Paraconductivity and upper critical field in inhomogeneous amorphous superconductors

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Correlation between enhanced paraconductivity σ' near the superconducting transition temperature T_{c0} and enhanced upper critical field H_{c2} at low temperature is observed in bulk amorphous superconductors. It is pointed out that the presence of inhomogeneities is responsible for this observation. Phase inhomogeneity causes σ' to diverge as $\epsilon^{-5/2}$ near T_{c0} where $\epsilon = (T - T_{c0})/T_{c0}$; while statistical fluctuation in alloy composition yields the usual result $\sigma' \propto \epsilon^{-1/2}$. Various models of enhanced H_{c2} are discussed. Comparison with new data on both homogeneous and inhomogeneous amorphous Zr_3Pd samples is made.

Recently, the temperature dependence of upper critical field $H_{c2}(T)$ in glassy superconductors has been a subject of substantial interest.[1–4] It was reported that in some amorphous transition-metal-alloy superconductors, enhancement of $H_{c2}(T)$ above the values predicted by the Ginzburg-Landau-Abrikosov-Gorkov (GLAG) theory was observed.[1,3,4] Meanwhile, it was noted that in other alloys $H_{c2}(T)$ followed the theoretical curve.[2] The authors of Refs. 2 and 4 suggested that the unusual behavior of $H_{c2}(T)$ could be explained by spatial inhomogeneities on a scale of the order of the superconducting coherence length. Recently, Clemens *et al.*[3] studied the effects of inhomogeneities on $H_{c2}(T)$ in neutron irradiated samples. In this paper, we point out a correlation between the temperature dependence of upper critical field $H_{c2}(T)$ at low temperature ($T \lesssim 0.6 T_{c0}$) and paraconductivity $\sigma'(T)$ near T_{c0} which lends additional support to the above suggestion. Since the degree of spatial inhomogeneities depends on the metallurgical conditions of the samples, new data on both homogeneous and inhomogeneous amorphous Zr_3Pd samples will be reported. Using a distribution in critical temperature which can describe either statistical fluctuation in alloy composition or phase inhomogeneity, expressions for $\sigma'(T)$ near T_{c0} are derived. Various models of enhanced $H_{c2}(T)$ are discussed. These results are compared with experimental data obtained thus far.

Amorphous ribbons of Zr_3Pd were prepared according to the method outlined in Ref. 5. The amorphicity of the ribbons was checked using a standard x-ray diffractometer (Ni filtered Cu $K\alpha$ radiation). The specimens used in the measurements were long strips of width $\sim$ 1 mm, length $\sim$1–2 cm, and thickness $\sim$25 μm. Sample resistivity was measured from T_{c0} to $\sim 2T_{c0}$ in a four-point probe. The current used was 5 mA. Temperature was monitored using a carbon resistor and a Hg nanometer with an accuracy of 1–2 mK. Temperature in the liquid-helium bath was regulated to equal accuracy. This allowed an accurate determination of conductivity near the transition temperature. The virgin samples used in this experiment had transition width (defined by 10% and 90% point on the resistivity curve) of $\sim$5 mK. Upper critical field was measured using a superconducting magnet in fields up to $\sim$60 kG and temperatures down to $\sim$1 K. The temperature was measured from the vapor pressure of helium. The overall technique had been given elsewhere.[6] The transition width at constant temperature in a high field was typically $\sim$4 kG. The critical field was taken at the 50% point on the resistivity curve.

We point out here that for all the glassy superconductors with the exception of Zr_3Rh reported in Refs. 7 and 8, $\sigma'(T)$ near T_{c0} (the temperature at which the sample resistivity vanishes) diverges faster than $\epsilon^{-1/2}$ ($\epsilon = (T - T_{c0})/T_{c0}$), the theoretical prediction of Aslamazov and Larkin (AL). Incidentally, all samples except Zr_3Rh exhibit enhanced H_{c2} values above the GLAG curve. Earlier, it was suggested that the rapid divergence of $\sigma'(T)$ near T_{c0} for one-dimensional samples could be accounted for by a distribution in T_c.[9] Thus, it is suggestive that the enhancement in $H_{c2}(T)$ might be an unique property of inhomogeneous glassy superconductors. This assertion can be tested by studying samples of the same alloy treated under different metallurgical conditions. We start with two samples numbers 1 and 2 of amorphous Zr_3Pd which show no detectable crystallization in x-ray diffraction. The reduced paraconductivity $\ln(\sigma'/\sigma_0)$ (σ_0 is the normal state conductivity at low temperature) plotted as a function of $\ln\epsilon$ for both samples are shown in Fig. 1. They follow the AL prediction near T_{c0}. Sample 1 was then annealed in vacuum at 280 °C for 10 h. Evidence of the onset of

