

## Superconductivity, normal-state resistivity, and magnetic susceptibility of amorphous Zr-Co alloys

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Disordered Zr-Co alloys are studied in the concentration range from 45 to 80 at. % Zr. Particular experimental concerns are described including the control of nonuniform sample cross section, possible aging effects, and the influence of small crystallites on one sample surface. Results are obtained for the concentration dependence of the first peak in the structure factor, the superconducting transition temperature  $T_c$ , the temperature and field dependence of the magnetic susceptibility  $\chi$  in the range 4.2–300 K and 0–1.5 T, and for the normal-state resistivity and its temperature dependence  $d\rho/dT$  at 270 K.  $\chi$  is found to be field dependent, behavior which is ascribed to ferromagnetic clusters. The weight fraction of these clusters increases with decreasing temperature and decreasing Zr concentration and amounts to at most 0.2 wt. % at 45 at. % Zr close to the ferromagnetic phase boundary.  $|d\rho/dT|$  decreases with decreasing Zr concentration and approaches 0 close to the ferromagnetic phase boundary. This behavior is well described by the observed  $T_c$  and a model which relates  $d\rho/dT$  to the electron-phonon interaction  $\lambda$ . The decrease of  $T_c$  is mainly due to a decreasing  $\lambda$ .

### I. INTRODUCTION

In recent years there has been an intensive interest in binary amorphous alloys, in particular, in those based on Zr. These alloys can be rather conveniently formed in melt spinning over wide composition ranges and therefore provide a useful basis for a systematic study of the element and concentration dependence of various properties. Examples include structural properties, relaxation phenomena, crystallization, resistivity, magnetic susceptibility, specific heat, electronic structure, and superconducting and ferromagnetic properties.

Nevertheless, the problem remains of how to adequately characterize an amorphous material. There is no well-defined structure, even for identical chemical compositions, and the basic question of how to correlate microstructure with observed properties of amorphous metals is still too difficult a problem. Furthermore, besides conventional concerns with sample purity and homogeneity, the experimentalist on amorphous metals must also take into account a number of possible influences on the measured properties such as the time dependence and the effects from processing parameters, e.g., melt temperature, cooling rate, and substrate temperature.

Methods developed to deal with these problems are so far mainly aimed at empirical characterization. One line of research is to modify the structure of a glass of given chemical composition, e.g., by heat treatment,<sup>1</sup> by varying the melt temperature,<sup>2</sup> by different quenching rates<sup>3,4</sup> or by different substrate temperatures.<sup>5</sup> Another approach is to report on several different experimental results for each sample to characterize it by its physical properties.

We present results of x-ray scattering, superconducting transition temperature  $T_c$ , normal-state magnetic susceptibility, and electrical resistivity measurements of disor-

dered Zr-Co alloys in the range 45–80 at. % Zr, with particular attention given to some of the pitfalls encountered with experiments on amorphous alloys. Furthermore, glassy Zr-Co is one of the interesting alloy systems where one can pass continuously in a disordered state from a superconducting (Zr-rich) phase to a ferromagnetic (Co-rich) phase. We study this phase transition from the superconducting side.

### II. EXPERIMENTAL METHODS

#### A. Sample preparation

The nominal purities of the elements used were 99.8 wt. % for Zr from Alfa Ventron and 99.998 wt. % for Co from Johnson and Matthey. Alloys were prepared in an arc furnace by repeated melting on a water-cooled copper hearth under reduced pressure of Ar gettered by molten Zr. Weight losses were negligible in this process.

Samples of mass of about 2 g were melt spun onto a rotating copper drum. The sample space could not be evacuated, but prior to melting, liquid N<sub>2</sub> was poured into a large container below the copper wheel which boiled off gas in sufficient quantities to preclude oxidation. Observations which support the view that this technique was adequate will be described below.

Care was taken to maintain similar process parameters for each alloy. Thus, by allowing the cast bands to drop into the cooled container, one should minimize post-quenching annealing effects. The ejection pressure and roller speed were kept constant, producing bands of about 30  $\mu\text{m}$  thickness, and the quenching rates are presumably similar. The temperature of the melt  $T_m$  was not measured. We used similar heating power, heating time, and sample mass in each case however and differences in  $T_m$  are expected to be small.

### B. Conventional measurement techniques

Both sides of the samples were examined by x-ray diffraction at room temperature. The position of the first peak in the structure factor was determined in a setup with a curved monochromator of LiF in the diffracted beam, a scintillation counter, and a step scanning control. Readings were taken for a fixed time in steps of  $0.1^\circ$  in  $\theta$ .

The superconducting transitions were determined by dc resistance measurements. We checked these results by a mutual inductance measurement on the  $Zr_{80}Co_{20}$  sample.  $T_c$  was then about 40 mK lower ( $\approx 1\%$ ) and the transition width was similar. In these measurements the temperature was obtained from a calibrated carbon resistor. The temperature coefficient of resistance at 270 K was measured by a similar four-probe dc technique. Temperatures were regulated and read from a calibrated Pt resistor.

The temperature and field dependence of the magnetic susceptibility  $\chi$  was measured in a Faraday balance in the range 4.2–300 K and 0–1.5 T. Samples of masses down to 10 mg were suspended in Au wires which had been separately calibrated.

### C. Resistivity measurements

The best results for the resistivity  $\rho$  of amorphous metals are usually obtained from density measurements<sup>6</sup> of the cross-sectional area  $A$ . Such measurements are now widely used. However, accurate results may require sample lengths of the order of a meter. It must then furthermore be assumed that the variation of  $A$  is small over the length used in the resistance measurement.

In our case, we could only obtain band lengths of the order of several cm for  $Zr_{45}Co_{55}$ . Therefore we have developed a photographic method to obtain accurate resistivity measurements on short samples.<sup>7</sup> This method allows for measurements of  $\rho$  and  $A$  on the same piece of a sample so that any variation of  $A$  over the sample length can be controlled.

