

Electronic disorder in superconducting amorphous Zr-Co-P: Comparison with results for T_c and B_{c2} of amorphous alloys

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The superconducting transition temperature and the upper critical magnetic field of amorphous $Zr_{67}Co_{33-x}P_x$, $x=0,5,11$, are studied. Comparison of critical-field parameters for several different amorphous alloys show that an anomalously enhanced critical field cannot be simply correlated to other material properties. Results from different methods to increase disorder in three-dimensions are compared. The normalized T_c of $Zr_{67}Co_{33-x}P_x$ samples, and published results for H-doped samples and neutron-irradiated samples all show a similar dependence of the resistivity increase. This relation extends to below 20% of the initial T_c and it can be obtained from the Fukuyama-Ebisawa-Maekawa theory with a single adjustable parameter. The widths of the superconducting transitions in the magnetic field decrease strongly with decreasing temperature for Zr-Co-P but remain finite at the lowest measuring temperatures. The critical magnetic field increases with increased disorder, which agrees with recent observations from neutron irradiation and cannot be explained by current theories for disorder effects.

I. INTRODUCTION

The upper critical magnetic field of amorphous superconductors has been a controversial field of study for several reasons. On the one hand, the coherence length ξ for amorphous transition-metal superconductors is often of order 50 Å, while the elastic electronic mean free path l_e is at most 10 Å, and these materials are in the dirty limit $l_e \ll \xi$, where one would expect the traditional Werthamer-Helfand-Hohenberg theory¹ (WHH) to be applicable. However, although the WHH theory in many cases describes the upper critical field $B_{c2}(T)$ quite well,²⁻⁴ there are several reports on deviations.⁵⁻⁷ It has not been clarified if this is due to system-dependent properties or what would be the decisive parameters in that case, or if such deviations are due to sample inhomogeneities or to incorrect conclusions based on data collected over a too limited temperature range.

A second area of controversy is the question of whether effects from the electronic disorder in amorphous metals are observable in $B_{c2}(T)$. In amorphous metals at low temperatures, one reaches the regime where the inelastic electronic mean free path $l_i \gg l_e$. Quantum corrections are then observed in transport properties, which, at least qualitatively, can be explained within the framework of weak localization and electron-electron interaction theories. The influence of disorder on superconducting properties is less well understood, particularly what concerns $B_{c2}(T)$, where different theories predict enhancement⁸ or reduction⁹ of the normalized critical field with increased disorder.

In the present paper, we study $B_{c2}(T)$ of amorphous $Zr_{67}Co_{33-x}P_x$ ($x=0,5,11$). Substituting Co with P at constant Zr concentration is similar to hydrogen substitution in Zr-based amorphous superconductors¹⁰ and represents an alternative route to increased disorder, be-

sides neutron¹¹ or ion¹² irradiation studied previously. By choosing materials with low transition temperatures $T_c \leq 3$ K, $B_{c2}(0)$ is limited and $B_{c2}(T)$ can be measured over an extended temperature range, down to $t = T/T_c < 0.1$, where deviations from the WHH theory, if they exist, can be detected. Comparison is made with other amorphous samples by using similar standard analyzing techniques for the critical magnetic field.¹³ This is necessary to detect trends in the small variations of the critical-field parameters which can be achieved by changes in controlled parameters, such as doping concentration and resistivity increase.

Sample preparation and measurement techniques are briefly described in Sec. II. The results are presented in Sec. III and discussed in Sec. IV. It is found that critical-field results are quite system dependent with no simple correlations between critical-field properties. The depression of T_c is found to scale with increased resistivity in a similar way as observed previously for neutron-irradiation-induced disorder.¹¹ Published data for hydrogen-doped Zr-based alloys,¹⁰ when plotted as normalized T_c vs resistivity increase, confirm and extend this analysis. The Fukuyama-Ebisawa-Maekawa (FEM) theory⁹ describes the depression of T_c with an assumed initial value of the disorder parameter. The critical magnetic field is found to be enhanced by increased disorder.

