

ENHANCEMENT OF SUPERCONDUCTIVITY IN METAL FILMS

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It has been found by Kammerer and Strongin¹ that tungsten films consisting of very small crystallinities have anomalously high transition temperatures T_c . It was suggested^{1,2} that the presence of oxide-metal interfaces gives rise to an enhanced effective electron-phonon interaction ρ and, therefore, an increased T_c , as proposed by Ginzburg.³ In this Letter, we report the effect of crystallite size on the T_c 's of several other metals. We have found that small crystallite size can increase the T_c 's of many superconductors.

The films were prepared by admitting controlled amounts of oxygen into the evaporation system as the metals were being evaporated. The results are summarized in Table I, which lists the highest T_c 's obtained for a particular metal and the corresponding average crystallite size d as determined by electron microscopy. For the Al, Sn, and In films, the electron diffraction patterns were diffuse and were characteristic of the particular metal. No extra rings corresponding to an oxide or any other impurity were detected. For the Pb film, the diffraction patterns revealed the presence of both Pb and PbO crystallites. In the case

Table I. Enhancement of superconductivity in several metal films. The films were prepared by admitting controlled amounts of oxygen during evaporation. Column 2 lists the highest T_c obtained for a particular metal. The transition widths were narrow ($\sim 0.01^\circ\text{K}$), and the T_c 's of all films did not change upon storing at room temperature. Columns 3 and 4 list the enhancement T_c/T_{c0} (T_{c0} is the transition temperature of the ordinary metal) and the corresponding average crystallite size. Column 5 gives the effective interaction ρ_0 for the ordinary metal as calculated from the formula [D. Pines, Phys. Rev. **109**, 208 (1958)] $T_{c0} = \frac{1}{2}\Theta_D \times \exp(-1/\rho_0)$. The thickness of the Al film was 800 \AA , while the thicknesses of the other films were greater than 2000 \AA .

Metal	T_c ($^\circ\text{K}$)	T_c/T_{c0}	d (\AA)	ρ_0
Al	3.0	2.6	40	0.19
Ga	7.2	6.5	...	0.20
Sn	4.1	1.1	110	0.31
In	3.7	1.1	110	0.36
Pb	7.2	1.0	...	0.53

of Ga, the crystallinity was so poor that it is not possible to give a meaningful value of d .

We have made a detailed study of the effect of varying crystallite size on the T_c of aluminum films. The aluminum was evaporated onto either a quartz or glass substrate from an aluminum-wetted tungsten filament⁴ at a rate of about $100 \text{ \AA}/\text{sec}$. The T_c 's were determined by the vanishing of dc electrical resistance. The lowest temperature we could reach in our measuring system was 1.26°K . In Fig. 1(a) is shown an electron micrograph and an electron diffraction pattern of a film which was evaporated at the lowest attainable pressure in our evaporator. Figures 1(b) and 1(c) are micrographs and diffraction patterns of films which were evaporated while oxygen was bled into the system. The nominal oxygen pressures, as indicated during the evaporation on an ionization gauge, were $1 \times 10^{-5} \text{ mm Hg}$ for film 1(b) and $5 \times 10^{-5} \text{ mm Hg}$ for film 1(c). The substrate was at a temperature of 300°K . Figure 1 demonstrates that as more

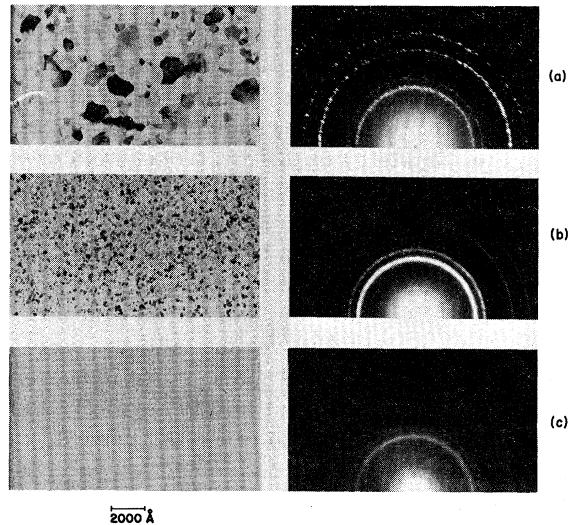


FIG. 1. Electron micrographs and diffraction patterns of aluminum films: (a) no oxygen admitted, normal resistivity $r_n = 1.5 \mu \Omega\text{-cm}$, average crystallite size $d = 1000 \text{ \AA}$, $T_c < 1.26^\circ\text{K}$; (b) oxygen pressure $1 \times 10^{-5} \text{ mm Hg}$, $r_n = 10 \mu \Omega\text{ cm}$, $d = 180 \text{ \AA}$, $T_c = 1.6^\circ\text{K}$; (c) oxygen pressure $5 \times 10^{-5} \text{ mm Hg}$, $r_n = 610 \mu \Omega\text{ cm}$, $d = 45 \text{ \AA}$, $T_c = 2.3^\circ\text{K}$. The films were 800 \AA thick and were evaporated on to a quartz substrate at 300°K .

oxygen is admitted during the deposition, T_C increases, d decreases, the electron diffraction patterns become more diffuse, and higher order rings diminish in intensity. The thickness of the films in Fig. 1 was approximately 800 Å. At a given oxygen pressure, variation of the film thickness from 300 to 3000 Å did not produce any significant variation in either T_C or crystallite size.

