Proximity-effect-induced superconductivity in very dilute Pb-Zn composites

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Very dilute bulk dispersions of micrometer-sized particles of Pb in Zn show resistive superconducting transitions at up to 3 K, far above that of Zn itself (0.8 K), although the Pb volume fraction is only 0.006. The I-V characteristics contain reproducible structure that is not understood. At lower temperatures the samples expel a small, but significant, amount of flux. The superconducting transition can be explained in terms of proximity-effect coupling of the Pb grains through the Zn matrix.

The study of inhomogeneous superconductors has grown enormously in the past few years,[1] but most of the work has been on two-dimensional (2D) systems. In this paper we report on the behavior of clean 3D composites of superconductor (Pb) randomly dispersed in normal metal (Zn) that show resistive superconducting transitions at temperatures well above T_c(Zn) for a remarkably small volume fraction of Pb (Fig. 1). Although the Pb particles have average spacing an order of magnitude larger than the appropriate superconducting coherence length of the Zn matrix, we believe that the residual weak proximity-effect coupling suffices to induce bulk superconducting behavior.

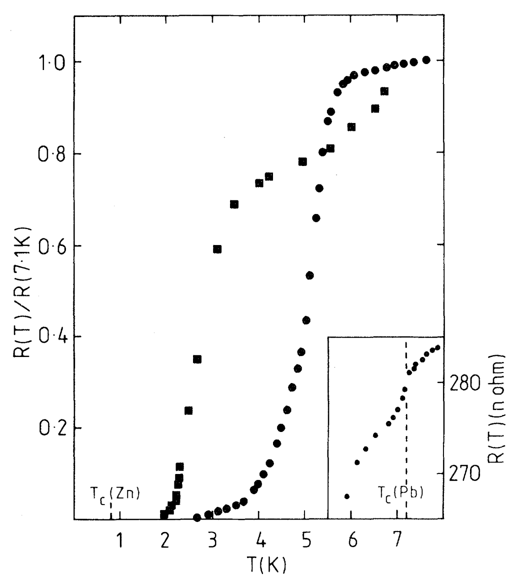

FIG. 1. Normalized resistance for samples Pb-Zn-1 (squares; $I = 10$ mA, $J = 900$ A m^{-2}) and Pb-Zn-3 (circles; $I = 1$ mA, $J = 400$ A m^{-2}). The higher current density in sample Pb-Zn-1 compared with that in sample Pb-Zn-3 has depressed the transition in the former by at most 0.3 K. The more pronounced temperature dependence for Pb-Zn-1 above 5 K is because of the larger relative phonon contribution to the resistance in that sample. Inset: Resistance near T_c(Pb) for sample Pb-Zn-3.

Some years ago Tsuei and Newkirk found that Cu containing similarly small amounts of Nb showed a high T_c.[2] They attributed the superconductivity to precipitated small particles of Nb coupled by the proximity effect through the normal matrix. However, because the metallurgy of the Cu-Nb system is more complicated than that of Zn-Pb, the morphology of their samples was much less well defined and, consequently, quantitative analysis of their data was impossible. We have been able both to characterize our samples and to measure their transport properties in detail; this has enabled us to make a semiquantitative comparison with a simple model for the composite material.

Our preparative technique depends on the solubility of Pb in liquid Zn (0.3 at.% at the melting point, equivalent to $f = 0.006$) and its insolubility (less than 10^{-4}at.%) in solid Zn.[3] Thus, when liquid Zn saturated with Pb freezes, liquid Pb droplets phase separate and become entrapped within it. The size and distribution of the Pb particles depend somewhat on the details of the freezing process and so vary between samples,[4] but the volume fraction is always the same. In contrast, Nb has limited solubility in solid Cu, about 1 at.% at 1100 °C, diminishing to ~ 0.1 at.% at room temperature. Thus in Tsuei and Newkirk's Cu-Nb composites, the size, shape, and distribution of the Nb particles depended sensitively on details of the metallurgical treatment and were much less uniform than that of the Pb particles in our composites. Indeed, the particles may even have formed a continuous, spongelike three-dimensional network.[5]

We were aware that small amounts of filamentary superconductor can confer apparent superconductivity of the entire sample,[6] but scanning electron microscope (SEM) examination showed the Pb particles to be spheroidal, as would be expected of particles that had phase separated as liquid droplets. Furthermore,

TABLE I. Sample characteristics.