II. EXPERIMENTAL DETAILS

Samples of mass 4–5 g were prepared as described previously for amorphous Zr-Cu from repeatedly arc-molten master ingots which were rapidly quenched by melt-spinning in a helium atmosphere.¹³ The wheel speed was 35–40 m/s. Samples were checked to be x-ray amorphous by diffraction at room temperature. The samples were analyzed with an x-ray fluorescence spectrograph

from which it was concluded that deviations from nominal compositions were small.¹⁴

Standard techniques were employed for the measurements. The density was determined by an Archimedian method, which gave results for the electrical resistivity which were accurate to about 1%. Electrical resistance was measured with a four-probe dc technique with excitation levels down to 1 μ A at low temperatures.

A dilution refrigerator with a superconducting solenoid to 7 T was used for low-temperature measurements. $B_{c2}(T)$ was determined from the resistive mid-points of transition curves at constant fields. The widths of the transitions in the magnetic field, $\Delta B_{c2}(T)$, were defined from the 10–90 % interval of the resistance drop. These points were conveniently located in the B, T plane from alternating field sweeps at constant temperature and temperature sweeps at a constant magnetic field.

III. RESULTS

The results of the critical-field measurements of $Zr_{67}Co_{33-x}P_x$ are displayed in Fig. 1. The transition widths in zero field were 11, 3, and 60 mK for $x=0, 5$, and 11, respectively. The larger ΔT_c for $x=11$ at. % P indicates that this sample may be somewhat more inhomogeneous than the other samples. However, the widths in magnetic field were found to decrease with decreasing temperature for all samples. This will be further discussed below. Critical-field slopes $-dB_{c2}/dT$ at T_c were 3.31, 3.11, and 3.04 T/K for $x=0, 5$, and 11, respectively. The value for $Zr_{67}Co_{33}$ is in fair agreement but slightly smaller than an average value of 3.45 T/K obtained previously for nearby compositions in this alloy system.³

The critical-field data were analyzed using the WHH theory.¹ According to this theory, the reduced critical field $h^*(t) = -B_{c2}/(T_c dB_{c2}/dT)_{t=1}$ with $t = T/T_c$ is obtained from an implicit function $f(B_{c2}, t, \alpha, \lambda_{s.o.}) = 0$, with two parameters α and $\lambda_{s.o.}$. The critical-field slope at T_c

gives $\alpha = 0.528[-dB_{c2}/dT]_{t=1}$ with B_{c2} in tesla. The spin-orbit interaction $\lambda_{s.o.}$ is related to the spin-orbit scattering rate $\tau_{s.o.}^{-1}$, measured, e.g., in the normal-state magnetoresistance, by¹⁵ $\tau_{s.o.}^{-1} = 3\pi k_B T_c \lambda_{s.o.}/2\hbar$.

One could thus use the WHH theory with only one adjustable parameter $\lambda_{s.o.}$. As pointed out by Wong, Cotts, and Poon⁴ this procedure can easily underestimate α due to the curvature of the data close to T_c and hence overestimate h^* , particularly $h^*(0)$, i.e., produce an artificial enhancement of the critical field in the region where disorder effects, if observable, are most likely to show up. Therefore it is preferable to analyze critical-field data with both $\lambda_{s.o.}$ and α as adjustable parameters. The observed slope at T_c can be used as a consistency check in such an analysis.

This analysis is shown in Fig. 2 with $Zr_{67}Co_{28}P_5$ as an example. The best fit, corresponding to $\lambda_{s.o.} = 2.7$ and $\alpha = 1.84$, is shown by the square. The crosses mark the area in $(\lambda_{s.o.}, \alpha)$ space where the rms value of the fit is within twice the best value. The vertical solid lines show the region of α which is consistent with the observed slope at T_c and thus give upper and lower bounds for variations of α . This procedure gives estimates of errors in $\lambda_{s.o.}$ and α . We thus find $\lambda_{s.o.} = 2.7 \pm 0.7$ and $\alpha = 1.84 \pm 0.07$ for $Zr_{67}Co_{28}P_5$.

The results of $h^*(t)$ are shown in Fig. 3. It can be seen that there is a systematic enhancement of $h^*(t)$ with increasing phosphorous concentration and that $h^*(0)$ remains below the WHH maximum value of 0.693 for all samples.

