Variation of disorder in superconducting glassy metals

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The impact of increased disorder on superconducting T_c and H_{c2} of amorphous Zr-Cu and Hf-Co has been studied. In these highly disordered materials, disorder was incrementally increased by irradiation with fast neutrons of low intensity. Increased resistivity, increased magnitude of $d\rho/dT$, and smearing of the x-ray-diffraction patterns, confirm the increased disorder. The irradiation effects on ρ and T_c depend on the amorphous system, but when the T_c depression is plotted vs resistivity increase, all data fall on the same curve. T_c data are well described by the Fukuyama-Ebisawa-Maekawa theory. The normalized critical field $h^*(t)$ increases at low temperatures with increasing disorder. This cannot be explained by present theories.

I. INTRODUCTION

The electron motion in high-resistivity amorphous metals is diffusive, with a large elastic scattering rate $1/\tau$. Therefore, quantum corrections are expected at low temperatures, when the inelastic scattering time $\tau_i \gg \tau$. These effects have been amply demonstrated in the transport properties of disordered materials. Superconducting properties are also affected by strong disorder, although, as yet, no unified picture has been obtained. However, it is by now experimentally well established that disorder depresses the superconducting T_c.[1–5] This is in contrast to the old view[6] that superconductivity is unaffected by weak disorder. Theoretically several disorder-related effects, such as weak localization and electron-electron interaction, have been found which reduce T_c.[7–10]

As for the upper critical field, H_{c2}, of amorphous metals, there is no agreement on the influence of disorder. Several experimental results suggest an anomalous enhancement of the normalized critical field at low temperatures,[11–15] above values consistent with the standard Werthamer-Helfand-Hohenberg (WHH) theory.[16] However, other results show good agreement with WHH theory.[17–19] The enhancement may occur from delocalization effects in magnetic field on the Coulomb pseudopotential μ^*.[20] On the other hand, according to the Fukuyama-Ebisawa-Maekawa (FEM) theory,[8] weak localization effects on H_{c2} are so small that they are almost indistinguishable from WHH theory.[21] In addition, it has been shown that inhomogeneities, even on a length scale of below 100 Å, can cause enhancement of the critical field.[22,23]

There are difficulties to perform controlled experiments to test predictions of disorder effects on superconductivity. When structural disorder is changed in a crystalline material, e.g., band structure will change and superconducting properties will be affected by changes in the density of state $N(0)$. In this case the variation of T_c can have either sign. In two-dimensional (2D) films the variation of film thickness may lead to varying dimensionality affecting the interpretation. If disorder is varied by means of compositional variation, changes in a number of other parameters are expected in addition to varying disorder.

We have studied the effect of increased disorder on superconductivity by irradiation with fast neutrons of 3D amorphous metal ribbons. In this way we start with an already strongly disordered material, and only an incremental increase of disorder can be achieved by the irradiation. However, we can control the varying disorder and monitor changes by the changing resistivity ρ.

In the present paper we study resistive properties, x-ray diffraction, the superconducting T_c, and the upper critical field $H_{c2}(T)$, and the effect of neutron irradiation on these properties. We have chosen amorphous ribbons of $Zr_{50}Cu_{50}$ and $Zr_{60}Cu_{40}$. In addition some results for $Hf_{67}Co_{33}$ are also included. These alloy systems are suitable since the whole $H_{c2}(T)$ curves can be studied at moderate magnetic field strengths in a dilution refrigerator. It is important to reach the region $T/T_c \leq 0.1$ in these experiments, since deviations in the similar shape of critical field curves for different amorphous alloys are most clearly displayed in that region. In fact, the confusion about the upper critical field of amorphous alloys is to some extent due to the limited temperature ranges sometimes used. In addition these ribbons have appropriate mechanical properties for an experiment that lasts over a long period of time and requires several mountings and dismountings of electrical contacts. Finally, many amorphous systems are not suitable for neutron irradiation, i.e., although nuclear reactions are minimized, activation of slowly decaying radioactive nuclei inhibits convenient handling of the samples. This is not the case for Zr-Cu and Hf-Co.

A short paper on some T_c results of Zr-Cu samples has been published previously.[4] The present paper is organized as follows: In Sec. II, sample preparation, neutron-irradiation conditions, and measurement techniques are described. In Sec. III we describe special precautions taken to rule out changes in properties due to thermal relaxation of the structure and to control possible effects of surface oxidation. In Sec. IV evidence for increased dis-

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order by neutron irradiation is presented. This comprises results for $\Delta\rho/\rho$, $\rho(T)$ and x-ray results. Section V contains results for T_c and H_{c2}, which are analyzed and discussed in Sec. VI.

