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Enhancement of Superconductivity in Aluminum Films

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Mixtures of Al and Al_2O_3 were sputtered at room temperature, while mixtures of Al and Ge were sputtered at 77 °K yielding, respectively, a maximum transition temperature of 2.5 and 3.6 °K. The phonon spectrum of an Al film with 3.6 at.% Ge($T_c = 3.48$ °K) is very similar to that of normal Al ($T_c = 1.2$ °K) and only slightly lower in energy. The magnitude at 0 °K and the temperature dependence of the energy gap of the enhanced Al are extremely well fitted by the BCS theory. Density measurements were performed in two different ways on the two mixtures (10 wt% of Al_2O_3 and 10 wt% of Ge) with maximum T_c. Density measurements by a direct weighing technique yielded a decrease in density of 5.5%. Electron diffraction experiments showed that the lattice spacing increased from 4.05 (normal aluminum) to 4.19 Å for the most enhanced aluminum, which corresponds to a 10.5% increase in volume. The observed increase in volume is sufficient to explain the increase in T_c without invoking any other mechanism.

INTRODUCTION

The transition temperature of Al and other superconductors has been raised in various ways. The first approach was to deposit Al films at liquid-helium temperatures.[1,2] The same result was obtained by Abeles *et al.*[3] by evaporating Al at 300 and 77 °K with a partial pressure of oxygen. The enhancing effect of a dielectric layer first demonstrated by Rühl[4] was used by Strongin *et al.*[5,6] who deposited at 4 °K alternating metallic and dielectric layers. The same increase in T_c can be obtained if one deposits at 4 °K alternating thin layers of different superconductors or superconductor-normal metals.[7] Another approach consists in codepositing a film of the superconductor with another material: coevaporating superconductors and organic materials at helium temperatures,[8,9] cosputtering Al and SiO_2 at room temperature,[10] and coevaporating superconductors and semimetallic (or semiconducting) materials at liquid-He temperatures.[11] It is also possible to increase the T_c of Al by depositing thin films at room temperature. The T_c is found to increase with decreasing film thickness.[12-14] Although many other experiments have been used to enhance the transition temperature of superconductors, the above-mentioned experiments are the most typical. One advantage of the codeposition technique of Al with either oxygen[3] or other materials[8-11] is that it does not require thin films, and one can therefore hope to enhance the T_c in very thick films which do not present the ambiguous physical properties of ultrathin layers. Furthermore, the coevaporation of Al with 10% Ge at helium temperature yielded the highest reported transition temperature for Al of 6.45 °K.[11]

Numerous theoretical studies have tried to explain the enhancement of T_c in superconducting films. Almost all explanations are based on the fact that such films are either disordered or composed of very small grains which leads to a high surface-to-volume ratio. As a result the enhancement was attributed to surface superconductivity[15] and to an attractive interaction between electrons at the surface of a metallic crystallite via a dielectric polarization wave.[16] Cohen and Douglass[17] suggested that electrons could pair across thin dielectric barriers thereby reducing the Coulomb part of the interaction. Parmenter[18] invoked the quantization of electron levels in small granules. Many explanations of the enhancement are based on McMillan's strong-coupling theory[19] and the occurrence of soft surface phonons.[7,20,21] Although there is some agreement between certain theoretical hypotheses and certain experiments one cannot say that any given theory has been established with certainty. For example, the experiments of Meunier *et al.*[11] seem to establish that the nature of the dielectric is important and consequently that Hurault's model[16] plays an important role. On the other hand, the enhanced values of T_c for various superconductors can approximately be fitted by the strong-coupling theory.[7,19,20] This suggests that the increase in T_c is caused by the lowering of the phonon frequencies possibly through the formation of "membrane" and "edge" modes in granular films.[21] Such soft surface modes have never been clearly established except perhaps in the phonon-assisted tunneling experiments in granular Al of Klein and Leger.[22] They report[22] a peak at 36 mV corresponding to the longitudinal phonons and two peaks (22.5 and 28 mV) corresponding to two transverse modes. It may be possible that the 22.5-mV peak is the transverse mode while the 28 mV is the suggested membrane mode.[21] In view of this, it would be interesting to observe the phonon structure of granular Al as the strong-coupling deviation from the BCS density of states and compare it with that of normal Al. It has been widely reported that superconducting films with enhanced T_c's have a small grain size; one should also find out if the physical properties of such granular films (such as the density) are different from bulk aluminum.

