NRL Report 6962

Proceedings
of
First Symposium

1969 Spring Superconducting Symposia

Sponsored by

The Office of Naval Research
and
The Naval Research Laboratory

March 28, 1969

NAVAL RESEARCH LABORATORY
Washington, D.C.

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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, has 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 first of four to appear. In order to provide an atmosphere of free uninhibited discussions in the afternoon, no recordings were made. As will be noted, Dr. McMillan's paper in this volume is a reprint of his formally published article.

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

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

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

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

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

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

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

Mrs. E. Shaperio, Magnetism Branch 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

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WELCOME

Captain James C. Matheson, USN
Director, Naval Research Laboratory

It is a genuine pleasure to welcome you to the Naval Research Laboratory for the first of four one-day symposia. I hope your accommodations here are acceptable. From the program, I am convinced that the technical aspect of the symposium will be very stimulating.

It is our privilege today to have with us to open the meeting the Chief of Naval Research, RADM Thomas Owen. Admiral Owen is the head of the Office of Naval Research, one of the sponsors of the Symposia, and former Director of the Naval Research Laboratory, the other sponsor. He had a most distinguished career at sea during World War II, and subsequently served in senior research management positions in both the Department of the Navy and the Office of the Secretary of Defense. After receiving his Ph.D. in physical chemistry at Cornell University in 1950, he did postdoctoral studies at the University of Amsterdam in the Netherlands.

I am extremely pleased to introduce the former director of the Naval Research Laboratory and the present Chief of Naval Research — Admiral Tom Owen.

OPENING ADDRESS

Rear Admiral Thomas B. Owen, USN
Chief of Naval Research

Good morning, ladies and gentlemen. It is a privilege for me as a cosponsor of this symposium to welcome all of you to what I hope is the first in a very successful series of symposia designed to review and extend our knowledge in the field of superconductivity. I note that the audience is composed of scientists, engineers, and administrators, not only from the Washington area but from all over the country, who have a common interest in this apparently burgeoning field. The interest of the Office of Naval Research in low-temperature phenomena is certainly not new, and its Naval Research Laboratory has been actively engaged in cryogenics research for the past 20 years. In the period 1947 to 1950 the Office of Naval Research hosted or sponsored some seven different symposia involving cryogenics, thus emphasizing the fact that our interest in low and ultra-low-temperature phenomena certainly is not new.

In 1947 the Naval Research Laboratory was fortunate to secure one of the earliest commercial Collins liquifiers, making it possible to liquify helium gas at NRL as early as the spring of 1948. It was also in 1947 that NRL acquired a high-magnetic-field Bitter-type solenoid. These two facilities thus permitted NRL to embark on a program to study the electrical and magnetic properties of matter at low temperatures. Later, at NRL in 1951, the interest in low and ultra-low temperatures certainly brought about or fostered an interest in the phenomenon of superconductivity. In succeeding years the Lab found that tungsten is a superconductor with the lowest known critical temperature, namely 0.012°K, with some argument by a group on the West Coast that the figure should be 0.015°K. The Laboratory later discovered, in collaboration with Westinghouse, that the degenerate semiconductors GeTe and SnTe are also superconductors. Incidentally, I note that the class of materials known as degenerate semiconductors will be the subject of the second symposium scheduled for May 25th.

As can be seen, the last 20 years have resulted in tremendous progress in the field of superconductivity. Many materials have been found to exhibit this phenomenon, and I think that we may be at the beginning of a period of expanding interest in an area that has lain dormant for some years but which may be of as much importance in the field of science, engineering, and application as have masers and lasers. Certainly the potential of room-temperature superconductivity, perhaps by the use of organic compounds, holds promise. This idea will be reviewed in greater detail at a symposium sponsored by ONR and NASA to be held at the University of Hawaii this coming fall.

We in the Office of Naval Research sponsor an extensive program in support of the Stanford University superconducting linear accelerator. We seek in this effort the promise and application it may have in helping us engineer methods by which we can transfer microwave energy without losses, and we hope that we will be able to capitalize on much of the knowledge that we know will come out of this type of research.

In reviewing the progress made in superconductivity during the past 25 years, it would seem to me that the real purpose of this series of symposia is really to examine the field critically to find out what direction fundamental research, and of course applied research, might take.

My personal appreciation is expressed to Drs. Matthias, McMillan, Geballe, and Garland for the time they are taking to give us this morning's tutorial presentations, and I want to thank you all for participating. I wish this meeting and the others succeeding it only the best in what I call opportunities for the future.

HOW AND WHERE TO FIND HIGH-TEMPERATURE SUPERCONDUCTORS

Bernd T. Matthias
University of California, San Diego
La Jolla, California

and

Bell Telephone Laboratories
Murray Hill, New Jersey

Thank you for the introduction, Bob; I don't mind being harassed. I would also like to thank you for inviting me.

Tungsten was not the first element that I know of to have its superconductivity discovered here at NRL. It was iridium, which Bob Hein did many years ago. Of course, iridium's transition temperature was higher than tungsten. Ever since, I have been fond of this place (NRL) and this is the reason why I am delighted to be here.

I also want to begin with a friendly introduction because the rest of my talk will not be so friendly. As you probably gathered, I'm supposed to talk to you on how and where to find high-temperature superconductors. Actually, I will be glad to do this, and I will try. However, I think that what I should do is to tell you how not to find them, because much more effort these days has been going into how not to find them than into how to find them. The major part of my talk is not to give you all my latest, greatest, and newest discoveries (which you can read one way or the other), but to tell you where I think everyone has gone wrong. This is something you usually don't want to put in print, but I think the time has come to speak out.

I might as well start right in the beginning and tell you what I think is wrong with the field at present. You see, ever since 1911, people have been saying "wouldn't it be nice if we were at room temperature." This talk went on at sort of a steady rate until 1950, when it began to accelerate. Now it has become more pronounced, and you hear it wherever you go. My personal opinion is that there isn't even a hope of a chance right now, and this obsession of superconductivity at room temperature deflects the efforts of getting superconductivity up to liquid nitrogen temperatures. Our technology today is almost as good at nitrogen temperatures as at room temperatures — and it is much, much more likely that we will get to nitrogen temperatures than our ever getting to room temperatures. The essence of my talk will be how we got to where we are now, and how we are going to approach higher transition temperatures without clinging to radical and old attitudes.

As you know, there have been theories in superconductivity for the last 20 years — started originally by Bardeen and Fröhlich, and later by Bardeen, Cooper, and Schrieffer — theories based on the electron-phonon interaction. Undoubtedly, to an extent in a certain group of superconductors, superconductivity is strictly due to the electron-phonon interaction. However, in my opinion — from now on anything I say is only my opinion — the majority of superconductors are due to a mechanism which is different from the electron-phonon interaction. As a matter of fact, in addition to the electron-phonon interaction there are, today, at least three separate groups that can be distinguished. One is the group of the transition elements, where we have an electron-electron

interaction. There, the phonon interaction, in my opinion, is completely irrelevant and all predictions, assumptions, and hypotheses based on the phonon interaction will not work because it is strictly an electron-electron interaction.

As you know, for the transition elements, one can predict transition temperatures by counting the number of valence electrons in a very simple way. I am sure you all know what I am referring to, but perhaps I should elaborate. I can show you one figure and that is essentially the whole picture. [See Fig. 1.] If you plot the number of valence electrons per atom counted completely regularly (according to the periodic system) from one to ten, the transition temperature has a very symmetric behavior in that you have maxima a little below five and a little bit below seven with a minimum at six in tungsten. This is a curve that works beautifully for all transition elements and their compounds. However, it does not work at all for the nontransition elements and their compounds.

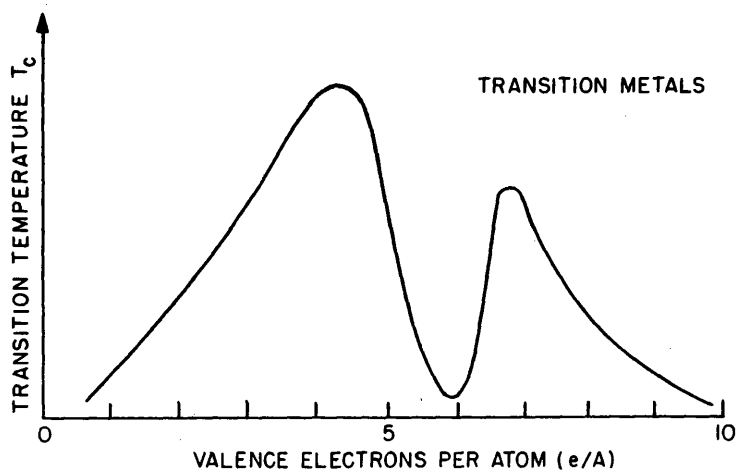

Figure 1

If you use the same parameter for the nontransition elements, the transition temperatures are really essentially like this [see Fig. 2] — that is to say, everything that is metallic amongst the nontransition elements is superconducting. During the last few years this has been elaborated on and proved to a large extent. As I will show you later on in another slide, we have discovered a large number of new superconducting elements in this range simply by one feature — making them metallic. The latest in this group, as you probably all know, is phosphorus which we were able to make superconducting by applying more or less hydrostatic pressure in the order of 80 kbars, resulting in a transition temperature of 6°K. This shows that everything among the metallic nontransition elements will be superconducting (phosphorus being the most spectacular so far, but there will be others). Sulphur will be superconducting at about 400 kbars, [and so will] iodine and maybe even xenon.

The thing to note is that everything in this part of the periodic system is superconducting, provided it is metallic. This is due, undoubtedly, to electron-phonon interaction. If you can remember a very early paper on the BCS theory by David Pines, he stated that the interaction parameter V in the equation $T_c \sim \theta \exp(-1/N(0)V)$ should be a constant. Later on, everyone else tried to extrapolate this to the transition elements and got into terrible difficulties. Had they remained with nontransition elements, everything would be fine because V, in fact, is constant. We have found many new superconductors, literally from tellurium to phosphorus. The specific heat is always pretty much the same.

LOCATING HIGH-TEMPERATURE SUPERCONDUCTORS

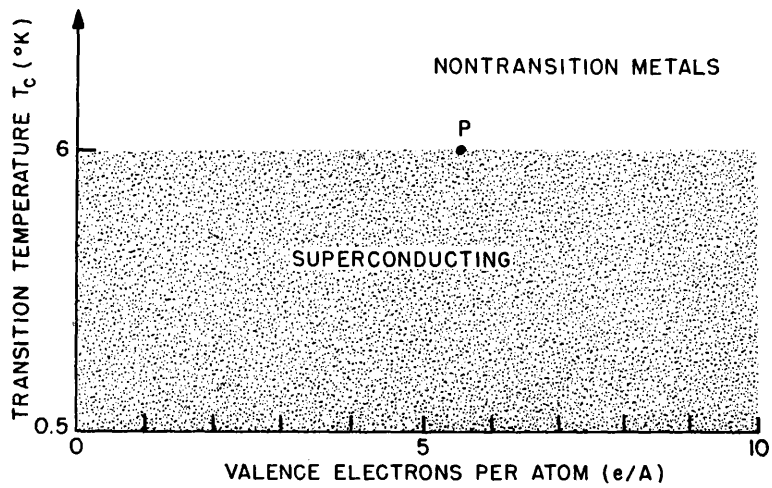

Figure 2

The transition temperature is always the same, between 0.5° and 5°K. It is very nice that everything (in this corner of the periodic chart) is superconducting. However, there is one major disadvantage; while everything is superconducting, all the transition temperatures are low. There has never been a nontransition element, or a compound formed by them, that exceeded 9°K at the very best. Whenever anyone has tried, they have failed to get to higher temperatures with these nontransition elements. Undoubtedly, here the phonon interaction is the correct one. It is beautifully described, and the temperature is essentially proportionate to the inverse square root of the atomic mass.

I want to talk to you now more about the two major and two minor groups of superconductors. The other major group, namely the transition elements, was different not just with respect to the transition temperatures and its variation with electron concentration, but it was different from just about every other angle. Let me comment a little bit on where these differences are because they are still there and I assure you they will be there for a long time to come. First of all, you see the electron concentration behavior for the nontransition elements where everything is superconducting. No dependence to speak of. For the transition elements, however, the regularity is an extremely rigid one and the transition temperatures vary here by a factor of 10^3 at least, and things are altogether quite drastic. Originally, when we tried to prove this point [that there was a fundamental difference between the mechanism for superconductivity in the transition and nontransition elements] we decided to measure the isotope effect for the transition elements, i.e., $T_c \sim M^{-1/2}$. Geballe and I found for the first time a case where the isotope effect was completely absent, that is, in ruthenium it was zero. Where you now have the square root, from now on let's call it alpha (i.e., $T_c \sim M^{\alpha}$) so that $\alpha = -0.5$. For ruthenium ($\alpha = 0$) there was just no dependence of T_c on the mass. This, of course, gave rise to a great deal of argument ever since, and by now I am sure the theory has sort of adapted itself in many ways trying to follow this absence of an isotope effect. One thing remains true — not one alpha in the transition elements has ever come close to -0.5. It is always either 0 or less than the square root [0.5]. That is true for all transition elements, and right now the most interesting one of course will be tungsten. You see, everything in the periodic system is symmetric, and when we found ruthenium to be zero, we could predict — which we did against theory — that there was a symmetric element, namely zirconium, which also had an isotope effect of zero. (You see I will be followed by two of my friends, the theorists, who will talk about this and I might as well anticipate what they are going to say.) We predicted that zirconium had to be zero, in disagreement

with Garland's paper, and in fact the Swiss found that the isotope effect in zirconium was indeed zero.

Now in the meantime, many isotope effects here have been measured and it seems to be sort of reminiscent of the curve of transition temperatures because again everything is symmetric. Therefore, we hope there will be a maximum of the isotope effect in the middle. Geballe and I measured molybdenum and we found -0.33 or -0.38 so the isotope effect pointed out this difference between the mechanisms for superconductivity in the transition and nontransition elements. There are many other effects which have shown this same difference, thin films for instance. When you make thin films of the nontransition elements [aluminum of course is the most famous one, the film which unfortunately has given rise to fantastically exaggerated hopes of high transition temperatures] — when you make aluminum in a thin film, the temperature goes from 1° to 5°K. When some of my lesser friends heard about it they got completely excited and sighed — "ah! factor 5" — applied it to niobium, and predicted 45°K. It was complete nonsense because this is typical for the nontransition element films only.

Almost all films of nontransition elements are higher in transition temperature than the bulk sample — indium films, gallium, aluminum — whatever film you make here except for lead, if it is a thin film, it is higher. And as you plot the film thickness eventually the temperatures come to the bulk value. Now, if you do exactly the same thing with the transition elements, i.e., thin films, you get exactly the opposite effect. The thin film is always lower — much lower — and as you raise the film thickness, you finally get to the bulk value.

Aside from the above formula and maybe another, I will not talk to you about any formulas, but you may be saying to yourself — what does that prove? The thin film of course will undoubtedly change the phonon spectrum. In other words, it will become softer on the surface because it is mostly surface. Therefore, if the phonon interaction is that crucial, it should enhance the superconductivity, and as you see, in fact it does for the thin films of the nontransition element. However, for the transition element, where in my opinion the phonon interaction has just the opposite effect — namely, it destroys superconductivity — there of course you will get the opposite behavior. The thinner the film, the larger the phonon spectrum, the worse the transition temperature, and that is why this sign is wrong. From this behavior, even though for the last five years an enormous amount of work has been put into it, no exception has even been found to date. There has never been a transition element film that was above the bulk material in transition temperature.

Now let me come to another parameter, pressure. Very often people say I should show that phonons have nothing to do with superconductivity. Obviously I can't stop a crystal from rattling. You know this as well as I do. However, there is one thing that can be done. You can squeeze it. By squeezing it, you of course heighten the potential well of the atomic vibrations and you will reduce the amplitude. Then you somehow restrict the phonon interaction. As a consequence, in this group of nontransition elements, whenever you squeeze them usually you reduce the transition temperature very drastically. For instance, you can squeeze cadmium, zinc, and aluminum until they become normal at the temperature they can be measured. Lead can be squeezed from a transition temperature of 7° down to 2°K. Whenever you squeeze any nontransition element, you really go down in transition temperature because you stop the crystal from rattling. Now what happens in the transition elements. Nothing that drastic, but usually the T_c goes up quite a bit. The phonons really have nothing much to do but inhibit a little bit. If you squeeze the crystals here, you will not get any drastic changes of the superconducting transition temperature.

Now, as I mentioned before, I told you there are several mechanisms — so far we've only discussed two. Let me now quickly show to you what the other two mechanisms are. [See Fig. 3.] Here is the first group I mentioned — the nontransition elements, phosphorus, etc., and the things that are missing are arsenic, sulfur, iodine, chlorine, etc. — they'll come. Here are the groups of the transition elements about which I have just talked. Now we come to the third group, the f elements.

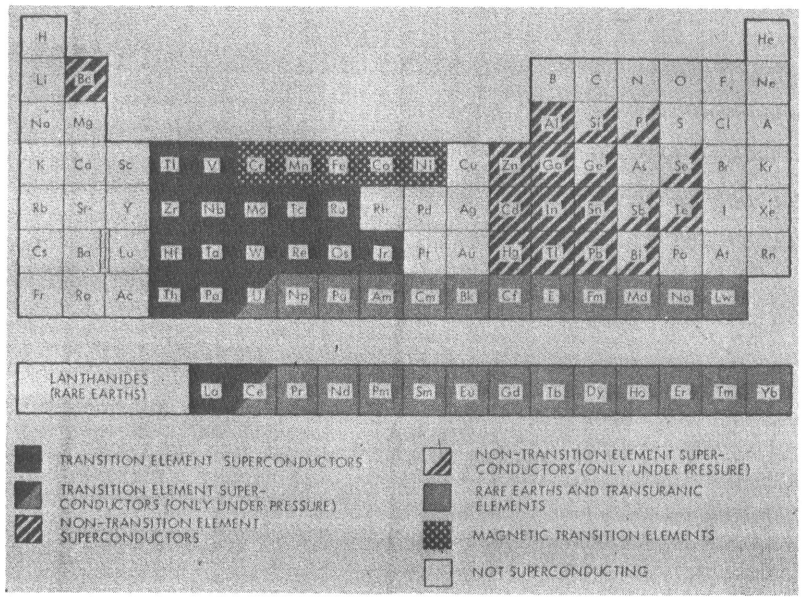

Figure 3

I am sure you heard about it before from me and there is no point of my dwelling too much upon it. Before the f electrons become localized, they go through a range of superconductivity. That is true for elements like lanthanum, cerium — where they are becoming localized. You know cerium has become superconducting, again under pressure. It is also true, in the same way, for things like protactinium and uranium. Cerium and uranium are essentially both magnetic and superconducting because you can interfere with the f electrons through pressure.

Now, what happens in this third group when you apply pressure? You get staggering effects. Namely, if you stop the lattice vibrations for these elements, since the f electrons are susceptible to pressure, and particularly susceptible to lattice vibration, then the effects are really drastic. As a consequence, when you squeeze uranium in bulk it becomes superconducting at two degrees — these two degrees coming from essentially nowhere. We don't know where but we do know that U certainly isn't superconducting above a tenth of a degree without pressure. If we squeeze lanthanum at 150 kbars, T_c = 12.5°, whereas normally the superconducting temperature of La is 6°K. Really a staggering effect! Recently we have extrapolated a little bit on this (lanthanum). The element next to it is barium — so we put pressure on barium, knowing that whatever is true for one element is probably true in its neighborhood. Recently, we haven't published it yet,

barium has become superconducting, again at a temperature which is very high, between 5° and 6°K for 155 kbars. Cerium behaves exactly as it should in the row of the transition element — it behaves like thorium. It is a four valence element superconducting at almost exactly the same temperature as thorium, which is at 1.4°K.

