ENHANCED SUPERCONDUCTIVITY IN LAYERED METALLIC FILMS*

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We have observed large increases in the transition temperature T_c of thin, quenched composite films consisting of alternating layers of dissimilar metals. We estimate the regions of the film which experience the greatest increase to be within a few monolayers of the metal-vacuum or metal-metal surfaces. A possible explanation for the increased T_c's is the shift in the electron-phonon coupling to larger values due to the lowering of the phonon frequencies.

Some years ago Hilsch and co-workers[1] investigated the superconducting-transition temperature T_c of metallic films of soft metals prepared by vacuum deposition onto substrates held at cryogenic temperatures. In general they found that quenched films produced this way were composed of small metallic particles and the increase in T_c of the metal correlated with the Debye temperature Θ_D. Theoretical work[2] and interest in obtaining high T_c's has renewed interest in this problem, and much work has recently been done[3-6] on films. To investigate the higher T_c's in these systems, recent work[5-7] was done on sandwiches consisting of alternating metallic and dielectric layers, and also on near-monolayer films.[6] In general, higher T_c's were obtained in Al, Sn, In, and Zn than previously reported in pure metal films. To explain these results it was suggested that electrons could pair across thin dielectric barriers,[5-7] thereby reducing the Coulomb part of the interaction and raising T_c. It was also recognized that "disorder" could play a role in these measurements. This is discussed in Refs. 4-6. We emphasize that no explanation of why "disorder" should raise T_c has been given. In the present work we report measurements on layered structures consisting of alternating layers of different metals which show the same large increases in T_c observed previously.[6] This eliminates the need for invoking pairing across dielectric barriers (Cohen-Douglass mechanism) as suggested in previous work on layered structures.[5-7] The rises in T_c are explained here using a model which considers quenched films as an aggregate of small crystallites, and then estimates changes in the phonon spectrum due to the surfaces. We do not consider quantization due to size, and surface effects are only considered in terms of their effect on the phonon frequencies.

The new data presented in Figs. 1 and 2 show effect of depositing successive layers of different metals in the Al-Cu and Al-Sn systems. The metals were deposited onto glass slides held near 4°K and the experiments are done in situ. The general features of the experimental setup are described in Ref. 5. One important difference in these experiments is that the edges of the film were masked, which eliminated essentially the effect of size distributions in the shadow regions of the film. Because the resistance transitions widths are sharp and are significantly narrower than the ΔT_c's caused by the next increment of metal, and because we can see the "peaked behavior" with thickness shown in Figs. 1 and 2, we believe that the deviations from the average thickness of a given layer are fairly small. This is in contrast to the work in Ref. 5, where the films were not masked, and where the size distributions in the film edges caused a smeared out behavior when T_c was plotted as a function of thickness, instead of the peaking of T_c as a function of thickness shown in Figs. 1 and 2. The random error in thickness due to readings on our quartz-crystal-oscillator thickness monitor is about 10% at a thickness of about 5 Å for Al and is less for the denser metals. Because of the porous nature of these materials the

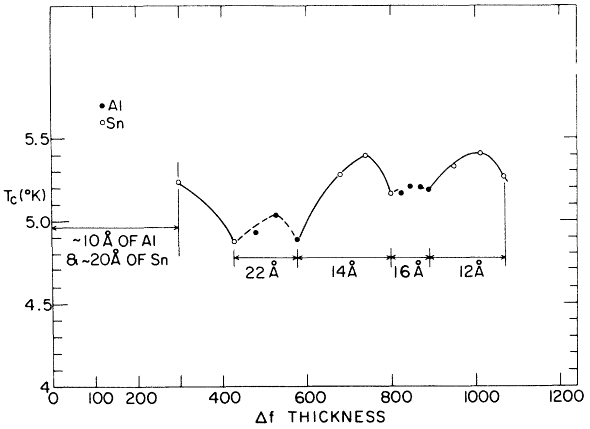

FIG. 1. Plot of T_c versus thickness for alternate layers of Al and Sn. The thickness scale is in units of frequency change on a crystal-oscillator thickness monitor. The characteristic thickness of the Sn layers (and the Cu layers in Fig. 2) may be as much as 50% higher than the values indicated, due to unknown geometrical factors.

