

**NRL Report 6972**

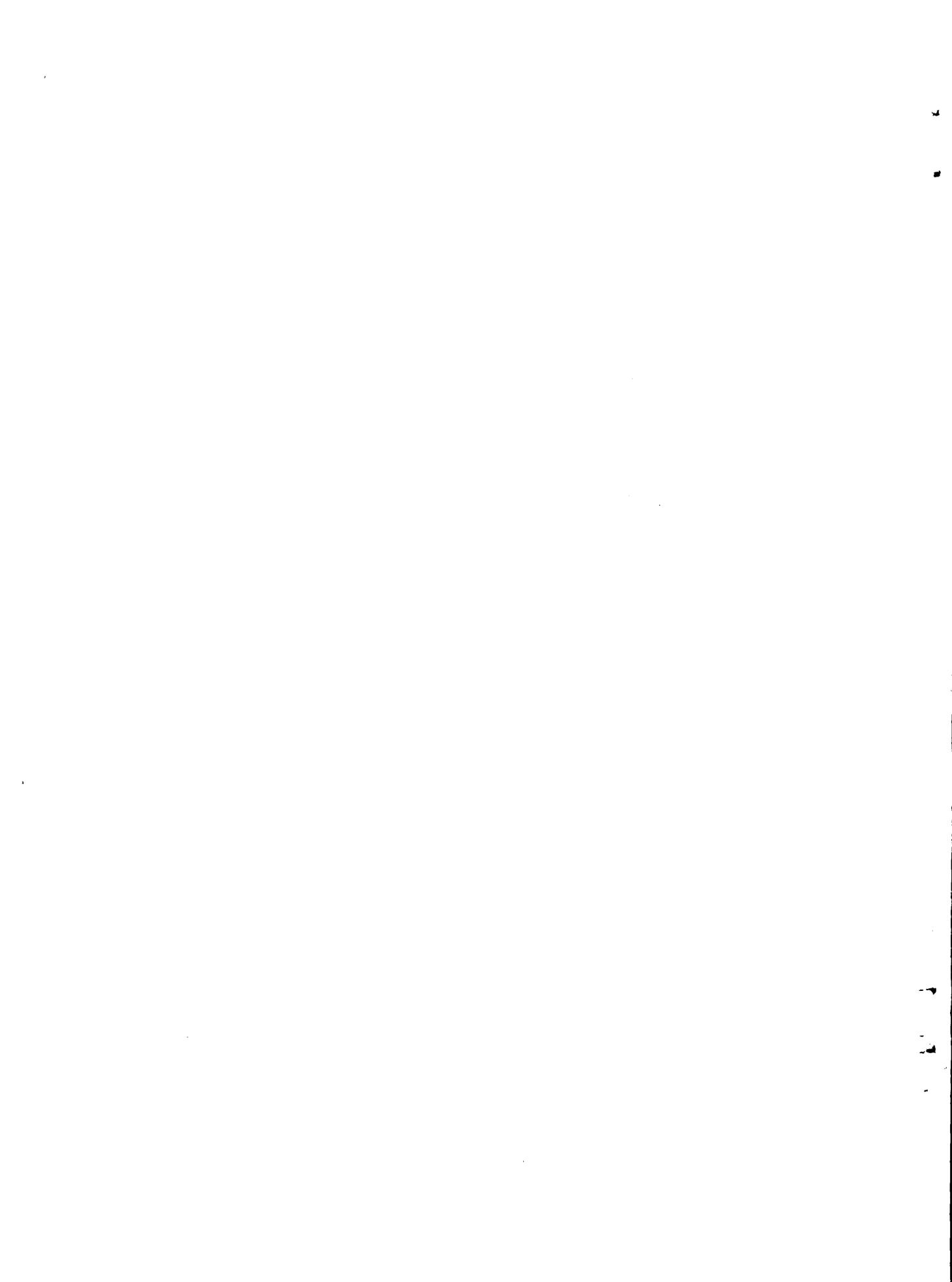
**Proceedings  
of  
Second Symposium  
1969 Spring Superconducting Symposia**

*Sponsored by*  
The Office of Naval Research  
and  
The Naval Research Laboratory

April 25, 1969



**NAVAL RESEARCH LABORATORY  
Washington, D.C.**



## 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 second 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. Klausung; 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, "Molecule's 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	iii
SUPERCONDUCTIVITY IN DEGENERATE SEMICONDUCTORS	1
LOW-CARRIER-DENSITY SUPERCONDUCTORS	19
SUPERCONDUCTIVITY IN LOW-CARRIER-DENSITY ROCK SALT COMPOUNDS	30
SUPERCONDUCTIVITY IN "FREE-ELECTRON-LIKE" SUPERCONDUCTORS	45

# SUPERCONDUCTIVITY IN DEGENERATE SEMICONDUCTORS

J. F. Schooley  
*National Bureau of Standards*  
*Washington, D.C.*

Well, it is very pleasant for me to be here at the Naval Research Laboratory which, as Bob [Dr. Hein] points out, is the home of the superconducting semiconductor. It is essentially the fifth anniversary of superconductivity in semiconductors and almost exactly the fifth anniversary of the National Bureau of Standards activity in this field and I think it is very fitting that the conference be held today.

Although my title is a fairly broad one, I will honor it principally by giving a few definitions of superconductivity in degenerate semiconductors so that we all are speaking the same language. I am sure that everyone here knows the definition of all of these terms, but yet it's perhaps worthwhile to be sure that we all are speaking about the same things. Then I want to take note of a certain number of similarities among the known superconducting semiconductors. Then I want to concentrate almost exclusively on the topic I know best — strontium titanate. I think Dr. Hulm will discuss germanium- and tin telluride in his own talk.

To start with, I want to define what I mean by semiconductor. For my purposes, a semiconductor shall have low carrier concentration, it shall have a variable carrier concentration in which the experimenter can — by doping or whatever mechanism — produce carriers variable over a factor of say 10 with a very scant change in the structure of the material, and finally a semiconductor shall possess a low Fermi energy. These are not very stringent rules but I think that they will suffice for my purposes.

A degenerate semiconductor has the Fermi energy measured from the bottom of the conduction band — much, much larger than  $kT$  — so that at low temperature the carriers don't drop out of the conduction band and leave you holding an insulator. I think it would be very nice some time to observe superconductivity in an intrinsic semiconductor such that at a certain temperature there would be enough conduction electrons to induce the superconducting state, and then at a lower temperature to see whether the electrons drop down into the valence band and leave you without superconductivity. I think that would be very cute — but I don't have a candidate right now.

Figure 1 depicts the differences among metals, semimetals and semiconductors for my purposes. I can tell you without a great deal of pride that I made this slide myself. On the left we have three pieces of the energy vs wave vector, and as an energy scale I have taken 0 to 1 Rydberg — 13 electronvolts. The Fermi energy is drawn the same for the metal, for the semimetal, and for the semiconductor. In the case of the metal, which I have chosen to be aluminum, we are looking in a (100) direction in reciprocal space and we see that it has electrons essentially partly filling a band which gives you the ductility and the high conductivity characteristic of a metal. It may or may not have overlapping bands. In the case of a semimetal, I have drawn a rough shot at bismuth. One finds that the valence band is almost full and the conduction band is almost empty, but these overlap and the Fermi surface penetrates both of them giving hole and carrier conduction.

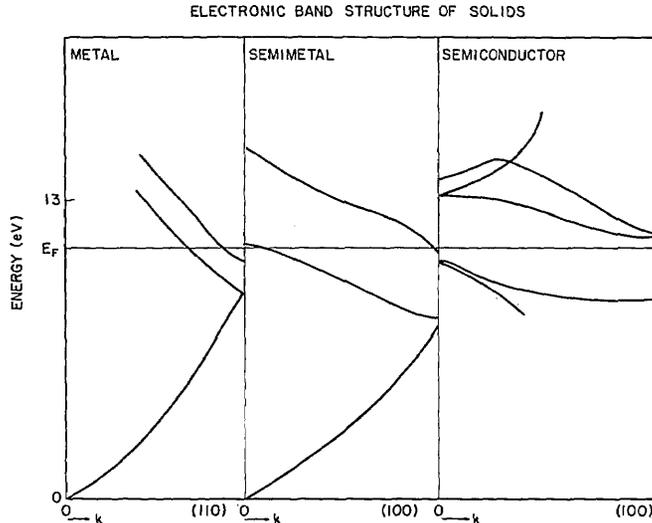


Figure 1

In a semiconductor, in this case silicon in the (100) direction, one sees that there is a forbidden band in which there are no states at all at the Fermi energy for any value of  $k$ . In that case electrons are, of course, excited from the filled valence band to the empty conduction band, and being thermally excited they simply drop back into the valence band (at low temperatures). All semiconductors become insulators at absolute zero.

In place of the intrinsic semiconductor, one can induce carriers that will stay in at low temperatures by doping or alloying a semiconductor with either a donor or acceptor atom. Roughly speaking, you can compute the energy of the impurity level as being something like the hydrogen energy divided by the square of the dielectric constant of the material and this means — for a polar material — one will find the impurity level fairly close either to the top of the valence band or the bottom of the conduction band.

I want to go on to strontium titanate now and show a little bit about the band structure of this material since that's quite relevant to the occurrence of superconductivity. Figure 2 shows the energy of the important atomic orbitals in strontium titanate on the ordinate, and assumes perfect ionicity in the material. You can see that you have a separation of about perhaps 16 electronvolts between what Arnold Kahn and Leyendecker took as the valence band (the oxygen 2p band) and the conduction band (the titanium 3d level). Kahn and Leyendecker chose the deviation from perfect ionicity — which you see in the vertical dashed line — as something like 17% covalency in order simply to take advantage of the change of the energy level and to produce a band gap of about 3 electronvolts which is observed in the optical measurements of strontium titanate. Figure 3 shows the results of Kahn and Leyendecker's tight-binding calculation of the energy band structure of strontium titanate. Tight binding of course is the physicists term for the linear combination of atomic orbitals in which you take the energies of the atomic orbitals and simply push the atoms closer and closer together and discuss the resulting band scheme in those terms. The important part of this figure is that here in the (100) direction you can see that the  $\Delta_2'$  is the lowest member of the conduction band, and Kahn and Leyendecker predicted that there would be at the zone edge a high effective mass electron valley. The existence of a flat valley has actually been verified, as you will see in a moment. If we use the rough rule that I mentioned, that impurity atoms will sit in the forbidden region at energies roughly the hydrogen energy divided by the square of the



Shall I define superconductivity? Well, I don't think I need to do this for this group. I think we should use the ordinary definitions as long as we can, and I'll simply state without proof that superconducting semiconductors show a decrease in the electrical resistance on the order of a factor of 100 over a short temperature region, characteristic of superconductivity. They show the heat capacity anomalies of reasonable size over a reasonable temperature span. They exclude magnetic flux in a reasonable way, as magnetization measurements which I will show indicate, and the energy gap appears to approximate that of BCS. There has not been enough work done on that particular facet to suit me, but in the one case where the energy gap of germanium telluride was measured, it appeared to be something like 4.1 for  $2\epsilon_0/kT_c$  rather than the BCS number of 3.5, but this is not an unusual discrepancy.

Normal-State Parameters

Material	Valleys	Mass	$\epsilon_0$	$\gamma$
GeTe	4 (111)	2	40	1.3
SrTiO <sub>3</sub>	3 (100)	5	10,000	1.7
SnTe	4 (111) (12 (110)) (6 (100))	1.7	1800	1.4

Figure 4

Now I would like to show you evidence that the occurrence of many shallow valleys in a polar material is essential for a superconducting semiconductor. Figure 4 shows some of the normal-state parameters of the known superconducting semiconductors. We have germanium telluride with four valleys in the (111) directions in momentum space, an effective mass of 2, which indicates shallow valleys, a static dielectric constant (indicated by  $\epsilon_0$  instead of  $\epsilon_s$ ) of 40, and a density of states  $\gamma$  of 1.3 millijoules per mole per degree square. Similarly, for strontium titanate we have three (100) valleys, as I have just shown, the density of states effective mass is about 5, the static dielectric constant is  $10^4$ , and the density of states is 1.7. These are numbers in the range of the superconductivity. For tin telluride we have what seems to me a currently more interesting case with four valleys in the (100) direction. Our host Dr. Hein and coworkers here at NRL, and Dr. Burke and coworkers at NOL, find the existence of another set of valleys which would apparently lie in the (110) direction, and if I do my arithmetic properly — with the help of my theoretical friends — the number of valleys involved will be 12. Dr. Hein in a recent publication — and when I say recent, I thank Dr. Hein for a preprint of a publication on tin telluride — indicates the possibility of the influence of a third set of valleys in the (100) direction. I am not sure whether this is just a desire to go for the course record in the number of valleys, or whether there is actually experimental evidence here, but we will wait and see what Dr. Hein says about that. Notice that all of these materials have respectable densities of states. These numbers correspond reasonably well with the density of states of aluminum or indium, which are reasonably legitimate metals, and the reason of course is that the number of valleys is high and the effective mass of the electrons is high.

Actually, each of the superconducting semiconductors which is indicated in Fig. 4 is a set of superconductors. This is in the same sense that an alloy system forms a set of superconductors. It has the added feature in the case of the superconducting semiconductors that the change from one member of the set to the next often involves no

perceptible change in the electronic or mechanical structure of the system. If we will look at the impurity level involved over the superconducting range, we will see that, for all of these materials, most likely — and we feel almost certain for strontium titanate — no severe change of the mechanical or electronic band structure takes place over the entire superconducting range. This is a change from the usual metal alloy system and should provide constant delight to the theoreticians.

Conduction Induction

Material	Dopant	Carrier Range ( $\text{cm}^{-3}$ )	Resistivity ( $\mu$ ohm-cm)
GeTe	2-6% Ge Def.	$0.8-1.5 \times 10^{21}$ p	30-300
	7-10% Ge Def. + 2-7% Ag	$2.7-6.4 \times 10^{21}$ p	--
SrTiO <sub>3</sub>	0.006-0.3% O Def.	$10^{18}-10^{20}$ n	200
	0.06-0.6% Nb	$10^{19}-10^{20}$ n	50-100
SnTe	0.5-4% Sn Def.	$0.3-2 \times 10^{21}$ p	30-50
	3% Sn Def. + 0.5-2.5% As	$0.4-1.3 \times 10^{21}$ p	--
	3% Sn Def. + 0.5-1% Sb	$0.3-1.0 \times 10^{21}$ p	--

Figure 5

In the case of germanium telluride, Fig. 5, there are two mechanisms of producing carriers. One is simply to use a germanium deficiency of 2 to 6 percent. This results in  $0.8$  to  $1.5 \times 10^{21}$  holes with a resistivity in the range listed. The other way is to use a rather larger germanium deficiency and 2 to 7 percent silver. In strontium titanate the loss of a wee little bit of oxygen is sufficient — up to 0.3 percent oxygen giving  $10^{20}$  carriers (electrons in this case). The alternative way of producing carriers is to introduce niobium, and about 1/2 percent of niobium also gives  $10^{20}$  carriers.

In tin telluride, three separate mechanisms have been used: that of tin deficiency up to 4 percent; that of a combination of tin deficiency and arsenic; and tin deficiency and antimony. Again, the rather high carrier concentration is equivalent to that of germanium telluride, and perhaps is an order of magnitude greater than that of strontium titanate.

Now I want to go on to work more or less exclusively on strontium titanate. I want to discuss the  $T_c$  curves for the strontium titanate systems including those with partial substitution of barium, calcium, or zirconium.

After looking at the  $T_c$  curves for the barium-, calcium-, and zirconium-substituted strontium titanates, then I would like to discuss some work which we have been doing on uniaxial and hydrostatic stress effects on strontium titanate, which are relatively quite large in this material. I think this offers a fertile field for a hustling theoretician. Finally, I would like to describe experiments on magnetization which show the type II character of strontium titanate and simply make the statement that it was expected that superconducting semiconductors would be type II superconductors.

Figure 6 shows the  $T_c$  vs  $n$  curve of strontium titanate. It is composed of points taken with single-crystal oxygen-deficient specimens, plus two or three polycrystalline niobium-doped specimens. The data point at  $T_c = 0.4$ ,  $n = 1.5 \times 10^{20}$  is for a niobium-doped specimen. It appears that the niobium doping produces an envelope somewhat

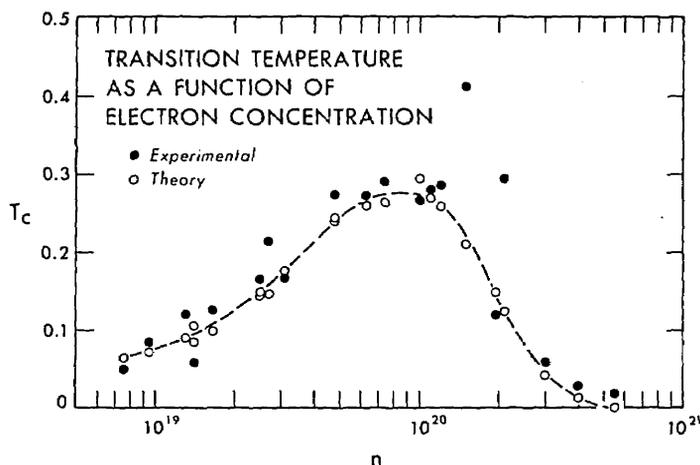


Figure 6

above the  $T_c$  vs  $n$  curve for the oxygen-deficient samples. The points were measured by the ac susceptibility method which Dr. Hein has shaken your faith in — I hope not too severely.

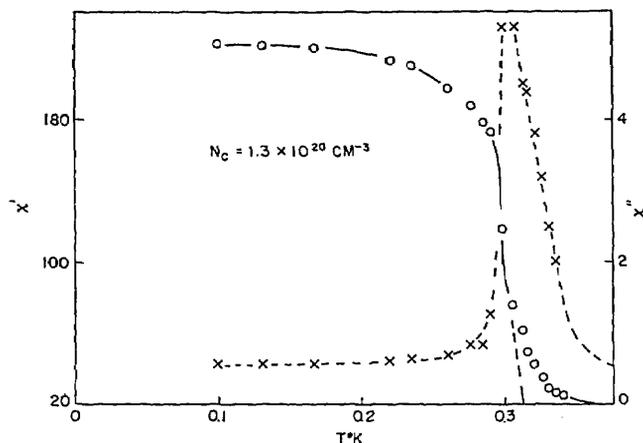


Figure 7

Primarily for the benefit of Dr. Hein, and again in gratitude for having his preprint, I would like to show what this type of ac susceptibility measurement looks like on strontium titanate in Fig. 7. This simply shows the transition in zero applied field and in a measuring field of the order of a few milligauss of a sample of  $1.3 \times 10^{20}$  hydrogen-reduced (or oxygen-deficient) strontium titanate. You see the real part or the inductive part rather, of the susceptibility dropping off in a way indicative of a broad transition and the "lossy" part or the  $\chi''$  shooting up in the region of the transition. Dr. Hein has shown this type of curve in his paper and gives a very adequate explanation as being due to magnetic hysteresis in the specimen, which becomes particularly pronounced in the transition region due to local areas being driven into the intermediate state. I would only add that in an ordinary superconductor one would have a very high loss in the normal

state. In other words, even at low frequency (this was taken at perhaps 270 cycles), you would have skin depth problems, perhaps; but in any case you would have a very high electromagnetic loss in an ac susceptibility measurement, so that this peak, even if present, wouldn't show up very well, unless, say, you had a strained specimen, but in the fairly high resistivity superconducting semiconductors, you then have very little loss in the normal material because the resistivity is so high so that this peaked loss region shows up fairly well.

Referring back to Fig. 6 — I want to comment that the dashed curve is the theoretical curve which fits the theoretical points. I am not going to go into the way that a theoretician gets theoretical experimental points, because I am not really sure that I understand it, and you wouldn't believe it anyway.

However, we do have the smooth curve and this is the work of Koonce and Cohen. I want to comment on it because in this theoretical fit they used best values; that is, experimental values (or the best ones they could guess at from experiments if their parameter wasn't directly measured) for some 18 normal-state parameters on strontium titanate. To this, they added a single number for the intervalley deformation potential (which can't be gotten simply from experiments), and with the use of all this data they ground out the curve that you see. Whereas the fit is very good, I think the real contribution of the theoretical work of Koonce and Cohen is that they really tried to apply the BCS theory to real strontium titanate specimens, warts and all! They considered every normal-state property that they felt would influence the superconducting state and I think this is the technique which will generate the quickest advance in the theory of superconductivity.

Figure 8 shows the effect of adding barium or calcium to strontium titanate. In this case we have a curve composed of data taken on ceramic samples of pure strontium titanate; of 7-1/2% barium substituted for strontium titanate; and of 7-1/2% calcium substituted for strontium titanate; and two points I see for 2-1/2% barium substitution. One finds now that the extent of the superconductivity appears to be rather larger and the transition temperature rather higher: a substantial change in the superconducting properties of the material. We believe that the influence of the calcium and barium is

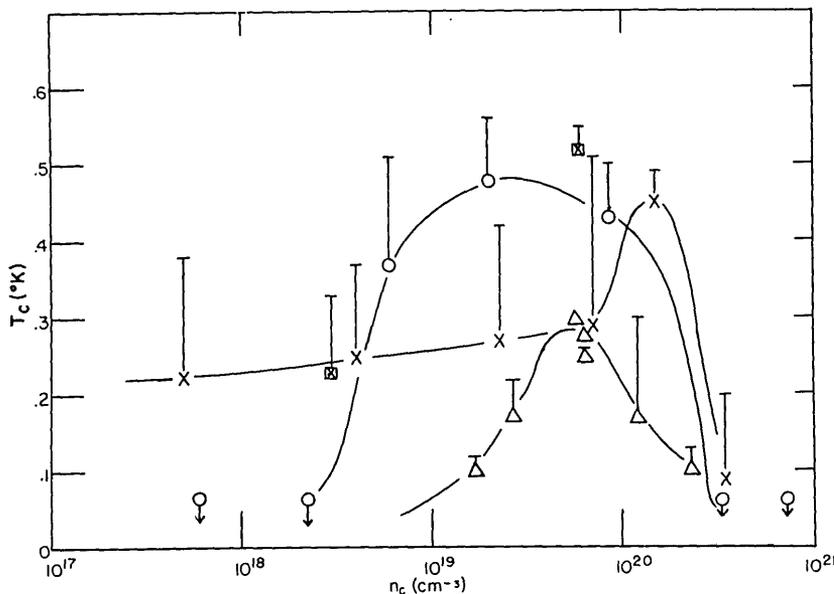


Figure 8

The Most Important Part of  
the Periodic Table

IA	IIA	IIIB	IVB	VB
K	Ca	Sc	Ti	V
Rb	Sr	Y	Zr	Nb
Cs	Ba	R.E.	Hf	Ta

Figure 9

primarily on the dielectric properties of the lattice and I will try to spend a little time to convince you that this is true.