Sample Pb-Zn	$\frac{R\,(300\text{ K})^{a}}{R\,(4.2\text{ K})}$	T_c(K) [b]	Pb volume fraction, f, determined from: Chem. anal.	SEM	Resistance	Magnetization
1	3900	2.00				
2	900	2.54	0.0057 ± 0.0003	0.006–0.02		
3	450	3.00	0.0065 ± 0.0003	0.007–0.02	0.004 ± 0.001	0.004 ± 0.001

[a]Measured with 1 A current, so that proximity-effect coupling is suppressed.
[b]Defined as the temperature at which a current density of 920 A m^{-2} restores 1% of the normal-state resistance.

measurements of the resistance, resistive critical field, and magnetization,[4] all of which are sensitive to particle shape, also indicated that the particles are nearly spherical. The typical radius r is 1 μm [considerably larger than the coherence length ξ_0(Pb) $=0.07$ μm] and typical separation is 5 μm. In addition to chemical analysis we have estimated the Pb concentration from the SEM backscattered images (Table I).

Electrical resistances were measured on spark-cut bars 0.1–0.2 cm^2 in cross section and up to 3 cm long using a superconducting quantum interference device resistance bridge.[7] The ambient magnetic field was less than 10 mOe, although data were taken also in an applied field.[4] Precautions taken to avoid extraneous causes of superconductivity included etching the sample surface and using nonsuperconducting solder for the voltage contacts. We checked also on sample homogeneity by examining different portions of the same ingot.

We have looked at samples from three different ingots, and all show qualitatively the same resistive behavior (Fig. 1); in every case the resistance drops to zero by 2 K. At the higher temperatures the Zn is sufficiently pure for the phonon contribution to the resistivity to be visible. Near 7 K there is an additional small change δR (inset to Fig. 1), associated with the Pb transition, broadened by the particle size distribution. For a matrix of resistivity ρ_{Zn} containing a volume fraction f of *spherical* particles that undergo a resistive transition from ρ_{Pb} to 0, effective-medium theory[8] predicts (to order f)

$$\delta R/R_n = 9f/[2+(\rho_{Zn}/\rho_{Pb})] ,$$

where $R_n = R(7.1\text{ K})$. We have used the observed δR and $\rho_{Pb} =$ 16 nohm cm (from a separate measurement) to obtain another estimate of f (Table I). Deviations below the resistance expected of Zn become apparent at 4 to 6 K, depending on sample, and at lower temperatures the resistance is strongly current dependent.

Direct recordings of the I-V characteristics (Fig. 2), which were reversible, show that in the superconducting state the resistance is less than 10^{-12} ohm, i.e., $10^{-5}R_n$. In all samples the onset of dissipation occurs at a well-defined critical current $I_c(T)$, which varies exponentially with temperature [Fig. 3(a)]. Furthermore, at larger currents the I-V characteristics always show distinct (but repeatable and reversible) changes of slope without any associated jump in voltage. The most striking example is shown in Fig. 2. The slopes of the almost linear regions between these "kinks" are two orders of magnitude less than R_n, appear to have nearly integer ratios to each other, and are approximately proportional to temperature [Fig. 3(b)]. Other samples exhibited rather less sharp kinks but still included unmistakable abrupt changes in slope. Similar kinks have been observed by one of us in the I-V characteristics of superconductor-insulator (Nb-KCl) composites[9] and by

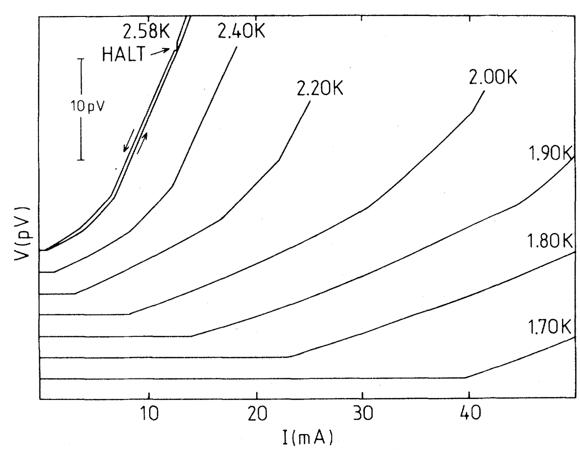

FIG. 2. Current-voltage characteristic at several temperatures below T_c for sample Pb-Zn-3. Each curve starts off at zero voltage but, for clarity, successive curves have been shifted vertically. The small displacement between the $T=2.58$ K curves for increasing and decreasing currents arises solely from recorder time constants, as demonstrated by halting the current sweep.

