

Evidence for a Surface-Phonon Contribution to Thin-Film Superconductivity: Depression of T_c by Noble-Gas Overlayers*

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When care is taken to prevent contamination, the superconducting transition temperatures of thin Al, Sn, Tl, and amorphous-Bi films are depressed by overlayers of Ne or Ar. For a given film, the ratio of the shift in T_c produced by Ar to that produced by Ne is observed to be 1.8. The results can be explained in terms of a modification of the phonon spectrum by the presence of the noble gas. A simple model predicts the observed ratio of the effect of Ar to that of Ne and the relative magnitudes of the shifts for the four different metals.

I. INTRODUCTION

In the theory of strong-coupling superconductors the transition temperature T_c is determined by the frequency dependence of the product of the electron-phonon coupling constant and the phonon density of states, $\alpha^2(\omega)F(\omega)$. Differences between the transition temperatures of thin films and that of the bulk metal are often explained in terms of a modification of $\alpha^2(\omega)F(\omega)$ in the film. It has been suggested that the enhancements of the superconducting transition temperature for amorphous or disordered films of many nontransition metals¹ are caused by a "softening" of the phonon frequencies in the film relative to those of the bulk metal.^{2,3} Based on the experimental observation that the low-temperature specific heat is the same for disordered as for ordered crystalline films,⁴ Bergmann⁵ has reached a somewhat different conclusion. He attributed the increase in T_c with disorder to a modification of the electron-phonon coupling constant $\alpha^2(\omega)$ by "forbidden" electron-phonon processes which are permitted when translational invariance is broken by the disorder.

It has also been suggested that true surface phonons⁶ as well as disorder may contribute to the enhancement of T_c in thin films.^{7,8} Theoretical calculations of the phonon spectrum for model films lend some support to this hypothesis.^{8,9} The presence of a free surface is expected to lower the average phonon frequency in the thin film and consequently increase its T_c with respect to that of the bulk. The contribution of surface phonons should become more important as the film thickness becomes smaller. The only evidence yet cited for the influence of surface phonons is the thickness dependence of T_c in some weak-coupling superconductors (see, e.g., Ref. 7). Although the surface phonons would be expected to produce an increase in T_c with decreasing film thickness, observation of such a thickness dependence of T_c for thin films does not constitute strong experimental

evidence for the influence of surface phonons since resistance measurements¹⁰ indicate that the degree of disorder of a thin film may decrease with increasing film thickness. Since the contribution of surface phonons to superconductivity is relatively small, a thickness dependence of the degree of disorder is sufficient to explain the enhancement of T_c with decreasing film thickness observed for some metal films. Recent studies^{11,12} have emphasized that neither surface phonons nor any mechanism other than disorder within the films is needed to explain some of the observed enhancements. Furthermore, an interpretation of the thickness dependence of the transition temperature of thin films appears to be complicated by at least one other mechanism which tends to depress T_c and which is not yet understood. In films of many metals the transition temperature is observed to decrease uniformly with decreasing film thickness.¹³ Even for those metals, Tl, Al, and Sn, which exhibit an initial increase in T_c with decreasing film thickness, for thicknesses below a certain value T_c decreases.¹⁴

Information concerning the role of surface phonons in superconductivity in thin films could be obtained from experiments which measure superconducting properties that are sensitive to the phonon modes as the surface modes are externally modified. Two such properties are the superconducting transition temperature and the phonon density of states, which can be measured with tunneling experiments. Unfortunately the contribution of the surface phonons is expected to be small and it is doubtful if the surface-phonon peaks could be detected in a tunneling experiment. Very small changes in the transition temperature, however, may be readily detected.

The surface-phonon modes should be drastically changed when an adsorbate layer is deposited on the film. It is well known that oxygen adsorbed onto the metal film will react chemically and produce rather large shifts in the transition temperature¹⁵

which are believed to be related to charge transfer or the "charge effect."^{16,17} If the principal effect of the adsorbate is to be only a modification of the surface-phonon modes, it should be a material which is physically, rather than chemically, adsorbed on the metal surface. Although the noble gases are rather strongly adsorbed on transition metals, perhaps even with charge transfer between adsorbate and metal, there is evidence that this adsorption is much weaker for simple metals.¹⁸ This paper reports experiments in which the influence of noble-gas adsorbates on the transition temperature of Sn, Al, Tl, and amorphous-Bi films was observed. Preliminary results have been reported previously.^{19,20} Similar experiments involving the influence of Ne and Xe on the transition temperature of thin superconducting films have recently been reported.²¹

In Sec. IV of the present paper, a simple model for the influence of the noble-gas overlayer on the vibration of the metal ions at the previously free surface is presented. The results of the model are used with expressions for the transition temperature of strong-coupling superconductors^{2,22} to predict the effect of the noble-gas adsorbate on T_c . Although it is improbable that the only effect of the noble-gas adsorbate is to modify the phonon spectrum, the surprisingly good agreement between the predictions and the experimental observations suggests that the principal influence of the adsorbate on T_c is through this mechanism.

II. EXPERIMENTAL PROCEDURE

The Al films were evaporated from a W filament and the Sn and Tl films were evaporated from Ta bands onto a quartz substrate held at 77°K. Before cooling to helium temperatures the films were partially annealed at 95°K. The amorphous-Bi films were evaporated from a Ta band and "quench condensed" onto the substrate which was held at 4°K. Although these films are referred to as amorphous Bi, the sample contained 6-at. % Tl, which helped to stabilize the amorphous phase.