The resistance was measured at a few different well-marked positions of the potential edges. The sample was then embedded in plastic and grounded down at right angles to its length and  $A$  was determined photographically at several positions. The accuracy of this method is mainly determined by errors in the photographic processes and is estimated to be within  $\pm 1.5\%$ .

### D. Influence of small crystallites

In melt spinning with one wheel, the side of the band in contact with the roller surface (inner side) is more rapidly cooled than the outer surface. Therefore, particularly at the limits of the glass-forming range, the critical cooling rate may be exceeded at the inner side and just barely reached on the outer side resulting in the formation of small crystallites on the surface of the more slowly cooled side of the sample.<sup>8,9</sup> Unless both sides of the bands are examined this fact may easily escape attention.

Figure 1 shows the x-ray spectra of a  $Zr_{80}Co_{20}$  sample. Three peaks were observed from the outer surface as quenched [Fig. 1(a)]. The  $d$  values of the two higher-

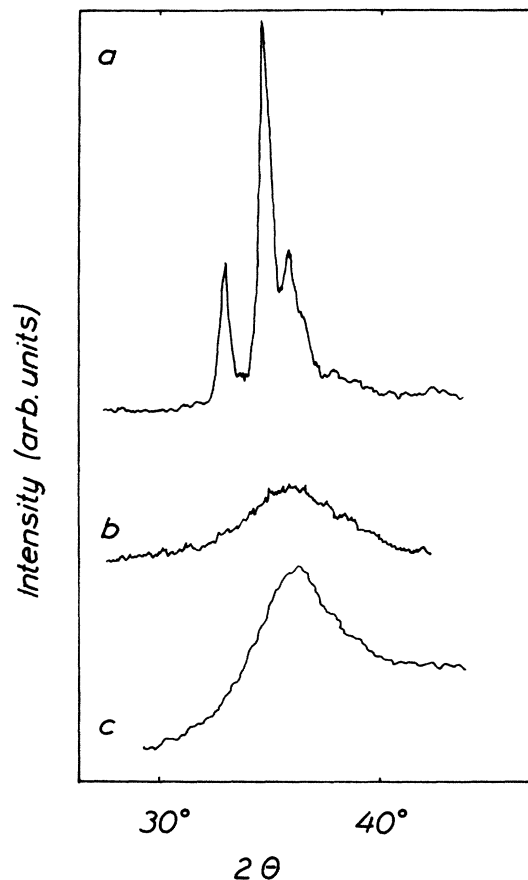


FIG. 1. A portion of x-ray scattering results with Cu  $K\alpha$  radiation from a  $Zr_{80}Co_{20}$  sample. (a) The slowly cooled side of the sample as quenched. (b) The same side after light grinding. (c) The rapidly cooled side as quenched.

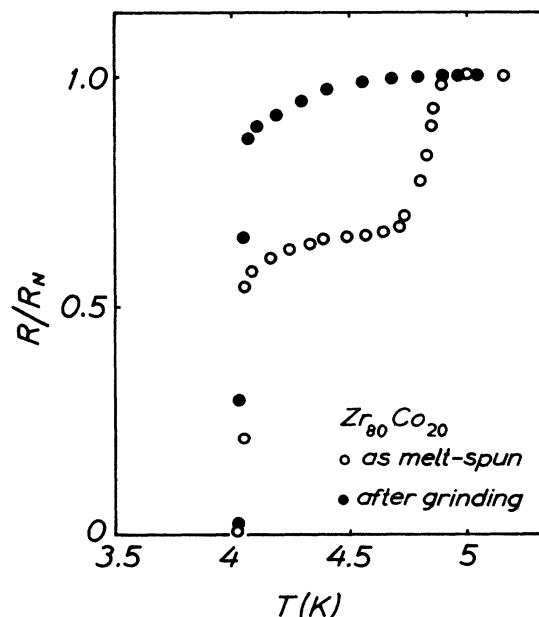


FIG. 2. Superconducting transitions for the same sample as in Fig. 1.  $R_N$  is the normal-state resistance.

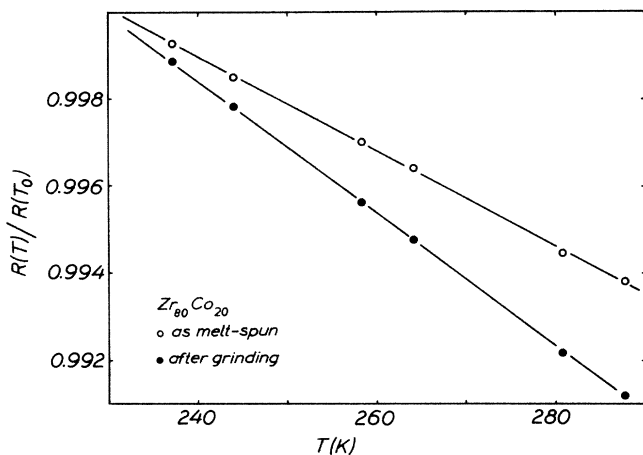


FIG. 3. Resistance versus temperature at higher temperatures for  $Zr_{80}Co_{20}$  as quenched and after grinding.  $R$  has been arbitrarily normalized to a temperature  $T_0$  of about 230 K to display that the temperature dependence is weaker for the sample as quenched.

angle peaks would suggest<sup>10</sup>  $Zr_4Co$ . After grinding this surface the peaks disappeared and the resulting diffractogram, shown in Fig. 1(b), resembles the result in Fig. 1(c) from the inner side in the as-quenched condition.

Although these crystallites presumably form a small fraction of the outer surface in the as-quenched condition they may have a strong influence on properties which are sensitive to surface conditions. This is illustrated in Figs. 2 and 3.  $T_c$  measured resistively shows a double transition in the as-quenched state (Fig. 2). After grinding, only the lower transition is observed, which we thus associate with the glassy state.

