

## Resistivity of amorphous Fe-B alloys: Measurements and implications

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Ribbons of amorphous alloys of composition  $\text{Fe}_{100-x}\text{B}_x$  ( $15 \leq x \leq 22$ ) were prepared by rapid quenching from the melt. The temperature dependence of the resistivity is linear for  $120 \leq T \leq 300$  K and quadratic for  $20 \leq T \leq 100$  K; this behavior is qualitatively consistent with predictions based on recent extensions of the theory of resistivity for liquid transition metals. Within this theoretical framework, an electronic stability criterion for metallic glasses is found not to be satisfied for the Fe-B system. The experimentally determined stable composition regime ( $x \approx 20$ ) agrees with predictions of random-packing models, where the boron atoms occupy voids inherent in such a structure. At the higher temperatures, the temperature coefficient of resistivity is positive and constant as a function of composition within experimental uncertainty. Based on these observations and a published structure factor for  $\text{Fe}_{84}\text{B}_{16}$ , it is suggested that the most probable values for the number of electrons per atom contributing to conduction are:  $z_{\text{Fe}} \leq 1$  and  $0 \leq z_{\text{B}} \leq 1$ .

### I. INTRODUCTION

The electrical transport properties of amorphous metals are just beginning to be investigated experimentally in a systematic way and theoretical predictions on the temperature dependence of resistivity have only recently appeared. From the point of view of understanding, the simplest systems would seem to be those with the fewest components. At least two components must be used to obtain amorphous alloys which will be stable at room temperature. Amongst these, we have chosen the Fe-B system for our studies.

All samples were prepared by the same method and verified to be amorphous by x-ray diffraction and electron-microscopy examination. The effect on resistivity measurements of various methods of making electrical contact to the samples was investigated, and no variations were found in our case, where only ratios of resistivity as a function of temperature are reported. The importance of properly mounting the sample for resistivity measurements and the effect of thermal expansion are discussed. It is found that the largest variation in our measurements at fixed composition results from sample-to-sample variations.

The results are compared with recent predictions based on extensions of the theory of resistivity for liquid transition metals,<sup>1,2</sup> and qualitative agreement is obtained. The higher-temperature measurements (up to room temperature) are used to deduce that a proposed stability criterion for metallic glasses,<sup>3,4</sup> does not appear to be satisfied for the Fe-B system. On the basis of our measurements we are also able to obtain estimates for likely values of the number of electrons per atom contributing to conduction. This is an important parameter which does not easily result from purely theoretical considerations.

### II. EXPERIMENTAL

Samples of amorphous alloys in the  $\text{Fe}_{100-x}\text{B}_x$  series were prepared by rapid quenching from the liquid onto a rotating drum.<sup>5</sup> The amorphous nature of the resulting ribbons was checked by x-ray diffraction and transmission electron-microscopy analysis. Amorphous samples with no indication of a crystalline component were obtained only in the compositional range  $15 \leq x \leq 22$ . The resulting ribbons ( $\sim 1$  mm wide and  $30 \mu\text{m}$  thick) were cut into 13 mm lengths for resistance measurements. Copper wires were attached for the standard four-probe resistance measurement technique by various methods (conducting epoxy, spot welding, indium solder) with identical results within experimental error. The samples were supported only by these copper leads of 0.13 mm diameter, to prevent changes in sample dimensions as a function of temperature which would be imposed by dimensional changes of the substrate if the samples were affixed to a substrate.

Changes in sample dimensions will occur during temperature cycling due to nonzero thermal-expansion coefficients of the samples. The ratio of resistivities at two temperatures is equal to the ratio of the resistances measured at those temperatures multiplied by  $b = (1 + A \Delta T)^2$ , where  $A$  is the thermal-expansion coefficient and  $\Delta T$  is the temperature difference. This correction factor is usually negligible in the case of crystalline alloys, where temperature coefficients of resistivity are large. However, it may be important in amorphous alloys, where temperature coefficients of resistivity are small ( $\sim 10^{-4} \text{ K}^{-1}$ ). For example, the ratio of the resistance at 20 K to that at 300 K might be 0.97, and the corresponding correction factor  $b$  would be 1.003 for

$A = 5 \times 10^{-6} \text{ K}^{-1}$ , a typical value<sup>6</sup> for amorphous alloys. This amounts to a 10% correction in going from a resistance ratio to a resistivity ratio and should be taken into account in precise work. Note that the thermal-expansion coefficient is a strong function of temperature and can be a strong function of composition as well.<sup>6</sup>

Values of  $A$  at the temperatures of interest (those below room temperature) have not been determined, and therefore we have not corrected the resistivity ratios reported here. These are, therefore, strictly speaking, resistance ratios, although that distinction is not made in the following. In the Fe-B series of amorphous alloys, values of  $A$  above room temperature change from positive to negative as a function of composition,<sup>6</sup> but the magnitude of the correction factor  $b$  is such that the conclusions in this paper would be unaffected by its inclusion.