The first thing I would like you to note is that barium or calcium substitution is not really doping at all. In Fig. 9 you can see that this is true because if you take strontium, titanium, and oxygen over in the less important region of the periodic chart you can see that calcium and barium are isoelectric with strontium. If you replace 7% of the strontium — or 2% or any percent — with calcium or barium you are really not affecting the carrier density. On the other hand, you can see that niobium — which goes in for the titanium — will act as a dopant, and we so treated it. Now, although the calcium and barium are innocuous as far as the carrier density is concerned, or at least we think it is ineffective on the electronic structure, various people have studied the effects of calcium and barium addition on the dielectric properties of strontium titanate, and the next figure shows some of this data.

Figure 10 shows the work of Granicker and Jakits.\* I want you to note that strontium titanate appears to be structurally tetragonal at low temperatures itself. Strontium titanate occupies the center vertical line here. In fact there is evidence that this shift to crystallographic tetragonality does not influence any sensible number of electrons, so that the semiconducting strontium titanate can be treated as if it were cubic at all temperatures. Again, here I refer to the magnetoresistance measurements done at NRL. The addition of either barium or calcium to strontium titanate — substituting for part of the strontium — you can see has drastic changes in the case of the structure on either side, although for 7% in neither case does it leave the tetragonal phase.

Figure 11 shows, however, the influence of barium titanate on the dielectric constant as a function of temperature. Strontium titanate is the bottommost curve, and as you compare this to Fig. 12, you can see the zero temperature dielectric constant measured here is 6000 — whereas it's listed as 10,000 on Fig. 12, which I think shows the difficulty of making measurements at a very high dielectric constant. In any case, the addition of a little barium gives the appearance of ferroelectricity, that is, you get the peak in the dielectric constant. The material is made more ferroelectric — (the temperature of the peak in  $\epsilon$  rises) — by the addition of 2, 4, 6, 8, and 10% barium.

Figure 12 shows a similar type of experiment for calcium strontium titanate; 4, 8, 12%, etc., calcium again produces a peak in the dielectric constant characteristic of ferroelectricity. Now Dr. Koonce reminds me — almost continually in fact — that it is the dielectric function  $\epsilon(q, \omega)$  that is the parameter that enters the superconducting gap equation and not the static dielectric constant which we have seen in these two figures. He also reminds me that the superconducting strontium titanate has carriers in it, and

\*Nuovo Cimento, Suppl. 3, 11:480 (1954).

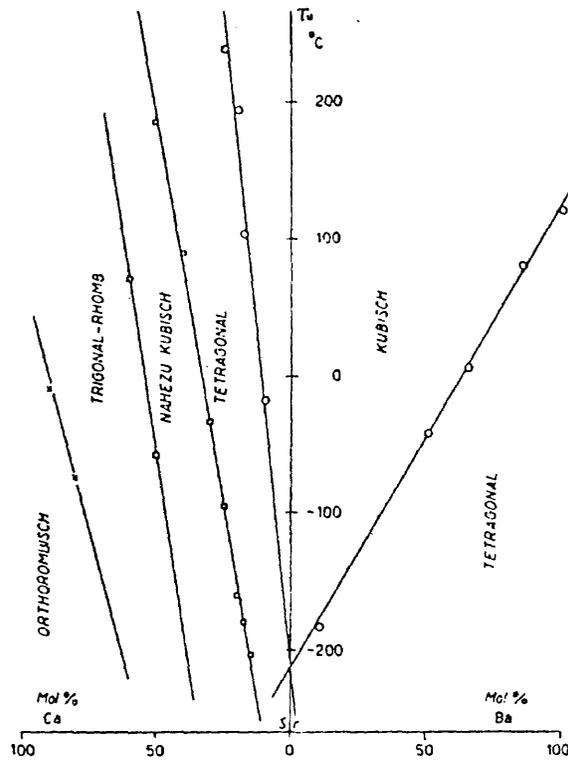


Figure 10

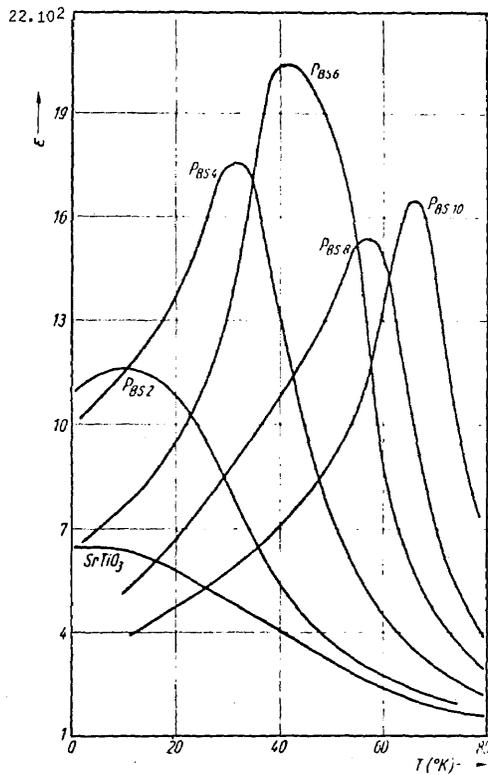


Figure 11

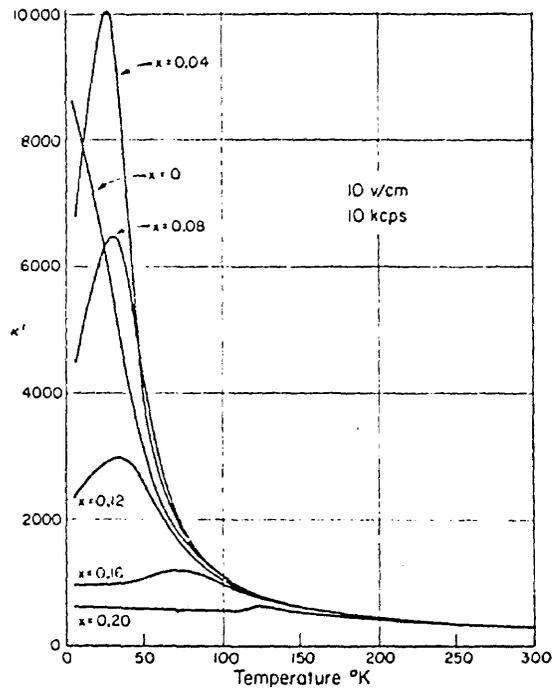


Figure 12

that these are insulating materials that have been examined. My only reply to that is "Don't bother me with facts, my mind is made up. It is the dielectric properties that are changing and that are causing the wide change in  $T_c$  by barium or calcium substitution."

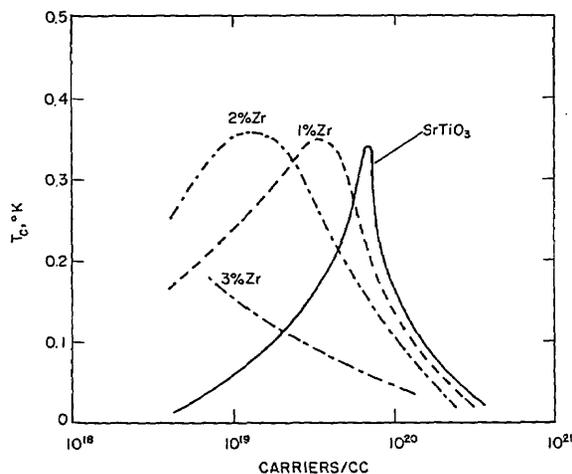


Figure 13

Hulm, Jones, Miller, and Tien have investigated the substitution of 1, 2, and 3% zirconium for titanium in oxygen-deficient strontium titanate (Fig. 13). This is again a set of ceramic samples which were made at Westinghouse and have very nearly the same envelope as the NBS standard variety, and one can see that the influence of a little bit of zirconium is fairly drastic.

Referring to Fig. 9, I just want to show that zirconium is isoelectronic with titanium; so again having made the substitution zirconium for titanium, one has done a similar thing to the calcium or barium substitution. That means that one has to add, besides that, carriers.

Now back to Fig. 13. The zirconium does not enhance the  $T_c$  particularly here, but it certainly affects it. It drives the peak  $T_c$  to lower and lower and, by George, lower carrier densities! Hulm, Jones, Miller, and Tien discuss their data in terms of a change of electronic properties of the crystal, and Dr. Eagles has written a theoretical discussion in the same vein.

This is polemics, so you can turn me off if you like. The presence of a sufficiently radical change in the electronic character of the mixed crystal strikes me as being an unlikely situation, and if I may be permitted, I will simply say that I think it is unlikely that there is a substantial change in the electronic character of these mixed crystals. It is very likely that here again we have a change in the dielectric properties. I am treading on dangerous ground here because Dr. Hulm was writing on dielectric properties before I knew what they were, so he may be able to shut me off very fast. However, the compound strontium zirconate is a well-known perovskite and, according to Roth at the Bureau of Standards, it is very nearly cubic. I haven't been able to find, on short notice, dielectric measurements either of strontium zirconate or of the mixed crystals with strontium titanate, but my guess — based on our experience with calcium and barium — is that this data will show a substantial change in the dielectric properties from strontium titanate as you add a small amount of zirconium. The corresponding change in the

electronic properties would require that the zirconium modify the entire band structure; you have to add the carriers by oxygen deficiency here as before, and, after all, 97% of the electrons generated go into the same old titanium 3d levels.

I would like to show you now some of the results we have obtained on stressing superconducting strontium titanate. Figure 14 shows a pictorial of the Fermi surface of strontium titanate. This is just to remind you that with compressional stress on a many-valley material — depending on the sign of the deformation potential — you either shrink or more heavily populate the valleys in the stress axis and either swell or shrink the ones in the perpendicular direction in  $k$  space. What we were after in these experiments was to shift the valley population enough by stress so as to depopulate one of the valleys, and this would drop out one or two terms in the superconducting gap equation and should plummet the transition temperature. This effect should make  $T_c$  go down very strongly as a function of uniaxial stress.

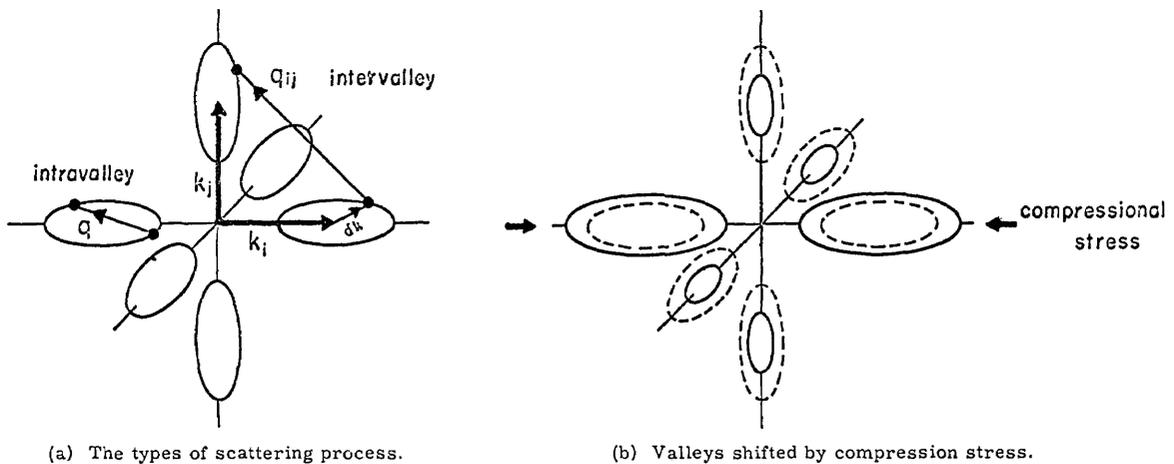


Figure 14

We realized in these experiments, of course, that many of the gap parameters depend on the molar volume. Among these are the dielectric function, the exchange phonon frequencies — that is the frequencies of the phonons critical to the electron scattering — and the  $q_0$ , the maximum phonon number at the edge of the zone. All of these are dependent on the molar volume so that a change in  $T_c$  need not necessarily indicate valley repopulation.

Figure 15 shows the first of two apparatus that Earl Pfeiffer, my colleague at the Bureau of Standards, built in order to examine these defects. This one simply shows an adiabatic demagnetization salt — potassium chrome alum — with a screw driver, which is detachable, and a germanium piezoresistor — which was our manometer. Also shown are the strontium titanate stress sample which sits in the same stress axis as the germanium piezoresistor, a reference specimen with its separate coil, and a thermometer sphere (CMN).

Figure 16 shows a relatively routine ice bomb. The fact that we had to work below 0.3K in general did complicate the apparatus substantially, particularly the previous one. In this case, what one has is simply a stainless steel bomb which one fills with water. We included a stress specimen of strontium titanate and a specimen of indium or tin

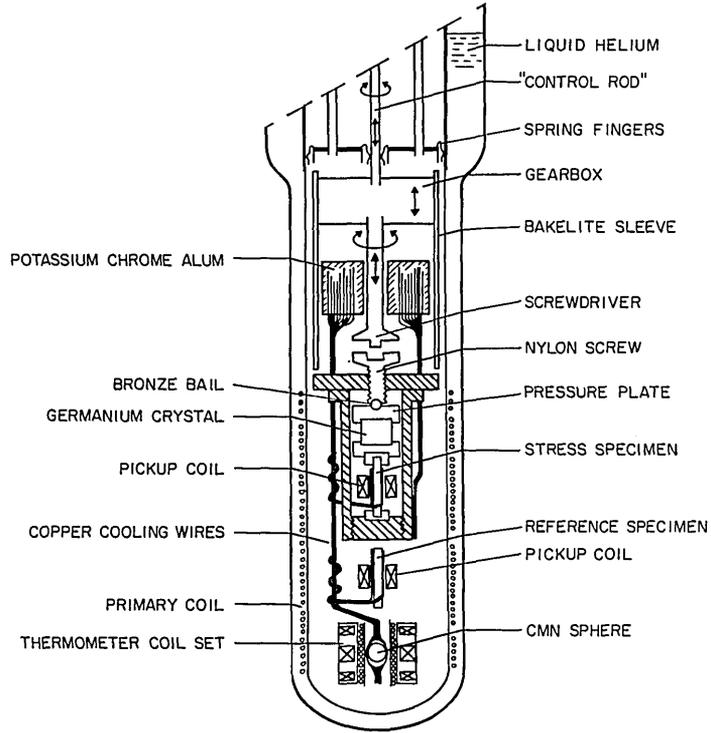


Figure 15

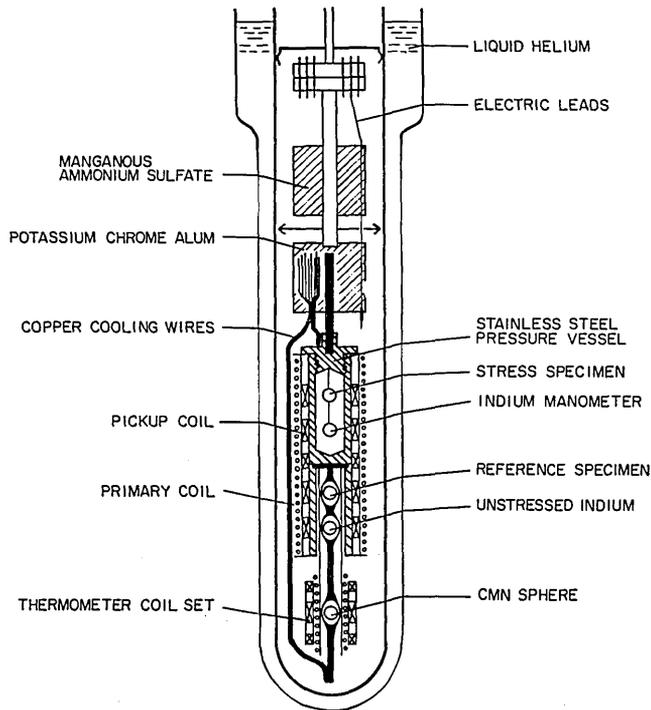


Figure 16

which would then show a shift in its transition temperature and act as a manometer. Also shown is a reference specimen of strontium titanate of the same carrier density and a reference specimen of unstressed indium in order to measure the shift of the transition temperature.

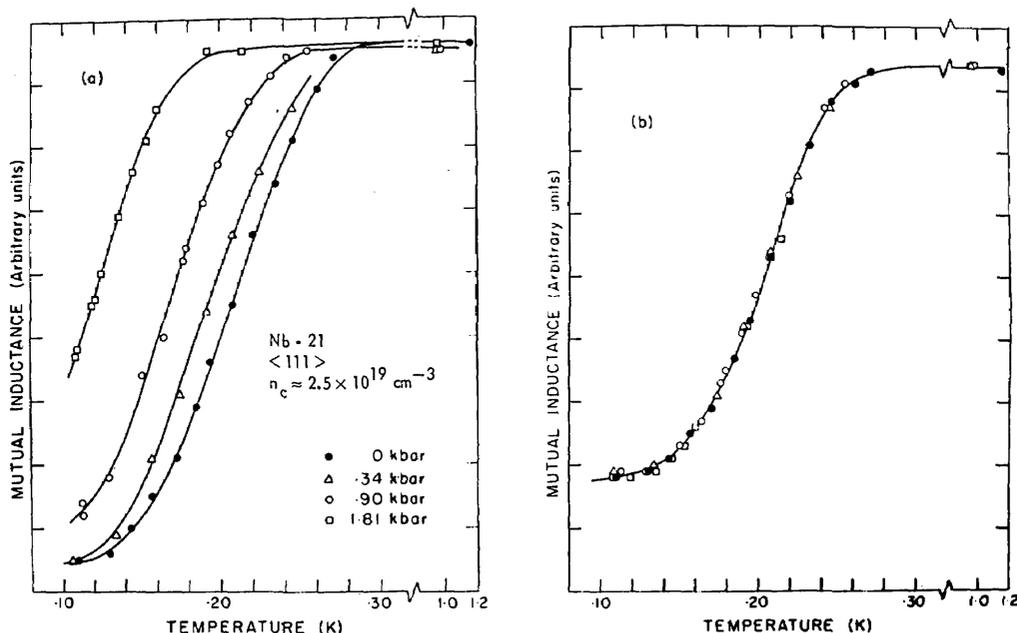


Figure 17

Figure 17 shows the type of data one gets with uniaxial stress apparatus. (This is a sample of niobium-doped  $\text{SrTiO}_3$  with  $2.5 \times 10^{19}$  carriers.) The transition temperature simply decreases as stress was applied in the (111) direction. The reference specimen in all these runs then either has or does not have the same transition curve, and to the extent that our thermometry is any good, it has the same transition curve. In any case one can then measure the shift in transition temperature rather nicely by comparing the two curves. It shows, I think, the value of including the reference specimen. What one has here are points at 0 pressure (solid circles) and in the same run, 300 atmospheres or so (which are the triangular points), then 900 atmospheres (the open circles), and finally 1800 atmospheres (the squares). One simply warms the sample up to  $1^\circ$ , screws down on the screwdriver to produce different pressures.

Figure 18 shows the similar result for the ice bomb in which tin was the manometer. The 1.48 kilobars pressure was deduced from the shift of the tin transitions. One assumes that the pressure is now temperature independent, and cools the sample to a tenth of a Kelvin or so and measures the shift of the strontium titanate transition. You can see here that the relative effect on strontium titanate is enormous as compared to metals. If we compare roughly a tenth of a degree (the shift of  $T_c$  per kilobar pressure on In) divided by 3.5K (the indium  $T_c$ ), or a 3% effect here, and roughly a 40% reduction of the strontium titanate  $T_c$  — this means that the stress is extremely effective in depressing superconductivity in this material.

Figure 19 shows a complete set of data taken on a specimen about  $6 \times 10^{19}$  oxygen deficient strontium titanate. One sees in the first place the very anisotropic defect of

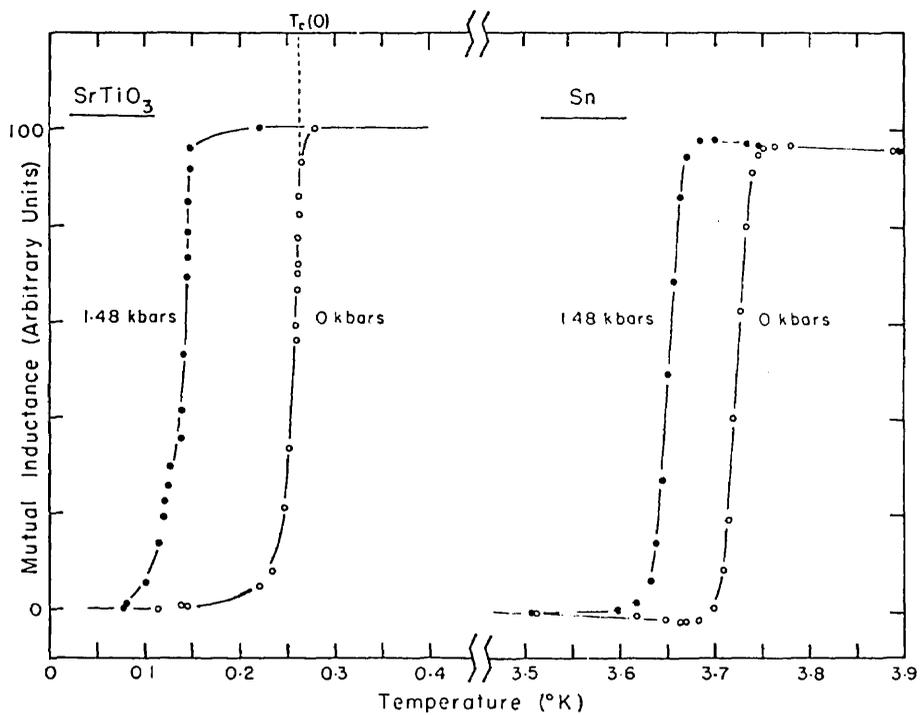


Figure 18

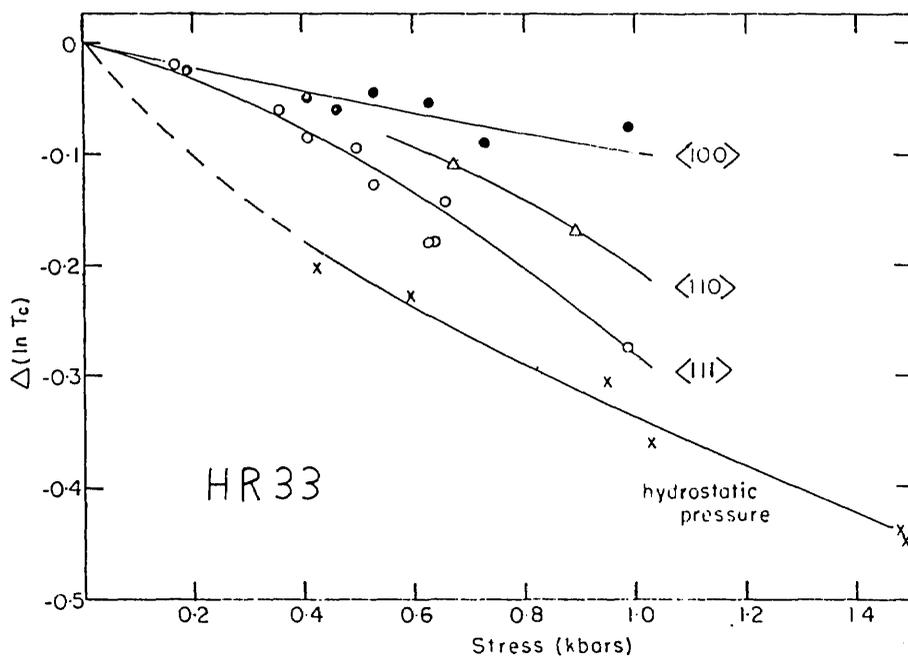


Figure 19

uniaxial stress, and then the ice bomb results showing that the effect is primarily due to molar volume change. The initial slopes of the uniaxial stress curves here are about a third of that for the hydrostatic case, which all adds together to indicate a change in molar volume. If we were to find valley depopulation, we would expect to find it in (100) stress and we would expect this curve simply to drop out of sight at some pressure when a valley depopulated. This we have not seen.