II. EXPERIMENTAL METHODS

A. Sample preparation and neutron irradiation conditions

Amorphous ribbons of $Zr_{50}Cu_{50}$, $Zr_{60}Cu_{40}$, and $Hf_{67}Co_{33}$ were prepared by arc-melting followed by melt spinning. All samples were checked by x-ray diffraction from both sides of the samples to be amorphous. Further details about preparation techniques and properties have been given previously.[19,24]

Structural disorder was increased by irradiation with fast neutrons ($E_n > 1$ MeV) of low intensity. Fast neutrons were used since they penetrate the samples and are expected to give a homogeneously distributed radiation damage. To minimize relaxation effects, the sample temperature must not increase during irradiation. Therefore a low-power reactor is appropriate. Sample pieces were placed in a container in an empty fuel element position at the reactor core edge, which was surrounded on all sides by water of a temperature less than 25 °C. The sample container was covered with Cd to avoid activation from thermal neutrons. In this way the samples could be cooled without contact with water. This prevented accumulation of hydrogen in the samples, which may occur from radiation-induced reactions in Zr-H_2O systems, particularly at elevated temperatures. On the other hand the cross section for (n,p) reactions in Zr is negligible at the neutron energies present in our reactor.[25]

Two neutron exposures were performed on the same pieces of a sample. The first dose was 0.75×10^{18} n/cm^2 and the second was 1.4×10^{18} n/cm^2. Thus the total dose was 2.2×10^{18} n/cm^2. The first exposure was performed in air. Before the second dose, the sample container was filled with He gas and sealed. The fast neutron flux at the sample position was about 1.5×10^{11} n/cm^2 s. Including time for intervening measurements and reactor maintenance the experiment lasted 1.5 years.

Nuclear reactions producing impurities are likely negligible. The large neutron absorption resonances in Hf between 1 and 10 eV will result in an initial production of Ta nuclei. However, the concentration of these according to a rough calculation is smaller than 1 ppm. For Co a corresponding estimate results in 0.1 ppm of Ni. For the other samples all reaction products will have a concentration of below 0.01 ppm.

B. Measurements

The increase in disorder was measured by the resistivity. Due to irregularities in sample geometry, resistivity measurements on small amounts of a metallic glass sample are accurate only to within 10%. This is not sufficient for our purpose. Instead we measured the relative resistivity change, by measuring the resistance over a well-defined sample length, before and after each irradiation. In repeated measurements the accuracy was about 0.2%.

X-ray analysis with Ni-filtered Cu $K\alpha$ radiation, with a monochromator in the diffracted beam, was made before and after each neutron exposure. To get good diffraction patterns from the small amounts of irradiated sample, data were taken in steps of $\Delta\theta=0.125°$ with exposure times of about 20 min for each step.

Stable four-pole electrical contacts were obtained by cutting two tounges in each end of the samples to which wires were tied and fixed with silver paint and epoxy. The temperature dependence of the resistivity from 4.2 K to 300 K was measured with slowly drifting temperature in a ^{4}He cryostat. The upper critical field was measured resistively in a dilution refrigerator equipped with a 7 T superconducting solenoid. The magnetic field was oriented parallel to the sample current. The temperature was obtained from a calibrated carbon resistor. $H_{c2}(T)$ was defined as the magnetic field at the 50% value of the resistance at 4.2 K and was measured by slowly sweeping the temperature in a fixed field. 10% and 90% resistance values were also taken to determine the magnetic field transition widths ΔH_{c2}. These measurements were made both by sweeping the temperature in a fixed field and by sweeping the field at a fixed temperature. The two methods gave identical results.

III. EXPERIMENTAL CONSIDERATIONS

A. Negligible relaxation effects

Amorphous samples are metastable and relaxation effects, which may occur during the long exposure time in the reactor must be carefully controlled. By cooling the sample can in the reactor we are assured that the sample temperature was not inappropriately increased. In a previous experiment on aging effects in similar metallic glasses, we found no observable relaxation effect after 36 months in air at room temperature.[26]

In addition we made a separate investigation of the effect of thermal relaxation of the present Zr-Cu samples. Two pieces of $Zr_{60}Cu_{40}$ were heat treated in 470 K for 1 h (sample A) and 2.5 h (sample B), respectively. T_c, the transition width, ΔT_c, H_{c2}, and the residual resistivity ratio, $R=\rho_{4.2\text{ K}}/\rho_{300\text{ K}}$, were measured before and after the thermal treatment. By comparison with irradiated samples we can distinguish possible relaxation effects.

For both heat-treated samples T_c decreased about 0.15 K. The transition width decreased from 47 mK to 10 mK for sample A, which indicates some thermal relaxation and increased homogeneity. For sample B, annealed for 2.5 h, ΔT_c increased from 40 mK to 210 mK. This might be a sign of incipient phase separation. The transition width in magnetic field was independent of field strength for both samples. The R value decreased from 1.0472 to 1.0459 for sample A, and from 1.0469 to 1.0441 for sample B. The result of this experiment is in agreement with reported annealing experiments,[27,28] or long time relaxation experiments,[29] which all show a less negative $d\rho/dT$ with increasing relaxation.