The resistance around 270 K is shown in Fig. 3, arbitrarily normalized to display that the temperature coefficient of resistance  $\alpha$  is less negative in the as-quenched state. Crystallites may be expected to have a lower resistivity than the bulk and a positive  $\alpha$ . Therefore they may contribute substantially to decrease  $|\alpha|$ . Similar conclusions were reached previously for Ni-Zr glasses.<sup>11</sup>

#### E. Absence of observable surface oxides

In spite of the precautions taken to avoid oxidation during melt spinning, some surface oxides may have formed. Therefore one may be concerned about a possible influence of such oxides on the measured properties. It will be seen below that the results for  $T_c$ ,  $\rho$ ,  $\chi$ , and the first peak in the structure factor are in good agreement with those obtained with samples from other sources, melt spun in an inert gas. The results for  $Zr_{80}Co_{20}$  discussed above also clearly indicate that a conducting phase is removed by grinding the surface.

For the field dependence of  $\chi$  there are no comparable results. Therefore we investigated the magnetic properties of a  $Zr_{65}Co_{35}$  sample melt spun in Ar gas. The results for  $\chi$  and its temperature dependence are similar to those displayed below,  $\chi$  being about 2% smaller at all temperatures for the Ar-quenched sample. If the field dependence  $\omega\sigma$  of  $\chi$  were due to magnetic oxides one would expect a

smaller  $\omega\sigma$  in the Ar-quenched sample. In contrast, the observed  $\omega\sigma$  was about 70% higher. This may be due to a somewhat lower cooling rate for the Ar-quenched sample.<sup>4</sup> We conclude that possible oxides on the surface of our samples apparently do not influence any of the present measurements.

#### F. Absence of significant aging effects

Since a glass is not in thermodynamic equilibrium, the question arises whether the observed properties are time dependent. Strong aging effects have been observed in the temperature dependence of resistance<sup>12</sup> of  $Zr_{40}Cu_{60}$  with a change of sign of  $\alpha$  at 250 K after 27 months. We have not performed a systematic study of aging in Zr-Co alloys. By remeasuring several properties after an extended time, however, we have ascertained that such effects are at most small in this alloy system.

Our samples were stored in air at room temperature. The positions of the potential edges in the resistance measurements were not marked on the samples since we were not worried by aging effects at the time of our first measurements. Therefore the samples may have been slightly displaced when remeasured and the scatter of these results include possible aging as well as variations over sample length.

The resistive results for  $T_c$ , however, all show a small decrease of below 2% after 20 months. Full relaxation usually produces a decrease of the order of 10%.<sup>2,13</sup> Our results thus suggest a small relaxation after 20 months. The results for  $\alpha$  were inconclusive since we observed lower as well as higher values of  $\alpha$  after aging. These results will be shown in Sec. III. In summary, possible aging effects are small and do not affect the conclusions drawn from  $d\rho/dT$ .

In the measurements of  $\chi$ , the samples were folded and wrapped with a suspension wire of Au. Stored in this way a sample of  $Zr_{59}Co_{41}$  was remeasured after 39 months. The results for  $\chi$  were within a few tenths of a percent of the original measurements at all temperatures. In the field dependence of  $\chi$  we found a measurable aging effect of about a 3% increase. Such a small change has no influence on the interpretation of these results.

### III. RESULTS AND INTERPRETATION

#### A. x-ray results

Disordered samples with 50, 78, and 82 at. % Zr could not be produced by our quenching methods. The x-ray diffractograms from the rapidly cooled side of these samples contained a few sharp Bragg peaks and they were discarded from further investigation. Grinding of the slowly cooled side was essential at 45 at. % Zr, and in general also for 80-at. % samples, and occasionally necessary for 70-at. % samples. In this way we obtained x-ray amorphous samples at 45, 59, 65, 67, 70, and 80 at. % Zr.

The magnitude of the scattering vector  $k_p$  at the first peak in the diffractograms was evaluated from  $k_p = 4\pi \sin\theta/\lambda$ . The results are shown in Fig. 4 together with published values. Our data for 65 at. % Zr include results for three samples of different cooling rates.<sup>4</sup> The

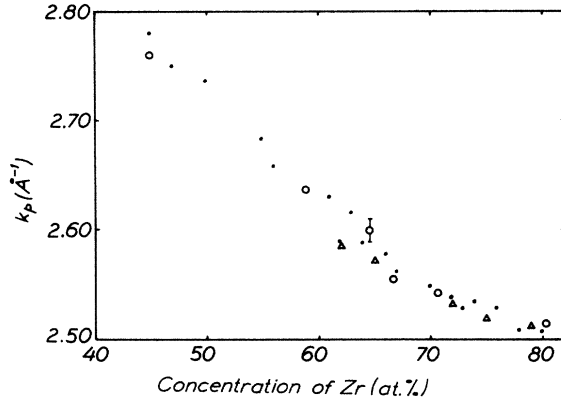


FIG. 4.  $k_p = 4\pi \sin\theta/\lambda$  at the first peak in the structure factor.  $\Delta$ , Ref. 9;  $\cdot$ , Ref. 14;  $\circ$ , present work.

results for samples from different sources agree fairly well. There appears to be a change of slope of  $k_p$  versus Zr concentration around 65 at. % but there is little evidence that this change is discontinuous as suggested by Buschow.<sup>14</sup>