### III. RESULTS

Only resistivity ratios are reported in this paper. Resistivity at a given temperature is normalized to that at room temperature for a fixed composition. The greatest experimental uncertainty in the measurements of resistivity versus temperature is the sample to sample variability illustrated in Fig. 1. Samples were taken from adjacent portions of the ribbon of amorphous  $\text{Fe}_{78}\text{B}_{22}$ . Each sample gave reproducible results when cycled in temperature but, as seen in the figure, a sample to sample spread of  $\sim 1\%$  occurs at the lowest temperatures. Similar results were found for other compositions.

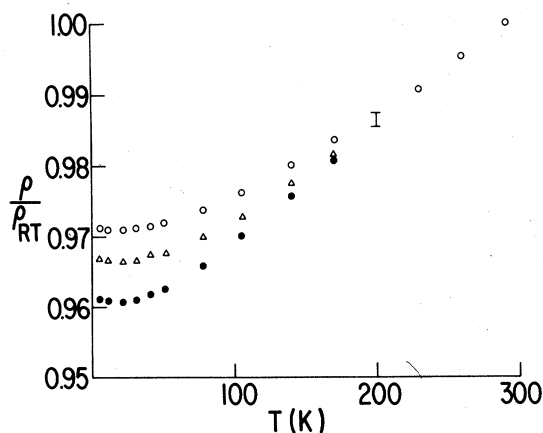


FIG. 1. Temperature dependence of resistivity normalized to the value at room temperature. Data are shown for three samples of  $\text{Fe}_{78}\text{B}_{22}$  cut from adjacent portions of an amorphous ribbon.

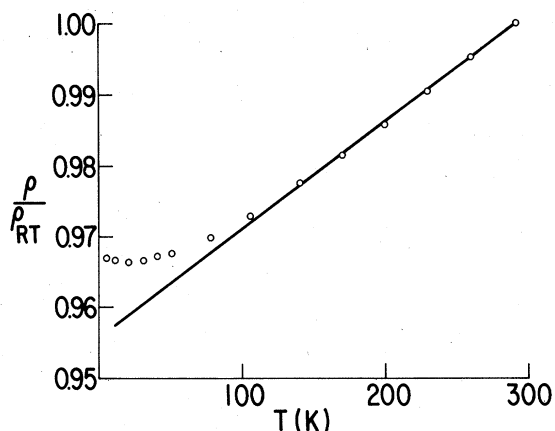


FIG. 2. Resistivity as a function of temperature for a sample of amorphous  $\text{Fe}_{78}\text{B}_{22}$ . A linear temperature dependence is obeyed at the higher temperatures.

Throughout the compositional range studied it was found that the temperature dependence of resistivity has a linear  $T$  dependence in the interval  $120 \leq T \leq 300 \text{ K}$  (e.g., see Fig. 2) and a  $T^2$  dependence at the lower temperatures  $20 \leq T \leq 100 \text{ K}$  (e.g., see Fig. 3). At the lowest temperatures, a clear minimum in resistivity occurs as has been reported for many amorphous alloys.<sup>7</sup>

Figure 4 shows the temperature coefficient of resistivity  $\alpha = \rho^{-1}(d\rho/dT)$  as a function of composition. It can be seen that  $\alpha$  is positive and approximately constant as a function of composition.

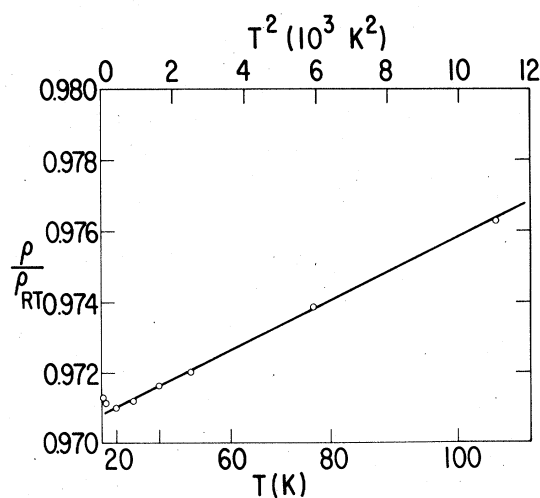


FIG. 3. Temperature dependence of resistivity in the lower-temperature regime for a sample of amorphous  $\text{Fe}_{78}\text{B}_{22}$ . The temperature is plotted on a  $T^2$  axis so that the straight line corresponds to a  $T^2$  dependence.

