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Comments

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Coupling and isolation: Critical field and transition temperature of superconducting granular aluminum

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Measurements have been made of the critical magnetic field of superconducting granular aluminum ($d \sim 30$ Å) down to temperatures well below T_c ($t^2 < 0.1$). The results show that it is possible to have the coupling between grains weak enough and the temperature low enough so that the critical field is that of the isolated grain while at the same time the large fluctuations expected in isolated grains of this size are suppressed. The results for T_c, together with those from other sources, indicate that the maximum T_c is a function of grain size only.

Granular metals have been studied increasingly during the last decade, and probably none more than granular aluminum. Nevertheless the property which seemed most intriguing from the start, namely, the enhanced superconducting transition temperature, continues to elude our understanding. The presence of the insulating material between the metallic grains, the coupling between electrons on adjacent grains, the disorder of the material, and the size of the grains, have all been suspected as causes of the enhancement.[1]

We have been led to reexamine the factors which influence the transition temperature in connection with our measurements of the critical fields. In this Comment we review the evidence for attributing the enhancement entirely to a size effect. The mechanism of such a size effect remains unclear. It could be related to the ratio of surface area to grain volume, or to the electronic mean-free path.

The role of the coupling between grains is nevertheless crucial. In isolated grains of 50 Å or less superconductivity is suppressed by fluctuation effects.[2,3] Coupling will decrease the fluctuations. For sufficiently weak coupling certain average thermodynamic properties can, however, remain equal to those of the isolated grains. The fact that different properties of the isolated grains are differently affected by fluctuations was already evident from Ref. 2. The additional fact that coupling has different effects on different properties has been discussed by Kawabata,[4] by Šimánek,[5] and by Deutscher *et al.*[6]

Figure 1 shows the upper critical fields extrapolated to zero temperature, $H_c(0)$, and the transition temperatures in zero field, T_c, for a series of granular aluminum specimens. The specimens were evaporated from an electron-beam source onto water-cooled glass substrates in a small amount of oxygen, and are similar to those which we have used in earlier investigations.[3,7] They consist of aluminum grains whose size is about 30 Å, with amorphous Al_2O_3 between the grains. The measurements were made in magnetic fields to 9 T, perpendicular to the plane of the specimens, at temperatures from 0.3 to 4 K. $H_c(T)$ and T_c were defined by the values of H and T where the resistance was equal to half its normal-state

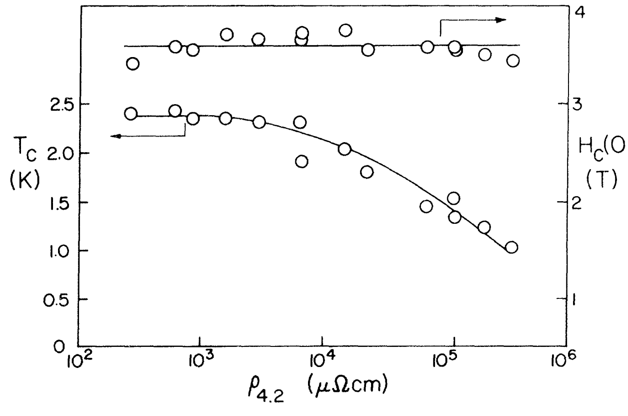

FIG. 1. The critical magnetic field extrapolated to zero temperature, $H_c(0)$, and the superconducting transition temperature, T_c, for a series of granular aluminum specimens.

value. Two of the specimens were also measured in parallel fields. The results for $H_c(0)$ were the same to 0.1 T, although at higher temperatures $H_c(T)$ showed the anisotropy previously observed by Deutscher and Dodds.[8]

The transition temperature is approximately constant for specimens whose resistivities are between 100 and 3000 $\mu\Omega$ cm.[9] It decreases for higher resistivities, presumably because of the destruction of the Josephson coupling by charging effects.[10,11] $H_c(0)$, on the other hand remains approximately constant while T_c decreases, as long as superconductivity can still be observed.