### B. Superconducting transition temperature

Our  $T_c$  results agree with those of other workers. Data from several different sources were shown recently.<sup>15</sup> We have fitted a second-degree polynomial  $T_c(c)$ , with Zr concentration  $c$  in at. %, to our data and to those of Ref. 16 given in a table. This function is convenient and will be used below. The result is

$$T_c(c) = 0.225(c - 49.7) - 0.00306(c - 49.7)^2, \quad (1)$$

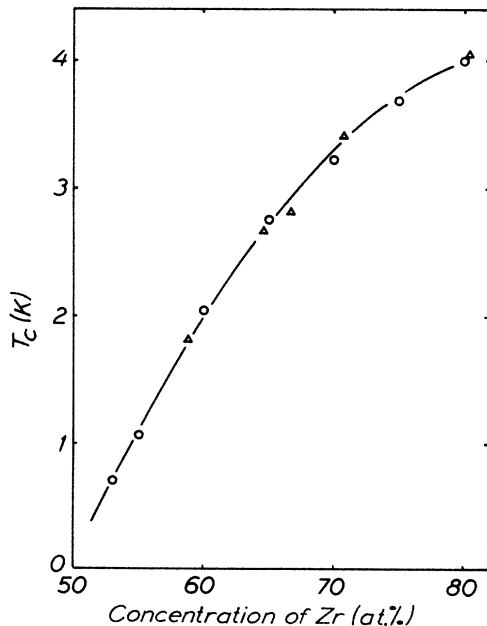


FIG. 5. Concentration dependence of  $T_c$ .  $\circ$ , Ref. 16;  $\Delta$ , present results. The curve, Eq. (1), is a least-square fit to the data.

with a standard deviation of below 50 mK for the data in the range 53–80 at. % Zr. Our results, those from Ref. 16, and Eq. (1) are shown in Fig. 5.  $Zr_{45}Co_{55}$  was found to be nonsuperconducting above 15 mK. The agreement between  $T_c$  results for samples from different sources is encouraging.  $T_c(c)$  for disordered Zr-Co alloys appears to be a well characterized function, independent within about 0.1 K of different processing parameters, in different laboratories, such as melt temperature, cooling rate, atmosphere in quenching process, possible post-quenching relaxation, and storage conditions.

### C. Magnetic susceptibility

The magnetic susceptibility was found to be somewhat field dependent in all samples. As previously reported<sup>17</sup> in disordered Zr-Fe this is ascribed to ferromagnetic Co-rich clusters of saturation magnetization  $\sigma$  and weight function  $\omega$ . The observed magnetization  $\chi_A B$  is thus assumed to consist of two parts:  $\chi B$  and  $\omega\sigma$ .  $\chi$  is the matrix susceptibility and is taken to be independent of the magnetic field  $B$  as in Honda plots of  $\chi_A$  versus  $1/B$ :

$$\chi = \chi_A - \omega\sigma/B. \quad (2)$$

$\chi$  at 300 K is shown in Fig. 6 as a function of Zr concentration. Our results agree very well with those of Babic *et al.*<sup>18</sup> in the range 80–65 at. % and are somewhat larger over the whole concentration range than those of Altounian and Strom-Olsen.<sup>16</sup>

It can be seen from Fig. 6 that  $\chi$  is weakly dependent on concentration for the superconducting alloys. At 45 at. % Zr, however,  $\chi$  appears to be substantially exchange enhanced. The temperature dependence of  $\chi$  is shown in Fig. 7 for some alloys.  $\chi$  increases slowly with temperature for the superconducting alloys at a rate of about  $3 \mu J/T^2 \text{ kg K}$ . This is similar<sup>19</sup> to polycrystalline Zr and supports observations by other methods.<sup>20–22</sup> that Zr  $d$  electrons dominate the Fermi-surface properties of these alloys.

At 45 at. % Zr,  $d\chi/dT$  is negative from 4.2 to 300 K. This temperature dependence is weak compared to that in a local-moment system. In amorphous  $Zr_{40}Cu_{60}$ , e.g.,<sup>23</sup> 1 at. % Fe replacing Cu causes  $\chi$  to increase by a factor of 2

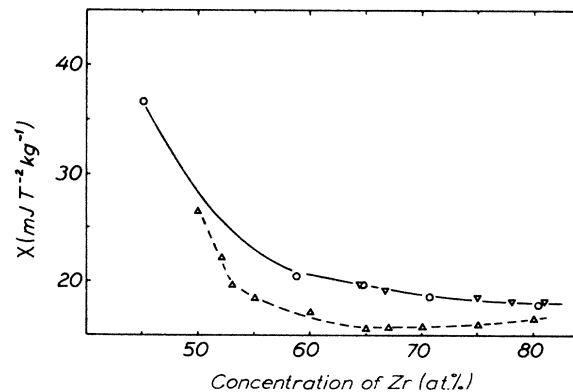


FIG. 6. Concentration dependence of the room-temperature magnetic susceptibility.  $\Delta$ , Ref. 16;  $\nabla$ , Ref. 18;  $\circ$ , present results.

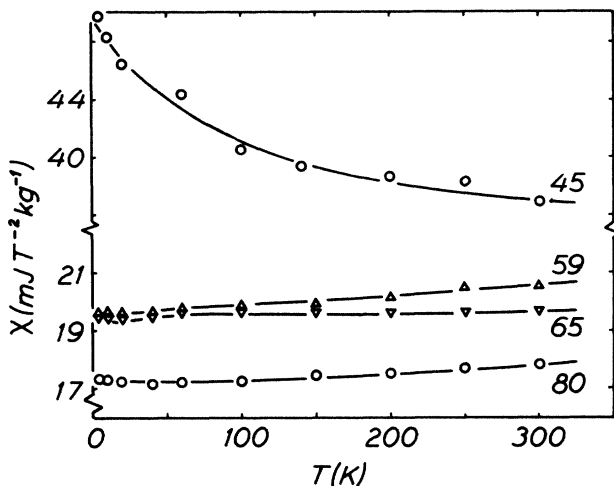


FIG. 7. Temperature dependence of  $\chi$  for some samples. The figures denote Zr concentration in at. %.

in the same temperature interval. Clearly, there is no well-developed local moment in disordered Zr-Co alloys at a few at. % of Co short of the ferromagnetic phase at 43 at. % Zr.<sup>24</sup>