Some details of the experimental apparatus are shown in Fig. 1. The outer helium shield, which entirely surrounded the films, was held at 4°K during and subsequent to the evaporation of the films. The pressure measured at the vacuum jacket remained below 5×10^{-8} Torr except during the actual evaporation. Groups of three to five films of different thicknesses were prepared simultaneously by progressively lowering the shutter next to the substrate and exposing more of the masked substrate. Evaporation was stopped by closing the rotary shutters on the nitrogen- and the helium-cooled shields and then turning off the evaporation current. Thus all five films with fresh, presumably clean, surfaces remained entirely enclosed by

a helium-temperature shield from immediately after preparation until conclusion of the experiment. The films were cooled to helium temperature and cycled several times between 4 and 25°K. T_c was measured at the end of each cycle. The excellent repeatability of the transition curves during this process over periods as long as three hours clearly demonstrates that the surfaces were not being contaminated by residual gases in the cryostat.

If, on the other hand, the films of different thicknesses were prepared by progressively raising the shutter next to the substrate and covering more of the substrate, the lower (thinner) films exhibited a smaller shift in T_c when the noble gas was deposited relative to the upper (thicker) films, which were the last to be covered. This indicated that some gas molecules from the residual gases in the vacuum or from the metal evaporation source were present during evaporation. However, when this shutter was progressively lowered so that evapora-

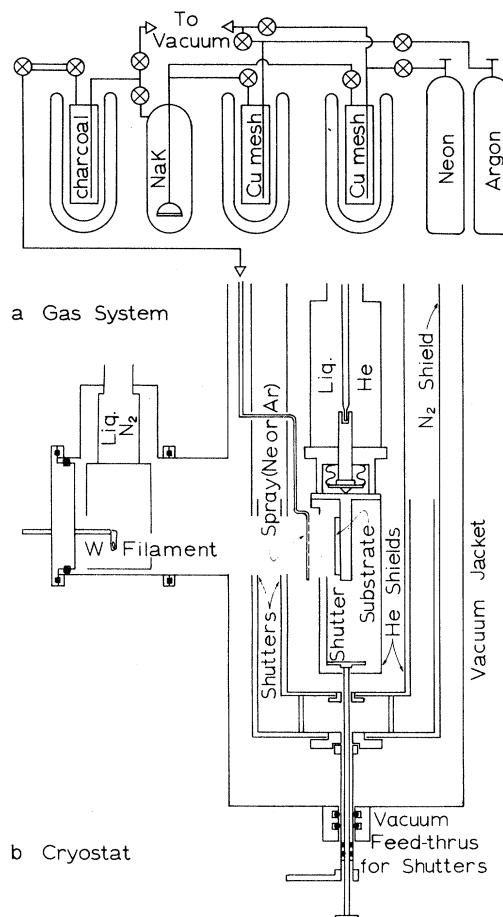


FIG. 1. Experimental configuration. (a) Gas flow and purification system including cryogenic traps and NaK alloy bubbler. (b) Cryostat for film deposition and noble-gas overlaying.

tion of all five films ended simultaneously, as was the case for all data reported in this paper, the surface contamination due to these gases should have been quite small. It is thus believed that the sample surfaces of the films discussed subsequently in this paper were relatively free of impurities and adsorbed gases.

Since the influence of the thin edges of the films must be considered, the groups of films for Sn, Tl, and Al were deliberately prepared with film thicknesses in the region where T_c is relatively insensitive to thickness, i. e., near the maximum in T_c as a function of film thickness. In each evaporation of three to five films, at least one of the films usually had a thickness which was thinner than that of the maximum in T_c and was in the region where T_c is observed to decrease with decreasing thickness. Thus, although the edges of the films were not scribed, the transition temperatures measured should be representative of the bulk of the films rather than its edges. This problem does not arise with the amorphous Bi films since their transition temperature decreases with decreasing film thickness.¹³

The transition curves for Sn, Al, and Tl films are shown in Fig. 2. After T_c for the clean film was established (right-hand curve), Ne was condensed onto the free surface at 4°K and T_c was measured (middle curve). When the film was warmed to 25°K to desorb the Ne, the transition returned to the original curve. Ar was then condensed onto the surface and the new T_c measured (left-hand curve). When the film was again warmed to 25°K, no further change in T_c was observed.

The film resistance was measured by a four-terminal technique and the temperature was measured with a Ge resistance thermometer. The resistive transition curves were recorded continuously on an X-Y recorder as the temperature was slowly varied. The resolution and repeatability of the transition curves were better than 5×10^{-4} °K. Measurements of the normal-state resistance were measured with a potentiometer to a precision of 5 parts in 10^5 .

At the conclusion of the experiments the films were warmed to room temperature, removed from the cryostat, coated with a reflecting silver film inside a second evaporation chamber, and examined with a Varian Å-Scope to determine the film thickness. The accuracy of the thickness measurements is ± 20 Å for those films thinner than 200 Å and $\pm 10\%$ for those thicker than 200 Å. These measured values of the thickness include the thin oxide layer which presumably formed during the short exposure to the atmosphere when the films were transferred from the cryostat to the second evaporation chamber.

