New Resistance Anomaly in the Superconducting Fluctuation Region of Disordered Cu-Zr Alloys with Dilute Magnetic Impurities

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In disordered superconducting Cu-Zr alloys with dilute magnetic impurities, we have observed a new type of resistance anomaly which gives rise to strongly increased scattering of conduction electrons in a narrow temperature range above T_c and appears to be due to interaction between superconducting fluctuations and spin. For a given level of impurities this phenomenon is peaked around $Cu_{50}Zr_{50}$, but is observable from 35 to 60 at.% Zr. When the Cr impurity concentration is varied in $Cu_{50}Zr_{50}$, a resistance peak can be observed for 100–600 ppm Cr with a maximum peak height of about 6% of the measured resistance. The effect is destroyed by a magnetic field of some tenths of a tesla.

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A new type of resistance anomaly has been observed in disordered Zr-Cu alloys. Samples with Zr concentration in the range 35–60 at.% which contain dilute magnetic impurities display, with increasing temperature, a maximum and a minimum in the electrical resistance in a narrow temperature range above the superconducting T_c, before the usual superconducting fluctuation region with a slowly increasing resistance. In these samples, T_c varies from about 0.1 to 1.6 K and the peak follows T_c over this range. The amplitude is largest for $Cu_{50}Zr_{50}$, where it can reach several percent above the minimum resistivity. This is comparable to the resistivity change from room temperature to liquid-helium temperature, which implies a dramatic change in the electron-scattering rate. A magnetic field of a few tenths of a tesla quenches the peak.

The samples are metallic glasses prepared by arc-melting appropriate amounts of Cu and Zr in argon atmosphere and melt-spinning onto a revolving copper wheel in an inert atmosphere. Three sources of elements were used, designated I–III. For source I, the starting materials were at least 99.99 wt% pure. Only one sample from this source was studied, $Cu_{50}Zr_{50}$(I). Details about preparation and properties have been given previously.[1,2] A series of samples, II, was prepared with elements of 99.9 wt% nominal purity. These samples were characterized recently.[3] In particular, T_c was found to agree reasonably with the bulk of published data, well within 100 mK, which is about the usual difference between samples from different laboratories.[4] Thus, there is no evidence of a depression of T_c from magnetic interactions. Samples denoted III were prepared by us[5] from 99.98 wt% nominally pure Zr and 99.9999 wt% Cu.

The temperature dependence of the electrical resistance in the region of the anomaly is shown for two $Cu_{50}Zr_{50}$ samples in Fig. 1. On the scale shown a peak is prominent in the sample from source II and absent in that from source I. The full superconducting transitions are shown in the inset and illustrate that the peak may not be observed unless measurements are densely made above T_c.

The magnitude of the peak can be measured as the ratio of the peak height ΔR and the minimum resistance R. This quantity is shown in Fig. 2 as a function of Zr concentration for a series of samples from source II. It can be seen that the peak maximum occurs around 50 at.% Zr, with a bell-shaped concentration dependence, and a fairly symmetrically decreasing amplitude for lower and higher Zr concentrations. The width of the peak at half maximum shows a similar concentration dependence with a maximum of 80 mK for $Cu_{50}Zr_{50}$ and about half that value for $Cu_{57}Zr_{43}$ and $Cu_{40}Zr_{60}$. The transition temperature, taken as resistive midpoint, is also shown in Fig. 2. The peak occurs at about 20–60 mK above T_c. The peak follows T_c over more than an order of magnitude, which suggests that superconducting fluctuations

