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1969 Spring Superconducting Symposia

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Edited by

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May 16, 1969

NAVAL RESEARCH LABORATORY
Washington, D.C.

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PREVIOUS REPORTS IN THIS SERIES

"Proceedings of First Symposium, 1969 Spring Superconducting Symposia," NRL Report 6962, March 28, 1969

"Proceedings of Second Symposium, 1969 Spring Superconducting Symposia," NRL Report 6972, April 25, 1969

PREFACE

The Office of Naval Research and the Naval Research Laboratory recognized a number of advantages in cosponsoring and conducting a series of four one-day symposia on superconducting materials and devices. These meetings, held at the Naval Research Laboratory during the spring of 1969, had as their primary motives ...

a. To bring together scientists, engineers, and science administrators from some 18 government, university, and industrial laboratories in the Washington-Baltimore area which are engaged in or sponsoring research programs involving superconductivity.

b. To provide an opportunity for these persons to meet each other, to hear formally prepared papers by their colleagues, and to engage in informal and frank discussions of their research programs.

c. To collect and disseminate comments and opinions of experts regarding the current status and the future of research on superconducting materials and devices.

The morning session of each symposium was devoted to four invited forty-minute papers. Each afternoon the four invited speakers formed a panel to discuss questions posed by the audience.

Recordings, transcripts, and then lightly edited manuscripts of the papers were prepared for publication in the Proceedings, this being the third of four to appear. In order to provide an atmosphere of free uninhibited discussions in the afternoon, no recordings were made.

Topics for presentation, speakers, and general planning of this series of symposia were the responsibility of the Organizing Committee. The sixteen papers given represented authors from three government laboratories, eight universities, and four industrial laboratories. Although this series was initially established for the Washington-Baltimore community, early publicity and announcements generated sufficient distant interests so that a number of attendees appeared from outside this geographic area.

It is a pleasure to acknowledge the efforts of the following individuals who significantly contributed to the success of these four symposia:

Mr. John J. Lister, Mr. David N. Ginsburgh, and Mr. John M. Hoggatt; Public Affairs Branch, NRL; arrangements and smooth operations of the symposia at NRL.

Mrs. Mary L. Taylor; Security Branch, NRL; internal security.

Mr. Warren H. Ramey and staff; Graphic Arts Branch, NRL; design and printing of announcements, programs, and proceedings.

Mr. Kenneth A. Klausing; Graphic Arts Branch, NRL; photography of persons and blackboard presentations.

Dr. Edward H. Takken and Mr. John E. Cox; Magnetism Branch, NRL; for their help in editing the transcriptions.

Mrs. E. R. Shapiro, Magnetism Branch, NRL; for her services as receptionist.

The programs for the four days follow.

SYMPOSIUM I, March 28, 1969, "SUPERCONDUCTIVITY AMONG METALLIC ELEMENTS AND ALLOYS"

Chairman and panel moderator — Dr. R. A. Hein

1. Dr. B. T. Matthias, "The Where and How to Obtain High Transition Temperatures."
2. Dr. W. L. McMillan, "Superconductivity and the Electron-Phonon Interaction."
3. Dr. T. H. Geballe, "Intermetallic Compounds — An Unlimited Source."
4. Dr. J. W. Garland, "Mechanisms for Superconductivity."

SYMPOSIUM II, April 25, 1969, "SUPERCONDUCTIVITY AMONG DEGENERATE SEMICONDUCTORS AND SEMIMETALS"

Chairman and panel moderator — Dr. R. A. Hein

1. Dr. J. F. Schooley, "Superconductivity in Degenerate Semiconductors."
2. Dr. C. S. Koonce, "Low Carrier Density Superconductors."
3. Dr. J. K. Hulm, "Superconductivity in Low Carrier Density Rock Salt Compounds."
4. Dr. P. E. Seiden, "Superconductivity in 'Free Electron Like' Superconductors."

SYMPOSIUM III, May 16, 1969, "EFFECTS WHICH ENHANCE THE SUPERCONDUCTING TRANSITION TEMPERATURE

Chairman — Dr. R. A. Hein; Panel Moderator — Dr. R. Glover

1. Prof. J. D. Leslie, "Electron Tunneling Investigations in Amorphous and Disordered Superconductors."
2. Dr. A. Paskin, "Enhancement of T_c in Thin Films."
3. Dr. F. R. Gamble, "Molecular Enhancement Effects."
4. Prof. J. R. Schrieffer, "Theories of Enhancement Effects."

SYMPOSIUM IV, June 6, 1969, "SUPERCONDUCTING DEVICES"

Chairman — E. A. Edelsack; Panel Moderator — Dr. W. Gregory

1. Prof. B. S. Deaver, Jr., "Superconducting Devices."

2. Prof. S. Shapiro, "Infrared Detectors."

3. Dr. W. Goree, "Superconducting Magnetometers."

4. Dr. Z. J. Stekly, "Superconducting Magnets."

Organizing Committee

R. A. Hein — NRL
E. A. Edelsack — ONR

CONTENTS

Preface i

ELECTRON TUNNELING INVESTIGATIONS IN AMORPHOUS AND DISORDERED SUPERCONDUCTORS 1
J.D. Leslie

ENHANCEMENT OF T_c IN THIN FILMS 14
A. Paskin

MOLECULAR ENHANCEMENT EFFECTS 27
F.R. Gamble

THEORIES OF ENHANCEMENT EFFECTS 36
J.R. Schrieffer

ELECTRON TUNNELING INVESTIGATIONS IN AMORPHOUS AND DISORDERED SUPERCONDUCTORS

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My collaborators on the work to be described here were Juei-Teng Chen and Tom Tung Chen, two graduate students of mine, and Dr. H. J. T. Smith, a colleague in the Physics Department at Waterloo.

INTRODUCTION

At the present time there is much interest in trying to obtain high T_c superconductors, for obvious technological reasons, and consequently there is much effort in trying to understand why certain superconductors have high T_c, and whether there are effects that might enhance T_c. In this regard we thought that it might be interesting to look at amorphous Bi and Ga because they are both materials that show dramatic changes in T_c when they go from the crystalline to the amorphous state. For example, crystalline Bi is nonsuperconducting down to 50 millidegrees (1), but when Bi is quench-condensed onto a substrate at helium temperature one obtains amorphous Bi with a T_c of approximately 6K (2). Similarly, the normal crystalline phase of Ga is superconducting with a T_c of 1.08K (3), but amorphous Ga has a T_c of approximately 8.5K (2). The variable influence of the crystalline to amorphous transition on T_c has been studied since 1954, and much work has been done on amorphous superconductors since then, primarily by Hilsch and Buckel and their coworkers. However, much of their work has been measurements of T_c as a function of alloying, annealing, etc. With T_c measurements alone it is difficult to determine the mechanism producing the changes in T_c. When we started our tunneling work on amorphous Bi and Ga a few years ago, there had been a measurement of the energy gap of amorphous Bi by Reif and Woolf (4) which suggested that amorphous Bi might be a strong-coupling superconductor. Hence it might be possible to see phonon structure in the tunneling curves and, by using the standard formalism of strong-coupling superconductivity theory, to determine the mechanism responsible for the high value of T_c.

EXPERIMENTAL METHODS

I would like to discuss briefly some of the experimental methods of our work. The tunnel junctions are prepared in situ in an evaporator-cryostat in the following manner. Three aluminum strips 0.6 mm wide are evaporated at room temperature onto a glass or sapphire substrate that is mounted on a copper block containing a He-3 evaporation pot. After partial oxidation of the aluminum strips to form the tunneling barrier, the substrate is cooled down to 1.5K, and then cross strips of the material to be investigated are quench-condensed onto the substrate to complete the three junctions. Typically these cross strips are 0.5 mm wide and 1000 Å thick as determined from resistance measurements. Temperatures are measured with a calibrated germanium resistor (5) attached to the

back of the substrate mounting block. Warming of the substrate by thermal radiation during the measurements is made negligible by the use of multiple heat shields and thermally anchored shutters. One point to note is that once the amorphous samples are prepared they have to be kept below certain "conversion" temperatures (approximately 20K for Bi and 15K for Ga), otherwise the amorphous phase converts to a crystalline phase.

The type of tunneling measurements that we make are the standard ones and the electronic circuits for making the measurements are essentially standard (6). We measure current-voltage (I-V) characteristics so that we can obtain the energy gap parameter Δ. In Fig. 1 we see typical I-V characteristics for an $A\ell$-$A\ell_xO_y$-Bi junction for various temperatures. The characteristic is analysed for Δ_{Bi} in the usual way: the maximum is taken to occur at $\Delta_{Bi}-\Delta_{A\ell}$ and the midpoint of the steep rise (or the point where an extrapolation of the steep rise cuts the voltage axis) is taken to occur at $\Delta_{Bi}+\Delta_{A\ell}$. Theoretically the current should show a vertical jump at $\Delta_{Bi}+\Delta_{A\ell}$, but experimentally there is always a finite slope to the sharp increase in current, and the uncertainty in where to take the sum of the two energy gaps leads to most of the estimated error of ± 0.02 meV in Δ.

The other types of tunneling measurements are derivative measurements. In Fig. 2 we see some typical results for an $A\ell$-$A\ell_xO_y$-Bi junction. We measure the slope of the I-V characteristic in the superconducting and normal states, i.e. $(dV/dI)_s$ and $(dV/dI)_n$, respectively, and then we plot up the ratio $(dV/dI)_n/(dV/dI)_s$. In Fig. 2 $(dV/dI)_n$ is shown as curve (a), $(dV/dI)_s$ as curve (b), and their ratio as curve (c). The ratio curve $(dV/dI)_n/(dV/dI)_s$ is related to the quantity of theoretical interest $N(\omega)$, the effective electron tunneling density of states in the superconductor. In Fig. 2 can be seen one of our main experimental difficulties, i.e., all these amorphous materials show large

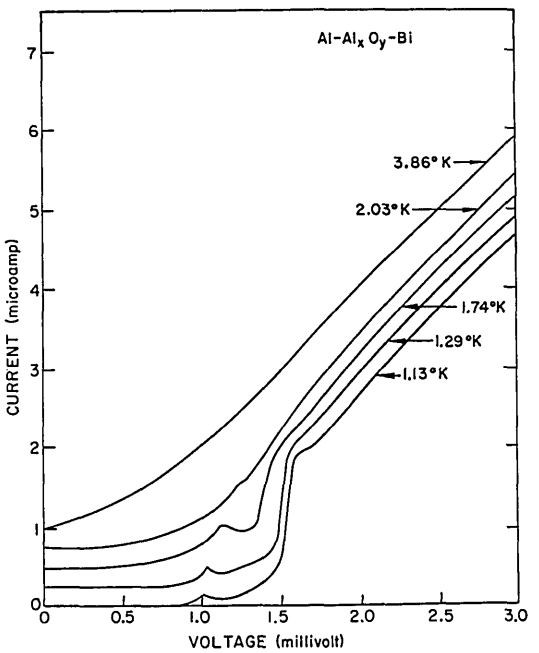

Fig. 1 - Current-voltage characteristics. For clarity the curves have been displaced by 0.25 μA intervals.

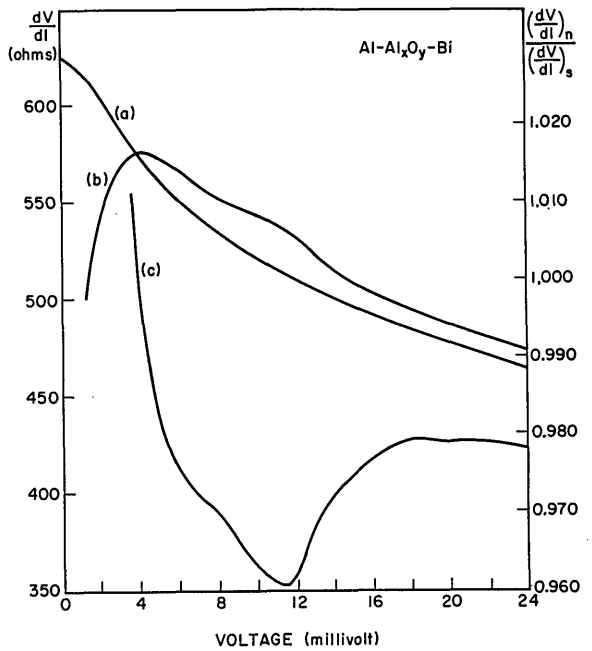

Fig. 2 - Curve (a): Incremental junction resistance $(dV/dI)_n$ of bismuth in normal state vs voltage at 6.90K. Curve (b): Incremental junction resistance $(dV/dI)_s$ of bismuth in superconducting state vs voltage at 1.15K. Curve (c): Relative differential conductance $(dV/dI)_n/(dV/dI)_s$ vs voltage derived directly from the data of curves (a) and (b). To correct for bismuth film resistance, curve (c) should be normalized to 1.000 at 24 meV. The same type of junction was used as in Fig. 1.

zero-bias anomalies. In our apparatus at present we cannot apply a magnetic field to force the films normal. So we have to take the $(dV/dI)_n$ curve at T greater than the T_c of the amorphous film, in this case at T = 6.90K, whereas the $(dV/dI)_s$ curve was taken at 1.15K. Ideally the two curves should be taken at the same temperature, but in the case of amorphous Bi and Ga, at least, we have some evidence that the temperature dependence of the zero-bias anomaly is not very strong, so we think that we are on fairly safe ground in taking the ratio as we do. Another complicating factor can be seen in Fig. 2, i.e., the ratio plot does not approach one at high voltage as it should theoretically. This is caused by the high resistivity of the amorphous Bi in the normal state, which causes a slight ac voltage drop across the width of the junction and leads to $(dV/dI)_n$ being lower than its true value. We correct for this by normalizing the ratio to 1.000 at high voltage. We also measure second derivatives of the I-V characteristic, but these are used just to check the accuracy of the first derivative curves in certain voltage regions and also to suggest the position and form of the phonon structure that we should use as an initial guess in our fitting procedure.

INVERTING THE GAP EQUATION

In strong-coupling superconductivity theory the energy gap is a function of energy:

$$\Delta(\omega) = \phi(\omega)/Z(\omega) \tag{1}$$

where $\Delta(\omega)$ is the energy gap function, $\phi(\omega)$ is the pairing self-energy, and $Z(\omega)$ is the renormalization function. $Z(\omega)$ can also be expressed in terms of $\xi(\omega)$, which is the normal self-energy. These functions are interrelated by the Eliashberg integral gap equations:

$$\xi(\omega) = [1 - Z(\omega)]\,\omega = \int_{\Delta_0}^{\infty} d\omega' \; \mathrm{Re}\left(\frac{\omega'}{(\omega'^2 - \Delta'^2)^{1/2}}\right)$$

$$\times \left\{ \int d\omega_q \, \alpha^2(\omega_q) \, F(\omega_q) \, [D_q(\omega' + \omega) - D_q(\omega' - \omega)] \right\} \tag{2}$$

and

$$\phi(\omega) = \int_{\Delta_0}^{\omega_c} d\omega' \; \mathrm{Re}\left(\frac{\Delta'}{(\omega'^2 - \Delta'^2)^{1/2}}\right)$$

$$\times \left\{ \int d\omega_q \, \alpha^2(\omega_q) \, F(\omega_q) \, [D_q(\omega' + \omega) + D_q(\omega' - \omega)] - \mu^* \right\} \tag{3}$$

where $D_q(\omega) = (\omega + \omega_q - io^+)^{-1}$ and ω_c is a cutoff energy. $F(\omega)$ is the phonon density of states, $\alpha^2(\omega)$ is an effective electron-phonon coupling function, and μ^* is the Coulomb pseudopotential. The quantities that can be extracted from the inversion procedure are the product $\alpha^2(\omega)F(\omega)$ and μ^*. Δ_0 is the measured value of the energy gap parameter and is given by the value of the energy gap function at an energy Δ_0, i.e., $\Delta_0 = \Delta(\Delta_0)$. Finally, the effective electron tunneling density of states $N(\omega)$ is given by

$$N(\omega) = \mathrm{Re}\left(\frac{\omega}{\sqrt{\omega^2 - \Delta^2(\omega)}}\right) \tag{4}$$

which we see is an expression that comes into Eq. (2).