Some further results are summarized in Fig. 4 in the form of the relative change compared to the $x=0$ sample. The bare density of states, $N(0)$, was obtained from the WHH theory¹ (with correction for the unrenormalized density of states):

$$N(0) = \frac{\pi}{4k_B L} \frac{M}{d\rho} \frac{1}{1+\lambda} \left[-\frac{dB_{c2}}{dT} \right]_{t=1}, \quad (1)$$

where L is Avogadro's number, M the atomic mass, d the density, and λ the electron-phonon interaction evaluated

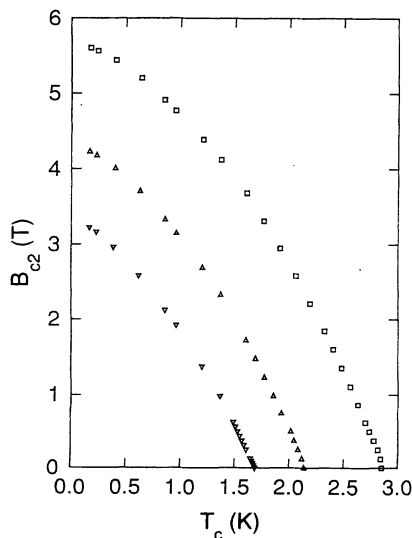


FIG. 1. Upper critical field for amorphous $Zr_{67}Co_{33-x}P_x$. $x=0$ (\square), $x=5$ (\triangle), and $x=11$ (∇).

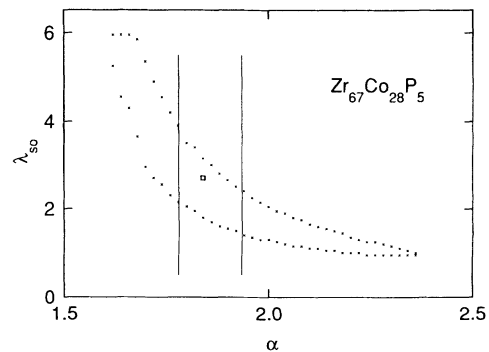


FIG. 2. Analysis of critical-field data exemplified by $Zr_{67}Co_{28}P_5$. On the dashed curve in the $\lambda_{s.o.}, \alpha$ plane, the rms value of the fit reaches twice the best value obtained for the square. The vertical lines give extrema for α which are consistent with the observed slope at T_c .

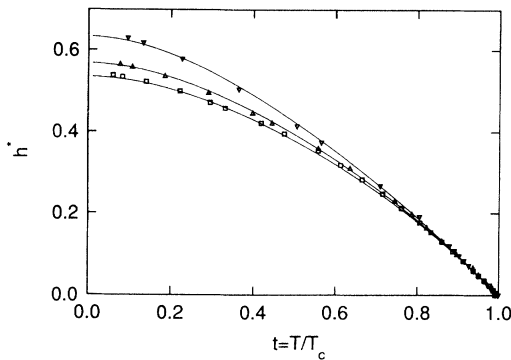


FIG. 3. Normalized critical field $h^*(t)$ for Zr-Co-P samples. The symbols are the same as in Fig. 1; i.e., in order of increasing $h^*(t)$ the P concentration is $x = 0, 5$, and 11 .

from McMillan's formula. The increase in ρ and decrease in M lead to a somewhat stronger decrease of $N(0)$ with x as compared to $-[dB_{c2}/dT]_{t=1}$.

It can be seen from Fig. 4 that the substitution of Co by 11 at. % P leads to a resistivity increase of 10%, a decrease in the density of states by 15%, and a decrease of T_c by 40%.

IV. DISCUSSION OF RESULTS

A. Comparison with other amorphous alloy systems

In order to investigate if there are systematic trends in critical-magnetic-field parameters for different amorphous alloy systems, we have collected data in Table I for several amorphous superconductors. These results have been obtained by the analysis methods described in the previous section on data which extend to T/T_c below or much below 0.1. For Nb-Ni alloys this required reanalysis of previously published results.⁷ The new

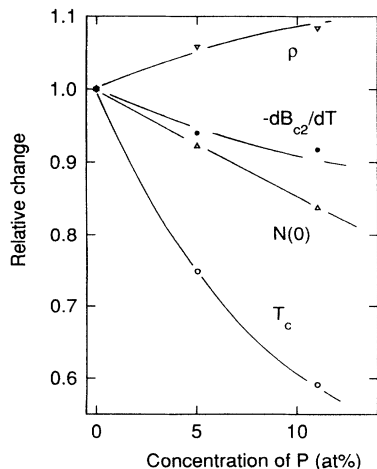


FIG. 4. Relative change of several properties of Zr-Co-P samples.