As for the critical field measurement no significant change could be observed in the reduced field $h^*(t)=-H_{c2}/[T_c dH_{c2}/dT]$ after relaxation. Laborde

TABLE I. Some results for Zr-Cu and Hf-Co. $\Delta\rho/\rho$ is the observed resistivity increase and $\Delta\rho_{ox}/\rho$ is a rough estimate of the maximum error due to surface oxidation, discussed in the text. ΔT_c is the width of the superconducting transition.

Sample	Dose (10^{18} n/cm^2)	$\frac{\Delta\rho}{\rho}$ (%)	$\frac{\Delta\rho_{ox}}{\rho}$ (%)	$\frac{\rho_{4.2\,K}}{\rho_{300\,K}}-1$ (%)	ΔT_c (mK)
$Zr_{50}Cu_{50}$	0.0			2.48	12.5
	0.75	9.8	4.0	4.07	41.7
	2.2	23.2	8.7	5.13	28.8
$Zr_{60}Cu_{40}$	0.0			4.75	31.8
	0.75	9.3	2.2	6.19	141
	2.2	23.5	2.9	7.97	151
$Hf_{67}Co_{33}$	0.0			5.55	16
	1.4	0.73	0.0	5.23	23

et al. measured H_{c2} close to T_c before and after annealing,[27] and found no significant change in shape. In another annealing experiment[30] $h^*(t)$ increased after heat treatment due to phase separation.

These R results for relaxed samples are opposite to the R results for irradiated samples shown in Table I and discussed in Sec. IV. Furthermore, for irradiated samples there are no such dramatic changes in ΔT_c in either direction, as observed in the relaxation experiments. We conclude that thermal relaxation effects seem negligible in the irradiated samples.

B. Surface oxidation effects

Surface oxidation could not be avoided during the irradiation. We estimated the degree of oxidation by measuring the mass change due to oxygen bound to the surface.

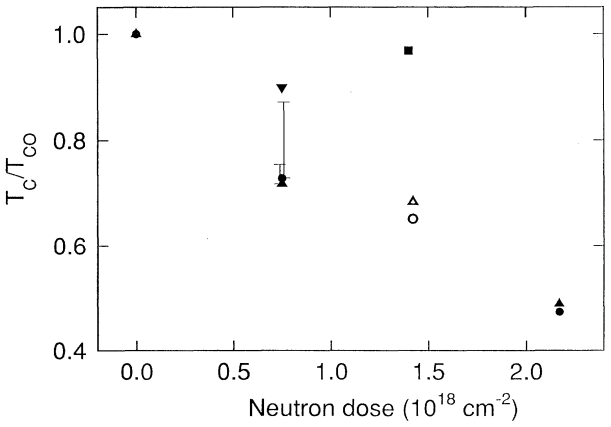

FIG. 1. Relative T_c reduction vs neutron dose. ●: $Zr_{50}Cu_{50}$, ▲: $Zr_{60}Cu_{40}$, ▼: $Zr_{75}Fe_{25}$, ■: $Hf_{67}Co_{33}$. Unfilled symbols show the T_c reduction after the second irradiation relative to the T_c values after the first neutron dose. The error bars are overestimates of possible surface oxidation effects (see text).

TABLE II. X-ray results. k_p is the scattering vector at the first peak in the structure factor and Δk_p is the full width at half maximum of this peak.

Sample	Dose (10^{18} n/cm^2)	k_p (nm^{-1})	Δk_p (nm^{-1})
$Zr_{50}Cu_{50}$	0.0	27.09±0.03	4.34
	2.2	26.96±0.03	4.98
$Zr_{60}Cu_{40}$	0.0	26.39±0.03	3.91
	2.2	26.25±0.03	4.48

The mass increase was typically of the order 0.3–0.4 mg, which corresponds to about 1% of the total sample mass. The precision of the measurement was better than 0.05 mg. Such an oxide layer gives an error to the measurements. We obtained rough overestimates of these errors from the following calculations.

Assuming that ZrO_2 was formed selectively at the surface,[31] the decrease of the metallic part of the sample cross section could be calculated from the measured mass increase. The results of these calculations are shown in Table I.

If oxidation is selective there is a risk for compositional changes in the sample. These changes would be negligible in ρ, but could affect, e.g., T_c, which decreases with decreasing Zr concentration. With selective Zr oxidation, the part of the T_c depression, shown by error bars in Fig. 1 below, could be due to Zr depletion of the matrix. Similar results were obtained for the larger irradiation dose.

Two observations lead to the conclusion that these errors are gross overestimates of the real effect. First, the structure factor is quite sensitive to sample composition.[32] A decrease in Zr concentration, corresponding to the calculation above, would shift the position of the first peak in the structure factor towards *higher* values of k_p by 0.1–0.3 nm^{-1} for different samples. This is not observed (Table II). Furthermore, the consistent behavior of the results for the depression of T_c for several different alloys, with different oxidation conditions, which will be discussed below, also suggests that the errors due to oxidation are much smaller than estimated above.