actual thickness may be somewhat different from our estimates based on the amount of material deposited. It is seen from Fig. 1 that T_c increases when Al is deposited onto Sn or Sn onto Al. Even Al on Cu has its T_c raised initially as shown in Fig. 2. From the position of the peaks in the curves of temperature versus thickness we estimate that the region of highest T_c is of the order of three or four monolayers in both Al and Sn. Similar peaks in the curves of T_c versus thickness have been observed for metal-insulator and metal-semiconductor systems, such as Al-SiO and Al-Ge, when the edges are masked. We show in Fig. 3 that the trend in the maximum T_c's that we have observed in layered structures is similar to the prediction of McMillan[9] for these elements, if it is assumed that increased electron-phonon coupling can be achieved by lowering the average phonon frequencies $\langle \omega^2 \rangle$. If this correlation is not a coincidence, we must ask why the phonon frequencies are lowered in these systems.

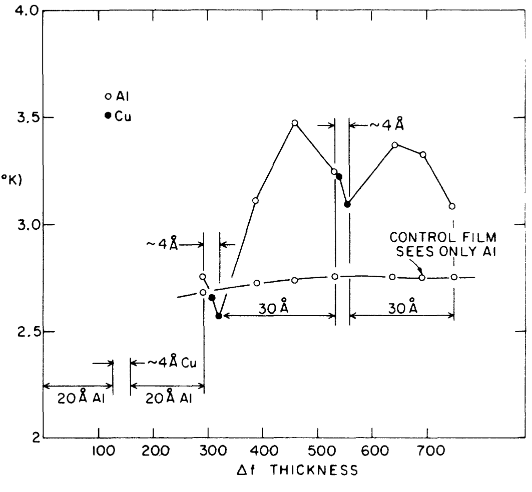

FIG. 2. Plot of T_c versus thickness for alternate layers of Al and Cu. The thickness scale is in units of frequency change on a crystal-oscillator thickness monitor. Some characteristic thicknesses are given in the figure. On this run there was also a control film. Every time Al was deposited to make the Al-Cu layers, Al was deposited at the same time under the same conditions on the control film. It can be seen that the control on which only Al is deposited stays at about 2.7°K, the T_c of thick Al films on cryogenic substrates. See Refs. 1 and 5.

We assume that these quenched films are composed of many small metallic crystallites separated by voids. At a surface, the fact that the surface atoms share fewer interatomic bonds will lead to a lowering of the phonon frequencies.[8] This effect will be accentuated when a new metal is first deposited on a dielectric or foreign metal since the new layer will be bounded by a free surface on one side and a "quasifree" (lattice-mismatched) surface on the other. A possible

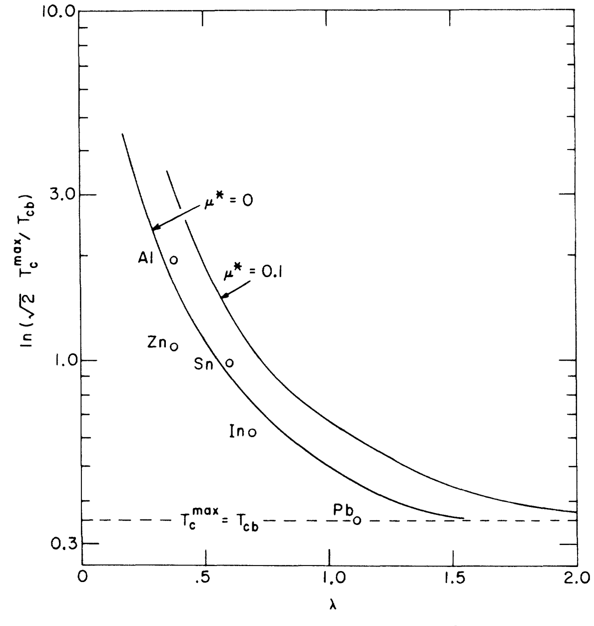

FIG. 3. Solid lines: dependence of $T_c^{\max}/T_{cb}$ on electron-coupling strength in bulk material λ, as predicted from the strong-coupling theory [Eq. (3)] with $\mu^*=0$, and for $\mu^*=0.1$. Open circles: values of $T_c^{\max}/T_{cb}$ obtained in thin films of Al, Zn, Sn, In, and Pb. Note that the quantity $\ln(\sqrt{2}\ T_c^{\max}/T_{cb})$ is plotted on a log grid which illustrates the strong λ dependence of $T_c^{\max}/T_{cb}$.

alternative picture of the structure of quenched films is that of disorder at the atomic level with an altered average lattice spacing. This effect also could lead to a lowering of $\langle\omega^2\rangle$ and an increase of T_c. However, except for the first layer on a foreign substance, it seems more likely that atoms will assume their usual arrangement in small crystallites.