To ensure that impurities, particularly oxygen,

were not present in the Ne and Ar deposited on the films, the gas system shown in Fig. 1 was evacuated to a pressure lower than 10^{-6} Torr and flushed several times with the gas to be deposited. Prior to deposition on the film, the gas (Linde, 99.998% purity) was passed successively through a cold trap filled with Cu mesh to condense any water vapor, a bubbler filled with NaK alloy to react chemically with trace oxygen impurities, and a cooled charcoal trap to adsorb remaining impurities. The

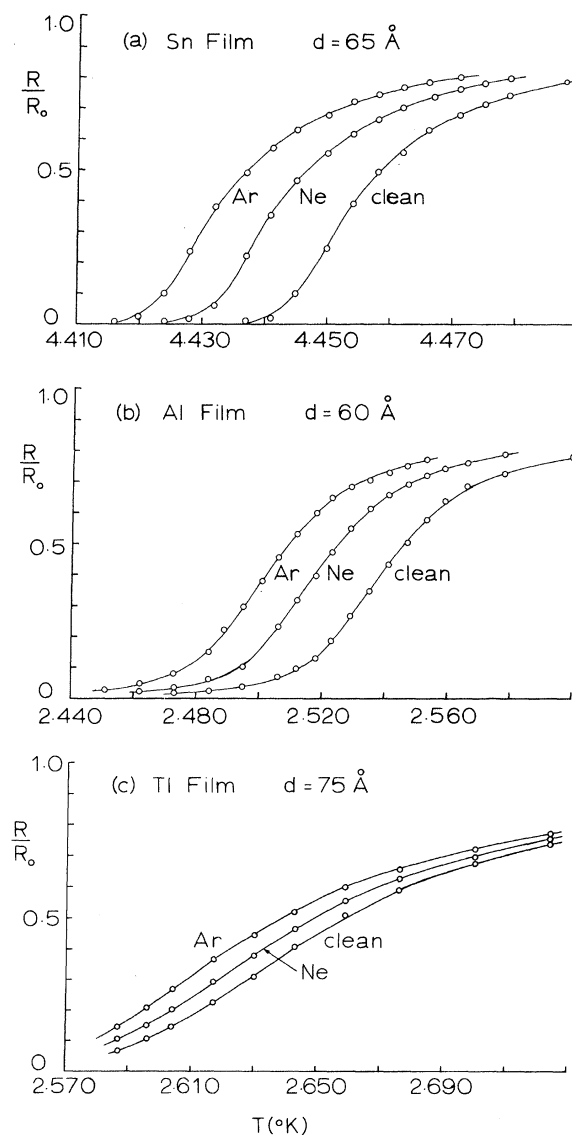


FIG. 2. Transition curves for (a) 65-Å Sn film, (b) 60-Å Al film, and (c) 75-Å Tl film. Transition curves marked "Ar" and "Ne" are taken with a thick overlayer of the noble gas covering the metal films. Curves marked "clean" were taken before the deposition of the noble-gas overlayer and after the Ne overlayer had been removed by warming to 25°K.

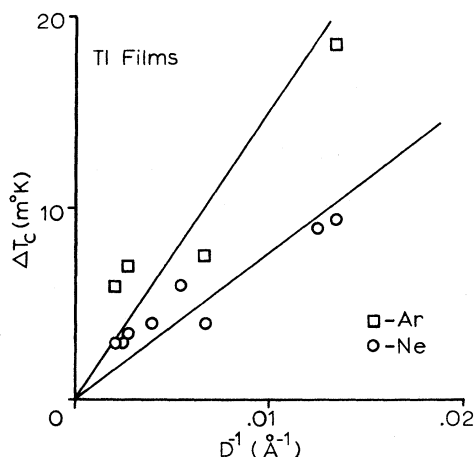


FIG. 3. Shift in transition temperature, ΔT_c , as a function of reciprocal film thickness D^{-1} , produced on Tl films by overlayers of Ar and Ne.

two traps were cooled with liquid nitrogen for the Ne overlayers and an alcohol-dry-ice mixture for Ar.

Small amounts of oxygen in the Ne or Ar were readily detected. During an early run a small leak developed around the stem of the valve that admitted the noble gas to the film which resulted in the inclusion of small amounts of oxygen as an impurity in the Ne and Ar depositions. The initial depression of T_c was of the same order as that for the pure noble gas. Warming the film to 25 °K appeared to allow the oxygen to concentrate at the film surface and react to form an oxide layer. The result was to increase T_c for Al and decrease T_c further for Sn, in agreement with the oxidation effect for these metals.¹⁵ Because of the sensitivity of Al to the oxidation effect, a control film of Al was included during the experiments with Sn. Since Tl films also show a shift opposite to that produced by the noble gas when they are oxidized, no control film was needed with them. For the data shown in Fig. 2, the fact that T_c returned to the value for the clean film when Ne was desorbed and that T_c remained unshifted when the Ar-coated film was warmed to 25 °K provides convincing evidence that the observed shifts result from the noble-gas layer rather than any impurity.

III. RESULTS

As indicated in Fig. 2 the noble-gas overlayers depress the transition temperature of thin Sn, Al, and Tl films. Associated with this decrease in T_c was a small increase in the residual resistance. The fractional change in residual resistance was approximately an order of magnitude smaller than that observed for the transition temperature. The transition temperature of the amorphous-Bi films

also decreased; however, for films of the same thickness, the fractional decrease in T_c for Bi was more than an order of magnitude less than that for Sn, Al, or Tl. Also associated with the decrease in T_c for Bi there was a decrease in the residual resistance.

In Fig. 3 the shifts ΔT_c produced by Ne and Ar overlayers on Tl films are plotted against reciprocal film thickness D^{-1} as measured with an interferometer. Over the range of film thicknesses in these experiments both ΔT_c and residual resistance were found to be approximately proportional to the reciprocal film thickness.