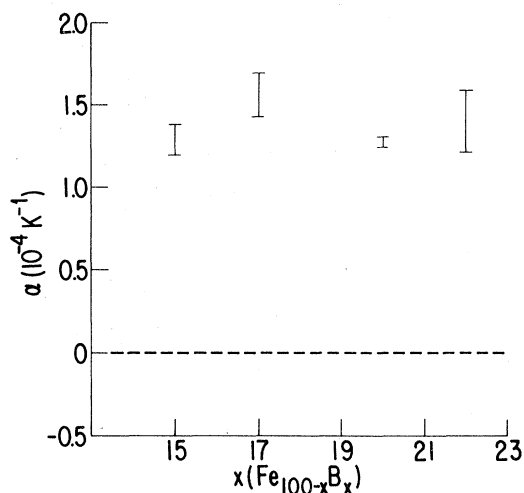


FIG. 4. Temperature coefficient of resistivity in the linear  $T$  regime ( $120 \leq T \leq 300$  K). The bars cover the values found for the following numbers of samples tested: 4 for  $x=15$ , 2 for  $x=17$ , 2 for  $x=20$ , and 4 for  $x=22$ .

#### IV. DISCUSSION

The  $T$  and  $T^2$  dependence of resistivity we have found at higher and lower temperatures, respectively, is in qualitative agreement with predictions of recent models based on extensions of the theory of resistivity for liquid metals.<sup>1,2</sup> We will use arguments based partly on these models although it should be noted that they do not include magnetic scattering. Magnetic scattering may be unimportant in the higher-temperature regime being considered. No changes in resistivity have been observed on traversing the Curie temperature of various ferromagnetic amorphous alloys,<sup>8,9</sup> and the extended theory of liquid metals in which the resistivity is primarily determined by the structure factor seems to be appropriate.<sup>8-10</sup>

An electronic criterion has been proposed<sup>3,4</sup> to explain the relative stability of metallic glasses against crystallization:  $2k_F \approx q_p$ , where  $k_F$  is the Fermi wave vector and  $q_p$  is the position of the first peak in the structure factor. For amorphous transition metals<sup>11</sup> the resistivity is proportional to  $a(2k_F)$ , i.e., the value of the structure factor at  $2k_F$ . The temperature dependence of the structure factor is such that negative temperature coefficients of resistivity are expected and observed,<sup>1,11</sup> when  $2k_F \approx q_p$ . Our observation that the temperature coefficient of resistivity is positive throughout the compositional region of stability implies, therefore, that  $2k_F \neq q_p$  in these alloys, and the electronic stability criterion is not satisfied for the Fe-B system. On the other hand, geometrical arguments of stability based on the random packing of hard spheres<sup>12</sup> (where the B atoms would occupy voids inherent in such a structure) predict stability at

compositions close to  $x=20$ . This is consistent with the region of stability  $15 \leq x \leq 22$  which we have experimentally determined.

A fundamental quantity which governs the resistivity is the number of electrons per atom contributing to conduction, defined as  $z$ . The value of  $z$  for the Fe-B system is  $z_e = z_{Fe}(1-x/100) + z_B(x/100)$ . The following line of reasoning leads to a determination of likely values for  $z_{Fe}$  and  $z_B$  based partly on our measurements of resistivity. We have determined that  $\alpha(x) > 0$ , and this implies<sup>1</sup> that  $a(2k_F) < 1$ , where  $a(2k_F)$  is the structure factor at  $2k_F$ ; this means that  $2k_F$  is not near the peak in the structure factor. Using measurements<sup>13</sup> of  $a$  for  $Fe_{84}B_{16}$ , it follows that  $2k_F > 3.50 \text{ \AA}^{-1}$  or  $2k_F < 2.55 \text{ \AA}^{-1}$ . Since  $k_F^3 = 3\pi^2 N z_e$ , where  $N$  is the number of atoms per unit volume, the inequality conditions on  $k_F$  can be converted to conditions on  $z_e$ . The density used was  $7.45 \text{ g cm}^{-3}$ , an average value of the density of  $Fe_{84}B_{16}$  reported in the literature.<sup>13,14</sup> We then have  $z_e < 0.74$  or  $z_e > 1.9$ , as shown schematically in Fig. 5. The value of  $z_{Fe} \approx 1$  is found to be generally valid in liquid-metal alloy systems,<sup>15</sup> and is also deduced<sup>16</sup> from calculations for solid Fe. Therefore, we conclude that the lower solution of Fig. 5 is more likely, i.e.,  $z_{Fe} \leq 1$  and  $0 \leq z_B \leq 1$ .