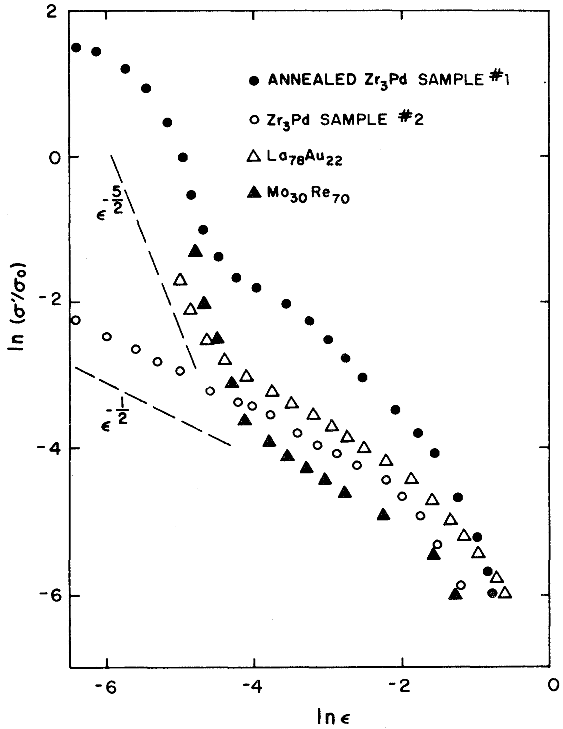

FIG. 1. $\mathrm{Ln}(\sigma'/\sigma_0)$ as a function of $\ln\epsilon$ for four amorphous superconductors, where ϵ is $(T-T_{c0})/T_{c0}$. Data on $La_{78}Au_{22}$ and $Mo_{30}Re_{70}$ are taken from Ref. 7. Data are to be compared with dashed straight lines for $\ln\epsilon < -4$.

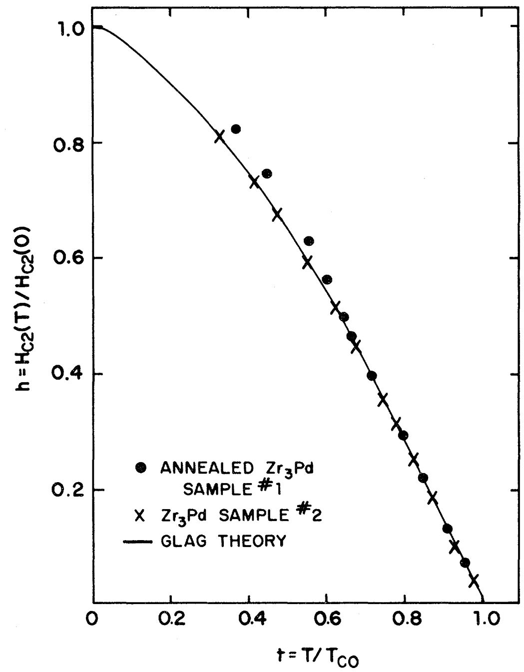

FIG. 2. Reduced upper critical field as a function of reduced temperature. $H_{c2}(0)$ is the GLAG value at $T=0$. The values of T_c for annealed sample 1 and sample 2 are 2.68 K and 3.04 respectively. The upper critical field gradients near T_{c0} are equal to 26 and 24.0 kG/K, respectively.

crystallization was observed in the sample and its paraconductivity measured. As can be seen in Fig. 1, the annealed sample 1 exhibits the same rapid divergence in $\sigma'(T)$ near T_{c0} as in most of the amorphous superconductors mentioned earlier. The transition width of the annealed sample is ~ 30 mK which is comparable to the other inhomogeneous samples. We have also included data on amorphous $Mo_{30}Re_{70}$ and $La_{78}Au_{22}$ from Ref. 7 for comparison. Normalized upper critical field versus normalized temperature for annealed sample number 1 and sample number 2 are shown in Fig. 2. It can be seen that the $H_{c2}(T)$ data for the homogeneous Zr_3Pd sample ($\Delta T_c \sim 5$ mK) follow the GLAG curve while those for the inhomogeneous sample ($\Delta T_c \sim 30$ mK) are enhanced above the theoretical curve.