EXPERIMENTAL PROCEDURE

The Al-Ge and Al-Al_2O_3 films were deposited using the getter-sputtering technique.[23] The target preparation was similar to the one used for the deposition of ferrite films.[24] A powder mixture of Al and Ge or Al and Al_2O_3 of the desired concentration is pressed into the form of a button and an aluminum stem is pressed into the button. The Al-Al_2O_3 films usually 5000 Å thick were sputtered unto glass substrates at room temperature at a rate of 200 Å/min. The Al-Ge films approximately 2000 Å thick were sputtered on glass substrates at 77 °K at a rate of 70 Å/min and were measured at helium temperatures without warming up above 77 °K. The direct density measurements were performed on 1.5-μ-thick Al-10 wt% Ge films and on pure Al films using a microbalance for the weight determination and an interferometer for the thickness measurement. The maximum possible error in the weight measurement is 5×10^{-6} g, corresponding to a 3% precision in the weight determination. The thickness was determined to one tenth of a wavelength (≈ 300 Å), i.e., with an accuracy of 2%. The electron diffraction experiments were performed on the same Al-Al_2O_3 and Al-Ge films used in the superconductivity experiments. The lattice parameters of these films were determined with great accuracy as they were measured relative to a 20 000-Å evaporated Al film, thus eliminating the errors inherent to an absolute measurement where the camera constants must be accurately known. The Al-Al (10 wt% Ge) tunnel junctions were prepared by thermal oxidation of an evaporated Al strip followed by the sputtering at 77 °K of a cross strip of Al-10 wt% Ge. The junctions were measured at helium temperatures without warming up above 77 °K.

EXPERIMENTAL RESULTS AND DISCUSSION

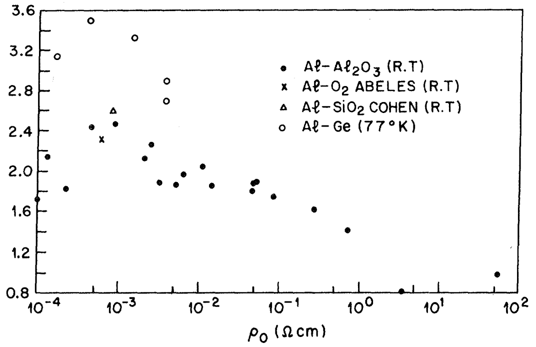

FIG. 1. Transition temperature of Al-10 wt% (3.6 at.%) Ge and Al-10 wt% Al_2O_3 (6 at.% O) films as a function of low-temperature resistivity. (R. T. = room temperature.)