analysis reinforces the conclusion that B_{c2} for this alloy system is anomalous with all three alloys having $h^*(0)$ larger than the WHH maximum. In a few cases in Table I, there are two alloys of the same composition. In the case of $Zr_{50}Cu_{50}$, this illustrates typical scatter between different acceptable samples of amorphous alloys.¹³ For $Al_{90}La_{10}$, however, it would seem that for sample II the normal-state transport properties are anomalous and possibly influenced by nanocrystallites.¹⁷

The widths of the transitions in magnetic field were measured for the alloys in Table I. For Zr-Cu samples these widths were found to increase slightly with decreasing temperature.¹³ This would seem to have been a small enough effect not to influence the results, and the WHH theory could be fitted to most of the data. Also, for Al-based samples, a small increase of ΔB_{c2} with decreasing temperature was observed, and inhomogeneities may thus contribute to the large $h^*(t)$ for these alloys. As discussed in Ref. 17, however, results from the normal-state magnetoresistance support that $h^*(t)$ is enhanced by intrinsic reasons. For the other samples in Table I, $\Delta B_{c2}(t)$ was constant or decreased with decreasing t . In summary, therefore, inhomogeneity effects would not seem to have essentially influenced the conclusions drawn from the data in Table I.

Attempts to understand critical-field data by relations to other properties have previously modeled inhomogeneities¹⁸ or found some correlations with the mass⁴ and with the resistivity.⁵ Increasing mass would increase $\lambda_{s.o.}$ and therefore also $h^*(t)$, and this was observed for a series of samples based on Ti, Zr, and Hf, respectively.⁴ Increasing resistivity indicates increased disorder, which would be expected to affect $h^*(t)$. Some support for such a relation was found in Ref. 5.

For the samples in Table I, there is no simple correlation with characteristic sample properties such as the mass or normal-state resistivity. For about half of the alloys, the WHH theory can describe the data with a finite $\lambda_{s.o.}$ while for the other alloys $h^*(0) > 0.693$, the WHH maximum value. The Al-based superconductors are particularly anomalous with low mass, α , and ρ , and large $h^*(0)$ and relatively high T_c 's. Even if these alloys were excluded, the superconductors where the WHH theory cannot fit the data may have larger ρ (Hf-based samples) or smaller ρ (Nb-Ni) than Zr-Cu or Zr-Co samples where the WHH theory fits the data or the mass can be similar in alloy systems that do or do not fit the WHH theory (Zr-Cu and Nb-Ni). The trend in Table I that an increasing $\lambda_{s.o.}$ is correlated with an increasing $h^*(0)$ for the eight samples where $\lambda_{s.o.}$ is finite is merely a consequence of successful fits to the WHH theory.

For individual alloy systems, correlations may be discerned in some cases, such as a weak trend for increased ρ and $h^*(0)$ with decreasing Zr concentration in Zr-Cu samples. For Zr-Co-P this will be further discussed in the next section.

Therefore it must be concluded that critical-magnetic-field properties of amorphous samples are strongly dependent on the alloy system and simple correlations with atomic mass or normal-state resistivity break down when results from several different systems are considered.

TABLE I. Critical magnetic field and resistivity data for amorphous alloys.

Sample	α	$\lambda_{s.o.}$	$h^*(0)$	$T_c (B=0)$ (K)	$\rho(4.2 \text{ K})$ ($\mu\Omega \text{ cm}$)	$\frac{\rho(4.2 \text{ K})}{\rho(2.95 \text{ K})}$
Zr ₆₇ Co ₃₃	1.91	1.9	0.54	2.88	183	1.055
Zr ₆₇ Co ₂₈ P ₅	1.84	2.7	0.58	2.15	193	1.052
Zr ₆₇ Co ₂₈ P ₁₁	1.60	6	0.64	1.69	197	1.048
Zr ₃₆ Cu ₆₄ ^a	1.22	3.0	0.63	0.179	184	1.028
Zr ₄₀ Cu ₆₀	1.41	6	0.65	0.274	184	1.029
Zr ₄₃ Cu ₅₇	1.44	∞	0.693	0.532	185	1.038
Zr ₅₀ Cu ₅₀ (I)	1.54	3.9	0.62	0.804	180	1.024
Zr ₅₀ Cu ₅₀ (II)	1.45	9	0.66	0.746	182	1.035
Zr ₆₀ Cu ₄₀	1.55	1.9	0.57	1.60	179	1.052
Nb ₆₀ Ni ₄₀ ^b	1.37	∞	0.70	1.91	158	1.017
Nb ₅₀ Ni ₅₀	1.45	∞	0.71	1.01	156	1.009
Nb ₄₀ Ni ₆₀	1.73	∞	0.70	0.254	179	1.023
Hf ₆₇ Ni ₃₃ ^c	1.79	∞	0.714	1.75	202	1.048
Hf ₆₇ Co ₃₃	1.88	∞	0.703	1.75	211	1.055
Al ₉₀ La ₁₀ (I) ^d	0.245	∞	0.719	3.98	52	0.9678
Al ₉₀ La ₁₀ (II)	0.275	∞	0.719	4.27	40	0.8857
Al ₉₀ Y ₁₀	0.269	∞	0.723	3.68	46	0.9880