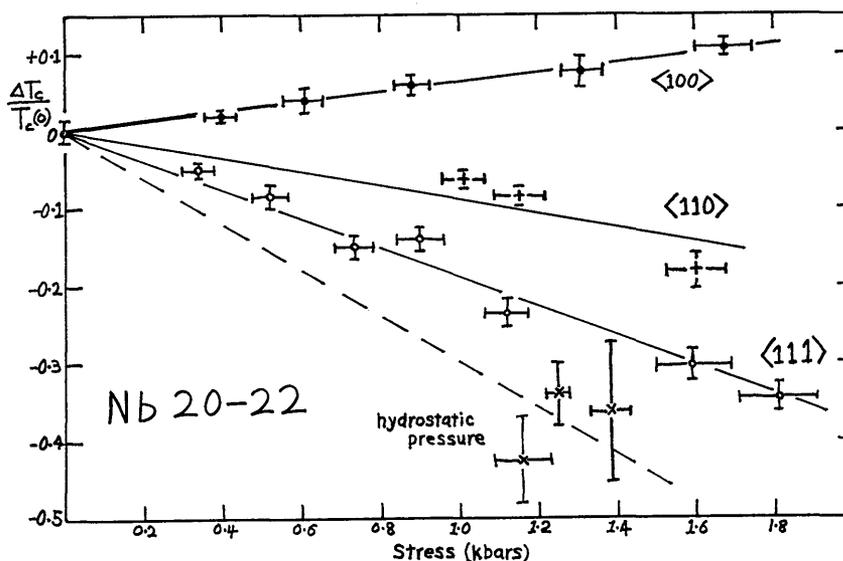


Figure 20

Figure 20 shows a set of results for a niobium-doped specimen of about  $3 \times 10^{19}$  carriers. Here the surprise is in the (100) case, where stress increases the transition temperatures by about 10% for 1.8 kilobars. Actually, what we decided to do was to go ahead and go for 25K by continuing to apply stress and taking advantage of the linearity of this curve, but the specimen broke at something like 2000 atmospheres. We feel that it realized the importance of the experiment to the national goals, and it just couldn't stand the strain.

Well, we understand in a qualitative way the lack of valley dumping by the fact that we did not see the depopulation of an electron valley. This is presumably due to just a low acoustic deformation potential. We can understand in a qualitative way the effects of the stress on the strontium titanate transition temperature because there are so many of the superconducting parameters which are volume dependent. We don't understand that increase on the niobium sample, and anyone who wants to have a crack at explaining is highly welcome.

I think the next thing I will go into is the magnetization to show the type II character of superconducting semiconductors. Figure 21 shows a magnetization curve, or at least the front end of it, for a sample of niobium-doped material of  $10^{20}$  carriers, and the first critical field ranges between 3 and 1 gauss, or oersteds, or minitesla (actually 0.1 to 0.3 millitesla). Figure 22 shows the high end of the transition and you can see that the material is extremely type II, going from a field of first penetration of a gauss or so out to a field for normality of a few hundred gauss. This made the measurement very difficult and both the Labs that have done this type of experiment have been driven to desperate

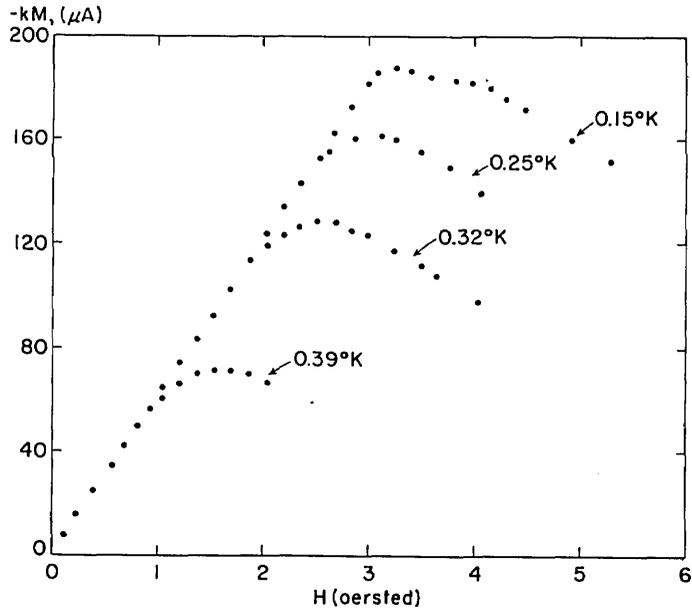


Figure 21

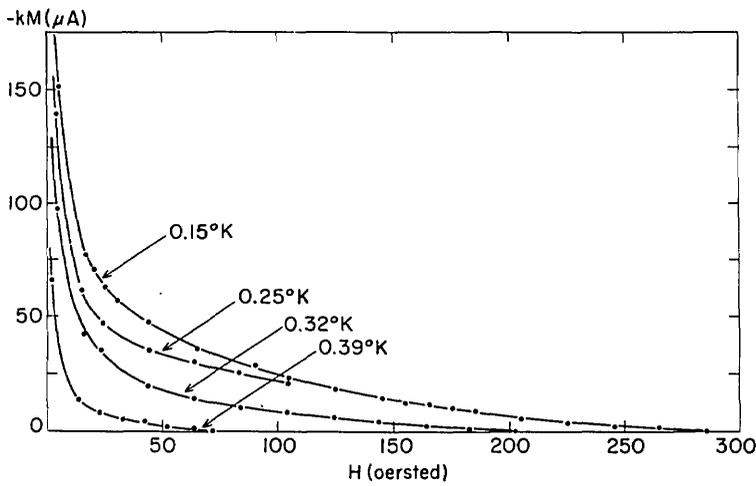


Figure 22

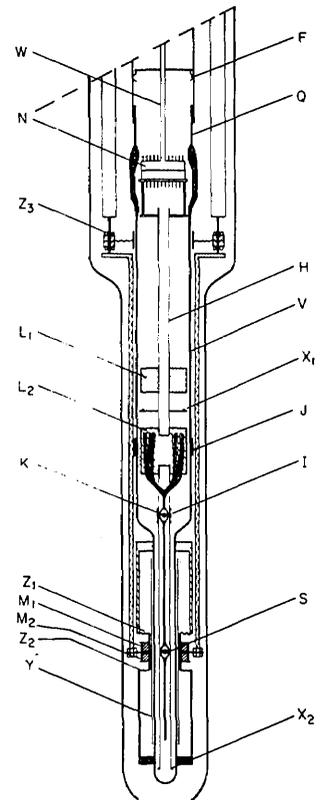


Figure 23

measures in order to measure it at all. In our own case, Dr. Ernest Ambler of NBS designed a sensitive vibrating coil magnetometer made for the measurements that we have, the heart of which is shown in Fig. 23. Here we simply have a vibrating coil surrounding the specimen and the specimen is then enclosed in an adiabatic demagnetization apparatus and held in a steady, constant, dc magnetic field. Thus, one simply measures the spatial variation of the moment about the small specimen — the signal is then proportional to the magnetization.

Dr. Hein in his forthcoming work on tin telluride describes his own solution, which is the incremental susceptibility technique. Now, he is a purist as you can see — 99.4% of all superconductors report their data with the magnetization curve minus  $M$  and it looks right side up and well; my hat is off to Dr. Hein but his curve is upside down — there is no getting around it. Again you can see for tin telluride — this is a specimen of  $10^{21}$  carriers at 12 millidegrees — God help us! and the first critical field is down around  $1/2$  a gauss and the second is up around 5. As we do, Dr. Hein uses a thermal purge after each run to drive out trapped flux. You can see that this is necessary from the return curve where, as the field is reduced to zero, there is a certain amount of trapped flux which gives in fact a paramagnetic moment. This can be seen as to disappear when you apply thermal purge after the return trace, and we see the same thing. One can simply drive the specimen normal, get rid of the trapped flux and have a virgin sample for the next magnetization measurement.

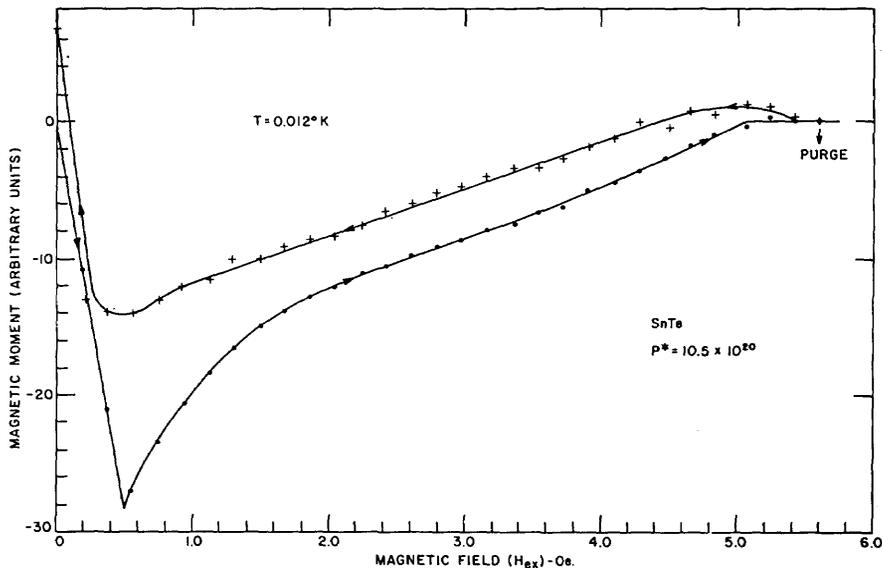


Figure 24

Figure 25 shows the results of our own measurements on the niobium-doped specimen that I showed previously for a set of temperatures up toward the transition temperature. The lower curve is the first critical field which goes to a value of perhaps 4 Oe, and the second critical field goes up to about 500. One can compute the Ginzburgh-Landau coefficient — the kappa value — following the theory of Marki, who has treated the case of impurity-limited mean free path. The value that I obtained in this result is 8.4. For tin telluride, Hein has found values ranging between 4 and 6 for specimens over the superconducting range, and values from 2 to 10, I guess, are ordinary for these materials.

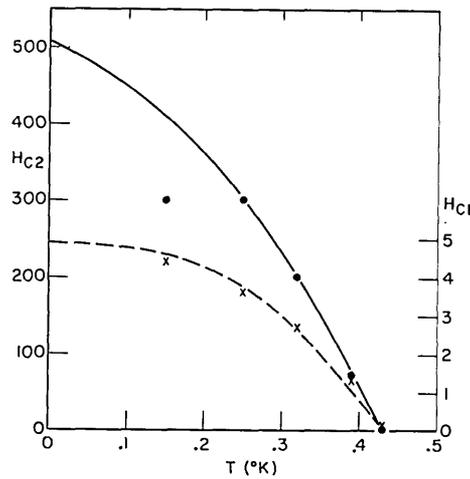


Figure 25

I want to close by giving the theoreticians the last laugh, by saying that after all this blood, sweat, and tears, they knew all along that the kappa was going to be very large. One can write it simply as the ratio of the London penetration depth divided by the full coherence distance:

$$\kappa \equiv \frac{\lambda_L}{\xi} = \frac{\sqrt{m^*c^2/n_s 4\pi e^2}}{(kT_c/0.18\hbar v_F + \ell^{-1})^{-1}} \approx \frac{10^{-4} - 10^{-5} \text{ cm}}{10^{-6} \text{ cm}} = 10 - 100.$$

The theoreticians simply point out that you have a big effective mass, and you have a very small number of super electrons. In the case of strontium titanate you are down by a factor of 1000 here and the lower part is the BCS coherence distance and the electronic mean free path. In these materials, electronic mean free path dominates this term because it is smaller and one obtains typically  $10^{-4}$  to  $10^{-5}$  cm divided by some  $10^{-6}$ , which then gives kappa values in the range of 10 to 100.

Thus, we did know ahead of time that it was going to be difficult to make the magnetization measurements but we had to do it because it was there. Well this has been a very fast trip through the field of superconducting semiconductors with its shallow valleys and its shimmering Fermi lakes situated along the favored axes of reciprocal space and I trust and hope that it has been somewhat illuminating. Thank you.

# LOW-CARRIER-DENSITY SUPERCONDUCTORS

C. S. Koonce  
*National Bureau of Standards*  
*Washington, D.C.*

I also feel honored to be here at NRL to discuss the BCS theory of superconductivity as applied to low-carrier-density systems, and I hope this discussion will complement the discussion to be given by Dr. Seiden later in the day on "Free-Electron-Like Superconductors." I recall that in the previous symposium, Prof. Matthias suggested that before theorists attempt to calculate transition temperatures for 2<sup>o</sup> superconductors, they should first learn to calculate the transition temperatures for 2<sup>o</sup> superconductors. While these words were spoken in the heat of debate, I'll address myself to the problem of calculating the transition temperature of a real material, in this case a low-carrier-density superconductor.

By a low-carrier-density system, I mean one in which the Fermi energy is of the same order of magnitude, or less than, the phonon frequencies of the phonons to which electrons are coupled. This more or less limits my field to the field of degenerate semiconductors. As we will see, some of the theoretical problems here are similar to the problems in the transition elements and in semimetals. In fact, at the present time there are only three materials that I would classify as a low-carrier-density superconductor, and two of these materials, germanium telluride and tin telluride, have Fermi energies which are 10 to 20 times larger than the phonon energies so that these materials form a transition region between the regime of metals and the regime of low-carrier-density superconductors. The other superconducting semiconductor, strontium titanate, is a true low-carrier-density system. For the carrier densities at which it has been found to be superconducting, the Fermi energy is always less than the highest phonon frequency, and at its low-concentration end the Fermi energy is as much as 60 times *smaller* than the phonon frequency.

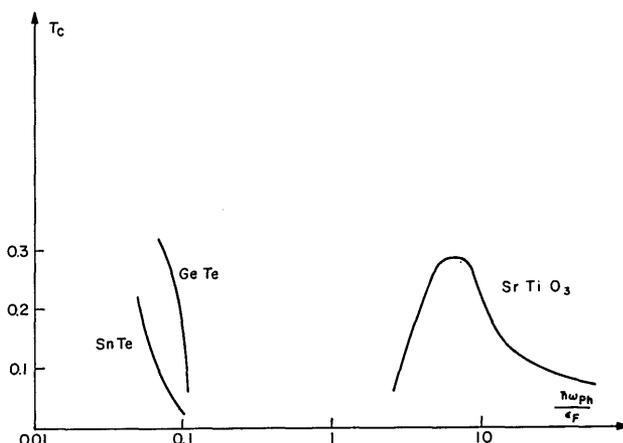


Figure 1

This information is shown in the first figure. The figure shows transition temperature plotted as a function of phonon energy divided by the Fermi energy, which is the inverse of the ratio that you usually see. On the left we have metals. In fact, metals lie to the left of the temperature axis shown. I have plotted tin telluride and germanium telluride on the basis of the data of Dr. Hein and coworkers, together with the data on strontium titanate by Dr. Schooley and coworkers. As you can see there is a big gap between the two. Tin telluride and germanium telluride have transition temperatures which are measurable for Fermi energies 10 times to 20 times larger than phonon energies, whereas strontium titanate has transition temperatures measurable only for phonon energies larger than Fermi energies.

Now I will discuss the methods for calculating the superconducting energy gap and superconducting transition temperature of low-carrier-density superconductors. I think this is interesting mainly because, as you can see on this first figure, in place of having one transition temperature for a given material, we actually have a whole series of transition temperatures for pretty much the same material. Since we are adding less than 1% of impurities to the strontium titanate, it is reasonable to assume that the band structure and other relevant properties are more or less unchanged. The same is more or less true for tin telluride and germanium telluride. Certainly, this is true near the low-carrier-density end where the band structure is most important.

- (1) Phonon Energy
- (2) Fermi Energy
- (3) Plasma Energy
- (4) Width of Conduction Band

Figure 2

Well, before developing a superconducting energy-gap equation, we first have to determine the relative order of magnitude of the normal state energies which are relevant to superconductivity. The four energies which are relevant are shown in Fig. 2. They are the phonon energy, that is, the energy of the phonons to which electrons are coupled; the Fermi energy; the plasma energy, which is Planck's constant times the plasma frequency; and the width of the conduction band. Now, this is a conduction band for an n-type material. In general, I mean here the width of the band in which conduction takes place. For a p-type material this would then be the valence band.

For ideal metals the phonon energy is small compared to all of the other energies that we have shown in the figure and this leads to great simplifications in the theory. As we have said, the phonon energy in low-carrier-density superconductors can be greater than the Fermi energy, as in strontium titanate.

In addition, for strontium titanate the plasma energy is approximately equal to the highest longitudinal optic phonon energy, which is a strong mode in this material, the plasma energy being approximately equal to the phonon energy at the peak of the  $T_c$  vs carrier concentration curve. The peak is at about  $10^{20}$  carriers per cubic centimeter. Thus the plasma energy can be smaller than the phonon energy, larger than the phonon energy, or equal to the phonon energy depending on how many carriers you introduce into the strontium titanate. Finally, for strontium titanate the width of the conduction band is also of the same order of magnitude as the relevant phonon energies.

The Fermi energy and the width of the conduction band are both of importance because they give the energy range over which the variation in density of electronic states can be expected to occur. In a metal, for example, where the phonon energy is small compared both to the Fermi energy and to the width of the conduction band, it is quite proper to take the electronic density of states as a constant over the range of phonon interaction. For a low-carrier-density system, of course, such as strontium titanate, this would be a very poor approximation.

The band structure is important for reasons other than the relative magnitude of the Fermi energies and phonon energies. For example, as Dr. Schooley pointed out, all of the known low-carrier-density superconductors have a many-valley structure and this means that electrons can scatter not only within a given valley, but they can also scatter from one valley into another valley. Therefore the gross features of the band structure, that is, where in momentum space the electrons are, determines what phonons are involved in scattering the electrons. Even if one considered only intravalley processes, the band structure would still be important because parameters which will always enter the theory, such as the Fermi wave-vector, will depend on the number of valleys in the conduction band. One must begin almost any calculation for a low-carrier-density superconducting system by considering the band structure.

The plasma energy or plasma frequency is important because it gives the range of the repulsive Coulomb interaction in much the same way that the phonon energy gives the range of attractive interaction through the phonon field. When the plasma energy and the phonon energy are the same order of magnitude, it means that the phonon attraction and the Coulomb repulsion have to be treated on an equal footing. This means, for example, that the interaction through the phonons must be screened by the full frequency- and wavevector-dependent electronic dielectric function. It also means that one cannot approximate the Coulomb repulsion with a pseudopotential. The approximations made in the Coulomb repulsion must correspond to the approximations made in the phonon attraction.

The first gap equations, that of BCS using a Bardeen-Pines interaction and the gap equation of Bogoluibov, used an instantaneous interaction through the phonon field. These theories had the advantage of allowing variation in electronic density of states to be included in a very natural manner into the equation. Unfortunately, the assumption of an instantaneous interaction caused these theories to be valid only in the limit of very large phonon frequencies. Of course, most superconductors are metals, and metals have phonon energies which are small compared to Fermi energies, so that the retardation, that is, the time lag between the time the phonon is emitted and the time it is reabsorbed, is really more important for most superconductors than is the variation in the electronic density of states.

This difficulty was removed by Eliashberg who developed a gap equation valid in the opposite limit, namely, when the phonon frequency is small compared to the Fermi energy. The Eliashberg theory was later generalized by Schrieffer and others to include renormalization or self-energy effects. A gap equation was then obtained which held for both strong and weak coupling, only requiring that the phonon frequency be much smaller than the Fermi energy.

Our next figure (Fig. 3) is a map which shows the regions of validity of the various gap equations we talked about. The region of metals is on the left while low-density systems are on the right. We see that for simple metals the Eliashberg theory and the Eliashberg theory with renormalization will always be good approximations. At the top we have weak coupling and at the bottom strong coupling. The dotted lines are, of course, only qualitative divisions, and the scale is totally arbitrary.

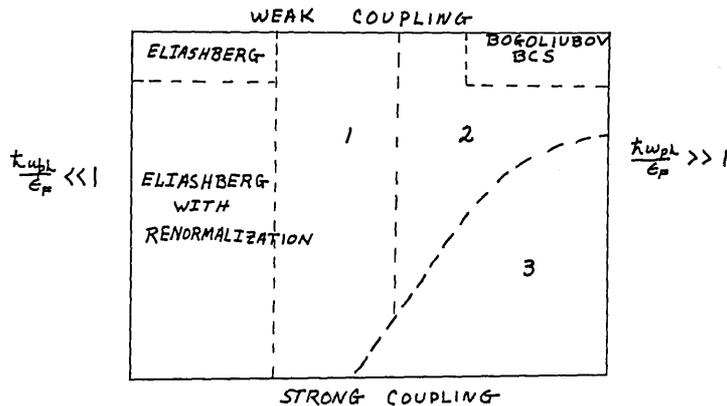


Figure 3

As we mentioned, the BCS and Bogoliubov equations assume an instantaneous interaction and, therefore, are valid only in the limit of very large phonon energies. I want to emphasize that I am distinguishing between the BCS gap equation with the Bardeen-Pines interaction and the BCS theory of superconductivity with the paired electrons interacting through a phonon field. Of course, all of the equations mentioned use the BCS theory of superconductivity. In addition, both the BCS and the Bogoliubov equations do not include renormalization and so are valid only here in the weak coupling limit. One can include renormalization effects into these equations, but the procedure is really not straightforward because of the fact that the equations are valid only in the limit of very large phonon energies.