The transition temperature of Al-Al_2O_3 films deposited at 300 °K and Al-Ge films deposited at 77 °K is plotted as a function of the residual resistivity (ρ_0) in Fig. 1. The increasing resistivity of the films was obtained by sputtering Al with increasing concentrations of Al_2O_3 or Ge; the concentration corresponding to the maximum in T_c was 10 wt% Al_2O_3 or Ge while the concentrations corresponding to the maximum resistivities (54 Ω cm for Al-Al_2O_3 and 4×10^{-3} Ω cm for Al-Ge) were, respectively, 40 wt% Al_2O_3 and 20 wt% Ge. Films with residual resistivities less than 10^{-3} Ω cm (which corresponds approximately to the maximum in T_c) are metallic, i.e., $\rho(\text{R.T.})/\rho_0 > 1$, while films with residual resistivities greater than 10^{-3} Ω cm show a semiconducting behavior, i.e., $\rho(\text{R.T.})/\rho_0 < 1$, where R.T. stands for room temperature. As all these films have a very short mean free path, the largest ratio observed is actually quite small [$\rho(\text{R.T.})/\rho_0 = 1.15$] while the smallest ratio obtained on the Al-Al_2O_3 film with $T_c = 1$ °K and $\rho_0 = 54$ Ω cm was 0.067. As shown in Fig. 1, the data obtained by Abeles *et al.*[3] who evaporated Al in a partial pressure of oxygen and by Cohen *et al.*[10] who sputtered simultaneously Al and SiO_2 are in excellent agreement with the Al-Al_2O_3 data. This seems to imply that for a given temperature of deposition, the T_c's correlate with the resistivities regardless of the type of dielectric used. Within the range of thickness investigated (1000–20 000 Å) the T_c's are independent of film thickness. There also seems to be a critical amount of dielectric (approximately 10 wt%) required to obtain the maximum T_c. Once this critical amount is exceeded, the excess dielectric is mainly rejected in the grain boundaries, thus leading to tunneling from grain to grain and to the observed increasing resistivity with decreasing temperature. These results seem to contradict the conclusions of Meunier *et al.*[11] who suggested that the nature of the inclusion may be of importance. As it is, however, difficult to control concentrations by evaporation, and as the resistivity was not monitored in these experiments,[11] it is possible that the various T_c's still reflected different resistivities rather than different dielectrics. It seems, on the other hand, that the temperature of deposition is an important parameter in determining the maximum T_c. Indeed, for a 10 wt % concentration of dielectric in Al, the maximum T_c for depositions at 300, 77, and 4 °K was, respectively, 2.5, 3.6, or 6.45 °K.[11] There are some differences between the Al-Al_2O_3 and Al-Ge experiments which should be stressed. First of all, it has been established[25] that when one sputters a target composed of several nonreacting elements the composition of the film is the same as that of the target because of the steady-state nature of the sputtering process. This is not true when one of the elements (such as oxygen) is chemically reactive. Consequently, while the oxygen concentration in the Al-Al_2O_3 films cannot be ascertained the Ge concentration of the Al-Ge films is that of the target. On the other hand, as the Al_2O_3 compound is stable at room temperature, the Al-Al_2O_3 films can be sputtered at room temperature and no change in the resistivity or in the transition temperature occurs upon aging. The solid solubility of Ge into aluminum is very limited and no known compound exists in the Al-Ge system. As a result, the Al-Ge films must be deposited at 77 °K. Upon annealing at room temperature, the resistivities of the films increase, the increase in resistivity with decreasing temperature becomes greater, and the transition temperature decreases. These facts can be interpreted by saying that the Ge which is insoluble in the Al is rejected at room temperature mainly in the grain boundaries. As the material in the grain boundaries becomes more resistive a lower temperature will be required before the adjoining grains can turn the grain boundary material superconducting via the proximity effect.[23,25] The same explanation could be used to interpret the decrease in T_c for films with $\rho_0 > 10^{-3}$ Ω cm as shown in Fig. 1. As the decrease in T_c may be linked to the reason for the enhancement in T_c, the final explanation for the decrease will have to be postponed until all the experimental data are analyzed. Most of the subsequent experiments pertain to the Al-Ge system which is best from the point of view of the lack of chemical reactivity between the two elements.

The T_c-vs-resistivity behavior shown in Fig. 1 suggests a comment about the resistivity values of granular films used in fluctuation experiments. Recently, Masker and Parks[26] reported that aluminum films with resistivities varying over five orders of magnitude exhibited a mean-free-path-dependent excess conductivity an order of magnitude larger than predicted by Aslamazov and Larkin (AL).[27] It is interesting to point out that although the films were thin (< 1000 Å), in agreement with the present study, the maximum transition temperature occurred again around a resistivity of 10^{-3} Ω cm and films with resistivities larger than 10^{-3} Ω cm were found to have a stronger semiconducting behavior. It is questionable, however, whether a resistivity which reflects to a large extent the tunneling from grain to grain should be used in the fluctuation theory. For two-dimensional films $[d \ll \xi(T)]$ the fluctuation rounding of the resistive transition is described by the relation[28]

$$[R_N - R(T)]/R(T) = \Delta R/R = \tau_0/\tau , \qquad (1)$$

where R is the measured resistance, R_N is the normal resistance, $\tau \equiv (T - T_c)/T_c \equiv \Delta T/T_c$, and τ_0 is the fitted width factor which is defined by AL as

$$\tau_{0\mathrm{AL}} = e^2 R_N^s/16\hbar = 1.52\times 10^{-5} R_N^s , \qquad (2)$$

where $R_N^s = RW/l = \rho_0/d$ is the sheet resistance for a film of width w and length l; ρ_0 is the residual resistivity of the film and d its thickness. If one fits relation (1) to the most resistive film shown in Fig. 1 ($T_c = 1$ °K, $\rho_0 = 54$ Ωcm, $d = 12\,000$ Å) with $\Delta R/R = 0.1$ one obtains $\Delta T = 67$ °K which is unreasonable. Actually such a film is most probably three dimensional $[d \gg \xi(T)]$ and one should use the approximate relation[28]