^aData for Zr-Cu from Ref. 13.

^bData for Nb-Ni from Ref. 7 presently reanalyzed.

^cData for Hf-based samples from Ref. 16.

^dData for Al-based samples from Ref. 17.

B. Disorder effects

We discuss disorder in terms of electronic disorder. Theoretically, one describes disorder⁹ in terms of the parameter $\hbar/\varepsilon_F\tau$ where $1/\tau$ is the elastic scattering rate and ε_F the Fermi energy. Experimentally, the measured R_{\square} in two dimensions (2D) or ρ in 3D then provides for measures of disorder. In crystalline materials, where disorder is varied, e.g., by different preparation conditions or by irradiation damage, the variation of T_c with disorder can have either sign, depending on competing effects in the density of states.¹⁹ This has been observed, e.g., in studies of radiation damage in a low-density-of-states A15 superconductor.¹²

For disordered materials, such as amorphous superconductors, T_c decreases with increased disorder. In this case the sometimes spiky nature of the density of states in crystalline materials has already been smeared by initial disorder. Further smearing effects due to increased disorder are therefore likely to be small.²⁰ Several theoretical and experimental studies, generally performed in 2D materials,²¹ have confirmed such a decrease in T_c . Weak localization and interaction effect theories often treat two different effects on T_c due to increased disorder: a decrease in the density of states and an increase in the Coulomb pseudopotential, reflecting poorer screening.

In 3D superconductors there has been comparatively little experimental work on this problem. One is faced here with the difficulty to control disorder in bulk metals. If one starts with a 3D crystalline material, the destruction of a lattice may dominate all changes of properties. Alloying in disordered materials may produce changes, e.g., in electronic structure, which mask changes due to

increased electronic scattering. Two methods seem to have been used to increase disorder in amorphous 3D superconductors: irradiation with high-energy neutrons of low intensity¹¹ and hydrogen substitution in amorphous samples of the type early-late transition-metal alloys.¹⁰

Why would there be no major alloying effects when P is substituted for Co in Zr-Co? For the other alloys in Table I, except perhaps the Al-based samples, one would expect changing properties to be dominated by such effects, e.g., changing electron concentration. However, it is well known that the electronic properties of the early-late transition metals are dominated by Fermi-surface electrons of the early transition metal.^{22,23} In fact, the late transition-metal atom has often been considered as a type of vacuum for Zr, or Hf electrons, and substitutions of that atom would therefore mainly increase the elastic scattering rate.

Also, in the case of hydrogen-doped Zr-based amorphous samples, as studied in Ref. 10, there is evidence that disorder increases with H concentration. Mizutani, Ohta, and Matsuda²⁴ found that the residual resistance ratio $\rho(4.2 \text{ K})/\rho(295 \text{ K})$ increased with H concentration in Zr-Pd samples, and Kokanovic, Leontic, and Likafella²⁵ observed a similar relation for H-doped Zr-Ni, which is one indication of increased disorder. Studies²⁵ of the normal-state magnetoresistance and magnetic susceptibility of Zr-Ni-H and Zr-Cu-H also indicate increased electronic disorder from, e.g., a decreased diffusion constant and an increased spin susceptibility in addition to increased elastic scattering rate.

Nevertheless, both neutron irradiation and doping may be subject to errors which are difficult to estimate, such as the introduction of small amounts of free volume affecting the density of states in the case of neutron irra-

diation and some nondisorder-induced changes in electronic structure in the case of doping also affecting the density of states.