The variation of T_C with d is shown in Fig. 2. The substrate temperatures are indicated in the figure. The maximum T_C obtained with the substrate at 300°K was 2.3°K. Further enhancement of T_C was obtained by evaporating onto a cold substrate. We have also determined energy gaps Δ from tunneling measurements on Al-Al_xO_y-Pb diodes, and the measured temperature dependence of the energy gap could be accurately fitted by the BCS function $\Delta(T)$ with $2\Delta(0)/kT_C = 3.4$.

Several mechanisms have been considered for the observed enhancement of T_C . In particular, we have explored a model in which each crystallite is considered to be an isolated superconducting system, so that the quantization of electronic motion plays an important role. This model is a three-dimensional generalization of a one-dimensional calculation by Thomson and Blatt.⁵ A detailed calculation yields an enhancement of T_C which is in reasonable agreement with experiment. For this model, the conductivity mechanism is tunneling through the crystallite boundaries. The normal resistivity, in this case, is given by $r_n \approx (\sigma_0 d)^{-1}$, where σ_0 is the normal conductance per unit area of a single tunneling junction. Using the value⁶ $\sigma_0 = 10^6 \Omega^{-1} \text{ cm}^{-2}$, the computed r_n is more than three orders of magnitude larger than the observed values. Therefore, it was concluded that the above model does not apply and that each crystallite is strongly coupled to its neighbor.

It has been suggested^{2,3} that surface enhancement of superconductivity may arise from an increased effective electron-phonon interaction near the geometric boundaries of a superconductor. We propose that this mechanism also applies to crystallite boundaries and is responsible for the observed increase in T_C in our films. A basic difference between our model and the work⁸ on the effect of impurities and defects on the transition temperatures of superconductors is that, in our case, the impurities or defects (such as the surface of a crystallite)

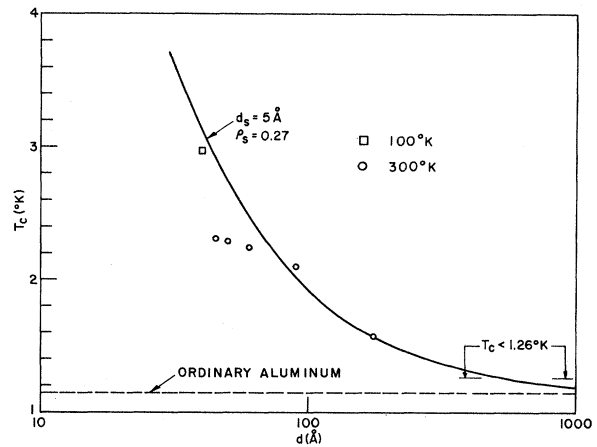


FIG. 2. Variation of T_C with the average crystallite size d of the aluminum films. The substrate temperature and the T_C of ordinary aluminum are indicated in the figure. The theoretical curve was computed from Eqs. (1) and (3).

are ordered in an array of boundaries, rather than randomly distributed throughout the sample. The question arises as to what specifically gives rise to the enhanced surface interaction. It is likely that the oxygen precipitates at the crystallite boundaries in the form of an oxide. In view of the suggestion^{1-3,7} that surface impurities may give rise to enhanced superconductivity, one is tempted to identify the oxide as such an impurity.

Following Strongin, Kammerer, and Paskin,⁹ we make use of the de Gennes¹⁰ layered-film model. We denote by ρ_s the electron-phonon interaction in a thin surface region of volume Ω_s encompassing the crystallite boundaries and let ρ_0 be the electron-phonon interaction of the ordinary metal, which has a volume $(\Omega - \Omega_s)$. If $\langle \hbar\omega \rangle$ is the BCS cutoff (which is assumed to be unchanged by the boundary), T_C is given by the expression

$$T_C = 1.14 \langle \hbar\omega \rangle \exp(-1/\rho), \quad (1)$$

where

$$\rho = \rho_0 + (\rho_s - \rho_0) \Omega_s / \Omega. \quad (2)$$

Equation (2) is simply a three-dimensional generalization of de Gennes's¹⁰ expression for a slab geometry. In the derivation of Eq. (2), it is assumed that the electronic density of states is unchanged by the surface interaction, and the coherence length for dirty superconductors¹¹ $\xi \sim [\xi_0 l]^{1/2}$ ($\xi_0 \sim 10^{-4}$ cm is the Pippard coherence length and l is the mean free path) is larger

than the dimensions of the system under consideration. In order for Eqs. (1) and (2) to apply to a film which consists of a system of small crystallites of varying size and shape, the number of crystallites in a volume $\sim \xi^3$ must be sufficiently large to establish a good statistical average of the quantity Ω_S/Ω . Using the electrical resistivity to estimate l , we find that for our films, at least 100 crystallites are contained in a volume ξ^3 . Therefore, Eqs. (1) and (2) are expected to be applicable.