Now if one knows $\alpha^2(\omega)F(\omega)$ and μ^*, one can solve the integral gap equations by an iterative technique. To start the iteration one puts in the BCS approximation that

$$\Delta(\omega) = \begin{cases} \Delta_0 \, , & \omega < \omega_0 \\ 0 \, , & \omega > \omega_0 \end{cases} \tag{5}$$

One integrates Eqs. (2) and (3) to get first-order expressions for $\xi(\omega)$ and $\phi(\omega)$, and hence for $\Delta(\omega)$, which can then be put back into Eqs. (2) and (3) and the process repeated. This is what Schrieffer, Scalapino, and Wilkins (7) did when they solved these equations first for a model phonon spectrum. Naturally, when programmed for a digital computer this iteration technique can be fast and accurate.

McMillan (8) took this process much farther by writing a digital computer program, the McMillan inversion program, which not only solves the gap equations for a given $\alpha^2(\omega)F(\omega)$ and μ^*, but compares the theoretical tunneling density of states $N_c(\omega)$ calculated from these parameters with the experimental tunneling density of states $N_e(\omega)$ and calculates how the computer should change $\alpha^2(\omega)F(\omega)$ and μ^* so that the theoretical and experimental density of states match better. The computer uses the new $\alpha^2(\omega)F(\omega)$ and μ^* in the gap equations and the process is iterated until, hopefully, it converges and one

finds an $\alpha^2(\omega)F(\omega)$ and μ^* that, when put in the gap equations, exactly reproduces the measured density of states.

Figure 3 shows the $\alpha^2(\omega)F(\omega)$ for crystalline Pb that McMillan and Rowell (8) obtained by the above inversion procedure. This figure shows the typical type of phonon spectrum that one gets for a crystalline superconductor. Note that there are few phonons at low energies and the transverse and longitudinal phonon peaks are fairly narrow. Now with this as a reference for what a crystalline material is like, we can go on to look at the type of phonon spectra that we find for amorphous superconductors.

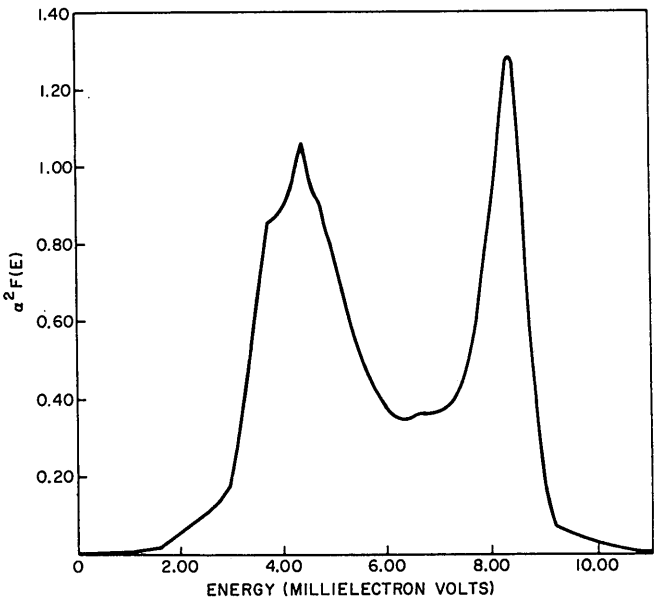

Fig. 3 - $\alpha^2(\omega)F(\omega)$ for crystalline Pb from McMillan and Rowell (Ref. 8)

PHONON SPECTRA OF AMORPHOUS Bi AND Ga

Figure 4 shows some tunneling results for amorphous Bi (9). The solid curve in Fig. 4(a) is the experimental $N(\omega)/N_{BCS}(\omega)$ data. The curve of Fig. 4(b) shows the phonon spectrum $\alpha^2(\omega)F(\omega)$ derived by using the McMillan program to invert the experimental $N(\omega)/N_{BCS}(\omega)$ data shown in Fig. 4(a). The dashed curve through the solid circles in Fig. 4(a) is the $N(\omega)/N_{BCS}(\omega)$ calculated from the gap equations using the phonon spectrum of Fig. 4(b). It can be seen that the fit between the experimental and calculated densities of states is quite good. The main points to note about the $\alpha^2(\omega)F(\omega)$ of amorphous Bi in comparison to what we have seen for crystalline Pb is that there is a much larger density of phonons at low energies and the phonon peaks are smeared out. Figure 5 shows tunneling results for amorphous Ga, presented in the same way as in Fig. 4. Once again, we see that the phonon spectrum $\alpha^2(\omega)F(\omega)$ is shifted towards lower energies and the phonon peaks are smeared out compared to what is found for a crystalline superconductor.

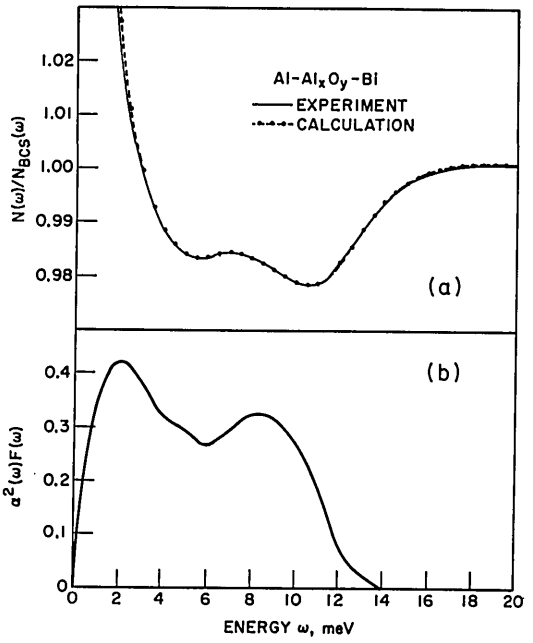

Fig. 4 - Tunneling results for amorphous bismuth. (a) The solid line is the plot of the experimental $N(\omega)/N_{BCS}(\omega)$ data. The dashed line through the solid circles is $N(\omega)/N_{BCS}(\omega)$ calculated from the gap equations using the phonon spectrum shown in (b). (b) The phonon spectrum $\alpha^2(\omega)F(\omega)$ derived by using the McMillan program to invert the experimental $N(\omega)/N_{BCS}(\omega)$ data shown in (a).

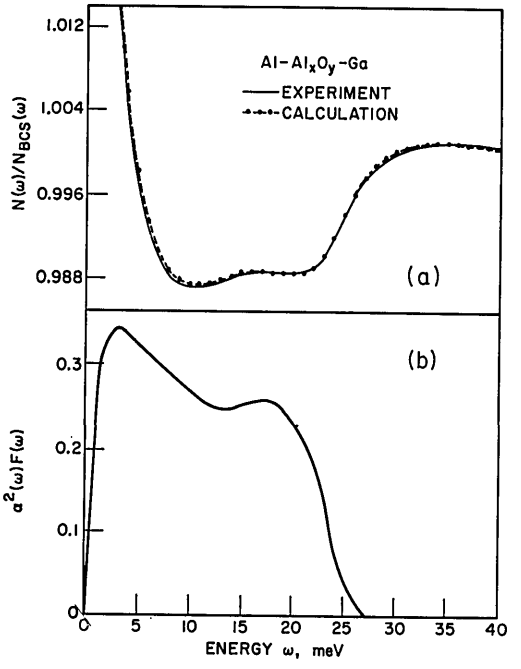

Fig. 5 - Tunneling results for amorphous gallium. (a) The solid line is the plot of the experimental $N(\omega)/N_{BCS}(\omega)$ data. The dashed line through the solid circles is $N(\omega)/N_{BCS}(\omega)$ calculated from the gap equations using the phonon spectrum shown in (b). (b) The phonon spectrum $\alpha^2(\omega)F(\omega)$ derived by using the McMillan program to invert the experimental $N(\omega)/N_{BCS}(\omega)$ data shown in (a).

COMPARISON WITH THEORY

The most direct check of our phonon spectra $\alpha^2(\omega)F(\omega)$ would be to put them in the temperature-dependent gap equations and find T_c by finding the temperature at which the gap parameter goes to zero. Also we could see if our spectra give T_c of 6.11K for amorphous Bi and 8.56K for amorphous Ga, i.e., the experimental values. However, since we do not have a program for this at the present, we have not been able to do this yet. However, if we assume that our phonon spectra are accurate, and the good agreement between the experimental and calculated tunneling density of states would suggest this, then we can use our results to test some of the approximate theories of the transition temperature of strong-coupling superconductors that involve parameters which are averages over the phonon spectrum $\alpha^2(\omega)F(\omega)$. The following parameters are useful for characterizing $\alpha^2(\omega)F(\omega)$, and some of them enter into these approximate theories:

a. the total electron-phonon interaction α_T^2, i.e., the total area under the $\alpha^2(\omega)F(\omega)$ plot,

$$\alpha_T^2 = \int \alpha^2(\omega)\, F(\omega)\, d\omega \ , \tag{5}$$

b. the electron-phonon coupling constant λ defined by

$$\lambda = 2 \int \alpha^2(\omega) F(\omega)\, \omega^{-1}\, d\omega \ , \tag{6}$$

c. the average phonon energy $\langle\omega\rangle$ and the average squared phonon energy $\langle\omega^2\rangle$, both introduced by McMillan (10),

$$\langle\omega\rangle = \left(\int \alpha^2(\omega)\, F(\omega)\, d\omega\right) \Big/ \left(\int \alpha^2(\omega)\, F(\omega)\, \omega^{-1}\, d\omega\right) \tag{7}$$

$$\langle\omega\rangle = \left(\int \alpha^2(\omega) F(\omega)\, d\omega\right) \Big/ \left(\int \alpha^2(\omega)\, F(\omega)\, \omega^{-1}\, d\omega\right) \ , \tag{8}$$

d. the endpoint of the phonon spectrum $\langle\omega_0\rangle$, and

e. the Coulomb pseudopotential μ^*.

Table I shows the values that we get for these parameters for amorphous Bi and Ga. The "softening of the phonon spectrum," i.e., the shift of the phonon density of states to lower energies, shows up in the low values of $\langle\omega\rangle/\omega_0$ — 0.24 for Bi and 0.22 for Ga — compared to what is found for crystalline superconductors — 0.53 for Pb (11) and 0.62 for Nb (10). Also the softening of the lattice shows up in a large λ — 2.46 for Bi and 2.25 for Ga — compared to what is found for crystalline superconductors — 1.6 for Hg and 1.5 for Pb (10).

McMillan (10) derived the following expression for the T_c of a strongly-coupled superconductor:

ELECTRON TUNNELING INVESTIGATIONS IN AMORPHOUS AND DISORDERED SUPERCONDUCTORS

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My collaborators on the work to be described here were Juei-Teng Chen and Tom Tung Chen, two graduate students of mine, and Dr. H. J. T. Smith, a colleague in the Physics Department at Waterloo.

INTRODUCTION

At the present time there is much interest in trying to obtain high T_c superconductors, for obvious technological reasons, and consequently there is much effort in trying to understand why certain superconductors have high T_c, and whether there are effects that might enhance T_c. In this regard we thought that it might be interesting to look at amorphous Bi and Ga because they are both materials that show dramatic changes in T_c when they go from the crystalline to the amorphous state. For example, crystalline Bi is nonsuperconducting down to 50 millidegrees (1), but when Bi is quench-condensed onto a substrate at helium temperature one obtains amorphous Bi with a T_c of approximately 6K (2). Similarly, the normal crystalline phase of Ga is superconducting with a T_c of 1.08K (3), but amorphous Ga has a T_c of approximately 8.5K (2). The variable influence of the crystalline to amorphous transition on T_c has been studied since 1954, and much work has been done on amorphous superconductors since then, primarily by Hilsch and Buckel and their coworkers. However, much of their work has been measurements of T_c as a function of alloying, annealing, etc. With T_c measurements alone it is difficult to determine the mechanism producing the changes in T_c. When we started our tunneling work on amorphous Bi and Ga a few years ago, there had been a measurement of the energy gap of amorphous Bi by Reif and Woolf (4) which suggested that amorphous Bi might be a strong-coupling superconductor. Hence it might be possible to see phonon structure in the tunneling curves and, by using the standard formalism of strong-coupling superconductivity theory, to determine the mechanism responsible for the high value of T_c.

EXPERIMENTAL METHODS

I would like to discuss briefly some of the experimental methods of our work. The tunnel junctions are prepared in situ in an evaporator-cryostat in the following manner. Three aluminum strips 0.6 mm wide are evaporated at room temperature onto a glass or sapphire substrate that is mounted on a copper block containing a He-3 evaporation pot. After partial oxidation of the aluminum strips to form the tunneling barrier, the substrate is cooled down to 1.5K, and then cross strips of the material to be investigated are quench-condensed onto the substrate to complete the three junctions. Typically these cross strips are 0.5 mm wide and 1000 Å thick as determined from resistance measurements. Temperatures are measured with a calibrated germanium resistor (5) attached to the

18.4 and 36.6K for amorphous Bi and Ga, respectively. However, there is uncertainty in what to take for θ_D, and perhaps this is an unfair comparison. If instead we use Eq. (10) and the values of λ and $\langle\omega^2\rangle$ derived from our phonon spectra to calculate T_c^{max}, we obtain T_c^{max} = 11.6 and 21.6K for amorphous Bi and Ga, respectively. With our values of λ, Eq. (11) would predict that $T_c = T_c^{max}$; however our values of T_c are much lower (by a factor of 2 to 2.5) than the predicted values of T_c^{max}. We would suggest that if our phonon spectra are typical of the extreme softening of the phonon spectra needed to obtain $\lambda \approx 2$, then Eqs. (9) - (11) are invalid in the limit $\lambda \approx 2$.

Recently Garland, Bennemann, and Mueller (13) have derived an expression for the transition temperature of disordered or amorphous superconductors. Their theory is based on the assumption that the average amplitude of ionic vibration is larger in a disordered lattice than a perfect crystal, and they conclude that this results in a decrease in $\langle\omega\rangle$, an increase in λ, and a broadening of the peaks in $F(\omega)$ in a disordered or amorphous superconductor in comparison with a crystalline one. Qualitatively our results agree with these conclusions.

The expression that Garland et al. derive is essentially a parameterized McMillan-type equation:

$$\ln\left(\frac{\langle\omega^2\rangle^{1/2}}{T_c}\right) = \frac{1+\lambda}{A\lambda\left(1-\frac{\mu^*\langle\omega\rangle}{\omega_0}\right)-\mu^*} \tag{12}$$

It is of the same form as the McMillan equation, except that it involves a parameter A which depends on the shape of the phonon spectrum. Garland (14) has informed us that A can be written in terms of measurable parameters in the approximate form

$$A = 0.52\left(1+\frac{\langle\omega^2\rangle^{1/2}}{\omega_0}\right) \tag{13}$$

Equation (12) can be made to look more like the McMillan equation (Eq. (9)) by rewriting it in the form

$$T_c = \langle\omega^2\rangle^{1/2}\exp\left(\frac{\sim(1+\lambda)}{A\lambda-\mu^*\left(1+\frac{\langle\omega\rangle}{\omega_0}A\lambda\right)}\right) \tag{14}$$

One sees that if A is taken to be 1, $\langle\omega\rangle/\omega_0$ is set equal to its value for Nb, i.e., 0.62, and $\langle\omega^2\rangle^{1/2}$ is taken to be $\theta_D/1.45$, then one recovers the McMillan equation except for a factor of 1.04 in the numerator of the exponent.

If we use our values of μ^*, λ, $\langle\omega\rangle$, $\langle\omega^2\rangle$, and ω_0, Eq. (14) predicts that T_c should be 5.1K for amorphous Bi (~18% lower than the experimental value of 6.11K) and 7.6K for amorphous Ga (~11% lower than the experimental value of 8.56K). The values of T_c predicted by Eq. (14) represent reasonable agreement of the theory of Garland et al. with our experimental results for amorphous Bi and Ga.