So you see there are already three mechanisms. In my opinion the fourth mechanism is a very intriguing one. It is that the metals with a very high Debye temperature are superconducting. The superconductivity of beryllium was found here (at NRL by Falge). Metallic beryllium (hexagonal) with $T_c = 0.026°K$ is a very good case in question. Many of the beryllium things — compounds, alloys, and amorphous films (where you rely on the high Debye temperatures) — are superconducting. In Germany, amorphous beryllium films have gotten up to as high as 10°K. What is true for beryllium is also true for boron. Geballe and I have made a large number of borides, all of which (hexaborides, dodecaborides, it doesn't matter as long as they are cubic, not magnetic, and not semiconductors) are always superconducting. So this is now the fourth group; that of the high Debye temperatures. I really don't want to talk very much about that any longer. I just wanted to show you how — by the occurrence of superconductivity, by the variation with electron concentration with pressure, with all these things — we can radically distinguish between all four groups.

For instance in the boride compounds, one might say "ah! yes — that of course must be an electron-phonon interaction." Nothing of the sort! What the borides really represent is the following. It's the matrix with an extremely high Debye temperature, a matrix in which we can suspend transition elements — whether it's yttrium, zirconium or thorium, scandium, lutetium — it doesn't matter. If we can suspend these transition elements in a matrix that doesn't shake, in other words, which does not have any phonon interaction, then we are alright, and we will get superconductivity. In order to show this, for instance, we recently did the isotope effect on ZrB_{12} — it is superconducting at 6°K (6 seems to be sort of a magic number, everything is at 6 degrees). We did the isotope effect because you can vary the mass of boron by 10 percent — of course there was no trace. We measured to within 1/2 a millidegree and there was no isotope effect — nothing at all.

Now just let me make one last comment about the isotope effect. In the third group, that of the f elements where the pressure has a staggering effect, the isotope effect should be of the opposite sign since pressure reduces the lattice interaction. Also, the lattice reaction can be reduced if we increase the mass, and therefore many years ago we predicted that for uranium (the only one we could do until now that we have barium) the isotope effect should have the opposite sign. True enough. A year and a half ago, Fowler, Hill, and several others of us found in Los Alamos that for uranium, the isotope effect essentially had changed its sign and also its order of magnitude and had become positive, as had been predicted under the assumption that the phonon interaction here is strictly detrimental.

The reason why I show all these things is to show you — under the assumption that we have several different groups of superconductivity — that we ought to do things on an empirical basis and then we will have no great problem at least to describe the occurrence of superconductivity, where it shows up and all that. As a consequence of the variation of transition temperatures, we managed to raise the transition temperature of the transition element compound niobium, aluminum, germanium to 21°K — 20.98°K to be exact. That is why I mentioned liquid nitrogen before and not liquid hydrogen, because we are now above liquid hydrogen. This empirical approach works very well. We really don't know exactly what we are doing, but at least we know when we are doing the right thing.

Why is it that so far none of the theoretical approaches have lead to any high-temperature superconductivity or to any new superconductors even at low temperatures? I have, first, some maybe not too relevant remarks to make. I think before one looks for high-temperature superconductivity, one should first get the feel for it by looking for superconductivity in itself. I think it is way too ambitious, and so far has been completely fruitless, to look for superconductivity at room temperature and all that if one cannot even find one at 2°K! A mechanism, a theory, that breaks down predicting superconductivity at 2°K undoubtedly will not be relevant at 2000 degrees, or whatever numbers that are quoted now. Then why are people so determined to make the electron-phonon interaction fit the transition element even though it doesn't work in films, isotope effects, or high temperatures? Here, I can tell you only one joke. The electron-phonon interaction always reminds me of the man who is looking for his keys under a street light and his friends say "but you didn't lose them here, you lost your keys over there." "I know, but it is too dark over there." Since the electron-phonon interaction worked so well here, they are absolutely unwilling (whoever they are) to stop applying the electron-phonon interaction in an area where it is completely irrelevant. You will hear again and again how the theory can be adapted and adapted and for the third time adapted to sort of agree with the experimental results. It's hopeless! It works beautifully in the nontransition elements and one should leave well enough alone and be happy about it and just start all over again. As long as one will try, as hard as one can, to apply the phonon interaction for the transition element, as long as you will have to patch things with one new parameter after the other — a new screening, another retarded potential and pseudo-potential on and on — they will have to go on and on and never be able to predict. In my opinion, until you can predict anything, it's probably the wrong theory.

For instance, we used — you probably won't believe it — I used BCS in order to squeeze phosphorus, because we know that according to BCS it had to become superconducting and so it did. But there is no verification of this by BCS again for the results in the transition elements — electron-phonon interaction rather works beautifully in the nontransition elements and it is essentially useless in the transition elements. I could go into many details with you now about density of states and all that sort of thing, but there is no point.

Let me make one comment which may arise in the discussion later, or certainly this afternoon. That is related to what I have said for applying electron-phonon interaction to the transition elements. I didn't think this was a good idea. This is a mild statement as to how I feel about applying the electron-phonon interaction to organic compounds. I'm sorry if I appear not to be friendly to my hosts here, but I think the organic superconductors have done a great deal of harm. First there aren't any! Three years or so ago, there was a review article on superconductivity in Naturwissenschaften which started out with the sentence, "Now that we have organic superconductors at room temperature," and as you heard in the opening of this conference there is a conference on high-temperature organic superconductors in Hawaii. I have nothing against Hawaii, but you see one might say — "Oh well, what harm is done?" The harm is considerable. I'm not talking about the money spent and all that, I'm talking about the people who are being led astray. I have a large number of students and it's hard enough to make physicists out of them but it is an extremely difficult job to convince them there are no organic superconductors.

The argument is — "look, so many people talk about it, there must be some." Sometimes this thing reminds me of the Virginia Wolf play where four people argue all night about the aberrations of a child, and when the play is over, it turns out that there never was a child. This is exactly how I feel about the organic superconductors. I've heard

descriptions of them — the sheen, black color ... it is unbelievable. It goes on and on. The literature has been led astray. The young people are being led astray and ask, "What else is there?" Really, it is a very sad story.

Again, I don't want to talk about the money because an enormous amount of money has been spent. Usually the proposals either read "in search for the truth" or something like that, or "now since we understand it." Good heavens! Have I become allergic to that sentence. "Now since we understand everything." It stares you in the face, not just in proposals, even in the journals.

Now, since everything is solved, my question is simply "What is solved in superconductivity?" Nothing! The theory over the last 13 years has not been able to produce one single superconductor, to predict one transition temperature, or to explain one of the various phenomena I mentioned. Yet everything is solved! I think that is a very awkward situation.

I don't know how many of you have heard of the recent Soviet paper as related by Litynski. In this paper the Russians are trying to be honest with themselves. It's a rarity, and it's really quite a fascinating document. In one section of the paper the two most important problems that face mankind today are mentioned: controlled fusion, obviously, and superconductivity at room temperature. But you see it is really true. Superconductivity at room temperature — even at nitrogen temperatures, could we ever get it that way — would change the face of this earth. Our whole technology would be different. Everything would be radically changed. You cannot exist today without electricity. (You could but it would be quite different.) Everything that is electric of course would be affected in an exceedingly drastic way by superconductivity at these very high temperatures.

I think that superconductivity at high temperatures is far too serious a problem to make jokes about it, to go to Hawaii for it, or to leave room for this type of argument. That "Oh yes, we will get there to room temperature, now we understand everything, it is only a matter of time." Three years ago, Kapitza in Moscow said "we are on the threshold of room temperature superconductivity." We have gone a half a degree higher since then! Room temperature is as far away as it always was — even the nitrogen temperature is as far away. The point I am trying to make is by just talking about it, we won't get there. On the contrary, by talking about it we will do some serious damage. It is essentially sort of a tranquilizer for the people who fail to get there — sort of like travel posters, you know. You look at it and you think "wouldn't it be nice." I think this is an extremely serious situation and I am determined, laughingly or not, to fight against it, because I think this kind of Madison Avenue approach to raise the transition temperature by words only is a very bad thing. As any good propaganda, you know what the criteria for good propaganda are — say it long enough, say it loud enough, say it clear enough, and repeat yourself and eventually everybody will believe you. Look at Naturwissenschaften. It is a respectable paper.

So this is essentially the essence of my talk. I wanted to talk to you much more about the actual superconductivity rather than the "hoped for" superconductivity because I think I know which way the theory should go. We've got to find a quantity that is reminiscent of the behavior of the transition temperature. The density of states is of course nonsense because there is essentially no correlation. What is there that resembles this curve? Let me quickly show you the second slide and you will see what I mean. [See Fig. 4.]

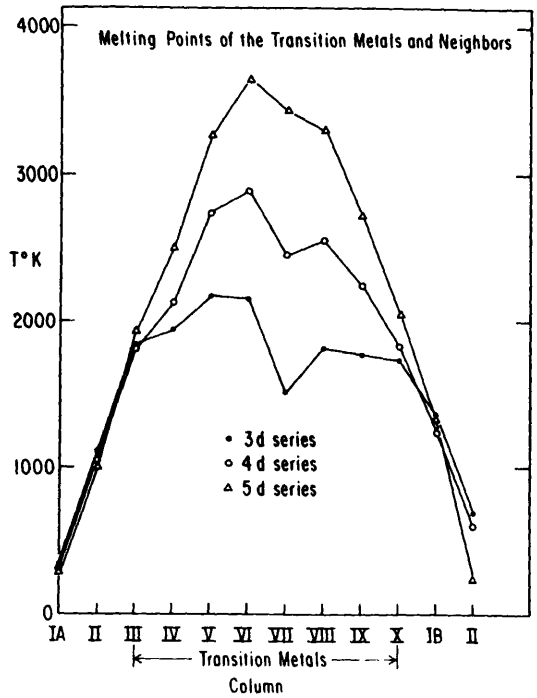

Figure 4

This is now a plot of the melting point of the elements, and you will see with a certain amount of imagination that you get the same behavior. You even get the dip here with the magnetic elements, but the difference between magnetism and superconductivity is only marginal. In other words, the melting point as we have found again and again is the only quantity that is profoundly related to superconductivity. For instance, the anomalous superconductors such as La and U all have anomalously low melting points. All the anomalous superconducting behaviors are reflected by melting points. Now then you might say "That is very good. All we have to do is stick to the melting point and the theory of melting, etc." And here I want to end with one friendly sentence at least. The theory of melting — in other words, the theory of where a metal will melt and the temperatures involved — is in worse shape than superconductivity! In other words, I have really managed to reduce superconductivity, which nobody understands, to something which people understand even less — the melting point.

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Transition Temperature of Strong-Coupled Superconductors

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The superconducting transition temperature is calculated as a function of the electron-phonon and electron-electron coupling constants within the framework of the strong-coupling theory. Using this theoretical result, we find empirical values of the coupling constants and the "band-structure" density of states for a number of metals and alloys. It is noted that the electron-phonon coupling constant depends primarily on the phonon frequencies rather than on the electronic properties of the metal. Finally, using these results, one can predict a maximum superconducting transition temperature.

I. INTRODUCTION

In this paper we derive a formula for the superconducting transition temperature, using the so-called "strong-coupled" theory, as a function of the coupling constants for the electron-phonon and Coulomb interactions. We take the point of view here that the theory of superconductivity is accurate and well-developed and that, given certain properties of the normal state of a given metal, we could calculate its superconducting properties, e.g., T_c, with an accuracy $\sim 1\%$. The necessary properties of the normal state are (a) the electron energy bands near the Fermi energy, (b) the phonon dispersion curves, (c) the fully dressed (screened) electron-phonon interaction matrix elements, and (d) the fully dressed Coulomb interaction between electrons. All these properties are not sufficiently well-known for any metal to make a first-principles calculation of its superconducting properties worthwhile. There is much to be learned, however, by approaching the problem from the other direction and asking what can be learned about the normal metal from its measured superconducting properties. There are available for a number of superconducting metals and alloys measurements of the superconducting transition temperature T_c, the Debye temperature Θ, and the electronic heat-capacity coefficient γ. Also, for a few metals, there are measurements of the phonon energies and of the isotope shift of T_c. By making use of our theoretical formula for T_c and experimental data, we can find empirical values for electron-phonon coupling constant λ and the phonon enhancement of cyclotron mass and specific heat. The measured isotope shifts can be used to find empirical values for the Coulomb coupling constant μ^*. With the addition of information about the phonon energies, we will be able to examine the makeup of λ and discuss the influence of the various metallic properties upon the variations of λ throughout the periodic table. Finally, it will be pointed out that the theory makes a reasonably definite statement about the maximum T_c that one should expect for a given class of materials.

The plan of the paper is as follows. In Sec. II we will write down the integral equations for the strong-coupled superconductor at the transition temperature and discuss an approximate, analytic solution. In Sec. III we will present accurate numerical solutions of the integral equations and show that these results for T_c fit a simple analytic function of the coupling constants λ and μ^*. In Sec. IV we use these theoretical formulas and experimental data to find empirical values of λ and the "band-structure" electronic density of states at the Fermi surface for a number of metals and alloys. In Sec. V we derive an expression for λ in terms of an average phonon energy $N(0)$, and an average of the electron-phonon matrix elements, and find empirical values for these quantities for a few elements. We

present a theoretical argument and empirical evidence that the coupling constant depends strongly on the phonon energies and only weakly on the other parameters in a given class of materials. With this observation, we derive in Sec. VI a maximum T_c for that class of materials.

II. THEORY

According to the Bardeen-Cooper-Schrieffer[1] (BCS) theory of superconductivity, one has a relation between the transition temperature T_c, a typical phonon energy $\langle\omega\rangle$, and the interaction strength $N(0)V$:

$$T_c = 1.14\langle\omega\rangle \exp[-1/N(0)V]. \tag{1}$$

Here $N(0)$ is the electronic density of states at the Fermi surface and V is the pairing potential arising from the electron-phonon interaction. Numerous authors have estimated $N(0)$ and V using Eq. (1) and experimental values of T_c, Θ, and γ (the coefficient of the electronic specific heat).

Since the BCS paper, much progress has been made in understanding the role of the electron-phonon interaction in normal and superconducting metals. Migdal[2] showed that, in normal metals, the electron-phonon interaction could be treated accurately [to order $(m/M)^{1/2}$] even for strong coupling. Eliashberg[3] and Nambu[4] have extended the Migdal treatment to the superconducting state using the Green's-function techniques of Gor'kov.[5] The Eliashberg theory takes into account the retarded nature of the phonon-induced interaction and treats properly the damping of the excitations. This strong-coupling theory is also accurate to order $(m/M)^{1/2}$. With the addition of the pseudopotential treatment[6] of the screened Coulomb interaction, the Eliashberg equations represent the present state of the art in superconductivity theory.[7] Comparison with tunneling experiments[8,9] and critical-field measurements[10] for strong-coupled superconductors has provided a strong confirmation of the theory in its present form.

The integral equations for the normal and pairing self-energies at the transition temperature are[11,12]

$$\begin{aligned}\xi(\omega) &= [1-Z(\omega)]\omega \\ &= \int_0^\infty d\omega' \int_0^{\omega_0} d\omega_q\, \alpha^2(\omega_q) F(\omega_q) \\ &\quad \times\{[N(\omega_q)+f(-\omega')][(\omega'+\omega_q+\omega)^{-1}-(\omega'+\omega_q-\omega)^{-1}] \\ &\quad +[N(\omega_q)+f(\omega)][(-\omega'+\omega_q+\omega)^{-1} \\ &\quad -(-\omega'+\omega_q-\omega)^{-1}]\}, \end{aligned} \tag{2a}$$

$$\begin{aligned}\Delta(\omega) &= [Z(\omega)]^{-1}\int_0^\infty \frac{d\omega'}{\omega'} \\ &\quad \times \mathrm{Re}[\Delta(\omega')]\int_0^{\omega_0} d\omega_q\, \alpha^2(\omega_q) F(\omega_q) \\ &\quad \times\{[N(\omega_q)+f(-\omega')][(\omega'+\omega_q+\omega)^{-1}+(\omega'+\omega_q-\omega)^{-1}] \\ &\quad -[N(\omega_q)+f(\omega')][(-\omega'+\omega_q+\omega)^{-1} \\ &\quad +(-\omega'+\omega_q-\omega)^{-1}]\} - \frac{N(0)V_c}{Z(\omega)}\int_0^{E_B}\frac{d\omega'}{\omega'} \\ &\quad \times \mathrm{Re}[\Delta(\omega')][1-2f(\omega')], \end{aligned} \tag{2b}$$

where $F(\omega_q)$ is the phonon density of states, ω_0 is the maximum phonon frequency, $\alpha^2(\omega_q)$ is an average of the electron-phonon interaction, V_c is the matrix element of the screened Coulomb interaction averaged over the Fermi surface, E_B is the electronic bandwidth, and $N(\omega)$ and $f(\omega)$ are the Bose and Fermi occupation probabilities $[\exp(\omega/kT_c)\mp 1]^{-1}$. The screened Coulomb interaction is described by the parameters $N(0)V_c$ and E_B, and the electron-phonon interaction by the function $\alpha^2(\omega_q)F(\omega_q)$, which we will discuss in more detail below.

We find an approximate solution to Eq. (2) by substituting a trial function for $\Delta(\omega)$ on the right-hand side of (2) and computing $\Delta(\omega)$ by performing the indicated integrations. We then require that the trial $\Delta(\omega)$ and the computed $\Delta(\omega)$ be as consistent as possible. Such a procedure was followed by Morel and Anderson,[6] who, in fact, used a better trial function than we will take; we depend more on the accurate numerical results of the next section. We choose

$$\begin{aligned}\Delta_t(\omega) &= \Delta_0, \qquad 0<\omega<\omega_0 \\ &= \Delta_\infty, \qquad \omega_0<\omega \end{aligned} \tag{3}$$

and compute $\Delta(0)$ and $\Delta(\infty)$ from Eq. (2). Neglecting

[1] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **106**, 162 (1957); **108**, 1175 (1957).
[2] A. B. Migdal, Zh. Eksperim. i Teor. Fiz. **34**, 1438 (1958) [English transl.: Soviet Phys.—JETP **7**, 996 (1958)].
[3] G. M. Eliashberg, Zh. Eksperim. i Teor. Fiz. **38**, 966 (1960); **39**, 1437 (1960) [English transls.: Soviet Phys.—JETP **11**, 696 (1960); **12**, 1000 (1961)].
[4] Y. Nambu, Phys. Rev. **117**, 648 (1960).
[5] L. P. Gorkov, Zh. Eksperim. i Teor. Fiz. **34**, 735 (1958) [English transl.: Soviet Phys.—JETP **7**, 505 (1958)].
[6] P. Morel and P. W. Anderson, Phys. Rev. **125**, 1263 (1962).
[7] J. R. Schrieffer, *Theory of Superconductivity* (W. A. Benjamin, Inc., New York, 1964).
[8] J. R. Schrieffer, D. J. Scalapino, and J. W. Wilkins, Phys. Rev. Letters **10**, 336 (1963); D. J. Scalapino, J. R. Schrieffer, and J. W. Wilkins, Phys. Rev. **148**, 263 (1966).
[9] W. L. McMillan and J. M. Rowell, Phys. Rev. Letters **14**, 108 (1965); also (to be published).
[10] J. C. Swihart, D. J. Scalapino, and Y. Wada, Phys. Rev. Letters **14**, 106 (1965).
[11] V. Ambegaokar and L. Tewordt, Phys. Rev. **134**, A805 (1964).
[12] D. J. Scalapino, Y. Wada, and J. C. Swihart, Phys. Rev. Letters **14**, 102 (1965).

the thermal phonons, we have three contributions to $\Delta(0)$:

$$\Delta^1(0)=[Z(0)]^{-1}\int_0^{\omega_0}\frac{d\omega'}{\omega'}\Delta_0\int_0^{\omega_0}d\omega_q\,\alpha^2(\omega_q)F(\omega_q)$$
$$\times\{f(-\omega')(\omega'+\omega_q)^{-1}-f(\omega')(-\omega'+\omega_q)^{-1}\}$$
$$\cong\frac{\Delta_0}{Z(0)}\int_0^{\omega_0}\frac{d\omega'}{\omega'}\tanh\left(\frac{\omega'}{2T_c}\right)2\int_0^{\omega_0}\frac{d\omega_q\,\alpha^2(\omega_q)F(\omega_q)}{\omega_q}$$
$$\cong[\Delta_0\lambda/Z(0)]\ln(\omega_0/T_c). \tag{4}$$