This leaves the remainder of the figure pretty much vacant — the dotted lines again are rough, depending on the error that you want to accept. For example, you can take the Eliashberg theory to the low Fermi energy side of this map as far as you like, but your error will increase the farther you go.

Before superconducting semiconductors were known, the Eliashberg theory with renormalization was an excellent theory for all materials, with the possible exception of transition metals with very narrow bands, and there was no problem. If one really wanted to calculate a transition temperature one just used the Eliashberg theory with renormalization and that was it. In tin telluride and germanium telluride, as we said, the highest phonon energy is between 5 and 10% of the Fermi energy. At higher carrier concentrations, the superconducting properties of these materials can certainly be calculated with the Eliashberg theory including renormalization. At the low-carrier-density end we may be getting into Region 1. In any case this is a borderline situation and the whole  $T_c$  vs carrier concentration curve can be calculated with the Eliashberg equation including renormalization, or the McMillan empirical equation which is obtained from the Eliashberg equation. At the low-carrier-concentration end I would expect deviations from the Eliashberg gap equation of the order of 5 to 10% in  $T_c$ , if one assumes that all of the valleys in the conduction band are at L in the Brillouin zone. These changes are probably less than the scatter in experimental results. It is probably less than the differences, for example, between the single crystal data of Dr. Hein and the sintered sample data of Dr. Hulm and coworkers on tin telluride, so essentially we are in the left-hand region with tin telluride and germanium telluride.

Strontium titanate on the other hand has been found to be superconducting for Fermi energy between 2-1/2 and 60 times smaller than the highest longitudinal optic phonon frequency, depending on the number of carriers involved as you saw in the first figure.

In addition, the electron-phonon coupling is relatively strong. There is a strong Coulomb repulsion as well as a strong phonon attraction, these tending to cancel. I would then put strontium titanate in Region 2, and possibly getting into Region 3 at low carrier densities. It is interesting to note that various equations — the Eliashberg equation without renormalization, the Bogoliubov equation, and the BCS model equation, with just a constant interaction up to the phonon energy — and also the BCS equation adjusted to include renormalization have all been used by various authors at various times to calculate the transition temperature of this one material, strontium titanate. It is interesting to see this scatter in the validity of the various approximations that have been used.

Professor Marvin Cohen and I attempted to find the approximate gap equations in Region 1 and Region 2. We looked for equations which would be more valid in these regions than the Eliashberg equation or the Bogoliubov or BCS equations, but equations which would reduce to these equations in the limit of large Fermi energies or weak coupling. When the Fermi energy is large, then our equations reduce to the Eliashberg theory — a gap equation with renormalization. When the coupling is weak and the Fermi energy is small and screening is neglected, our equations reduce to the equations derived by Liu using the Bogoliubov method. We obtained no equation in Region 3 because we neglected vertex corrections, a good procedure only if Fermi energy is very large or if the coupling is weak. We still have no equation that we have any confidence in at all in Region 3, the strong-coupling, low-Fermi-energy region.

$$\Sigma_{\text{ph}}(p_0) = -\frac{\Omega N(0)}{\sqrt{\epsilon_F}} \int_0^\infty dp_0' \operatorname{Re} \left( \frac{Z(p_0') p_0' \mathbf{I} + \varphi(p_0') \tau_1}{\{\epsilon_F + \chi + [(Z p_0')^2 - \varphi^2]^{1/2}\}^{1/2} + \{\epsilon_F + \chi - [(Z p_0')^2 - \varphi^2]^{1/2}\}^{1/2}} \right) \\ \times \{ \{\bar{g}_\lambda\}^2 [D_\lambda^u(p_0 + p_0') \pm D_\lambda^l(p_0 - p_0')] \},$$

$$\Sigma_{\text{ph}}(p_0) = -\Omega N(0) \int_0^\infty dp_0' \operatorname{Re} \left\{ \frac{Z p_0' \mathbf{I} + \varphi \tau_1}{[(Z p_0')^2 - \varphi^2]^{1/2}} \right\} \{ \{\bar{g}_\lambda\}^2 [D_\lambda^u(p_0 + p_0') \pm D_\lambda^l(p_0 - p_0')] \}$$

$$\Sigma(p) = [1 - Z(p)] p_0 \mathbf{I} + \chi(p) \tau_3 + \varphi_1(p) \tau_1 + \varphi_2(p) \tau_2,$$

$$\varphi(p) = Z(\hat{p}) \Delta(p)$$

$$p = (p, p_0)$$

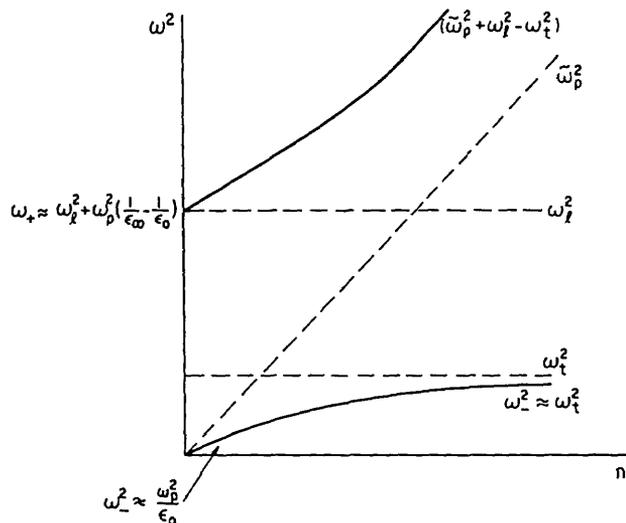
Figure 4

The equation that we obtained in Region 1 is on Fig. 4, above the Eliashberg equation. Don't let the subscripts trick you. I'm just going to talk about part of the equations. We used the same matrix notation used in the derivation of the Eliashberg equation. The Eliashberg equation with renormalization which was obtained previously is the equation used to calculate transition temperatures in metals. It is a matrix equation, the off-diagonal elements of the matrix giving the superconducting energy gap equation. The only difference between our equation and the Eliashberg equation with renormalization is contained inside the bracket of the real part. We get a different form in the denominator, simply because we have taken the Fermi energy to be finite. If one does an expansion of our term in brackets for phonon energies small compared to Fermi energies, the first term in the expansion is the term shown in the Eliashberg equation and the next terms

are of the order of phonon energy divided by the Fermi energy squared. Therefore, tin telluride and germanium telluride have about 1% corrections to the kernel of the gap equation. A 1% change in the kernel of the gap equation has a larger effect, of course, on  $T_c$ , but the end result is expected to be only 5 to 10% for these materials.

Unfortunately, as we saw in the first figure, there are no superconducting semiconductors between germanium telluride and tin telluride and the strontium titanate system. Most of the Region 1 that we have talked about is actually vacant at the present time. While this equation leads to very small effects in tin telluride and germanium telluride, the supposed materials that it would apply best to haven't been found yet. I want to emphasize again that we have tailored this equation to Region 1; it just contains the first effects of a finite Fermi energy and does not include, for example, the frequency dependence of the dielectric screening which is important for lower carrier concentrations.

Now, if we move into the second region where the phonon energy is as large or larger than the Fermi energy, the frequency dependence of the Coulomb interaction, screening, and the variation in the density of states becomes more important than the retardation or the time delay between emission and the absorption of the phonon. I think I will digress for awhile and talk about the importance of the frequency dependence of the electronic screening in low-carrier-density polar materials such as strontium titanate. We will first consider a material with just one polar mode, for simplicity (although strontium titanate has two strong polar modes, both of which should certainly be taken into account if you are interested in calculating a transition temperature). I will talk about one polar mode for simplicity. We then add electrons to the system. The electrons have their own collective mode, which is a plasma mode. This collective mode then couples to the longitudinal optic of phonon mode. Then we have two coupled modes at zero wavevector. When these modes couple we get the result shown on Fig. 5, which shows the frequency of the coupled modes plotted as a function of carrier concentration. Note that this is not a plot against wavevector. The whole figure is at zero wavevector and is plotted against the number of carriers in the sample.  $\omega_+^2$  is the upper mode and  $\omega_-^2$  is the lower mode.  $\omega_p$  is the plasma frequency, and you will recall that the plasma



$\frac{\epsilon_0}{\epsilon_\infty} = 4$  COUPLED PHONON-PLASMON MODES

Figure 5

frequency is  $(4\pi n e^2/m^*)^{1/2}$ . So the lower mode then starts out as the plasma energy screened by the static dielectric constant. At low carriers the upper mode is essentially the longitudinal optic phonon frequency. Thus for low  $n$  we start out with a longitudinal phonon frequency and the plasma mode screened by the static dielectric constant.

Now as we add carriers we see that these modes change character. The mode which began as a longitudinal optic phonon frequency moves up and, at large carriers, looks more and more like a plasma energy.  $\tilde{\omega}_p$  is the plasma frequency screened by the high frequency dielectric function  $\epsilon_\infty$ . At very high carrier densities, the upper mode looks more and more like a plasma mode and the lower mode approaches the transverse optic phonon mode. That means that at very high carriers, we again have a threefold degenerate phonon mode, that is, the polar nature of material which split the longitudinal and transverse mode in the undoped material is now shorted out and we have a threefold degenerate mode again. So the lower mode is then the phonon mode and the high mode becomes the plasma mode.

We should note that for strontium titanate the plasma frequency  $\tilde{\omega}_p$  screened by the high-frequency dielectric constant, which I believe is about 5.2, is approximately equal to the highest longitudinal phonon frequency. We are interested in the intermediate region of Fig. 5 for strontium titanate.

$$V(q, p_0 - p_0') = 4\pi e^2 / \Omega q^2 \kappa_T(q, p_0 - p_0'),$$

where

$$\kappa_T(q, p_0 - p_0') = \kappa_{ph}(q, p_0 - p_0') + \kappa_e(q, p_0 - p_0') - \kappa_\infty(q)$$

$$\frac{\kappa_\infty}{\kappa_T(q, p_0 - p_0')} = \frac{\kappa_\infty}{\kappa_T(q, 0)} + \int_0^\infty F(q, \omega) \left( \frac{1}{p_0 - p_0' - \omega + i\delta} - \frac{1}{p_0 - p_0' + \omega - i\delta} + \frac{2}{\omega} \right) d\omega.$$

Figure 6

We will next talk about what happens at finite wavevector. Figure 5 is all at zero wavevector with the number of carriers changing. We first note that the total interaction between electrons can be given, as on Fig. 6, by  $4\pi e^2 / \Omega q^2 \kappa_T$ , which is just a bare Coulomb interaction divided by the total dielectric function. The total dielectric function is the sum of polarizabilities from the lattice or the phonon contribution and from the electron gas. We can express the inverse of the total dielectric function by expanding it in the manner shown. The first term is the screening at zero frequency. The second term is an integral which we will talk about later. I want to point out now that the Coulomb interaction screened by the total dielectric function will be large when one approaches the zero of this total dielectric function. As one knows, the zeros of the dielectric function correspond to the longitudinal modes of the system, so when one approaches the longitudinal mode of the system the total interaction becomes large.

$$F(q, \omega) = - (1/\pi) \operatorname{Im} \left[ \frac{\kappa_{\infty}}{\kappa_T(q, \omega)} \right],$$

Figure 7

As shown on Fig. 7, the spectral weight function  $F(q, \omega)$  can be obtained by taking the imaginary part of the inverse dielectric function. As we discussed before, the longitudinal modes of the system occur when the total dielectric function is zero, so that  $F(q, \omega)$  will be large when the total interaction is large, and the longitudinal modes of the system can be obtained from the peaks of  $F(q, \omega)$ .

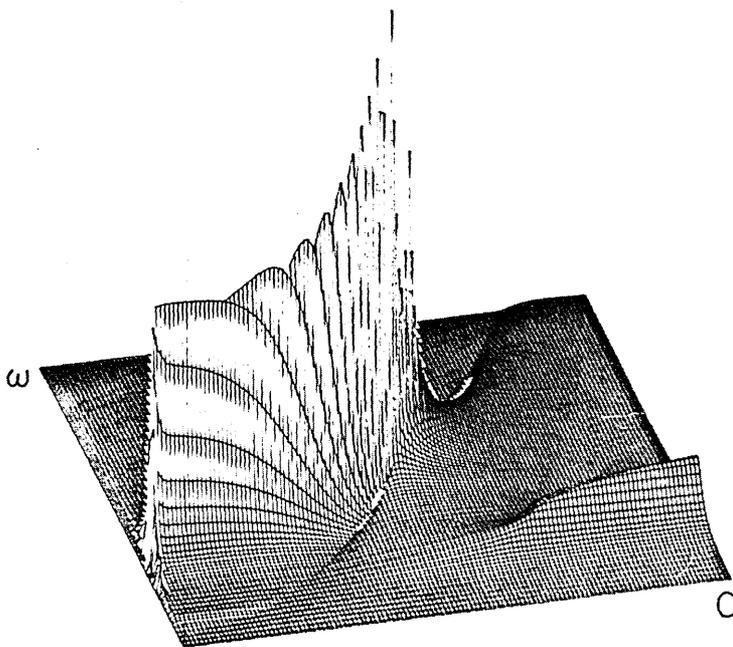


Figure 8

Figure 8 shows a plot of the spectral weight function plotted up from the frequency-wavevector plane. As you remember, we talked before about what happened at  $q = 0$ . Figure 5, which gave the longitudinal coupled modes as a function of carrier density, was all at zero momentum, which corresponds to the  $\omega$  axis of Fig. 8. You see that we do have two modes. The upper mode is the big peak that occurs above the longitudinal optic phonon frequency. The lower longitudinal mode is the low hump in this material at  $q = 0$ . The uncoupled longitudinal optic mode is a tenth of a volt. I've taken the plasma energy approximately equal to the longitudinal phonon optic frequency, as is the case in strontium titanate, but again I have only taken one phonon mode.

One can see that as momentum increases the energy of the upper mode increases. This is due to the partial plasma character of the coupled mode, since, as one knows, the

plasma frequency increases with increasing wavevector. We also notice the lower mode at  $q = 0$  that is just below the transverse optic phonon frequency. (I assume you can see the small hump. It looks like someone has a foot under the rug. It is a very weak mode here below the transverse optic phonon frequency.) This mode, as well as the stronger upper mode, damps out very strongly when one gets into the region of Landau damping, where real electron-hole pairs can be created. We can see that as the upper mode damps out a new mode is forming at large wavevectors.

I should put a scale on this wavevector plot. The maximum wavevector shown here is  $5.13 q_F$ . There is also a weighting factor which is essentially the momentum times this  $F(q, \omega)$  which will enter into our superconducting gap equation. If we are interested in a region of the intermediate  $q$  shown, it is clear that we can't talk about just one phonon frequency, because we have the large wavevector mode together with the small wavevector upper mode which is still prominent. So quite a large error would be made in this case if one simply replaced the three modes shown by one simple mode given as a function of wavevector.

Now that we have convinced ourselves that the frequency dependence of the dielectric function is very important, in fact that it determines the modes which couple the electrons, we will return to trying to obtain a gap equation in Region 2 of Fig. 3. We know now that we will have to include the frequency dependence of the dielectric function and also the variation in the electronic density of states. We obtained the equation shown on Fig. 9.

$$\Delta(\epsilon, p_0) = -\frac{1}{Z(\epsilon, p_0)} \int_{-\epsilon_F}^{\hbar\omega_{\text{ob}} - \epsilon_F} \frac{d\epsilon' \Delta(\epsilon')}{Z(\epsilon') E(\epsilon')} K_{\Delta}(\epsilon, \epsilon', p_0),$$

Figure 9

You see that it is of the BCS or Eliashberg form, that is, we have the gap times the kernel divided by the quasi-particle energy. We note here that the gap is a function of two variables. For most purposes we can evaluate  $p_0$  at the quasi-particle energy, namely  $E(\epsilon)$ , so we essentially have a gap equation which has the Eliashberg form, except that we notice that we have a renormalization factor  $Z(\epsilon, p_0)$ . If one evaluates this renormalization factor, one finds that it is quite important and that we are considering 50 or 60% changes in the kernel. This means we are talking about order of magnitude changes in the transition temperature or the energy gap. We see that the density-of-states variation will appear quite naturally in our equation. We are integrating now from  $-\epsilon_F$  to the width of the conduction band minus  $\epsilon_F$ .

The kernel that we have used is shown in Fig. 10. Again, don't let the complications fool you. This whole integrand is essentially the interaction after you have separated it into the Eliashberg terms. Here I have used the Coulomb interaction screened by the total dielectric function. If one separates out the Coulomb repulsion from the phonon attraction, that is, if in place of just screening by the total dielectric function one separates the kernel into two terms — one term rising from Coulomb repulsion and another term arising from phonon attraction — and in doing so one still keeps the frequency dependence of the dielectric screening as represented in the last term, one obtains the results shown on Fig. 11 for the phonon contribution to the kernel.

$$K_{\Delta} = \frac{\Omega m_b \pi}{(2\pi)^3 \hbar [2m_b(\epsilon + \epsilon_F)]^{1/2}} \int_{A(\epsilon, \epsilon')}^{B(\epsilon, \epsilon')} dq q V_c^B(q) \\ \times \left[ \frac{\kappa_{\infty}}{\kappa_T(q, 0)} + \int_0^{\infty} d\omega F(q, \omega) \left( \frac{1}{p_0 - E(\epsilon') - \omega + i\eta} \right. \right. \\ \left. \left. - \frac{1}{p_0 + E(\epsilon') + \omega - i\eta} + \frac{2}{\omega} \right) \right].$$

Figure 10

$$K_x(\epsilon, \epsilon', p_0)_{ph} = K_{\Delta}(\epsilon, \epsilon', p_0)_{ph} = \frac{\Omega m_b \pi}{(2\pi)^3 \hbar [2m_b(\epsilon + \epsilon_F)]^{1/2}} \int_{A(\epsilon, \epsilon')}^{B(\epsilon, \epsilon')} dq q \sum_{\lambda} |g_{\lambda}(q)|^2 \int_0^{\infty} d\omega' B_{\lambda}(q, \omega') \\ \times \left\{ \frac{\left[ \left( \frac{\kappa_{\infty}}{\kappa_e(q, 0)} \right)^2 + \int_0^{\infty} F_e'(q, \omega) \frac{2\omega' [p_0 - E(\epsilon')]}{\omega(\omega + \omega') [p_0 - E(\epsilon') - \omega + i\eta']} d\omega \right]}{[p_0 - E(\epsilon') - \omega' + i\eta]} \right. \\ \left. \frac{\left[ \left( \frac{\kappa_{\infty}}{\kappa_e(q, 0)} \right)^2 + \int_0^{\infty} F_e'(q, \omega) \frac{2\omega' [p_0 + E(\epsilon')]}{\omega(\omega + \omega') [p_0 + E(\epsilon') + \omega - i\eta']} d\omega \right]}{[p_0 + E(\epsilon') + \omega' - i\eta]} \right\}$$

$$A(\epsilon, \epsilon') = (2m_b)^{1/2} / \hbar |(\epsilon + \epsilon_F)^{1/2} - (\epsilon' + \epsilon_F)^{1/2}|,$$

and

$$B(\epsilon, \epsilon') = (2m_b)^{1/2} / \hbar |(\epsilon + \epsilon_F)^{1/2} + (\epsilon' + \epsilon_F)^{1/2}|.$$

Figure 11

The function  $\beta_{\lambda}(q, \omega')$  is essentially the phonon density of states. If one has a sharp phonon mode this will be a  $\delta$ -function, so that  $\omega'$  will be equal to the phonon energy. We notice that the terms here are of the Eliashberg form. We also notice that the first terms in the numerators arise from the zero frequency dielectric screening, while the second terms are due entirely to the frequency dependence of the screening. The  $F'(q, \omega)$  is a little different from the  $F(q, \omega)$  that we defined previously, being different only in that the total dielectric function is replaced by the square of the electronic contribution to the dielectric function, so that  $F'(q, \omega)$  will be large at the plasma energy. By looking at this equation, you can see when the frequency dependence of the dielectric screening will be important. You see the  $\omega' / (\omega + \omega')$  terms. As I have said,  $\omega'$  is essentially a phonon frequency.  $F(q, \omega)$  peaks near the plasma frequency so that we can replace  $\omega$  approximately by a plasma frequency. So if our phonon frequency is small compared to our plasma frequency, as it is in metals, these frequency-dependent terms will be small, containing a factor of phonon frequency divided by plasma frequency. Then, to a high degree of accuracy for simple metals, we can neglect these terms and simply screen our interaction by the square of the zero frequency dielectric function.

On the other hand, if we have a low-carrier-density superconductor, for example strontium titanate, for which the phonon frequency and plasma frequency are of the same order of magnitude, it means that the integral over  $\omega$  will be the same order of magnitude as the first term.

$$\left( \frac{\kappa_{\infty}}{\kappa_e(q, 0)} \right)^2.$$

Again we are talking about a 50% correction to our kernel, and as I said before, a 50% correction to a kernel means orders of magnitude change in the transition temperature. So if we are interested in calculating the transition temperature of a low-carrier-density superconductor, we must include terms arising from the frequency dependence of the dielectric function.

I think we can conclude from this last equation that any attempt to calculate the superconducting properties of strontium titanate must include the frequency dependence of the dielectric function as well as the renormalization. Thank you.

# SUPERCONDUCTIVITY IN LOW-CARRIER-DENSITY ROCK SALT COMPOUNDS

J. K. Hulm

*Westinghouse Research Laboratory  
Pittsburgh, Pennsylvania*

One of the pleasant things about working in this field has been the pleasant collaborations that we have had with several other groups, located at most points of the compass except to the north. To the East, we have worked with Bob Hein, John Gibson and Ray Falge, here at the Naval Research Laboratory. To the South, there is Dan Deis, Henry Fairbank, and Phil Lawless of Duke University, and in the West, Normal Phillips, Len Finegold, and Bailer Triplett at the University of California, Berkeley. I think I should commend the last group for getting results on the very difficult conditions in recent times! Finally there is our own group — Dan Deis, who came up to join us recently, Cliff Jones, Martin Ashkin, Bob Mazelsky, and Bob Miller. I probably left some out too, but those are most of the people involved.