ELECTRON TUNNELING INVESTIGATIONS IN AMORPHOUS AND DISORDERED SUPERCONDUCTORS

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At the present time there is much interest in trying to obtain high T_c superconductors, for obvious technological reasons, and consequently there is much effort in trying to understand why certain superconductors have high T_c, and whether there are effects that might enhance T_c. In this regard we thought that it might be interesting to look at amorphous Bi and Ga because they are both materials that show dramatic changes in T_c when they go from the crystalline to the amorphous state. For example, crystalline Bi is nonsuperconducting down to 50 millidegrees (1), but when Bi is quench-condensed onto a substrate at helium temperature one obtains amorphous Bi with a T_c of approximately 6K (2). Similarly, the normal crystalline phase of Ga is superconducting with a T_c of 1.08K (3), but amorphous Ga has a T_c of approximately 8.5K (2). The variable influence of the crystalline to amorphous transition on T_c has been studied since 1954, and much work has been done on amorphous superconductors since then, primarily by Hilsch and Buckel and their coworkers. However, much of their work has been measurements of T_c as a function of alloying, annealing, etc. With T_c measurements alone it is difficult to determine the mechanism producing the changes in T_c. When we started our tunneling work on amorphous Bi and Ga a few years ago, there had been a measurement of the energy gap of amorphous Bi by Reif and Woolf (4) which suggested that amorphous Bi might be a strong-coupling superconductor. Hence it might be possible to see phonon structure in the tunneling curves and, by using the standard formalism of strong-coupling superconductivity theory, to determine the mechanism responsible for the high value of T_c.

EXPERIMENTAL METHODS

I would like to discuss briefly some of the experimental methods of our work. The tunnel junctions are prepared in situ in an evaporator-cryostat in the following manner. Three aluminum strips 0.6 mm wide are evaporated at room temperature onto a glass or sapphire substrate that is mounted on a copper block containing a He-3 evaporation pot. After partial oxidation of the aluminum strips to form the tunneling barrier, the substrate is cooled down to 1.5K, and then cross strips of the material to be investigated are quench-condensed onto the substrate to complete the three junctions. Typically these cross strips are 0.5 mm wide and 1000 Å thick as determined from resistance measurements. Temperatures are measured with a calibrated germanium resistor (5) attached to the

minimum in going from Pb to Bi. We calculated the product $\lambda \langle \omega^2 \rangle$ and we see that it decreases by approximately 15% in going from Pb to Bi. McMillan proposed that $M\lambda \langle \omega^2 \rangle$, where M is the ionic mass, should be approximately a constant for the same class of materials and we find that this is verified within experimental error. (Since Pb and Bi are next to each other in the periodic table and are quite heavy, the variation in M can be neglected. Also the experimental uncertainty in λ and $\langle \omega^2 \rangle$ can probably account for a variation of 15% in their product.)

Table II
Phonon Spectra Parameters for
Disordered-Amorphous Pb-Bi Alloys

PARAMETER	Pb	$Pb_{.75}Bi_{.25}$	$Pb_{.25}Bi_{.75}$	Bi
α_T^2 meV	4·27	4·22	4·00	3·50
λ	2·15	3·00	2·93	2·46
μ^*	0·17	0·14	0·12	0·11
$\langle\omega\rangle$ meV	3·97	2·82	2·73	2·86
$\langle\omega^2\rangle$ $(meV)^2$	21·8	14·6	14·7	16·3
$\langle\omega^2\rangle^{1/2}$ meV	4·67	3·82	3·83	4·04

PARAMETER	Pb	$Pb_{.75}Bi_{.25}$	$Pb_{.25}Bi_{.75}$	Bi
ω_0 meV	9·0	11·0	11·6	12·0
A	0·79	0·70	0·69	0·70
$\lambda\langle\omega^2\rangle$ $(meV)^2$	46·9	43·8	42·9	40·1
T_C^{CAL} (°K) GARLAND ET AL	5·7	5·3	5·3	5·1
T_C^{EXP} (°K)	7·16	6·91	6·85	6·11

We have inserted the parameters of Table II into Eq. (14) in order to see the T_c that this equation would predict for these samples, and we have compared these calculated values to what is observed experimentally. The comparison is shown graphically in Fig. 7. Experimentally, we find that as a function of increasing Pb content, T_c increases rapidly in going from Bi to 25-at-% Pb, then increases more slowly and goes through a broad maximum at 50-at-% Pb, then goes through a shallow minimum around 80-at-% Pb, and finally shows a sharp increase in going to Pb. The T_c's predicted by the theory of Garland et al., are shown by the open triangle in Fig. 7, and we see that although the T_c values predicted are too low by 10 to 20%, the calculated behaviour of T_c in going from Bi to Pb is qualitatively correct.

In Fig. 7 we have also plotted some work from the literature that shows how the T_c's of crystalline Pb-Bi films behave as a function of composition. Starting at Pb with a T_c of 7.2K, as the at-% of Bi is increased T_c rises rapidly towards a maximum of approximately 8.5K near 60-at-% pb, then decreases at about the same rate down to 30-at-% Pb. At 25-at-% Pb, T_c has dropped to 7K, and below 25-at-% Pb, T_c is probably decreasing rapidly with further increase in the concentration of Bi since Adler and Ng (16) have shown that a $Pb_{0.05}Bi_{0.95}$ alloy is nonsuperconducting down to 1K. When we annealed our $Pb_{0.50}Bi_{0.50}$ and $Pb_{0.75}Bi_{0.25}$ quench-condensed films, their T_c increased to 8.1K and 8.0K, respectively, which is close to the values of T_c for the corresponding concentration crystalline films. So an amusing point that we should make is that one talks about "phonon softening" enhancing T_c, but in this alloy system at least, making the superconductor amorphous or disordered seems to reduce T_c below the crystalline value. Unfortunately, the tunneling data on the crystalline Pb-Bi alloys show multiple energy gaps and so we haven't figured out a way yet that we could invert the tunneling data to get phonon spectra.

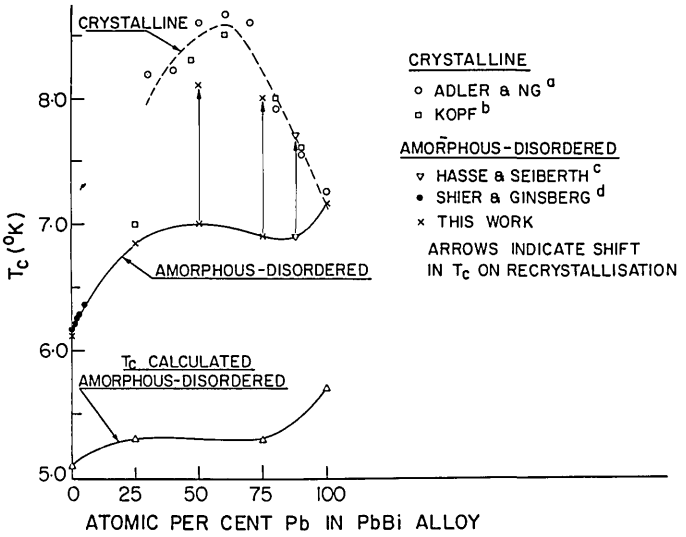

Fig. 7 - Superconducting transition temperature T_c (°K) versus atomic percent Pb for a series of crystalline and disordered-amorphous Pb-Bi alloys. The calculated T_c's for our disordered-amorphous Pb-Bi alloys are obtained by using the data of Table 2 in Eq. (14). The references indicated on the figure are: a. J.G. Adler and S.C. Ng, Can. J. Phys. 43:594 (1965). b. L. Kopf, Rev. Sci. Instr. 38:734 (1967). c. J. Hasse and J. Seiberth, Naturwiss. 8:51 (1964). d. J.S. Shier and D.M. Ginsberg, Phys. Rev. 147:384 (1966).

CONCLUSIONS

The approximate expression for T_c of Garland et al. (Eq. (14)) gives semiquantitative agreement with our results for amorphous Bi and Ga, and for the disordered-amorphous Pb-Bi alloy system, but it tends to always give too low a T_c by 10 to 20%. Whether this is due to the wrong choice of a characteristic phonon energy premultiplying the exponential in Eq. (14), or whether it is due to the parameter A overemphasising the importance of the change in the shape of the phonon spectra we cannot say at the present time. Of course there is always the possibility that a single formula like Eq. (14) cannot explain the T_c's for crystalline and amorphous superconductors over a wide range of λ, $\langle\omega^2\rangle$, etc. We feel that tunneling studies for the purpose of extracting phonon spectra will have to be carried out on a wide range of crystalline and amorphous-disordered superconductors before some of these questions can be resolved.

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ENHANCEMENT OF T_c IN THIN FILMS

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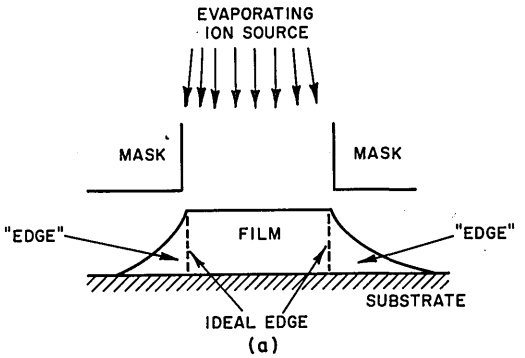
While listening to Jim Leslie's excellent detailed talk, I recalled some remarks that Fröhlich had made at one meeting, in which he said that the only thing more naive than an experimentalist's use of a theoretical formula was the theoreticians use of experimental data. Being a theoretician who has worked closely with experimentalists, I thought in my presentation this morning I would try to take neither the theories nor the experiments too seriously.

In hearing about the tales of the tunneling measurements, I thought, perhaps, it might be both more informative and certainly more entertaining if I try to tell the Brookhaven experiences with enhancement as they occurred, rather than as they appear in the Physical Review Letters. In doing this I think you will have a chance to learn along with us. Of course, one always emphasizes his own efforts, so I'd like to begin by pointing out that enhancements, as they are now called, were originally discovered by numbers of people, certainly intensively studied by Hilch and his coworkers. When I talk about the Brookhaven effort, we essentially rediscovered for ourselves what other people had known, but I think that the timeliness of the work changed the emphasis and the direction. Consequently, I'd like to tell it as a narrative, and I hope that you will bear with me if you know of other versions that don't sound exactly as I tell it.

About five years ago, we were working on tunneling measurements and resistivity measurements in thin films of aluminum. One of the things I might caution people who are not working in the field of thin films is that thin films, like all sort of relative parameters such as big, etc., mean different things to different people. To people working in superconductivity, I think thin films originally meant in the hundreds of Angstroms. I think now when we talk about thin films, we are thinking in the 50-Angstroms range, and possibly down to 5-Angstroms. When we say thin films, perhaps one should use a word like ultra-, or some other prefix, because materials in the 5-Angstrom range are a new and perhaps interesting field of physics in itself, possibly independent of the enhancement area. I would like to show a schematic of what these thin films look like when you actually evaporate them — Fig. 1(a) is an artist's concept — and then perhaps one will be able to understand the story. One starts with a substrate, and in evaporating, the desired film shape is determined by a mask. Evaporating this way, at least ideally, the film should build up as shown in Fig. 1(a). In actuality, you get something like a thin shadow of the mask, and this shadow region, in the jargon, is known as "edges."

When we started making measurements on aluminum, being somewhat new to tunneling, we weren't aware of edges. We evaporated the films and made resistivity measurements on aluminum and we got very excited because we noticed if you measure the resistivity as a function of temperature, you found there were long persistent tails. Aluminum

Figure 1(a)



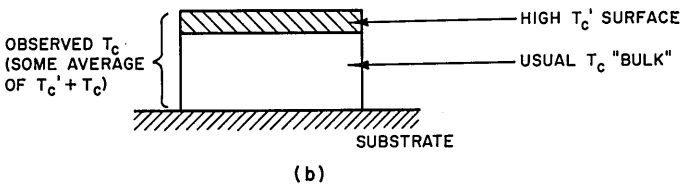


Figure 1(b)

should have a transition temperature about 1K, and these tails persisted up to 3 or 4K. We got very excited about that and in the course of speaking with more experienced people, they said, "Oh yes, that is just a well-known edge effect." We thought edges were just as physical as the main body of the film, so that was a pretty provocative statement. After we had become more sophisticated and appreciated that the effects we were seeing were occurring in the edges, we sent off a letter saying, somehow or other, the edges of aluminum were certainly at a much higher temperature than the bulk. This was very exciting at the time, partially because of speculations by the Russians, such as Ginzburg, that if you got to very thin films then the surfaces of these thin films might have very special properties. We thought that what had happened is that the edges, which have a large surface-to-volume ratio, might have had some sort of surface enhancement, and this was a demonstration of it. Consequently, we sent if off naively to Physical Review Letters, and we got the reply from the referee that this is a well known "dirt effect" in edges. We didn't understand what the dirt effect was, but it more or less crystallized our program. We said, "If somehow 'dirt' and 'edges' make critical temperatures go up, then we were going to study dirt and edges." And so, in our subsequent research we threw away bulk films and started to try to learn how to make films as thin as our edges.

When you are doing experiments of this sort, it's useful to have theories although they are not even handwaving speculations, such as Ginzburg's. Nevertheless, it was an exciting prospect. Ginzburg had suggested that many things might be occurring at the surface. There might be a dielectric effect. There might be phonon effects because the atoms vibrate more loosely at the surface. There might be some other things, all of which would be hard to pin down. The one thing that would be certain was that, if somehow or other you could do something on the surface, then from our understanding of superposed films it follows that the bulk of the film will reduce the observed critical temperature because of averaging effects (see Fig. 1(b)). It is apparent that somehow or other you want to get the bulk to be as small a fraction of the total sample volume as possible, and this was then the direction of the research as of about 5 years ago.

At this time, we were going to try to learn how to make films. The region of interest is less than about 10 Å so we had to somehow make thin films with characteristics that we could study in the region of less than 100 Å, and so enhance the enhancement effect. If we could just get these very thin films, then we would be able to study enhancement more directly. Technologically, the temperatures you're interested in is about 20K, but in the laboratory it was like one of the anecdotes that was told at the last meeting — "You do what you can do" — so most of the work always turns out to be on aluminum, tin, and lead. But when you go to the funders, you always mention niobium-tin and vanadium-silicone, and the like. These materials are very difficult to work with and so the experiments you do first of all are on the softer materials or the simple metals, and secondly, of course, they are always the materials that you've already seen some effect on. A systematic investigation was started by the Brookhaven group under Strongin's guiding spirit, and apparatus was set up in which one could grow thin films in a systematic way, with a minimum of oxygen contamination in the Angstrom region.

Figure 2 shows the body of the work in which so-called enhancement was found to exist. The plot shown here is the ratio of the critical temperature to the bulk value as a function of λ, the electron-phonon coupling constant. What you generally find is that in the ones that are already strong superconductors, such as lead, nothing very much seems to happen. However, the softer ones, such as aluminum, are moved up — aluminum got up to 5 or 7 — a considerable ratio between the bulk value and the pure value. The thing that was a little hard to demonstrate was the origin of the mechanism; Bob Schrieffer, perhaps, is going to review all the various mechanisms which have been suggested and, one by one, discarded. However, at this time in the Brookhaven story we learned of McMillan's paper which Jim Leslie has just gone through in great detail. The thing that is interesting is that if you take the maximum value that McMillan's formula would yield, then you get the lower curve shown in Fig. 2. Now you notice that the enhancement you get depends upon the value of the parameter μ^*, and that's essentially because the electron-phonon and the direct electron-electron interactions are in competition. You

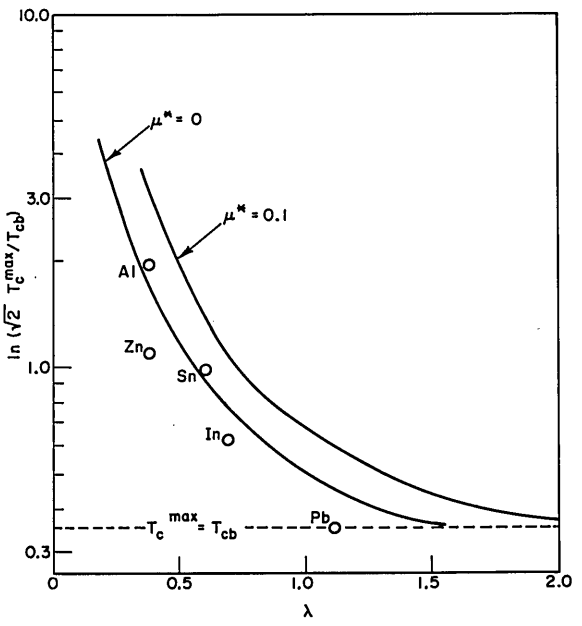


Figure 2

get the most enhancement when, to some degree, the electron-phonon interaction is partially being cancelled out by the electron-electron interaction. So the bigger the electron-electron interaction is when you somehow soften the phonons and get the electron-phonon up also, then you get more enhancement.