$$\Delta R/R = \tau_0 d/2\tau(\xi_0 l)^{1/2} , \qquad (3)$$

where l is defined by $\rho_0 l = 10^{-11}$ $\Omega\,\mathrm{cm}^2$. Using again $\Delta R/R = 0.1$ relation (3) yields $\Delta T = 6\times 10^{11}$ °K which is completely unphysical. As the fit to relation (1) or (3) becomes so unphysical for large sheet resistances (4.5×10^5 Ω/square) it is possible that large errors are also introduced whenever one uses the sheet resistance from a film displaying a marked semiconducting behavior ($R_N^s > 500$ Ω/square). It is precisely in this region that the experimental[26] τ_0 decreases rapidly towards $\tau_{0\mathrm{AL}}$ and one wonders whether most of this effect would disappear if one used instead of the measured resistivity a resistivity where the tunneling contribution between grains has been taken out. Thompson *et al.*[29] have reported that Pb films with high sheet resistance display a much narrower transition than predicted by AL and have fitted their data with a modified version of the AL theory. They also attribute the departure from the AL theory to the fact that the films consisted of weakly connected particles with a size larger than the effective coherence length.

Tunneling measurements were performed on the Al-10 wt% Ge (3.6 at.% Ge) films deposited at 77 °K which showed the maximum T_c enhancement. Films with T_c's around 2.5 °K had energy gaps at 0 °K ($2\Delta_0$) ranging between $3.44kT_c$ and $3.52kT_c$ in excellent agreement with the data of Cohen *et al.*[10] Other values of $2\Delta_0/kT_c$ reported in the literature are 3.4 by Abeles *et al.*[3] and 3 by Klein and Leger[22] on Al films evaporated in a partial pressure of oxygen, and 3.7 by Chubov *et al.*[14] on thin Al films (2000 to 50 Å). In agreement with Abeles *et al.*[3] the temperature dependence of the energy gap was very close to that predicted by the BCS theory. A plot of the tunneling first derivative (dV/dI) as a function of energy (V) is shown in Fig. 2. The structure which extends from 30 to 38 mV (after subtracting $2\Delta_0 = 1$ mV) represents a 0.18% devia-

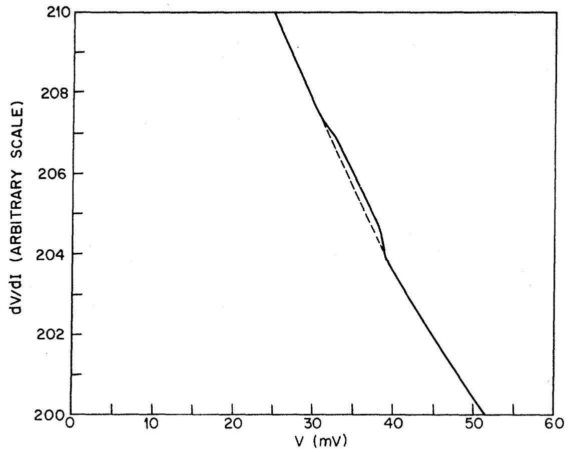

FIG. 2. Tunneling resistance (dV/dI) at 1 °K vs V for an Al tunnel junction with an Al-10 wt% Ge film ($T_c = 3.47$ °K) showing the longitudinal phonon structure.

tion from the background conductance and corresponds to the longitudinal phonons.[30] Shen[31] measured the tunneling conductance of evaporated Al with the bulk T_c of 1.2 °K and found a structure which deviates by 0.02% from the background conductance and extends in energy from 35 to 40 mV. As the strong-coupling deviation from the BCS density of states varies as $(T_c/\Theta_D)^2$, the magnitude of the phonon structure shown in Fig. 2 for Al with $T_c = 3.5$ °K scales exactly from the one observed by Shen[30] for Al with $T_c = 1.2$ °K. Owing to the spread in energy, it is difficult to say whether or not the longitudinal phonon is shifted from that of bulk aluminum. Following McMillan's strong-coupling theory[19] with a Coulomb pseudopotential $\mu^* = 0.1$, one expects a threefold transition temperature increase to arise from a 10% decrease in the average phonon frequency. This means that the longitudinal phonon frequency should be shifted to the range 31.5–36 mV and the data shown in Fig. 2 are consistent with such a requirement. The transverse phonon mode could not be observed with certainty most probably because it was too smeared in energy. As a result one cannot rule out the possibility of the surface modes suggested by Dickey and Paskin.[21] On the other hand, when Dickey and Paskin discuss[21] the 12% decrease in the average phonon frequencies required to explain the data of Strongin *et al.*[7] they rule out a pure density decrease as a possible explanation. This is mainly due to the fact that they request a 12% density decrease assuming a Grüneisen's constant of unity. But if the phonon spectrum of granular aluminum is close to that of bulk aluminum (as suggested by Fig. 2) one can use the bulk Grüneisen's constant which is approximately 2.[32] The density decrease then required[7] is only 6% which as we shall shortly see is what occurs.