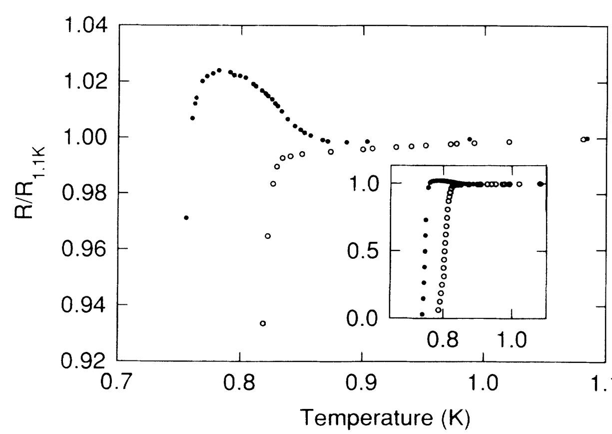

FIG. 1. The electrical resistance in the temperature region above T_c for two $Cu_{50}Zr_{50}$ samples, normalized to the values at 1.1 K. ○, elements from source I; ●, elements from source II. Inset: The full resistive transitions for both samples. The analyses of these alloys are given by samples No. 3 and No. 4 in Table I.

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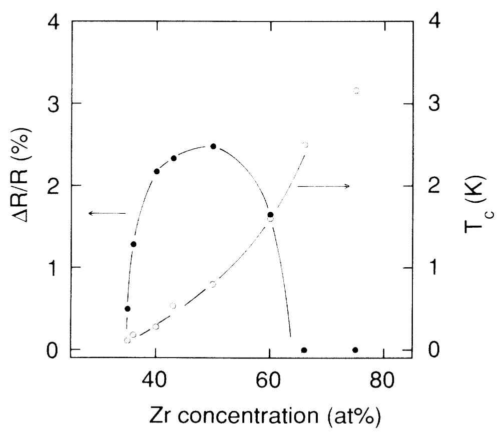

FIG. 2. ●, normalized peak height vs Zr concentration for a series of Cu-Zr(II) samples. ○, resistive midpoint of the superconducting transitions. The peak maximum is 20–60 mK above T_c for all samples in the range 35–60 at.% Zr. Three of these samples have been analyzed in Table I (samples Nos. 1–3).

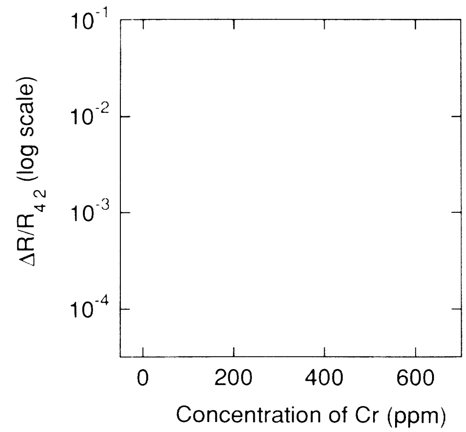

FIG. 3. Normalized peak height on a logarithmic scale vs Cr dopant concentration. The host alloy is $Cu_{50}Zr_{50}$ with elements from source III. The arrow marks the absence of a peak at the estimated level of experimental sensitivity. The analyses of the four Cr-doped alloys are given by samples Nos. 7–10 in Table I.

are involved in the interaction. The absence of an observable peak at 66 at.% Zr implies in our experiment that it is smaller than about 0.01%.

Several samples of composition $Cu_{50}Zr_{50}$ were prepared with elements from source III and small amounts of magnetic impurities. Results for Cr-doped samples are shown in Fig. 3. T_c was within 0.8 K ± 10% for all samples in the figure. The peak magnitude increases with Cr doping up to a very large value of 6% at about 300 ppm Cr and then decreases for larger Cr concentrations. At 600 ppm the peak is barely observable with a magnitude of 2.8×10^{-4} and a full width at half maximum of 7 mK. With Mn impurities instead of Cr, T_c was depressed to 420 mK already at 11 ppm and no peak was observed. With nominal Fe impurities of 700 and 1400 ppm (as analyzed, 259 and 1650 ppm, respectively), T_c was normal for the lower concentration and depressed to 460 mK for the higher one, and the peak was absent in both cases.

Several samples were analyzed by atom absorption spectroscopy to determine impurity levels. In the initial phases of this work two different facilities were used[6] to make sure that consistent results were obtained. The results are shown in Table I.