The main reason for studying superconducting semiconductors, as far as I am concerned, is to try to get a better grip on the material parameters that enter into the superconducting interaction. There are quite a few theoretical expressions that exist for the superconducting transition temperature, mostly qualitative, some quantitative. We need work to quantify these in order to get exact numerical results, and of course our ultimate goal — at least one I have — is to be able to predict what upper critical temperature is possible in superconductors and to be able to predict new directions that we might go in materials to get higher critical temperatures. It seems rather peculiar that to try to do this we are working with quite low critical temperature materials down in the millidegree range, but I think it would be obvious from what I say as to why we are doing this.

The things that we think that  $T_c$  is a function of are shown in Fig. 1. Certainly we know that electron parameters such as the carrier density  $n$ , the electronic density of states which is related to the heat capacity coefficient  $\gamma$ , the effective mass  $m^*$  — which may be, of course, a multiple thing — and the Fermi energy  $\epsilon_f$  play a role in the determination of the transition temperature. We know that there are probably detailed band

$$T_c = \text{function of } \left[ \begin{array}{l} \text{Electron parameters, } n, \gamma, m^*, \epsilon_f, \\ \text{band structure factors,} \\ \text{s, p, d, f, character,} \\ \text{Phonon parameters, } M, a, \omega, \\ \text{lattice mode spectrum} \\ \text{Electron-phonon interaction strength} \end{array} \right]$$

Figure 1

structure effects where several bands may be involved in the conduction band of the material. There is indication that we have to take into account the nature of the bonding. Certainly the behavior of the transition metals and the rare earth metals and alloys is different from that of the simple s-p material. There are phonon parameters such as the atomic mass, lattice parameter, and the frequencies; and in fact we would like to take into account the lattice mode spectrum in some detail. Then, of course, there is the electron-phonon interaction strength which is a cause of superconductivity. Now all of this, by the way, is for bulk material in the absence of other influences such as geometric effects which are present in thin films, or things like localized magnetic moments, which themselves can cause depairing in superconductivity.

Although we don't have a precise general theoretical expression for the function, special forms have been derived for application to particular materials or for idealized models of solids. You have already heard about intervalley scattering in strontium titanate. There is a useful free-electron calculation due to Morrel and Anderson which has recently been extended by Phil Seiden, who will speak after me. If one has more detailed information on the phonon spectrum — for example inelastic neutron scattering measurements — it is possible to calculate  $T_c$  in simple metals and this has already been done just quite recently by Carbotte and Dynes for aluminum, sodium, and potassium. For the last two cases you get very low values — way below any temperature that one can obtain at the present time.

Now, what is the experimental situation? In complex materials, much has been learned by varying the solid-state parameters delineated in Fig. 1. The classic case, of course, is the dependence of  $T_c$  upon  $M$  (isotope effect) which essentially stimulated the creation of the original BCS theory. One of the limitations with this effect is that  $M$  can be varied only over a quite narrow range. By alloying, that is, making solid-solution alloys as has been done extensively for the transition metals, one can vary  $\gamma$ , which is proportional to the density of states, but unfortunately this simultaneously varies  $n$ ,  $a$ , and  $\omega$  and the band character as well. Consequently it is pretty hard to distinguish between these various parameters. Another possibility was given to us by the discovery of the superconducting semiconductor materials, for in this class of materials we can make orders of magnitude changes in  $n$  and corresponding great changes in  $T_c$ . The other factors may change somewhat while we are doing this, but to a lesser extent than they do in the case of alloy. Thus, we have here a fairly clear-cut case of single variable change, and the rest of my talk will be concerned with what we have learned from this so far.

First of all, I would like to summarize the experimental data on five materials in this class, shown in Fig. 2. Here we see  $T_c$  as a function of the carrier density  $n$ . Strontium titanate is on the left [followed by] tin telluride, germanium telluride, indium telluride, and lanthanum selenide. I am not going to discuss strontium titanate — it has already been covered — and I think Dr. Seiden will talk about lanthanum selenide. I am focusing my attention on the three compounds on the right which all belong to the sodium chloride lattice, which is one of a fairly simple structure to handle from a theoretical viewpoint. You notice that in all these materials, with the exception of strontium titanate,  $T_c$  increases monotonically with increasing carrier density. I should say that germanium telluride isn't exactly sodium chloride structure. It shows a small deviation from the sodium structure to a rhombohedral phase around 300°C, and this creates some difficulties experimentally. Also, indium telluride, which was found by Geller and co-workers at North American Rockwell, is in the sodium chloride phase only at high pressures. It can be stabilized to some degree at atmospheric pressure, but it is a difficult material to work with.

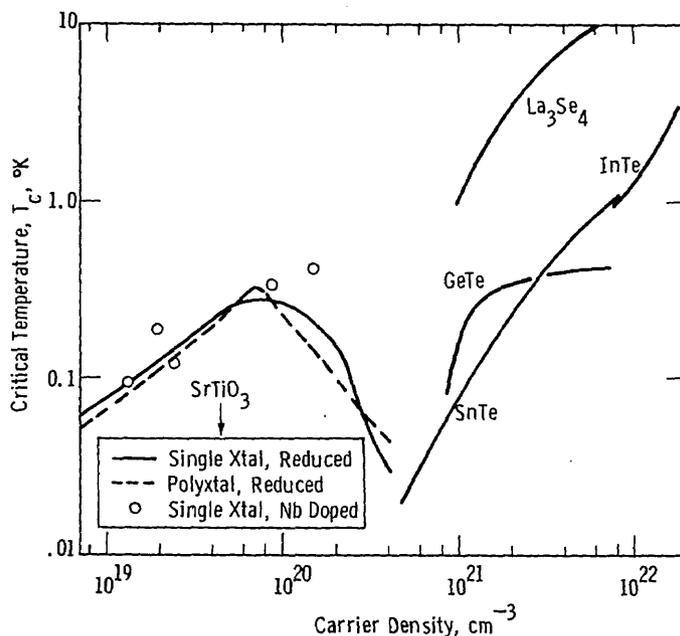


Figure 2

We have focused most of our attention, in fact, to tin telluride, and that explains the range of  $T_c$  and  $n$ ; tin telluride is the greatest among these materials. You notice  $T_c$  changes by two orders of magnitude in this material and in fact we were limited at the lower end, certainly, by the temperatures that we can reach in our cryostats at Westinghouse. We intend to extend the range down to a few millidegrees, hopefully in the very near future.

It is important to understand how the carriers are produced in these materials and this is shown in Fig. 3.

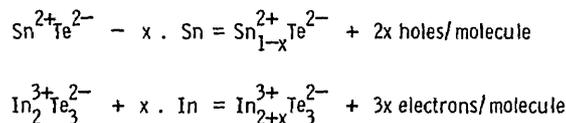


Figure 3

These materials are commonly referred to in the semiconductor business as polar semiconductors. This simply means that they presume some degree of ionicity in the lattice, and if you are treating them as ionic crystals we think that tin is divalent, which is a common valence state of tin, and if you abstract a fraction  $X$  of tin from this material, you go off stoichiometry as shown. In order to maintain the charge balance, you have to have two holes per molecule of tin telluride. Consequently the compound on the right, which is the one we normally work with, is deficient in tin — there are tin vacancies in the material. In germanium telluride, the doping mechanism is exactly the same as for tin telluride. In the case of indium telluride, it is somewhat different because of the trivalent state of indium. The balance case for the charge is off stoichiometry already.

The thing on the left doesn't look like sodium chloride, but you've got two indiums and three telluriums so you have already one sixth of the indium sites vacant, but you also have charge neutrality and you should have an insulator. If you add indium to this material to bring it toward stoichiometry, you get 3X electrons per molecule, so it is n-type, whereas tin telluride is p-type. Of course, in both of these cases, certainly in the case of tin telluride, X is fairly small and in most of our work it is less than one percent. There is a small change of lattice parameter associated with this shift, which violates what I said about all the other things being constant, but it is a small change. The actual carrier density in these materials is measured directly by the Hall effect and roughly agrees with the chemical composition shown in these equations but not exactly. This is what we refer to as self-doping.

You can also dope these materials by substitutional doping, which is a more common type of doping. This is necessary for the elemental semiconductors such as germanium and silicon, and we have substituted antimony, arsenic, copper, gold, and silver in the tin telluride lattice. You will notice that these are all valences different from two — which is what you need for substitutional doping. Careful work on the solid solubility and the phase diagrams is necessary for this kind of doping and I am not going to go into any detail on it, but quite a bit of work has been done.

The critical temperature vs n relationship in tin telluride seems to be essentially unaffected by the nature of the dopant, at least for low doping concentration. This is illustrated in Figs. 4 and 5.

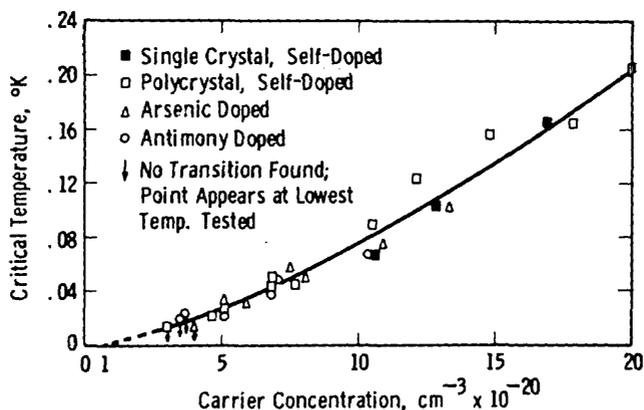


Figure 4

In Fig. 4, you see that you have quite a few self-doped points, including some single crystals which were investigated here at the Naval Research Laboratory in collaboration with the Naval Ordnance Laboratory. Also shown are our own polycrystalline self-doped — and arsenic antimony doped — samples, and as far as we can tell there is no significant trend to the impurity doped samples. They scatter around the self-doped points — and there is considerable scatter! There doesn't seem to be any systematic deviation from the  $T_c$  vs n curve.

Recently we have extended this up to higher carrier concentrations by means of copper, silver, and gold doping and that is shown in Fig. 5. The smooth curve here is the smooth curve taken from Fig. 4. It doesn't look quite the same because we are plotting

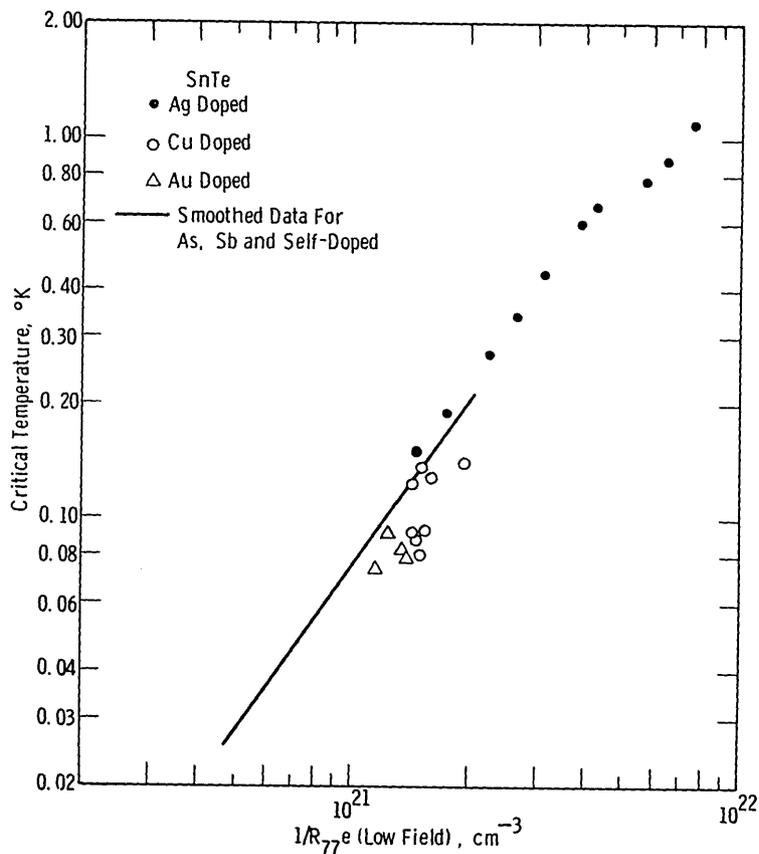


Figure 5

on the log-log scale. The black points are for silver. We really don't understand why — you can put a lot more silver in substitutionally than we can copper or gold — but by using silver we have been able to get the transition temperature up to slightly over 1°K.

Certain nonbelievers in semiconducting superconductors believe that this entire business is mythological in the sense that they believe superconducting transitions are due to impurity phases, such as free tin in tin telluride or free titanium in strontium titanate. It is hard to see why free tin would have a critical temperature down in the millidegree range, but people say these things, at least they use to say them. I think that Dr. Schooley would agree with me that there has been sort of a double standard operating here in the sense that the critics who are imposing this kind of demanding existence criteria on these low-carrier-density materials don't normally impose these criteria on the other superconducting alloys and compounds at higher temperatures. Be that as it may, I believe that most of the doubt is now being dispelled. The careful characterization of the semiconductors by x-rays, metallurgical studies, phase diagram studies, etc., has largely ruled out pseudosuperconductivity due to impurity phase. Of course one of the clinchers is one can determine the bulk effects by some direct means, such as heat capacity studies, and heat capacity data exist for most of these materials. I would like to show a typical heat capacity curve in the case of the germanium telluride measured by Len Finegold on our samples in Fig. 6. For a pure type I superconductor, one would expect the heat capacity to rise rather steeply at the transition temperature and drop down at lower temperatures. This doesn't look quite like that and we've never achieved a

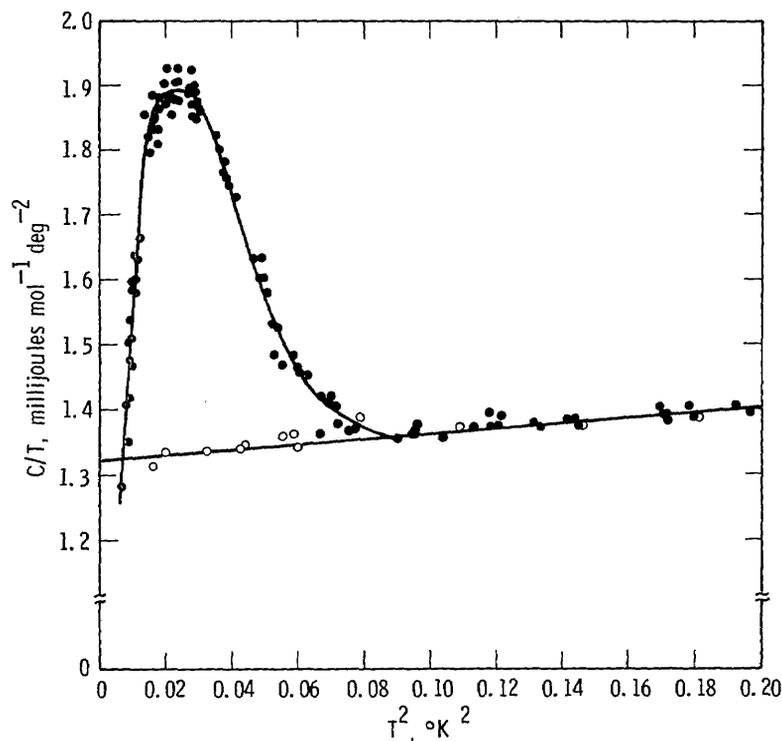


Figure 6

behavior close to the very sharp anomaly of a metal. I think this is mainly due to the fact that one has to work (in heat capacity) with very large samples and it is difficult to get a uniform distribution of carrier densities in these materials. Similar anomalies have been found for tin telluride and strontium titanate and I think these are undoubtedly bulk superconductors.

The further clincher is the work of Schooley and Esaki and Stiles on tunneling. Tunneling in germanium telluride shows that this material does develop a superconducting energy gap below  $0.3^\circ\text{K}$ .

Now there are some semiconductors that have been reported superconducting in which real doubt exists regarding the bulk effects. For example, about a year ago Lalevic reported lead telluride to be superconducting around  $5^\circ\text{K}$ . We've made a very careful examination of lead telluride samples with the compositions that he used, and other compositions in the same vicinity, and we feel that he had free lead — sort of a lead herring! One of the reasons for our conclusion is that it is impossible to achieve carrier densities much above  $10^{19}$  by self-doping in lead telluride. You can, however, increase the carrier density to  $5 \times 10^{20}$  by adding sodium or lithium. We tested such a sample down to  $0.009^\circ\text{K}$  and it does not show superconductivity, but I think it might become superconducting at lower temperatures simply by analogy with tin telluride, a very similar material.

Obviously since there are several rock-salt-structure superconducting semiconductors and an even larger group of normal semiconductors which belong to the rock salt lattice, such as lead telluride, lead selenide, lead sulfide, tin arsenide, tin antimonide, and so on, some interesting alloys can be made. Quite a bit of work has been done on

such alloys. Here you have sort of a problem with the number of variables. First of all, in the basic material itself you can vary  $n$  over a large range, and in addition to that, you can mix these things. Thus there is a second degree of variation so there is a lot of work that should be done, but I have only got time to mention one system which is rather interesting and unique. This is the alloy system between tin telluride and indium telluride.

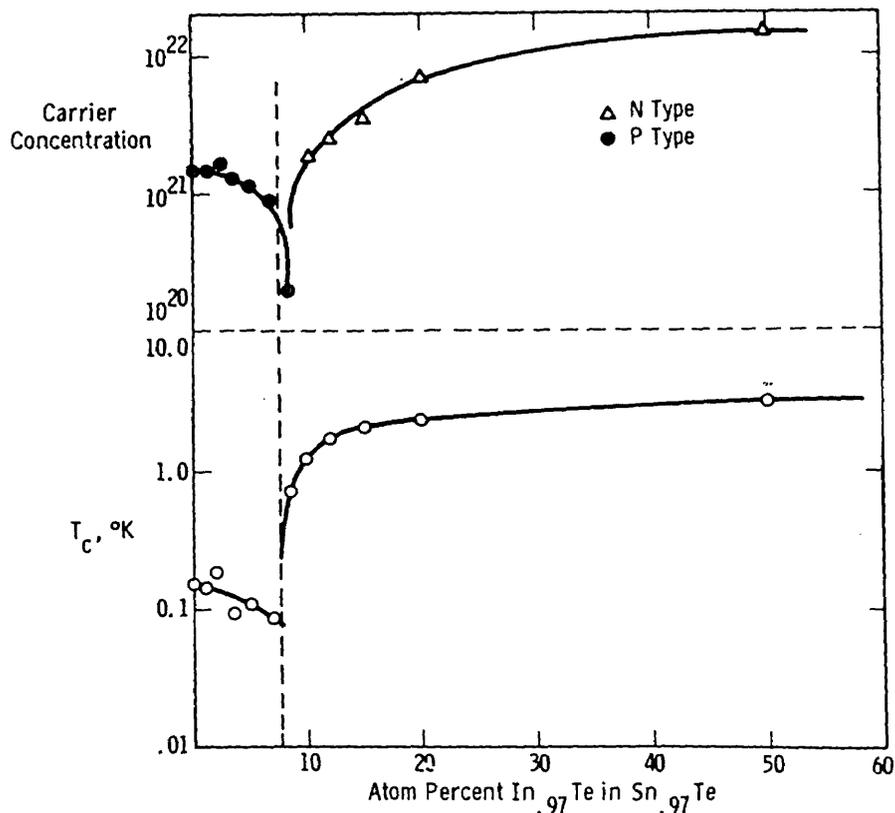


Figure 7

The results for this are shown in Fig. 7. On the top you see the variation of carrier density. You may recall that I said that indium telluride is n-type, and that you have to apply high pressures to stabilize the rock salt phase. If you add tin telluride to indium telluride then you don't need the pressure. The alloying also acts to stabilize the phase. From about 50% tin telluride to 100% tin telluride we have the phase at atmospheric pressure, and this is the range with which we are concerned here. The carrier concentration starts out in the p-type tin telluride phase. As we add n-type indium telluride, the carrier concentration falls off towards compensation — goes down to  $10^{20}$  — and then suddenly jumps up again into the n-type region of indium telluride. The critical temperature does the same thing. It follows the carrier concentration pretty close, dropping off as you would expect, and then it rises again quite steeply for the indium telluride phase. We thought at first that there might have been some kind of lattice transformation, a phase anomaly in the system. At times, the behavior of critical temperatures in superconductors like this occurs in the case of phase transformations. We looked at this very carefully and there is no evidence of such a transformation. It appears to be a solid solution over the entire range. So what we've got here is essentially a pure electronic

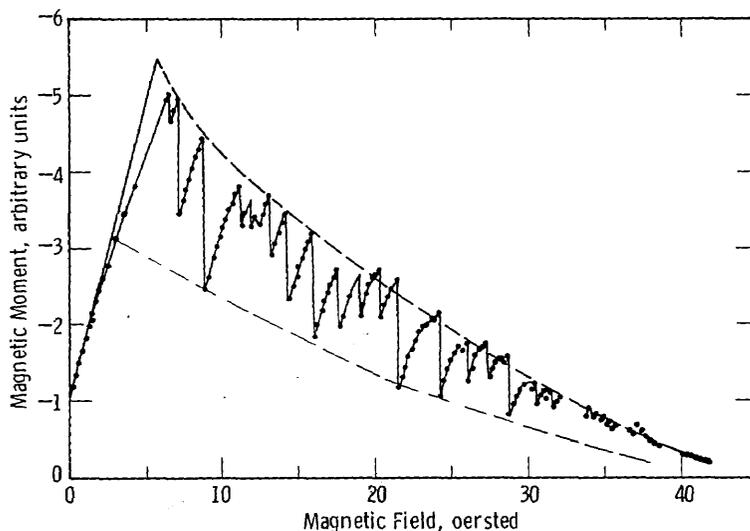


Figure 8

anomaly and I think it is unique. It is the only one I know of anyway — going from p-type to n-type.

I would like to say a word about the other superconducting properties of these materials. Because of the low critical temperatures, you might be surprised that they're type II, as Dr. Schooley mentioned, but this is well illustrated in the magnetization curve which Bob Hein obtained in germanium telluride on our samples, as shown in Fig. 8. The envelope of the magnetization curve here is clearly of the type II variety. The spikes you see on it are typical of flux jumping, which is more commonly found in a heavily deformed alloy and things like niobium zirconium that are used in superconducting magnets, and it is surprising to find flux jumping in material like this. Bob Hein suggested, and I think that I agree with it, that it is possibly due to the fact that we have in germanium telluride a lattice transformation which produces a very finely divided germanium structure. We don't really have a single crystal, and this finely divided domain structure is apparently on a scale, or produces enough local strain in lattice, that you have pinning of fluxoids. When you have a high critical current density, you get flux jumping on the magnetization curve. One thing that supports this conclusion is the similar curve for tin telluride which doesn't have the domain structure, as far as we know, and does not show flux jumping although it shows a similar envelope in the magnetization curve. Hein's data on  $H_{c1}$  and  $H_{c2}$  on this typical sample of germanium telluride is shown in Fig. 9. The lower curve is  $10 H_{c1}$ . Again the type II behavior is pretty obvious with the separation of  $H_{c1}$  and  $H_{c2}$ . The variation of  $H_{c2}$  with composition is shown in Fig. 10. Here is shown  $H_{c2}$  and you will see that the magnitude of  $H_{c2}$  changes quite rapidly with composition, essentially as you go toward stoichiometry. In other words, as you lower the carrier density,  $H_{c2}$  is dropping very fast. Now we can check up on this quite simply using the GLAG theory of superconductivity.