In Fig. 8 the temperature dependence of  $\omega\sigma$  in Eq. (2) is shown for some samples. It can be seen that  $\omega\sigma$  increases with decreasing temperature and increases at each temperature with decreasing Zr concentration. For  $Zr_{45}Co_{55}$  the field-dependent part of  $\chi$  is quite large at all temperatures. From Fig. 7 it can be seen that  $\omega\sigma/B$  at 1 T for this sample is comparable to  $\chi$ . The large field dependence and the possibility that some clusters are unsaturated in the available field range up to 1.5 T make the results

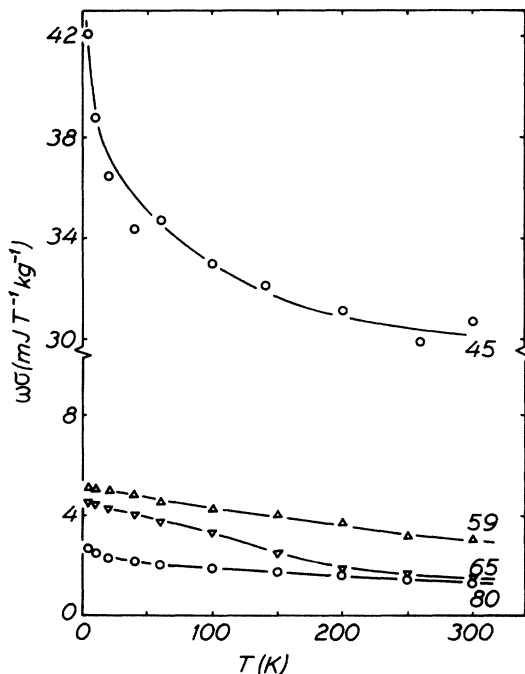


FIG. 8. Temperature dependence of  $\omega\sigma$ , defined in Eq. (2). The figures give Zr concentration in at. %.

for  $\chi$  and  $\omega\sigma$  somewhat less accurate for this sample. Therefore the data are more scattered in this case.

This fact does not affect the conclusion that  $\omega$  is small even close to the ferromagnetic boundary. If these clusters consist of Co spins of  $1.7 \mu_B/(\text{Co atom})$ , then about 250 wt. ppm of such clusters would be required at 45 at. % Zr. If the clusters are diluted ferromagnets close to the critical concentration with moments of about<sup>24</sup>  $0.2 \mu_B/(\text{Co atom})$  then they would reach about 0.2 wt. %. These values give upper and lower bounds for the cluster concentration in this sample.

For the superconducting alloys,  $\omega$  is an order of magnitude smaller. It was found previously that  $\omega\sigma$  could be varied by about a factor of 3 by different cooling rates without any appreciable influence on  $T_c$ .<sup>4</sup> We concluded that up to at least 35 at. % Co there is no significant interaction between these clusters.

$\chi$  and  $\omega\sigma$  follow a similar concentration dependence with a small increase down to 59 at. % Zr. At 45 at. % Zr there appears to be a significantly increased exchanged-enhanced magnetic susceptibility and a strong increase in the ferromagnetic cluster fraction. Ferromagnetism may therefore emerge from the percolation of such clusters. More likely, however, an increased exchange enhancement of  $\chi$  in combination with an increased polarizing effect from the clusters are the dominating reasons for the ferromagnetic phase transition.

#### D. Electrical resistivity

The electrical resistivity was measured with the photographic technique on three samples. These results are shown by the open circles in Fig. 9 together with several results from density measurements. Our results are similar to the two sets of data marked by triangles. In particular, taking the variation of  $A$  into account does not give

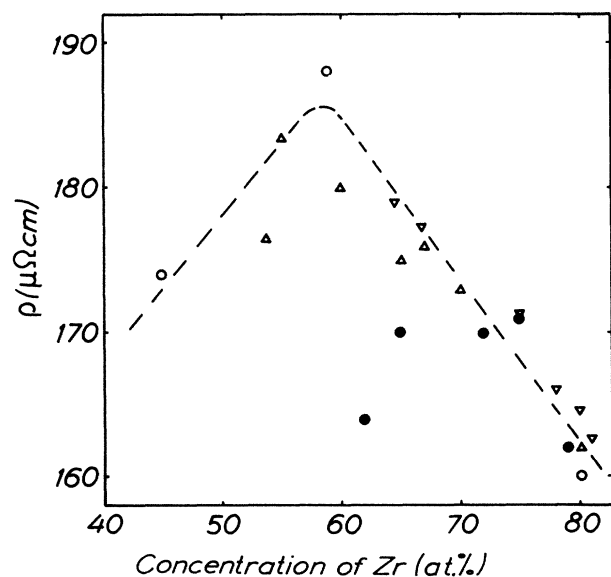


FIG. 9. Concentration dependence of the room-temperature resistivity. ●, Ref. 9; △, Ref. 16; ▽, Ref. 18; ○, present work. The dashed curve is only a suggestive summary of most of the data.

systematically lower values of  $\rho$  compared to results from density measurements which, as pointed out,<sup>25</sup> would be the case if  $A$  were seriously nonuniform. We conclude that in general there would be no need for a more laborious photographic technique unless only short samples were available.

The dashed curve in Fig. 9 is a guide to the eye suggesting a concentration dependence of  $\rho$  which is similar to that in other disordered Zr-based alloys.<sup>16,18</sup> The filled circles<sup>9</sup> were said to be accurate to about 5% and were disregarded. The scatter around the dashed curve is generally within  $\pm 2\%$ . It was suggested recently<sup>26</sup> that a maximum in  $\rho$  may arise with decreasing Zr concentration from a combination of a decrease in the density of Zr  $d$  electrons, which increases  $\rho$ , and an increased pressure on the Zr sites, which decreases  $\rho$ .

The results for  $d\rho/dT$  at 270 K are shown in Fig. 10. We were concerned about assessing the validity of such results since very differing values have been reported in the literature. E.g., the concentration dependence of  $\alpha$  was found<sup>18</sup> to have the opposite sign compared to our previous results.<sup>27</sup> Furthermore, the strong time dependence of disordered Zr-Cu alloys<sup>12</sup> would seem to require precautions which have rarely been considered.