For $Zr_{50}Cu_{50}$ all measurements were performed both with the oxide layer present and with the oxide layer carefully removed. As expected the results were identical.

IV. EVIDENCE FOR INCREASED DISORDER

It can be seen in Table I that the resistivity increases with irradiation for all samples. This is a strong sign of increased disorder. In each of the neutron exposures, the resistivity change is almost identical for both Zr-Cu samples, while only a small increase of the resistivity is observed for Hf-Co. Oxidation effects, estimated as above, are negligible for the Hf-Co sample and we believe that this small resistivity increase is significant.

These changes can be compared with recent results[33]

for neutron-irradiated $Zr_{75}Fe_{25}$. After a dose of 0.75×10^{18} n/cm^2 the resistivity had increased by $4\pm2\%$. In an experiment[34] on Mo-Ru-B irradiated with 10^{19} n/cm^2 accumulated in 66 h, no resistivity change could be observed within the measurement accuracy, which was $\pm10\%$.

A further observation is that $d\rho/dT$ for Zr-Cu samples becomes more negative with increasing irradiation for all samples. Results for the resistivity ratios are shown in Table I.[35] For Hf-Co on the other hand, a small decrease of R is observed after irradiation. This result is not understood. All samples were handled in a similar way but small differences in strain from the mounting of contacts and sample cannot be excluded and could affect the temperature dependence of the resistivity. However, in our experience, variations in $\rho_{4.2\ K}/\rho_{300\ K}$ between measurements on one sample with different contact arrangements are usually within 0.002. The presently observed change of 0.0032 is somewhat larger. We note from Table I that the observed variations in R values from neutron irradiation of Zr-Cu samples are much larger than this effect. The measurements of the resistivity increase induced by neutron irradiation in contrast were made at constant temperature under edges gently pressed into the sample surface and do not contain this possible source of error.

The negative slope in $\rho(T)$ is related to disorder. According to the well-known Mooij correlation[36] the slope becomes negative above a critical resistivity of $\rho_c\approx150$ $\mu\Omega$ cm. In the light of more available data[37] this universal critical resistivity has been questioned, but there is still agreement on a system-dependent ρ_c. However, there is no unified picture of how to explain the temperature dependence of ρ in amorphous metals. Attempted explanations are based on, e.g., the extended Ziman theory or quantum corrections due to the short mean free path.

The connection between a more negative slope and increased disorder has support in several experiments. Crystalline $LuRh_4B_4$ was irradiated by α-particles.[38] Initially $d\rho/dT$ was positive, but with irradiation the slope first decreased and then changed sign. In an experiment on amorphous $Zr_{67}Ni_{33}$, disorder was increased by substituting extra scattering centers of hydrogen into the alloy.[39] With 12.3 at. % of H, R had increased from 1.035 to 1.061. In $Zr_{75}Fe_{25}$ the resistivity ratio increased from 1.025 to 1.055 by neutron irradiation with 0.75×10^{18} n/cm^2.[33,40]

X-ray investigations were made for the Zr-Cu samples. The results show that the amorphous structure remains after irradiation. The position and half width of the first peak in the structure factor before irradiation and after full dose, are given in Table II. For both samples the half width of the first peak is about 15% larger after irradiation. Such a smearing of the spatial repetition frequency is expected when disorder is increased. The position of the first peak is slightly shifted towards smaller values of the scattering vector k_p. This is probably related to a small, irradiation-induced volume increase. In the Mo-Ru-B experiment,[34] Δk_p increased by 7% due to irradiation. Garoche *et al.*[41] found a 4% decrease of Δk_p, after full thermal relaxation in amorphous $Zr_{54}Cu_{46}$.

We thus find that the electrical resistivity, the resistivity ratio, and x-ray data for the Zr-Cu samples all support that increased disorder has been produced by neutron irradiation. For Hf-Co this conclusion is supported by the measured resistivity increase only. On the other hand, these measurements are more accurate than for Zr-Cu.

V. RESULTS FOR T_c AND H_{c2}

Figure 1 shows the relative change of T_c as a function of neutron dose for all samples. A datum for $Zr_{75}Fe_{25}$ from Ref. 33 has also been included. It can be seen that T_c is depressed by neutron irradiation for all samples. The depression rates are system dependent, with the strongest effect in Zr-Cu alloys and only a weak effect in Hf-Co. This conclusion is not affected by including the maximum error in T_c from possible Zr depletion by selective oxidation, as discussed above and illustrated by the error bars for Zr-Cu samples at one irradiation dose.