In Fig. 11, the three columns on the right are essentially free-electron-theory values calculated from the measured carrier density  $n$ , the effective mass  $m^*$ , as determined from specific heat data and the measured normal state resistivity. Note that the penetration depth  $\lambda_p$  and the coherence length  $\xi_0$  are on the order of a few microns ( $10^4 \text{ \AA}$ ), whereas the mean free path  $\ell$  is the order of a few hundred angstroms. This is really the reason that these materials are type II. They are quite short electron-mean-free-path materials.

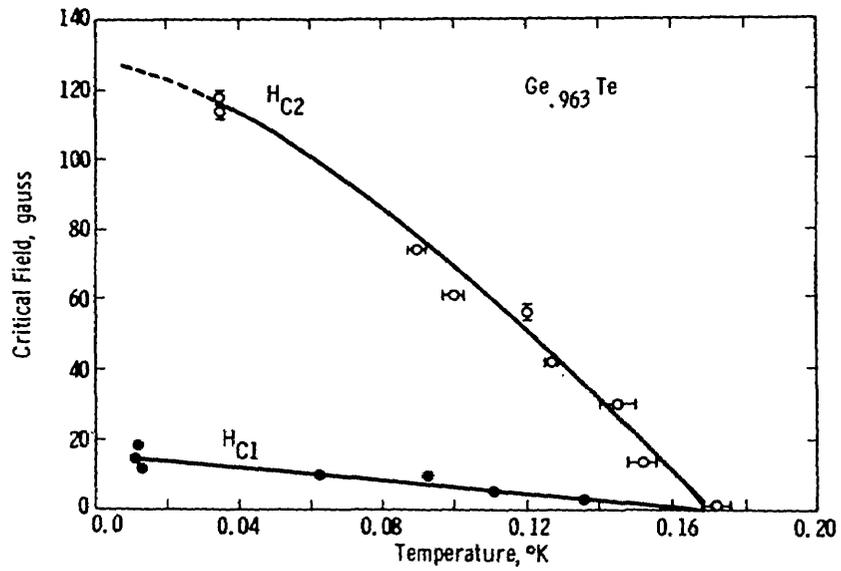


Figure 9

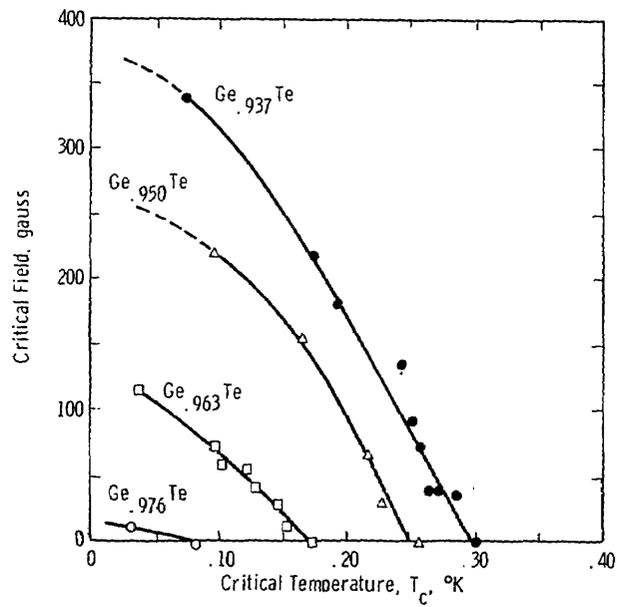


Figure 10

	$n$ ( $\times 10^{-20}$ )	$T_c$ °K	$H_{c2}(0)$ calc Gauss	$H_{c2}(0)$ meas Gauss	$l$ Å	$\epsilon_0$ Microns	$\lambda_p$ Microns
Ge <sub>.976</sub> Te	8.6	.080	43.4	16.2	296	3.86	0.85
Ge <sub>.963</sub> Te	9.3	.172	103	125	262	1.84	0.88
Ge <sub>.950</sub> Te	11.8	.250	180	304	201	1.37	0.92
Ge <sub>.937</sub> Te	15.2	.310	266	379	156	1.20	0.96
SnTe(xtal)	10.5	.065	19.9	5.4	394	6.20	0.69
"	12.5	.100	39.1	13.1	296	4.27	0.75
"	16.5	.174	84.5	69.6	219	2.69	0.79
"	20	.210	125	85.0	168	2.38	0.85

Figure 11

Using the mean free path and the density of states, which you measure from heat capacity and  $T_c$ , one can calculate the  $H_{c2}(0)$  — the extrapolated value of  $H_{c2}$  to absolute zero — as a function of carrier density. In comparison to the measured values you see that the agreement isn't really very good, although the higher field values are not too bad. The highest fields both for tin telluride and for germanium telluride are in the right ball park, but as you go to lower fields in tin telluride a big discrepancy occurs — a factor of 4, and about a factor of 3 in germanium telluride. I don't have any explanation for this at the present time; however we are talking about the low  $n$  part of the data and this discrepancy may be connected with a some kind of kink in the density of states in this region.

Quite a lot of work on the electronic properties has been done, particularly by Esaki and Stiles at IBM, and Allgaier, Burke, Houston, and Savage of the Naval Ordnance Lab, and also Babiskin and Seibenman at NRL — so I guess to talk about the subject at all in Washington is like bringing coals to Newcastle. However, I have to make some comment on the electronic structure. In tin telluride, the Fermi surface is thought to consist of four dumbbell-shaped surfaces along the (111) directions. There is a possibility there are two valence bands, the second one being occupied above about  $2 \times 10^{20}$  carriers per cc. In that case, if that is true, then we are always operating in the two-band region for the superconducting studies that I have reported here. Esaki and Stiles' tunneling measurements indicate that tin telluride has a semiconductor energy gap of about 0.3 eV. We've done quite extensive heat capacity measurements on the material in the two-band region, and we find that the density of states on the basis of about four points looks as though it's proportional to  $n^{1/3}$ , which is what you would expect on a quasi-free-electron picture. However, I should hasten to add that on the basis of four points — which cover the range — we can't say there isn't some kink in the density of states somewhere along the line. From the slope of the density of states vs carrier density curve, we can estimate the effective mass, and it comes out about 2.

The properties of germanium telluride are rather similar, except that the filling of the second valence band seems to occur. It is thought to occur somewhat higher at about  $4 \times 10^{20}$  carriers, but again it is below the range of the superconducting measurements. Since we have a pretty well defined  $T_c$  vs  $n$  curve, extending over two orders of magnitude of  $n$  for tin telluride, what can we learn about superconductivity from this curve?

Rather than trying to take into account the obviously complicated electronic structure of the material, we prefer to use a free-electron approach. I think the only justification for this is that it seems to work moderately well. The departure point for this

$$\begin{array}{ll}
 \text{B. C. S.} & k_B T_c = 1.14 \hbar \omega_c \exp \left[ -\frac{1}{N(0) V} \right] \\
 \\
 \text{Morel \& Anderson} & N(0) V = \lambda - \mu^* = \lambda - \frac{\mu}{1 + \mu \ln (\epsilon_F / k_B \theta_D)} \\
 \\
 \text{McMillan} & T_c = \frac{\theta_D}{1.45} \exp \left[ -\frac{1.04 (1 + \lambda)}{\lambda - \mu^* (1 + 0.62 \lambda)} \right]
 \end{array}$$

Figure 12

analysis is shown in Fig. 12, and I'll try to limit the number of equations I throw at you. The first one I am sure is well known to all of you — the good old primitive BCS expression of 1957 for the critical temperature. In this expression  $\omega_c$  is some kind of critical phonon frequency,  $N(0)$  is the density of states of the Fermi surface, and  $V$  is the pairing potential which was not calculated in the BCS theory but was simply introduced as an arbitrary parameter. We know physically that  $N(0)V$  must consist of two parts. Using the notation used by Morrel and Anderson in 1961 there is a component  $\lambda$  which is a positive part of the interaction representing the phonon-induced electron attraction, and a term  $\mu^*$  which represents the Coulomb repulsion — the normal Coulomb repulsion between electrons. Actually, this starts out as  $\mu$  but is modified by the expression in the denominator due to the fact that the attractive term is derived from electron energies within a thin shell of thickness  $k_B \theta_D$  in the vicinity of the Fermi surface, whereas the repulsive term is calculated for all electron energies. This introduces both the Fermi energy and the Debye temperature in the denominator. The chief knowledge of this  $\mu^*$  comes about from isotope experiments. In the primitive BCS theory, this term was ignored. Thus  $N(0)V$  was essentially independent of mass, and on this basis you get an isotope effect of  $T_c$  proportional to  $M^{-1/2}$ . Later on, it was discovered that lots of materials have different isotope effects — for example, some elements such as Ru and Zr have no isotope effect while other transition metals have a mass dependence for  $T_c$  quite different than the BCS prediction. Consequently, a correction had to be put in, and this of course also contains the mass (see Morrel and Anderson expression in Fig. 12). From isotope experiments on different metals, values of  $\mu^*$  have been derived. Morrel and Anderson calculated  $\lambda$  and  $\mu$  from a quasi-free-electron picture using a jellium model of a solid, which is one in which you ignore the periodicity of the ionic lattice and derive the lattice modes on the basis of positive ion plasma. I think Phil Seiden is going to discuss this theory in more detail so I won't go into it, but I have to use the results. It is sufficient to say that on this model  $\lambda$  and  $\mu$  come out to be essentially functions of only electronic parameters, that is to say, the carrier density and the effective mass. Actually, for the computation we used a slightly modified BCS expression recently introduced by McMillan for strong coupling, see Fig. 12. McMillan's expression is only slightly different numerically from the BCS expression if  $\lambda - \mu^*$ , in the form given in Fig. 12, is substituted for  $N(0)V$ . An important point in my considerations is that the  $\lambda$  has two contributions within it which arise from the different scattering processes for the electrons.

Figure 13 illustrates this kind of an elementary experimentalist view of what goes on. With a simple Fermi surface and a simple Brillouin zone, you have scattering electrons involved in the phonon-induced attraction and repulsion,  $k$  to  $k'$  scattering. When you have a normal phonon exchange involving  $q_N$ , this gives rise to the term  $\lambda_N$ . When you can have an umklapp exchange involving  $q_U$ , which introduces a reciprocal lattice vector  $\vec{g}$ , this gives rise to the term  $\lambda_U$ . The crucial point is all I want to point out, and though it is very obvious I think it needs saying anyway. If the Fermi sphere is very

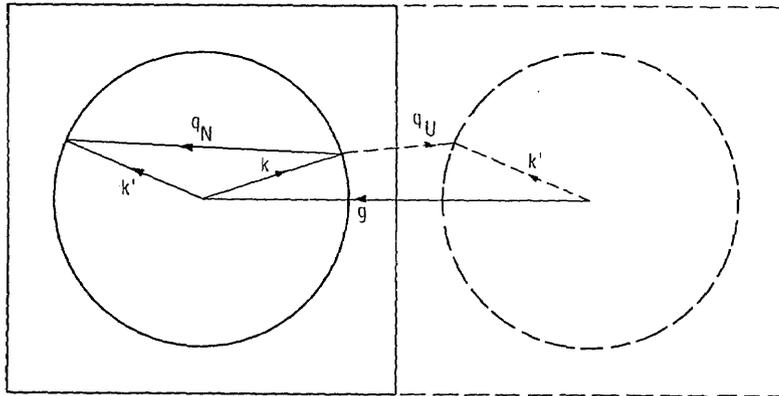


Figure 13

small compared with a Brillouin zone — in other words if it were a very tiny sphere in the center — the normal processes are the ones that dominate the situation. The  $q_N$  is small in that case and  $q_U$  is very large. As the Fermi sphere grows in size and becomes very large, then  $q_U$  can actually be smaller than  $q_N$ , and the umklapp processes begin to be quite probable.

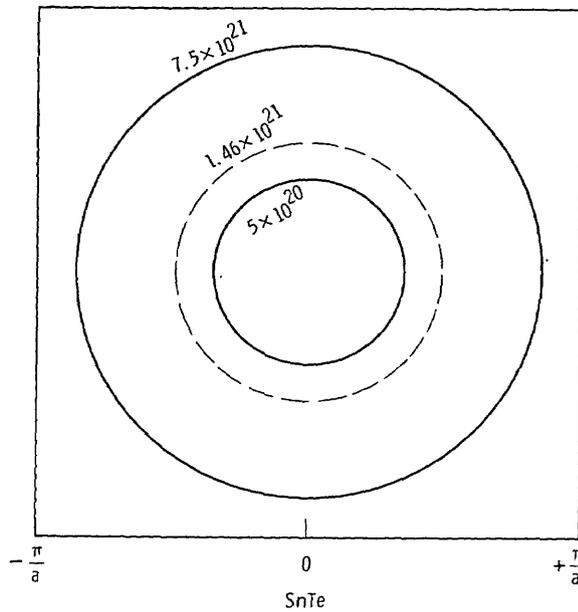


Figure 14

Just to illustrate this for tin telluride I have drawn a couple of Fermi spheres for the free-electron picture corresponding to different carrier densities. This is shown in Fig. 14 relative to the reciprocal lattice. The reciprocal lattice isn't square — its cross section would be a polyhedron, but this is all qualitative anyway. The onset of umklapp processes occurs roughly when the Fermi sphere diameter equals half the zone edge. For SnTe this occurs at a carrier density corresponding to the dotted circle in Fig. 14.

Thus the experimental data involve carrier densities which cover the range from that where normal processes should dominate to that where umklapp processes should dominate. Qualitative considerations of this kind seem to be borne out by our results.

Figure 15 shows the theoretical value of  $\lambda_N$  and the  $\mu^*$  repulsive term as a function of carrier density calculated strictly on the Morrel and Anderson picture. I'll say more about  $\lambda_U$  in a moment. What we have simply done is this. We have taken the calculated  $\mu^*$  on this model, and the experimental  $T_c$ 's, plugged them into McMillan's expression for  $T_c$ , Fig. 12, and derived the attractive component  $\lambda$ . In other words,  $\lambda$  is derived here, but it is sort of a quasi-experiment thing. It requires an assumption on  $\mu^*$  but it is essentially an experimental  $\lambda$  and this is plotted as  $\lambda(\text{exp})$  over the range that we are dealing with in tin telluride. Note that  $\lambda(\text{exp})$  lies remarkably close to the theoretical  $\lambda_N$  of the low carrier densities.

Let me say just physically what these two terms  $\lambda_N$  and  $\mu^*$  do as a function of carrier density. As you go down to a dilute electron gas — as you approach very low carrier densities — both of these functions approach 1/2, and the difference  $\lambda - \mu^*$  is what determines the critical temperature. As you would expect, when you go to zero density,  $T_c$  goes to zero. Now as  $n$  increases, this difference also increases, but eventually it will pass to a gradual maximum for only normal scattering. That is somewhere around  $10^{22}$  electrons per cc, corresponding to a critical temperature of just a few degrees. If you have only normal scattering you have quite a low transition temperature superconductor. What we find experimentally is that  $\lambda(\text{exp})$  is tending towards  $\lambda_N$  at low carrier densities and deviates from it as the carrier density increases.

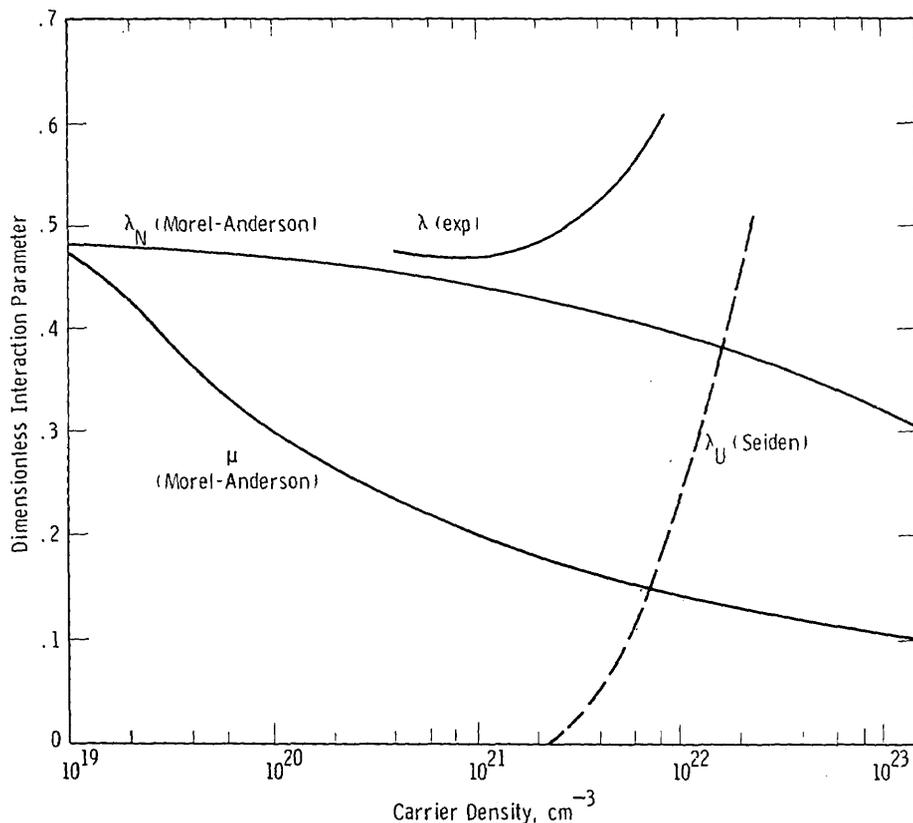


Figure 15

Morrel and Anderson also calculated  $\lambda_U$ , but they did a very crude averaging sort of thing which isn't very useful. Dr. Seiden computed the  $\lambda_U$  more accurately for the case of lanthanum selenide, and we have adapted his values to tin telluride but shifted the curve slightly to correspond to where we think the umklapp processes should start. We expected  $\lambda_U$  — and this is fairly qualitative — to rise in some fashion like this, and it would explain why we see an experimental rise of the total attractive component of the interaction. I think this physically makes some sense if you ignore all the other approximations that we've made in talking about spherical Fermi surfaces — and clearly, we know the Fermi surfaces aren't that type in this material.

One other thing we can do is to compare the results on tin telluride with some results on some other rock-salt-structure materials in which we have made heat capacity measurements, giving us a density of states. These are materials like niobium nitride, niobium carbide, etc. Although these are transition-element-containing materials — the materials in which the Fermi surface is away from the d-band — and the density of states is low, essentially derived from s and p electrons, I think they are roughly comparable to tin telluride in the free-electron sense that we are talking here. We don't know the effective mass so we can't make a comparison on the carrier density curve, but we can convert the tin telluride data into density-of-states data because we do know the effective mass here — so I have done that in Fig. 16. The tin telluride curve is replotted against the band-density-of-states cubed, which is essentially proportional to  $n$ , and then I have put onto this plot the  $\lambda$  values derived for hafnium nitride, niobium carbide, zirconium nitride, and niobium nitride. You see that they fall roughly in line with the tin telluride data as if  $\lambda$  is simply going on increasing by the umklapp scattering. In fact, in the case of niobium nitride it would be a major contribution to the total superconducting interaction. If any of this makes sense, I think what we have learned is that we have in tin

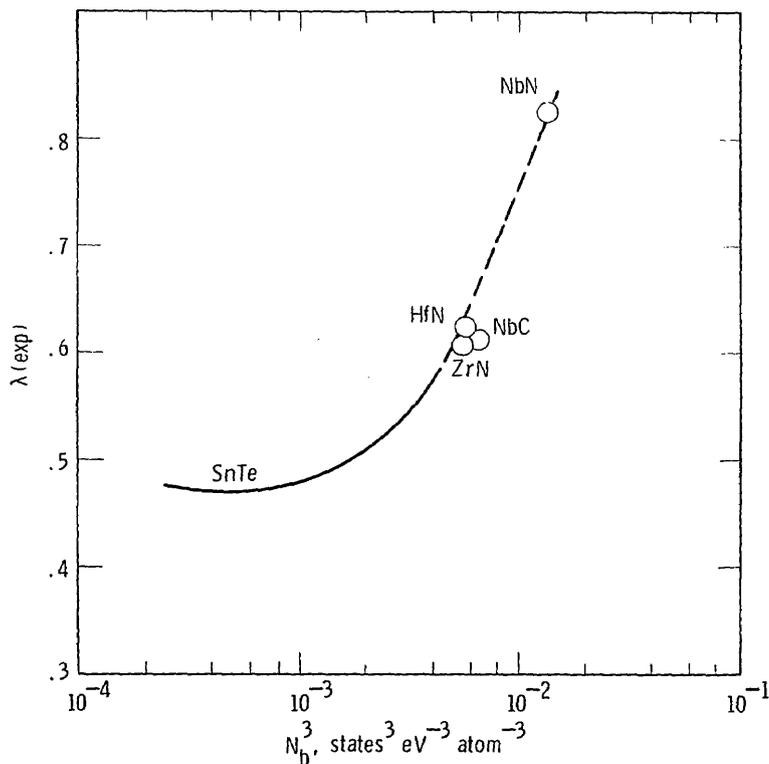


Figure 16

telluride a material in which, on one extreme, we have normal scattering dominating, and on the other extreme, umklapp scattering is dominant.

I would like to say just a few words about other possible materials. We have tested a lot of the materials of this class for superconductivity and some of them shown in Fig. 17. Some of these points are data from other people. I won't pick out all of them but you see lead telluride as previously mentioned, bismuth telluride — these other tellurides — many of which are thought to be semiconducting. Some of them have pretty high carrier densities. In fact, this is sort of a selected list of materials that have carrier densities exceeding  $10^{20}$  in most cases. Gallium nitride was reported superconducting by the Russians, but nobody believes that — its probably free gallium. None of these are superconductors.