This result is consistent with recent work on Al-Ge,[6] where it was shown that there is a range of resistivities for which the coupling between grains is sufficiently strong for zero electrical resistance to be observed, but sufficiently weak so that the observed values of the critical field are those expected for the isolated grains.[12]

It is shown in Ref. 6 that the observed critical field at $T=0$ is that of the isolated grain if $4S^2\sigma\rho_n >> \xi^2(0)$. Here $\xi(0)$ is the coherence length at $T=0$ of the superconductor from which the grains are made, equal to $0.85\sqrt{\xi_0 l}$, l is the electronic mean-free path, ξ_0 is the BCS coherence length, S is the distance between grain centers and therefore close to the grain diameter, σ is the bulk resistivity of the metal of the grain, and ρ_n is the specimen resistivity.

For comparison with our data we use $S=30$ Å, $l=S/2=15$ Å, $\xi_0=10^4$ Å (the value for pure aluminum adjusted for the higher T_c), and $l/\sigma=10^{-11}$ Ω cm^2. With these numbers the observed value for $H_c(0)$ is expected to become that of the isolated grain for $\rho_n >> 2000$ $\mu\Omega$ cm. For the larger grains of Ref. 6 ($S\sim 100$ Å) the isolated grain limit is reached at resistivities lower by a factor of about 10. In that case, for films whose normal-state resistivity at 4.2 K is greater than 2000 $\mu\Omega$ cm, the observed $H_c(T)$ is in good agreement with the values calculated for an isolated sphere of diameter S.[12]

For our material, with its smaller grain size, the situation is more complicated for two reasons. The first is that $H_c(0)$ (~ 3.6 T) is limited by the Pauli paramagnetic effect.[13] Tedrow and Meservey[14] have demonstrated that the paramagnetic limit is reached in aluminum films with thickness between 37 and 77 Å. For nine films in this range, with the field parallel to the film, they found $H_c(0)/T_c$ to be approximately constant and equal to (1.9 ± 0.2) T/K, in good accord with the value expected from recent theoretical considerations of the paramagnetic limit.[15]

The second complication is that our grains are so small that when they are sufficiently weakly coupled thermodynamic fluctuations broaden the superconducting transition to the extent that the discontinuity in the heat capacity is no longer observed.[2,3] Nevertheless, since the fluctuations die out as T goes to zero, the critical field at zero temperature can still be given a meaning analogous to that in larger grains. It is the critical field which would be observed in grains of that size in the absence of any fluctuations.

Figure 1 shows $H_c(0)$ to be approximately constant. The constant value and isotropy of $H_c(0)$ confirm that it is characteristic of the isolated grains and that is does not depend on the coupling between them. The experiment demonstrates that the magnetic transition to the normal state occurs because of destruction of superconductivity in the grains, rather than through the destruction of the coupling.

Although the observed T_c for the specimen is not proportional to $H_c(0)$, we nevertheless define a quantity T_{c0} which is proportional to $H_c(0)$, related as in the Pauli limit. In large grains T_{c0} would be the transition temperature of the isolated grain; in our grains it would not be observable as a property of the isolated grain because of fluctuation effects. If the proportionality constant is again 1.9 T/K then for our observed field of 3.6 T, T_{c0} would be about 1.9 K.

We note that this value is close to the maximum value of T_c (~ 2.4 K) observed for our series of specimens. We now make the hypothesis that the maximum observed T_c for the system of coupled grains is equal to the quantity T_{c0} which is related to the properties of the isolated grain, and which for larger grains would be the observed transition temperature of the isolated grain.

On Fig. 2 we have gathered the results of several measurements of grain size, d, and the corresonding values of the transition temperature in the region where T_c has its maximum value and is approximate-

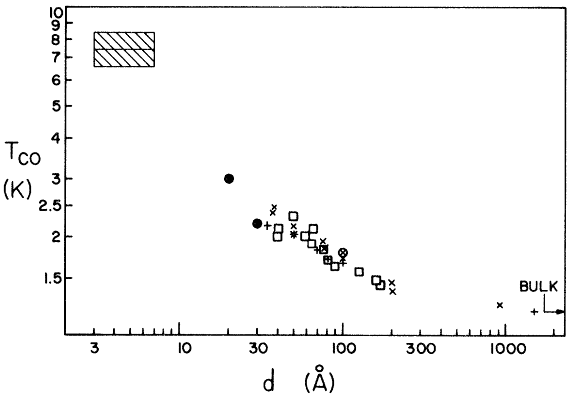

FIG. 2. The transition temperature as a function of grain size for a variety of aluminum-based specimens: ● Refs. 9 and 16; ○ Ref. 6; □ Ref. 17; × Ref. 14; and + Ref. 18. For Refs. 14 and 18 the points are plotted at the value of the film thickness. The shaded region at the left top represent the values of T_c for films evaporated onto liquid-helium-cooled substrates (Ref. 24) and implanted with Ge and Si (Ref. 25).