To obtain  $d\rho/dT$ , one usually measures  $\alpha$ . We want to stress that the well-known fact that  $\alpha$  in disordered alloys is small should not be taken to imply, as has often been the case, that the temperature dependence of  $\rho$  is small in these alloys. The physically interesting quantity is  $d\rho/dT$  and its magnitude, in contrast, is generally large in disor-

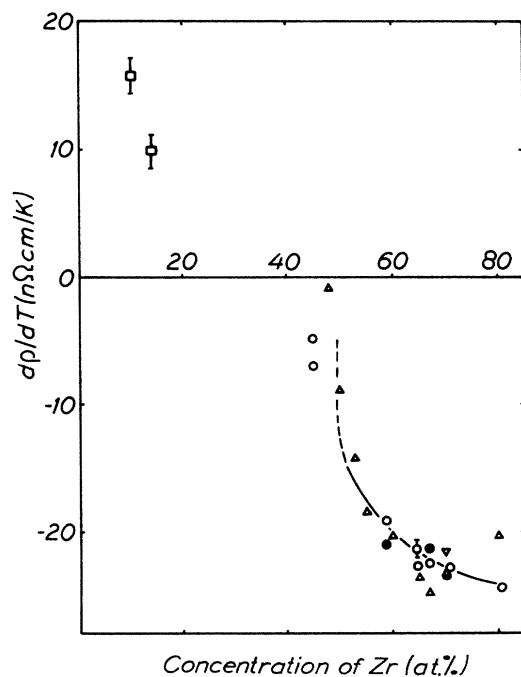


FIG. 10.  $d\rho/dT$  at 270 K versus Zr concentration.  $\Delta$ , from Ref. 29;  $\square$ , from Ref. 30;  $\nabla$ , Ref. 21;  $\delta$ , four measurements on different portions of a sample band from Ref. 4;  $\circ$ , present samples within a few months from casting;  $\bullet$ , present samples after prolonged aging. The curve is a calculation of  $d\rho/dT$  for the region  $T > 0$  based on Eqs. (1), (3), and (4).

dered alloys. This is immediately clear from Fig. 10, recalling that  $d\rho/dT$  of Cu at 270 K is about  $7 \text{ n}\Omega \text{ cm/K}$ .<sup>28</sup>

Data for samples in various conditions and from different sources have been collected in Fig. 10. The open circle with a bar represents four measurements on samples taken from different parts of a band studied in Ref. 4 and of thickness comparable to the present ones. The data  $\nabla$  was obtained from the present  $\rho$  data and the result<sup>21</sup> for  $\alpha$  for a sample, from a different source. Unfilled circles represent measurements of  $d\rho/dT$  performed within a few months from the casting of the bands. Filled circles were obtained from samples aged for at least 21 months at room temperature. The data marked  $\Delta$  were obtained from recent results<sup>29</sup> for  $\rho$  and  $\alpha$ , and the squares are estimates from a graph of  $R$  versus  $T$  for ferromagnetic samples.<sup>30</sup> The curve was calculated independently as described in Sec. III E.

The aging experiments were somewhat inconclusive since  $d\rho/dT$  changed differently for different samples. Therefore we do not know if there is an unexpected concentration dependence of aging effects or if measurement errors, including possible small changes in the positions of the potential contacts, have caused these results. The latter possibility seems more likely. Nevertheless, we can conclude that possible aging effects are, at most, small for these alloys.

The results from Ref. 29 generally agree with ours. The notable exception is the 80-at. % Zr sample. As discussed above, samples at the edge of the glass-forming range may contain crystallites and minute fractions of these can distort resistivity results.  $d\rho/dT$  for our as-quenched 80-at. % Zr sample (Fig. 3) is  $\sim -16 \text{ n}\Omega \text{ cm/K}$ , which is numerically even smaller than the result from Ref. 29. Therefore,  $|d\rho/dT|$  of this sample may be too small in Ref. 29 due to some minor crystallites.

Figure 10 shows that  $|d\rho/dT|$  decreases rapidly below 60 at. % Zr where  $T_c$  vanishes. The data suggest a change of sign of  $d\rho/dT$  close to the ferromagnetic phase boundary. Sign reversals have been observed in various transport properties such as  $d\rho/dT$ , the Hall coefficient  $R_H$ , and the thermoelectric power  $S$ , of several Zr-based glasses.<sup>31-35</sup> These phenomena are an interesting part of the study of transport properties of metal glasses. No consensus seems yet to have been reached as to their origin.  $R_H$  and  $S$  may be related but the sign reversal in  $d\rho/dT$  is probably of a different origin. E.g., in Zr-Co,  $R_H$  changes sign at about<sup>34</sup> 70 at. % Zr where  $|d\rho/dT|$  is still large. The proximity of this apparent sign reversal of  $d\rho/dT$  to the ferromagnetic phase boundary in Zr-Co may of course be accidental. On the other hand, the correlation of both decreasing Zr concentration,  $|d\rho/dT|$ , as well as  $T_c$ , is common in Zr-based glasses.

### E. Interpretation of the resistivity results

For a number of different Zr-based glassy metals the electron-phonon interaction  $\lambda$  is proportional to  $d\rho/dT$  evaluated at about 270 K.<sup>21</sup> With  $\lambda$  calculated from McMillan's formula,<sup>36</sup> and the observed  $T_c$ , and  $\mu^* = 0.13$ , one finds<sup>37</sup> for  $d\rho/dT$  in  $\text{n}\Omega \text{ cm/K}$

$$\lambda = -0.028 d\rho/dT . \quad (3)$$

A possible explanation for this observation was based on the generalized Ziman model.<sup>21</sup> Equation (3) was found to break down for Zr-Ni glasses.<sup>38</sup> Recent results, on the contrary, suggest that a similar relation holds also in this case.<sup>39</sup> For glassy Nb-Ni, Eq. (3) appears to be violated.<sup>40</sup> The reason for these different behaviors is not understood. Obviously the application of Eq. (3) to glassy metals is more problematic than for crystalline alloys and must be carefully empirically established in each case.