NON-SUPERCONDUCTING COMPOUNDS

Compound	Doping Method	Carrier Density $\text{cm}^{-3}$	Lowest $T_n$ °K
PbTe	Li, Na	$5 \times 10^{20}$	0.009
$\text{Bi}_2\text{Te}_3$	Iodine	$1 \times 10^{21}$	0.019
$\text{AuTe}_2$	As Made	$2.5 \times 10^{21}$	0.051
SbTe	As Made	$5 \times 10^{20}$	0.051
$\text{CoGe}_2$	As Made		0.051
$\text{PtSb}_2$	Tin	$3.7 \times 10^{20}$	0.037
GaP	Silicon	$1 \times 10^{19}$	0.051
GaN	As Made		2.00
$\text{SrNbO}_3$	Sr vacancies	$2.7 \times 10^{21}$	0.044
$\text{CaTiO}_3$	0 vacancies	$3.7 \times 10^{19}$	0.10
$\text{BaTiO}_3$	0 vacancies	$1.3 \times 10^{20}$	0.059
$\text{Sr}_{.99}\text{La}_{.01}\text{TiO}_3$	0 vacancies	$3.1 \times 10^{20}$	0.078
$\text{SrTiO}_3 + 10\% \text{KTaO}_3$	0 vacancies	$4.8 \times 10^{19}$	0.051

Figure 17

Quite a few materials are being tested but of course there are an awful lot that haven't been tested down below  $1^\circ\text{K}$ , and this may explain why we only really have five materials to talk about in any detail here. There are some other candidates that I might mention. One which the Bell people worked on a little bit, but on which I think more extensive work could be done is silver fluoride, which is a dilute metal, and another one is their silver clathrate compounds, which are also dilute metals. In these compounds,  $n$  can be varied over quite a wide range. There are some substituted metal bronzes which probably fall in the same category. I think these are interesting things that should be investigated in the future.

# SUPERCONDUCTIVITY IN "FREE-ELECTRON-LIKE" SUPERCONDUCTORS

P. E. Seiden  
*IBM Watson Research Center  
Yorktown Heights, New York*

I would like to discuss a theory of superconductivity which is useful from an experimentalist point of view. That is, I want an experimental theory in the sense that you can use it as a model. You can say "Well, if it works for one material and then I change the material, the theory can make some predictions of what is going to happen." That is basically what Morel and Anderson tried to do, and as we just saw from a slide that John Hulm had, it is quite a simple theory. It has few parameters so that you can actually take a desk calculator and calculate values for  $T_c$  in a short period of time, say 1/2 hour. That is the kind of theory I would like to have. Unfortunately, I have not quite been able to find it.

The right way to do things has recently been done by Carbotte and Dynes. They have done a really complete calculation, complete in the sense that it is up to date in modern many-body theory. The approximations they make are ones they are forced into because we just don't know how to do any better. However, their calculations are very complicated, which means long programs and running times and, what is even more serious, extensive experimental information — for example, complete neutron diffraction data on the phonon spectra. These data are not generally available for many materials. Even if I can't do calculations on a desk calculator and have to go to a computer it would be nice to have something which is short and takes a minimum of experimental data. Well, that is the kind of calculation I have been able to do in certain cases.

I now want to state the necessary approximations. First, it is a free-electron-like theory. Let's pursue exactly what "free-electron-like" means and how far we can stretch the idea. Well, the first approximation was discussed in detail by Cal Koonce, and let's write it down. The phonon frequency  $\omega_p$  must be small compared to everything else. That was essentially what Koonce called the renormalized Eliashberg region. I will stick to that region, and as you will remember from Koonce's talk, that means the only thing I can't talk about is strontium titanate, and I won't.

Now, what is the problem. We know that BCS gave their result for the transition temperature as

$$T_c = 1.14\theta_D e^{-1/N(0)V} ,$$

where  $N(0)V$  is the ad hoc parameter which gives the coupling. Well, McMillan has extended the renormalized Eliashberg theory and obtained the following more complete analytic result

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

The parameters  $\lambda$  and  $\mu^*$  have the same meaning as they had on Dr. Hulm's figures. Now, what is the problem? The problem is not really to calculate  $\mu^*$ . This is fairly easy, and furthermore  $\mu^*$  doesn't vary very much. In fact, it has been suggested that if you are in doubt about  $\mu^*$ , for transition metals take a value 0.13, and for nontransition metals take a value of 0.1, and you will be doing all right. The  $\mu^*$ 's do turn out to be pretty much these values, and the reason for the lack of sensitivity is that the relationship for  $\mu^*$  has a logarithmic dependence on practically every parameter in sight. Unless you really get drastic, things just don't change very much.

The problem comes down to calculating the electron-phonon interaction  $\lambda$ , and that is indeed really a problem if you are going to do it properly. Now the question is just what materials are you going to test against if you carry out the calculation. The original Morel and Anderson calculation, which has an explicit expression for  $\lambda$ , tested against the elements. This test really doesn't tell you much. After all you are doing a many-body calculation. You can have, depending on the generality you use, one or more adjustable parameters and you are trying to calculate a single number — so you don't have to have too good a theory to come out with the right number. Whether you can justify it or not is another question. Even for metals like aluminum or sodium and potassium it is still, in general, a very complicated problem.

What you would much rather do and what has been the brunt of discussion today is to look at the functional dependence, and experimentally the functional dependence that has been looked at mostly has been that of electron concentration. I'll have one other example which I have looked at and which I will discuss today, but the electron concentration dependence provides the best results. If you can do this sort of calculation you are still well off even if you are left with an adjustable parameter. You just normalize the curve some place, and although you can't predict the transition temperature per se you can at least examine the functional dependence. From the experimental point of view, this is what you really want to do. You start off from some base. You have tested one group of materials and you want to know what is going to happen if you make a certain change. Well, you have already got some of the answer, so you are interested in extrapolating this from what you already know. Therefore, what you are interested in, of course, is just the functional dependence. The goal, then, is to determine this functional dependence, a problem that is much, much easier than actually calculating a transition temperature. As a matter of fact, as you'll see when I show you a slide [see Fig. 11] of the absolute transition temperatures I calculate from the simplest model with no adjustable parameters, these results look pretty ludicrous, although they do tell you something. I'll get to that later.

Now what's wrong with Morel and Anderson? Well, there are two basic things that are wrong. One, they use the Coulomb potential for the interaction. It is well known from the theory of metals that this potential is too strong and that a pseudopotential is much better. I have used the first approximation to this pseudopotential, just taking the core repulsion into account. You know that an electron can't get into an ion because of a strong repulsion there. The electron is not really free to move throughout the lattice. The equation  $V = -ze^2/r$  applies everywhere except inside the ion. You can take care of the problem very easily by putting on a delta function potential as

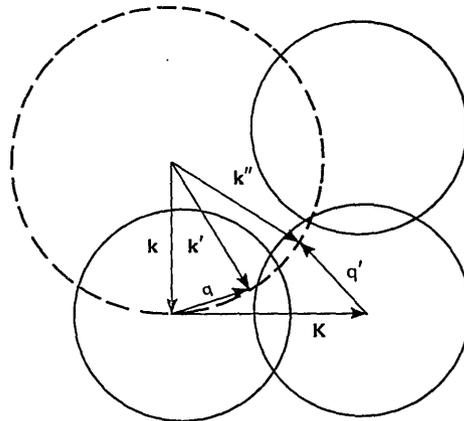
$$V = -\frac{ze}{r} + \beta\delta(0) .$$

This actually reproduces practically all of the aspects of the more accurately calculated pseudopotential that you need for superconductivity. The reason is that the effects of a better pseudopotential theory are felt at very large momentum transfers which never occur in superconductivity. You don't get momentum transfers greater than  $2k_f$ .

Secondly, Morel and Anderson considered only one Brillouin zone for normal metals and an average over one higher-order zone for polyvalent metals. We have lots of zones contributing, and for most materials this gives you a much larger contribution. Thus, the reason they got answers that look at all reasonable was the fact that they had these two more or less compensating errors. They used an interaction that was too big, but then they didn't take the whole interaction, which reduced the error. I'll show you some of the results later, and you will see what kind of numbers they get.

Well, what goes into the calculation of the transition temperature? I am using the Eliashberg equation. This gap equation is isotropic. Therefore, since the anisotropy has been thrown out of the problem, why put it back now? The next assumption is that we have spherical Fermi surfaces and spherical Brillouin zones, i.e., I will take the spherical approximation for the Brillouin zone.

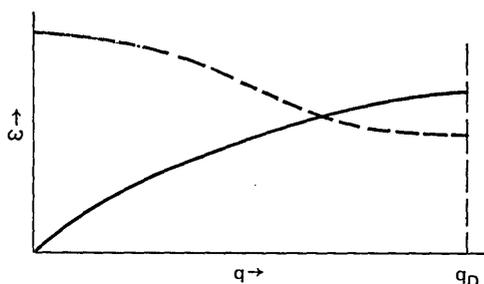
Now, we also have to take into account in some realistic manner the reciprocal lattice and the high-order Brillouin zones. After all, what are we doing when we change electron concentrations, especially if the lattice parameter remains constant as it strictly does with lanthanum selenide and as it more or less does with tin telluride? We are shrinking the Fermi sphere with respect to the Brillouin zones and, therefore, continuously changing the ratio of normal to umklapp processes. You therefore can't expect to get any kind of a realistic answer if you assume just one or the other. Let me draw a picture:



I will represent the Brillouin zone as a solid circle, and one reciprocal lattice vector away I draw another zone. In the spherical approximation these zones overlap. I can draw several other zones as shown here. Now, let us draw in the Fermi surface as a dotted circle. If the electron is in a state represented by the wave vector  $k$  it can then be scattered to a new state  $k'$ . If  $k'$  lies in the normal zone, there exists a phonon of wave vector  $q$  of the required size to have  $k = k' + q$ . But if the scattered state  $k'$  lies outside the normal zone as shown for  $k''$ , I must make use of a reciprocal lattice vector and hence  $k = k'' + q' + K$ . Now it is just a geometry problem to figure out the various phonon processes. You know how far you can vary the angle between  $k$  and  $k'$  and still stay in a certain zone — it's just determined by the reciprocal lattice geometry. That's no big deal to solve. It amounts to knowing the size of the Fermi wave vector, the Debye wave vector, and the reciprocal lattice structure. So, this is done and is the second thing I have included in the calculation. Although it is a jellium model, I have put the reciprocal lattice back in. That is, the matrix elements for the transitions are jellium matrix elements. They depend just on the magnitude of the momentum transfer  $|k - k'|$ . This is in accord with deformation potential theories and is not really a very serious approximation. Now when you do this calculation, things are very simple. You have only

one integral over angle involving the phonon transfer. As a matter of fact, if you want, you can do this integral analytically although the result comes out to be terribly large and not very informative, so it is just as easy to do it by numerical integration.

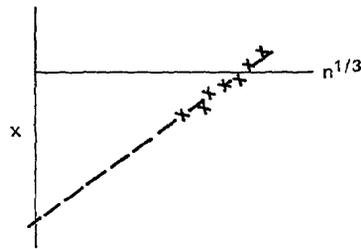
The one other basic assumption I have used is that of a jellium phonon spectrum. This is the weakest part of the theory and we'll talk about the problem a little bit more later. However, the jellium phonon spectrum is renormalized by the Coulomb pseudo-potential. It is not then strictly jellium. The point is that the spectrum looks something like this (solid line):



We can normalize this spectrum so that either the slope at  $q = 0$  or the point  $q = q_D$ , that is, the velocity of sound or the Debye frequency, comes out to be right. We are, however, still using a spectrum of the jellium type, which is certainly not valid for all materials, and you will see some of the consequences later. Just a hint, I predict that the transition temperature for lead is  $10^{-34}$ , but the jellium spectrum is clearly not good for lead. By the way, that's with no corrections and no adjustable parameter — listen, anybody will believe that lead has *at least* a transition temperature of  $10^{-34}$ .

Now, we want to test the theory, so what kind of tests do we have? The first one I used was lanthanum selenide which was actually the impetus for my calculations to begin with. From all the measurements we have so far this material appears to have electronic properties that are really understood. Lanthanum selenide exists all the way from  $\text{La}_3\text{Se}_4$  to  $\text{La}_2\text{Se}_3$ . Now if you take the normal valences of these materials, triple plus for lanthanum and double minus for selenium, you find for  $\text{La}_3\text{Se}_4$  that you have nine electrons for La, minus 8 for Se, or one electron/formula unit left over to go into a conduction band — a very simple-minded model — while for  $\text{La}_2\text{Se}_3$  you have 6 minus 6 or 0, and it is an insulator. In fact, you can write this material  $\text{La}_{3-x}[\ ]_x\text{Se}_4$  where [ ] are vacancies in the lattice and  $0 \leq x \leq 1/3$ . On this simple model, then, you'd say that the carrier concentration varies as  $n = n_0(1 - 3x)$ , where all you need to calculate now is  $n_0$ , which from the lattice parameter is found to be  $n_0 = 5.4 \times 10^{21}$ . Now the reason you only need the lattice parameter is that it is constant for the whole range of  $x$ . As accurately as we have measured x-ray diffraction, the lattice parameter is constant. This is very nice because starting out with the electron concentration which, although not large compared to metals, is still reasonably significant, you can go all the way down to zero, and without a lattice parameter change. This indicates that metallic binding must be negligible in this material since the structure and lattice parameter don't change. These electrons are probably really free because there is no great interaction with the lattice. Well, we have done Hall effect measurements in these materials and find exactly this  $n_0$  for  $\text{La}_3\text{Se}_4$  and just the  $(1 - 3x)$  behavior of  $n$ .

That's nice. Now, the next thing we looked at was the temperature independent susceptibility  $\chi$  as a function of measured carrier concentration, and there you get something that looks like this:



We haven't gone all the way, but it is a fairly nice straight line. If you fit a straight line to this data, and extrapolate back toward  $n = 0$ , you find that this diamagnetic susceptibility is within 4% of the diamagnetic susceptibility calculated for the insulating lattice just using the Landolt-Bornstein values for  $\text{La}^{+++}$  and  $\text{Se}^{--}$ . From the slope of this curve you get an effective band mass equal to 1.3, a very nice value for something you would call free electrons.

Then you can measure the specific heat and get  $m^*$ , the specific heat effective mass which is equal to the band mass  $m_B$ , times  $1 + \lambda$ . So you measure  $\chi$  to get  $m_B$  and measure specific heat to get  $m^*$  and  $\theta_D$ . Then you plug that in McMillan's formula with a calculated  $\mu^*$ , and get just the  $T_c$  observed for this material. So the whole thing hangs together very nicely. This is really a free-electron-like material.

One problem in this thing is that lanthanum selenide is crystallographically very complicated. It is a thorium phosphide structure, which is basically body-centered cubic but contains, unfortunately, 28 atoms per unit cell. The assumption there is that we take one phonon band. There are three times 28 bands around, but if you assume all the rest to be way above the lowest band then, since the interaction  $\lambda$  is proportional to  $q^2/\omega_q^2$ , the correction of all these higher bands is on the order of 10 to 15% provided one of the higher bands doesn't come way down (dotted curve on dispersion curve figure). If this were to happen, I'm in trouble, so I make a very nice assumption — it doesn't happen!

The parameters involved are the following:

$$Z, a_0, m_B, \theta_D, \beta, \text{ and } \sigma.$$

The valence  $Z$  is defined essentially as the number of electrons per primitive unit cell. This is consistent with how you usually define valences for elements.  $a_0, m_B, \theta_D, \beta,$  and  $\sigma$  are the lattice parameter, the band mass, Debye temperature, the pseudopotential core repulsion parameter, and a correction to the phonon frequencies. I mentioned that we can correct the phonon frequencies to give the right slope at  $q = 0$  or the right intercept at the band edge. We do this by multiplying the integral by the square of  $\sigma$ , which is equal to the jellium sound velocity over the measured sound velocity or the maximum jellium frequency over the Debye frequency. Now, do we know these parameters. Well, we know  $Z$  because we know the carrier concentration and  $a_0$ , which gives us  $Z$ . We know the band mass, we have measured that. We measured the Debye temperature. We calculate  $\sigma$  by correcting by the Debye temperature, so the only thing that is unknown is  $\beta$ . Well, as I mentioned before, we'll fit  $\beta$ . That is, I am going to determine  $\beta$  by fitting the theory to the  $T_c$  curve at  $\text{La}_3\text{Se}_4$ .

Now, we can see that this is on Fig. 1. Here are the experimental points. The point that I fitted is not on the curve for some anomalous reason, but here are the rest of the experimental points and the theoretical curve for  $T_c$  vs  $n$ . It is really quite a good fit for something this complicated. There are some very interesting things. Unfortunately, we have an experimental sad story. We haven't gotten our dilution refrigerator working, but there are some interesting things that might happen out at the low  $T_c$  end. It turns

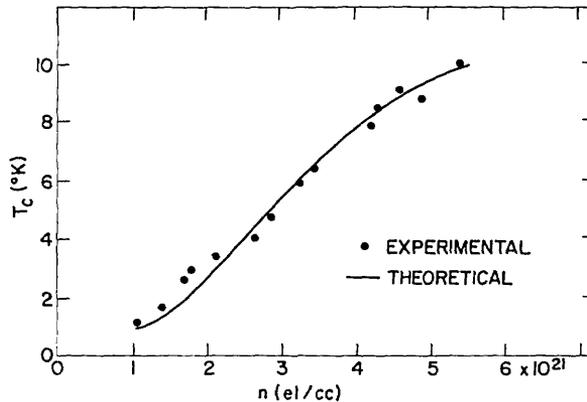


Figure 1

out the theory predicts a little bump. This may be an artifact of the calculation, due to the fact that I am assuming spherical Fermi surfaces and spherical Brillouin zones, or it may be real. In any event, one would like to look for it, and although I was hoping to look for it sometime in the last three years we haven't been able to do it because of technical difficulties.

Now let's look at what the theory predicts for the behavior of  $T_c$  as a function of the other various parameters. Figure 2 shows the behavior as a function of the valence. You can expect this variation to happen because the valence essentially determines the ratio of the Fermi wave vector to the Brillouin zone vectors. In fact, that is exactly what it is,  $2k_f/q_D = (4Z)^{1/3}$ , so  $Z$  determines the overlap with the high-order Brillouin zones, and therefore determines how much umklapp contribution you get. But you notice it is flattening out. It is not increasing continuously. That's because as you start to overlap higher-order Brillouin zones you do get an increased contribution. As you keep going, however, you do keep picking up higher zones, but some of the zones in the middle start dropping out because the Fermi surface completely encloses them and you don't get any contribution from them. So eventually it is going to tail off, as the figure shows.

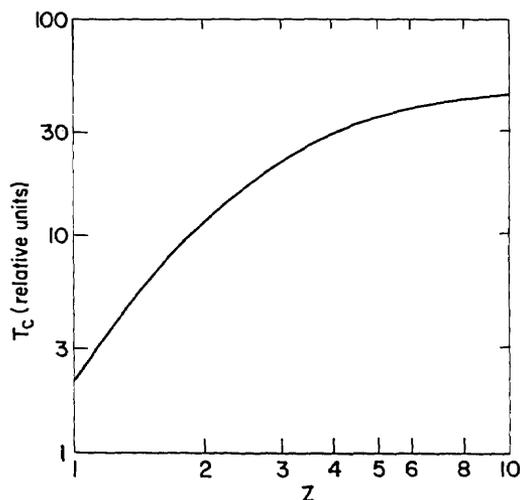


Figure 2

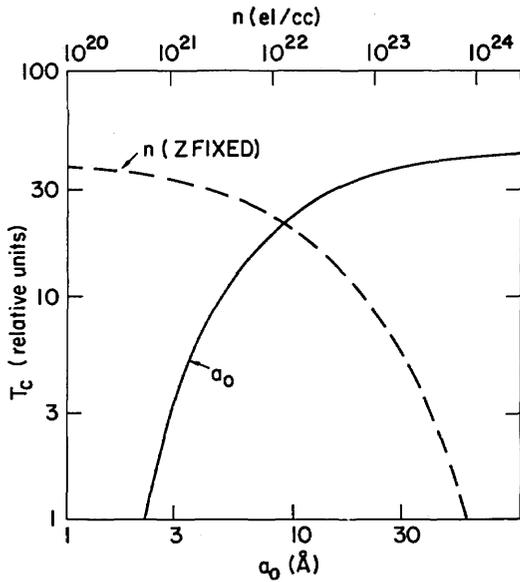


Figure 3

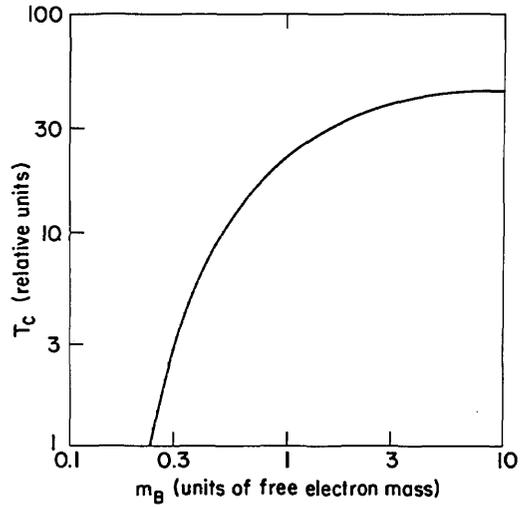


Figure 4

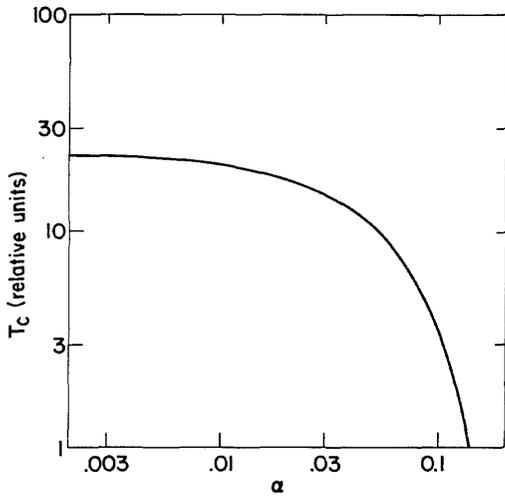


Figure 5

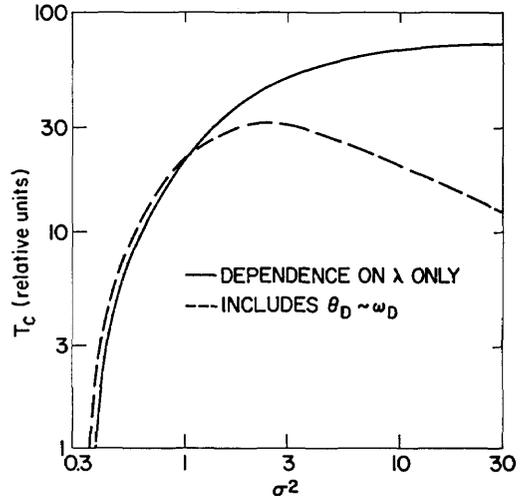


Figure 6

Figure 3 is a plot of what happens when the lattice parameter varies, with the valence being fixed. Again, you see a behavior that is tending toward a maximum. Figures 4 and 5 show  $T_c$  as a function of band mass and as a function of the pseudopotential parameter  $\alpha$ , and again the same thing is happening. You see, by the way, in Fig. 5, the error that Morel and Anderson make for lanthanum selenide. This  $\alpha$  is a dimensionless parameter proportional to  $\beta$ . The  $\alpha$  for lanthanum selenide is 0.08, and they, of course, used an  $\alpha$  of zero, so you can get an idea of the error.