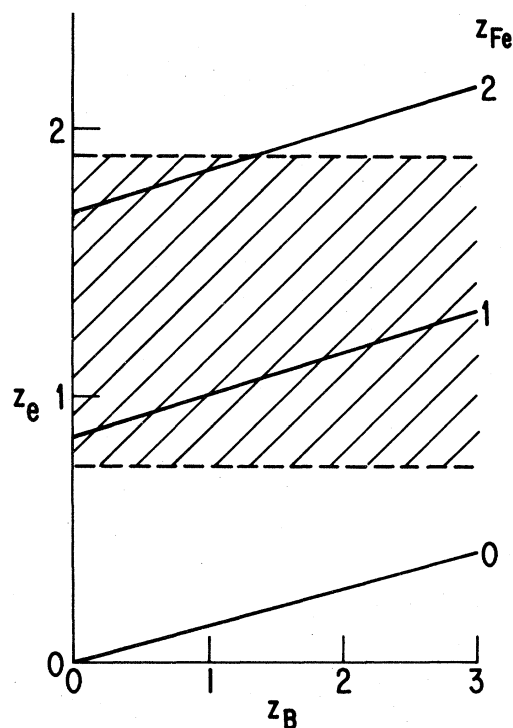


FIG. 5. Schematic plot of the allowed values of  $z$ . The value of  $z$  for the Fe-B system,  $z_e$ , is shown as a function of  $z_B$ . Lines are drawn for the cases  $z_{Fe} = 0, 1, 2$ . The shaded area is excluded by the condition  $\alpha(x) > 0$ , which follows from the results shown in Fig. 4.

The value of  $z_B$  cannot be determined more precisely, but the following considerations support the conclusion that it is low, i.e.,  $0 \leq z_B \leq 1$ . A value of  $z_B \sim 0$  means that the three boron electrons which might otherwise contribute to conduction have been transferred to localized energy levels of the Fe-B system. Cluster orbital calculations for  $\text{Fe}_{80}\text{B}_{20}$  (R. P. Messmer, private communication) show that this is indeed the case. The value  $0 \leq z_B \leq 1$  also must be consistent with measurements of variations in magnetic moment per atom as a function of composition. Results for  $B$  in various ferromagnetic amorphous alloys,<sup>17</sup> including Fe-B,<sup>18</sup> show that approximately one boron electron must remain localized to explain the changes in magnetic moment. In our picture, the other two boron electrons would also be localized, but with opposite spins so that they would not contribute to magnetic properties; this implies  $z_B \approx 0$ . Recent measurements of changes of magnetic moment as a function of composition in the Fe-B system<sup>19</sup> imply that approximately two electrons per B atom become localized, which would mean that  $z_B \approx 1$  as an upper limit.

One can use the value of  $z_e$  deduced above to test a simple condition<sup>20</sup> for the validity of the theory of resistivity invoked in this paper: that the mean free path of conduction electrons,  $L$ , be longer than the mean atomic radius  $R$ . The absolute resistivity of the Fe-B samples in this study was measured to be  $120 \mu\Omega \text{ cm}$  at room temperature, within  $\sim 10\%$  uncer-

tainty. Using this value of resistivity together with  $z_e = 0.7$ , and a density of  $7.4 \text{ g cm}^{-3}$ , one obtains  $L = 6.2 \text{ \AA}$  and  $R = 1.4 \text{ \AA}$ . The computed value of  $2R$  can be compared to the position of the first peak in the pair distribution function of  $\text{Fe}_{84}\text{B}_{16}$  which is at  $2.5 \text{ \AA}$ .<sup>13</sup> Thus, the condition for the validity of the theory is satisfied.

## V. SUMMARY AND CONCLUSIONS

The temperature dependence of resistivity has been determined for amorphous ribbons of composition  $\text{Fe}_{100-x}\text{B}_x$ . The temperature dependence is linear for  $120 \leq T \leq 300 \text{ K}$  and quadratic for  $20 \leq T \leq 100 \text{ K}$ . At the higher temperatures, the temperature coefficient of resistivity is positive and constant as a function of composition. From these observations, it is concluded that an electronic stability criterion is not satisfied for this system, and that  $z_e \leq 1$ , with likely values of  $z_{\text{Fe}} \leq 1$  and  $0 \leq z_B \leq 1$ .

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