When the Brookhaven group first saw McMillan's paper, the first thing they did was to take the approximation $\mu^* = 0$, and of course, the poorer the approximation the better the agreement. They got extremely good agreement by using $\mu^* = 0$, but then it became quickly apparent that a more reasonable approximation based on experiences of both McMillan and other people is that μ^* should be in the vicinity of 0.1. This raises the maximum obtainable transition temperature and the agreement begins to vanish. There is always great reluctance to throw away curves that agree, and so the curve $\mu^* = 0$ was also published.

Figure 3 is displayed to point out a few things about growing very thin films, and is meant to give one a feeling of confidence of the fact that one can start to make controllable films in the Angstrom region. The idea is that one evaporates a controlled film of aluminum and simultaneously the film that one is making measurements on. Now the idea is that one evaporates a certain amount of aluminum, pauses, does an experiment, then evaporates more aluminum, pauses, does an experiment, etc. If the vacuum conditions are not good enough, then you would keep getting monolayers of oxide, and then you would expect that the aluminum that you simultaneously evaporated as a control would have a resistivity that just kept going up and up and up. This did not happen. The aluminum control layer just went on continuously with the same characteristics, which was very encouraging. I hope no one asks the actual vacuum pressure because it seems, from results of this sort, that the amount of oxygen seen by the cold substrate is much lower than the pressure that you would monitor in the general environment.

What is it that one sees, on the assumption that one is willing to believe that what is building up is films of the orders of Angstroms? The thing that almost universally

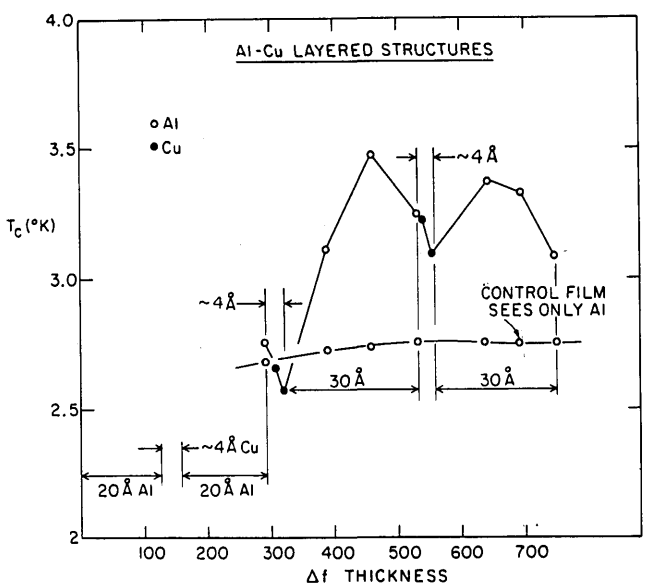


Figure 3

happens is that you have at $\Delta f \approx 300$ (Fig. 3) a film, and then copper is put on. Based on the superposition principle, one expects copper, which is not superconducting, to throw in a little zero T_c average, and thus lower it. When you put a little copper on, it lowers it, and then you start putting on aluminum, and the first couple of Angstroms of aluminum drastically increase the temperature until eventually, when you get up to a certain thickness, it begins to go down. Now the interpretation of this is that the effect is somehow occurring at the surface and there is an optimum amount of surface to volume that you can obtain before eventually the temperature goes down. The idea is that — at least in terms of the electron-phonon interaction — the surface is causing softening of the lattice spectrum and this is having an increase in the temperature.

McMillan's formula for T_c is

$$T_c = \frac{\theta_D}{1.45} \exp\left(\frac{1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)}\right)$$

where θ_D is the Debye temperature, μ^* is the Coulomb pseudopotential, and λ is the electron-phonon coupling constant. We have already seen this formula and I would like to make a couple of editorial comments. The interaction parameter λ which appears in this formula is, prior to some of the approximations used to evaluate it, given as

$$\lambda = 2\int_0^{\omega_0} \frac{d\omega\ \alpha^2(\omega)\ f(\omega)}{\omega}$$

where ω is a phonon frequency, ω_0 is the maximum phonon frequency, $f(\omega)$ is the phonon density of states, and $\alpha^2(\omega)$ is an average of the electron-phonon interaction, and hence describes the strength of the interaction.

Now the thing that McMillan did, which I think is his contribution, was to try to extract the phonon dependence or the frequency of the phonon dependence out of this interaction and relate it in terms of things that one knew something about. What he did was essentially to multiply and divide by an electron matrix element $\mathcal{I}^2$ which one knows something about. So somehow he multiplied and divided by this quantity $\mathcal{I}^2$ and then was left with a frequency ratio which he then made some approximations on. The point that he made was to try to extract this term, which he didn't want to evaluate, in terms of a product of an electronic matrix element and a frequency dependence. His result was that $\lambda \approx N(0)\mathcal{I}^2/M\langle\omega^2\rangle$. Now this kind of approximation is generally very useful. Somehow or other, you seize upon the slowly varying part and separate out the rapidly varying part. After this, McMillan went through a series of data on T_c's of various materials and noticed that, in general, in certain classes of materials this electronic term was fairly insensitive or very slowly varying for families of materials. He found that the more rapidly varying parameter was the quantity $\langle\omega^2\rangle$ which I will describe in a moment. Now if one is going to get something about enhancement — that is if you assume that the material you make in very very thin films would have the same quantity $\mathcal{I}^2$ — then it is apparent that if you can make the average of ω^2 much smaller, the temperature would go up. But I think there has to be some words of caution. First of all, this is an artificial separation. $\mathcal{I}^2$ and ω^2 as they occur are the same animal, interwoven, and so you have to be very careful when you separate them because the whole electron interaction in simple metals gives, as a consequence, the electron-phonon interaction.

The electron-phonon, and the electron-electron, interactions are, to some approximation, different facets of the same animal, so when you separate them you have to be

careful because it is somewhat of an arbitrary separation. In fact, you know that if you change $\langle \omega^2 \rangle$, this really has to change the electron interaction too.

Even though I am going to give detailed calculations of how I think ω^2 changes, I would like to point out that I am not trying to convey the impression that just by changing $\langle \omega^2 \rangle$, enhancement results, because there must also be some change in $\mathcal{J}^2$. If I emphasize this point, it is because I think Dr. Leslie went over that rather rapidly, and it's something you have to keep in mind. When you use the formula, you are making the approximation that $\mathcal{J}^2$ is constant.

To be specific, for example, suppose you envision what's happening at a surface of a very thin film — then the atoms are vibrating at a lower frequency because the forces at the surface are weaker. Simultaneously, the electron density of states is also changing near the surface because of the new boundary conditions, and so although one ascribes everything to the ω^2, I think that in doing so one has to appreciate that this must be some sort of upper limit, that in actuality the density of states most likely is going to be going down and somewhat compensating for the frequency change.

Well, with this reservation, let's go ahead and see if we can estimate this quantity λ. If you assume that the electronic matrix element is going to stay constant, then λ is proportional to $\langle 1/\omega^2 \rangle$ and this ω^2 is not really a mean squared frequency. It is just dimensionally a squared frequency — it's actually the average of the frequency divided by the average of one over the frequency. Now it's this quantity, $1/\omega$, which is obviously going to be very sensitive to what the shape of the spectrum is because, if you shift the frequencies down, this $1/\omega$ weighting factor would make a considerable difference in this average of ω^2. So one would expect, if one somehow induces the softening that shifts the frequency spectrum down, that this quantity ω^2 would become smaller, and therefore λ would become larger and one would get an enhancement.

Going back to the narrative form, at the time that Strongin and coworkers discovered (for themselves) the McMillan formula, it became apparent that if this is going to be a possible explanation, one would like to have some sort of quantitative estimate of how ω^2 changes. Now you can do a handwaving argument, and I think the handwaving argument probably gives about half the answer. Unfortunately, λ enters into the formulation for T_c exponentially, and thus T_c is very sensitive to changes in ω^2. Let me go through the handwaving argument because I think that the physics is all there. The handwaving argument is that, in the bulk, any given atom is surrounded by other atoms and the restoring force is essentially proportional to the number of atoms around it. Now when they get to the surface, to some approximation, say about a half or a third of the atoms are missing, and therefore the restoring force on the atoms at the surface is 1/2 or 1/3 less than that. If we remember our simple harmonic approximation, the restoring force ω^2 goes approximately as the force, and so if the force is down, ω^2 is down. You might expect that the atoms at the surface are missing about 50% of their neighbors, thus the average of ω may be down 25 or 30%, and so the handwaving argument gives about the right order of magnitude for explaining the softening. If you are really worried about, or take seriously, this $1/\omega$ function that has to be evaluated in the McMillan formulation, then you would like to have a better calculation.

During the time that Strongin and his people were discovering the softening aspects, we had been using a computer to study the lattice dynamics for Lennard-Jones potentials — or we like to say rare gas solids. It seemed like a very easy thing to convert this program from calculating the lattice dynamics of large particles to the lattice dynamics of a surface. In fact, this is exactly the kind of thing that a computer does much better than the analytic kinds of approaches, because the computer can handle the finite number

of atoms and it handles boundary conditions very easily, whereas theoreticians who work on lattice dynamics generally like to have infinite arrays of atoms with perfect periodic conditions. I won't go into how one calculates lattice dynamics, but I'll just say in a couple of sentences what you do. Lattice dynamics, as done on a computer, consists of solving Newton's equations for a finite number of atoms and essentially simulating a real crystal. You put the atoms in, you put some force law between them, and the atoms vibrate, and you just keep following them as a function of time — you follow their velocity, their positions, etc. You are doing it as if it were a computer experiment in which you are simulating the atomic motions in a system. You want to calculate the frequency distribution. If you monitor the velocity as a function of time, and then do a Fourier transform of the velocity, you obtain the frequency distribution as shown in Fig. 4. In essence, you take the velocity of the atoms and a particle at some time t and then compare them with the velocity at some earlier time t_0. Taking the ratio of $v(t)/v(t_0)$ and Fourier transforming gives you the distribution in normal modes of a system.

Frequency Distribution $f(\omega)$ is given by the Relationship

$$f(\omega) = \frac{2}{\pi} \int_0^\infty \frac{\langle v(t)\, v(0)\rangle}{\langle v(0)^2\rangle}\, dt \cos \omega t \ ,$$

where the Integrand is the Velocity Autocorrelation.

Figure 4

The way we try to simulate the thin films is to set up on the computer something three-atom-layers thick — which seems about the maximum we should use — and then one sets the system in vibration and follows it as a function of time. We were trying to simulate the motion of atoms at very low temperatures, and a very low temperature system is perfectly harmonic. What we thought to be a very easy problem turned out to be very complicated. We threw in the velocities seemingly at random. However, we might recall that harmonic oscillators can't transfer any energy from one to another and the atoms kept vibrating ad infinitum in the computer, exactly as they were put in initially. It sounds funny now, but it wasn't very funny then because it took some time to appreciate. We had previously been working at high temperatures where there is anharmonicity. In that case we just throw them in the box and high temperature makes things uniform and you get equilibrium the way you do in nature. For these small particles, we similarly threw them in and hoped they would come into equilibrium. The theoreticians may be not only naive about experiments, but they are also sometimes naive about their own work. Of course, we had some very exciting spectra to begin with, because we got the spectra of the distribution that we threw in rather than the equilibrium one, and that had peaks all over the place. So we had to learn how to randomize the system so it would vibrate something like a real platelet. Finally, after learning these little subtleties, we did get frequency spectra. One always has to establish some feeling of confidence about such results. How one goes about this depends upon which group one is talking to. If one talks to Yeshiva's statistical mechanics groups, then the way you convey the fact that your calculations are very good is to compare them to other calculations and this gives theoreticians a feeling of confidence.

Our calculation for something that resembles an infinite rare gas solid is compared with an analytic solution of Grindley and Howard in Fig. 5, and within experimental error they are in excellent agreement. This is the experimental error on the computer.

Having established that we were able to do it for the bulk, we believe that the small particles for which our calculations were done are a good simulation of thin films, at least thin Lennard-Jones films. Figure 6 shows the results. Here we see the spectrum of a solid where the top plot is the longitudinal frequency and the bottom two are the transverse modes, and they are relatively sharp. They are not real peaked as a number of these theoretical curves are. Figure 6 shows the spectrum for a small particle, three-atom-layers thick and about 30 Å long. It's a disc, and in using the disc there is no periodic boundary condition. This disc is free to come to equilibrium at whatever pressure it wants to, and it expands a little bit. It simulates what you might expect to happen in a real film and that's why, presumably, the longitudinal frequency is a little shifted from the bulk value even though we start out with the same density in the film as in the bulk. In other words, the computer was allowed to let the atoms come to whatever density they wanted to. They came to a slightly lower density than the bulk value. One can also see the transverse and two new low-frequency modes which are the ones that we call the softening.

The detective work consisted of trying to trace down how the two soft peaks arise. The peak a little below 0.1 we thought we understood as the surface one — the peak at about 0.03 we didn't initially understand, and everything you don't understand you tend to get excited about. The 0.03 peak was a very exciting peak and we tried to trace it down.

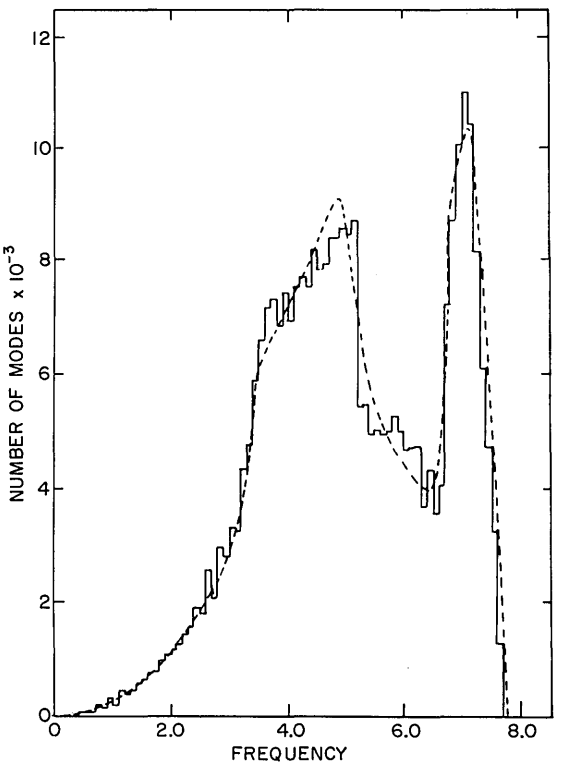


Figure 5

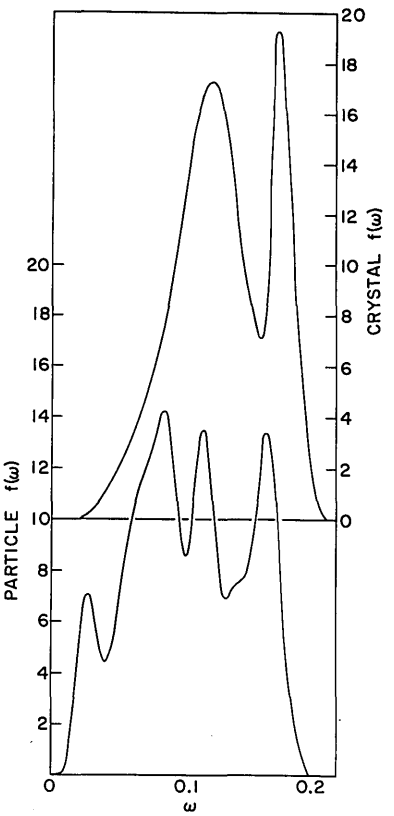


Figure 6

There were various ways available of trying to trace these peaks down. One can make the particle thicker and thicker, and eventually it should go to the bulk values, and watch how these two peaks disappear. The other thing is to get rid of the edges because even these thin particles have edges too. We tried both of these things. Figure 7 shows the particle without the edges. Now first of all, for the people unfamiliar with these kinds of curves, the wiggles are Fourier transform truncation errors and they don't mean anything. You have to learn which are real and which aren't real. The main thing is that the left and central curves are for the x and y directions. These are the motions in the planes of an infinite film. In the right-hand figure is the frequency distribution in the z direction. In the z direction, which contains vibrations normal to the surface, there are a tremendous number of atoms that are vibrating with the low frequency which we can identify as being the surface mode. In the x and y direction, the surface mode doesn't appear, nor does that low-frequency peak. The lowest frequency peak vanishes in the x-y or infinite plane directions, and so we are able to identify the lowest frequency peak of Fig. 6 as being something that occurs at the edge. It is easy to understand that the atoms at the edge of a film have almost no atoms around them, and they obviously have very weak bending forces and so their frequency should be lowest.