It has been widely reported[33] that thin films usually have a lower density than the bulk material. In particular, Hartman[34] has shown that Al films in the 500–2000-Å thickness range evaporated at 25 °C have a density of 2.6 as compared to 2.7 for bulk aluminum. The direct density measurements were performed on thick (1.5 μ) pure evaporated Al films and on Al-10 wt% Ge (3.6 at.% Ge). The density measurements on the pure Al films were used to test the accuracy of the technique; two measurements yielded densities of 2.69 and 2.75 as compared to the reported value of 2.7, which is within the 5% accuracy of the measurements. As the Al-10 wt% Ge films had to be warmed up to room temperature for the density measurements, some of the T_c enhancement was lost: The T_c decreased from 3.5 to 2.74 °K. The density of the bulk Al-3.6 at.% Ge mixture is 2.8. Three different density measurements on the Al-3.6 at.% Ge films gave the following results: 2.60, 2.65, and 2.70 where the mean corresponds to a 5.5% decrease in density from the bulk. As the decrease in density is within the accuracy of the measurements it was decided to check this result with electron diffraction experiments.

The electron diffraction experiments on the various films were always taken with respect to an evaporated Al film with the bulk T_c of 1.2 °K and with the bulk lattice parameter of 4.05 Å of which the sharp electron diffraction rings are shown in

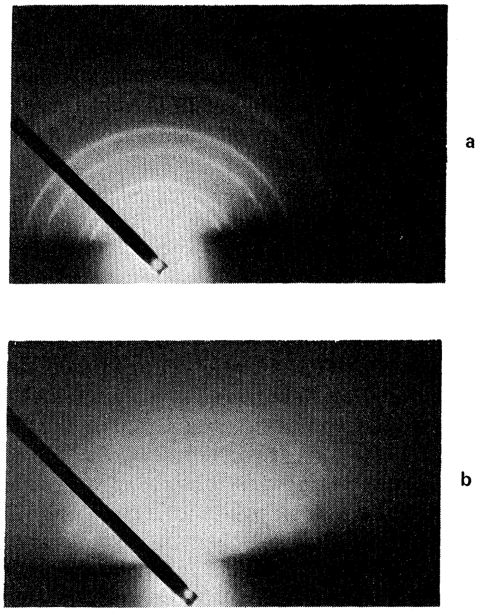

FIG. 3. (a) Electron diffraction of Al film evaporated at R. T. ($T_c = 1.2$ °K.) (b) Electron diffraction taken at R. T. of Al-10 wt% Ge film sputtered at 77 °K ($T_c = 2.74$ °K). (R. T. = room temperature.)

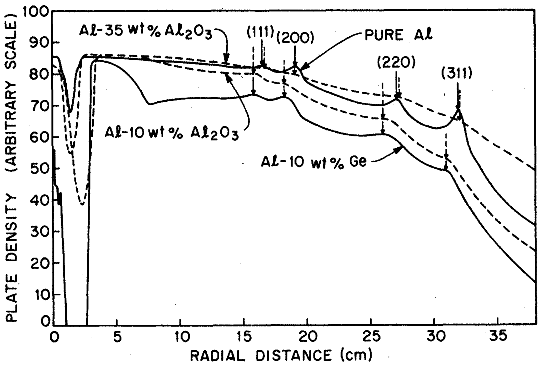

FIG. 5. Densitometer traces taken from electron diffraction plates of Figs. 3 and 4 showing the first four diffraction lines for the following films: pure evaporated Al ($T_c = 1.2$ °K), Al-10 wt% Al_2O_3 ($T_c = 2.47$ °K), Al-10 wt% Ge ($T_c = 2.74$ °K), Al-35 wt% Al_2O_3 ($T_c = 1.43$ °K).

