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Enhanced Superconductivity in Ultrarapidly Quenched Bulk Aluminum-Copper Alloy

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Transition temperatures T_c of up to 2.95 °K have been obtained in bulk samples of an aluminum-copper alloy containing 0.85-at.% Cu that had been subjected to the process of ultrarapid quenching. The samples were obtained by a new method of ultrarapid quenching which secures large thin samples that had undergone cooling rates from the melt of about 10^6 °K $\sec^{-1}$. At the same time, samples conventionally prepared from the same melt showed the normal behavior expected from such an alloy. The rise of T_c is linked to the quenching speed and is proportional to the residual resistance. A possible explanation of the phenomenon is offered by evoking a phonon surface-mode mechanism.

Considerable amount of work has been done on the problem of dealing with the shift in the transition temperature of bulk metals containing various impurities. More specifically, for metals such as aluminum, theoretical models[1–3] have been made to account for small shifts in T_c due to nonmagnetic impurities. Measurements made on such systems[4–6] indicate good agreement with the theoretical predictions. Generally, dilute alloys prepared conventionally and either annealed or cold worked show small shifts in T_c.

On the other hand, thin metallic films deposited on cold substrates have exhibited deviations of T_c from the bulk value,[7] which in some cases can be very large. Metallic-film sandwiches[8] and alloyed films[9] exhibit unusually large effects of this kind and attempts have been made to explain this in terms of the increase of electron-phonon coupling through the lowering of the phonon frequencies.[8] A more detailed theoretical model has been put forward by Dickey and Paskin[10] to account for this effect through surface modes in small particles that produce changes in the phonon spectrum.

We report here observations of a large increase in T_c on the bulk dilute alloy of aluminum with 0.85-at.% Cu which has been subjected to ultrarapid quenching (URQ) from the liquid state at a rate of 10^6 °K $\sec^{-1}$. The samples of URQ alloy were prepared by a method described elsewhere[11] starting from wires of conventionally prepared alloy. The latter were prepared by melting 99.997%-pure Al with the corresponding quantity of electrolytically pure Cu, homogenizing the alloy by heating for three days at 540 °C in a neutral atmosphere, and then quenching it to obtain a solid solution. The alloy was then drawn into wires 1 mm in diameter. At the same time as the URQ samples were prepared, some wire was melted in the same way and using the same procedure as for UR quenching, but instead it was quenched normally in iced water and rolled to a thin foil. Samples were made of this foil, as well as the original wires, and electrical measurements were made on these in order to eliminate any possible effects of impurities accidentally included in the URQ samples. The latter were obtained as thin (20–30 μm), long (15 mm), and narrow (0.5–1.0 mm) strips and they were mounted for electrical measurements by a method[12] we normally use for very small samples. Two samples of URQ pure aluminum were included in the measurements to test the possible effect of UR quenching on pure aluminum.

All URQ samples show large residual-resistance ratios, about an order of magnitude higher than those exibited by a conventional alloy (Table I). While none of the samples conventionally prepared shows any deviation from Matthiessen's rule down to the lowest temperature reached in our cryostat (1.48 °K), the URQ samples exhibit superconducting transitions at temperatures which are considerably higher. No superconducting transition was observed for URQ pure-Al samples down to 1.48 °K. These transitions were measured by the standard method of compensation and simultaneously by the use of signal recorders. Temperature readings were kept within 0.01 °K and all transitions were covered several times going in both directions. Some of the curves thus obtained are shown in Fig. 1. It seems

TABLE I. Transition temperatures T_c given as two values. The first corresponds to a complete absence of detectable signals, while the second value corresponds to the center of the transition curves. The residual resistance ρ, the mean free path l, and the values of λ are calculated from expressions given in the text.

Sample	T_c(°K)		ρ	$1/l$ (10^6 cm^{-1})	λ
A	1.48	1.95	0.68	0.42	0.43
B	1.56	1.97	0.72	0.45	0.43
C	1.96	2.30	0.95	0.59	0.50
D	2.30	2.95	1.12	0.69	0.56

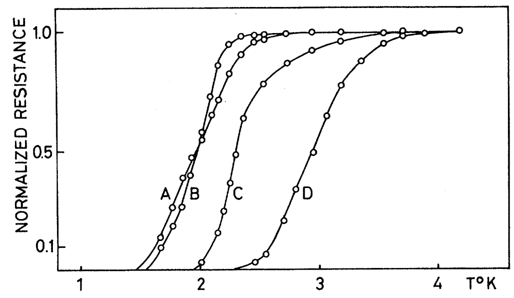

FIG. 1. Transition curves obtained from traces on the signal recorder. The points correspond to the signal level obtained through several passages across the temperature scale. Samples marked A–D are made from the same alloy but quenched at different speeds.

reasonable to assume that these transition temperatures would bear some simple relationship to the mean free path l which we can calculate for each sample from the simple relationship[5]

$$1/l = 0.62\times10^{6}\rho ,$$

where

$$\rho = R_{4.2}/(R_{293} - R_{4.2}).$$

As expected, the values of l, or for that matter of ρ, thus plotted as a function of T_c for various samples fall on a straight line (Fig. 2). Since the only parameter relevant for the measurements in question which varies from sample to sample is the quenching speed, it appears reasonable to assume that the shift in T_c observed is only a function of this speed, since Cu concentrations are the same for all samples. We have therefore made Debye-Scherrer diagrams from our samples and these reveal considerable smearing of lines characteristic for a highly disordered alloy. We estimate that the grain size in these samples falls in the interval of 100 to 1000 Å.