In the spirit of the above discussion, if we now assume that the electron-phonon coupling strength (and therefore T_c) depends mainly on the phonon frequencies and is fairly insensitive to electronic properties, we can use the analysis of McMillan.[9] Following McMillan, we can predict the maximum value of T_c obtainable by reducing the phonon frequencies. Numerical solutions of the gap equations have been carried out by McMillan[9] for a Nb-like phonon density of states and the results are well fitted by the analytic expression

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

where Θ_D is the Debye temperature and μ^* is the Coulomb pseudopotential; μ^* is generally found (using isotope experiments) to be 0.10 ± 0.02 for nontransition metals. The quantity λ involves the details of the phonon density of states $F(\omega)$, and the electronic matrix elements $\alpha^2(\omega)$ are needed to determine λ which is given by

$$\lambda = 2\int \frac{\alpha^2(\omega)F(\omega)}{\omega}\,d\omega = \frac{N(0)\langle \mathscr{I}^2\rangle}{M\langle\omega^2\rangle}, \qquad (2)$$

where $N(0)$ is the (bare) density of states at the Fermi surface, M is the nuclear mass, $\langle\omega^2\rangle$ is an average over the phonon frequencies, and $\langle\mathscr{I}^2\rangle$ is a Fermi-surface momentum average over the electronic matrix elements. Empirically one finds that $N(0)\langle\mathscr{I}^2\rangle$ is roughly constant[9] for a given structure and that the major dependence of λ is therefore not on the electronic properties directly but, instead, on the "softness" of the lattice as measured by the lattice frequencies $\langle\omega^2\rangle$. From Eq. (1) we can determine the maximum obtainable transition temperature $T_c^{\max}$ compared with the bulk value T_{cb} which depends only upon the bulk phonon coupling. The result (taking for convenience $\mu^* \sim 0$ and McMillan's result[9] that $T_c^{\max}$ for $\mu^* = 0$ corresponds to $\lambda \approx 2$) is given by

$$\sqrt{2}\,T_c^{\max}/T_{cb} = \lambda^{\frac{1}{2}}e^{1/\lambda-\frac{1}{2}}. \qquad (3)$$

In Fig. 3, $\ln(\sqrt{2}\,T_c^{\max}/T_{cb})$ is plotted as a function of λ from Eq. (3) where $\mu^* = 0$, and also for the more realistic case where $\mu^* = 0.1$, together with our experimental data on Al, Zn, Sn, In, and Pb films. The values of λ are those quoted by McMillan.[9] The data are for the maximum transition temperatures observed for ultrathin films or film sandwiches deposited onto low-temperature substrates. The experimental values of $T_c^{\max}$ for Al, Sn, Zn, Pb, and In are about 5.7, 7, 1.8, 7.1, and 4.4°K, respectively.[10] The value for each element corresponds to the largest one observed in various experiments on layered films. On the basis of Eq. (1), with $\mu^* = 0.1$, λ must increase from 0.38 to 0.55 to explain the rise of T_c of Al from 1.2 to ~5.7°K, and for Sn λ must change from 0.6 to about 0.80 to explain the rise in T_c from 3.7 to 7°K. Since from Eq. (2) λ goes as $\langle\omega^2\rangle^{-1}$, decreases in $\langle\omega^2\rangle$ of about 31 to 25%, respectively, are necessary to account for the above increases in Al and Sn. Molecular-dynamics (computer) calculations by Dickey and Paskin[11] show that an isolated plate about three atoms thick will have $\langle\omega^2\rangle$ reduced to half the bulk value, and their result is insensitive to the diameter of the plate. On the basis of the above, the required decrease in $\langle\omega^2\rangle$ of about 30% in the first few monolayers of Al or Sn is entirely reasonable, especially when one considers that the grains composing this new layer are in mechanical contact with the film below it, and with each other. Of course, as more metal is added the layers become thicker and $\langle\omega^2\rangle$ approaches the bulk value. We believe that the correlation between the predicted maximum increase in T_c and that observed in Fig. 3, plus the discussion above, renders plausible the explanation of the observed increase in T_c in terms of changes in the phonon spectrum. Clearly, tunneling data showing the low-frequency modes would offer the conclusive test of the above explanation.