First we investigated if the disappearance of the peak in the region 60–65 at.% Zr was due to any (accidental) difference in impurity concentration. In each of the analyses (A) and (N) there are fairly small differences between samples Nos. 1 and 2. Except for some differences in Cr concentration, analyses (A) and (N) are also in fair agreement with each other. Therefore, we conclude that a certain level of impurities is not a sufficient condition for observation of the peak and that the concentration dependence of the constituent elements must also be considered.

TABLE I. Results of analyses of several samples. The roman letter after the sample denotes source elements used. P (or NP) after the sample means that a peak (or no peak) was observed in the resistivity. (A) and (N) denote two companies which performed the analyses. Samples 1 and 2 were also analyzed by (A) for impurities of Zn, V, Co, Ni, and Ti with similar results for both samples of 5, <20, <3, 15, and 140 ppm by weight, respectively.

Sample No.	Analysis	Impurity (ppm by weight) Fe	Cr	Mn
1, $Cu_{40}Zr_{60}$(II) P	(A)	620	57	3.4
	(N)	576	19	1
2, $Cu_{34}Zr_{66}$(II) NP	(A)	690	59	4.5
	(N)	520	19	2
3, $Cu_{50}Zr_{50}$(II) P	(N)	460	23	1
4, $Cu_{50}Zr_{50}$(I) NP	(N)	Probably <50 [a]	1	1
5, $Cu_{50}Zr_{50}$(III) NP +20 ppm Mn	(N)	63	14	11
6, $Cu_{50}Zr_{50}$(III) NP +700 ppm Fe	(N)	259	14	2
7, $Cu_{50}Zr_{50}$(III) P +140 ppm Cr	(N)	40	148	1.7
8, $Cu_{50}Zr_{50}$(III) P +323 ppm Cr	(N)	44	319	1.9
9, $Cu_{50}Zr_{50}$(III) P +501 ppm Cr	(N)	21	515	1
10, $Cu_{50}Zr_{50}$(III) P +602 ppm Cr	(N)	21	597	1
11, Zr(III) (99.98 wt%)	(N)	119	21	2

[a]See Ref. 7.

Samples Nos. 3, 4, and 6 in Table I have similar Zr concentration and T_c's. It can be seen that a peak is absent at low levels of magnetic impurity concentration (Nos. 4 and 6) and observable at somewhat larger impurity concentration (No. 3). The analyses of samples Nos. 7–10 confirm that the result in Fig. 3 is due to Cr doping. We have indications that Fe also may cause a peak and we cannot rule out Mn. In particular, the peak magnitude is much smaller for sample No. 7 than for sample No. 3 (the maximum in Fig. 2), albeit the former contains more Cr and, from Fig. 3, is in a concentration range where the peak increases with Cr content. Therefore the larger Fe concentration in sample No. 3 apparently contributes to the resistivity peak.

In all our experiments we see no peak samples where the magnetic impurity level is sufficient to cause strong magnetic interactions, leading to a depression of T_c. From this we can give tentative upper limits of the impurity concentrations, below which a peak may be observable. For Fe this limit is about 1600 ppm and for Mn about 10 ppm, while, as mentioned, for Cr the peak disappears at about 600 ppm.

It is interesting to note the strong effect of Mn impurities. The depression of T_c for 11 ppm Mn corresponds to dT/dc of -400 K/at.%. There is little work on magnetic impurities in metallic glasses. However, this rate is comparable to the effect of Mn in elemental superconductors such as[8] Cd or[9] Zn.

Some samples were investigated in a magnetic field. It was found that the peak is destroyed by a comparatively weak magnetic field. An example is shown in Fig. 4 for $Cu_{57}Zr_{43}$(II). ΔR has decreased to half its zero-field value at about 0.1 T. The peak in Fig. 4 moves towards lower temperatures at -0.27 K/T, more slowly than the decrease of T_c in magnetic field of -0.36 K/T (corresponding[3] to dB_{c2}/dT close to T_c of -2.7 T/K). The strong negative magnetoresistance is further evidence that the resistance anomaly is due to the interaction between conduction electrons and a dilute magnetic spin.