The transition widths in zero field, ΔT_c, taken as the temperature interval where the resistance changes from 10% to 90% of the normal-state value, were given in Table I. With one exception ΔT_c increases slightly with irradiation. $\Delta T_c/T_c$ is within 10% except for $Zr_{60}Cu_{40}$, where the strong increase of ΔT_c with irradiation may suggest inhomogeneities in the sample. However, the results for ΔH_{c2} discussed below do not suggest this interpretation.

The upper critical field of nonirradiated and irradiated Zr-Cu samples are shown in Fig. 2. Before irradiation the magnetic field transition widths ΔH_{c2} were constant or weakly increasing with increasing field.[19] For the irradiated samples the transition widths in magnetic field were constant or even decreasing with increasing field. Figure 3 shows the transition widths after the first neutron exposure. The primary data of Fig. 2 display only small differences to the eye except for the depression of T_c. These results will be discussed and analyzed in Sec. VI.

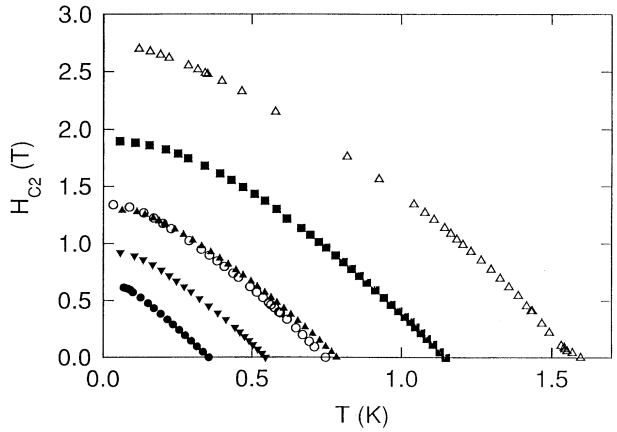

FIG. 2. H_{c2} of nonirradiated and irradiated amorphous Zr-Cu samples. $Zr_{60}Cu_{40}$: △ nonirradiated, ■ 0.75×10^{18} n/cm^2, ▲ 2.2×10^{18} n/cm^2. $Zr_{50}Cu_{50}$: ○ nonirradiated, ▼ 0.75×10^{18} n/cm^2, ● 2.2×10^{18} n/cm^2.

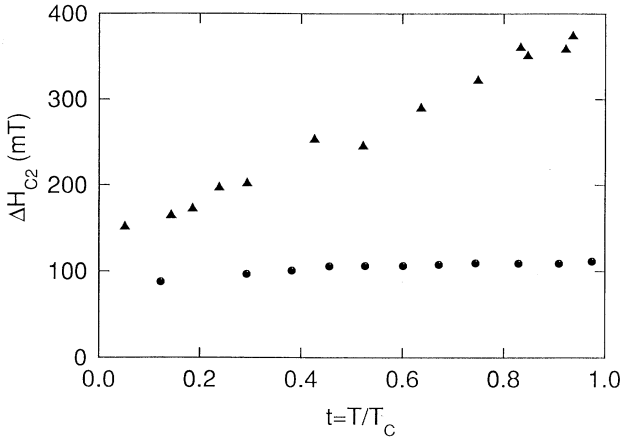

FIG. 3. Transition widths in magnetic field, taken as 10% to 90% of the normal-state resistivity, after the first neutron dose. ●: $Zr_{50}Cu_{50}$, ▲: $Zr_{60}Cu_{40}$.

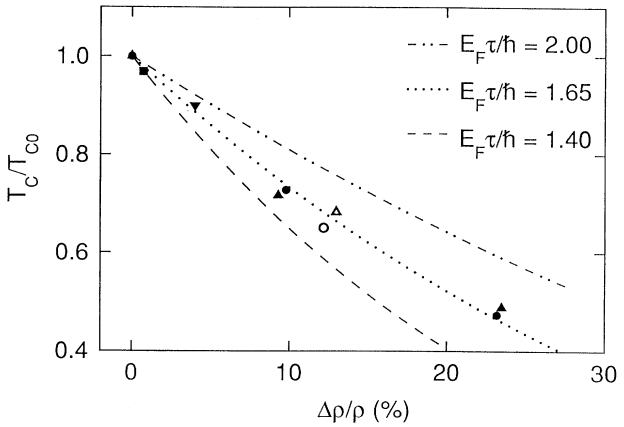

FIG. 4. Relative T_c reduction vs resistivity increase. ●: $Zr_{50}Cu_{50}$, ▲: $Zr_{60}Cu_{40}$, ▼: $Zr_{75}Fe_{25}$, ■: $Hf_{67}Co_{33}$. Unfilled symbols show the T_c reduction after the second irradiation relative to the T_c values after the first neutron dose. The curves are FEM calculations for three different starting values of the disorder parameter $E_F\tau/\hbar$, which encompass the present observations and take the uncertainty of the resistivity measurements into account.