Before we apply the model of T_c distribution to discuss the $\sigma'(T)$ curves, several comments are made on the general shape of these curves for bulk superconductors. Near T_{c0}, say $\ln\epsilon \lesssim -4$, the Maki-Thompson (MT) contribution to σ' is negligible.[10] However, for $\ln\epsilon \gtrsim -3$, the MT term becomes comparable to the AL term for a pair breaking parameter of $\epsilon_c \simeq 0.5$. This value is typical of amorphous transition metal superconductors.[11] In addition, this regime also signifies the breakdown of the slow variation approximation in the Ginzberg-Landau free energy functional.[7,8] Recently, it has been pointed out that a short-wavelength cutoff is also required for the MT contribution.[11] Because of these complications and in lieu of a complete theory, it is meaningful to consider only the region dominated by the AL contribution, that is $\ln\epsilon \lesssim -4$ in the present model. Then, only inhomogeneities on the scale of $\gtrsim 8\xi_0$ (the zero-temperature coherence length) contributes to the composition fluctuation. Below and above T_{c0}, say $T \simeq 0.5$ and $1.5T_{c0}$, inhomogeneities on the scale of ξ_0 becomes important. We also restrict our discussion to the case of composition fluctuation due to incipient decomposition or crystallization on the scale of ξ_0 in the amorphous host. Then, this fluctuation well below and above T_{c0} would be larger than that near T_{c0}. Macroscopic phase separation with two phases percolating each other such as in Pb-Sb-Au alloys will not be discussed.[12] Extending the model in Ref. 9 to a three-dimensional superconductor, the total resistivity near T_{c0} can be written in the following form:

$$\frac{R(T)}{R_0} = \frac{1}{\gamma}\int_0^\infty \frac{\sigma_0}{\sigma'_{AL}(T_c)+\sigma_0}\, g\left(\frac{T_c - T_{c0}}{\gamma}\right) dT_c \,, \quad (1)$$

where g is the normalized T_c distribution function, γ is the characteristic width of this function, and $\sigma'_{\rm AL}(T_c)$ is the AL contribution from the sample region with transition temperature at T_c. T_{c0} is the temperature at which resistivity vanishes. By changing variables to $y=(T_c-T_{c0})/\gamma$, expression (1) becomes

$$\frac{R(T)}{R_0}=\int_{-\infty}^{\infty}\frac{(T-T_{c0}-\gamma y)^{1/2}}{(T-T_{c0}-\gamma y)^{1/2}+\tau_1(T_{c0}+\gamma y)^{1/2}}g(y)\,dy\ , \tag{2}$$

where $\tau_1=e^2/32\hbar\xi_0\sigma_0$. Without loss of generality, we have extended both the lower and upper limits of integration to $-\infty$ and $+\infty$, respectively.[9] Defining the moments of the distribution function as $M_n=\int_{-\infty}^{\infty}x^n g(x)\,dx$, we obtain the following expression for $\sigma'_{\rm AL}(T)$ up to its second moment:

$$\frac{\sigma'_{\rm AL}(T)}{\sigma_0}=\frac{\sigma'_{\rm AL}(T_{c0})}{\sigma_0}\left[1+\left(\frac{\gamma M_1}{2\epsilon}+\frac{3\gamma^2M_2}{8\epsilon^2}\right)\left(1+\frac{\sigma'_{\rm AL}(T_{c0})}{\sigma_0}\right)\right]\ . \tag{3}$$

If one takes $g(T_c-T_{c0}/\gamma)$ to be an even function, then for $\sigma'_{\rm AL}(T_{c0})/\sigma_0<1$, the additional divergence in $\sigma'_{\rm AL}(T)$ varies as $\epsilon^{-5/2}$. As discussed beforehand, the characteristic width γ depends on the coherence length $\xi(T)$. Thus one would expect that very near T_{c0}, say $\ln\epsilon<-6$, the inhomogeneities will be averaged out on the scale of $\xi(T)$ and the usual $\epsilon^{-1/2}$ dependence should be recovered. Straight lines of slopes $-1/2$ and $-5/2$ are drawn in Fig. 1 for comparison. The agreement is reasonable.

Next we consider the case of statistical fluctuation in bulk samples. For a large number of atoms $N(\xi)$ enclosed within a characteristic volume ξ^3 at alloy composition x, the composition fluctuation varies as $[x/N(\xi)]^{1/2}$. Putting the temperature dependence into ξ, this becomes $[x/N(\xi_0)]^{1/2}\epsilon^{3/4}$ for $\xi\sim\epsilon^{-1/2}$. Then the characteristic width γ for the T_c distribution function is given by the approximate expression

$$\gamma\simeq\left(\frac{x}{N(\xi_0)}\right)^{1/2}\left(\frac{dT_c}{dx}\right)\epsilon^{3/4}\ . \tag{4}$$

Taking $N(\xi_0)$ to be 10^4 atoms and $(dT_c/dx)\simeq 0.1$ K/at.% for amorphous Zr-Pd alloys,[11] one obtains $\gamma\simeq 0.08\epsilon^{3/4}$. To observe positive deviation from the AL term, one requires that $\epsilon\sim\gamma$ as can be seen from expression (3). This puts an upper limit on $\epsilon\lesssim 4\times10^{-5}$ K or $\ln\epsilon\lesssim-10$. Therefore, within the temperature resolution of the present experiments, the correction term is very small. It can be said that statistical fluctuation in composition does not alter the temperature dependence of AL paraconductivity. This can be compared with the nonstatistical fluctuation where a simple relationship between γ and ϵ cannot be obtained. The present result agrees well with the data on the otherwise homogeneous Zr_3Pd and Zr_3Rh samples.