The fractional shifts may be expressed by

$$\frac{\Delta T_c}{T_c} = \frac{-K}{D}, \quad \frac{\Delta R_0}{R_0} = \frac{K'}{D}, \quad (1)$$

where the constants K and K' depend on both the metal and the noble-gas adsorbate. Values of K and K' for an Ar coating are listed for the different metals in Table I. Although precautions are taken to ensure that the surfaces of the films were relatively clean, one might expect a small variation in surface cleanliness and surface roughness among the different metals. Thus, although a comparison of the magnitudes of the K_{Ar} 's for the different metals provides a measure of the relative sensitivity of their transition temperatures to a noble-gas overlayer, there may be some aberration. Perhaps of more significance, however, are the relatively large errors in K and K' which are principally due to the uncertainty in film thicknesses.

Since the shifts in T_c for both Ne and Ar were measured on the same film, a much more precise comparison of the relative effects of the two noble gases for a given metal may be obtained. For this comparison no thickness measurement need be considered and the surface cleanliness is approximately the same since the Ne appears to be boiled off completely by warming to 24 °K. For the weak-coupling materials studied the ratio of the shift ΔT_c produced by the Ar layer to that produced by Ne was close to 1.8. For the twelve individual films the values of this ratio ranged between 1.7 and 2.0, with average values of 1.95, 1.80, and 1.85 for

TABLE I. Coefficients K_{Ar} and K'_{Ar} for the linear dependence on inverse film thickness D^{-1} of the relative shifts in transition temperature, $\Delta T_c/T_c$, and residual resistance, $\Delta R_0/R_0$, respectively, due to an Ar overlayer.

Metal	K_{Ar} (Å)	K'_{Ar} (Å)
Al	0.85 ± 0.20	0.085 ± 0.025
Tl	0.56 ± 0.15	0.15 ± 0.05
Sn	0.30 ± 0.07	0.045 ± 0.015
α -Bi	0.02 ± 0.01	-0.006 ± 0.004

the Tl, Sn, and Al films, respectively. The deviations of the values of the ratio for the individual films from the average was consistent with the error in measurement of the ΔT_c . The value of the ratio of the change in ΔR produced by Ar to that produced by Ne was approximately the same as that for ΔT_c ; however, the scatter was considerably larger as a result of the larger error in the determination of ΔR . Since the shifts in transition temperature for the amorphous-Bi films were more than an order of magnitude smaller than those for the weak-coupling materials, and thus barely within our resolution capability, the ratio of the shift for Ar to that for Ne could not be precisely determined; however, the observed ratio lies between 1.5 and 3.

IV. DISCUSSION

A. Comparison with Previous Experiment

The decreases in T_c for Ar and Ne coatings reported in this paper are consistent with those reported for Ne and Xe coatings on Sn, Tl, Pb, α -Ga, and α -Bi films by Felsch and Glover,²¹ and that for Ar on a Tl film by Rühl.²³ The observation by Felsch and Glover that the noble-gas coating increases the residual resistance of Sn and Tl films but decreases the resistance of α -Bi films is also confirmed in these experiments. The values of K_{Ne} observed in this experiment agree very well with those calculated from the data given for 150-Å-thick Sn and α -Bi films by Felsch and Glover, but K_{Ne} observed in this experiment for Tl films is approximately three times as large as that computed from their data for a 150-Å-thick Tl film. The value of K_{Ar} (~ 0.4) computed from Rühl's data for a single Tl film, however, agrees very well with that listed in Table I.

It is somewhat difficult to explain the smaller effect on Tl observed by Felsch and Glover. It is perhaps related to the fact that the films were surrounded in the present experiment by a liquid-helium-cooled shield and in Rühl's experiment by a liquid-hydrogen-cooled shield from the time of preparation until completion of the experiment, whereas in the experiments of Felsch and Glover the film was surrounded only by a liquid-nitrogen-cooled shield for a short period between the time it was prepared and the time it was cooled to liquid-helium temperature. During the short time in which the films were exposed to a poorer vacuum, one might expect that the surface of the Tl films would be more readily contaminated than that of the Sn films, because of the strong affinity of Tl for oxygen.

Felsch and Glover also observed that the heavier noble gas, Xe, produced a larger shift in T_c than Ne, as was the case with Ar in this experiment. The ratio of the shift in ΔT_c produced by Xe to that

produced by Ne appeared to vary from 1.8 for Sn to 9 for α -Ga films, in contrast to the constant value 1.8 reported here for Ar to Ne. Such a large variation in the relative effect of Xe and Ne for the different metals is surprising in view of the present results for Ar and Ne. It should be noted, however, that whereas the Ne and Ar overlayers in our experiments were deposited on the same film to provide a high precision for the ratio $\Delta T_{c, Ar} / \Delta T_{c, Ne}$, the comparison of the effects of Xe and Ne is based on data from different films of the same metal. It would be very desirable to see data for the influence of Xe and Ne on the same film to determine if the variation between metals is indeed so great.

Rühl¹⁵ has demonstrated that oxidation of the surface of a thin film will produce a shift in the transition temperature. Other workers²⁴⁻²⁶ have shown that different dielectric coatings can produce similar shifts. The shifts produced by the dielectric coatings in these previous experiments are markedly different from those produced by the noble-gas layers. For example, SnS, Tl₂Se, SiO, and Ge overlayers on Sn films and SiO overlayers on Al films have been observed to depress the transition temperature of the film, while TlCl, Tl₂Se, and Ge overlayers produced an increase in the transition temperature of Tl films. Comparison with electrostatic-charging experiments,^{16,17,27} which indicate that removal of electrons decreases the transition temperature for Sn and Al films but increases T_c for Tl films, suggests that, in most cases, these shifts are related to charge transfer.