The dominant contribution to the ω' integral is from small ω', and we neglect ω' relative to ω_q in the phonon propagators $(\omega'+\omega_q)^{-1}$. The natural definition of a dimensionless electron-phonon coupling constant is

$$\lambda\equiv 2\int_0^{\omega_0}\alpha^2(\omega_q)F(\omega_q)\frac{d\omega_q}{\omega_q}, \tag{5}$$

and λ corresponds roughly to the $N(0)V$ of the BCS model. Further, we have

$$\Delta^2(0)=[Z(0)]^{-1}\int_{\omega_0}^{\infty}\frac{d\omega'}{\omega'}\Delta_\infty\int_0^{\omega_0}d\omega_q\,\alpha^2(\omega_q)F(\omega_q)\frac{2}{\omega'+\omega_q}$$
$$\cong[\Delta_\infty/Z(0)](\langle\omega\rangle\lambda/\omega_0), \tag{6}$$

where $\langle\omega\rangle$ is an average phonon frequency;

$$\langle\omega\rangle=\int_0^{\omega_0}d\omega_q\,\alpha^2(\omega_q)F(\omega_q)\Big/\int_0^{\omega_0}\frac{d\omega_q}{\omega_q}\alpha^2(\omega_q)F(\omega_q)$$
$$\cong 0.5\omega_0, \tag{7}$$

and we have neglected ω_q relative to ω'. The first two contributions are from the electron-phonon interaction; the third term from the Coulomb interaction is

$$\Delta^3(0)=-[N(0)V_c/Z(0)]$$
$$\times[\Delta_0\ln(\omega_0/T_c)+\Delta_\infty\ln(E_B/\omega_0)]. \tag{8}$$

At high energies the only contribution is from the Coulomb interaction:

$$\Delta(\infty)=-[N(0)V_c/Z(\infty)]$$
$$\times[\Delta_0\ln(\omega_0/T_c)+\Delta_\infty\ln(E_B/\omega_0)]. \tag{9}$$

The renormalization is easily found to be

$$Z(0)=1+\lambda,\qquad Z(\infty)=1. \tag{10}$$

We satisfy our consistency requirement at low and high energies:

$$\Delta(0)=\Delta_0$$
$$=[\Delta_0\lambda/Z(0)]\ln(\omega_0/T_c)+[\Delta_\infty/Z(0)](\langle\omega\rangle/\omega_0)\lambda$$
$$-[N(0)V_c/Z(0)][\Delta_0\ln(\omega_0/T_c)+\Delta\ln(E_B/\omega_0)], \tag{11}$$

$$\Delta(\infty)=\Delta_\infty$$
$$=-N(0)V_c[\Delta_0\ln(\omega_0/T_c)+\Delta_\infty\ln(E_B/\omega_0)]$$
$$=-\frac{N(0)V_c\Delta_0\ln(\omega_0/T_c)}{1+N(0)V_c\ln(E_B/\omega_0)}$$
$$=-\mu^*\Delta_0\ln(\omega_0/T_c), \tag{12}$$

where μ^* is the Coulomb pseudopotential of Morel and Anderson[6]

$$\mu^*=\frac{N(0)V_c}{1+N(0)V_c\ln(E_B/\omega_0)}. \tag{13}$$

Substituting (12) into (11), we find

$$\Delta_0=\frac{\Delta_0[\lambda-\mu^*-\mu^*\lambda(\langle\omega\rangle/\omega_0)]\ln(\omega_0/T_c)}{1+\lambda}. \tag{14}$$

The strong-coupling formula analogous to Eq. (1) is then

$$\frac{T_c}{\omega_0}=\exp\left(\frac{-(1+\lambda)}{\lambda-\mu^*-(\langle\omega\rangle/\omega_0)\lambda\mu^*}\right). \tag{15}$$

In weak coupling ($\lambda\ll 1$), Eq. (15) reduces to the BCS result with $\lambda-\mu^*$ playing the role of $N(0)V$. The strong-coupling features are (1) that the interactions are renormalized by $Z=1+\lambda$ and (2) that the Coulomb interaction changes the gap function in such a way that the phonon contribution is reduced from λ to $\lambda[1-(\langle\omega\rangle/\omega_0)\mu^*]$.

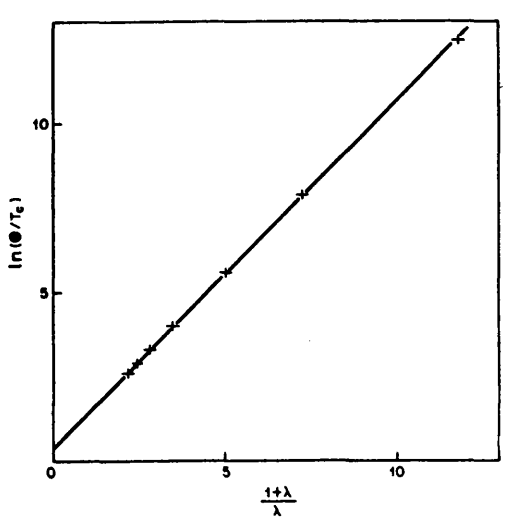

FIG. 1. The logarithm of Θ/T_c versus $(1+\lambda)/\lambda$ from a solution of the integral equations of the strong-coupled theory with $\mu^*=0$. The straight-line fit determines the constants (1.04 and 1.45) in the theoretical formula [(Eq. (18)].

III. NUMERICAL RESULTS

In order to find a more accurate solution of the gap equation, we go to the computer. We solve Eq. (2) by

TABLE I. Values of the coupling constant λ for various values of the Coulomb term μ^* and transition temperature T_c (in °K).

T_c \ μ^*	0	0.088	0.149	0.157	0.245
20	0.85	1.12	1.34		
15	0.68	0.93	1.12		1.47
10	0.55	0.75	0.91		1.20
5	0.40	0.58		0.72	
1	0.25	0.39		0.50	
0.1	0.16	0.28		0.38	
0.001	0.09			0.25	

a simple iterative procedure. We write (2) in the form

$$\Delta_{n+1}(\omega)=\int d\omega'\,K(\omega,\omega')\,\Delta_n(\omega'),\qquad(16)$$

and choose $\Delta_1(\omega)$ to be the solution found in Sec. II. We substitute $\Delta_1(\omega)$ into the right-hand side of (16) and perform the indicated integration to find $\Delta_2(\omega)$, which is, we hope, closer to true solution. We find, in fact, that after four to eight iterations, $\Delta(\omega)$ has converged in the third decimal place. During the iteration it is convenient to fix T_c and μ^* and to adjust α^2 at each stage so that $\Delta_{n+1}(0)=\Delta_n(0)$. We must choose a particular $\alpha^2(\omega_q)F(\omega_q)$, and, since we will be interested in the bcc transition-metal alloys in the next section, we take $F(\omega_q)$ to be the phonon density of states of Nb found from the neutron work.[13] $\alpha^2(\omega_q)$ is taken to be a constant α^2 over most of the phonon spectrum; however, we take $\alpha^2F(\omega)=0$ for $\omega<100$°K to eliminate the coupling to the long-wavelength transverse phonons (see Fig. 4). We have performed the numerical calculations for several values of T_c and μ^* with T_c in the range 10^{-3} °K$<T_c<20$°K and μ^* between 0 and 0.2. The results for λ for various values of T_c and μ^* are given in Table I. Instead of plotting the numerical data as a family of curves, we will use the analytic formula (15) to fit the data. A plot (Fig. 1) of $\ln(\Theta/T_c)$ versus $(1+\lambda)/\lambda$ for $\mu^*=0$ yields a straight line with a slope of 1.04 and an intercept of $0.37=\ln 1.45$. In order to determine the constant $\langle\omega\rangle/\omega_0$ from the numerical data, we plot in Fig. 2 the quantity

$$y=\left(\lambda-\frac{1.04(1+\lambda)}{\ln(\Theta/1.45T_c)}\right)\Big/\mu^*\qquad(17)$$

[which should be equal to $1+(\langle\omega\rangle/\omega_0)\lambda$] versus λ. A straight line with a slope of $\langle\omega\rangle/\omega_0=0.62$ and an intercept of 1 provides a good fit to the numerical data. The scatter of the points about the straight line is partly due to numerical inaccuracies of the computer program which are magnified in taking the difference to calculate y. The final formula for the transition temperature is then

$$T_c=\frac{\Theta}{1.45}\exp\left[-\frac{1.04(1+\lambda)}{\lambda-\mu^*(1+0.62\lambda)}\right].\qquad(18)$$

We have used the Debye Θ for the characteristic phonon frequency. We could just as well have used the maximum phonon frequency ω_0 or the average phonon frequency $\langle\omega\rangle$ [see Eq. (24) below]. For niobium, $\Theta=277$°K, $\omega_0=330$°K, and $\langle\omega\rangle=230$°K. We illustrate the accuracy of this analytic formula by plotting $y'=1.04(1+\lambda)/\ln(\Theta/1.45T_c)$ versus λ in Fig. 3. The analytic formula gives the family of straight lines $y'=-\mu^*+(1-0.62\mu^*)\lambda$ for a fixed μ^*. The numerical data points (for the same μ^* values) are shown by crosses. The analytic formula does give a good fit to the numerical values over a wide range of parameters.

The energy-gap function $\Delta(\omega)$ for a typical set of parameters ($\lambda=0.91$, $\mu^*=0.149$, $T_c=10$°K) corresponding roughly to those of Nb is shown in Fig. 4, together with the phonon density of states of Nb.

Since we will find empirical values of λ in the next section, we are interested in the definition of λ in terms of the electronic matrix elements and the phonon frequencies. We have used $\alpha^2(\omega)F(\omega)$, which is defined by

$$\alpha^2(\omega)F(\omega)=\int_S\frac{d^2p}{v_F}\int_{S'}\frac{d^2p'}{(2\pi\hbar)^2v_{F'}}\sum_\nu g_{pp'\nu}{}^2\delta(\omega-\omega_{p-p'\nu})\Big/\int_S\frac{d^2p}{v_F},\qquad(19)$$

where the integral $\int d^2p$ is taken over the Fermi surface and the electron-phonon matrix elements are given by[14]

$$g_{pp'\nu}=(\hbar/2MNV\omega_{p-p'\nu})^{1/2}\mathcal{g}_\nu(p,p'),\qquad(20)$$

where $\mathcal{g}_\nu(pp')$ is the electronic matrix element of the change in the crystal potential $\mathfrak{U}$ as one atom is moved:

$$\mathcal{g}_\nu(pp')=\int\psi_p{}^*(\boldsymbol{\varepsilon}_{p-p'\nu}\cdot\nabla\mathfrak{U})\psi_{p'}d\mathbf{r}.\qquad(21)$$

Note that g^2 is inversely proportional to the phonon energy $\omega_{p-p'}$, so that the first moment of $\alpha^2(\omega)F(\omega)$ is independent of the phonon frequencies:

$$\int_0^\infty d\omega\,\omega\alpha^2(\omega)F(\omega)=\int\frac{d^2p}{v_F}\int\frac{d^2p'}{(2\pi)^2v_{F'}}\sum_\nu\frac{\hbar}{2MNV}\mathcal{g}_\nu{}^2(pp')\Big/\int\frac{d^2p}{v_F}$$
$$=\frac{N(0)\hbar\langle\mathcal{g}^2\rangle}{2M}.\qquad(22)$$

[13] Y. Nakagawa and A. D. B. Woods, Phys. Rev. Letters 11, 271 (1963).
[14] J. M. Ziman, *Electrons and Phonons* (Oxford University Press, London, 1960), p. 182.

Here $\langle g^2\rangle$ is the average over the Fermi surface of the square of the electronic matrix element (21). Finally, from the definition of λ, we have

$$\lambda=2\int\frac{d\omega\,\alpha^2(\omega)F(\omega)}{\omega}=\frac{N(0)\langle g^2\rangle}{M\langle\omega^2\rangle},\qquad(23)$$

where $\langle\omega^2\rangle$ is an average of the square of the phonon frequency:

$$\langle\omega^2\rangle=\int d\omega\,\omega\alpha^2(\omega)F(\omega)\Big/\int\frac{d\omega\,\alpha^2(\omega)F(\omega)}{\omega}$$

$$\cong\int d\omega\,\omega F(\omega)\Big/\int\frac{d\omega\,F(\omega)}{\omega}\qquad(24)$$

The transition temperature (18) depends on the isotopic mass[6,15] directly through the factor Θ and implicitly through the ω_0 dependence of μ^*. Using (18) and (13), we find $T_c\propto M^{-\alpha}$, with

$$\alpha=\frac{1}{2}\left(1-\frac{(1+\lambda)(1+0.62\lambda)\mu^{*2}}{[\lambda-\mu^*(1+0.62\lambda)]^2}\right)$$

$$=\frac{1}{2}\left[1-\left(\mu^*\ln\frac{\Theta}{1.45T_c}\right)^2\frac{1+0.62\lambda}{1+\lambda}\right],\qquad(25)$$

which differs very little from the weak-coupling result.

The velocity of electrons near the Fermi surface is renormalized by the electron-phonon interaction. To see this, we find the self-energy for electrons in the normal state [Eq. (2a)] for $T=0$ and $\omega\ll\omega_0$:

$$\xi(\omega)\cong-\lambda\omega.\qquad(26)$$

The energy of the electronic excitations is determined from the poles of the Green's function, or from

$$\omega-\epsilon_k-\xi(\omega)=0,\qquad(27)$$

where ϵ_k is the energy of the Bloch state (measured from the Fermi energy) with momentum k. Substituting

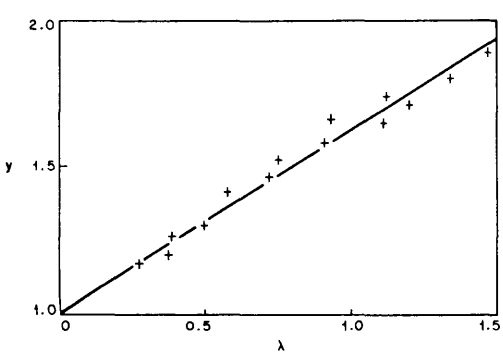

FIG. 2. The quantity y defined in Eq. (17) versus λ; the straight-line fit determines the third parameter (0.62) in the theoretical formula [Eq. (18)].

[15] J. W. Garland, Jr., Phys. Rev. Letters **11**, 114 (1963).

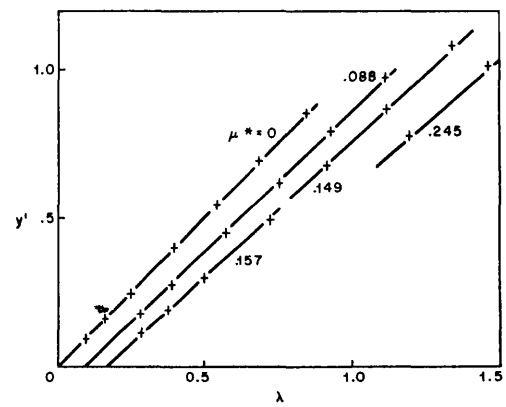

FIG. 3. The quantity $y'=1.04(1+\lambda)/\ln(\Theta/1.45T_c)$ versus λ according to (+++), the computer program, and (——), the analytic formula [Eq. (18)], demonstrating that the analytic formula does fit the numerical results.

(26) into (27), we find for the energy ω of the elementary excitation,

$$\omega=\epsilon_k/(1+\lambda).\qquad(28)$$

The electronic heat-capacity coefficient γ,[2,16] the cyclotron masses,[17,18], and the Fermi velocity measured in the Tomash-Rowell experiments[19–22] are all renormalized by the factor $(1+\lambda)$.

This completes the theoretical portion of the paper, and we will summarize the results. Our central result is Eq. (18), which expresses T_c in terms of a characteristic phonon energy Θ, the electron-phonon coupling constant λ, and the Coulomb "pseudopotential" μ^*. This formula was derived from accurate numerical solutions of the integral equations of the (accurate) theory of superconductivity with, however, a special assumption about the shape of the phonon density of states. The superconductor was assumed to be isotropic, but this is not a serious approximation. The definitions of λ and μ^* in terms of the basic metallic properties are given in Eqs. (23) and (13). Several observable properties of the metal are modified from their "band-structure" values by the electron-phonon interaction. The velocity of electrons near the Fermi surface is reduced by the factor $(1+\lambda)$; this velocity is measured in the Tomash-effect experiments. The electronic heat capacity and cyclotron mass are enhanced by the factor $(1+\lambda)$. The cyclotron-mass enhancement is in fact anisotropic

[16] G. M. Eliashberg, Zh. Eksperim. i Teor. Fiz. **43**, 1005 (1962) [English transl.: Soviet Phys.—JETP **16**, 780 (1963)].
[17] S. Nakajima and M. Watabe, Progr. Theoret. Phys. (Kyoto) **30**, 271 (1963).
[18] R. E. Prange and L. P. Kadanoff, Phys. Rev. **134**, A566 (1964).
[19] W. J. Tomasch, Phys. Rev. Letters **15**, 672 (1965); **16**, 16 (1966).
[20] W. L. McMillan and P. W. Anderson, Phys. Rev. Letters **6**, 85 (1966).
[21] W. J. Tomasch and T. Wolfram, Phys. Rev. Letters **16**, 352 (1966).
[22] J. M. Rowell and W. L. McMillan, Phys. Rev. Letters **16**, 453 (1966).

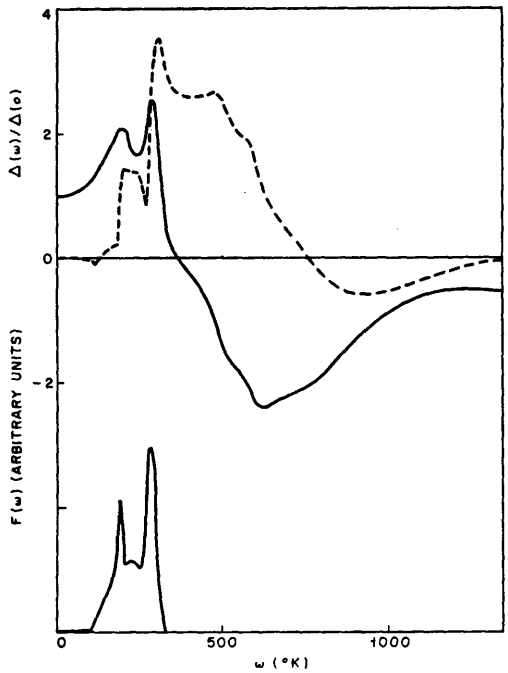

FIG. 4. The real (——) and imaginary (- - -) parts of the energy-gap function versus energy at the transition temperature for parameters (T_c=10°K, λ=0.91, μ^*=0.149) corresponding roughly to niobium, together with the phonon density of states for niobium used in the calculations.

and will vary from orbit to orbit; λ is an isotropically averaged quantity, and $(1+\lambda)$ gives an average enhancement factor. The strong-coupled formula (25) for the isotope shift was obtained directly from (18) and (13), and is numerically very close to the weak-coupling result.

IV. EMPIRICAL RESULTS

We begin now the empirical portion of the paper, making use of the theoretical equations and experimental results to extract the coupling constants λ and μ^*. We first determine μ^* for those few metals for which the isotope shift has been measured. Then, taking reasonable values of μ^* for the other metals, we will find empirical values of λ from T_c and Θ. Finally, we use these empirical numbers for λ to estimate the "phonon enhancement" of the electronic heat capacity γ and deduce from the measured γ the bare or "band-structure" electronic density of states at the Fermi energy.