VI. ANALYSIS AND DISCUSSION

A. T_c

The large differences in depression of T_c for comparable neutron-irradiation doses in Hf-Co and in Zr-Cu in Fig. 1 can be understood from the large absorption cross sections for neutrons both in Hf and in Co. In the present case Hf plays a minor role, since its resonance region is mainly at energies lower than the energy ($\approx$25 eV) required to displace one atom from its equilibrium value. Co has, however, very large resonance cross sections around 150 and 5000 eV. The effects of these on the induced structural changes of the amorphous sample are difficult to estimate, since it depends, among other factors, on the detailed shape of the fast-neutron spectrum and of the actual structure of the sample itself. However, if the resonance integral for Co, calculated from 10 eV to 1 MeV, is effective in reducing the neutron flux and if the absorption of Hf is included, one arrives at the estimate that the number of atomic displacements are smaller by a factor of 5 in Hf-Co as compared to Zr-Cu. Thus the increase of disorder is much smaller in Hf-Co than in Zr-Cu for similar neutron flux.

When the relative decrease in T_c is plotted against resistivity change in Fig. 4, all data are seen to fall close to one universal curve. It should be noted that Zr-Cu data are plotted in Fig. 4, corresponding to the changes in ρ and T_c after three irradiation doses, i.e., after the first irradiation experiment, after both irradiation experiments, and after the second experiment only. In the latter case, the properties after the first experiment were taken to be the initial values. This observation strengthens the consistency of the data and suggests a logarithmic relation between the depression of T_c and the resistivity increase.

In recent years several theoretical papers have discussed disorder effects on T_c. Andersson, Muttalib, and Ramakrishnan[7] (AMR) argue that increased disorder will enhance the Coulomb pseudopotential μ^*, and thus increase the repulsion between the electrons in the Cooper pair. The effect on T_c is calculated by use of McMillan's formula. The AMR theory was recently used[5] to analyze T_c results in hydrogen-doped Zr-based amorphous alloys. To account for our results such an analysis would require an enhancement of μ^* of about 25%. In a tunneling experiment on thin films of A15 compounds[42] no evidence was found for an increased Coulomb interaction with increased disorder. On the other hand, the highest resistivity among the examined thin films was only 62 $\mu\Omega$ cm. In amorphous Zr-based superconductors, where disorder is roughly characterized by $\rho\approx 170$ $\mu\Omega$ cm, evidence was obtained from $d\rho/dT$ and T_c measurements[43] showing that there is an enhancement of μ^* by about 20% over the traditional value of 0.13 for crystalline transition metals.

Fukuyama, Ebisawa, and Maekawa[8] (FEM) used a perturbative approach to study localization effects on superconducting properties in the weakly localized regime, i.e., where the disorder parameter $E_F\tau/\hbar \gg 1$. E_F is the Fermi energy and τ is the elastic relaxation time. FEM found two contributions to the suppression of T_c. One is increased Coulomb interaction and the other is a depression of the electron density of states. The FEM expression is

$$\ln\left[\frac{T_c}{T_{c0}}\right]=\frac{-3\sqrt{3}\hbar^2}{8\pi(E_F\tau)^2}\left\{\left[\frac{1}{g^*}\right]^2+2\pi\left[\frac{1}{g}-\left[\frac{\mu^*}{g}\right]^2\ln\left[\frac{k_B\Theta_D\tau}{\hbar}\right]\right]\right\}, \quad (1)$$

where

$$g^*/g=[1+\mu\ln(E_F/k_B\Theta_D)]/[1+\mu\ln(E_F\tau/\hbar)]\ . \quad (2)$$

Θ_D is the Debye temperature, $g=\lambda_{\text{e-ph}}-\mu^*$, where $\lambda_{\text{e-ph}}$ is the electron-phonon coupling constant and μ^* is defined above. μ is the unrenormalized screened Coulomb interaction. For amorphous metals, estimates of $E_F\tau/\hbar$ fall in the range[21] 1.3–2.5 or[19] 2.5–3.1. In Fig. 4 we have used the FEM expression to calculate the T_c depression due to increased disorder from three different starting values of $E_F\tau/\hbar$. The validity of a perturbative treatment can possibly be questioned in this region. $E_F\tau/\hbar$ was assumed to be proportional to ρ^{-1}. The other parameters were given reasonable values for our samples: $E_F\approx 2$ eV, $\Theta_D=220$ K, $\lambda_{\text{e-ph}}=0.55$, and $\mu^*=0.14$. For $E_F\tau/\hbar=1.65$ we observe fair agreement with FEM theory. In this comparison the small shift of the initial disorder parameter for the open symbols in Fig. 4 has been neglected.

Different effects on T_c could be difficult to rule out. E.g., in addition to changes in $N(0)$ considered in disorder theories there may be changes due to smearing or due to volume increase. It has been pointed out, however,[7] that when starting from an already strongly disordered material, further smearing is likely to be small. The x-ray results indicate a small volume increase of about 1.5%, which would affect $N(0)$. The irradiation-induced volume increase in Mo-Ru-B (Ref. 34) was also 1.5%. In this case T_c was instead found to increase by 2%.