It was shown previously¹¹ that results from several different alloy systems, where nondisorder effects are expected to be significantly different, nevertheless collapse onto one curve when plotted as normalized T_c reduction vs resistivity increase. This gave empirical evidence that the increasing elastic scattering rate is the dominating effect of neutron irradiation.

This analysis is useful also for comparing different experimental techniques to increase disorder. In Fig. 5 we show T_c/T_{c0} vs $\Delta\rho/\rho$ for the present P-doped Zr-Co samples, for three amorphous alloy systems with hydrogen doping¹⁰ and for three alloy systems which were neutron irradiated.¹¹ The consistency between data for different samples and different treatments is remarkable.

These results support the contention that increased electronic disorder is the dominating effect in the observed changes of T_c in all cases shown in Fig. 5. The dashed curve was hence calculated from the FEM theory⁹ with initial values at $T_c=T_{c0}$ and $\Delta\rho=0$ of $(\hbar/\epsilon_F\tau)^{-1}=1.65$ and $\lambda_0=0.55$ and with $\epsilon_F=2$ eV, Debye temperature $\Theta=220$ K, and the Coulomb pseudopotential $\mu^*=0.14$. These parameters are the same as chosen previously¹¹ and are reasonable estimates for Zr and Hf-based amorphous superconductors. Furthermore, the form of the calculated curve is not sensitive to small changes in the parameters. If λ_0 is decreased by 20% to 0.45, an increase in the initial value of $(\hbar/\epsilon_F\tau)^{-1}$ by 20% produces an identical curve for T_c/T_{c0} .

The data in Fig. 5 are fairly well described by one universal curve from the FEM theory over a range of T_c values down to 0.2 of T_{c0} . The largest deviations are of order 15% in T_c/T_{c0} and are observed for one datum in hydrogen-doped $Zr_{60}Cu_{40}$ and for 11% P in Zr-Co. This scatter may be due to small differences in initial conditions for different samples or to an influence by alloying

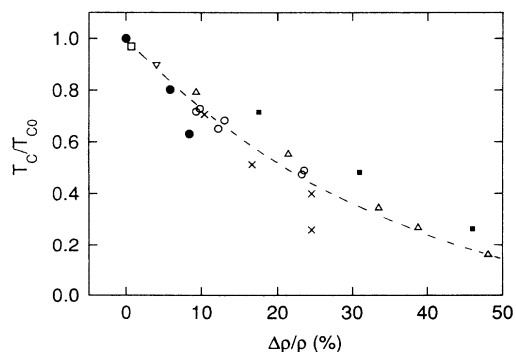


FIG. 5. Relative change of T_c vs resistivity increase. Present Zr-Co-P samples (●). Neutron-irradiated samples from Ref. 11 are $Zr_{60}Cu_{40}$ and $Zr_{50}Cu_{50}$ (○), $Hf_{67}Co_{33}$ (□), and $Zr_{75}Fe_{25}$ (▽). Hydrogen-doped samples from Ref. 10 are $Zr_{67}Ni_{33}$ (△), $Zr_{70}Cu_{30}$ and $Zr_{60}Cu_{40}$ (×), and $Zr_{65}Pd_{35}$ (■). The dashed curve is calculated from Fukiyama-Ebisawa-Maekwa theory with the initial value of $\epsilon_F\tau/\hbar$ of 1.65.

on other properties besides the elastic scattering rate. For the samples of Ref. 10, there may be some additional uncertainty at low T_c 's since data were not measured but calculated from a weak localization contribution to the normal-state magnetoresistance.

Recently, a parametrization of disorder effects on T_c was performed in terms of three renormalization quantities.²⁶ Comparing with experimental data requires fitting of three parameters, viz., the resistivity at the metal-insulator transition, the clean limit T_c , and a special value of the integrand in the T_c equation. The fit in Fig. 5 is simpler since it uses in principal only one parameter, i.e., $(\hbar/\epsilon_F\tau)^{-1}$. However, our procedure can be expected to be successful only for fairly similar initial samples, such as in Fig. 5. In more general cases, a more elaborate fitting technique will probably have to be used.