As a first approximation, the binding forces between adsorbed noble-gas atoms and a metal would be expected to be van der Waals' forces with no charge transfer. It has been suggested that a "non-bond-charge transfer" may play a role in noble-gas adsorption¹⁸; however, this mechanism would invariably result in a transfer of electrons to the metal. Comparison of the direction of the shifts produced by the noble-gas overlayers with electrostatic-charging experiments, dielectric-coating experiments, and oxidation experiments given in Table II convincingly excludes the possibility that the influence of noble gases is related to charge transfer.

It has been observed that the transition temperature of thin metallic films is often a smooth function of the residual resistance per square of the film, $R_{0\Box}$. For sufficiently thin films of a particular metal a larger $R_{0\Box}$ is generally associated with a lower transition temperature.^{13,14} Strongin *et al.*¹⁴ have suggested that the observed increase in transition temperature when Ge is deposited on Pb films is associated with a decrease in $R_{0\Box}$ due to the increased conductivity provided by the Ge layer. It should be pointed out, however, that no general relationship of this type is observed in di-

electric-coating experiments. For example, deposition of TlCl , Tl_2Se , and Ge on Tl films has been observed to increase both the residual resistance and the transition temperature of the film.^{24,25} In particular, there appears to be no general correlation between the sign of the change in resistance and the change in transition temperature produced by a noble-gas overlayer. For the metals Sn , Al , and Tl the direction of the shifts in T_c and those in $R_{0\Box}$ anticorrelate; however for α - Bi , α - Ga , and Pb they appear to correlate.

B. Modification of the Phonon Frequencies

One effect of the noble-gas overlayer is to modify the surface-vibrational frequencies of the metal film. In order to obtain a rough estimate of the shift in T_c resulting from this mechanism, we adopt the following Einstein model: Noble-gas atoms in the overlayer are assumed to have an effective force constant $k_n = M_n \omega_n^2 \propto M_n \Theta_n^2$, where M_n and Θ_n are respectively the atomic mass and Debye temperature for the bulk noble-gas solid. Metal ions in the interior of the film are assumed to have the effective force constant $k_m = M_m \omega_m^2 \propto M_m \Theta_m^2$, where M_m and Θ_m are, respectively, the atomic mass and Debye temperature of the bulk metal. The effective force constant for an ion at the metal surface is assumed to be k_m for vibrations parallel to the surface. For vibrations perpendicular to the surface, the effective force constant for a surface ion is assumed to be $\frac{1}{2}k_m$ before and $[\frac{1}{2}k_m + \frac{1}{2}(k_m k_n)^{1/2}]$ after the overlayer is added; i. e., roughly speaking, we assume that the noble-gas-metal force constant is given by the geometric mean of noble-gas-noble-gas and metal-metal force constants. If N is the total number of ions in the film and N_s is the number of surface ions, then before the overlayer is added there are $(3N - N_s)$ vibrational frequencies equal to ω_m and N_s frequencies equal to $(k_m/2M_m)^{1/2} = \omega_m/\sqrt{2}$, so that

$$\langle \omega^2 \rangle = [(3N - N_s)\omega_m^2 + \frac{1}{2}N_s\omega_m^2]/3N = (1 - \frac{1}{6}r)\omega_m^2, \quad (2)$$

with $r = N_s/N$. After the overlayer is added, the frequency $\omega_m/\sqrt{2}$ is changed to $\omega_m(1 + \alpha)^{1/2}/\sqrt{2}$, where

$$\alpha = (k_n/k_m)^{1/2} = (M_n \Theta_n^2/M_m \Theta_m^2)^{1/2}, \quad (3)$$

so that

$$\langle \omega^2 \rangle = [1 - \frac{1}{6}r(1 - \alpha)]\omega_m^2.$$

If we interpret $\langle \omega^2 \rangle$ as the McMillan average²² and use Eq. (23) of Ref. 22, then for $r \ll 1$ the change in the coupling constant λ is given by

$$\Delta\lambda/\lambda = -\frac{1}{6}\alpha r. \quad (4)$$

If $\Delta T_{c,Ar}$ and $\Delta T_{c,Ne}$ are, respectively, the shifts in T_c due to modification of the phonon frequencies when Ar and Ne are deposited on a given film, then Eqs. (3) and (4) imply that

$$\frac{\Delta T_{c,Ar}}{\Delta T_{c,Ne}} = \frac{(dT_c/d\lambda) \Delta\lambda_{Ar}}{(dT_c/d\lambda) \Delta\lambda_{Ne}} = \frac{\alpha_{Ar}}{\alpha_{Ne}} = 1.8, \quad (5)$$

independent of the particular model for T_c . (It is assumed that the dependence of T_c on the phonon frequencies can be written as a dependence on λ alone, to a good approximation, and that $\Delta\lambda$ is small.) This result is in surprisingly good agreement with the experimental data, as mentioned above. Our model also predicts that $\Delta T_{c,Xe}/\Delta T_{c,Ne} = 2.2$.

The magnitude of the shift which would be produced by the phonon modification alone may also be estimated. If the ratio r of the number of surface ions to total number of ions in the metal film were known, the expression for T_c developed by McMillan²² or by Garland *et al.*^{2,3} could be used to estimate this shift. For an order of magnitude estimate it may be assumed that the surface of the film is perfectly smooth and perfectly clean, in which case $r = a_0/D$, where a_0 is the distance between lattice planes parallel to the surface and D is the film

TABLE II. Summary of the effect of surface modifications on the transition temperature T_c and residual resistance R_0 of some weak-coupling superconductors.