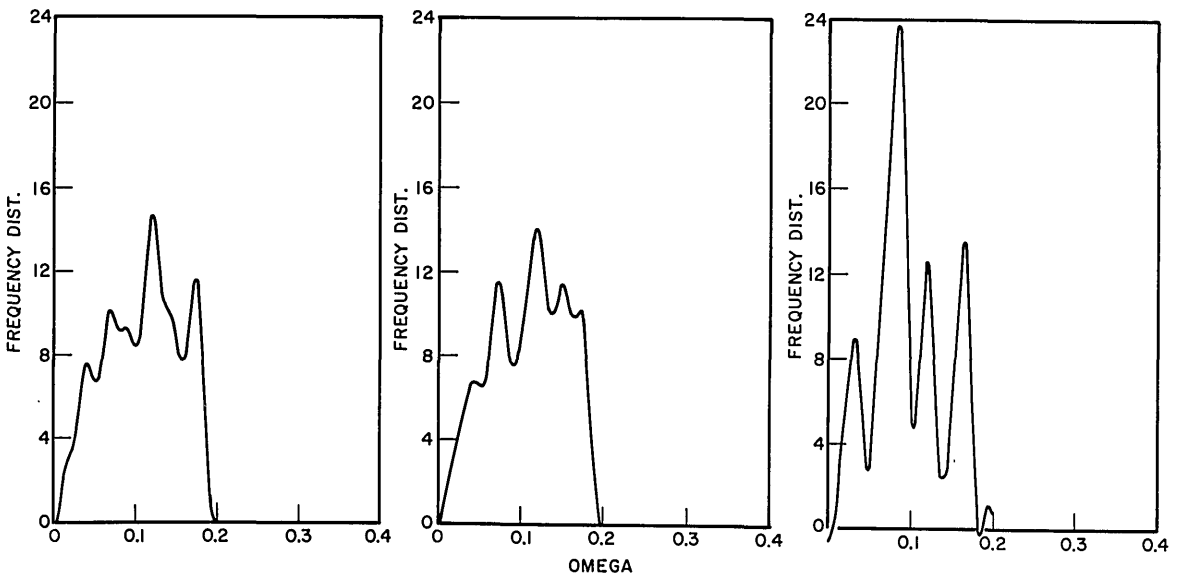


Figure 7

More recently, Allen and DeWitt have done different crystallographic orientations and have nicely demonstrated the fact that the less atoms you have in certain crystallographic directions, the softer the frequencies are. In Fig. 8 the films were made thicker. When you make the film thicker, you begin to find that the surface mode is a smaller fraction of the total. The right-hand figure is again the z direction. In the last figure the low-frequency peak had a value of $f(\omega) = 9$, while in this case $F(\omega) \approx 4.00$. These films show very little surface relative to the 3 Å films. These data also demonstrated that frequency is a very rapidly varying function of the thickness.

Figure 9 is an intellectual curiosity, I suppose. This is the mean square displacement of the atoms as a function of the time. People working in low-energy electron diffraction (LEED) see something related to the Debye-Waller factor, and the Debye-Waller

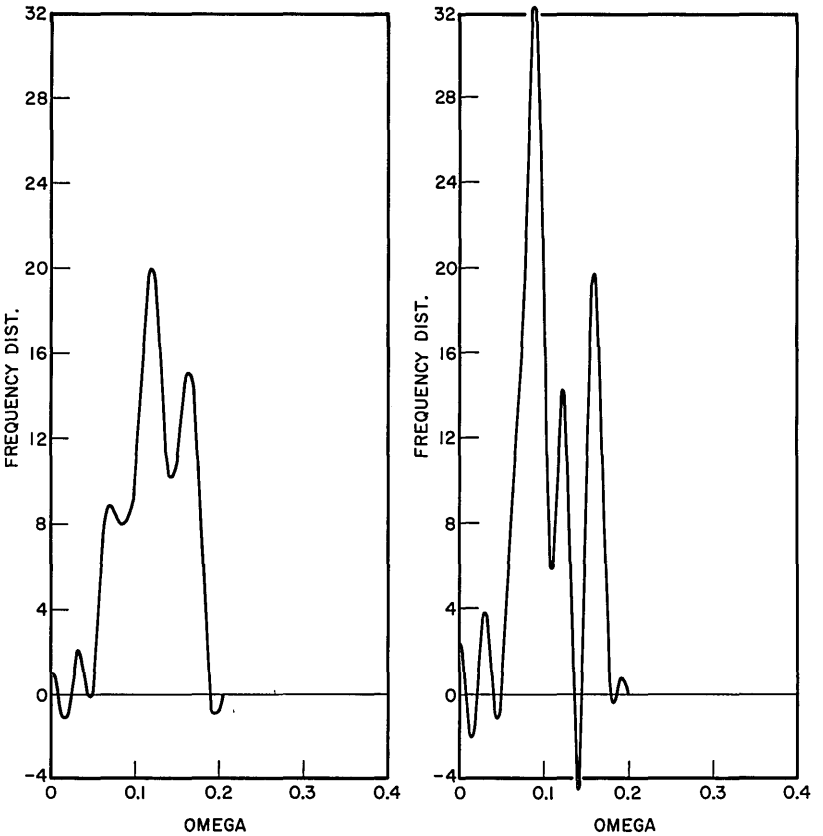


Figure 8

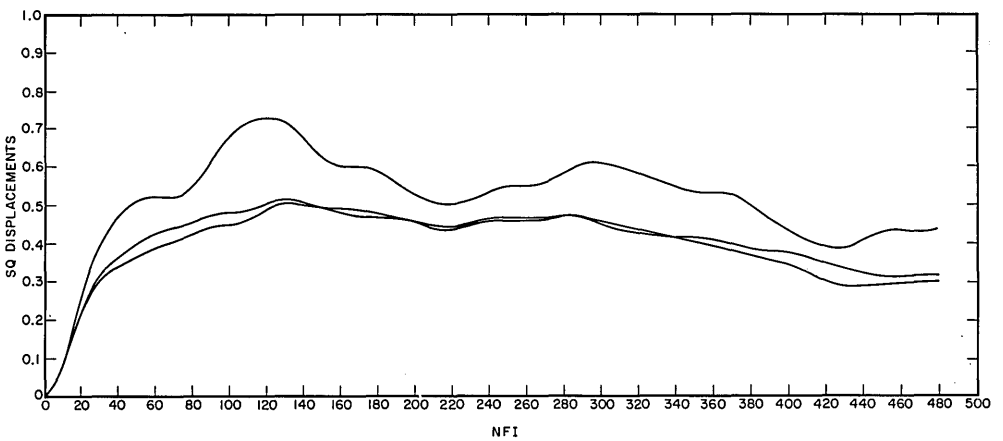


Figure 9

ELECTRON TUNNELING INVESTIGATIONS IN AMORPHOUS AND DISORDERED SUPERCONDUCTORS

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My collaborators on the work to be described here were Juei-Teng Chen and Tom Tung Chen, two graduate students of mine, and Dr. H. J. T. Smith, a colleague in the Physics Department at Waterloo.

INTRODUCTION

At the present time there is much interest in trying to obtain high T_c superconductors, for obvious technological reasons, and consequently there is much effort in trying to understand why certain superconductors have high T_c, and whether there are effects that might enhance T_c. In this regard we thought that it might be interesting to look at amorphous Bi and Ga because they are both materials that show dramatic changes in T_c when they go from the crystalline to the amorphous state. For example, crystalline Bi is nonsuperconducting down to 50 millidegrees (1), but when Bi is quench-condensed onto a substrate at helium temperature one obtains amorphous Bi with a T_c of approximately 6K (2). Similarly, the normal crystalline phase of Ga is superconducting with a T_c of 1.08K (3), but amorphous Ga has a T_c of approximately 8.5K (2). The variable influence of the crystalline to amorphous transition on T_c has been studied since 1954, and much work has been done on amorphous superconductors since then, primarily by Hilsch and Buckel and their coworkers. However, much of their work has been measurements of T_c as a function of alloying, annealing, etc. With T_c measurements alone it is difficult to determine the mechanism producing the changes in T_c. When we started our tunneling work on amorphous Bi and Ga a few years ago, there had been a measurement of the energy gap of amorphous Bi by Reif and Woolf (4) which suggested that amorphous Bi might be a strong-coupling superconductor. Hence it might be possible to see phonon structure in the tunneling curves and, by using the standard formalism of strong-coupling superconductivity theory, to determine the mechanism responsible for the high value of T_c.

EXPERIMENTAL METHODS

I would like to discuss briefly some of the experimental methods of our work. The tunnel junctions are prepared in situ in an evaporator-cryostat in the following manner. Three aluminum strips 0.6 mm wide are evaporated at room temperature onto a glass or sapphire substrate that is mounted on a copper block containing a He-3 evaporation pot. After partial oxidation of the aluminum strips to form the tunneling barrier, the substrate is cooled down to 1.5K, and then cross strips of the material to be investigated are quench-condensed onto the substrate to complete the three junctions. Typically these cross strips are 0.5 mm wide and 1000 Å thick as determined from resistance measurements. Temperatures are measured with a calibrated germanium resistor (5) attached to the

Now the Debye spectrum is essentially the match of some average property to the true spectrum. You take an average property — like the specific heat — and you take the average that corresponds to the specific heat moment of the spectrum and compare it with experiment. If you look at the Debye approximations to Fig. 11 then you realize that you can always choose a Debye θ that will approximate any particular moment. The ratio of the various moments in some dimensionless unit is easier to compare than the actual moments and so in Fig. 10 we have the ratio of the McMillan ω^2 to the real ω^2, and the thing that turns out to be rather interesting is that in doing this the Debye θ cancels out and we see that the Debye approximation (which means that the frequency is going as ω^2) is an excellent approximation to the infinite crystal. It predicts 0.83 and the actual crystal ratio is 0.85.

However, if you go to the particle, you see that the particle average is considerably different. In fact, to obtain agreement you have to go to a two-dimensional approximation which means that $f(\omega)$ goes as ω rather than ω^2. If you are going to match these ratios of the moments, it is important to remember that if you change the number of degrees of freedom, then the Debye frequency spectrum and the Debye θ you choose has to be changed by the appropriate weighting factor.

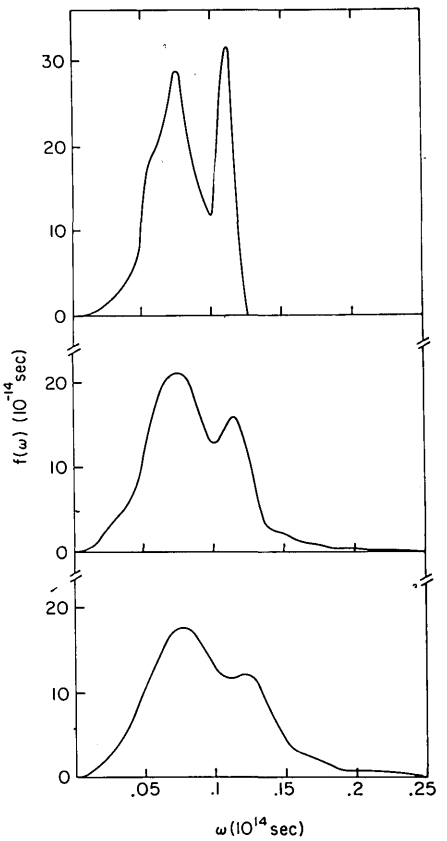

Figure 11

In the minutes left, I would like to make some remarks about amorphousness because this little particle we dreamed up may or may not correspond to reality. The question arises as to what is happening to these frequency moments in amorphous-like particles. Now again the computer has an advantage over analytic work because it doesn't care where the atoms are and it will just as soon work with a random arrangement of atoms as a periodic one. We quenched in, from high temperature, an amorphous-like structure which means that we just essentially have a liquid that's at very low temperature. That's what happens on a computer. When you lower the temperature down to about 0K rapidly you quench in a very high temperature state.

I don't have a figure showing our results; we are still trying to convince ourselves that the quenched state really corresponds to an amorphous film. However what you get is very similar to the high-temperature frequency spectrum of a solid. Figure 11 shows the frequency spectra at low temperature (top curve) relative to the frequency spectra at high temperature (bottom curve) for a Lennard-Jones solid. At high temperatures you see that all the things have been spread out. There is one thing that happens which is a little unexpected, but very important if true, and it is that at high temperatures you get a very long high-frequency tail. The bottom curve of Fig. 11 is for an infinite bulk sample at high temperatures. When we have quenched in this sort of a bulk to low temperatures, we get very close to the same spectrum as this. If we took the moments of a spectrum of this sort, the average frequencies that appear in the McMillan formula would shift up because the high-frequency tail more than compensates for the low-frequency shift. This either means that our calculation is not of a real amorphous solid, or it offers the

possibility, that is so nice from a theoretical point of view, that you could have it both ways. You can perhaps make amorphousness shift frequencies up. Since surfaces introduce soft modes, you can then get any answer you want, enhancement or de-enhancement, and that's a very nice state for a theoretician to end a talk.

MOLECULAR ENHANCEMENT EFFECTS

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Probably the first indication that organic molecules might ever play a role in superconductivity came with the 1937 paper by Fritz London, "Supraconductivity in Aromatic Molecules" (1). However, current interest in this subject can be more easily traced to Little's 1964 paper, "Possibility of Synthesizing an Organic Superconductor" (2), where he described a highly idealized molecular structure possessing two principal features: (a) a long polymer-like highway for itinerant electrons, and (b) localized electrons in highly polarizable molecules attached to the highway by chemical bonds. Little's consideration of the coulomb interaction between itinerant and localized electrons led him to an effective attractive interaction between itinerant electrons, like that produced by the electron-phonon interaction, and hence to a superconducting ground state. Applying the BCS formalism, Little predicts an extraordinarily high critical temperature for this model, in fact 2000K.

I can say without fear of contradiction that this paper has been responsible for a considerable amount of subsequent theoretical and experimental effort. However, much — perhaps most — of the theoretical activity has been to take issue with the proposal. This criticism frequently deals with aspects peculiar to the model which Little selected, for instance its unidimensionality, and may not concern us if we turn our attention more to what I consider the essence of Little's proposal: that itinerant electrons might be coupled attractively by mutual interaction with organic molecular electrons. Much attention has been given to the problems associated with Little's model; not so much to the possibility that his idea might be used otherwise. Perhaps one reason for this state of affairs is that his one-dimensional model presents to the theoretician an interesting and approachable problem. If we eliminate the one-dimensional problems, the problems of the semiconducting energy gap of the central highway, and the question of bond alteration, and perhaps some other problems which are thought to be peculiar to the polymer, then we are left with the exciton mechanism. The application of the exciton mechanism, as it is now called, to other systems has been proposed by McConnell (3,4) and coworkers in this country, and in Russia by, among others, Ginzburg (5), Geilikman (6), and Keldysh (7), each of whom has described a system of more than one dimension in which the itinerant electrons are furnished either by a metal film or a metal matrix, and the localized electrons by molecules which are placed on the metal surface or inserted within the metal matrix.

