients are al-

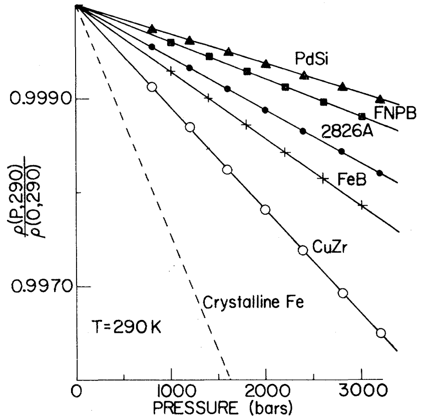

FIG. 6. Relative resistivity as a function of pressure at room temperature for various materials.

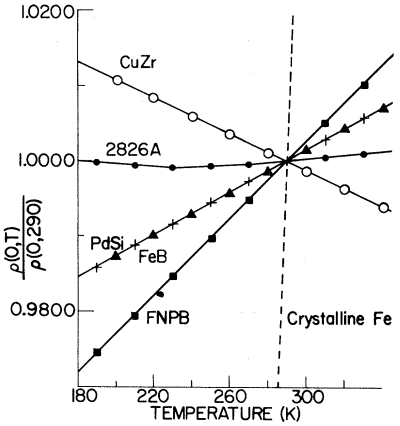

FIG. 7. Relative resistivity as a function of temperature at atmospheric pressure for various materials.

most identical, but the pressure coefficients are quite disparate. FNPB has the largest temperature coefficient, but the second smallest pressure coefficient. The comparison with crystalline Fe is also telling—the pressure coefficients of the amorphous materials are about four or five times smaller than that of Fe, but the temperature coefficients are ten times smaller. It can therefore be concluded that thermal scattering, the dominant mechanism in crystalline metals, makes only a very small contribution to the resistivity of amorphous alloys.

In crystalline ferromagnetic materials above the Curie temperature there is a significant contribution to the resistivity from the scattering of electrons from the spin disorder. At the Curie point the spins become ordered, and this contribution vanishes, leading to a sharp anomaly in the resistivity as a function of temperature. Of the five alloys examined in this study the Curie points of two (FNPB and 2826A) fell within the temperature range available. In neither of these materials was an anomaly seen at T_c in the resistivity at atmospheric pressure. There was also no detectable difference between the pressure coefficients of the magnetically ordered and disordered states. It therefore seems clear that in these materials scattering from spin disorder plays a negligible role, although the Hall coefficient is clearly related to the magnetic state.

It appears from the considerations discussed above that the dominant contribution to the resistivity in amorphous alloys is the scattering from the intrinsic disordered atomic arrangements. This mechanism is usually modeled using the Ziman theory of the resistivity,[28–34] which was originally developed for liquid metals. In this theory the electrons are assumed to be nearly free and the resistivity is given by

$$\rho=\frac{12\pi m^2 N}{\hbar^2 e^2 k_F^2 V}\int_0^1\left[\frac{q}{2k_F}\right]^3 a(q)\,|u(q)|^2\, d\left[\frac{q}{2k_F}\right], \tag{1}$$

where N is the number of conduction electrons, V is the volume, k_F is the Fermi wave vector, q is the scattering vector, $a(q)$ is the scattering structure factor, $u(q)$ is the Fourier transform of the single-ion pseudopotential, and the other symbols have their usual meanings. This expression is strictly appropriate only for elastic scattering of the conduction electrons, but the correction due to inelastic scattering is negligible.

The function $a(q)$ which appears in Eq. (1) can be measured through x-ray or neutron scattering, and for a typical liquid metal resembles Fig. 8. For amorphous metallic alloys the shape is quite similar, although for many alloys a shoulder appears on the high-q side of the initial peak.

For transition metals the pseudopotential $|u(q)|^2$ is replaced by the single-site transition matrix, which can be expressed as a function of phase shifts, η_l. The contribution of the d-wave phase shift η_2 is much stronger than that of the s and the p waves.