Fig. 3(a). The electron diffractions for an Al-10 wt% Ge warmed up from 77 °K to room temperature with a resulting T_c of 2.74 °K are shown in Fig. 3(b) while the electron diffraction for an Al-10 wt% Al_2O_3 ($T_c = 2.47$ °K) is shown in Fig. 4(a). The grain size as estimated from the broadening of the electron diffraction lines is 50 Å for Al-10 wt% Ge [Fig. 3(b)] and the Al-10 wt% Al_2O_3 [Fig. 4(a)]. As the Al_2O_3 content is increased from 10 to 40%, the T_c decreases (as shown in Fig. 1) and the electron diffraction patterns become more diffuse [Figs. 4(a) –4(c)] to the point where Fig. 4(c) corresponds to a completely amorphous film. The electron diffraction plates shown in Figs. 3(a), 3(b), 4(a), and 4(b) were run on a densitometer and the result is shown in Fig. 5. It is immediately apparent from Fig. 5 that both Al-10 wt% Al_2O_3 and Al-10 wt% Ge have a larger lattice parameter (i.e., a smaller density) than pure Al. In both these cases the lattice parameter increased from 4.05 Å for pure Al to 4.19 ± 0.04 Å which corresponds to a 10% increase in volume. As it is very likely that the O or Ge are interstitially located, this would then correspond to a net 6% decrease in density after taking into account the 4% interstitials. This density decrease is in very good agreement with the direct density measurements quoted above. Levy and Olsen[35] using hydrostatic pressure on Al with a resulting decrease in volume as high as 2.5% reported a value of −22 for $\Delta T_c/(\Delta V/V_0)$. Using this value with the observed 10% increase in volume yields an enhancement in T_c of 2.2 °K in quite good agreement with the experimental increase in T_c. Furthermore, for the observed increase in T_c (1.2 °K to 2.5–2.7 °K) the required 6.5% decrease in the average phonon frequency (assuming no electronic changes[19]) can be explained even with a Grüneisen's constant of unity.

Although the determination of the diffraction peaks for the Al-35 wt% Al_2O_3 is hampered by the diffuseness of the electron diffraction rings [Fig. 4(b)], Fig. 5 seems to show that they register fairly well with those of pure Al. The density effect can therefore be used as well to explain the decrease in T_c for $\rho > 10^{-3}$ Ω cm shown in Fig. 1. One can argue that if one tries to force a larger content of interstitials than the one corresponding to the peak in T_c (≈ 5 at.%), the interstitials get rejected mainly in the grain boundaries and the aluminum matrix returns to its normal density and therefore to its usual T_c. It is interesting to point out that two more explanations can be given for the observed decrease in T_c. The first one is based on a prediction by Anderson[36] that superconductivity should disappear when the separation between electronic levels becomes of the order of the energy gap. Us-

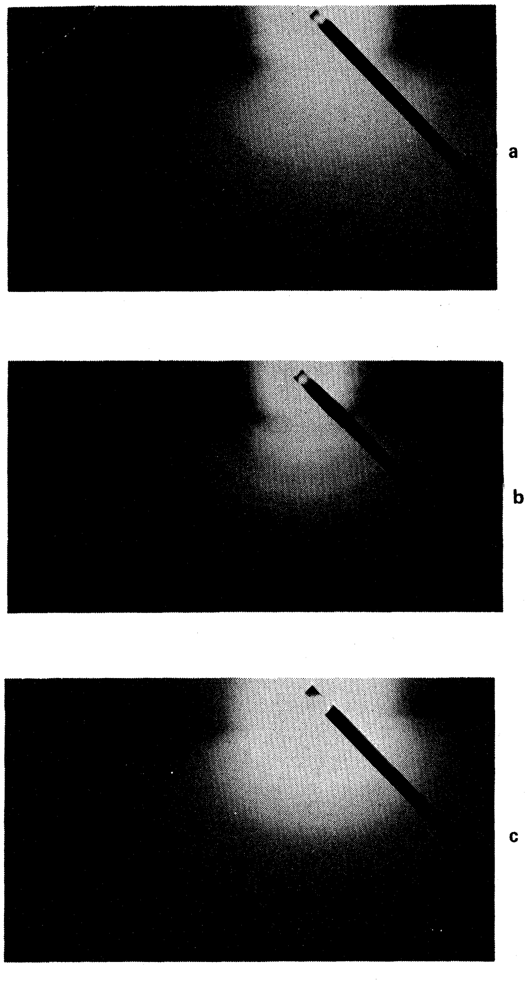

FIG. 4. Electron diffractions of Al-Al_2O_3 films: (a) Sputtering target was Al-10 wt% Al_2O_3, $T_c = 2.47$ °K. (b) Sputtering target was Al-35 wt% Al_2O_3, $T_c = 1.43$ °K. (c) Sputtering target was Al-40 wt% Al_2O_3, $T_c = 0.8$ °K.