Before we examine the various models of H_{c2}, it is appropriate to discuss the possible forms of inhomogeneities in amorphous samples. For the alloy systems studied, they undergo eutectic crystallization into phases with different compositions from the amorphous hosts. For example, evidence of crystalline La_2Au and α-Zr embedded in amorphous La-Au and Zr-Pd alloys was observed.[11] If crystallization were not suppressed during the supercooling process, there would be a tendency for the composition of the regions in the neighborhood of these crystallites to fluctuate. Another form of inhomogeneity might occur, for example, in alloys where several intermetallic compounds or a sizable homogeneity range for an intermetallic compound exists in the composition of interest. Then, there would be a tendency towards microscopic incipient decomposition. This happens especially in ternary alloys where a large choice of short-range order is available. Examples of macroscopic phase separation ($>\xi_0$) had been reported in several amorphous ternary alloys.[13] We have noted in our paraconductivity studies that the characteristic distribution in T_c on a scale of $\sim10\xi_0$ is approximately 30 mK. The deviation from GLAG prediction on the $H_{c2}(T)$ curve is more noticeable for $\epsilon>0.6$ corresponding to a scale of $<1.3\xi_0$. On such a scale, the degree of inhomogeneity is expected to be quite large. Thus, it is meaningful to incorporate distributions in T_c and H_{c2} in any model attempting to discuss the trend in $H_{c2}(T)$. Various authors have developed models along this line.[2–4]

We would like to point out that an additional mechanism for the enhancement of $H_{c2}(T)$ might be taking place in inhomogeneous samples. If inhomogeneous superconducting regions are present in a sample, there will be inhomogeneous normal regions as well. From free energy considerations, the flux lines will be more favorably trapped or pinned in the normal regions. It would be difficult to mathematically formulate this problem for three-dimensional superconductors. However, one can imagine bundling and twisting of flux lines as they seek for the normal regions. Normally, these vortices would have filled a homogeneous type-II supercondutor. In an inhomogeneous superconductor, as ξ decreases with temperature to the point when it is comparable to the scale of inhomogeneities, vortex pinning by the normal regions becomes appreciable. There will be a redistribution of vortices and as a result, the density of vortices in the still superconducting regions will decrease. This in turn allows an increased critical field for these regions. From our experimental results, this suggests that the inhomogeneities are on the scale of ξ_0. This idea is similar to the case of layered superconductors where anomalous $H_{c2}(T)$ parallel to the layers were observed.[14] This was attributed to the fact that when ξ is comparable to the period of the layers, the normal cores of the vortices can fit between the layers where they have no pair-breaking effect on the superconducting layers. For inhomogeneous bulk samples, similar effect might have played a role on the upper critical field. However, from a naive topological point of view, one would expect this effect to be less dominant than in layered compounds.

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[1]M. Tenhover, W. L. Johnson, and C. C. Tsuei, Solid State Commun. 38, 53 (1981).
[2]W. L. Carter, S. J. Poon, J. W. Hull, and T. H. Geballe, Solid State Commun. 39, 41 (1981).
[3]B. M. Clemens, M. Tenhover, and W. J. Johnson, Physica 107B+C, 319 (1981).
[4]K. Agyeman, C. C. Tsuei, and P. Chaudhari (private communication).
[5]S. J. Poon *et al.* (unpublished).
[6]J. L. Vicent, S. J. Hillenius, and R. V. Coleman, Phys. Rev. Lett. 44, 892 (1980).
[7]W. J. Johnson and C. C. Tsuei, Phys. Rev. B 13, 4827 (1976).
[8]W. L. Johnson, C. C. Tsuei, and P. Chaudari, Phys. Rev. B 17, 2884 (1978).
[9]P. M. Horn, Phys. Lett. 41A, 361 (1972). For random distribution of inhomogeneities in a three-dimensional alloy, we sum over the distribution function the sample resistivity since all parallel paths are equally favorable for the conduction electrons.
[10]K. Maki, Prog. Theor. Phys. 45, 1016 (1971).
[11]S. J. Poon, in *Amorphous Metallic Alloys,* edited by F. Luborsky (in press), Chap. 20.
[12]C. O. Kim and W. L. Johnson, Phys. Rev. B 23, 143 (1981).
[13]U. Köster and U. Herold, in *Topics in Applied Physics: Glassy Metals I,* edited by H.-J. Güntherodt and H. Beck (Springer-Verlag, New York, 1981), Vol. 46, p. 225.
[14]M. R. Beasley, in *Inhomogeneous Superconductors—1979,* edited by D. U. Gubser *et al.*, AIP Conf. Proc. No. 58 (AIP, New York, 1980), p. 186.