2. B_{c2}

From Fig. 3 it was seen that $h^*(t)$ is enhanced with increasing phosphorous concentration. However, before drawing any conclusions, it is important to rule out effects from inhomogeneities since these, if present, could easily mask the consequences of the increased elastic scattering rate.

There are several theoretical^{18,27,28} and experimental²⁹⁻³¹ results supporting the idea that inhomogeneities lead to a broadening of the superconducting transitions in a magnetic field. Striking illustrations for Zr-based amorphous alloys were given in Ref. 28, where transition widths $\Delta B_{c2}(t)$ in a magnetic field increase linearly with the magnetic field to well above 1 T at $t=0.5$. This behavior was, in one case, accounted for by inhomogeneities on a length scale of about half the zero-temperature coherence length, i.e., about 30 Å, and this model led to the prediction that ΔB_{c2} should reach above 2 T at $t < 0.1$.

The transition widths in a magnetic field for Zr-Co-P samples decrease with the magnetic field as illustrated in the inset of Fig. 6. This is clearly very different from the results quoted above and gives evidence that inhomogeneities do not contribute to an anomalous enhancement of $h^*(t)$. In fact, from Fig. 6 it can be seen that $\Delta B_{c2}(t)$ decreases in an accelerated way with decreasing temperature. This behavior is not understood. It does not seem to have been reported before for dirty superconductors. When previously observing a decreasing transition width, we found $\Delta B_{c2}(t)$ to be linear in t .¹¹ There is an old prediction³² that first-order superconducting transitions could occur in magnetic fields at low temperatures, but this has not been observed. In such a case, $\Delta B_{c2}(t)$ would, of course, decrease strongly before the first-order transition. Judging from the curvature in Fig. 6, however, it does not seem likely that $\Delta B_{c2}(t)$ goes to zero at $T \geq 0$ for any of the three samples.

The zero-field transition widths ΔT_c described in Sec. III suggest some inhomogeneity-induced broadening for the 11 at. % P sample. This is in contrast to the results for $\Delta B_{c2}(t)$. The reason for this difference is not understood. However, we note that inhomogeneities increasing B_{c2} would be expected also to increase $\Delta B_{c2}(t)$,^{27,28} and

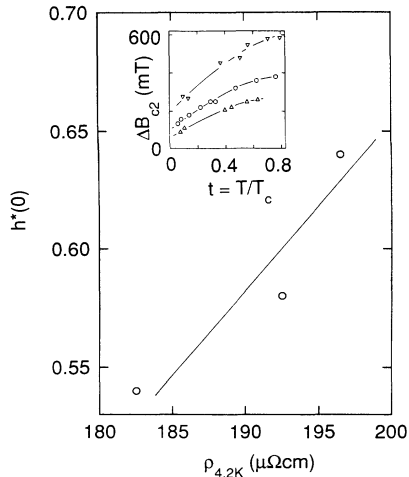


FIG. 6. Increase of $h^*(t)$ with resistivity for $\text{Zr}_{67}\text{Co}_{1-x}\text{P}_x$. The straight line is a guide to the eye. The inset shows the decrease of the transition widths for decreasing reduced temperature t . The samples are, from top to bottom, $x = 11, 0$, and 5 .

this is not observed. Therefore we conclude that inhomogeneities affecting the interpretation of critical-field results have likely not been introduced by phosphorous doping.

An increase in $\lambda_{s.o.}$ which could account for an increased $h^*(0)$ is unlikely. In fact, if changing at all, the spin-orbit scattering rate would be expected to decrease by P substitution. Even with a constant $1/\tau_{s.o.}$, one could account for at most an increase in $\lambda_{s.o.}$ by 70% from a decrease of T_c by 40%, and not a factor of 3 as observed in Table I. The strong increase in $h^*(0)$ is thus not mainly due to an increasing $\lambda_{s.o.}$. In contrast, the increase in $\lambda_{s.o.}$ with P concentration is mainly an effect of a successful attempt to the fit WHH theory to data with increasing h^* .

Other effects from P substitution, besides an increased elastic scattering rate, are likely to be small, as argued above. Nevertheless, some change of α cannot be ruled out, e.g., from a decreasing $N(0)$ due to a changing electron concentration. A decrease of α would increase h^* by its definition. However, at 11% P the observed decrease of α by 18% (Table I) could only lead to an increase of $h^*(0)$ by at most 6%, as compared to the observed increase of about 20%. Even if $\lambda_{s.o.}$ increased proportionally to $1/T_c$ (which is likely not justified) and in addition the full change of α were ascribed to nondisorder effects, a significant fraction (of order $\frac{1}{3}$) of the observed enhancement of $h^*(0)$ would not be accounted for.