Quantum corrections to the resistivity may be observed in disordered metals.<sup>41,42</sup> Since disorder is not expected to depend strongly on concentration in these alloys, such a contribution would not significantly influence the concentration dependence of  $d\rho/dT$ .

For the present alloys we calculate a function  $d\rho(c)/dT$  from Eq. (3), the observed  $T_c(c)$  [Eq. (1)], and McMillan's equation

$$\lambda = \frac{1.04 + \mu^* \ln[\Theta/1.45T_c(c)]}{(1 - 0.62\mu^*) \ln[\Theta/1.45T_c(c)] - 1.04}, \quad (4)$$

with  $\mu^* = 0.13$  and  $\Theta = 200$  K independent of alloy concentration. The result is shown in Fig. 10. The solid part of the curve covers the range where  $T_c$  has been observed and the dashed part the extrapolated part of Eq. (1). This extrapolation extends to 49.7 at. % Zr where  $T_c = 0$ ,  $\lambda \approx 0.14$  from Eq. (4), and  $d\rho/dT = -5$  nΩ cm/K from Eq. (3). The observed data are fairly well described by this calculation. In particular, the agreement between calculation and experiments in the region of the rapid decrease of  $|d\rho/dT|$  close to the superconducting phase boundary suggests that  $T_c$  vanishes due to a decreasing  $\lambda$ .

It is worth noting that there is no adjustable parameter in this calculation. The value of the proportionality constant  $k$  in the relation  $\lambda = kd\rho/dT$  was obtained from other experimental results, McMillan's formula, and the mentioned assumptions about  $\mu^*$  and  $\Theta$ . The calculation is insensitive to the choice of  $\Theta$ . In principle, though, one could use  $k$  and  $\mu^*$  as two adjustable parameters to obtain a best fit to the observed  $d\rho/dT$ , but this possibility has not been explored here.<sup>43</sup> The fit in Fig. 10 also provides further evidence that Eq. (3) is useful for disordered Zr-Co alloys.

#### IV. CONCLUSIONS

Glassy Zr-Co alloys in the range 45–80 at. % Zr have been studied. Particular attention was paid to some problems with experiments on glassy metals. The influence of small crystallites on one side of the ribbons was illustrated. The cross-sectional area of the ribbons was measured

by a photographic method. The time dependence of the measured properties was found to be small.

We have obtained results for the concentration dependence of the position of the first peak in the structure factor  $k_p$ , the superconducting  $T_c$ , the resistivity and its temperature derivative, and the field and temperature dependence of the magnetic susceptibility. Several of these results such as  $k_p(c)$ ,  $T_c(c)$ ,  $\rho(c)$ , and  $\chi(c)$  confirm published data. We point out that there is apparently no discontinuity in the slope of  $k_p(c)$  and that the magnitude of the temperature derivative of the resistivity is large in most of these alloys.

In all alloys  $\chi$  is field dependent, which suggests a small fraction  $\omega$  of ferromagnetic clusters in the samples of saturation magnetization  $\sigma$ .  $\omega\sigma$  increases with decreasing temperature for each alloy and with decreasing Zr concentration at each temperature.  $\omega$  is a small fraction of the matrix, below 0.2 wt. % even at 45 at. % Zr close to the ferromagnetic boundary. For the superconducting alloys the normal-state temperature dependence of  $\chi$  is small and positive, similar to that of crystalline Zr. At 45 at. % Zr there is still no well-developed local moment. The magnitude of  $\chi$  at this composition suggests some exchange enhancement.

$d\rho/dT$  is negative and its magnitude decreases with decreasing Zr concentration and tends to zero close to the ferromagnetic phase boundary. This result is correlated with a decreasing electron-phonon interaction.

The results suggest that Co plays a rather passive role in Zr-rich glassy Zr-Co. Except for a small increasing fraction of ferromagnetic clusters, the addition of Co would seem to have mainly a diluting effect on the observed properties. Ferromagnetism appears to emerge rather abruptly by an increased polarization of the matrix through an increased interaction with the growing ferromagnetic clusters. A number of different observations suggests that there are no significant magnetic interactions depressing  $T_c$  in disordered Zr-Co alloys.

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<sup>1</sup>H. S. Chen, in *Amorphous Metallic Alloys*, edited by F. E. Luborsky (Butterworths, London, 1983), p. 169.

<sup>2</sup>Z. Altounian, J. O. Strom-Olsen, and J. L. Walter, *J. Appl. Phys.* **55**, 1566 (1984).

<sup>3</sup>P. Allia, R. Sato Turtelli, F. Vinai, and G. Rionto, *Solid State Commun.* **43**, 821 (1982).

<sup>4</sup>Ö Rapp and L. Hedman, *Phys. Rev. B* **30**, 5135 (1984).

<sup>5</sup>S. J. Poon, P. L. Dunn, R. E. Elmquist, and L. M. Smith, *Solid State Commun.* **42**, 267 (1982).

<sup>6</sup>E. Babic, Z. Marohonic, and J. Ivkov, *Solid State Commun.* **27**, 441 (1978).