ly independent of specimen resistivity. In accordance with our hypothesis we refer to this value as T_{c0}. The full circle at $d = 30$ Å is for specimens similar to ours.[9,16] If the specimens are deposited on substrates cooled with liquid nitrogen the grain size becomes about 20 Å, and T_c rises to 3 K.[16] There is a point at $d = 100$ Å and $T_{c0} = 1.8$ K for the Al-Ge specimens of Ref. 6. Other measurements of grain size and T_c for oxidized aluminum films are those of Pettit and Silcox,[17] who measured T_c and d for 12 films with d between 40 and 160 Å.

We have also included on Fig. 2 the points corresponding to the thin-film specimens of Tedrow and Meservey,[14] and of Cherney and Shewchun,[18] plotted at the values for their film thickness. It is likely that their specimens consisted of islands of aluminum whose extent along the film was approximately equal to the film thickness. This is supported by their measured resistivities, which are of the same order as the resistivities of the granular films. We see that the transition temperatures for the granular specimens lie near the same curve of T_c against d.[19–22]

Figure 2 also shows that the points lie on approximately the same curve regardless of the material of the dielectric, Ge or Al_2O_3.[23] In the case of the films of Refs. 17 and Ref. 18 the islands are also likely to be separated by regions of oxide.

Considerably higher transition temperatures have been observed for films deposted on liquid-helium cooled substrates,[24] and for films implanted with Ge and Si at 8 K.[25] The structure of these films is not known, but it is quite likely that they are either granular or that the effective size of the metallic region is not far from the interatomic spacing, i.e., several angstroms. Figure 2 shows that a size of that order would be quite consistent with the other results on the figure, i.e., that the T_c enhancement could also in these cases be ascribed to the same size-related effect.

In truly isolated grains it is no longer possible to measure an electrical transition. Susceptibility and heat-capacity transitions can be observed, but only in sufficiently large grains. The transition is broadened, and T_c is lowered. This is apparent in the susceptibility measurements of Buhrman and Halperin,[26] and in specific-heat measurements on Al-Al_2O_3 (Ref. 3) and Al-Ge.[27]

We cannot rule out the possibility of some influence by a disordered region surrounding the grains, but the experimental results on different systems seem to indicate that the effect is at least approximately independent of the material of such a layer. The absence of any influence of the nature of the dielectric confirms conclusions which have been reached somewhat more indirectly before.[16]

We conclude that for weakly coupled grains the evidence of Fig. 2 is consistent and persuasive. The maximum measured transition temperature for any system is equal to that expected for isolated grains with the fluctuation effects suppressed, and it is a function of grain size only. However, it seems that the transition temperature characteristic of small isolated grains can only be measured when some small amount of coupling remains between the grains.

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thickness the resulting points are similar to the others on Fig. 2.

[21] Results different from those of Fig. 2 were obtained by M. Strongin, O. F. Kammerer, H. H. Farrell, and D. L. Miller, Phys. Rev. Lett. 30, 129 (1973). They quote values of T_c between 1.37 and 1.48 K for films with thicknesses between 30 and 150 Å, grown epitaxially on silicon and covered with germanium. The grain size is not known, and it is possible that the structure of these films is different from that of the other films to which we have referred.

[22] Films with grain sizes of about 150 Å were investigated by A. Saxena, J. E. Crow, and M. Strongin, Bull. Am. Phys. Soc. 17, 333 (1972). The observed T_c (near 1.4 K) has been quoted (Refs. 21 and 26) to show that there is little dependence of T_c on d. It is, however, quite consistent with the results shown on Fig. 2.

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