Because I am more familiar with McConnell's proposal and because I believe it contains features of special merit, I shall describe part of it as an example of what is an experimentally tractable approach to molecular exciton superconductors. A suitable molecule will have a set of molecular orbitals which may be approximated by linear combinations of atomic orbitals. Typically these orbitals have appreciable magnitude throughout the structure and are thus delocalized within the boundaries of the molecule. In a model system it will be possible to sort the orbitals on the basis of symmetry. If this molecule is allowed to interact with a metal surface or if it is inserted into a metal matrix, we would expect there to be a new set of eigenfunctions for the metal-molecule system, some of which, in a favorable case, have significant amounts of both metallic

and molecular character. Benzene in a vanadium lattice is shown in Fig. 1. In certain cases if the mixing is sufficient, there will be eigenfunctions with the fermi energy of this character. In this regime a current which passes through the metal will also pass through the molecules. In other words, the electrons responsible for conductivity and superconductivity will be found in states of partial molecular character. Now we further imagine that, for reasons of symmetry or for other reasons, there remains a set of molecular orbitals, some occupied, some empty, which do not mix well with the metallic orbitals and thus remain located mostly on the molecule. The energy level scheme we would require is shown in Fig. 2. The levels π_3^n and π_5^n are, in an idealized case, sharp and entirely associated with the molecule. An electronic excitation of the molecule would correspond to promotion of an electron from π_3^n to π_5^n.

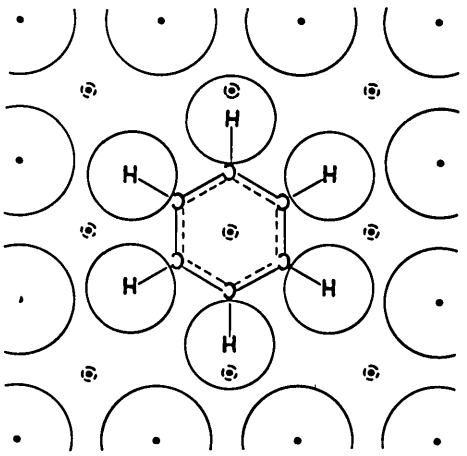


Figure 1

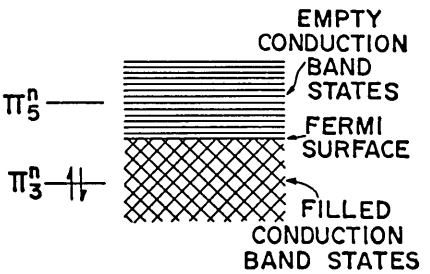


Figure 2

The coulomb interaction between the localized and the itinerant electrons in this system is very great because both electrons are sometimes on the same atom, and this is a feature of special merit. Other mechanisms usually require the itinerant electron to pass next to, but not through, the molecule. The weaker interaction in this system places severe and, according to my organic chemist friends, difficult-to-meet constraints on the nature of the molecules. Little (8) has said that he feels a dye molecule should absorb at 1 eV with an extinction coefficient of at least 10^5, and transition moment located at the ends, before it would be worth considering. This difficulty, which may in the face of the virtuosity of the modern organic chemist prove surmountable, is in any case not of concern if sufficiently strong interaction is obtained.

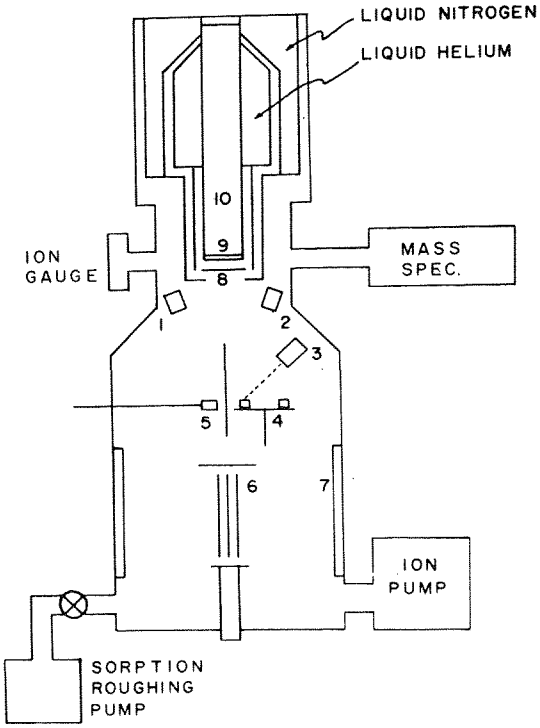
Now I would like to review the results of experimental investigations with emphasis on our own. At Stanford, McConnell, Hoffman, and I began studying the interactions between organic molecules and metals by coating thin superconducting films of vanadium with various planar aromatic molecules. We measured the effect of about a dozen compounds on the critical temperature of these films, but after the first few experiments were able to predict the sign of the effect prior to the experiment with satisfying reliability (9). This was because the effect depended on the magnitude of the sum of the first ionization potential and the election affinity of the molecule. This sum divided by two is known as the molecular electronegativity. Molecules with low electronegativities produced enhancements; those with high electronegativity depressions. The films were about 100 Å thick and the effects were about 5% of the critical temperature. These results are given in Table 1. The molecular electronegativity is a parameter which is large for

molecules that will happily take on an additional electron, and small for the other kind. The most likely explanation of the observed effects then is that the molecules either charge or discharge the film, producing a contact potential. Molecules with an electronegativity greater than the work function of the metal withdraw electrons and vice versa. Earlier, Glover and Ruhl (10) demonstrated conclusively that the effects of molecular oxygen on the critical temperature of thin superconducting films could be duplicated by positive electrostatic charging. We coated several vanadium films with oxygen and observed an effect of the usual magnitude, but of the wrong sign to support the electrostatic charging hypothesis for our results. The nature of these results then is unclear, but upon further examination I think they should be understandable in terms of the contact potentials established. Other work of a similar nature has been reported for a variety of inorganic coatings by P. Hilsch and D. Naugle (11). These enhancements and depressions were interpreted by the authors as the result of electrostatic charging.

Table 1

No.	Compound	ΔT_c (°K)	T_c (°K)	d (Å)	I^b (eV)	A^h (eV)	ψ (eV)
1	Anthracene	+0.10	2.3	90	7.40	0.42	3.91
2	Tetracene	+0.075	2.8	130	6.88	1.0	3.94
3	Perylene	+0.08	2.9	205	7.22	0.85	4.04
4	Hexabenzacoronene	+0.10	2.7	120	~7.6[c]		~4
5	Phenothiazine	+0.09	2.2	65	7.28[d]		
6	3,4,7,8-tetramethyl-1,10-phenanthroline	+0.09	2.5	85	8.65[e]		
7	2-Aminoanthraquinone	+0.06	2.6	115	$\lesssim$9.34[f]	<0.5[e]	$\lesssim$4.9
8	1,4,5,8-Tetrachloro-anthraquinone	+0.025	2.2	50	$\gtrsim$9.34[f]	0.66[e]	$\gtrsim$5.0
9	Pyromellitic dianhydride	-0.11	2.3	65		0.85	
10	Chloranil	<0[a]	—	—	$\gtrsim$9.68[g]	1.37	$\gtrsim$5.5
11	Tetracyanoquinodimethan	-0.10	2.3	60		1.7	

At Stanford we turned to metal-molecule codeposition whereby we were able to place organic molecules within a metal-metal matrix by the simultaneous condensation of the two onto a cold surface. A schematic of the vacuum apparatus for this work and subsequent work at Stanford is shown in Fig. 3. Items 1 and 2 are crystal oscillator deposition rate monitors. Item 3 is an electron beam gun; 4 is the metal source; 5, the organic source. Item 6 is a titanium sublimation pump. The liquid helium cryostat is placed above the vacuum system. A photograph of this system from the outside is shown in Fig. 4.



COEVAPORATION SYSTEM

Figure 3

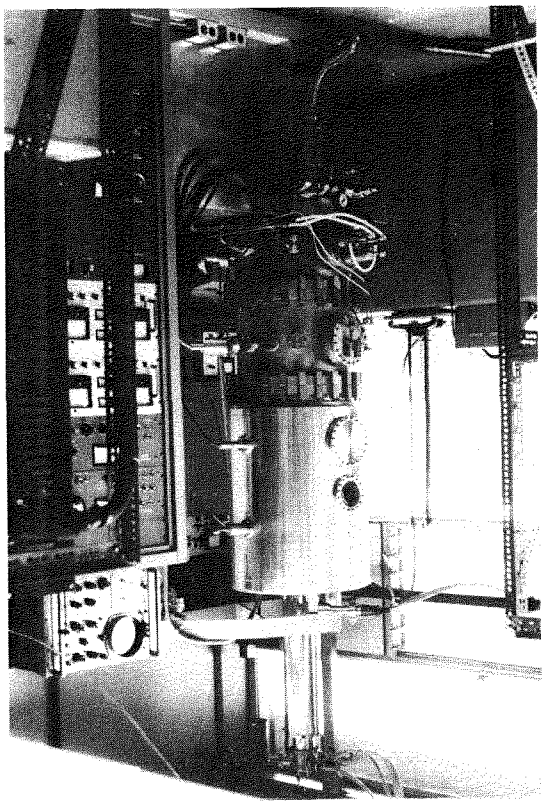


Figure 4

Using niobium or vanadium we found that molecular inclusions decreased the critical temperature drastically and in a manner which is almost independent of the nature of the molecule. The results for niobium are shown in Fig. 5. For aluminum the inclusions produced a large enhancement, raising the critical temperature to between 5 and 6K. These data are shown in Fig. 6. The critical temperature at first rises rapidly with increasing concentration, in this case of TCNQ (tetracyanoquinodimethane), but soon approaches five plus degrees asymptotically. Annealing the films at room temperature reduces the critical temperature in each case, but films containing the molecule still are enhanced. In Fig. 7 the effect of the molecular inclusions on the normal state resistivity is shown before and after annealing. The stabilizing influence of the molecules is evident in the small effect that annealing has on the more concentrated specimens. All samples had a positive temperature coefficient of resistance, as is evident in Fig. 8. The depressions observed for the transition metals are probably produced by disturbing a bond structure particularly favorable to superconductivity.

The aluminum results came after the Chicago-Brookhaven paper (12) on the multilayer sandwich film. Because the highest critical temperature reported in that paper for aluminum, 5.7K, and the maximum critical temperature we obtained, 5.2K, were close I felt that we were probably seeing the same effect. A look into the literature confirmed this. Many years ago Buckel and Hilsch (13) reported that condensing nontransition metal superconductors onto a cold surface would produce a disordered film with a higher

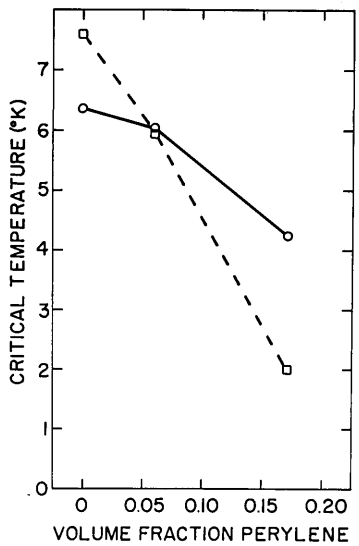


Figure 5

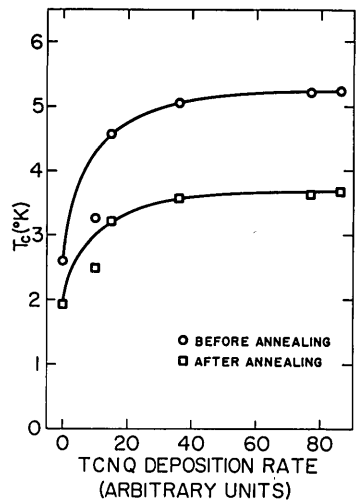


Figure 6

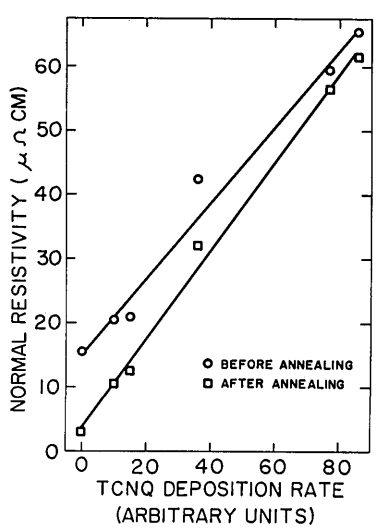


Figure 7

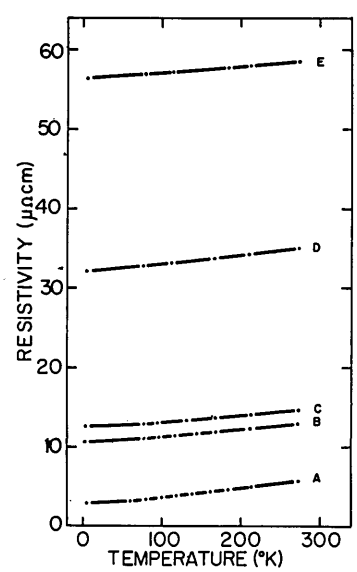


Figure 8

critical temperature. They also reported that the simultaneous addition of foreign materials would increase this disorder and raise the critical temperature. The highest temperature reported for aluminum was 5.5K (14). With this at hand I reexamined the Chicago-Brookhaven paper and noted that the enhancements reported for the several elements investigated were related to the enhancements obtained by Buckel and Hilsch by quench condensation in a rather straightforward manner. This comparison is presented in Table 2. The first column of numbers is the ratio of the enhanced critical temperature reported by Buckel and Hilsch to the normal critical temperature of the bulk. The next column indicates that the further enhancement obtained at Brookhaven were the result of taking further advantage of each element's susceptibility to disorder enhancement. We published these findings along with our aluminum results (15), but at the time we had no idea what disorder enhancement was. I should mention here that a paper by the Orsay group (16) on indium-anthraquinone mixtures appeared shortly after our own. They reached 4.5K and rationalized the effect as we had.

Table 2
Comparison of Low Temperature
Condensation and Layer Results

	$\frac{T_c \text{ (quenched)}}{T_c \text{ (bulk)}}$	$\frac{T_c \text{ (layered)}}{T_c \text{ (quenched)}}$
Al	2.30	2.10
Zn	1.64	1.30
Sn	1.26	1.26
In	1.20	1.07
Pb	1.00	1.00

The trend which was patently clear by this time was that the weak coupling *nontransition* metal superconductors could be enhanced and that the enhancement was greater the higher the Debye temperature of the bulk. It was also clear then that, except for the charging effects, all the enhancements which had been reported thus far were of this nature. A compendium of enhancement reports demonstrates this convincingly (17). In Table 3 the elements are listed with the most weakly coupling first. The ratio of the enhanced to the normal critical temperatures is presented for each element for several treatments. The first column of numbers is for annealed thin films about 100 Å thick. These enhancements were initially sometimes attributed to the quantization of electron modes, as first proposed by Blatt. The second column is the enhancements reported by Buckel and Hilsch for low-temperature deposition. These workers in 1954 did not feel obliged to interpret their results theoretically. The third column of numbers is for the work of Abeles and colleagues at RCA who condensed the elements in an oxygen atmosphere. The Brookhaven results are next (column 4); then our own and those of the Orsay group (column 5). Finally (column 6) that of the Corning people who found that, when pressed into the fine pores of porous Vycor, some metals showed an increase in the critical temperature. Of course, the remarkable thing about Table 3 is that there is a unique ordering of the elements which arranges them according to their susceptibility to enhancement. All the specimens examined may be characterized either by small grain sizes, by limited physical dimensions, or by both. It was not until Geballe told me of McMillan's work (18) that I understood this ordering or the nature of the effect. The calculated maxima predicted by McMillan appear in the last column. They seem a most

ELECTRON TUNNELING INVESTIGATIONS IN AMORPHOUS AND DISORDERED SUPERCONDUCTORS

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EXPERIMENTAL METHODS

I would like to discuss briefly some of the experimental methods of our work. The tunnel junctions are prepared in situ in an evaporator-cryostat in the following manner. Three aluminum strips 0.6 mm wide are evaporated at room temperature onto a glass or sapphire substrate that is mounted on a copper block containing a He-3 evaporation pot. After partial oxidation of the aluminum strips to form the tunneling barrier, the substrate is cooled down to 1.5K, and then cross strips of the material to be investigated are quench-condensed onto the substrate to complete the three junctions. Typically these cross strips are 0.5 mm wide and 1000 Å thick as determined from resistance measurements. Temperatures are measured with a calibrated germanium resistor (5) attached to the

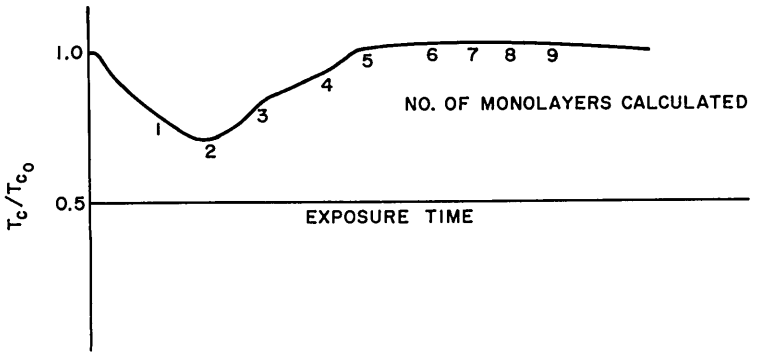

Figure 9

Regarding the exciton mechanism this proves, I believe, only that we're not likely to stumble upon it. Not every Tom, Dick, and Harry molecule is going to do it. Only a dozen or so of the more easily tested have been examined and only a few metals. Of course, this is the natural way to start, but not the way to finish.