Neglecting the "strong-coupling" correction $(1+0.62\lambda)/(1+\lambda)$ in Eq. (25), we find an expression for the Coulomb pseudopotential μ^* in terms of the isotope-shift coefficient α, the transition temperature, and the Debye Θ:

$$\mu^*=(1-2\alpha)^{1/2}/\ln(\Theta/1.45T_c). \qquad (29)$$

The experimental values of α, T_c, and Θ are given in Table II, together with the empirical value of μ^* obtained using Eq. (29). For the transition metals, we see that there is some variation about the average value of $\mu^*=0.13$. The higher T_c transition metals have higher densities of states and smaller effective bandwidths, and somewhat larger values of μ^* are appropriate. However, for these metals, μ^* is less important relative to λ, and we take below the value 0.13 for all transition metals. For the nearly-free-electron metals, the theoretical estimate $\mu^*=0.1$ is reasonable, and this is confirmed by the empirical μ^* for zinc.

Next, we rewrite Eq. (18) in a convenient form for finding an empirical electron-phonon coupling constant λ from the experimentally determined transition temperature T_c and Debye Θ:

$$\lambda=\frac{1.04+\mu^*\ln(\Theta/1.45T_c)}{(1-0.62\mu^*)\ln(\Theta/1.45T_c)-1.04}. \qquad (30)$$

Here we use $\mu^*=0.13(0.1)$ for the transition (polyvalent) metals. The experimental T_c and Θ are listed in Table III for the superconducting metals, together with the empirical coupling constant λ found using Eq. (30). The coupling constant found in this way is reliable for weak and intermediate coupling strengths $\lambda<1$. However, for the strong-coupled case $\lambda>1$, the resulting λ is sensitive to the details of the phonon spectrum, and it is desirable to have more information about the phonon density of states than just the Debye Θ. For lead, where the phonon density of states is known from the analysis of the tunneling experiments to be quite similar to that for niobium, Eq. (30) works reasonably well; the coupling constant deduced from the tunneling data is 1.3, and Eq. (30) yields 1.1. For mercury, however, the tunneling experiment yields a phonon spectrum quite different from niobium, and Eq. (30) fails; the tunneling experiment gives $\lambda=1.6$, whereas Eq. (30)

TABLE II. Empirical values of the Coulomb pseudopotential μ^* found from the isotope shift α, T_c, and Θ using Eq. (29).

Metal	α	T_c (°K)	Θ (°K)	μ^*	Reference
Zr	0.00±0.05	0.55	290	0.17	a
Mo	0.37±0.04	0.92	460	0.09	b
Re	0.38	1.69	415	0.10	c
Ru	0.0±0.15	0.49	550	0.15	d, e
Os	0.21	0.65	500	0.12	e
Zn	0.30±0.01	0.85	309	0.12	f

[a] E. Bucher, J. Muller, J. L. Olsen, and C. Palmy, Phys. Letters 15, 303 (1965).
[b] B. T. Matthias, T. H. Geballe, E. Corenzwit, and G. W. Hull, Jr., Phys. Rev. 129, 1025 (1963); E. Bucher and C. Palmy, Phys. Letters 24A, 340 (1967).
[c] E. Maxwell, Rev. Mod. Phys. 36, 144 (1964).
[d] T. H. Geballe, B. T. Matthias, G. W. Hull, Jr., and E. Corenzwit, Phys. Rev. Letters 6, 275 (1961); D. K. Finnemore and D. E. Mapother, *ibid.* 9, 288 (1962); J. W. Gibson and R. A. Hein, Phys. Rev. 141, 407 (1966).
[e] T. H. Geballe and B. T. Matthias, IBM J. Res. Develop. 6, 256 (1962); R. A. Hein and J. W. Gibson, Phys. Rev. 131, 1105 (1963).
[f] R. E. Fassnacht and J. R. Dillinger, Phys. Rev. Letters 17, 255 (1966).

TABLE III. Empirical values of the electron-phonon coupling constant λ and the "band-structure" density of states $N_{bs}(0)$ found from T_c, Θ, and γ for the superconducting metals.

Element	T_c (°K)	Θ (°K)	γ (mJ/mole °K^2)	λ	$N_{bs}(0)$ (states/eV atom)	$N_{bs}(0)/N_{fe}(0)$	Reference
Be	0.026	1390	0.184	0.23	0.032	0.31	a, b
Al	1.16	428	1.35	0.38	0.208	1.08	c
Zn	0.85	309	0.64	0.38	0.098	0.61	d
Ga	1.08	325	0.60	0.40	0.091	0.46	e
Cd	0.52	209	0.69	0.38	0.106	0.53	e
In	3.40	112	1.69	0.69	0.212	0.89	f
Sn	3.72	200	1.80	0.60	0.238	0.82	g
Hg	4.16	72	1.79	1.00	0.146*	0.70	h
Tl	2.38	79	1.47	0.71	0.182	0.66	h
Pb	7.19	105	3.00	1.12	0.276*	0.87	i
Ti	0.39	425	3.32	0.38	0.51		j, k
V	5.30	399	9.9	0.60	1.31		j, k
Zr	0.55	290	2.78	0.41	0.42		j, k
Nb	9.22	277	7.8	0.82	0.91		k
Mo	0.92	460	1.83	0.41	0.28		j, k
Ru	0.49	550	3.0	0.38	0.46		j, k
Hf	0.09	252	2.16	0.34	0.34		l, k
Ta	4.48	258	6.0	0.65	0.77		j, k
W	0.012	390	0.90	0.28	0.15		m, k
Re	1.69	415	2.3	0.46	0.33		j, k
Os	0.65	500	2.3	0.39	0.35		j, k
Ir	0.14	420	3.2	0.34	0.51		j, k

[a] R. L. Falge, Jr., Phys. Letters 24, 579 (1967).
[b] E. Gmelin, Compt. Rend. 259, 3459 (1964).
[c] Norman E. Phillips, Phys. Rev. 114, 676 (1959).
[d] G. Seidel and P. H. Keesom, Phys. Rev. 112, 1083 (1958).
[e] Norman E. Phillips, Phys. Rev. 134, A385 (1964).
[f] H. R. O'Neal and N. E. Phillips, Phys. Rev. 137, A748 (1965).
[g] C. A. Bryant and P. H. Keesom, Phys. Rev. 123, 491 (1961).
[h] B. J. C. van der Hoeven, Jr., and P. H. Keesom, Phys. Rev. 135, A631 (1964).
[i] B. J. C. van der Hoeven, Jr., and P. H. Keesom, Phys. Rev. 137, A103 (1965).
[j] B. W. Roberts, *Progress in Cryogenics* (Heywood and Co., Ltd., London, 1964).
[k] F. Heininger, E. Bucher, and J. Muller, Physik Kondensierten Materie 5, 243 (1966).
[l] K. Andres (private communication).
[m] R. T. Johnson, O. E. Vilches, J. C. Wheatley, and S. Gygax, Phys. Rev. Letters 16, 101 (1966).

gives $\lambda=1.0$. The point is that whenever Eq. (30) yields a coupling constant greater than 1 and there is no information available for the phonon density of states, the results should be treated with some caution.

The electronic heat-capacity coefficient γ is proportional to the electronic density of states at the Fermi surface (the "band-structure" density of states) times the enhancement factor $(1+\lambda)$ from the electron-phonon interaction. If λ and γ are known, we can find the band-structure density of states $N_{bs}(0)$:

$$N_{bs}(0)=3\gamma/2\pi^2k_B^2(1+\lambda). \tag{31}$$

Strictly speaking, $N_{bs}(0)$ contains the enhancement due to the Coulomb interactions between electrons. In Table III are listed the experimental heat capacity γ and the empirical electronic density deduced from Eq. (31) and the empirical coupling constant λ.[23] For lead and mercury, we have used the λ found from the tunneling experiments. For the polyvalent metals, we list the ratio of $N_{bs}(0)$ to the electronic density of states at the Fermi surface from the free-electron model

$$N_{fe}(0)=\tfrac{3}{4}(Z/E_F), \tag{32}$$

where Z is the valence and E_F the Fermi energy.

[23] J. W. Garland, Jr., has performed a similar service (to be published).

This procedure for extracting the band-structure density of states is particularly interesting when the experimental data (T_c, Θ, γ) are available for a series of alloys with the same crystal structure. Consider the bcc alloy system Ta–W. According to the rigid-band model, which seems quite reasonable for the alloy systems considered here, the band structures of Ta and W are very similar, and in alloying from Ta to W, one is merely increasing the Fermi energy so that the volume contained in the Fermi surface increases from 5 electrons/atom to 6 electrons/atom. Using the same procedure described in the above paragraphs for metals, we can find the band-structure density of states at the Fermi energy for each alloy and plot out the band-structure density of states as a function of either electron/atom ratio or energy. It is quite reasonable to compare this empirical density of states versus energy curve with that calculated from the computed band structure of either Ta or W. There are sufficient data available to construct the density of states versus electron/atom ratio for four alloy series of the transition metals.

(1) $N_{bs}(0)$ for the bcc $3d$ transition-metal alloys of Ti–V and V–Cr are given in Table IV and plotted in Fig. 5. The V–Cr alloys with more than 60% Cr are not superconducting above 0.025°K, and the coupling con-

TABLE IV. Empirical values of λ and $N_{bs}(0)$ found from T_c, Θ, and γ for the bcc $3d$ transition-metal alloys and for "paramagnetic" chromium. The values of λ in parentheses were obtained by extrapolation.

Alloy	% second metal	T_c (°K)	Θ (°K)	γ (mJ/mole °K²)	λ	$N_{bs}(0)$ (states/ eV atom)	Reference
TiV	20	3.5		6.9	0.54	0.95	a
	30	6.14		10.0	0.62	1.31	a
	50	7.30		10.8	0.65	1.39	a
	75	7.16		10.6	0.65	1.36	a
	85	7.02		10.3	0.65	1.32	a
VCr	10	3.21	370	8.15	0.53	1.13	b
	20	1.90	400	7.15	0.48	1.02	b
	25	1.36	425	6.75	0.45	0.99	b
	40	0.37	450	5.4	0.38	0.83	b
	50	0.10	470	4.85	0.33	0.77	b
	60	<0.025		4.0	(0.28)	0.67	b
	80			2.1	(0.20)	0.37	c
	90			2.07	(0.20)	0.37	c
	94.5			2.33	(0.20)	0.41	c
"Cr"				2.9	(0.25)	0.49	c

[a] C. H. Cheng, K. P. Gupta, E. C. van Reuth, and P. A. Beck, Phys. Rev. 127, 2030 (1962).
[b] K. Andres and E. Bucher (private communication).
[c] F. Heiniger, Physik Kondensierten Materie 5, 285 (1966).

stants are found by extrapolation. The γ value for Cr is that for "paramagnetic" Cr found by extrapolating the γ for paramagnetic Mo–Cr alloys.

(2) The most complete data are for the bcc $4d$ transition-metal alloys of Zr–Nb, Nb–Mo, and Mo–Tc (Table V and Fig. 6). We have used, in addition, the $4d$–$5d$ alloys of Mo–Re which should give $N_{bs}(0)$ values reasonably close to Mo–Tc. Heiniger *et al.*[24] have noted that the γ values for Zr–Rh alloys appear to lie on the same curve as for the Zr–Nb alloys, and we have in-

TABLE V. Empirical values of λ and $N_{bs}(0)$ found from T_c, Θ, and γ for the bcc $4d$ transition-metal alloys.

Alloy	% second metal	T_c (°K)	Θ (°K)	γ (mJ/mole °K²)	λ	$N_{bs}(0)$ (states/ eV atom)	Reference
ZrNb	50	9.3	238	8.3	0.88	0.93	a
	75	10.8	246	8.9	0.93	0.98	a
NbMo	15	5.85	265	6.3	0.70	0.79	b
	40	0.60	371	2.87	0.41	0.43	b
	60	0.05	429	1.62	0.31	0.26	b
	70	0.016	442	1.46	0.29	0.24	b
	80	0.095	461	1.49	0.33	0.24	b
	90	0.30	487	1.67	0.36	0.26	b
MoRe	5	1.5	450	2.2	0.45	0.32	c
	10	2.9	440	2.6	0.51	0.36	c
	20	8.5	420	3.8	0.68	0.48	c
	30	10.8	395	4.1	0.76	0.49	c
	40	12.6	340	4.4	0.86	0.50	c
	50	11.5	320	4.4	0.85	0.50	c
MoTc	50	12.6	300	4.6	0.91	0.51	c
ZrRh	3	3.1	244	3.62	0.59	0.48	d
	4	3.8	226	3.83	0.64	0.50	d
	5	4.8	210	5.08	0.70	0.63	d
	6	5.75	196	6.80	0.78	0.81	d
	7	5.95	192	7.36	0.80	0.87	d

[a] F. Heiniger, E. Bucher, and J. Muller, Physik Kondensierten Materie 5, 243 (1966); R. D. Blangher, J. K. Hulm, J. A. Rayne, B. W. Veal, and R. A. Hein, in *Proceedings of the Eighth International Conference on Low-Temperature Physics, London, 1962*, edited by R. O. Davies (Butterworths Scientific Publications, Ltd., London, 1963).
[b] B. W. Veal and J. K. Hulm, Ann. Acad. Sci. Fennicae A210, 108 (1966).
[c] F. J. Morin and J. P. Maita, Phys. Rev. 129, 1115 (1963).
[d] G. Dummer, Z. Physik 186, 249 (1965).

[24] F. Heiniger, E. Bucher, and J. Muller, Physik Kondensierten Materie 5, 243 (1966).

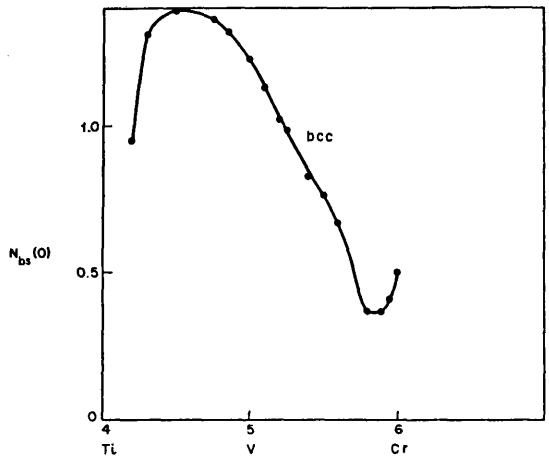

FIG. 5. The band-structure density of states versus electron/atom ratio for the bcc $3d$ transition-metal alloys from the data in Tables III and IV.

cluded those data as well, although it is by no means clear that the rigid-band model is valid for alloys of metals whose valence differs by 5.

(3) The values of $N_{bs}(0)$ for the bcc $5d$ alloys of Hf–Ta, Ta–W, and W–Re, as well as the hcp $5d$ alloys of W–Re and Re–Os, are given in Table VI and plotted in Fig. 7. Again it is necessary to interpolate for λ where the T_c has not been measured. The densities of states of the three bcc alloy series are similar, exhibiting a peak for electron/atom ratio $n=4.5$, a deep minimum near $n=5.8$, and a shoulder at $n=6.2$. Figure 8 shows a plot of the electron-phonon coupling constant λ versus electron/atom ratio, and Fig. 9 gives λ plotted versus density of states for these alloy series.

It is most interesting at this point to compare our empirical results with the theoretical density of states

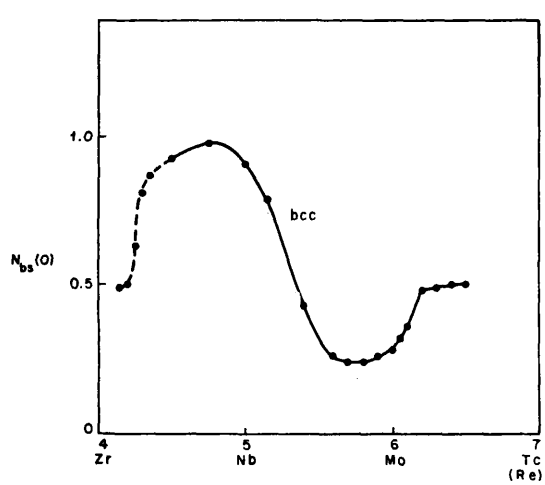

FIG. 6. The band-structure density of states versus electron/atom ratio for the bcc $4d$ transition-metal alloys from the data in Tables III and V.

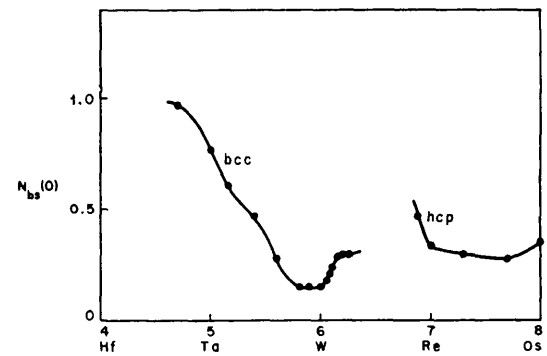

FIG. 7. The band-structure density of states versus electron/atom ratio for the bcc and hcp $5d$ transition-metal alloys from the data in Tables III and VI.

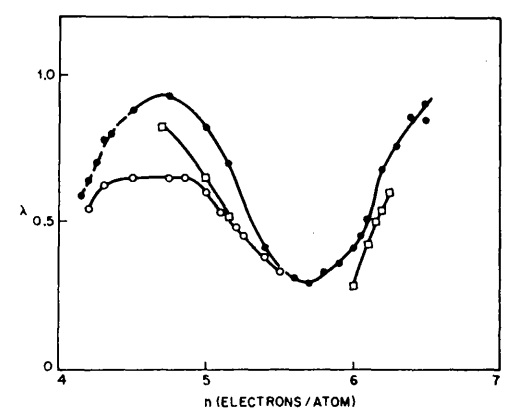

FIG. 8. The empirical electron-phonon coupling constant versus electron/atom ratio for the bcc $3d$ (○○○), $4d$ (●●●), and $5d$ (□□□) transition-metal alloys from the data in Tables III–VI.

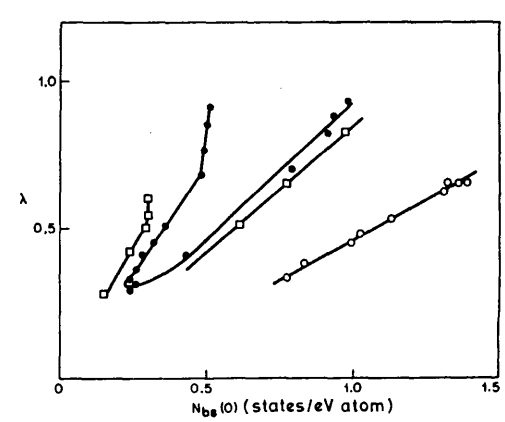

FIG. 9. The empirical electron-phonon coupling constant versus the band-structure density of states for the bcc $3d$ (○○○), $4d$ (●●●), and $5d$ (□□□) transition-metal alloys from the data in Tables III–IV.

TABLE VI. Empirical values of λ and $N_{bs}(0)$ found from T_c, Θ, and γ for the bcc (*hcp) 5*d* transition-metal alloys. The values of λ in parentheses were obtained by interpolation.

Alloy	% second metal	T_c (°K)	Θ (°K)	γ (mJ/mole °K²)	λ	$N_{bs}(0)$ (states/ eV atom)	Reference
Hf–Ta	70	6.81	209	8.30	0.82	0.97	a, b
Ta–W	16	1.85	265	4.36	0.51	0.61	a, b
	40		291	3.08	(0.39)	0.47	a
	60		317	1.63	(0.25)	0.28	a
	80		354	0.88	(0.26)	0.15	a
	90		368	0.92	(0.27)	0.15	a
W–Re	5		380	1.14	(0.32)	0.18	a
	7.5		378	1.40	(0.38)	0.21	a
	10	0.7	375	1.63	0.42	0.24	a, b
	15	2.26	365	2.10	0.50	0.29	a, b
	20	3.20	359	2.20	0.54	0.30	a, b
	25	4.64	351	2.30	0.60	0.30	a, b
W–Re*	88	7.47	332	3.76	0.70	0.47	a, b
Re–Os*	30	1.45	351	2.05	0.47	0.30	a, b
Re–Os*	70		382	1.86	(0.42)	0.28	a

[a] E. F. Bucher, F. Heiniger, and J. Muller, in *Proceedings of the Ninth International Conference on Low-Temperature Physics, Columbus, Ohio,* edited by J. A. Daunt *et al.* (Plenum Press, Inc., New York, 1965), p. 1059.
[b] E. Bucher (private communication).

from band-structure calculations. Matthies[25] has calculated the band structure of tungsten using the augmented plane-wave (APW) method for two potentials (labeled W_1 and W_2), and has computed the electronic density of states versus energy. Figure 10 shows the theoretical density of states for potential W_2, together with the empirical density of states (solid circles) for the Hf–Ta–W–Re alloys from Tables III and VI. For the empirical data, the energy was determined from the electron/atom ratio, using the theoretical curve (dotted line of Fig. 10). As can be seen in Fig. 10, the agreement between the theoretical and empirical densities of states is excellent for this potential (W_2). The *d* band is about 25% narrower for potential W_1 than for W_2, and the density of states correspondingly higher. The shoulder at $n=6.15$ (Fig. 7) or at $E=1.17$ Ry (Fig. 10) is a critical point and can probably be identified with the saddle point in the Matthies band structure about half-way between the symmetry points H and N and lying just above the tungsten Fermi energy.