Several theoretical models have been put forward to account for the very large enhancement of the superconductivity in granular films.[13] The effects of lattice disorder on T_c have also been considered[14] with a view toward explaining the same behavior. Experimental results[8] have generally been interpreted in terms of the McMillan expression[15] for T_c which is given in the form

$$T_c = \frac{\Theta}{1.45}\,\exp\left[-\left(\frac{1.04(1+\lambda)}{\lambda-\mu^{*}(1+0.62\lambda)}\right)\right].$$

The Coulomb pseudopotential μ^* is taken as ≈ 0.1, and λ involves the phonon frequency spectrum and the electronic matrix elements,

$$\lambda = 2\int \alpha^{2}(\omega)\,F(\omega)\,\frac{d\omega}{\omega} = \frac{N_0\langle g^2\rangle}{M\langle\omega^2\rangle},$$

where N_0 is the electronic density of states at the Fermi surface, M is the nuclear mass, $\langle g^2\rangle$ is the Fermi-surface momentum averaged over the electronic matrix elements, and $\langle\omega^2\rangle$ is an average over the phonon frequencies. The increase in T_c would then be due to the increase in the value of λ owing to the lowering of the $\langle\omega^2\rangle$, since[15] $\lambda = \text{const}\times 1/M\langle\omega^2\rangle$ in the experimental situation considered. Dickey and Paskin[10] have considered in detail a mechanism where the $\langle\omega^2\rangle$ is lowered in material consisting of small plateletlike particles where low-frequency modes result in a shift of the frequency spectrum sufficiently large to account for the observed increases in T_c. Thus, for particles which consist of the order of 150 atoms arranged in plates three atoms thick, they find that the phonon frequency distribution $F(\omega)$ is sufficiently altered with respect to that in a normal crystal to give the observed effects. The authors obtain surface modes which they identify in considerable detail, and these are quite specific for relatively thin platelets. The question arises as to what extent one can apply their conclusions to the grains in our bulk samples. It appears probable that the longitudinal and transverse modes characteristic of a solid are likely, in our case, also to break up into surface modes whose relative magnitude will of course be different according to how far the thickness of our grains differs from the Dickey-Paskin platelets. Our grains still have to be in the form of plates, since an increase in thickness reduces the importance of surface modes. However, the process of URQ will presumably favor such grain formation.[16] Whatever the mechanism whereby the $\langle\omega^2\rangle$ is decreased, however, we can find the λ from our data using an approximate expression given[15] in the form

$$T_c/T_c^{\max} = (2/\lambda)^{1/2}\,\exp(\tfrac{1}{2} - 1/\lambda),$$

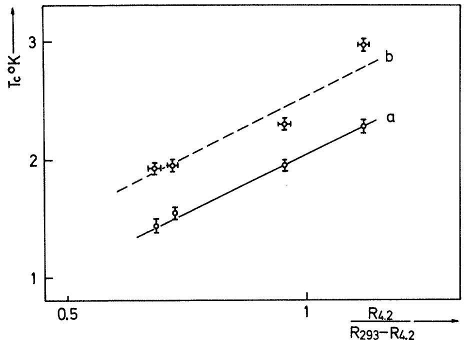

FIG. 2. Dependence of the transition temperatures T_c of samples A–D on the residual resistance. The straight line (a) corresponds to the temperatures where no more detectable signal is observed from the samples, while (b) corresponds to T_c defined as the transition midpoint. The slope of both straight lines is $\Delta T_c/\Delta\rho \approx 2$ °K.

where the T_c is the observed transition temperature. The values of λ that correspond to each of our samples are given in Table I.

It appears, therefore, that the effect reported here may be due to the formation of very small grains in the aluminum alloy owing to URQ, and that the presence of a small quantity of Cu is only incidental to the physical picture. However, pure UR-quenched aluminum shows no such effect, at least not nearly as great. This is probably due to the fact that the addition of Cu impurity greatly facilitates the formation of small platelike grains which are difficult to obtain in pure aluminum no matter how great the quenching speed. This hypothesis is further strengthened by other observers,[17] who find in working with Cu-doped quenched Al films that these crystallize in smaller grains than when pure metal is used.

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Motion of the Order Parameter in Type-II Transition-Element Superconductors in a High Magnetic Field

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The resistive state of type-II transition-element superconductors in a high magnetic field is studied using a technique due to Maki *et al.* The order parameters for the individual bands have similar Abrikosov-type solutions. Assuming a common upper critical field for the two bands, it is seen that the motions of the *s*- and *d*-electron pairs are controlled by different diffusion equations. The diffusion constants for the *s*- and *d*-pair motions are obtained for a typical transition-element superconductor. It is found that the *s*-band diffusion constant is not affected by the presence of the second band, but that the *d*-band diffusion constant is affected.

I. INTRODUCTION

When placed in a perpendicular magnetic field, a type-II superconductor exhibits a triangular array of vortices through which the magnetic field penetrates the superconductor. Using the Ginsburg-Landau equations, Abrikosov[1] showed the existence of a mixed state containing an array of quantized flux lines. Recently, a number of experiments[2] have been performed to investigate the motion of