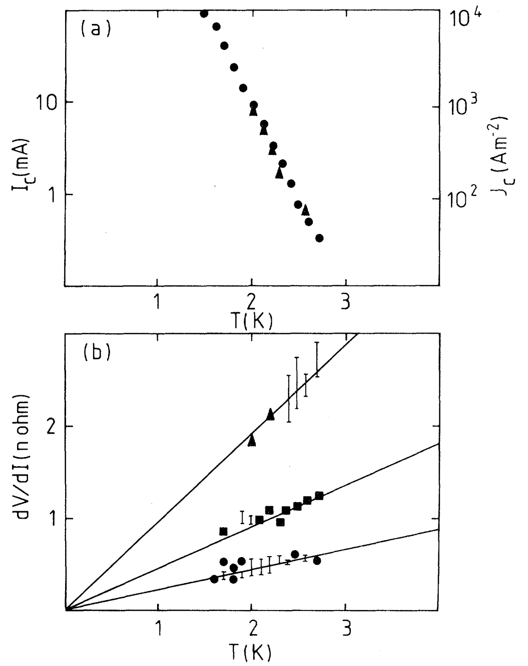

FIG. 3. (a) Critical current and critical current density (log scales) for samples Pb-Zn-2 (b) (triangles) and Pb-Zn-3 (circles). (b) Differential resistances of the first three "linear" regions of the I-V's of Pb-Zn-3 (Fig. 2). Some of the regions appear to be perfectly straight (single point), others contain a succession of line segments with minor changes of slope between them (multiple data points), and some are slightly curved (error bar). The straight lines drawn through the data points have gradients in the ratio 1:2.1:4.4.

another group in pressed Nb-In composites.[10]

Magnetization measurements were made in a vibrating sample magnetometer on a needle-shaped sample; these will be described in detail elsewhere.[4] Only at temperatures below those of the resistive transition did flux exclusion (of a slowly applied field) become significant, and even at 1.5 K the diamagnetic susceptibility was only 50% of the full Meissner value of $-1/4\pi$. This phenomenon, the same as seen by Tsuei and Newkirk, suggests a small average amplitude of the superconducting order parameter. A separate experiment, in which the sample was cooled in a constant weak applied field, showed that over the same temperature interval a small amount of flux, corresponding to 3% of the sample volume, was actually expelled. Magnetization measurements above 5.5 K allowed another estimate of the Pb volume fraction to be made (Table I).

In order to see whether the proximity effect can account for induced superconductivity at such a small superconducting fraction, we have made estimates based on a greatly simplified model[4] with the same fraction of Pb distributed as spheres of uniform radius $r = 1$ μm on a simple cubic lattice of spacing a (9 μm for $f = 0.006$). We treat the supercurrent carried by each of the bonds as independent. The temperature dependence of the critical current is dominated by an exponential factor[11]

$$I_c(T) = I_c(0)\exp[-K(T)\bar{b}] \ . \tag{1}$$

$K(T)$ is given approximately by $2\pi k_B T/\hbar v_F$, and $\bar{b}$ is the appropriately averaged distance between the Pb particles. For Zn, we estimate $T[K(T)]^{-1} L \approx 1.0$ μm K. The observed exponential variation of I_c with temperature for two different samples [Fig. 3(b)] corresponds to $\bar{b} = 4.8$ and 5.3 μm, whereas for the regular array $\bar{b} = a - 2r = 7$ μm. In the real random composite the important current paths will be those on which the steps are shorter than average, so that to find a value of $\bar{b}$ that is somewhat smaller than predicted by the crude lattice model seems physically very reasonable.

Our crude model suggests that the prefactor in Eq. (1) corresponds to a current density given by[11] $J_c(0) \approx (\pi r^2/a^2)\hbar en/m\bar{b}$, where m and n are the electronic mass and number density. For our model parameters $J_c(0) = 10^{10}$ A $\mathrm{m^{-2}}$, the measured prefactors [from Fig. 3(b)] are 10^7 and 10^8 A $\mathrm{m^{-2}}$. These estimates are exceedingly rough, to be relied on only to factors of 10, but they do show that proximity-effect coupling between the Pb particles, weak as it is, suffices to provide the observed magnitude of critical currents.

Because the coupling between the Pb particles is weak, it is important to check whether it can withstand thermal fluctuations. In the lattice model thermal fluctuations become important when $J_c(T) \lesssim (2e/ha^2)k_B T$, equivalent to 500 A $\mathrm{m^{-2}K^{-1}}$. The measured critical current densities [Fig. 3(b)] encompass this criterion, implying that in the real random composite material, where there is a broad spectrum of coupling strengths along different paths, at all temperatures there are plenty of weaker paths that are susceptible to thermal fluctuations. Thus the current distribution will not be a static one (although the rate of change will be limited by the high conductivity of the Zn matrix). This picture suggests that fluctuations are important to the sudden onset of dissipation (Fig. 2), which is presently not understood.

We do not have any explanation either for the discontinuities in slope of the I-V characteristics. Our Zn-Pb system is the third in which they have been seen and is very different in composition from the other two, so they are probably a general feature of superconductivity in 3D composites.

We have seen very recently the same kind of proximity-effect-induced superconductivity in a Pb-Al composite ($f = 0.006$) made by the same technique. The results of these experiments, together with a fuller description of the measurements on the Pb-Zn composites, will be published elsewhere.[4]

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