Matthies[26] has also computed the band structure and electronic density of states for hcp rhenium using the relativistic APW method. The theoretical density of states is in good agreement with the empirical data for the hcp W-Re-Os alloys (see Fig. 5 of Ref. 26).

V. ELECTRON-PHONON COUPLING CONSTANT

Having found empirical values of the electron-phonon coupling constant λ for a number of metals and alloys, we now wish to investigate the dependence of the coupling constant on the various metallic properties.

[25] L. F. Matthies, Phys. Rev. 139, A1893 (1965).
[26] L. F. Matthies, Phys. Rev. 151, 450 (1966).

A. Empirical Results

According to Eq. (23), in order to calculate the coupling constant, we need to know the electronic density of states $N_{bs}(0)$, an average phonon frequency $\langle\omega\rangle$, and an average squared electronic matrix element, $\langle\mathcal{I}^2\rangle$. The least accessible of these quantities is the last, $\langle\mathcal{I}^2\rangle$, and we will first adopt the empirical approach and determine $\langle\mathcal{I}^2\rangle$ from the experimental data for λ, $N(0)$, and $\langle\omega\rangle$. For this purpose the Debye Θ does not provide a sufficiently reliable estimate of the average phonon frequency, and we must restrict this discussion to those metals for which neutron scattering or electron tunneling measurements of the phonon frequencies are available. The phonon density of states of Nb (Fig. 4) is typical for fcc and bcc lattices, and for that case the average phonon frequency [Eq. (24)] is approximately the mean of the frequencies of the longitudinal and transverse peaks. In Table VII we give the average phonon frequency found in this way, together with the empirical λ and $N(0)$ values from Table III for the bcc transition metals, three polyvalent metals, and V_3Si. From these three empirical quantities, we find the empirical values for $\langle\mathcal{I}^2\rangle$ given in Table VII by rewriting Eq. (23)

$$\langle\mathcal{I}^2\rangle=[\lambda M\langle\omega^2\rangle/N(0)]. \tag{33}$$

Dimensionally, $\mathcal{I}$ is an electronic quantity with units of energy/length. The characteristic energy—the electronic-bandwidth or Fermi energy—is of the order of a few electron volts, and the characteristic length is the lattice spacing, a few angstroms; we expect $\mathcal{I}$ to be a few eV/Å, as observed. Note that for the bcc transition metals, $N(0)\langle\mathcal{I}^2\rangle$ (Table VII) is constant $\sim$7 eV/Å² within experimental uncertainty, even though $N(0)$ and

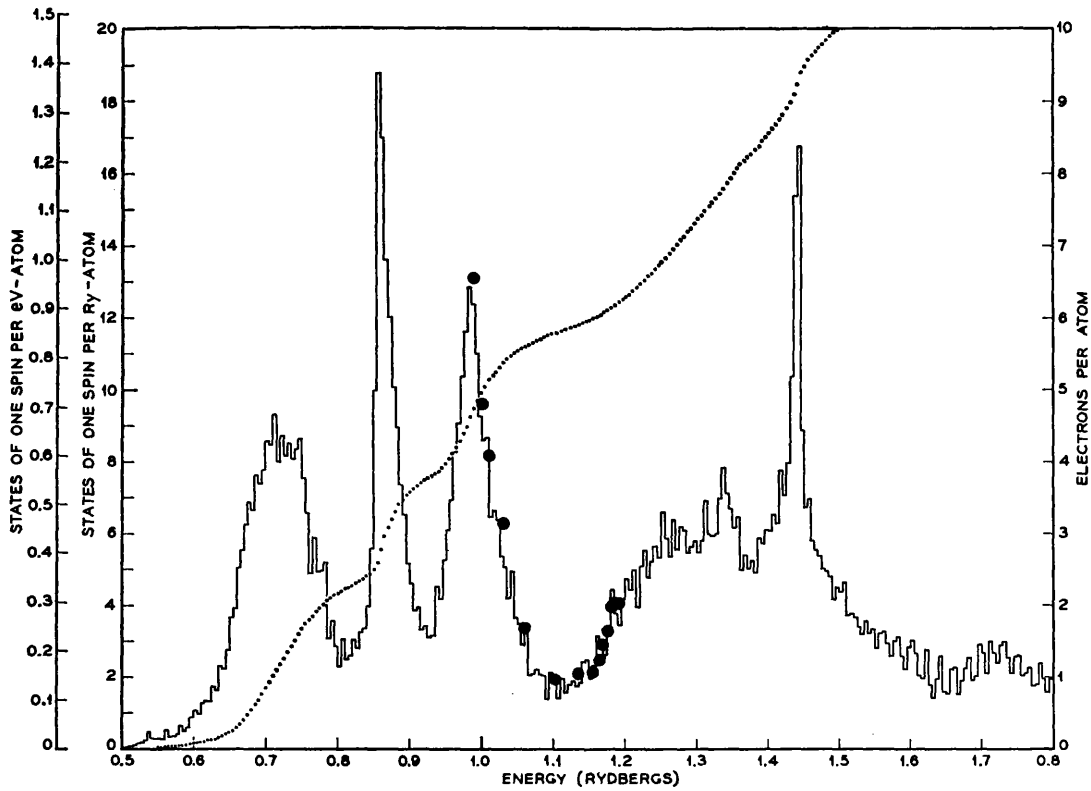

FIG. 10. The theoretical band-structure density of states versus energy for tungsten according to Matthies (Ref. 25), together with the empirical (solid-circles) data for the bcc 5*d* alloys from Tables III and VI.

$\langle g^2 \rangle$ individually vary by a factor of 10 [for vanadium $N(0)\langle g^2 \rangle$ is somewhat low, but the uncertainty in $\langle g^2 \rangle$ because of the uncertainty in $\langle \omega \rangle$ is greater]. This is a remarkable result: We find empirically that for this class of materials, the electronic factor $N(0)\langle g^2 \rangle$ remains constant and that the coupling constant (or transition temperature) is governed by the phonon factor $M\langle \omega^2 \rangle$ or by the stiffness of the lattice. This is in marked contrast to the statement that is usually made—that the coupling constant (or transition temperature) is

TABLE VII. Empirical values of the average electronic matrix element $\langle g^2 \rangle$ found from λ, $N_{bs}(0)$, and $\langle \omega^2 \rangle^{1/2}$ using Eq. (33). The T_c, Θ, and γ values are taken from Table III.

Metal	(°K)	T_c (°K)	γ (mJ/mole °K²)	λ	$N_{bs}(0)$ (states/eV atom)	$\langle \omega^2 \rangle^{1/2}$ (°K)	$\langle g^2 \rangle$ (eV² Å⁻²)	$N(0)\langle g^2 \rangle$ (eV Å⁻²)	Reference
V	5.30	399	9.9	0.60	1.31	290	3.5	4.6	a
Nb	9.22	277	7.8	0.82	0.91	230	7.9	7.2	b
Ta	4.48	258	6.0	0.65	0.77	170	7.9	6.1	c
Mo	0.92	460	1.83	0.41	0.275	310	24.6	6.8	d
W	0.012	390	0.90	0.29	0.148	250	42.5	6.3	e
Al	1.16	428	1.35	0.38	0.206	330	9.7	2.0	f
In	3.40	112	1.69	0.71	0.21	110	8.4	1.76	g
Pb	7.19	105	3.00	1.12	0.300	75	7.8	2.34	h, i
V_3Si	17	520	21[j]	0.82	2.33[j]	390	4.9	11.3	k, l

[a] K. C. Tuberfield and P. A. Engelstaff, Phys. Rev. **127**, 1017 (1962).
[b] Y. Nakagawa and A. D. B. Woods, Phys. Rev. Letters **11**, 271 (1963).
[c] A. D. B. Woods, Phys. Rev. **136**, A781 (1964).
[d] A. D. B. Woods, and S. H. Shen, Solid State Commun. **2**, 223 (1964).
[e] S. H. Shen and B. N. Brockhouse, Solid State Commun. **2**, 73 (1964).
[f] R. Stedman and G. Nilsson, Phys. Rev. **145**, 492 (1966).
[g] J. M. Rowell and W. L. McMillan (to be published).
[h] B. N. Brockhouse, T. Arase, G. Caglioti, K. R. Rao, and A. D. B. Woods, Phys. Rev. **128**, 1099 (1962).
[i] W. L. McMillan and J. M. Rowell, Phys. Rev. Letters **14**, 108 (1965).
[j] Per vanadium atom rather than per molecule.
[k] J. E. Kunzler, J. P. Maita, H. J. Levinstein, and E. J. Ryder, Phys. Rev. **143**, 390 (1966).
[l] Bernard Mozer (private communication).

governed by the electronic density of states, being given by $\lambda = N(0)V_{\rm ph}$, with $V_{\rm ph}$ reasonably constant. The coupling-constant variation is certainly correlated with the density-of-states variation, but only because the high-density-of-states materials are elastically softer. We have at present no theoretical explanation of this fact; we have only the empirical observation for these five bcc transition metals.

B. Theory for the Simple Metals

For the polyvalent metals (e.g., Al, In, Pb), the pseudopotential theory[27–29] enables one to calculate all the properties of the metal from a knowledge of the electron-ion pseudopotential. One can calculate the Fermi surface, the electron-phonon matrix elements, and the phonon frequencies. We do not intend to perform detailed calculations here, but rather we will discuss how the coupling constant depends on the pseudopotential, and will obtain some rather simple results.

Within the pseudopotential model, the Hamiltonian of the metal is the sum of (1) the kinetic energy of the electrons, (2) the Coulomb interaction between electrons, (3) the kinetic energy of the bare ions, (4) the Coulomb interaction between ions, and (5) the bare electron-ion interaction given by the pseudopotential $V(R_i - r_e)$. This bare atomic pseudopotential is screened by the conduction electrons, and in momentum space the screened potential is just v_q/ϵ_q, where v_q is the Fourier transform of the bare pseudopotential, and ϵ_q is the dielectric constant. With the atoms located on the lattice sites, the crystal potential is just the sum over lattice sites of this screened potential, and the Fermi surface is determined by the values of v_q/ϵ_q at the reciprocal lattice vectors. For the metals of interest, one finds a Fermi surface distorted slightly from the free-electron sphere, and for this discussion we neglect this distortion and take the wave functions to be plane waves. The electron-phonon matrix elements are now readily calculated from Eqs. (20) and (21). We find

$$g_\nu(p, p') = i(\mathbf{p}-\mathbf{p}')\cdot\epsilon_{p-p',\nu} v_{p-p'}, \tag{34}$$

and, average g^2 over the spherical Fermi surface, we find

$$\langle g^2\rangle = \sum_\nu \int_0^{2k_F} (\epsilon_{q\nu}\cdot q)^2 v_q^2 q\,dq \Big/ \int_0^{2k_F} q\,dq$$
$$= \tfrac{8}{9}k_F^2 E_F^2 \langle v_q^2\rangle, \tag{35}$$

where E_F and k_F are the Fermi energy and wave number, and we have defined a dimensionless average of the pseudopotential squared

$$\langle v_q^2\rangle \equiv \int_0^{2k_F} v_q^2 q^3 dq \Big/ \int_0^{2k_F} v_0^2 q^3 dq. \tag{36}$$

For the free-electron gas, the density of states of one spin per atom is

$$N(0) = 3Z/4E_F, \tag{37}$$

where Z is the valence of the ion. Finally, expressing the average phonon frequency in units of the ionic plasma frequency

$$\Omega_p^2 = 4\pi N Z^2 e^2/M, \tag{38}$$

we find an expression for the coupling constant

$$\lambda = N(0)\langle g^2\rangle / M\langle\omega^2\rangle$$
$$= \tfrac{1}{2}\pi \frac{E_F}{k_F e^2} \frac{\langle v_q^2\rangle}{(\langle\omega^2\rangle/\Omega_p^2)}. \tag{39}$$

The factor $E_F/k_F e^2$ is just $0.96/r_s$, where r_s is the radius in atomic units of a sphere containing one electron. We find a simple expression for the electron-phonon coupling constant for a nearly-free-electron metal, involving a dimensionless average of the pseudopotential and a dimensionless phonon frequency:

$$\lambda = \frac{1.51}{r_s} \frac{\langle v_q^2\rangle}{(\langle\omega^2\rangle/\Omega_p^2)}. \tag{40}$$

For lead, the tunneling experiments[9] yield the values $\langle\omega^2\rangle/\Omega_p^2 = 0.02$ and $\langle v_q^2\rangle = 0.04$.

Within the pseudopotential model, the phonon frequencies are also determined by the pseudopotential. One starts with a calculation of the phonon frequencies Ω_p of the bare ions and then subtracts the electronic contribution $E_{\rm bs}^2$, which is proportional to $v_q^2(1-1/\epsilon_q)$:

$$\omega_q^2 = \Omega_q^2 - E_{\rm el}^2. \tag{41}$$

The point that we wish to make here is that for the polyvalent metals, there is a large cancellation between the ionic term Ω_p^2 and the electronic term $E_{\rm el}^2$ so that the observed phonon frequencies are extremely sensitive to small changes in $E_{\rm el}^2$ or in the pseudopotential (for lead, the observed ω_q^2 are about $\frac{1}{10}$ of the ionic term Ω_p^2 at the zone boundary). The important dependence of the coupling constant λ upon the pseudopotential arises from the $\langle\omega^2\rangle$ term in the denominator of Eq. (40), rather than from the $\langle v_q^2\rangle$ in the numerator. Thus, for the polyvalent metals, the pseudopotential theory predicts that the coupling constant varies inversely with the (dimensionless) phonon frequency squared:

$$\lambda \cong C/(\langle\omega^2\rangle/\Omega_p^2), \tag{42}$$

[27] J. C. Phillips and L. Kleiniman, Phys. Rev. **116**, 287 (1959).
[28] B. J. Austin, V. Heine, and L. J. Sham, Phys. Rev. **127**, 276 (1962).
[29] W. A. Harrison, Phys. Rev. **126**, 497 (1962); *Pseudopotentials in the Theory of Metals* (W. A. Benjamin, Inc., New York, 1966).

or, more approximately,

$$\lambda \approx C'/M\langle\omega^2\rangle. \tag{43}$$

From Table VII we see that $C'=N(0)\langle g^2\rangle$ is constant within experimental accuracy for Al, In, and Pb.

To conclude this section, we (1) observe empirically that for a given class (bcc) of transition metals the coupling constant is equal to a constant divided by the ionic mass times the average phonon frequency squared, and (2) show theoretically for the polyvalent metals that this should be the case.

VI. MAXIMUM T_c

For a number of years the highest observed superconducting transition temperature has been 18°K,[30] the "Matthias limit." There has been a great interest, possibly for technological reasons, in the search for higher T_c materials. Recently Matthias *et al.*[31] have found superconductivity at 20°K in a solid solution of Nb_3Al and Nb_3Ge. In that paper the authors state that "there is no theory whatsoever for high transition temperatures of a superconductor." In this section we discuss an upper limit for the transition temperature of a given class of materials.

The strong-coupled theory of superconductivity will predict accurately the transition temperature of a metal from its fundamental properties. The difficulty in trying to predict a maximum T_c is that one does not have an accurate theory of metals from which to calculate the band structure, the phonon spectrum, etc. We can, however, make use of the observation of the preceding section that, within a given class of materials, the coupling constant depends mainly on the phonon frequencies. Given the freedom to adjust the phonon spectrum and therefore the coupling constant, say, by alloying, we show here that T_c has a maximum value.

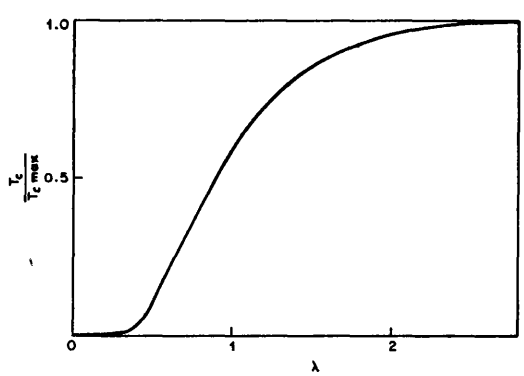

FIG. 11. The superconducting transition temperature according to Eq. (18) with $\mu^*=0.13$, assuming that the coupling constant obeys Eq. (45). Given the transition temperature and coupling constant for a material, the maximum T_c expected for similar materials can be found from this graph.

TABLE VIII. The predicted maximum superconducting transition temperature for four classes of materials found from the observed T_c and λ and Fig. 11, together with the observed maximum T_c.

Metal	T_c (°K)	λ	T_c^{max} (°K)	Observed maximum T_c	Material
Pb	7.2	1.3	9.2	8.8	Pb–Bi
Nb	9.2	0.82	22	10.8	Zr–Nb
V_3Si	17	0.82	40		
Nb_3Sn			28	20	Nb_3Al–Nb_3Ge

We begin with a simplification of the theoretical formula for T_c:

$$T_c \approx \langle\omega\rangle \exp[-(1+\lambda)/\lambda]. \tag{44}$$

Now, using the observation of Sec. V, we write for the coupling constant

$$\lambda = C/M\langle\omega^2\rangle, \tag{45}$$

where C is fixed for a given class of materials, e.g., for the bcc alloys in the neighborhood of Nb. We have

$$T_c = \langle\omega\rangle \exp[-M\langle\omega^2\rangle/C-1], \tag{46}$$

which takes on its maximum value as a function of $\langle\omega\rangle$ for $\langle\omega\rangle=(C/2M)^{1/2}$, and

$$T_c^{max} = (C/2M)^{1/2}e^{-3/2}. \tag{47}$$

What is happening here is that we increase the coupling constant to maximize the exponential factor in Eq. (44) by decreasing the average phonon frequency. But the average phonon frequency premultiplies the exponential, and the product is maximized for $\lambda=2$. It is useful to express T_c/T_c^{max} as a function of λ:

$$T_c/T_c^{max} = (2/\lambda)^{1/2}e^{(1/2-1/\lambda)}.$$

This expression has a broad maximum at $\lambda=2$ and falls off sharply for $\lambda<1$. In Fig. 11, we show T_c/T_c^{max} calculated from the accurate expression for T_c [Eq. (19)] rather than from Eq. (44), and taking $\mu^*=0.13$. Given the T_c and λ for a given material, we can find the maximum T_c for a class of "similar" materials from Fig. 11. The theoretical maximum T_c (Table VIII) for Pb-like materials, that is, for the lead-based alloys, is 9.2°K, and there is in fact a Pb–Bi alloy with $T_c=$

[30] T. H. Geballe, B. T. Matthias, J. P. Remeika, A. M. Clogston, V. B. Compton, J. P. Maita, and H. J. Williams, Physics 2, 293 (1966).

[31] B. T. Matthias, T. H. Geballe, L. D. Loninotti, E. Corenzwit, G. W. Hull, R. H. Willens, and J. P. Maita (to be published).

8.8°K.[32] For Nb-like materials, the maximum observed T_c is about half the theoretical maximum. The value of T_c^{max} for Nb_3Sn was found by scaling the T_c^{max} for V_3Si with the square root of the mass ratio.