Experiment	Property	Sn	Tl	Al
Coating with noble gases, Xe, Ar, Ne	T_c	decrease ^{a,b}	decrease ^{a-c}	decrease ^a
	R_0	increase	increase	increase
Oxidation	T_c	decrease ^d	increase ^d	increase ^d
Removal of electrons by electrostatic charging	T_c	decrease ^e	increase ^e	decrease ^f
	R_0	decrease	increase	decrease
Coating with dielectric and semiconductors	T_c	decrease ^{g,h}	increase ^{g,h}	decrease ⁱ
	R_0	increase	increase	increase

^aPresent work.

^bReference 21.

^cReference 23.

^dReference 15.

^eReference 17.

^fReference 27.

^gReference 24.

^hReference 25.

ⁱReference 26.

TABLE III. Values of the coefficient K (in \AA) which describes the shift of T_c for various noble-gas overlayers on thin Sn films, $\Delta T_c/T_c = -K/D$. The values in the first row are predicted from Eq. (6) and the McMillan expression for T_c (Ref. 22). Those in row two come from Eq. (7) and the expression for T_c of Garland *et al.* (Ref. 2). The experimental values for Ne and Ar are taken from this work while that for Xe is taken from Felsch and Glover (Ref. 21).

Noble gas	Ne	Ar	Xe
McMillan	0.09	0.16	0.20
Garland <i>et al.</i>	0.11	0.20	0.25
Experiment	0.17	0.30	0.37

thickness. According to the McMillan formula²² the expression for the shift is

$$\frac{\Delta T_c}{T_c} = \left(\frac{1.04\lambda}{(0.94\lambda - 0.1)^2} - \frac{1}{2} \right) \frac{0.17a_0}{D}, \quad (6)$$

where it has been assumed that $\langle \omega \rangle / \omega_0 = 0.62$ and $\mu^* = 0.1$.

According to the formula given by Garland *et al.*² the expression for the shift is

$$\frac{\Delta T_c}{T_c} = \left(\frac{\lambda [\mu^*(1 - 0.5A) + A]}{[A(1 - 0.5\mu^*)\lambda - \mu^*]^2} - \frac{1}{2} \right) \frac{0.17a_0}{D}. \quad (7)$$

In our estimates, the value of λ in a given formula was determined so as to yield the T_c measured for the experimental films when used in this formula. In the expression of Garland, Bennemann, and Mueller, the values of μ^* and A for disordered films given in Ref. 2 were used to estimate $\Delta T_c/T_c$ for Sn, Al, and Tl films. For a -Bi the modified version of the Garland formula for T_c given in Ref. 3 was used to determine a modified form of Eq. (7). The values of λ , $\langle \omega \rangle$, $\langle \omega^2 \rangle$, ω_0 , and μ^* given in Ref. 3 were used with this modified expression. Since we are attempting only an order of magnitude estimate, a_0 was taken to be 2.5 \AA for all of the metals.

The estimated values of K for Sn films coated with Ne, Ar, and Xe are compared with the experimental values in Table III. The agreement between the predicted and the measured values is remarkable in view of the simplicity of the model and the inaccuracies in the expressions for T_c . The fact that the predicted values are somewhat lower than the measured values can be readily rationalized, since the surface of a thin film is far from smooth. It is quite reasonable that surface irregularities might increase the actual surface area by as much as a factor of 2. Thus the magnitude of the shift to be expected from modification of the surface vibrational frequencies alone is sufficiently large to account for the entire measured shift.

Of as much interest as the magnitude of the shifts

of a given film is the ratio of the shifts for the different metals. Table IV lists the ratio of the coefficients K , which describe the magnitude of the shifts for the different metals normalized to that for Sn. The ratios estimated from Eq. (7) for a change in phonon frequencies only are given for comparison with the experimental ratios. As may be seen from these values, the relative magnitude of the shifts for the different metals to be expected from a modification of the surface vibrational frequencies is in good agreement with the experimental observations.

Although other factors (see Sec. IV C) may have some influence on the change in T_c , the agreement of our model with the experimental results strongly suggests that the *dominant* factor is modification of the phonon frequencies.

C. Other Influences

Recent experiments²⁸ have indicated that the quench condensation of a film may stress the substrate. In regard to the present experiments, one must ask if stresses on the metal film produced by condensation of the noble gas are sufficient to produce the observed effect. It is difficult to estimate the magnitude of the stresses which are developed; however, the experiments by Buckel²⁸ indicate that the stresses produced when metallic films are quench condensed are generally tensile. If this is true for the stresses produced by the quench-condensed noble gases, the stress would tend to increase the transition temperature of the films, as pointed out by Felsch and Glover,²¹ in contrast to the observed behavior.

If the stresses were not always tensile, one expects that they would sometimes be tensile and sometimes compressive, depending on the choice of metal and adsorbate, so that T_c would sometimes be increased in opposition to the observations. However, even if the stresses were always compressive for noble-gas condensation on a metal film, there is no reason to expect an appreciable difference between the magnitude of such a stress on a weak-coupling superconductor such as Sn or Al and that on a strong-coupling superconductor such

TABLE IV. Magnitudes of the shifts for different metals normalized to that for Sn. The first row gives the ratios predicted from Eq. (7) on the basis of a modification of the surface vibrational frequencies alone. The second row gives the experimental ratios from measurements reported in this paper.