The factor $(q/2k_F)^3$ in the integral in Eq. (1) heavily weights the values of q near $2k_F$, which correspond to electrons scattered through large angles. It is therefore a reasonable approximation to consider only the d-wave phase shift and to evaluate the structure function at $2k_F$, to give the expression

$$\rho=(C/Vk_F^2E_F)a(2k_F)\sin^2\eta_2(E_F)\,, \tag{2}$$

where E_F is the Fermi energy and C is a product of fundamental constants.

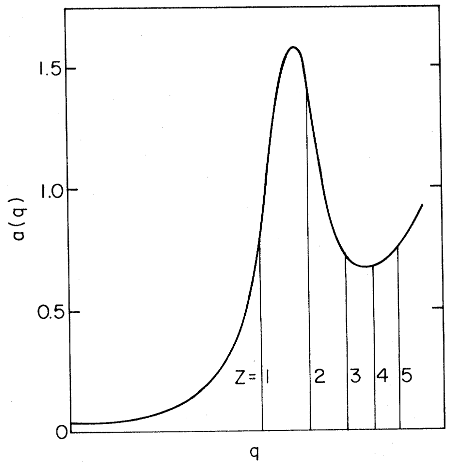

FIG. 8. Scattering structure factor for a typical liquid metal. The vertical lines mark $q=2k_F$ for the valences indicated (Ref. 30).

The value of $q = 2k_F$ is determined by the number of conduction electrons, which is controlled by the valence of the constituent atoms. As can be seen in Fig. 8, for monovalent species $2k_F$ falls below the first peak in $a(q)$. For higher valence $2k_F$ falls nearer the peak or even beyond it, and it is this characteristic which is usually invoked to explain the sign of the temperature dependence of the resistivity. If $2k_F$ falls very near the peak of $a(q)$, then at higher temperatures, when $a(q)$ has broadened and its peak height has fallen, $a(2k_F)$ may be smaller than at a lower temperature, and the temperature coefficient of the resistivity would be negative. For a lower valence species $a(2k_F)$ would increase with temperature as the peak broadened and the temperature coefficient would be positive.

The pressure derivative of ρ in this formulation is composed of three terms: the derivative of $(Vk_F^2E_F)^{-1}$, the derivative of $a(2k_F)$, and the derivative of $\sin^2\eta_2(E_F)$.

The derivative of the term $(Vk_F^2E_F)^{-1}$ can be found from simple scaling by noting that in a nearly-free-electron model with a spherical Fermi surface, k_F is proportional to $V^{-1/3}$ and E_F is proportional to $V^{-2/3}$, so $(Vk_F^2E_F)^{-1}$ scales as $V^{1/3}$, and the logarithmic derivative of $C/(Vk_F^2E_F)$ is simply $-\beta$.

To first order $a(2k_F)$ would not change at all with pressure, as the interatomic spacing and the Fermi wave vector would both scale as $V^{-1/3}$. The peak in $a(q)$ and the position of $2k_F$ would simply shift together toward higher values of q, and $d\ln a(2k_F)/dP$ would vanish. However, there is some indication that $a(q)$ may not simply shift without change of shape: Tsuji and co-workers[53] measured the x-ray interference function of liquid Na under pressure, and found that the position q_p of the first peak of the structure function did not simply scale as $V^{-1/3}$. The discrepancy was quite small, on the order of 1% at 3.8 kbar, but the first peak in the interference function did appear to fall at a slightly lower value of q than would be predicted by simple scaling. If this effect occurs in amorphous alloys as well, it could influence the resistivity by changing $a(2k_F)$ with pressure. If $q = 2k_F$ fell below the peak in the structure factor, then as $2k_F$ shifted closer to q_p the contribution of $d\ln a(2k_F)/dP$ would be proportional to $da(q)/dq$ in the neighborhood of $2k_F$. Even a small shift could have a significant effect if the slope of the structure factor were large, as it would be near q_p. However, the discrepancy between the measured values of $d\ln\rho/dP$ and the first term in the derivative of the Ziman expression, $-\beta$, requires that the remaining terms contribute only negative values. According to this analysis, $d\ln a(2k_F)/dP$ would be negative only if $q = 2k_F$ fell beyond q_p, which would presumably not be true for all of the materials studied here.