There are a number of refinements of the theory of T_c^{max} which should be attempted. The most important one is to test the relationship [Eq. (45)] between the coupling constant and the phonon frequencies for a wider range of materials and also, of course, to attempt to understand this result theoretically for the bcc transition metals. We should note that we have extrapolated the theoretical formula [Eq. (18)] for T_c versus λ, which was derived for $\lambda \lesssim 1$, to larger values of λ. The errors are probably not serious, but the calculations should be carried out for the extreme strong-coupled case. We have assumed that the average phonon frequency can be decreased indefinitely by (for the pseudopotential model) cranking up the pseudopotential. Of course, this is not the case. We are likely to drive some phonon mode unstable, so that the metal prefers a different crystal lattice, before the average phonon frequency is decreased very far. This would set an upper limit on the coupling constant that one could obtain experimentally and provide a stronger upper bound on T_c (a lattice instability of this nature has been observed for V_3Si).[33,34] The fcc Tl–Pb–Bi alloys are an interesting case to study experimentally in this respect, since the coupling constant is already large for lead and apparently increases with bismuth concentration.

VII. CONCLUSIONS

The central result of this paper is Eq. (18), which relates the superconducting transition temperature to the electron-phonon and Coulomb coupling constants according to the strong-coupled theory of superconductivity. This theory is believed to be accurate for real metals to lowest order in an expansion parameter $\hbar\omega_{ph}/E_F \sim 10^{-2}$–$10^{-3}$. The equations were originally derived for the Frohlich Hamiltonian, but recent studies[35–37,9] of the Coulomb interaction indicate that the only effect of the Coulomb interactions is to renormalize the energy bands and the electron-phonon matrix elements, and that the structure of the self-energy equations used here is correct. Band-structure effects are properly included in the definition of λ. We have neglected the anisotropy of the energy gap, but this introduces only a small error in T_c. The effects of persistent spin fluctuations, which are important for the nearly ferromagnetic case, are believed to be unimportant for the metals considered here. These effects could probably be included within the present formalism by choosing a somewhat larger Coulomb term μ^*. We have made one special assumption by using the phonon density of states for niobium. This introduces important errors only for the strong-coupled ($\lambda > 1$) superconductor with a wildly different phonon spectrum. We note that the strong-coupled theory has received strong experimental support from the analysis of the tunneling experiments on lead which probes the detailed structure of the self-energy equations. We regard Eq. (18) as just the numerical consequence of the established and verified theory of superconductivity. We have made no attempt to verify the theory of superconductivity in this paper, but rather have used that theory to examine the electron-phonon interaction in those metals which are superconducting. Equation (18) proves to be very useful in estimating the electron-phonon interaction strength and in stripping away the "phonon enhancement" of the specific heat and cyclotron mass to reveal the "band-structure" values. We have examined the variation of the coupling constant over limited portions of the periodic table and have found a surprising result—namely, that the coupling constant depends mainly on the phonon frequencies and is insensitive to large variations in the electronic properties, e.g., the band-structure density of states. This observation has been used to predict a maximum transition temperature for a given class of materials.

ACKNOWLEDGMENTS

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[32] B. W. Roberts, *Progress in Cryogenics* (Heywood and Co., Ltd., London, 1964).
[33] B. W. Batterman and C. S. Barrett, Phys. Rev. Letters **13**, 390 (1964).
[34] L. Testardi, T. B. Bateman, W. A. Reed, and V. G. Chirba, Phys. Rev. Letters **15**, 537 (1965).
[35] E. G. Batyev and V. L. Pokrovskii, Zh. Eksperim. i Teor. Fiz. **46**, 262 (1963) [English transl.: Soviet Phys.—JETP **19**, 181 (1964)].
[36] V. Heine, P. Nozieres, and J. W. Wilkins, Phil. Mag. **13**, 741 (1966).
[37] R. E. Prange and S. Sachs, Phys. Rev. **158**, 672 (1967).

INTERMETALLIC COMPOUNDS: AN UNLIMITED SOURCE

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We have heard what I can conservatively say is two different points of view this morning, and there is probably some room for interplay between the two. Intermetallic compounds afford an unlimited testing ground of various theoretical and experimental approaches to an understanding of superconductivity, in addition to their being an unlimited source of new superconductivity. We are all familiar with interplay between theory and experiment that has been fruitful in the past. One of the most well-known cases is the role of the electron-phonon interaction. The exploration of the effect of mass on superconductivity goes back even before most of you were born. According to the "Leiden Communications," Kamerlingh Onnes himself with Tuyn looked for the difference in T_c between "uraniun lead" and ordinary lead. If one tries to reconstruct what happened, it looks like their quoted reproducibility and temperature shift we now know the isotope effect would cause, were just the same — so they probably saw a little something but it was just within experimental error. However, the idea lay dormant, although Justi in Berlin obtained negative results in a similar experiment during the war years, until it was brought up again — this time simultaneously from both the theoretical and experimental viewpoints, and the dominant role of the lattice was actually discovered. Several other models have come to the front since the work on phonon interaction and the advent of the BCS theory. For example, pairing of electrons via their p-states by spin waves, which was proposed in the late 50's, has not been verified. Given a system of electrons ard some sort of a low-lying spectra of excitations, you can have a coupling mechanism for pairing the electrons, and therefore that's a source of superconductivity. Other examples that we have heard about are surface superconductivity, which Ginsburg has been proposing, and an interaction in the side chains of special organic molecules or polymers that was proposed by Bill Little. Little recently gave a seminar in which he described some interesting experiments on infrared absorption spectra in organic molecules and how the edge should shift as various groups are incorporated into the molecule. While this may not be a direct way of finding out about high-temperature superconductors, the shifts of the excitation spectra may give a clue as to whether superconductivity in such systems is possible.

In summary, either empirically, or theoretically, you take a model seriously and it will suggest something. Then you go ahead and look. If you get anywhere, then you keep going — otherwise — well, it depends how stubborn you are and in that respect I'd like to say a little about my feeling in the matter (since I am the speaker, I get that choice). I like to look for systems that have some noticeably unusual properties — superconducting properties, say — and then try to find out in these systems what the source is and what other unusual properties there are. To be able to do this we are indebted to Matthias, Hulm, and their coworkers in the 1950's, who sort of systematized the occurrence of superconductivity, which was discussed in the first part of Matthias' talk. Before you can find out something unusual about superconductivity, you have to know what is unusual,

and this we know from their pioneering work throughout the periodic system. Indeed Matthias discussed today how superconductivity changes with pressure, mass, and other external parameters. I am now going to talk about chemical effects, i.e., by changing chemical composition, one changes atomic spacing, the electron-to-atom ratio, and moves the Fermi surface; all this results in a change in superconductivity.

Some unusual superconducting effects occur in the compound $AuGa_2$ on which Wernick, Menth, et al., and myself have been working on at Bell Labs. A lot is known about $AuGa_2$. At the APS meeting in Philadelphia a few days ago Swittendeck from Sandia gave a detailed calculation of the band structure which had some interesting characteristics that may relate to the superconducting behavior. Eventually, we may be able to look at the Fermi surface and say here are electrons in a region in momentum space which can be isolated, and attribute an enhanced superconducting interaction to them. $AuGa_2$ and like compounds belong to the calcium fluoride structure; they are good metals but have very strong covalent features. For instance, they contract when they melt. It's easy to purify them, and as a result they have high residual resistance ratios.

$AuGa_2$ came to light as an interesting material because of some nuclear magnetic resonance work Jaccarino, Blumberg, and Wernick reported in '61. They found a temperature-dependent Knight shift in a material with an s-p conduction band where one would expect to find temperature-independent (Pauli) susceptibility and Knight shift. There are two other related compounds — $AuIn_2$ and $AuAl_2$ — which have almost all the same properties except their Knight shift is temperature independent and they are not superconducting until below 0.1°K. $AuGa_2$ is superconducting slightly above 1°K. It is hard to dissolve other elements in $AuGa_2$. For instance, $PtGa_2$ is also in the same family with a similar lattice constant, but you can't get any $PtGa_2$ to dissolve in $AuGa_2$. But Wernick found that Pd is soluble in $AuGa_2$. In Fig. 1 you can see the heat capacity and the superconductivity of $AuGa_2$ respond to the addition of Pd. Here heat capacity divided by temperature is plotted vs temperature in a conventional way. The measurements were made and the data reduced by J. P. Maita of B.T.L.

$AuGa_2$ is superconducting at temperatures slightly below where we could measure the heat capacity (about 1°K). However, with 5% of palladium replacing gold, there is a sharp transition at 1.8°K. We then went back and measured a sample with 2% of the gold replaced by Pd, and one with 10%. Not only does $AuGa_2$ have a markedly higher T_c than the $AuAl_2$-$AuIn_2$, but its T_c changes very rapidly as the palladium is substituted for the gold. In Fig. 2 you can see as a function of palladium concentration how the transition temperature changes, and it correlates with the change in the electronic density-of-states coefficient. As the palladium goes into solution, evidently there is a very rapid change in density of states, which then saturates. The rapid change in transition temperature saturates even at a slightly lower Pd concentration. Putting the palladium in is going to lower the Fermi level since it has one less electron than the gold. Swittendeck's calculation shows a feature which may explain the above results and also be responsible for the temperature dependence of the Knight shift. Namely, he finds a very small but flat region of the s band just below the Fermi level in $AuGa_2$. When you first add the palladium, the density of states increases at a rate of about one state per ev per atom, which is very typical of the d band material, whereas with no addition of Pd, the density of states is at just about 0.15 or 0.2 states per ev per atom, which is normal s-p material. Figure 3 is just to show the solubility. You can get up to 15% palladium to replace the gold, as judged by the response of the lattice constant, but the very sharp feature of the band occurs over a very small region in energy. Figure 4 shows what the susceptibility looks like. I put it on to show that $AuAl_2$ and $AuIn_2$ both have a temperature-independent susceptibility. They behave just the way you would expect for an s-p metal

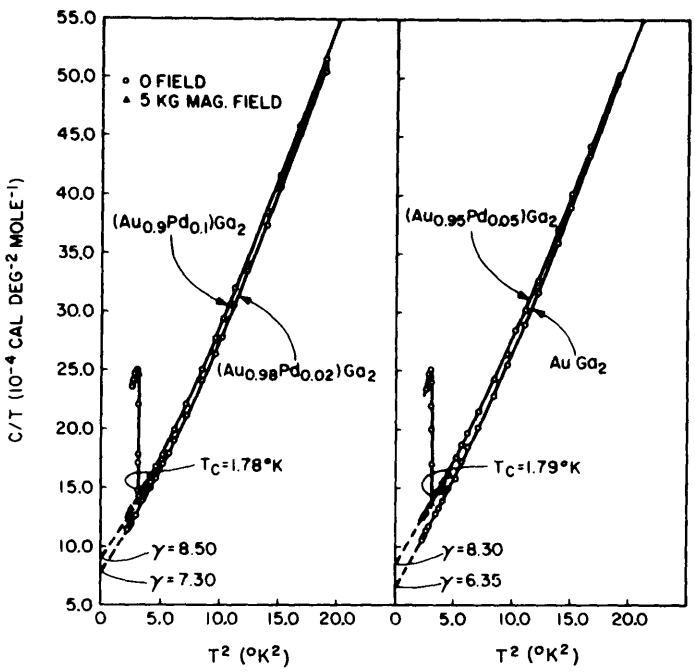

Figure 1

with paramagnetism, associated with the names of Pauli and Landau and Pierels, would do. However $AuGa_2$ has a very large temperature dependence. As we put palladium in, we get a paramagnetic response. Figure 5 shows all four members of this family which have some very similar properties. It is only the $AuGa_2$ which has the superconductivity above 1°K and it is the only one that has temperature-dependent properties, which, on intuitive grounds, may be associated with the one electron states Swittendeck finds in a flat part of the band. Incidentally, $AuAl_2$ — this member of the family which is purple here [slide was in color] — I understand from friends in the integrated circuit business, is referred to as the "purple plague." When integrated circuits were first made, people were bonding gold onto aluminum or aluminum onto gold. The bonds started falling apart and the things looked purple. Consequently, it was called the purple plague. Apparently Au and Al can react in film form near room temperature. It is a good chemical compound but not what people wanted on their leads because it's brittle. To return to $AuGa_2$, note how a study of it has become a fruitful way of finding out more about superconductivity.

I want to say a little about the interstitial compounds because other unusual superconducting behavior is found in these materials. When you look at the transition temperature of niobium carbide-nitride as a function of carbide-to-nitride ratio, as Matthias did back in the early 50's, you find a maximum in the transition temperature at about 30% carbon. Now maxima in pseudobinary systems are rather rare indeed, and so we decided to investigate this particular system in more detail. While these results are a few years old there recently has been renewed interest in the interstitial compounds. Among others, Jones and coworkers at Westinghouse can sputter niobium nitride films and are able to produce ribbons with very good high-field-current carrying properties. We studied the various microscopic parameters which could be extracted from McMillan's theory, such

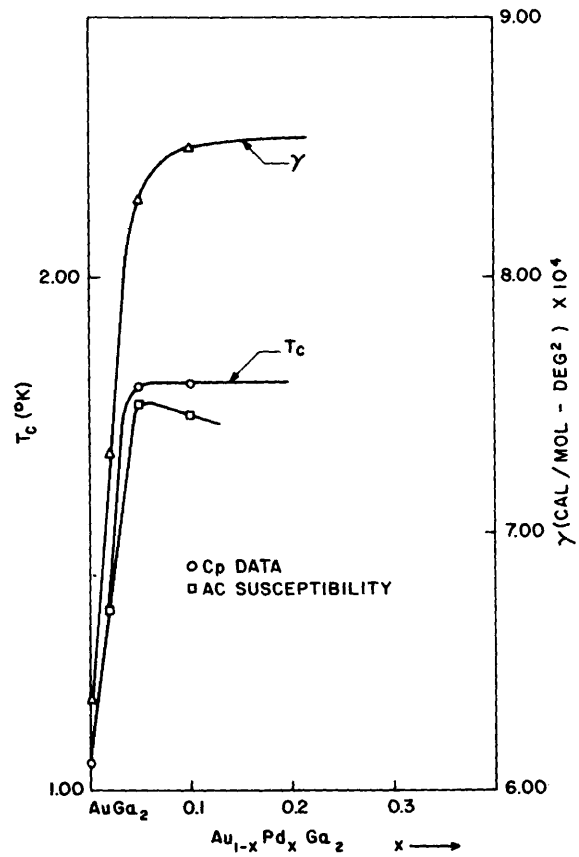

Figure 2

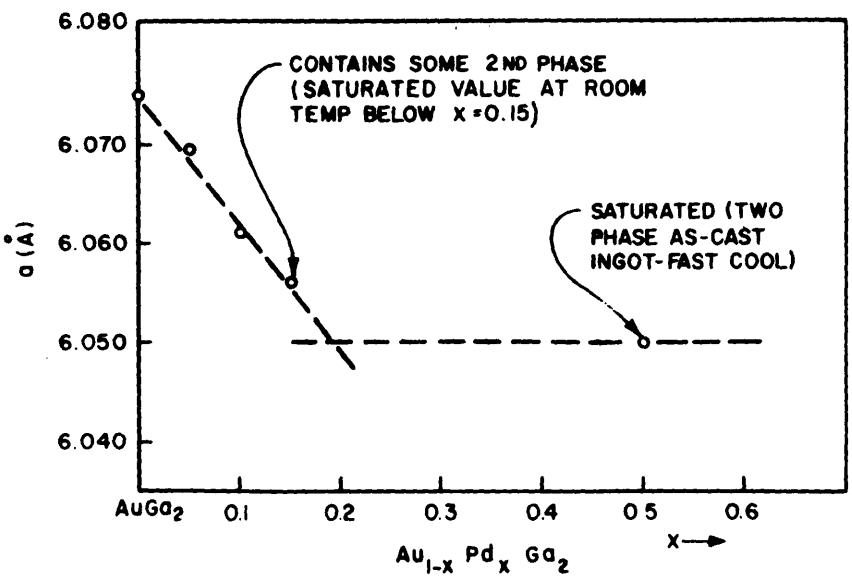

Figure 3

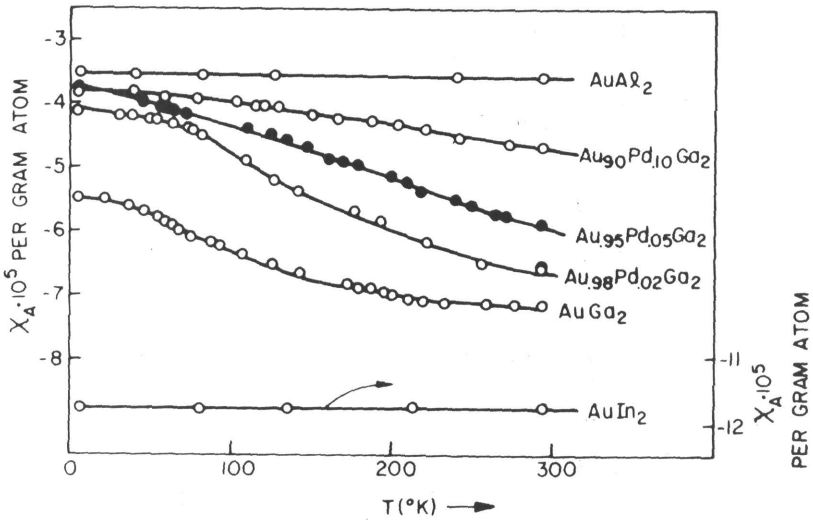

Figure 4

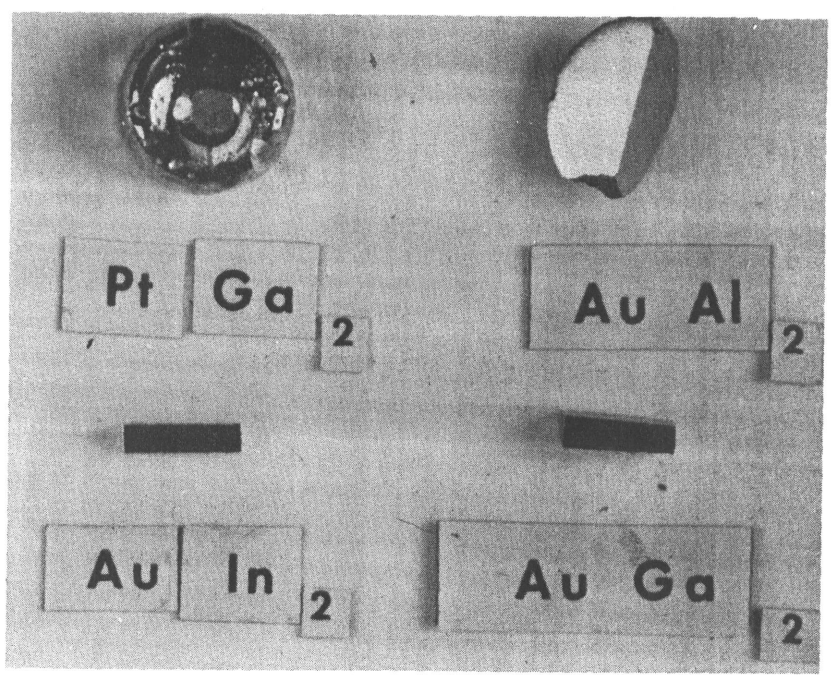

Figure 5

as the electron-phonon interaction. The density of states, etc., stayed about constant as one starts adding C to NbN, but the Debye temperature goes up. Most of the superconductivity appears to be due to s-p electrons — there is not much evidence for d-band electrons in this system. The low density of states and the strong electron-phonon coupling are more reminiscent of Pb than Nb. In fact, it looked like [it was the] s-p electrons from the nitrogen that were responsible for the superconductivity, and Matthias suggested entitling the paper "Superconducting Nitrogen." Clogston, who was also in on this work, suggested "Stiff Lead" because it had properties the same as lead except the Debye temperature was about three times as big. Now how does NbN form so there are no d-electron states at the Fermi surface? After getting some suggestions from P. W. Anderson and V. Heine, we proposed the following plausible scheme to accommodate the ten electrons per NbN (five from the Nb and five from the N), i.e., how can they be distributed? First, we put two into the 2s band formed from the nitrogen — that's obviously going to be filled. That leaves eight more electrons to play with. The 2p band of the nitrogen can hybridize with the 4d bands of the Nb, the former being lowered and the latter raised. The lowered p band will then accommodate six electrons. Of course, the raised d bands are then not occupied because the last two electrons would be mainly in a broad s-p conduction band, and the Fermi level would be in it. This, of course, is oversimplified, but may retain the essence. Now if you do your bookkeeping, you would find that there are on the average about six electrons in nitrogen orbitals and four in Nb orbitals making an ionic N^-Nb^+ configuration. I've just received a preprint from Nordling and coworkers at Uppsala in Siegbahn's group. They have looked at some carbides by the electron spectroscopy for chemical analysis (ESCA) technique. It is simply a photoemission experiment where x-rays are used to eject inner shell electrons which are then energy analyzed and show chemical shifts. For the rock-salt-structure carbides — niobium carbide, tantalum carbide, and vanadium carbide in the fifth row — they find evidence from the chemical shift that the carbon is indeed negatively charged and the niobium is positively charged. They have also studied variation in ionicity with variation in carbon (these compounds can be made with varying stoichiometry). Previously Giorgi and Sklar have found that as one-to-one metal-to-carbon stoichiometry is approached, the superconducting transition temperature increases. Now Nordling and his group find as they approach stoichiometry that the ionicity of the niobium and tantalum decreases and vanadium increases. Since vanadium carbide is not superconducting and the other two are, there may be a relationship between the ionicity of the bond and the superconductivity. This might require some rethinking on just how the transition temperature is related to the Debye θ, measured from the heat capacity. Charge contrast effects may also be important in compounds such as $ThPt_3$ ($T_c < 0.44°K$) and $ThPt_5$ ($T_c < 3°K$) where the d band is almost filled. There are nine valence electrons per atom in $ThPt_5$, and since platinum does not like to be superconducting this is quite a high temperature. The large charge contrast means that there could be a large charge fluctuation as you go along the lattice, if you happen to be an electron, that is.