However, the behavior of T_c found in Fig. 4 is consistent for three different amorphous systems. Other effects, if present, would be expected to give different contributions for different alloys and irradiation conditions. This observation strongly supports the conclusion that the observed depression of T_c is mainly due to the increased disorder.

B. H_{c2}

The standard theory for H_{c2} in systems with a short electron mean free path is the WHH theory.[16] It was derived by use of the Abrikosov-Gorkov theory and includes corrections for Pauli paramagnetism and spin-orbit interaction. The model used by WHH assumes,[44] e.g., spherical Fermi surfaces, weak-coupling superconductivity, constant $N(0)$ close to E_F, and small spin-orbit scattering compared to the total scattering. In spite of these simplifications the WHH theory has been very successful.

Possible quantum corrections are not included in the WHH theory. When fitting the theory to experimental data, it is convenient to use the reduced parameters $h^*(t)=-H_{c2}/[T_c(dH_{c2}/dT)_{T=T_c}]$ and $t=T/T_c$. In principle there is one free parameter in the theory, λ_{so} the spin-orbit interaction parameter. The theory also contains the Maki paramagnetic limitation parameter[45] α, which can be determined from the normal-state resistivity and the normal-state specific heat. α can also be determined from the critical field slope close to T_c by the relation

$$\alpha=-0.528(dH_{c2}/dT)_{T=T_c}\ . \quad (3)$$

If α is determined in this way it is, however, easily underestimated due to the negative curvature in data. Therefore it is advantageous to regard both α and λ_{so} as adjustable parameters and determine them from a fit to all data.[18] Then the slope at T_c can be determined from α. The WHH theory predicts an upper limit for $h^*(t)$ above which data cannot reach. In particular, $h^*(0)\leq 0.693$, and this maximum value is obtained, e.g., for $\lambda_{so}=\infty$. It is thus important not to underestimate the slope at T_c since $h^*(t)$ then will be overestimated, which can lead to fictitious deviations from WHH theory.

Methods for fitting to the WHH theory and procedures to estimate the accuracy with which α and λ_{so} can be determined from critical field measurements were described in some detail previously.[19] We found that typical results with standard methods are within about ±4% for α and within a factor of 2 for λ_{so}. It was also found that the Zr-Cu system could be well described by WHH theory.[19]

These methods were applied to the present results. The results are given in Table III. We obtain good fits, except for $Zr_{50}Cu_{50}$ after the second neutron dose, where data go beyond the theory. A systematic trend is observed in the extracted parameters; α decreases and λ_{so} increases with irradiation.

Figure 5 and 6 display H_{c2} data in reduced parameters. For both samples $h^*(t)$ increases with irradiation. This behavior cannot be explained within the WHH theory. Although $h^*(t)$ will increase if the paramagnetic limitation gets weaker, that effect is very small compared to what is observed.

The enhancement of the critical field for $Zr_{50}Cu_{50}$ after the second neutron dose is in the same direction as for the other irradiations, but is particularly anomalous, since the curve increases above the maximum WHH curve. For this sample special care was taken not to underestimate the slope at T_c. Different attempts to fit various sections of $H_{c2}(T)$ to WHH failed. Then a straight line was fitted to data in the vicinity of T_c and the slope of this line was corrected for the curvature of the data in that region. The curvature was taken to be the same as for the WHH max curve. Sample inhomogeneities are not expected to influence this analysis. ΔT_c is small as shown in Table I and the results for ΔH_{c2} of this sample are similar to those displayed in Fig. 3 and are discussed

TABLE III. Results from critical field data analysis.

Sample	Dose (10^{18} n/cm^2)	$\left[\frac{dH_{c2}}{dT}\right]_{T=T_c}$ (T/K)	λ_{so}	$h^*(0)$	rms (10^{-3})
$Zr_{50}Cu_{50}$	0.0	2.75	8.6	0.655	4.70
	0.75	2.62	10.5	0.663	2.96
	2.2	2.42		0.74±0.01	
$Zr_{60}Cu_{40}$	0.0	2.94	1.87	0.572	4.67
	0.75	2.73	3.3	0.616	2.32
	2.2	2.56	8.6	0.659	2.26

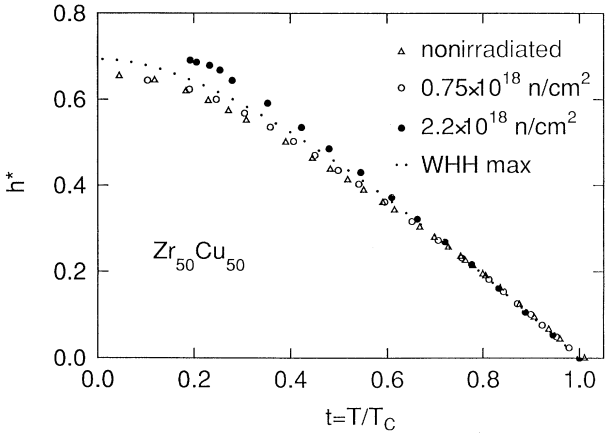

FIG. 5. Critical field data for $Zr_{50}Cu_{50}$ in reduced parameters. h^* increases with irradiation. After full neutron dose data reach above the WHH maximum.

below. In summary we have obtained strong indications that data for this sample go beyond the WHH regime.