For a while every enhancement was explained by its discover in terms of an exciting new mechanism. The fact that we now understand these effects in other terms should not discourage us.

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THEORIES OF ENHANCEMENT EFFECTS

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I must say that I am not one of the theorists who has been involved in enhancement effects and, therefore, I hope I can give a somewhat more dispassionate speech than most other theorists, if that is ever possible for a theorist. My own feeling is that this venture into "Alice in Wonderland" has not been totally useless and, much like the Moon program, there has been a lot of scientific fallout from chasing a distant star or moon, independent of whether you get there or not. The analogy, I'm afraid, at least in my view, stops there because I think we are going to get to the moon, while I wouldn't hazard much of a guess about 2000K, or even room-temperature, superconductors.

I thought I'd just briefly go over some of the ideas which have been discussed here this morning, and perhaps some other ideas in this quest for pay-dirt of high T_c. Roughly speaking, I've divided the mechanisms into three parts: (a) enhancing what we already know, i.e., the phonon mechanism, (b) nonphonon mechanisms and what one can do there, and (c) geometrical effects which don't work directly on the mechanism but try to increase T_c by influencing the density of states.

As for the first part, that is, the phonon-like mechanisms, we've heard that there has been a certain amount of progress in the prediction of how T_c should vary with metal parameters over and beyond the original simple idea that Bardeen, Cooper, and I had some twelve years ago. Our original ideas predicted that T_c was of the order

$$\theta_D \, e^{-1/N(0)V}$$

where θ_D is the Debye temperature, $N(0)$ is the density of states at the Fermi surface of the metal, and V is some "pairing interaction." For simplicity, and because we didn't know what better to do, we said that V was the sum of a phonon interaction V_{ph} plus a repulsive Coulomb interaction V_c. We had in mind for V_{ph} something like the Bardeen-Pines-Fröhlich interaction. This Bardeen-Pines-Fröhlich interaction was later pointed out to be incorrect in detail, although correct in its general form that the interaction is attractive at low frequency and repulsive at high frequency. We saw this morning the equations of strong-coupling superconductivity due to the Soviet physicist Eliashberg. We know that in the limit of weak coupling the Eliashberg equations go over exactly to the Bardeen-Pines-Fröhlich interaction and the BCS expression for T_c.

The Coulomb potential was originally included in the theory in a cutoff form and the so-called Coulomb pseudopotential effects were not taken into account. A couple of years after our original work, Bogoliubov, Shirkov, and Tolmachev suggested that the effective Coulomb interaction V_c^* is weaker than V_c for a simple physical reason, although they didn't mention this reason in their paper. All three of them are distinguished field theorists and they prefer to talk in terms of Fredholm solutions to integral equations rather than the physics of electrons pushing on one another; but the V_c^* vs V_c story is basically the fact that things that repel stay apart, and if they stay apart their interaction energy is less than it would be if they were to move in an uncorrelated fashion. That is, suppose

you take two particles moving along in space and ask how strongly they interact with each other. If they move in an uncorrelated fashion their interaction energy is large when they are on top of one another. If they interact via a repulsive potential, then they detour around one another and the strength with which they interact, including the correlation or detour effects, is certainly less than in the case where you don't include those effects. The detour correlation effects reduce the Coulomb interaction energy by a factor of roughly two or three for typical metals. So it is all very simple when viewed in this way.

For strong-(phonon)-coupling superconductors, V_c^t is not of importance, while for weak-coupling materials the correlation effects, depending implicitly on the Debye frequency, lead to a reduction of the isotope effect from $\alpha = -1/2$ toward $\alpha = 0$. Turning to the phonon interaction for strong-coupling superconductors, Eliashberg wrote down the correct equations some years ago. Solutions of these have been carried out for various types of models, and the one that has received the most fame is that of McMillan. As we saw earlier for the case of a transition metal vibration spectrum, namely for niobium, McMillan found that, except for small numerical corrections, T_c is of the order

$$T_c \approx \theta_D \, e^{-\frac{1+\lambda}{\lambda-\mu^*}}$$

where μ^* is given by the density of states at the Fermi surface times V_c^*, and λ, by definition, is the density of states at the Fermi surface times V_{phonon}, namely $\mu^* = N(0)V_c^*$ and $\lambda = N(0)V_{ph}$. So except for the factor $1 + \lambda$ in the numerator, the new theory and the old theory are, in fact, identical.

Now this $1 + \lambda$ factor has a very simple origin. It has to do with what is called renormalization effects. We know that the electron-phonon interaction in a crystal changes the electron's band mass m to a quasi-particle effective mass m^*, the ratio being $m^*/m = 1 + \lambda$. You can derive this relation from perturbation theory very simply. Thus, the mass enhancement of an electron moving through a normal metal measures exactly the electron-phonon coupling constant. The quasi-particle density of states, being proportional to m^*, *increases* with λ, and therefore you would have a factor of $1 + \lambda$ in the denominator from this mass enhancement effect, i.e., $N(0) \to (1+\lambda)N(0)$. In addition to the mass enhancement, there is another factor entering T_c. Not only is the mass of the electron renormalized, but so is its interaction with phonons renormalized. The electron-phonon matrix elements are *decreased* by the factor $1 + \lambda$. Since the λ in the denominator of the expression for T_c involves this matrix element squared, this matrix element renormalization gives you a *reduction* of the effective interaction $V_{ph} \to V_{ph}/(1+\lambda)^2$ by the square of the mass enhancement. Therefore, the phonon interaction is changed according to

$$N(0)\, V_{ph} \to [N(0)\,(1 + \lambda)]\,[V_{ph}/(1 + \lambda)^2] \to N(0)\, V_{ph}/(1 + \lambda)$$

in accord with the strong-coupling result.

Why have I gone into this detail? It is to try to take a little of the mystery out of formulas that are being used and accepted as being correct. There is no mystery, and, in fact, I don't think they are really correct in detail either. As McMillan writes it,

$$\lambda = \left\langle \frac{N(0)\, g^2}{m\, \omega^2} \right\rangle$$

Here g is the electron-phonon matrix element in suitable units, M is the ionic mass, ω is the phonon frequency, and the expression is to be averaged over all phonon modes.

Now in simple metals, that is, nontransition metals, there is a scheme called the pseudopotential scheme which says that an electron scatters off an ion via an effective potential which is not the Coulomb potential, but a potential much weaker than the Coulomb potential. This is due to the simple fact that if you take an atomic potential $V(r)$ which goes something like $e^{-\alpha r}$, then an electron coming along and scattering from this atom will see not only the attractive Coulomb potential, but it will also see an effective repulsive potential which comes about from the Pauli principle. As the electron comes near the atom the Pauli principle forbids the electron that's coming in from having wiggles in its wave function which match the wiggles in the wave function of the occupied core states. Since the incoming electron has, of necessity, wiggles which are similar to those of the core electrons the incoming electron must deform its wave function in such a way that the core pushes the conduction electron away from the core region. The incoming electron is thereby not allowed to feel the strong Coulomb attraction, and hence the effective potential, i.e., the Coulomb potential plus this effective repulsive Pauli potential, leads to a weak residual potential. The weakness of this total effective potential (pseudopotential) accounts for the fact that conduction electrons in most simple metals are almost free electron in character. The electron-phonon interaction g is just the Fourier transform of this pseudopotential.

Now it turns out that in simple metals one can roughly, very roughly, calculate the phonon frequencies of the wave vector q (denoted as ω_q) in the following way. If you calculate the frequencies of phonons for the ionic lattice with the electrons in the conduction band held fixed, that is, you allow the ions to vibrate without the conduction electrons moving, then the result is, in effect, the ionic plasma frequency Ω_q, which is of a very high frequency. From this quantity, to get the physical or observable phonons you must subtract the electronic part ω_q^{ℓ} in the form $\omega_q^2 = \Omega_q^2 - (\omega_q^{e\ell})^2$. This subtraction is the screening effect that corresponds to the fact that when two ions vibrate, the electrons move in between them to screen out the fields generated by the moving ions. Now, $\omega_q^{e\ell}$ is the response of the electrons to moving ions. From this picture we see that $\omega_q^{e\ell}$ is proportional to the electron-phonon coupling — just as Dr. Paskin said this morning. So, $(\omega_q^{e\ell})^2$ is proportional to g^2. You can now see why λ is supposed to vary mainly with ω^2, rather than through $N(0)g^2$. The reason is rather simple, namely that the observed frequencies are very small compared to the bare frequencies, and therefore $(\omega_q^{e\ell})^2 \propto g^2$ has cancelled almost all of the ionic plasma term Ω_q^2 for the observed coupling strengths. $(\omega_q^{e\ell})^2$ is about 75 to 95% of Ω_q^2 even for zone boundary phonons. Therefore, for a given percentage change of g, you see, the change in ω_q^2 is amplified greatly by having the dominant effect already cancelled out by ω_q^2. In the expression for λ, the percentage variation of the explicit $N(0)\, g^2$ is small compared to the variation of the ω_q^2. Again, this is just because the leading effect for the phonons is cancelled out and the small percentage change of g makes a much larger percentage change of ω_q.

I think that these arguments, while not precise for nontransition metals in infinite crystals which are perfectly ordered, are more questionable when you go to simple metals which are amorphous, or to thin films. I don't know of any theoretical justification which is as good as the one I outlined above for a constant $N(0)g^2$ in λ and which applies to the cases of amorphous or thin-film superconductors, or both, and yet these are the situations to which people apply the formula. So I put up a red flag here: there might be troubles.

A case where there is definitely trouble is when one takes this formula for λ and applies it blindly to transition metals. For transition elements there is no theoretical

reason that I know, as to why the above expression for λ, with $N(0)\mathcal{I}^2$ roughly constant, has anything to do with nature. The phonons in transition metals have their frequencies determined in a way which is very different from that discussed above because the pseudopotential concept mentioned above doesn't work for transition metals. The d-electrons have to be described more by a tight-binding scheme. The d-shell d-shell interactions are very important and this simple pseudopotential idea just doesn't work. A consequence of this is that while you can parameterize T_c phenomenologically by saying, roughly speaking, that the ω_q^2 should be the observed one and $N(0)$ is the density of states at the Fermi surface, I don't think this is more than a rough parameterization for the transition elements, since $\mathcal{I}^2$ is not expected to be a constant in these materials.

An interesting point is that if you look at the pressure effect for nontransition metals, if you squeeze the crystals, then the atoms getting closer together have stronger repulsive interactions. Vibrational frequencies go up so that, as the pressure goes up on nontransition elements, the frequencies go up, and hence λ, being proportional to $1/\omega_q^2$ goes down. If the interaction goes down, T_c should go down and this argument works for nontransition metals. Yet, for transition elements, the same condition of increasing pressure makes ω_q^2 go up as the lattice gets more rigid or stiff, but that doesn't bother superconductivity. T_c goes up, in general! Therefore, either you don't talk about the predicted pressure dependence for transition elements, or else you get worried about it — and people do both things. One has to take the argument about $\lambda \propto 1/\langle\omega^2\rangle$ with a great grain of salt when you look at transition elements.

Now, you might say, why does T_c go up for the transition elements? We know when you squeeze on them, the bands broaden. Broader bands make weaker screening. Weaker screening makes stronger interactions, so $\mathcal{I}^2$ should probably go up. But $N(0)$ is going down and ω_q^2 is going up, and so you see it's a rat's nest trying to figure out the chicken or the egg of why T_c goes up. The reason is probably very complicated.

Let me mention another possible way of increasing T_c within the phonon mechanism. This one I am interested in because I think it has some possibilities. Suppose you look at the density of states $N(E)$ for transition metals as a function of E, as shown in Fig. 1(a). You know there are all sorts of peaks, depending on which row and which particular element you are looking at. For example, niobium, which has a fairly high T_c, is sitting near a peak in the density of states. Molybdenum, which has a very low T_c, is sitting down in the minimum. Thus, for the purer elements you would say naively that if $N(0)$ is high, so is T_c, while if $N(0)$ is low, T_c is low. If you make disordered films, make short mean free paths, you would expect that the sharp peaks in the density of states, which after all come from coherent scattering off of many atoms, will be diminished so that you smear out $N(E)$. The minima get filled up and the maxima decrease, probably giving something more like the dotted line in the figure. If you are able to make samples with a very short mean path, the whole curve would just be smeared out and you wouldn't see anything particularly interesting. So, one effect of the short mean free path of amorphous materials is to make low-T_c superconductors into medium-T_c materials by making them more like everybody else. The other effect is to make high T_c into medium T_c. If you are in the business of making high T_c you can advertise that you have raised T_c from a millidegree to 5K for a low-T_c element, but what you are actually doing is bringing it into a democratic situation where everybody is roughly the same T_c. I would characterize bismuth as a good example of this, plus a lot of other examples. There may be other residual effects, but I would say this change of T_c is a zero-order effect, and unfortunately, as such, it is something that is often not discussed (for obvious reasons). I hope you don't mind the side comments here. I get a kick out of them after being chided for so many years about not being able to produce a 2000K superconductor.

So where does that leave us? Well you might say, "How about making a bunch of alloys which are perfectly periodic and hence not mean-free-path spoiled. Then maybe we can find a density of states which is fantastically high." Well, when you talk with experimentalists, they will tell you that high density of states doesn't necessarily mean high T_c. There are many examples of this situation. You raise the density of states, as measured by γ, and T_c goes down. Then the theorist says, "Well, things are complicated because V can have the reverse dependence and more than compensate for the change in N(0)." I think it is still an interesting and profitable game to try to find very high density-of-states materials. Nb_3Sn has a very high density of states. Moreover, I think there is a particular type of high density of states which should be sought for, namely a density of states which has a *high, sharp* peak, as shown in Fig. 1(b). This is probably the most desirable case, for a rather simple reason. If you have a high, sharp peak of the density of states at the Fermi surface, then while N(0) is large, the screening tends to be small, since, as we know, the screening effects depend on an average of the density of states over a relatively large region in energy about the Fermi surface. Therefore, while the average density of states (which determines the screening) may be relatively low, and hence the interactions strong, the density of states at the Fermi surface can be high for this case, and you can have your cake and eat it too. One must take care, however, that the reduced screening does not increase $\langle \omega^2 \rangle$ unduly, thereby reducing $\langle \mathcal{G}^2/\omega^2 \rangle$.