Our results therefore support that the critical field increases with increasing disorder. In Fig. 6 we find an approximately linear increase of $h^*(0)$ with the resistivity.

As mentioned previously, there is some support for an increasing $h^*(0)$ with increasing ρ also for the Zr-Cu samples listed in Table I. However, in this case one must expect that changing electron concentration between different samples would give significant contributions to the observed changes in sample properties, and these

samples are therefore excluded from the present discussion.

Results on the critical magnetic field of irradiated Nb_3Ir displayed an increase in the critical-field slope and α , with increasing resistivity.¹² Since the starting material in that case was a low-density-of-states crystalline compound, it seems likely that the observed α is dominated by an increased $N(0)$ through smearing of the density of states. In amorphous $\text{V}_{1-x}\text{Si}_x$ it was found that $h^*(t)$ decreased with increasing x and decreasing T_c .³³ Since the magnetoresistance was positive, the theory by Coffey, Muttalib, and Levin⁸ should not be applicable. Unfortunately, ρ was not measured and the relation to increased disorder is unclear.

Support for an increase of $h^*(0)$ with ρ was obtained previously in Mo-Ru- and Mo-Re-based amorphous superconductors.⁵ In this case, however, the magnetic field transition widths increased somewhat with decreasing field, and furthermore, the measurements were extended only down to $t = 0.3$, and both of these factors may introduce some uncertainty in the analyses. In neutron-irradiated Zr-Cu samples,¹¹ with constant or decreasing $\Delta B_{c2}(t)$ and with critical-field curves analyzed to below $t = 0.1$, the results agree qualitatively with present observations, and increasing disorder, manifested in increasing ρ , leads to an increase in $h^*(t)$.

The Fukuyama-Ebisawa-Maekawa theory⁹ predicts a decreasing critical magnetic field with increasing disorder and cannot therefore explain the present data. This raises the question why the FEM theory would be successful in the description of T_c and not for the critical field. The observation that similar effects on $h^*(t)$ were obtained in quite different methods to increase $1/\tau$, that is, P substitution as studied presently and neutron irradiation,¹¹ supports our interpretation and would thus suggest that theory must be remedied.

According to Coffey, Muttalib, and Levin, disorder can increase the critical field.⁸ However, in their model the disorder-induced enhancement of the Coulomb pseudopotential μ^* at $B = 0$ decreases with increasing magnetic field, leading to an enhancement of $h^*(t)$. Such an effect would imply a negative normal-state magnetoresistance $\Delta\rho/\rho$, i.e., weak spin-orbit scattering in the dominating weak localization contribution to $\Delta\rho/\rho$. This is not the case for Zr-based amorphous alloys where $1/\tau_{s.o.}$ is strong enough that $\Delta\rho/\rho$ is positive for not too strong magnetic fields [e.g., below about 30 T at 4 K (Ref. 34)]. Thus this theory⁸ does not seem to be applicable to our results. In fact, we do not know of a theory which can explain these results.

V. CONCLUSIONS

Data for the critical magnetic field of several amorphous superconductors were analyzed in a consistent way to detect possible reasons for an anomalous enhancement of $h^*(t)$. By our procedures some proposed explanations can be ruled out, i.e., inhomogeneities or too limited temperature range in the measurements. However, we have not found any simple relation between $h^*(0)$ and other sample properties. The conclusion is thus that the criti-

cal magnetic field is enhanced for some amorphous superconductors and that the reasons are not known.

For amorphous Zr-Co-P it was found that ρ and $h^*(0)$ increase with P concentration and that T_c decreases. The changes in ρ and T_c are consistent with results for differently treated amorphous samples, both neutron irradiated and hydrogen doped, and cover together a large range of T_c depressions down to 20% of T_{c0} . This variation can be described by the Fukuyama-Ebisawa-Maekawa theory with an initial value of $\epsilon_F\tau/\hbar$ of 1.65.

The critical magnetic field $h^*(t)$ is enhanced by increasing disorder. This result is not understood. It agrees qualitatively with observations for neutron-irradiated Zr-Cu samples.

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