<sup>7</sup>See AIP document No. PAPS-PRBMD-34-4558-19 for 19 pages describing a photographic method for accurate resistivity measurements applied to melt-spun Zr-based alloys. Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335

- East 45th Street, New York, NY 10017. The prepaid price is \$1.50 for a microfiche or \$5.00 for a photocopy. Airmail additional. Make checks payable to the American Institute of Physics.
- <sup>8</sup>Ö. Rapp, M. Flodin, Å. Östlund, and H. Fredriksson, *Physica Scr.* **25**, 804 (1982).
- <sup>9</sup>M. G. Karkut, and R. R. Hake, *Phys. Rev. B* **28**, 1396 (1983).
- <sup>10</sup>JCPDS, file No. 23-945 (Joint Committee for Powder Diffraction Standards) (unpublished), 1601 Park Lane, Swarthmore, PA 19081.
- <sup>11</sup>Z. Altounian, T. Guo-hua, and J. O. Strom-Olsen, *J. Appl. Phys.* **54**, 3111 (1983).
- <sup>12</sup>B. L. Gallagher and D. Greig, *J. Phys. F* **12**, 1721 (1982).
- <sup>13</sup>A. J. Drehman and W. L. Johnson, *Phys. Status Solidi A* **52**, 499 (1979).
- <sup>14</sup>K. H. J. Buschow, *J. Phys. F* **14**, 593 (1984).
- <sup>15</sup>Q.-R. Zhang, H. U. Krebs, and H. Freyhardt, *Physica* **126B&C**, 1313 (1984).
- <sup>16</sup>Z. Altounian and J. O. Strom-Olsen, *Phys. Rev. B* **27**, 4149 (1983).
- <sup>17</sup>L. Hedman and Ö. Rapp, *Phys. Lett.* **100A**, 251 (1984).
- <sup>18</sup>E. Babic, R. Ristic, M. Miljak, and M. G. Scott, in *Proceedings of the 4th International Conference on Rapidly Quenched Metals, Sendai, 1981*, edited by T. Masumoto and K. Suzuki (Inst. of Metals, Sendai, 1982), p. 1079.
- <sup>19</sup>E. W. Collings and J. C. Ho, *Phys. Rev. B* **4**, 349 (1971).
- <sup>20</sup>P. Oelhafen, E. Hauser, H. J. Guntherodt, and K. H. Benneman, *Phys. Rev. Lett.* **43**, 1134 (1979).
- <sup>21</sup>Ö. Rapp, J. Jäckle, and K. Froböse, *J. Phys. F* **11**, 2359 (1981).
- <sup>22</sup>R. H. Fairlie, W. H. Temmerman, and B. L. Gyorffy, *J. Phys. F* **12**, 1641 (1982).
- <sup>23</sup>F. R. Szofran, G. R. Gruzalski, J. W. Weymouth, and D. J. Sellmeyer, *Phys. Rev. B* **14**, 2160 (1976).
- <sup>24</sup>N. Heiman and N. Kazama, *Phys. Rev. B* **17**, 2215 (1978).
- <sup>25</sup>S. J. Poon, *Phys. Rev. B* **31**, 7442 (1985).
- <sup>26</sup>J. Destrey, M. El Amrani, and R. W. Cochrane, *Phys. Rev. B* **31**, 2499 (1985).
- <sup>27</sup>Ö. Rapp, M. Flodin, and L. Hedman, in *Superconductivity in d- and f-band Metals—1982*, edited by W. Buckel and W. Weber (Kernforschungszentrum, Karlsruhe, 1982), p. 351.
- <sup>28</sup>G. T. Meaden, *Electrical Resistance of Metals* (Heywood, London, 1965), p. 15.
- <sup>29</sup>Z. Altounian, R. J. Shank, and J. O. Strom-Olsen, *J. Appl. Phys.* **58**, 1192 (1985).
- <sup>30</sup>Y. Obi, L. C. Wang, R. Motsay, and D. G. Onn, *J. Appl. Phys.* **53**, 2304 (1982).
- <sup>31</sup>Z. Altounian, C. L. Foiles, W. B. Muir, and J. O. Strom-Olsen, *Phys. Rev. B* **27**, 1955 (1983).
- <sup>32</sup>R. W. Cochrane, J. Destrey, and M. Trudeau, *Phys. Rev. B* **27**, 5955 (1983).
- <sup>33</sup>B. L. Gallagher, D. Greig, M. A. Howson, and A. A. M. Croxon, *J. Phys. F* **13**, 119 (1983).
- <sup>34</sup>J. Ivkov, E. Babic, and R. L. Jacobs, *J. Phys. F* **14**, L53 (1984).
- <sup>35</sup>D. Pavuna, *Solid State Commun.* **54**, 771 (1985).
- <sup>36</sup>W. L. McMillan, *Phys. Rev.* **167**, 331 (1968).
- <sup>37</sup> $k = -0.028 \text{ K/n}\Omega \text{ cm}$  is obtained by  $-0.025(200/176)$ , where  $-0.025 \text{ K/n}\Omega \text{ cm}$  was obtained previously (Ref. 21) from  $\alpha$  and  $T_c$  and a rough average value of  $\rho = 200 \mu\Omega \text{ cm}$ .  $176 \mu\Omega \text{ cm}$  is an average value of  $\rho$  from Fig. 9.
- <sup>38</sup>Z. Altounian, R. Harris, and J. O. Strom-Olsen, *J. Non-Cryst. Solids* **61& 62**, 1185 (1984).
- <sup>39</sup>A. Inoue, K. Matsuzaki, H. S. Chen, and T. Masumoto, *J. Mater. Sci.* **21**, 1258 (1986).
- <sup>40</sup>P. Lindqvist and Ö. Rapp, 5th European Physical Society Meeting on Condensed Matter Physics, Berlin (1985) (unpublished).
- <sup>41</sup>E. Abrahams, P. W. Anderson, D. C. Licciardello, and T. V. Ramakrishnan, *Phys. Rev. Lett.* **42**, 673 (1979).
- <sup>42</sup>B. L. Altshuler and A. G. Aronov, *Zh. Eksp. Teor. Fiz.* **77**, 2028 (1979) [*Sov. Phys.—JETP* **50**, 968 (1979)].
- <sup>43</sup>Such an analysis [Ö. Rapp, *Phys. Rev. B* **34**, 2878 (1986)] recently suggested  $\mu^* = 0.15$  and  $k = -0.0292 \text{ K/n}\Omega \text{ cm}$ . On the scale of Fig. 10 this has a small influence on the calculated curve.