ing the enhanced energy gap results in a critical radius of 25 Å which is approximately the grain size at the peak in T_c. Recently,[37] Maki *et al.* calculated the fluctuation effects in zero-dimensional superconductors and defined the width of the critical region by

$$\Delta T_c \approx 10^2/r^{3/2}\,, \qquad (4)$$

where r the radius of the grains is in Å. Although this theory was calculated for an aggregate of small particles embedded in an insulating matrix, one can apply this theory to the present experiments as the films with the highest resistivity seem to approach that state. Using relation (4) with $r = 25$ Å (corresponding to the grain size where T_c is maximum) one finds $\Delta T_c = 0.8$ °K which is in fair agreement with an experimentally observed width of 0.5 °K. If one sets $\Delta T_c = 3$ °K in relation (4) one will find the critical grain size where superconductivity has been suppressed by fluctuations; this corresponds to 10 Å which is the limit for crystallinity and occurs as shown by Fig. 4(c) for the films with the highest resistivities.

SUMMARY

It has been shown that regardless of all other suggested explanations, the observed enhancement in T_c to 3.6 °K can be fully accounted for by the observed 5–10% increase in volume. The enhancement in T_c can be expressed in terms of a lowering of the average phonon frequency consistent with the volume increase without invoking new surface phonon modes.

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[1] W. Buckel and R. Hilsch, Z. Physik 138, 109 (1954).

[2] I. S. Khukhareva, Zh. Eksperim. i Teor. Fiz. 43, 1173 (1962) [Soviet Phys. JETP 16, 828 (1963)].

[3] B. Abeles, R. W. Cohen, and G. W. Cullen, Phys. Rev. Letters 17, 632 (1966).

[4] W. Rühl, Z. Physik 186, 190 (1965).

[5] M. Strongin, O. F. Kammerer, D. H. Douglass, Jr., and M. H. Cohen, Phys. Rev. Letters 19, 121 (1967).

[6] M. Strongin and O. F. Kammerer, J. Appl. Phys. 39, 2509 (1968).

[7] M. Strongin, O. F. Kammerer, J. E. Crow, R. D. Parks, D. H. Douglass, Jr., and M. A. Jensen, Phys. Rev. Letters 21, 1320 (1968).

[8] F. R. Gamble and H. M. McConnel, Phys. Letters 26A, 162 (1968).

[9] F. Meunier, J. P. Burger, G. Deutscher, and E. Guyon, Phys. Letters 26A, 309 (1968).

[10] R. W. Cohen, B. Abeles, and C. R. Fuselier, Phys. Rev. Letters 23, 377 (1969).

[11] F. Meunier, J. J. Hauser, J. P. Burger, E. Guyon, and M. Hesse, Phys. Letters 28B, 37 (1968).

[12] D. H. Douglass, Jr. and R. Meservey, Phys. Rev. 135, A19 (1964).

[13] M. Strongin, O. F. Kammerer, and A. Paskin, Phys. Rev. Letters 14, 949 (1965).

[14] P. N. Chubov, V. V. Eremenko, and Yu. A. Pilipenko, Zh. Eksperim. i Teor. Fiz. 55, 752 (1968) [Soviet Phys. JETP 28, 389 (1969)].

[15] V. L. Ginzburg, Phys. Letters 13, 101 (1964).

[16] J. P. Hurault, J. Phys. Chem. Solids 29, 1765 (1968).

[17] M. H. Cohen and D. H. Douglass, Phys. Rev. Letters 19, 118 (1967).

[18] R. H. Parmenter, Phys. Rev. 154, 353 (1967); 166, 392 (1968).

[19] W. L. McMillan, Phys. Rev. 167, 331 (1968).

[20] J. W. Garland, K. H. Bennemann, and F. M. Mueller, Phys. Rev. Letters 21, 1315 (1968).

[21] J. M. Dickey and A. Paskin, Phys. Rev. Letters 21, 1441 (1968).

[22] J. Klein and A. Leger, Phys. Letters 28A, 134 (1968).

[23] J. J. Hauser, H. C. Theuerer, and N. R. Werthamer, Phys. Rev. 136, A637 (1966).

[24] J. J. Hauser, Phys. Rev. Letters 23, 374 (1969).

[25] J. J. Hauser, H. C. Theuerer, and N. R. Werthamer, Phys. Rev. 142, 118 (1966).

[26] W. E. Masker and R. D. Parks, Phys. Rev. B 1, 2164 (1970).

[27] L. G. Aslamazov and A. I. Larkin, Fiz. Tverd. Tela 10, 1104 (1968) [Soviet Phys. Solid State 10, 875 (1968)].