There are also considerable data showing that thick quenched films[1] and metal-insulator-metal layers[5] have increased transition temperatures. Again, we believe that it is the softened phonon spectrum associated with the porous structure (characterized by the presence of "internal free surfaces") of such films that is responsible for the enhancement. The experimental work of Hilsch[1] on thick quenched films gave for T_c(quench)/T_c(bulk) 2.3, 1.64, 1.26, 1.20, and 1.00 for Al, Zn, Sn, In, and Pb, respectively, which shows roughly the same dependence upon λ as for the results shown in Fig. 3. However, the observed changes are smaller in the case of the thick quenched films. We also mention that even in films prepared at room temperature and composed of small particles,[3] the "soft phonons" due to the particle surfaces can explain the increased T_c.

We emphasize that perhaps the most convincing evidence for the importance of the surface (or interface) is the layered-film results shown in Figs. 1 and 2, which shows that it is the presence of the interface region which causes the dominant change in T_c. Thus, whenever a superconductor is evaporated, T_c is first increased, and then as the number of noninterface layers are increased the average coupling decreases again.

Finally, one may estimate the maximum value of T_c obtainable for different materials using Eq. (1). The estimates for Pb, Nb, V_3Si, and Nb_3Sn are 9.2, 22, 40, and 28°K,[9] respectively. We are now preparing thin V_3Si films to see how close we can come to the theoretical limit of 40°K.

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[1] For the T_c of thick Al, Sn, In, Pb, and Bi films deposited at cryogenic temperature see V. Buckel and R. Hilsch, Z. Physik 132, 420 (1952), and 138, 109 (1954); R. Hilsch, Non-Crystalline Solids, edited by V. D. Freschette (John Wiley & Sons, Inc., New York, 1958).

[2] V. L. Ginsburg, Phys. Letters 13, 101 (1964); V. L. Ginsburg and D. A. Kirznits, Zh. Eksperim. i Teor. Fiz. 46, 397 (1964) [translation: Sov. Phys.–JETP 19, 269 (1964)]; D. A. Kirznits and E. G. Maksemov, Zh. Eksperim. i Teor. Fiz.– Pis'ma Redakt. 2, 442 (1965) [translation: JETP Letters 2, 274 (1965)]; W. Silvert, Physics 2, 153 (1966); G. J. Thomson and J. M. Blatt, Phys. Letters 5, 6 (1963); A. Paskin and A. D. Singh, Phys. Rev. 140, A1965 (1965); E. A. Shapoval, Zh. Eksperim. i Theor. Fiz.–Pis'ma Redakt. 5, 57 (1967) [translation: JETP Letters 5, 45 (1967)]; R. H. Parmenter, Phys. Rev. 166, 392 (1968).

[3] M. Strongin, O. F. Kammerer, and A. Paskin, Phys. Rev. Letters 14, 949 (1965); B. Abeles, R. W. Cohen, and G. W. Cullen, Phys. Rev. Letters 17, 636 (1966); O. F. Kammerer and M. Strongin, Phys. Letters 17, 242 (1965); W. L. Bond. A. S. Cooper, K. Andres, G. W. Hull, T. H. Geballe, and B. T. Matthias, Phys. Rev. Letters 15, 260 (1965); S. Basavaiah and S. R. Pollack, Appl. Phys. Letters 12, 259 (1968); K. L. Chopra, M. R. Randlett, and R. H. Duff, Appl. Phys. Letters 9, 402 (1966).

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

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

[8] See, for example, E. Montroll, J. Chem. Phys. 18, 183 (1950).

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

[10] It is difficult to achieve the maximum of T_c in a single film because of the loss of metallic character and the quenching of superconductivity which occurs for films a few monolayers thick (see Ref. 6). This problem is not encountered when using the layered structures.

[11] J. M. Dickey and A. Paskin, private communication, and to be published.