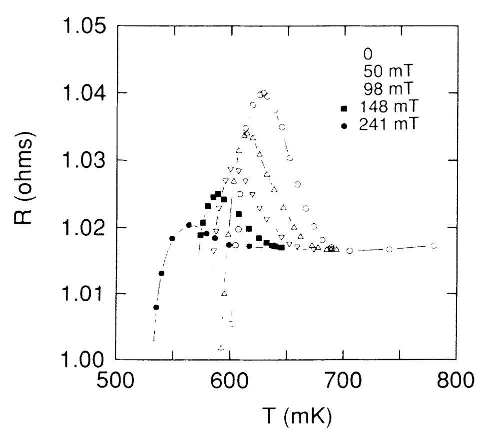

FIG. 4. The resistance above T_c for $Cu_{57}Zr_{43}$(II) in different magnetic fields.

There are few reports in the literature that show the superconducting transition on a scale that allows for comparison with the present results. An exception is Fig. 3 of Ref. 10 where it is clearly seen that a peak is absent in both $Cu_{40}Zr_{60}$ as well as in $Cu_{35}Zr_{65}$. In that investigation 99.98% pure Zr and 99.999% pure Cu were used and the absence of a peak is thus consistent with our results. The magnetic properties of Fe in glassy $Cu_{60}Zr_{40}$ have been investigated. In one report[11] there was a temperature dependence of the magnetic susceptibility χ, characteristic for the development of a moment, already at the lowest concentration studied of 1 at.% Fe. In another report,[12] Fe was still nonmagnetic when 5 at.% replaced Zr, with a temperature-independent χ, and a superconducting T_c of 0.11 K in agreement with our result for 35 at.% Zr. The reason for such discrepancies is not understood. It was pointed out[12] that the Fe magnetic moment seems to be extremely sensitive to its local environment and that differences in chemical short-range order between differently prepared samples may be of importance. Furthermore, internal oxidation and control of 3D impurities in Cu are frequently occurring problems.[13,14]

The role of disorder for the observation of a resistance peak is not known. We note, however, that the short electronic mean-free path in metallic glasses is a necessary condition for an extended region of superconducting fluctuations, and in our observations, the peak always occurs in the lower temperature range of the fluctuation region. Furthermore, it is interesting to note the possible relation to weak localization phenomena which are frequently observed in metallic glasses. In recent experiments on disordered Zr-Fe alloys, enhanced magnetic interactions could be induced by increasing disorder, as predicted by localization theories, and these changes were accompanied by the development of a resistance peak in the superconducting fluctuation region similar to those observed presently.[15]

Summarizing, we have found that dilute magnetic impurities in disordered Cu-Zr alloys under certain conditions can give rise to strongly enhanced electron scattering in a narrow temperature region above the superconducting T_c. This phenomenon is quenched by a weak magnetic field. From the strong Zr concentration dependence it appears that there is a resonance between impurity level and Fermi energy. The peak follows T_c over more than an order of magnitude, from which we infer that interactions between superconducting fluctuations and spins are important. The observation of this peak requires, in addition to conditions on the Zr content, that the impurity concentration is within restricted limits. For Cr, the relevant concentration range is about 100–600 ppm. For Fe our results suggest tentatively that the upper limit is below 1600 ppm, while for Mn, if it can produce a peak, the concentration should be below

10 ppm.

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[6](A): Analytica AB, Täby, Sweden; (N): Nordisk Analys Service, Hällefors, Sweden.

[7]The analysis of (N) originally gave 900 ppm Fe $\pm$ 20%. Only 7 mg of the sample was available, however, in contrast to >100 mg for all the other analyses. It appears that this analysis was in error due to accidental Fe contamination. The Zr used for this sample was the same as that of Ref. 1, and it was stated there to be of at least 99.99 wt%, i.e., of better quality than our best Zr sample No. 11 in Table I. Therefore a smaller Fe concentration than for samples Nos. 5 and 7–10 is expected.

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