Figure 6 is essentially the dependence of  $T_c$  on phonon frequency. I put it as a function of  $\sigma$ , which basically is the phonon frequency. The solid curve includes just the

dependence on  $\lambda$ , while the dotted curve includes the fact that the Debye temperature, of course, depends on the phonon frequency. The dotted curve shows a maximum, which is exactly what McMillan has talked about. He has shown that there should be a maximum  $T_c$  as a function of phonon frequencies. This is because you'd like a very soft lattice for the electron-phonon coupling so that when an electron comes along it can really move the ions — then they can transmit this to another electron. However, if you do this the Debye energy is very small so that the number of states available, since you can only scatter to states at the Fermi surface  $\pm$  the Debye energy, starts getting very small. Then although each interaction is very, very large, there are too few of them.

Now, in addition to this maximum, you notice that there was an asymptotic tendency to a maximum for all the other parameters. You can understand this tendency for a maximum in two ways. One, if you examine the kernel of the integral it is always of the form  $a/(a+1)$ ; so you tend to a maximum by just letting  $a$  get very large. So, in addition to the fact that McMillan has shown that making  $\lambda$  very large due to the phonon properties doesn't get you very much, making it very large period doesn't get you very much, simply because of the fact that it seems you can't do it.

There is another argument for that. If you make the electron-phonon-electron interaction very large, then you are also making the phonon-electron-phonon interaction very large. Eventually it is going to get so large that it is going to distort the lattice, and you are going to have some other lattice structure with a smaller electron-phonon interaction. In fact, this has been noticed in the  $\beta$ -tungsten structures. People have tried to get high transition temperatures where, by extrapolating, they are indicated at certain compositions. As that composition is approached, all of a sudden a phase transformation appears, a certain concentration will give a high  $T_c$  but you can never get there because of the phase transformation.

Well, formally you can take the theory and do this. Make the approximation imposing the maximum condition on  $\lambda$ , and the remaining problem is just geometry. You have to evaluate an integral of the form  $\int x dx$ , which even an experimentalist like me can do. That is, it turns out to be this integral over limits that you determine by the geometry of the reciprocal lattice. You can see the results of that on Fig. 7 where I do show them as a function of the valence. Now you can see that the valence is the only thing that is important because the valence determines the geometrical factor. It tells how much of the high-order Brillouin zones or how much of any Brillouin zone overlaps the Fermi surface. The figure shows  $\lambda$  going out to some maximum on the order of 1.7. I think this is for an fcc structure. It changes a bit depending on what the structure is, but not really very much.

You can see what this predicts. Let's take the best case. The parameter  $a$  I was telling you about is just the screening constant over the Fermi wave vector  $a = k_s^2/4k_f^2$ .

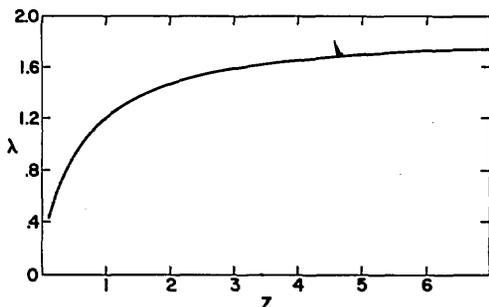


Figure 7

We let that get very much greater than one.

Let's assume that  $\mu^*$  is equal to zero. Then the transition temperatures one gets are on Fig. 8. You see that there is some dependence on crystal structure, although not too much.  $\mu^* = 0$  is an ideal case, which, of course, is not realizable. Let's take cases which are realizable. I mentioned to you that  $\mu^*$  is the order of 0.1. Sometimes you can get a little bit lower. In the best materials, like the high-temperature superconductors,  $k_s^2/4k_f^2$  is of the order of 1 — not very much greater than 1. Figure 8 shows what you get, which is remarkably close to values that are found from

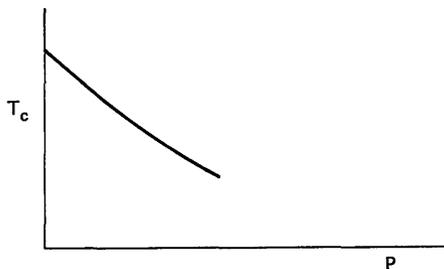
Maximum transition temperature for  
four crystal structures

LATTICE	$T_c^{\max} (^{\circ}K)$	
	$k_S^2/4k_F^2 \gg 1 \quad \mu^* = 0$	$k_S^2/4k_F^2 \sim 1 \quad \mu^* = 0.1$
sc	54	25
bcc	46	18
fcc	53	24
hcp	51	22

Figure 8

maximum  $T_c$ 's. So I don't really think that the metallurgical approach is going to get us very much unless there is a new interaction involved. This is predicated just on the electron-phonon interaction. If you say that you can mediate it with some magnetic interactions or that you have the sort of interaction Bill Little has in mind for organic superconductors, then all bets are off; but, so far, we have no case of superconductivity that can't be explained on the electron-phonon interaction, and we have no indication of any other interaction giving superconductivity. So until this comes along I think this is the best we can do.

Now, what's the next test? I'd like to extend this approach to something else and, in fact, try to go from lanthanum selenide for which the electronic properties look very simple to something a bit more complicated. Well, the natural thing would be to go to the elements. I have mentioned part of the difficulties there. However, again, I will point out that I am looking for functional dependencies. Is there a functional dependency that can be used for the elements? Yes, there is — the pressure dependence. I want to look at the pressure dependence of  $T_c$ . If you look at the pressure dependence in simple metals, not transition metals,  $T_c$  is a function of pressure, something like the figure:



The question is, can you account for that? Well, again, looking at the parameters that enter the theory we have the valence, which is well known, and the lattice parameter, which is directly measurable (with tables given in many books). The band mass is assumed independent of pressure. This is probably not a bad assumption as long as you don't have a Fermi surface near a Brillouin zone boundary. That is, if you find that the

Fermi surface is moving through a zone boundary then  $m_B$  is going to be a strong function of pressure which, in fact, is probably the case in thallium. For most metals that is not a problem. We will assume  $\beta$  to be independent of pressure because, after all,  $\beta$  only tells you how much of an ion core is forbidden. Unless you compress the sample to nuclear densities you don't expect  $\beta$  to really change. And the other two parameters are  $\theta_D$  and  $\sigma$  which, of course, do depend on pressure and, in fact, in similar ways since they are both phonon frequencies. Well, to take care of this pressure dependence we go to the simplest approximation — the Grüneisen approximation where

$$\partial(\ln \omega)/\partial(\ln V) = -\gamma .$$

Essentially what that says is that  $\omega$  varies as  $V^{-\gamma}$ . These parameters have been measured, so the data exist. Unfortunately, the accuracy on these measurements is not very great. There is a reasonable amount of scatter, and it turns out when you apply the superconductivity theory that the error on this measurement of  $\gamma$  is greater than the scatter in the data of the pressure dependence, so we will turn it around and use the theory to fit  $\gamma$  and see if  $\gamma$  is reasonable.

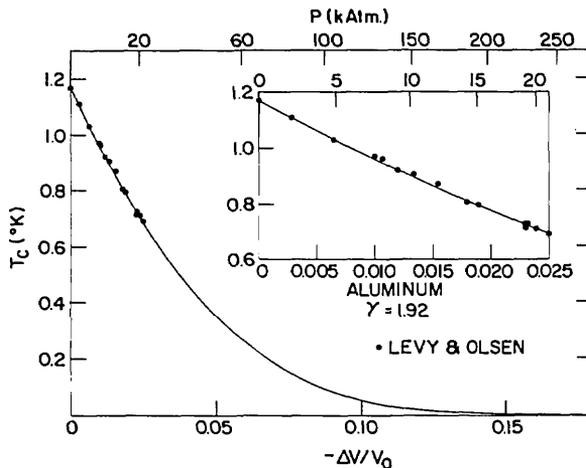


Figure 9

Figure 9 shows the pressure dependence of aluminum.  $\gamma = 1.92$  comes out to be right in the range of the other measured values, which I think for aluminum go between 1.8 and 2.2. So it is a reasonable value. So if you believe in the theory this perhaps is the best measurement of  $\gamma$  available. So, this is a very nice fit and I am reasonably happy with it. I have done it for lead, cadmium, zinc, tin, and indium and the results are all pretty much similar. There are a few little anomalies here and there, but I think I understand them. In general, things work out very well.

You can go further on this, and you can say "When is  $T_c$  going to zero?" We have a theory now which supposedly goes over the whole range of pressure. The only real approximation here is the fact that the Grüneisen constant is assumed to be independent of pressure. That is certainly not true, but it's not bad for many different metals. Figure 10 shows a table of values for the pressure at which the predicted  $T_c$  goes down to 5 millidegrees, which is about zero for experimentalists, and when it really goes to zero you can see that there are two interesting cases here — those of zinc and cadmium. Their pressures are perhaps within the measurable range. I am hoping somebody will

Critical Values and Pressures

	$\gamma$	$T_c = 5 \times 10^{-3} \text{ }^\circ\text{K}$		$T_c = 0 \text{ }^\circ\text{K}$	
		$-\Delta V/V_0$	P(kAtm)	$-\Delta V/V_0$	P(kAtm)
Al	1.92	0.143	200	0.329	860
Pb	2.11	0.425	1200	0.587	5000*
	2.27	0.387	900	0.543	3400
Zn	2.65	0.122	120	0.290	660
Cd	2.35	0.125	92	0.317	700
In	1.92	0.429	1600*	0.758	50,000*
Sn	1.65	0.297	410	0.540	3800
	1.79	0.269	320	0.484	2400

\*Extrapolated values from existing  $v = f(P)$  data at lower pressures.

Figure 10

pick this up and try it. In fact, it may be measurable for aluminum at 200 kilootmospheres.

Now what about the transition temperatures of the elements per se? In the pressure case, I just chose the zero pressure value of  $\sigma$  to be that value which gave me the right temperature. You can actually calculate  $T_c$  here if you assume the jellium spectrum. If I get values like  $10^{-34} \text{ }^\circ\text{K}$  for Pb you might wonder what value this has. It does have one certain value. It predicts a lower limit for  $T_c$ . The jellium spectrum almost always overestimates the phonon frequencies for nontransition metals. As a matter of fact, if you calculate the correction factors using the Debye temperature and the velocities of sound, these  $\sigma$ 's are always greater than one. If you now calculate for a number of elements that are not superconducting you will at least get a lower bound for the possible  $T_c$ . Now, this lower bound is only good if it shows you something. I'll show you it does.

First, I promised to show you what the Morel and Anderson results look like. Figure 11 shows the  $\lambda$  and  $T_c$  from Morel and Anderson, and the significant thing is, I think, that you can see by comparing with the experimental  $T_c$  that their results are sometimes too big and sometimes too small. Here are the  $T_c$  calculated in the present work with no further approximations besides using jellium spectrum (directly — *not* normalized) as I promised you. Oh! excuse me, I lied to you. It's  $10^{-35} \text{ }^\circ\text{K}$  for Pb, but the interesting things are these numbers 0.3 and 0.5 millidegree for Li and Rb. The 60 microdegrees for Cs is a little tougher. (The barium result is not reliable since we do not have a pseudopotential in this case.) So, if these calculated  $T_c$  are really minimum temperatures, those are the materials to look at for superconductivity at very low temperatures.

It is very interesting that Carbotte and Dynes looked at Na and K which, unfortunately, are the bad ones to look at. They have very low transition temperatures, but since Carbotte and Dynes did such a good calculation and needed so much information, they were stuck. They needed details on the phonon spectrum that have not been obtained for these other elements. I'm hoping in the future that one can do somewhat better than the present calculation and bring these numbers up slightly, but for three cases here it gives you some useful information.

Element	M-A		Exp.	Present Work		$\mu^*$
	$\lambda$	$T_c$	$T_c$	$T_c$	$\lambda$	
Li				$0.3 \times 10^{-3}$	.26	.14
Na	.25	.083		$10^{-18}$	.16	.12
K	.25	.052		$10^{-10}$	.18	.12
Rb				$0.5 \times 10^{-3}$	.24	.11
Cs				$60 \times 10^{-6}$	.22	.11
Be				$10^{-26}$	.10	.08
Ma	.32	2.6		$10^{-34}$	.12	.11
Zn	.25	.52	.93	$10^{-34}$	.088	.087
Cd	.23	.15	.54	$10^{-34}$	.091	.085
Ca	.27	.48		$10^{-20}$	.16	.13
Ba				$32 \times 10^{-6}$	.23	.12
Al	.33	5.5	1.17	$10^{-34}$	.115	.102
In	.34	1.9	3.40	$10^{-16}$	.125	.090
Tl	.32	1.5	2.39	$10^{-35}$	.095	.084
Sn	.34	3.4	3.73	$10^{-11}$	.137	.089
Pb	.40	3.9	7.22	$10^{-35}$	.102	.093

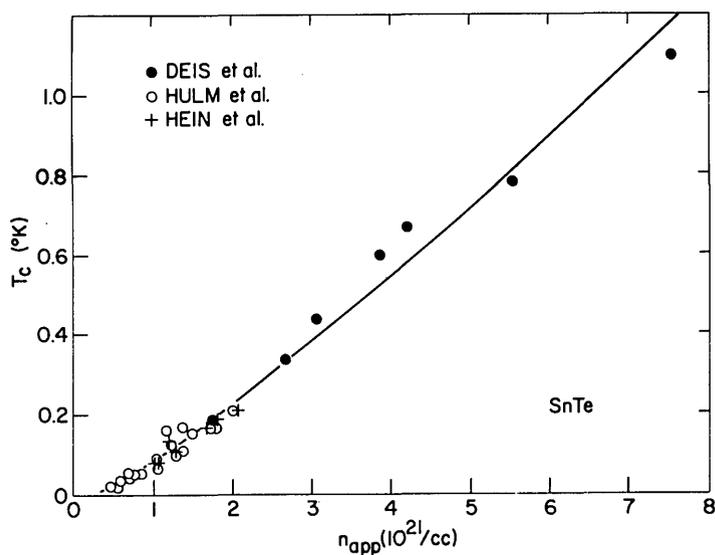
Figure 11

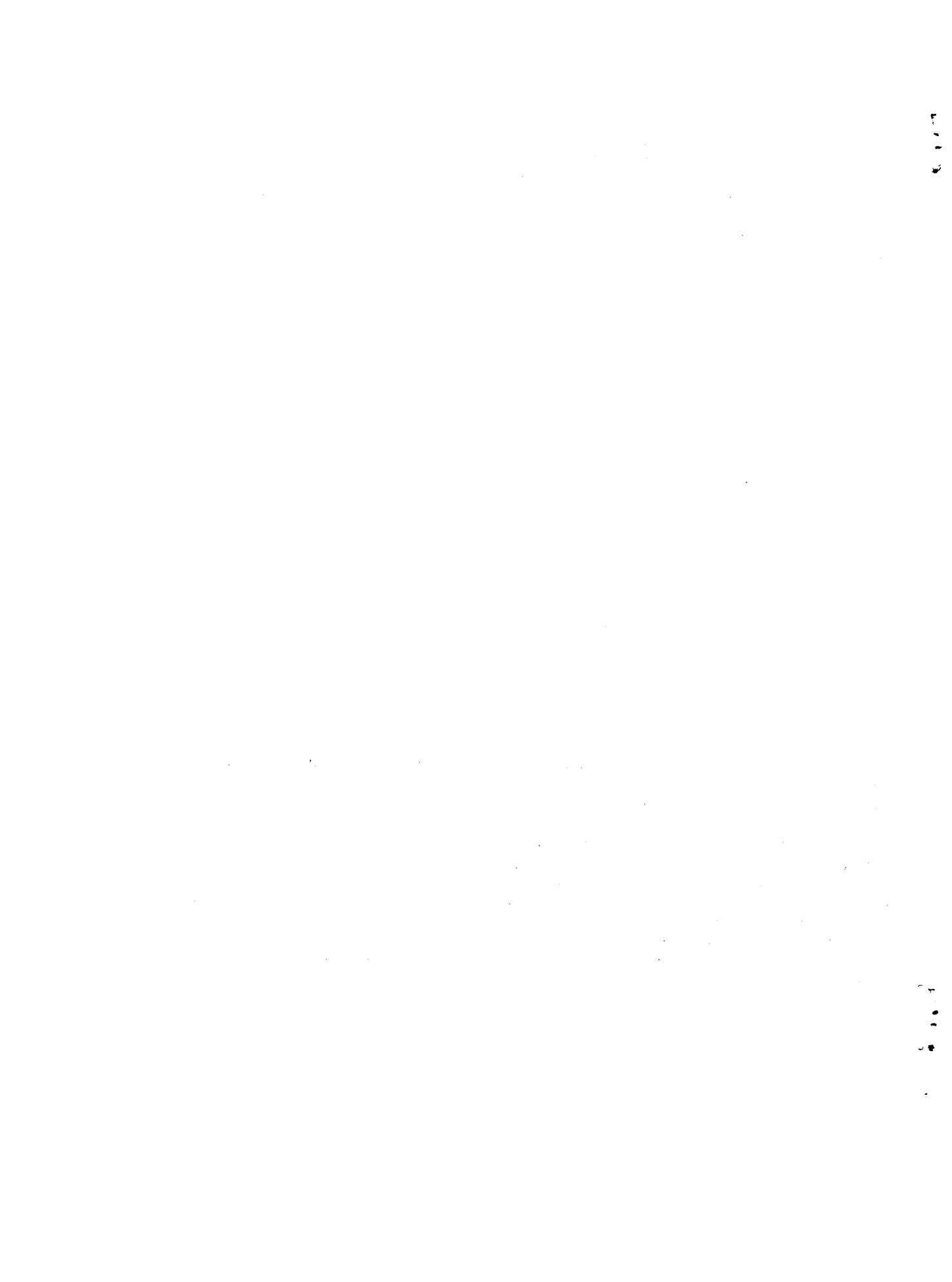
Now, just to keep in the swing of things, how far can we push this, and can we extend it to semiconducting superconductors? I already promised you that I am not going to talk about strontium titanate but I will talk about tin telluride. Now, John Hulm talked to you about what is basically the application of this theory to tin telluride, but I'd like to expand on this a little bit. One, tin telluride is really not a free-electron metal. If you look at the work of people who have measured the band properties (Tsu, Howard, and Esaki, for example), they have curves of the Fermi wave vector and the Fermi energy as a function of apparent electron concentration,  $(1/e)R_{77}$ , where  $R_{77}$  is the Hall coefficient at 77°K. They have results over a reasonably large range of electron concentrations, but not the whole range that has been measured for superconductivity. So I take their curves and perform what you might call a "French curve" analytical continuation. I just continue them out to cover the necessary region to get all the parameters I need. This gives  $k_f$  and  $E_f$ . The density of states is just the slope of the  $E_f$  curve, so you have all the parameters necessary. The theory doesn't need the parameters I listed previously,  $Z$ ,  $a_0$ ,  $m_B$ ,  $\theta_D$ ,  $\beta$ , and  $\sigma$ . Really what enters here is  $k_f$ ,  $E_f$ ,  $N(0)$ ,  $\theta_D$ ,  $\beta$ , and  $\sigma$ . It is only when you take an effective mass approximation that you reduce them to the first set.

In the case of tin telluride you clearly can't do that because one of the bands that John Hulm discussed is linear! You clearly can't use an effective mass approximation in the normal sense for a linear band. But you don't have to. You can use these numbers for  $k_f$ ,  $E_f$ , and  $N(0)$  directly and calculate  $T_c$ . I've done this, and this doesn't give much of a better agreement than the simple theory. What it does, I think, is straighten out the curvature. The simple theory has the curvatures even going in the wrong direction at the lower end — this I think straightens out the curvature a little bit but it still doesn't do much for the  $T_c$ .

Now you look at umklapp processes. Do these really contribute? The answer is no, because the real  $k_f$  is actually smaller than the free-electron  $k_f$  and the Fermi sphere for tin telluride is very small. There is no overlapping with the higher zones so there are no umklapp processes.

Now, what's left? Well, I think we all know what's left. It's the intervalley scattering. I can also take that into account in the McMillan formula in a rather ad hoc manner. I have the density of states, and I will assume an interaction parameter of the BCS type. Now I'll let  $\lambda$  become  $\lambda$  for the normal processes, plus some  $N(0)V$  for intervalley scattering, and I can again do what I did for lanthanum selenide — fit  $T_c$  at some point to get  $V$ . This is in the spirit of the Allen-Cohen calculation where they have done tin telluride and germanium telluride.





## DOCUMENT CONTROL DATA - R &amp; D

*(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)*

1. ORIGINATING ACTIVITY <i>(Corporate author)</i> Naval Research Laboratory Washington, D.C. 20390		2a. REPORT SECURITY CLASSIFICATION Unclassified	
		2b. GROUP	
3. REPORT TITLE PROCEEDINGS OF THE SECOND SYMPOSIUM, 1969 SPRING SUPERCONDUCTING SYMPOSIA			
4. DESCRIPTIVE NOTES <i>(Type of report and inclusive dates)</i> Proceedings of the second in a series of four symposia.			
5. AUTHOR(S) <i>(First name, middle initial, last name)</i> Papers delivered by J.F. Schooley, C.S. Koonce, J.K. Hulm, and P.E. Seiden			
6. REPORT DATE April 25, 1969		7a. TOTAL NO. OF PAGES 64	7b. NO. OF REFS 1
8a. CONTRACT OR GRANT NO. NRL Problem P05-02B		9a. ORIGINATOR'S REPORT NUMBER(S) NRL Report 6972	
b. PROJECT NO.		9b. OTHER REPORT NO(S) <i>(Any other numbers that may be assigned this report)</i>	
c.			
d.			
10. DISTRIBUTION STATEMENT This document has been approved for public release and sale; its distribution is unlimited.			
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Department of the Navy (Office of Naval Research), Washington, D.C. 20360	
13. ABSTRACT 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 second 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.			

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Superconductivity Transition temperature Electron phonon interactions Semiconductors (materials) Electron density (concentration) Metalloids						