There are several reports on deviations from WHH theory. In some cases, even if no enhancement above the WHH max curve is observed, the spin-orbit scattering strength extracted from the theory can be unphysically large. Enhancements of the critical field are often explained in terms of fine-scaled inhomogeneities in the sample. There is strong theoretical[22,23] and experimental[15,22,30,46] support for such a mechanism. However, an inhomogeneity-induced enhancement is accompanied by a significant broadening of the transition width ΔH_{c2} with increasing magnetic field.[15,22,46] This is in contrast to the observations in Fig. 3, where it is seen that the transition widths in field remain constant or even decrease somewhat with decreasing temperature and increasing field. We thus find that our observations cannot likely be explained by inhomogeneity effects. Similar arguments have been used previously to rule out inhomogeneities in samples where deviations from WHH theory were observed.[12,13,24] Tenhover and Johnson[11] dismissed inhomogeneities after electron microscopy examination with a resolution of 15 Å.

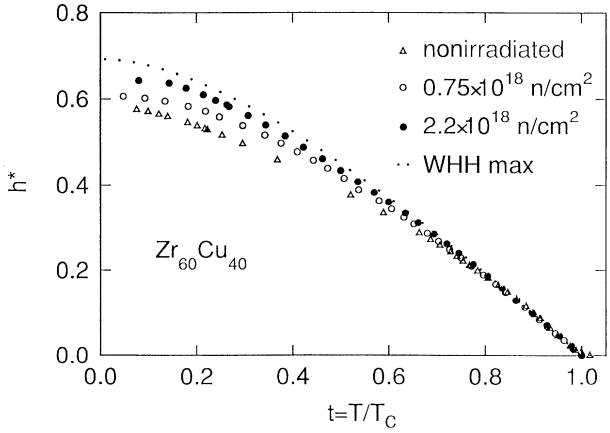

FIG. 6. Critical field data for $Zr_{60}Cu_{40}$ in reduced parameters. h^* increases with irradiation.

Coffey, Muttalib, and Levin[20] (CML) calculated localization effects on strongly disordered three-dimensional superconductors. They found that field-induced suppression of localization enhances the critical field at low temperatures. The main effect comes from a reduction of μ^* in magnetic field. According to AMR,[7] μ^* is enhanced by localization in zero field. The CML theory, however, does not seem to be applicable to the present results, as the proposed mechanism is closely related to a negative normal-state magnetoresistance. This is found in amorphous samples which contain light-metal elements, e.g., Cu-Mg and Ca-Al. For Zr-Cu, spin-orbit interaction is important and the magnetoresistance is positive.[47]

FEM[8] used their perturbative approach to calculate disorder effects on H_{c2} in the weakly localized regime. The effects on H_{c2} were found to be small. For $E_F\tau/\hbar > 1.5$ the FEM theory is almost indistinguishable from the WHH max curve. As pointed out above, the perturbative approach may be questionable in this region of disorder. Furthermore the FEM theory cannot explain enhancement of $h^*(t)$ above WHH theory as it only predicts values less than or equal to the WHH max curve. In particular, according to the FEM theory $h^*(0)$ decreases with increasing disorder, while we observe an increase as seen in Table III. We conclude that our observations cannot be explained by the FEM theory.

According to FEM theory the slope of H_{c2} close to T_c is slightly increased by localization. FEM theory thus predicts a somewhat enhanced $N(0)$ calculated from H_{c2}, as compared to $N(0)$ from specific-heat data.[21] Some experimental support has been found for such an enhancement.[19,21,48] According to the CML calculations,[20] localization does not affect the slope at T_c. The present observation of a weak decrease in the critical field slope at T_c with increased disorder may disagree with both theories. However, other density-of-states effects might contribute to the change in α, such as effects from a small volume increase or some smearing of the density-of-states curve. For a more firm conclusion on this point further studies are required, presumably on a system with larger disorder effects than those studied presently.

VII. CONCLUSIONS

Disorder has been continuously increased in amorphous $Zr_{50}Cu_{50}$, $Zr_{60}Cu_{40}$, and $Hf_{67}Co_{33}$ by irradiation with high-energy neutrons of low intensity. The impact on superconducting T_c was strong. When the relative T_c depression is plotted vs resistivity increase, data from all alloys fall on the same curve. The normalized critical field increases with disorder. This enhancement cannot however, be explained by present theories.

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