	$\frac{K_{Al}}{K_{Sn}}$	$\frac{K_{Tl}}{K_{Sn}}$	$\frac{K_{Bi}}{K_{Sn}}$
Garland <i>et al.</i>	2.1	1.4	0.01
Experimental	2.8	1.8	< 0.07

as α -Bi, α -Ga, or Pb. An estimate of the relative magnitudes of the shifts $\Delta T_c/T_c$ for the different metals may be obtained from the values of $T_c^{-1}(dT_c/dP)$ for the bulk material under a uniform hydrostatic pressure. Values of (dT_c/dP) are of course not available for α -Bi and α -Ga; however, it is reasonable to assume that these materials are somewhat similar to the high-pressure phases Bi II and Ga II, which have approximately the same superconducting transition temperatures as α -Bi and α -Ga. The values of (dT_c/dP) taken from Levy and Olsen²⁹ indicate that, if the shifts were principally due to stresses, the value of $\Delta T_c/T_c$ for the strong-coupling films α -Bi, α -Ga, and Pb should be about one-half to one-third that observed for the weak-coupling material Sn. The fact that the shifts $\Delta T_c/T_c$ for α -Bi reported in the present work and for α -Ga and Pb reported by Felsch and Glover²¹ are at least an order of magnitude smaller than those for Sn indicates that the results cannot easily be explained in terms of stresses.

One might expect that a stronger argument against the influence of stresses could be made using the fact that (dT_c/dP) for Tl has the opposite sign from (dT_c/dP) for the other non-transition-metal superconductors. Care, however, must be taken when considering a material as anisotropic as Tl, where the sign of (dH_c/dP) is observed to change with the direction of a uniaxial stress P . Indeed preliminary experiments in this laboratory appear to indicate that the transition temperature for Tl films under a uniaxial stress parallel to the plane of the film changes in the same manner as for Sn films, in contrast to the behavior of bulk Tl under a uniform pressure.³⁰

There is another effect which might also influence the transition temperature of the films with the noble-gas overlayer. This is the influence of the noble gas on the boundary conditions for the normal-state electrons. Shapoval³¹ has considered the modification of T_c for a thin film due to the influence of the electronic boundary conditions. He assumes that the normal-state wave functions vanish at the clean surface of the sample, so that $|\psi_n|^2$ is somewhat larger inside the sample. This effective reduction in the volume available to the electrons reduces the density of states; however, this reduction is more than offset by the enhancement of $|\psi_n|^2$ inside the sample, and thus he predicts that the transition temperature of the thin film will be larger than that of the bulk.

If the presence of the noble-gas overlayer modifies the electronic wave functions at the boundary of the film such that they are drawn out of the metal into the noble gas, one would expect a reduction in T_c as observed in these experiments. One might even attribute the larger ΔT_c for Ar to the larger polarizability of Ar atoms as compared to Ne atoms:

An electron would be more strongly attracted by the more polarizable atoms, and so an Ar adsorbate would more strongly pull electrons out of the metal and thus produce a larger ΔT_c in accordance with Shapoval's hypothesis. However, such an argument is not really valid because it is based on classical electrostatics and omits the quantum-mechanical aspects of the problem. In particular, the Pauli principle will result in an effective *repulsion* of the electrons in the metal by those in a noble-gas atom, so it is possible that the electrons in the metal will be effectively compressed when the noble-gas adsorbate is deposited. In fact, the idea of Ref. 18—that the noble-gas atoms tend to lose electronic charge to the metal rather than *vice versa*—suggests that the electrons are more likely to be compressed than drawn out of the metal by a noble-gas adsorbate. According to Shapoval's ideas, such a compression would increase T_c , in opposition to the observed decrease. We therefore feel that it is impossible to predict even the sign of the shift ΔT_c due to a modification of the electronic states.

Furthermore, the prediction that ΔT_c for the strong-coupling materials is more than an order of magnitude smaller than that for the weak-coupling materials depends on a cancellation between the decrease in T_c provided by the decrease in λ and the increase in T_c provided by the increase in ω_0 , which multiplies the exponential factor. It is difficult to see how a modification of the boundary conditions would provide two competing processes of this type. Thus it appears that values of ΔT_c for strong-coupling superconductors predicted by boundary-condition modifications should be somewhat larger than the values which are predicted by phonon modification and which are observed experimentally.

V. SUMMARY AND CONCLUSIONS

It has been firmly established in at least three different laboratories that the presence of an adsorbed noble-gas layer on the free surface of a metal film alters both its superconducting and normal properties. The noble-gas overlayer increases the residual resistance and depresses the transition temperature of weak-coupling non-transition-metal superconductors. For the strong-coupling non-transition-metal superconductors, both the residual resistance and transition temperature are decreased. The magnitude of the depression of T_c for the weak-coupling superconductors is almost an order of magnitude larger than that for the strong-coupling superconductors. The influence of the heavier noble gas Ar is approximately 1.8 times that of Ne.