Now another example of materials with unusual behavior is the β-W class. Most of the people here are familiar with Nb_3Sn, V_3Si, etc. Fifteen years, or something like that, have elapsed since Hardy and Hulm first found superconductivity in V_3Si at 17°K and the time in 1967 that Matthias, myself, and coworkers found superconductivity above 20°K in the niobium-aluminum-germanium system. In between that time an awful lot of samples were measured, and unusual properties in the β-W structure have been found, in addition to high-temperature superconductivity. I am referring to the Martinsitic transition at low temperatures, the temperature-dependent susceptibility, the temperature-dependent Knight shift, and the high density of states. Clogston and Jaccarino suggested that the temperature-dependent susceptibility could follow from sharp structure in the density of states — those two things go together. Weger at the Colgate Conference on Superconductivity suggested a one-band model due to the Nb chains in the crystal. Subsequently,

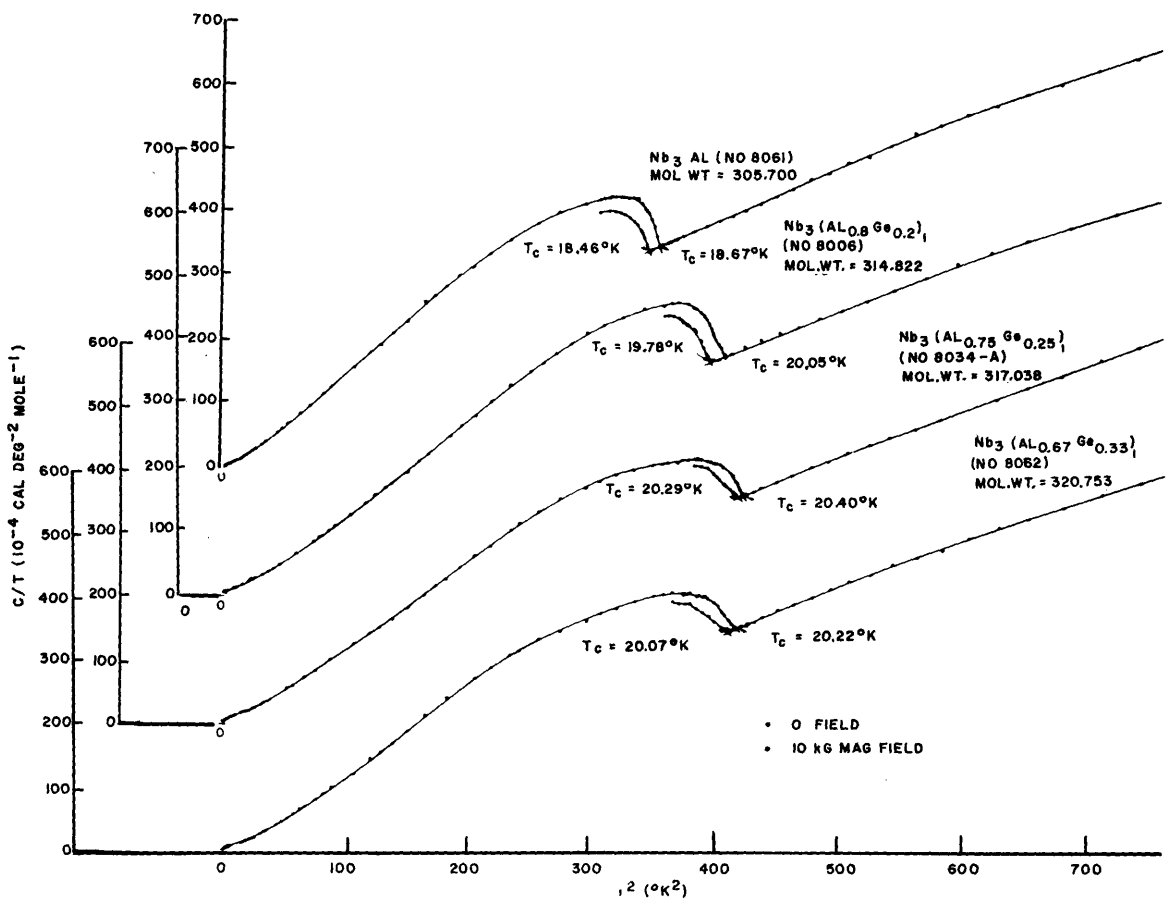

Figure 6

Friedel, Labbe, and Barasic, and also Cohen and Cody at RCA, have developed detailed models. These explain lots of the already measured phenomena but haven't predicted new things. New data in the Nb_3Al system doesn't seem to fit the theories so well. Afte the discovery of the superconductivity above 20°K in $Nb_3Al_{0.8}Ge_{0.21}$ we did a set of experiments on arc-melted and annealed material in which the Al-to-Ge ratio was varied. Figure 6 is taken from a paper I gave at Austin in 1967 in which the heat capacity data were analyzed and showed no unusual properties other than the superconductivity. We can draw such conclusions regarding the Nb_3Al and further don't see any marked change as Ge is substituted for Al for instance in the $Nb_3Al_{0.75}Ge_{0.25}$ sample of Fig. 6 (T_c = 20.4). We can then infer that even though the latter is multiphase, and examination of it alone might be unconvincing, that it also doesn't follow the one-dimensional band model predictions. Willens, Gossard, Menth, and myself have recently looked at some rather pure, almost single-phase, Nb_3Al samples. Essentially, we find a temperature-independent susceptibility which is flat but not much smaller than Nb_3Sn at room temperature. But whereas in Nb_3Sn the susceptibility increases as it is cooled, Nb_3Al doesn't. Using the measured heat capacity anomaly at the transition the Labbe-Friedel-Barasic theory says we should have measured a 35 times bigger variation in susceptibility than we did. But maybe there is still something there, but not right at the Fermi

surface, as in $AuGa_2$. If there were pronounced structure in the density-of-states curve a little bit below the Fermi surface, it would perhaps show up in some of the experiments which explore the band near the Fermi surface. We still don't have our hands on the reason for the high T_c. A lot of people, especially here in the audience, are doing ordering experiments on these systems and studying the effects of putting atoms on the different sites. Ordering experiments are another way of watching the response as superconducting parameters are changed.

Figure 7 shows an example of a fairly unusual structure — the hexagonal tungsten bronze. Superconductivity was discovered out in La Jolla several years ago in this structure. This figure looks down the C axis through the WO_3 octahedra. Big hexagonal channels where alkali metals go are evident. The compounds are supposed to be very inert. We were not getting a full superconducting signal one day and so we decided that we had some second phase which we tried to dissolve in mineral acid. The superconducting transition temperature went up from 1°K to 5°K. Upon analysis we found that the mineral acid — it didn't matter if it was hydrochloric or acetic or sulfuric — take your pick — was removing alkali metal atoms. We found about half the alkali metal atoms were removed. While this seems relatively straightforward from a spatial point of view, i.e., there is just enough room in the channel to accommodate a Rb ion, the superconducting response is not yet understood on a microscopic basis. Finding out why the transition temperature increases, which is the kind of thing that I have been advocating today, will keep us all in business for some time to come.

Thank you.

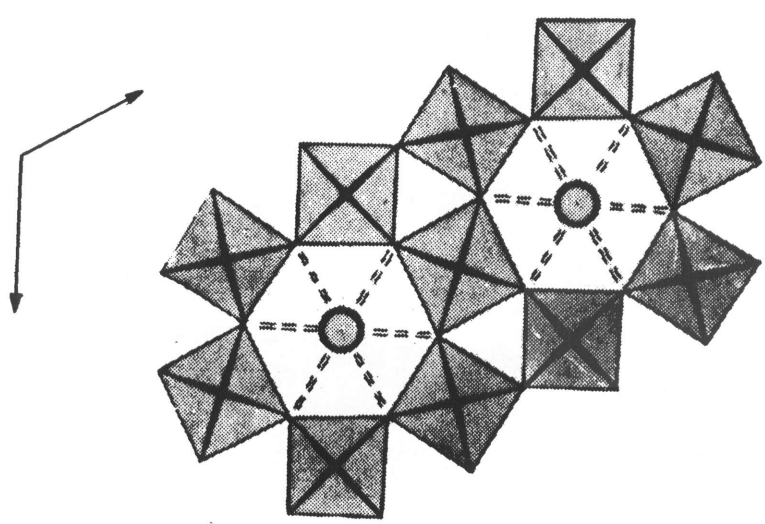

Figure 7

MECHANISMS FOR SUPERCONDUCTIVITY

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We shall start with the elementary BCS theory and the law of corresponding states. One may consider the BCS theory to have consisted of three parts: (1) the basic theory, which has just been described by Bill McMillan, (2) the postulate that the electron-phonon interaction was responsible, and (3) the BCS square-well model. The model, which included the assumption that the electron-phonon interaction was responsible for superconductivity, gave a law of corresponding states. The many exceptions found experimentally to this law of corresponding states have given rise to many conjectures as to other mechanisms for superconductivity in many materials. Particularly prominent exceptions to the law of corresponding states are (1) the isotope effect, $T_c \propto M^{\alpha}$, where α differs qualitatively from the BCS value -0.5 in many metals, (2) pressure effects and (3) enhancement effects in thin films, both of which go all over the map and may have either sign, and (4) stoichiometry effects which certainly could not be explained by the BCS model. Also, the BCS equation cannot really predict the variation of T_c or the occurrence of superconductivity except in the simple metals.

In fact, there are undoubtedly other mechanisms which could give rise to superconductivity. However, today I want to discuss those interactions I believe to be important in most materials in which superconductivity has been found. The electron-phonon interaction, as has been pointed out by Phil Anderson, is localized in space and retarded in time. The interaction extends over distances less than or approximately equal to an interatomic distance and is retarded by a time of order the inverse of the Debye frequency. The second interaction, the screened Coulomb interaction, is also of rather short range because of the short screening wavelength in metals. Although it is much less so than the electron-phonon interaction, it also is retarded. When considering the Coulomb interaction, it is very important to consider both its magnitude and its retardation. Its retardation is very different in different metals, being of the order of the inverse of the plasma frequency in simple metals and of the order of twice the inverse of the d-band width or more in the transition metal superconductors.

The basic equations for superconductivity, if we consider only these two interactions, at $T = 0$ have the form shown in Fig. 1. The kernel of the gap equation, which is denoted by K_+, peaks at frequencies corresponding to a typical longitudinal phonon frequency and also at a transverse phonon frequency. It changes sign at approximately the maximum phonon frequency. The electron-phonon interaction is most effective in inducing superconductivity if most of the phonons have approximately the same frequency. Thus, if some physical effect leads to a broadening of the phonon spectrum, this broadening will in turn reduce the effectiveness of the electron-phonon interaction in inducing superconductivity. This effect is easily seen physically, since the phonons contribute to superconductivity only to the extent that they are coherent after a time of order the retardation time. The effect also can be seen by inspection of the form of the kernal K_+, or by direct computation.

Basic Equations

$$\Delta(\omega) = Z^{-1}(\omega) \int_0^\infty d\omega' \, \mathrm{Re} \left\{ \frac{\Delta(\omega')}{\sqrt{\omega'^2 + \Delta^2(\omega')}} \right\} K_+(\omega,\omega') \, ,$$

$$Z(\omega) = 1 - \frac{1}{\omega} \int_0^\infty d\omega' \, K_-(\omega,\omega') \, ,$$

$$K_\pm = K_\pm^{\,ph} + K_\pm^{\,e} \, ,$$

$$K_\pm^{ph}(\omega, \omega') = N(\omega') \int_0^\infty d\omega_q \, F(\omega_q) \cdot \alpha^2(\omega_q)$$

$$\times \frac{1}{\omega' + \omega_q + \omega - i\delta} \pm \frac{1}{\omega' + \omega_q - \omega - i\delta} \, ,$$

$$Z(\omega) - 1 \rightarrow 0 \, ,$$

$$K_+^{\,e}(\omega,\omega') \rightarrow \mu^* \, N(\omega') \langle |M^2(\omega-\omega')| \rangle / N(0) \langle |M^2(0-0)| \rangle \, .$$

Figure 1

Using Eliashberg equations such as those shown in Fig. 1, but at finite temperature, Bill McMillan derived via extensive computer calculations the very useful formulas shown in Fig. 2. The first equation gives T_c as a function of the phonon-induced coupling constant λ, the effective Coulomb coupling constant μ^*, and the Debye temperature θ_D. The second equation gives λ, and hence the phonon contribution to the electronic mass renormalization, as a function of θ_D/T_c and μ^*. The third and fourth equations give the isotope effect and the pressure dependence of the transition temperature. In the formula for μ^*, $N(0)$ is the electronic density of states at the Fermi level, V_e is the average Coulomb interaction between two states on the Fermi surface, E_c is an effective Coulomb interaction cutoff energy, and ω_0 is the maximum phonon energy.

These equations are useful for a number of practical calculations, in particular, in calculating any effects in which the shape of the phonon spectral weight function does not change and is not of great importance. One can evaluate the isotope effect assuming that one can calculate μ^* and that there is no important critical point in the band structure, particularly near the Fermi level. One can also readily use the McMillan equations in calculating the pressure dependence of T_c in the simple metals or just to calculate T_c for the simple metals. Finally, one can use the McMillan equations to analyze and interpret the systematic variations of T_c in the transition metals as a function of ionic mass, Debye temperature, valence, row in the periodic table, and electronic density. The McMillan equations could be used in calculations of T_c or of the pressure dependence of T_c in the transition metals, except that calculations of λ and $\partial\lambda/\partial V$ have been too difficult to be done thus far. Such calculations are underway and should, at least partially, indicate the relative importance of the electron-phonon interaction for superconductivity in the transition metals. On the other hand, the McMillan equations are not at all useful for studying α-uranium, because of the f-band critical point near the Fermi level. Also, these equations should not be used in studying the properties of disordered systems or very anisotropic metals because such materials will have a phonon spectrum very

Eliashberg, Nambu formalism with
Coulomb and electron-phonon interactions

Given functional form of $\alpha^2(\omega)\ F(\omega)$

$+$

Extensive computer calculations

$\Longrightarrow$

McMillan Equations

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

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

$$\frac{\partial \ln T_c}{\partial \ln M} = -\frac{1}{2}\left[1 - \left(\mu^* \ln \frac{\theta_D}{1.45\ T_c}\right)^2 \left(\frac{1 + 62\lambda}{1+\lambda}\right)\right] = -\frac{1}{2}(1 - \zeta),$$

$$\frac{\partial \ln T_c}{\partial \ln v} = -\left[\lambda\left(\frac{1 + .38\mu^*}{1.04(1+\lambda)^2}\right)\left(\frac{\partial \ln \lambda}{\partial \ln v}\right) - \left(\frac{1 + .62\lambda}{1+\lambda}\right)\left(\frac{\partial \mu^*}{\partial \ln v}\right)\right] \ln \frac{\theta_D}{1.45}$$

$$\mu^* = \frac{N(0)V_e}{1 + N(0)V_e \ln (E_c/\omega_0)}, \quad \lambda = 2\int \frac{d\omega\ \alpha^2(\omega)\ F(\omega)}{\omega}$$

Figure 2

different from the niobium phonon spectrum used by McMillan in his numerical calculations. This point was made by McMillan himself. Finally, for the same reason, these equations should not be useful in studying stoichiometry effects.

Let us look at those calculations which have been made using the McMillan equations or similar equations. The results of experimental measurements of the isotope effect

$$T_c \propto M^{-\alpha} = M^{-0.5(1-\zeta)}$$

are compared with calculated values of ζ in Fig. 3. One finds generally good agreement with the simple metals; however, the experimental results of Dillinger for zinc are in rather bad disagreement with our calculated value. The difference in the measured quantity α is only 0.05 out of 0.4, a fairly small error, but this difference is outside the combined range of estimated errors for theory and experiment. For the transition metals one can estimate the value of ζ qualitatively by doing a model calculation rather than a full-blown band structure calculation, which would take of order one year for each element. Being too lazy to do the separate band structure calculation for each transition element, I merely used simple models for the calculation of ζ. Unlike Dr. Matthias, I cannot walk on water without getting my feet wet, so as he pointed out, I obtained a bad answer for zirconium. However, I did predict the correct value of ζ for rhenium. More important, even the earliest calculations were in good agreement with experiment for those elements having no critical points in their band structure close to the Fermi level, those for which the calculations should have been most reliable. Improved calculations,

Deviations ζ from the Ideal BCS Isotope Effect

Metal	ζ^{expt}	ζ^{calc}	Agreement
Al		0.20 ± .04	
Cd	0.0 ± .2	0.18 ± .03	?
Hg	0.0 ± .06	0.04 ± .01	good
In		0.05 ± .02	
Pb	0.04 ± .02	0.03 ± .01	excellent
Sn	0.06 ± .04	0.07 ± .02	excellent
Tl	0.0 ± .2	0.03 ± .01	?
Zn	0.25 ± .03	0.15 ± .03	poor
Mo	0.34 ± .10	0.3 ± .2	
Zr	0.8 ± .1	0.6 ± .2	
W	0.18	0.3 ± .3	qualitatively
Re	0.22 ± .02	0.3 ± .1	good
Ru	1.0 ± .2	0.9 ± .3	
Os	0.6 ± .1	0.6 ± .2	
Ir		1.05 ± .35	
Ta		0.35 ± .1	
Nb		0.35 ± .1	
V		0.6 ± .3	
α-U	5 ± 1	3.4 ± 3	
γ-U	-0.06 ± .04	0.05 ± .1	
La		<< 0	

Figure 3

the results of which are shown in Fig. 3, are in qualitatively good agreement with experiment for all of the transition metals. Because detailed calculations of oscillator strengths, wave functions, etc., were not performed, better agreement could not be expected. On the other hand, the calculations do not rule out the possibility of other interactions. However, they do indicate that the sum total of all interactions, except the electron-phonon interaction, would not yield superconductivity in the transition metals, so that the electron-phonon interaction is necessary and dominant for superconductivity in the transition metal elements.