Taking $\Omega \sim d^3$, where d is the average size of a crystallite, and letting d_S be the (constant) width of the surface interaction region, Eq. (2) becomes

$$\rho = \rho_0 + (\rho_S - \rho_0)[1 - (1 - 2d_S/d)^3]. \quad (3)$$

For the case of aluminum, we take the values¹² $\langle \hbar\omega \rangle = \frac{1}{2}\Theta_D = 190^\circ\text{K}$ (Θ_D is the Debye temperature), $\rho_0 = 0.19$, and choose $d_S = 5 \text{ \AA}$, the approximate size of a monolayer. The best fit to the experimental data, shown by the solid curve in Fig. 2, is obtained for the value $\rho_S = 0.27$. Comparison of the enhancement T_C/T_{C0} for films of Al, In, and Sn having the same value of d (110 \AA) shows that T_C/T_{C0} decreases as the strength of the interaction ρ_0 increases. This fact indicates that ρ_S does not vary appreciably from metal to metal.

Our present results might be related to early work on enhancement of superconductivity by Buckel and Hilsch¹³ and Khukhareva.¹⁴ These workers evaporated metal films at 4°K and, without admitting oxygen, obtained films made up of small crystallites with enhanced T_C 's. However, upon warming to room temperature, the films recrystallized, and the T_C 's approached the ordinary values. If these results are interpreted in terms of the model of surface enhancement by crystallite boundaries, one would conclude that oxide at boundaries is not necessary for surface enhancement, and the only role of the oxide in our films is to inhibit the growth of large crystallites. If, in-

deed, the oxide is not necessary for the enhancement of superconductivity, one must consider other mechanisms³ for the surface enhancement, such as the effect of surface states and/or exchange of surface phonons at the crystallite boundaries and the geometric boundaries of the film. In addition, image forces at the surfaces may reduce the Coulomb repulsion.

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¹O. F. Kammerer and M. Strongin, *Phys. Letters* **17**, 224 (1965).

²M. Strongin, A. Paskin, O. F. Kammerer, and M. Garber, *Phys. Rev. Letters* **14**, 362 (1965).

³V. L. Ginzburg, *Phys. Letters* **13**, 101 (1964).

⁴We have also been able to obtain aluminum films with T_C 's as high as 3.7°K without an external supply of oxygen by evaporating from alumina inserts. Presumably in this case the heated alumina inserts provide a supply of oxygen. Such Al films have been used in microwave phonon-assisted tunneling measurements [for example, Y. Goldstein and B. Abeles, *Phys. Letters* **14**, 78 (1965)].

⁵C. J. Thomson and J. M. Blatt, *Phys. Letters* **5**, 6 (1963).

⁶This value of σ_0 corresponds to that of very low resistance Josephson junctions, which are believed to be approximately 10 \AA thick.

⁷W. Silvert, *Physics* **2**, 153 (1966).

⁸See, for example, D. M. Ginsberg, *Phys. Rev.* **136**, A1167 (1964).

⁹Myron Strongin, O. F. Kammerer, and Arthur Paskin, *Phys. Rev. Letters* **14**, 949 (1965).

¹⁰P. G. de Gennes, *Rev. Mod. Phys.* **36**, 225 (1964).

¹¹See, for example, P. G. de Gennes, *Superconductivity of Metals and Alloys* (W. A. Benjamin, Inc., New York, 1966), p. 225.

¹²D. Pines, *Phys. Rev.* **109**, 280 (1958).

¹³W. Buckel and R. Hilsch, *Z. Physik* **138**, 109 (1954).

¹⁴I. S. Khukhareva, *Zh. Eksperim. i Teor. Fiz.* **43**, 1173 (1962) [translation: *Soviet Phys.-JETP* **16**, 828 (1963)].

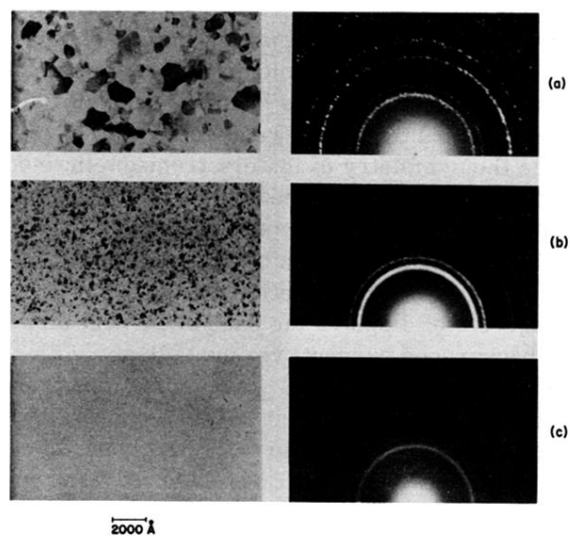


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