[28] L. R. Testardi, W. A. Reed, P. C. Hohenberg, W. H. Haemmerle, and G. F. Brennert, Phys. Rev. 181, 800 (1969).

[29] R. S. Thompson, M. Strongin, O. F. Kammerer, and J. E. Crow, Phys. Letters 29A, 194 (1969).

[30] G. Gilat and R. M. Nicklow, Phys. Rev. 143, 487 (1966).

[31] L. Y. L. Shen (private communication).

[32] P. E. Seiden, Phys. Rev. 179, 458 (1969).

[33] K. L. Chopra, *Thin Film Phenomena* (McGraw-Hill, New York, 1969).

[34] T. C. Hartman, J. Vac. Sci. Tech. 2, 239 (1965).

[35] M. Levy and J. L. Olsen, in *Physics of High Pressures and Condensed Phase*, edited by A. van Itterbeek (North-Holland, Amsterdam, 1965), Chap. 13.

[36] P. W. Anderson, J. Phys. Chem. Solids 11, 26 (1959).

[37] K. Maki, J. L. Hurault, and M. T. Béal-Monod, Phys. Letters 31A, 526 (1970).

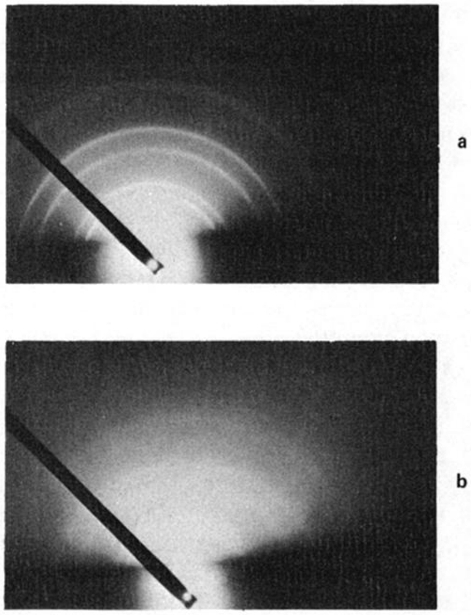

FIG. 3. (a) Electron diffraction of Al film evaporated at R. T. ($T_c = 1.2\,°\mathrm{K}$.) (b) Electron diffraction taken at R. T. of Al-10 wt% Ge film sputtered at 77 °K ($T_c = 2.74\,°\mathrm{K}$). (R. T. = room temperature.)

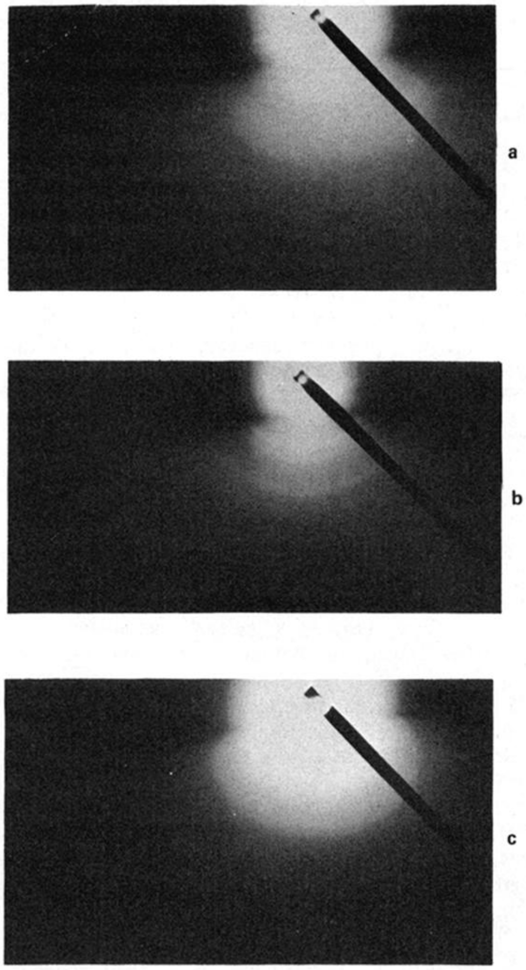

FIG. 4. Electron diffractions of Al-Al_2O_3 films: (a) Sputtering target was Al-10 wt% Al_2O_3, $T_c = 2.47$ °K. (b) Sputtering target was Al-35 wt% Al_2O_3, $T_c = 1.43$ °K. (c) Sputtering target was Al-40 wt% Al_2O_3, $T_c = 0.8$ °K.