Although the depression in T_c and the change of residual resistance are small, it appears that these

effects do not result from small strains which could be formed when the noble-gas overlayer is quenched condensed and also are not related to the charge effect, which has been used in the past to account for changes in T_c produced when metal-dielectric boundaries are formed. Although it is impossible to rule out contributions from more subtle effects which cannot be estimated, such as the modification of the boundary conditions for the normal-state electrons, the simple model for the influence of the adsorbed gas on the vibrational frequencies of the metal-surface ions can adequately explain all the features of the observed shifts ΔT_c in transition temperature. These are (i) the fact that ΔT_c is always negative, (ii) the fact that ΔT_c is much larger for weak-coupling than for strong-coupling materials, (iii) the fact that ΔT_c is about 1.8 times as large for an Ar overlayer as for an Ne overlayer on any given film, (iv) the values of the ratio of ΔT_c for one metal to that for another metal, and (v) the magnitudes of ΔT_c for a given metal film and a given overlayer. The dominant contribution to the depression of T_c therefore appears to arise from modification of the phonon spectrum. No satisfactory explanation for the resistance changes, however, has been offered.

Our model for the modification of the phonon modes by the noble-gas overlayer indicates that only about 15% of the surface-phonon³² contribution to T_c is suppressed by the Ne overlayer and 25% by the Ar overlayer. A limit on the surface-phonon contribution to T_c may be obtained from the assumption that the measured depressions can be

completely attributed to modification of the surface vibrations. This conclusion implies that, for Al and Sn films characterized by the same "bulk" disorder as those used in the present experiments, the T_c for a 50-Å film is increased by about 0.1 °K relative to the T_c for a very thick film solely because of the effect of a surface on the phonon frequencies. This increase in T_c due to surface-phonon effects should be only somewhat larger in clean (well-ordered) films. Thus the maximum enhancement of T_c to be obtained for a film sufficiently thick to be metallic would be of the order of 1–3 °K and much of that enhancement would be lost on exposure to the atmosphere. Surface-phonon enhancement thus does not appear to offer a practical means for producing high-temperature superconductors.

Recent experiments³³ indicate that physisorbed O₂ depresses the transition temperature of Sn films. The effect was attributed entirely to the paramagnetic moment of the O₂ molecule. Using our model and the measured shifts for Sn with Ar and Ne overlayers, we estimate that nearly half of the depression of T_c is attributable to modification of the phonon frequencies rather than magnetic effects.

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contribution" to represent the shift in T_c which is caused by the effect of a surface on all the phonon modes of the metal. The surface causes (i) surface phonons, which are localized near the surface, to be present and (ii) the bulk phonon frequencies to be modified.

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PHYSICAL REVIEW B

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Thermally Induced Flux Motion in Superconducting Tin*

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Direct evidence is presented for thermally induced flux motion in a superconductor. The method consists of setting up the macroscopic Landau domain structure in a thin single crystal of tin and imposing a temperature gradient along the sample. Motion is monitored with the Sharvin point-contact technique, enabling one to deduce an experimental value for the actual velocity of flux motion. The dependence of this velocity on the applied temperature gradient is found to be in fair agreement with a theory due to Clem.

Theory^{1,2} and experiment³⁻⁵ are in agreement in that it is possible to set flux into continuous motion in a superconductor by applying a thermal gradient. However, the available experimental evidence, in both type-I and type-II superconductors, is restricted to the measurement of various macroscopic time-independent electric fields associated with the presumed motion. In addition, the geometry of the flux structures involved is often unclear and so no detailed test of the various theories has been possible. However, it is known⁶ that the well-defined Landau domain structure can be set up in a type-I superconductor by applying a magnetic field at a small angle to a thin flat plate. Moreover, this structure can certainly be set into motion with an electric current and the motion observed directly, either over the whole sample with the magneto-optic technique⁷ or at a single point using Sharvin's method.^{8,9} We wish to report the results of an experiment, using the latter method, which clearly demonstrate that continuous regular motion can also be realized with a thermal gradient. Furthermore, our observations allow us to deduce an experimental value for the actual velocity of flux motion and so, for the first time, allow a comparison of this fundamental aspect of the phenomena with theory.

The experimental arrangement is shown in Fig. 1(a). A temperature gradient was obtained, in the usual way, by mounting the sample in an evacuated can and raising the temperature of one end with a heater, the other end being thermally linked to a helium bath by means of a copper post. The indicated temperature difference ΔT was obtained by measuring the temperature at two points 1.5 cm

apart on the sample which was a single crystal of dimensions $40 \times 5 \times 0.75$ mm cast from tin of 99.9999% purity. A magnetic field was applied at a small angle β to the plane of the sample in order to set up the Landau structure. Domain motion was monitored using the Sharvin point-contact technique,⁸ the contact resistance of a fine copper wire affixed to the sample in the vicinity of its geometric center being recorded as a function of time.

A direct chart-recorder trace of resistance fluctuations observed in the presence of a thermal gradient is shown in Fig. 1(b), with the experimental conditions identified in the caption. The vertical axis records resistance with the maxima corresponding to material under the point being completely normal and minima to its being superconducting. Occasional extended sequences of fluctuations have been observed which are extremely regular, but the trace displayed in Fig. 1(b) is typical of that which could be reproducibly obtained under a variety of experimental conditions. The spatial periodicity a [identified in Fig. 1(a)] of the domain structure in tin is known^{6,9} with about a 10% uncertainty for a given value of T , β , and C_N , where the last quantity, the volume fraction of the sample in the normal state, is obtained directly from traces, such as Fig. 1(b), by averaging over ~ 15 fluctuations. Using similar averaging, one obtains the number of domains/sec passing under the point, and multiplication by a gives an average velocity of domain motion for the given values of β , C_N , T , and ΔT . The variable of main interest is ΔT and Fig. 1(c) shows the result of varying this while holding β , C_N , and T constant. The error bars represent the maximum variation encountered in the velocity