The remaining term in the pressure coefficient of the resistivity is

$$d\ln[\sin^2\eta_2(E_F)]/dP = 2\cot\eta_2(E_F)(d\eta_2/dP) .$$

Ratti, Evans, and Gyorffy[54] have calculated the volume dependence of η_2 for crystalline Pd and Fe, and they find that the typical S-shaped curve of $\eta_2(E)$ is maintained at smaller volume but the sharpness of the resonance is reduced and it is shifted to higher energy values. As a result, at any particular energy E, $\eta_2(E)$ is reduced as the volume is reduced. Of course, E_F also shifts to higher energy at lower volume, and since $\eta_2(E)$ increases monotonically with E the two effects partially cancel, particularly since in these metals $\eta_2(E_F)$ lies well above the resonance. The actual change in $\eta_2(E_F)$ with volume would be small, but $\eta_2(E_F)$ would definitely decrease as the volume is reduced, so $d\eta_2(E_F)/dP < 0$. For $\eta_2(E_F) > 3\pi/4$ (as is the case in the pure transition metals), $\cot\eta_2(E_F) < 0$, so

$$d\ln\sin^2\eta_2(E_F)/dP > 0 .$$

This correction to the pressure coefficients is probably small, and it is not clear that $\eta_2(E)$ necessarily varies in the same way with pressure in an amorphous alloy as it does in a pure crystalline metal. In any case, however, the term has the wrong sign to explain the discrepancy between $d\ln\rho/dP$ and the first-order term $-\beta$, which amounts to about a factor of three.

On the basis of his study of $Pd_{82-x}V_xSi_{18}$ alloys, Lazarus[42] found that, within his error limits, all the resistivities apparently scale with pressure as $d\ln\rho/dP = -\beta$. This was taken as confirmation of the validity of the Ziman model. It now appears that with our present limited understanding of the behavior with pressure of the various terms involved in Eq. (2), this simple formulation of the Ziman theory as it stands cannot adequately account for the observed pressure dependence of the resistivity of the amorphous metals included in this study. A detailed study of the pressure dependence of the various quantities in the more general expression in Eq. (1) could yield some insight into these phenomena.

The Hall effect measurements do not appear to be particularly sensitive to pressure. Any variation due to the increase in electron density is within the error associated with the measurements, and no large changes due to shifts in the magnetic ordering with pressure appear to be present.

The behavior of the pressure coefficient with temperature in FeB remains unexplained, but it may be related to the fact that the atomic volume of the metalloid atoms is only 0.51 of the volume associated with the metal atoms, in contrast to the situation in PdSi and 2826A (among others), where the relative volumes are 0.94 and 0.90, respectively.[55] This indicates that in PdSi and 2826A the metalloid atoms occupy spaces comparable in size to those of the metal atoms, in a two-sphere dense random packing, whereas in FeB the metalloid atoms occupy the interstices of the metal-atom dense-random-packing structure. This difference may well affect the behavior of the resistivity under pressure, but no firm conclusions can be drawn at this time.

It can be seen from the analysis presented above that, within the present state of understanding of the variation with pressure of the different contributions to the resistivity, it is not possible to draw any definite conclusions about the origins of the phenomena observed in this study. It seems clear that thermal and magnetic scattering play negligible roles, but a simple nearly-free-electron model gives a better quantitative description of the variation of the disorder scattering with pressure than does a simple version of the more sophisticated Ziman model.

This is particularly surprising in view of the success the Ziman model has had in explaining the magnitude and temperature dependence of the resistivity and also, particularly, of the thermopower.[56] One would expect that a model which correctly predicts the behavior of a complicated and sensitive quantity such as the thermopower would be equally successful in describing a seemingly simpler quantity such as the pressure coefficient of the resistivity.

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