You might say, how do you find things that have very high peaks? One way is to make *ordered* binary alloys. People have been doing this for many years and little dramatic has occurred. Maybe what you are doing is hopping through parameter space in steps that are much too big, because the distance between different binary alloys is fairly

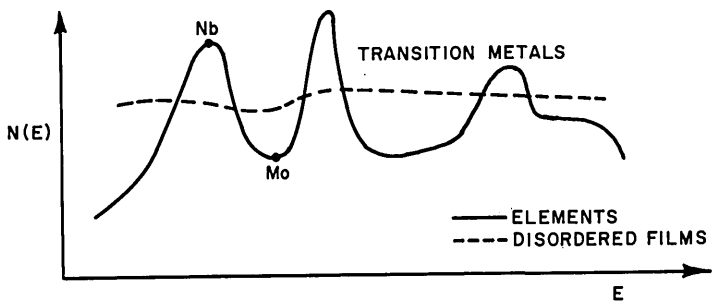

Figure 1(a)

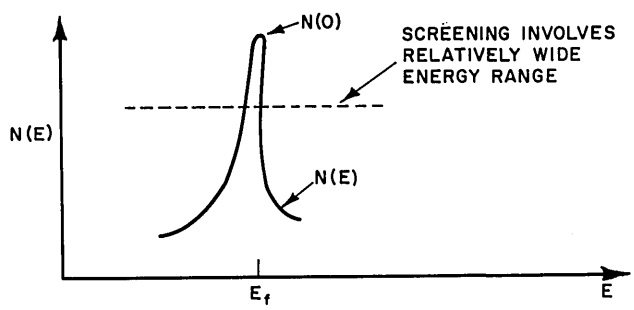

Figure 1(b)

ELECTRON TUNNELING INVESTIGATIONS IN AMORPHOUS AND DISORDERED SUPERCONDUCTORS

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My collaborators on the work to be described here were Juei-Teng Chen and Tom Tung Chen, two graduate students of mine, and Dr. H. J. T. Smith, a colleague in the Physics Department at Waterloo.

INTRODUCTION

At the present time there is much interest in trying to obtain high T_c superconductors, for obvious technological reasons, and consequently there is much effort in trying to understand why certain superconductors have high T_c, and whether there are effects that might enhance T_c. In this regard we thought that it might be interesting to look at amorphous Bi and Ga because they are both materials that show dramatic changes in T_c when they go from the crystalline to the amorphous state. For example, crystalline Bi is nonsuperconducting down to 50 millidegrees (1), but when Bi is quench-condensed onto a substrate at helium temperature one obtains amorphous Bi with a T_c of approximately 6K (2). Similarly, the normal crystalline phase of Ga is superconducting with a T_c of 1.08K (3), but amorphous Ga has a T_c of approximately 8.5K (2). The variable influence of the crystalline to amorphous transition on T_c has been studied since 1954, and much work has been done on amorphous superconductors since then, primarily by Hilsch and Buckel and their coworkers. However, much of their work has been measurements of T_c as a function of alloying, annealing, etc. With T_c measurements alone it is difficult to determine the mechanism producing the changes in T_c. When we started our tunneling work on amorphous Bi and Ga a few years ago, there had been a measurement of the energy gap of amorphous Bi by Reif and Woolf (4) which suggested that amorphous Bi might be a strong-coupling superconductor. Hence it might be possible to see phonon structure in the tunneling curves and, by using the standard formalism of strong-coupling superconductivity theory, to determine the mechanism responsible for the high value of T_c.

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$4\pi e^2/q^2$ divided by the dielectric constant $\varepsilon(q,\omega)$, where q and ω are Fourier transform variables. This is what enters for an electron which goes from k to $k + q$, its mate going from $-k$ to $-k-q$. Thus the effective interaction is

$$\theta\ (q,\omega) = \frac{4\pi e^2/q^2}{\varepsilon(q,\omega)}$$

The dielectric constant gives the dynamic "screening" effects. Now, in a crystal we know the dielectric constant has the form

$$\varepsilon(q,\omega) = 1 + 4\pi\ \alpha_{ion}\ (q,\omega) + 4\pi\ \alpha_{e\ell}\ (q,\omega)$$

where the α's are the ionic polarizability and the electronic polarizability. From this interaction all of superconductivity should flow. This is the effective interaction including all the effects of phonons, Coulomb repulsion, excitons, etc.

For example, the phonon frequencies are given in the following way. A set of zeros of the dielectric constant for a given q as a function of ω are at the phonon frequencies ω_q. You can see, then, that when the electrons exchange a phonon the interaction $\theta(q,\omega)$ has a singularity if the phonon that is involved is exchanged with its natural frequency.

Now, how about the electronic polarizability $\alpha^{e\ell}$? The way people usually treat this, for simple metals, is to say that the typical frequency variation $\alpha^{e\ell}$ is on the scale of electron volts. It is the electronic plasma frequency which determines the frequency scale of $\alpha_{e\ell}(q,\omega)$, while the frequency variation of $\alpha_{ion}(q,\omega)$ is on the scale of hundredths of an electron volt, i.e., the ionic plasma frequency. Therefore, the standard scheme, which doesn't say anything about excitons or plasmons being involved in superconductivity, replaces $\alpha_{e\ell}(q,\omega)$ by its static value $\alpha_{e\ell}(q,o)$. Matthias, Little, and others suggest that we should look more carefully at this quantity $\theta(q,\omega)$. As shown schematically in Fig. 3 they suggest that the effective interaction has structure not only at the phonon frequencies, where $\varepsilon(q,\omega)$ is going to zero due to the phonons, but also out at higher frequencies where there are dielectric anomalies associated with electronic transitions. Unfortunately, a standard pitfall that some people have gotten into over the

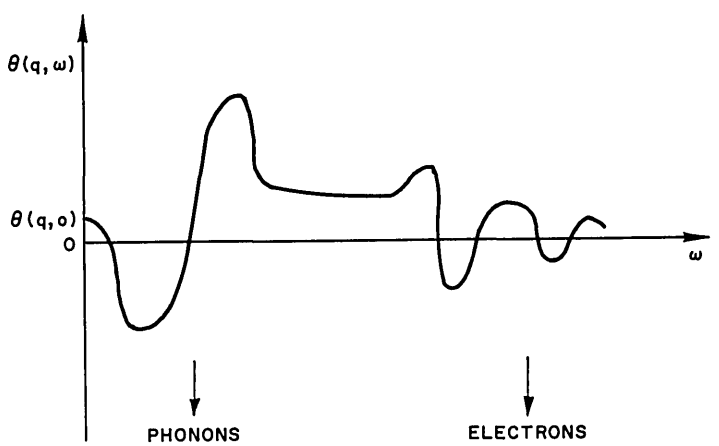

Figure 3

years (with the aid of some wishful thinking) amounts to saying that, neglecting the ions, $1/\varepsilon$ is given approximately by

$$\frac{1}{\varepsilon(q,\omega)} = \frac{1}{1 + 4\pi\ \alpha_{e\ell}(q,\omega)} \approx 1 - 4\pi\ \alpha_{e\ell}(q,\omega), \text{ if } 4\pi\ \alpha_{e\ell}(q,\omega) \ll 1 .$$

It is clear that the electronic polarizability *reduces* the Coulomb repulsion. However, they use this $1 - 4\pi\alpha$ approximation, which is good only for $4\pi\ \alpha_{e\ell}(q,\omega) \ll 1$, in the regime where $4\pi\ \alpha_{e\ell}(q,\omega) > 1$. So you start with an interaction $V(q)$ that is positive definite. By forgetting what you did the day before, you then crank $4\pi\ \alpha_{e\ell}$ up to make it bigger than 1, so that $1 - 4\pi\ \alpha_{e\ell} < 0$ and hence you *predict* an attraction. There were a number of papers which did this some time ago until the difficulty was pointed out. It may sound naive, but this has been a source of confusion for some time, because people did not calculate consistently.

You can show from very general arguments that, for $\omega = 0$, $\varepsilon(q,o)$ is necessarily nonnegative, and hence that the effective interaction $\theta(q,\omega)$ must be *positive* at zero frequency. If $\theta(q,\omega)$ were negative (attractive) for zero frequency, the system would be unstable, and it would simply polarize chargewise, making a transition to a normal state of different symmetry, e.g., doubling of the unit cell, or some such transformation, such that the system would become stable at least within the Hartree approximation. Thus, the Hartree effects correspond to the zero-frequency terms, and Hartree instabilities, involving large energies, must be stabilized first. Then you have to again ask how $\theta(q,\omega)$ varies with frequency in the new Hartree stabilized state.

Since the potential is nailed down by the Hartree stability condition to be repulsive at zero frequency, you then have to play on a beating of the attractive and repulsive regions of θ as a function of ω to get superconductivity. Thus, to make a calculation of what T_c is, you see, is a pretty subtle matter. It is for this reason one can get any answer one likes depending on how you emphasize the attractive versus repulsive regions in various approximate treatments.

The Matthias argument is basically that as an electron comes by an atom, it polarizes the atom by polarizing the core, and then another electron uses that polarization to get an attraction. I think, in principle, this is a perfectly good mechanism if you could ever predict or measure how strong an effect it is. Proposals have been made to measure the optical properties of crystals, and hence determine the size of the dielectric anomaly associated with atomic (electronic) polarization. A difficulty with the proposal is that light waves have wavelengths which are very long compared to atomic sizes for the frequencies of interest, and hence by this means you can only see electric dipole transitions in atoms. For example, you cannot see transitions between states of the same parity. If you had a p to f transition in an atom, the levels have the same parity, and hence there is no dipole field generated. It is a quadrupole field that is generated. Hence you will not couple to that transition by long-wavelength light waves. This doesn't bother the electrons because the electrons, having wavelengths of the order of an angstrom, can work as well on a quadrupole field as they can on a dipole field. So it may be that by doing optical experiments you miss something which is in fact present to produce an actual attraction between electrons. On the other hand, you may see an anomaly at the small q accessible to light waves which is *not present* for large q , which are those of overwhelming importance in determining T_c, thereby overestimating the effect.

There has been a proposal by Matthias for alpha uranium suggesting that the material is superconducting because of the core polarization mechanism and gave the "proof" that this was the case because of the isotope effect in uranium being M^{+2}. I am sorry

that I don't have time to go through the theoretical discussion here, but you might ask how a nonphonon mechanism can give an isotope effect if the ion vibrations aren't involved. You should see $T_c \propto M^{\alpha}$ if phonons are not involved. Matthias suggested that a Mössbauer-like effect is involved here. A careful treatment of this particular mechanism gives only $\alpha \simeq 0.01$! There is an argument however, which gives a *large* positive isotope effect for this nonphononic mechanism. The argument given by Capellmann and Schrieffer involves modulation of the energy levels by zero-point vibrations of the atoms. This mechanism gives an effect which is $\alpha \simeq 1/2$, although I am sorry I don't have time to talk about this topic in detail. So, at least we can't rule out for uranium this other mechanism, although I think the importance of the mechanism is highly unlikely for any metal, including U. In addition, experimentalist friends tell me to eye the experimental results with considerable skepticism, since the experiments are very difficult to perform and the scatter of the data is uncomfortably large.

One can essentially rule out nonphononic mechanisms for transition metals from the tunneling experiments of Rowell, et al., of which niobium and tantalum tunneling studies similar to those Dr. Leslie talked about today, show nice, well-developed phonon anomalies. The experiments show, at least for these transition metals, that they are phononic in nature and, by implication, since there is no difference in superconductivity between these and the other transition elements, that all transition elements are phononic.

That brings me to the end, except for a few words about geometrical effects. The problem of a thin film has been looked at as far as how the thinness of the film changes

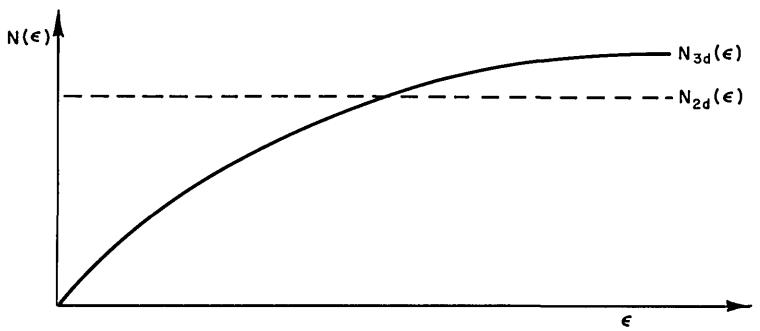

Figure 4(a)

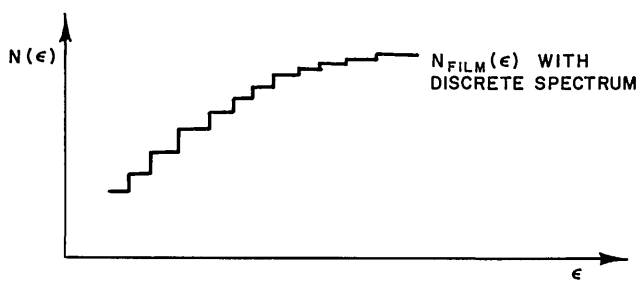

Figure 4(b)

the density of electron states. We know that the density of states for a simple three-dimensional electron gas varies as $N_{3d}(\varepsilon) \propto V\varepsilon$, Fig. 4(a). A two-dimensional film in principle has a square density of states, $N_{2d}(\varepsilon)$ being just a constant out to infinity. If you worry about how the motion goes not only in the film direction but in the transverse direction, and if you put in the discreteness of a spectrum in the third dimension, you find that $N_{film}(\varepsilon)$ has kinks or steps instead of just being flat, as shown in Fig. 4(b).

Parmenter has looked at these quantization effects on the density of states to see what happens to T_c, i.e., whether T_c increases, decreases, or stays the same. He assumes that the matrix elements are constant, that is, that the quantization effects on the bands and density of states don't affect the matrix element, and he concludes that T_c goes up when you go from a smooth to a rough density of states. I am personally doubtful of this scheme and feel that more careful work, including matrix element effects and sample inhomogeneities, must be included before one can assess the validity of the scheme.

Well, where does all this leave us? I am reasonably pessimistic, except for fallout. Maybe one fallout would be the brilliant student who accidentally hits on the right idea or experiment, and that would be great. I think some of the ideas having to do with looking at the dielectric function as a function of frequency, or the phonon modes near phase transitions, might be interesting in themselves, and perhaps there is something there. By and large, I guess, I am still of the view that intelligent experimentalists will win out by doing the same thing that drug manufacturers do: get 4000 bottles off of the shelf and mix them together, along with a liberal dose of inspired intuition gained from previous experiments, and hope for the best.

ELECTRON TUNNELING INVESTIGATIONS IN AMORPHOUS AND DISORDERED SUPERCONDUCTORS

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My collaborators on the work to be described here were Juei-Teng Chen and Tom Tung Chen, two graduate students of mine, and Dr. H. J. T. Smith, a colleague in the Physics Department at Waterloo.

INTRODUCTION

At the present time there is much interest in trying to obtain high T_c superconductors, for obvious technological reasons, and consequently there is much effort in trying to understand why certain superconductors have high T_c, and whether there are effects that might enhance T_c. In this regard we thought that it might be interesting to look at amorphous Bi and Ga because they are both materials that show dramatic changes in T_c when they go from the crystalline to the amorphous state. For example, crystalline Bi is nonsuperconducting down to 50 millidegrees (1), but when Bi is quench-condensed onto a substrate at helium temperature one obtains amorphous Bi with a T_c of approximately 6K (2). Similarly, the normal crystalline phase of Ga is superconducting with a T_c of 1.08K (3), but amorphous Ga has a T_c of approximately 8.5K (2). The variable influence of the crystalline to amorphous transition on T_c has been studied since 1954, and much work has been done on amorphous superconductors since then, primarily by Hilsch and Buckel and their coworkers. However, much of their work has been measurements of T_c as a function of alloying, annealing, etc. With T_c measurements alone it is difficult to determine the mechanism producing the changes in T_c. When we started our tunneling work on amorphous Bi and Ga a few years ago, there had been a measurement of the energy gap of amorphous Bi by Reif and Woolf (4) which suggested that amorphous Bi might be a strong-coupling superconductor. Hence it might be possible to see phonon structure in the tunneling curves and, by using the standard formalism of strong-coupling superconductivity theory, to determine the mechanism responsible for the high value of T_c.

EXPERIMENTAL METHODS

I would like to discuss briefly some of the experimental methods of our work. The tunnel junctions are prepared in situ in an evaporator-cryostat in the following manner. Three aluminum strips 0.6 mm wide are evaporated at room temperature onto a glass or sapphire substrate that is mounted on a copper block containing a He-3 evaporation pot. After partial oxidation of the aluminum strips to form the tunneling barrier, the substrate is cooled down to 1.5K, and then cross strips of the material to be investigated are quench-condensed onto the substrate to complete the three junctions. Typically these cross strips are 0.5 mm wide and 1000 Å thick as determined from resistance measurements. Temperatures are measured with a calibrated germanium resistor (5) attached to the

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