The experimentally observed variation of T_c with hydrostatic pressure is shown in Fig. 4. The simple metals fall near the empirical curve

$$\varphi \equiv \partial \ln [\ln (T_c/\theta_D)]/\partial \ln v = 2.5 ,$$

as was first noted by Olsen. The transition metals do not fall anywhere near this curve (with the exception of thorium, which has a very wide d-band), some of them even having a positive pressure dependence of T_c. Uranium, for example, is way below this graph. To date, no one has calculated the pressure dependence of T_c for any transition metal; however, there are many calculations of the pressure dependence of T_c for simple metals. To illustrate the accuracy which one can (or cannot) obtain in such calculations, some of our values for the pressure dependence of T_c and $N(O)$ for the simple metals are compared in Fig. 5 with the corresponding experimental values. The second column lists approximate calculated values of a correction factor δ which arises from changes in screening and in Brillouin zone size. The third and fourth columns give values of φ calculated in the weak-coupling BCS limit and calculated from the Eliashberg equations or McMillan's equations, respectively, assuming a nearly-free-electron (NFE) model.

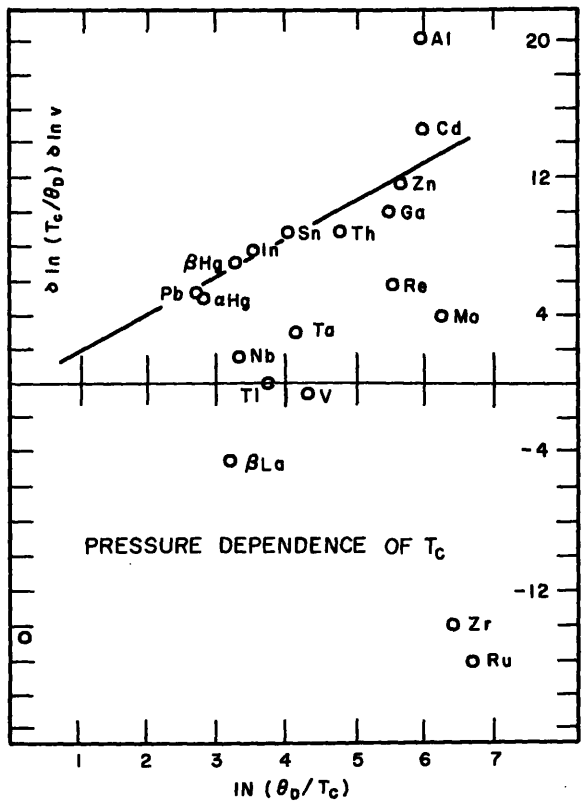

Figure 4

CALCULATED AND EXPERIMENTAL PRESSURE DEPENDENCE OF T_C AND N(O) IN THE SIMPLE METALS

Metal	δ	$\varphi_{BCS} = 2\gamma_G + \delta$	NFE calc	φ_{calc}	φ_{expt}	g_{calc} (φ_{calc})	g_{calc} (φ_{expt})	g_{expt}
Pb	+0.5	5.7	2.3	2.3	2.0	+0.9	+0.9	+0.7
αHg	~-.6	~3.8	~1.7	?	1.8	+0.9	+0.9	+6.3 (?)
In	~- 1	~3.7	~2.0	1.8	2.0	+0.7	+0.7	0.0
Tl	~-1.1	~4.3	~2.2	.6	0.0	0.0	-0.3	-5.
Sn	~-1.2	~3.1	~2.5	2.5	2.3	+0.6	+0.6	0.7
Zn	~-1.8	~2.2	~2.0		2.2	+0.3	+0.3	
Cd	~-2	~2.4	~2.3		2.6	+0.4	+0.4	
Al	-1.95	2.35	2.9	2.9	3.5	+0.7	+0.7	0.7

$\varphi = \partial \ \ln(\ln 1.14\, \theta_D/T_c)/\partial \ \ln v$

$g = \partial \ \ln N(0)/\partial \ \ln v \sim \partial \ \ln(m^*/m)\partial \ln v - \frac{1}{3}$

Figure 5

The next column lists values of φ obtained by correcting the NFE model according to the experimental values of $g \equiv \partial(\ln N(O))/\partial \ln V$. The two columns labelled g_{calc} were calculated using values of λ determined from φ_{calc} and φ_{expt}, respectively. Note, that the weak-coupling BCS approximation gives bad results, but that the Eliashberg equations give values of φ in very good agreement with experiment, except for the case of thallium, a notorious bad actor with extreme anisotropies in the pressure dependence of all quantities, presumably due to Fermi surface effects near the Brillouin zone boundaries. For thallium, the agreement with experiment is greatly improved if one takes account of these effects by allowing $N(O)$ to vary with pressure, as is measured experimentally. The calculated values of g are in excellent agreement with experiment except for α Hg, for which there is violent disagreement. For Tl and α Hg, neither the experimental nor the calculated value of g is very meaningful because of the large anisotropies in those two cases. Significant uncertainties also enter the calculations of pressure effects from the lack of knowledge of the pressure dependence of the phonon spectra.

Seiden has calculated the pressure dependence of T_c for large volume changes and obtains good agreement with experiment, as is shown in Figs. 6 and 7. The discrepancy between theory and experiment for cadmium at very high pressure presumably arises from Fermi surface effects not described within the NFE approximation.

Looking at φ, the pressure dependence of T_c, for the transition elements as shown on Fig. 8, one sees a correlation between φ and ζ, the deviation from the BCS isotope effect. Even α-uranium, which is way off the graph, qualitatively follows the empirical relationship

$$\varphi \simeq 2.4 - 5.5\,\zeta\ .$$

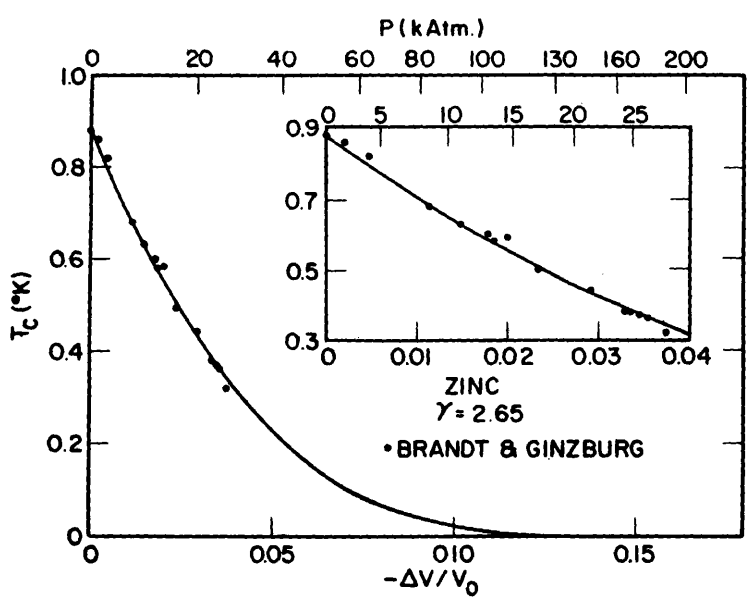

Figure 6

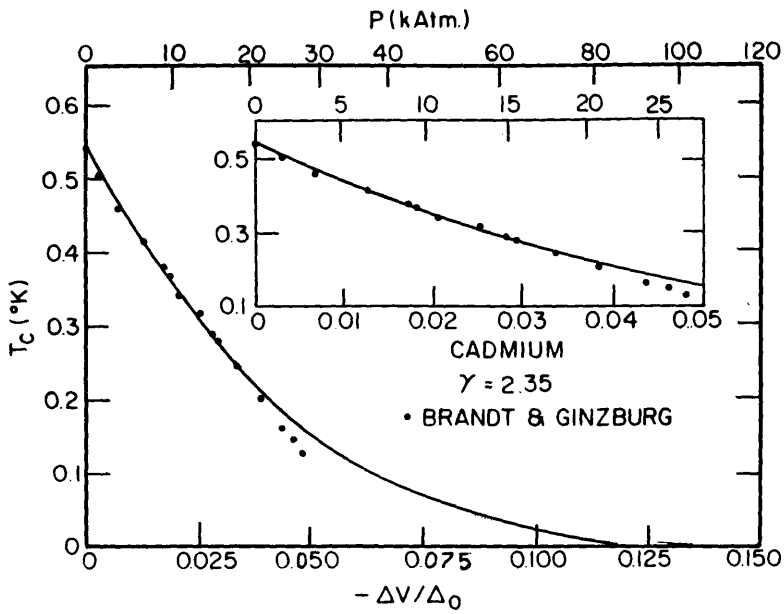

Figure 7

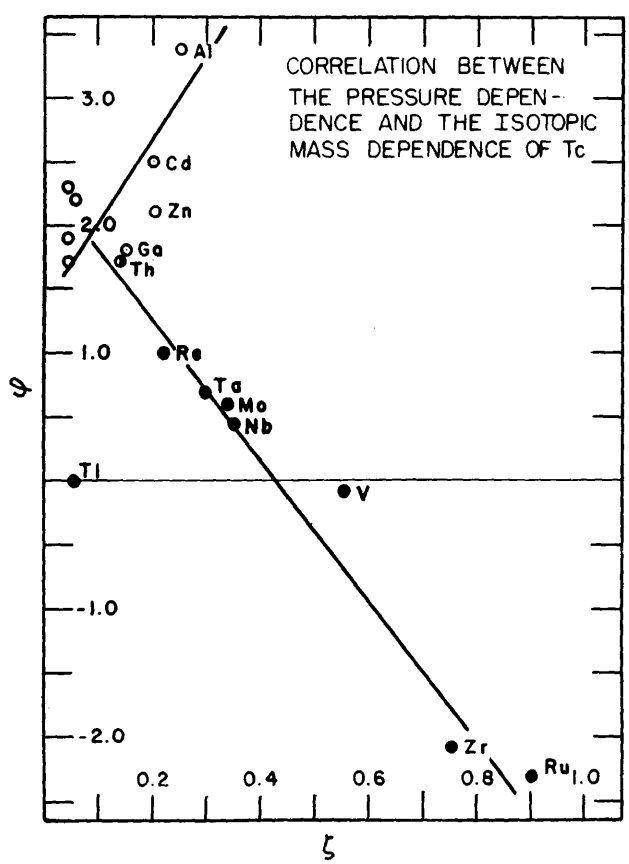

Figure 8

This correlation is not really well understood theoretically. The application of pressure should increase the d-band widths and make the electronic wave functions more like plane waves and less like LCAO wave functions, thus reducing the effectiveness of the repulsive Coulomb interaction. This could lead to a positive pressure dependence of T_c; if so, it would give a φ which decreases rapidly with increasing μ^*, hence with increasing ζ, as is observed. Also, the positive pressure dependence of T_c may follow from the increase in the matrix elements of $\exp(i\underset{\sim}{q} \cdot \underset{\sim}{r})$ between different d-band wave functions with increasing pressure. Clearly, the pressure dependence of T_c should be either weaker or of the opposite sign in the transition metals than in the simple metals. No calculation of T_c or of the pressure dependence of T_C has been attempted for any transition metal. However, our understanding of the band structure should now be sufficient to allow such calculations. Using the formalism of Sinha, with slight modifications, we are now preparing such a calculation for niobium.

Now let us look at some slides that show the difficulties associated with such calculations. First, Fig. 9 shows the form factors $|\langle k|\exp(i\underset{\sim}{q} \cdot \underset{\sim}{r})|k'\rangle|^2$ which enter into the calculation. One can see they vary rapidly with wave vector q, the momentum transfer. What actually enters into the calculation is an average of q^2M^2, which for intraband transitions is more like M^2, the matrix element squared for transitions from one sub-band to a different sub-band. One has to know the type of curve shown in the figure quite accurately, and then of course, one of these curves is accurate only for a given transition at a given point in the Brillouin zone to another point. The matrix element changes as one changes from one point to another in the Brillouin zone, so one has to do elaborate computer calculations to integrate over all these factors. Also, the density of states $N(E)$ itself can vary widely. Figure 10 shows the density of states calculated for platinum by a new technique developed by Mueller and myself. One can calculate the density

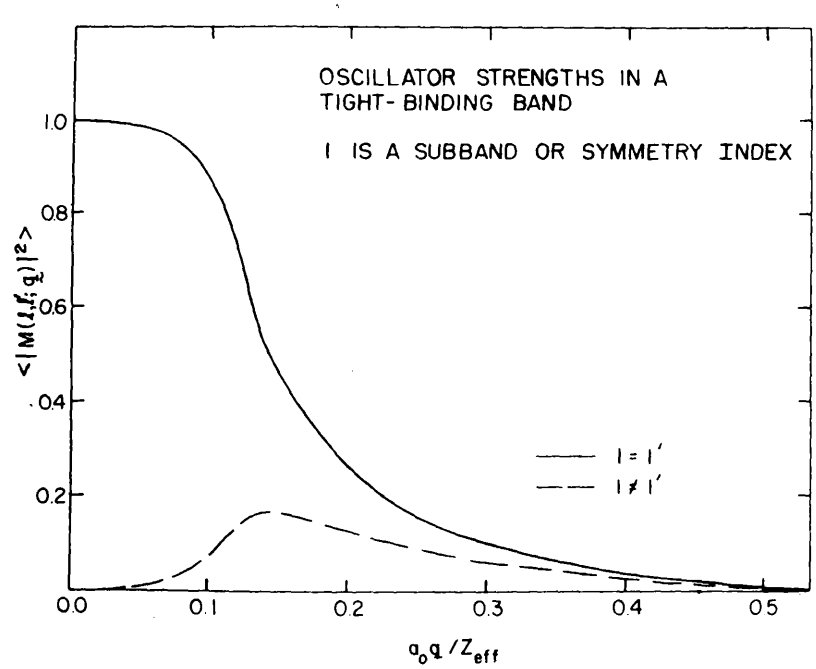

Figure 9

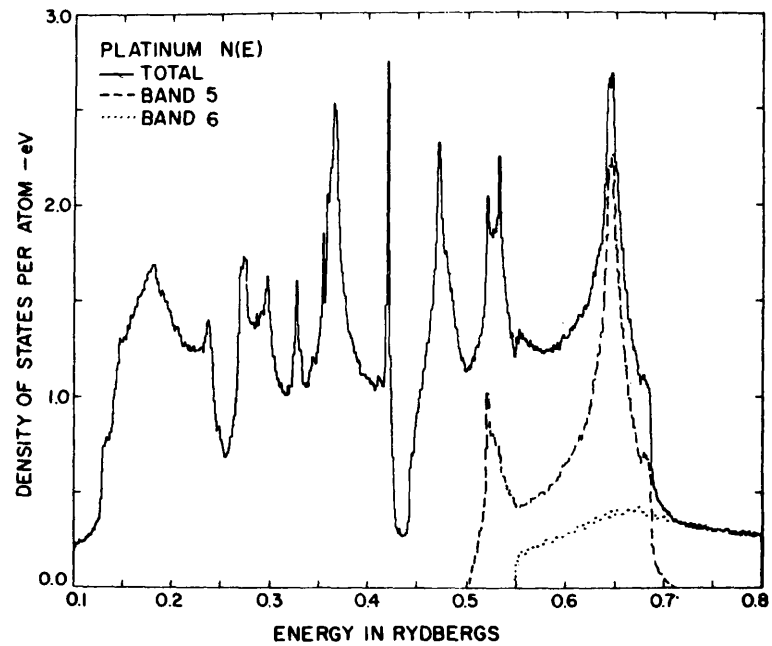

Figure 10

of states with a histogram width of only a thousandth of a Rydberg, which corresponds roughly to a 70th of an electron volt, and can look at the density of states in the different sub-bands. It is easily seen that a combination of all these factors yields sufficient complications to have prevented any calculation of T_c for a transition metal to date.

Furthermore, complications arise even in the calculation of screening, because not only the density of states $N(O)$ for virtual excitations of electrons from just below to just above the Fermi level enters, but the densities of states $N(E)$ for virtual excitations of electrons to energies all around the Fermi level. If $q = 0$, just the Fermi level is involved, but the screening of an interaction for momentum transfers of the order of the Fermi momentum is very complex. Figure 11 illustrates the dependence of the dielectric function $\kappa(q,\omega)$ upon the density of states $N(E)$ away from the Fermi level by showing the reduction in $[\kappa(q,\omega=0) - 1]$ caused by the cutoff of a simple free electron band at an energy $E_c > E_F$. One sees that for $q \simeq k_F$ only one half of the total screening arises from excitations to states within an energy $E_F/2$ of the Fermi level for this simple free-electron model. Of course, this effect is quantitatively somewhat different for a tight-binding d-band, but qualitatively the effect is the same. In short, it is very important to take into account variations of the density of states around the Fermi surface. It was a failure to take full account of this effect within our first model which led to an initial serious underestimate of ζ for zirconium.

Now, let us consider the systematic variation of λ among transition metals, as has been done by McMillan, myself, and others. As is shown by the equation

$$\lambda \propto N(O)\, M^{-1}\theta_D^{-2} \left\langle V_{e-i}^2 \right\rangle ,$$

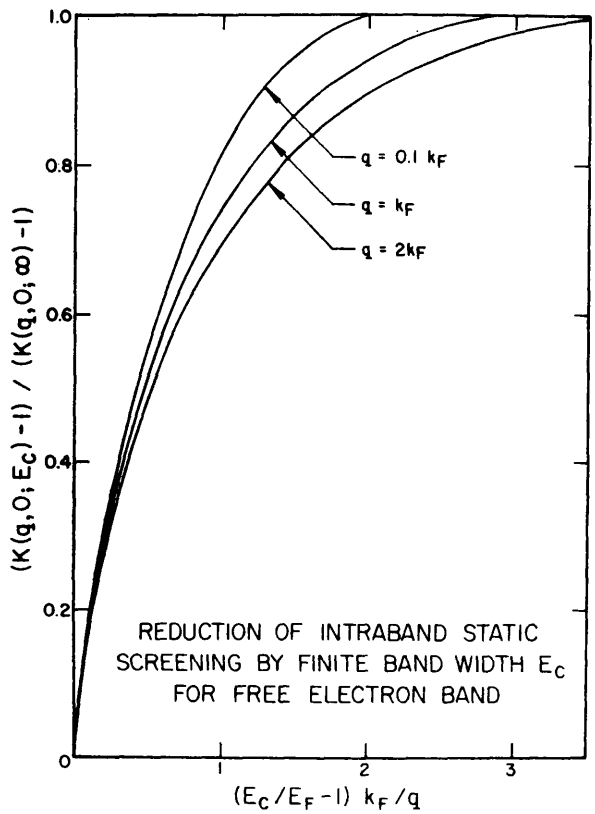

Figure 11

λ should be proportional to the density of states, inversely proportional to the nuclear mass, inversely proportional to the square of an average phonon frequency, and proportional to the average of the square of an electron-ion matrix element V_{e-i}. The electron-ion matrix element V_{e-i} for the transition metals will be proportional to the square of the oscillator strength for momentum transfer q times the electron-ion interaction between plane wave states,

$$\langle V_{e-i}^2 \rangle \propto \langle |qM(q)|^2 V_{e-i}^2(q) \rangle$$

In turn, the matrix element $V_{e-i}(q)$ will be proportional to some energy "E_f" which measures its strength at $q = 0$ and to the factor $N(O)/\langle N(E) \rangle$ which gives the change in screening due to band structure effects away from the Fermi level. This gives

$$\lambda \propto N(O) M^{-1} \theta_D^{-2} \langle |q\, M(q)|^2 \rangle \, [\text{"}E_f\text{"}\, N(O)/\langle N(E) \rangle]^2 ,$$

or

$$\lambda \propto M^{-1} \theta_D^{-2} \, [N(O)/\langle N(E) \rangle]^2 \, f_1(N(O)) \, f_2(Z,n,M) ,$$

where M and θ_D are known experimentally and $N(O)/\langle N(E) \rangle$ can be calculated fairly well. Assuming the dependence of λ upon $N(O)$ to be much stronger than its dependence upon Z, n, and M through the function f_2, and calculating λ from McMillan's equations, one can then determine $f_1(N(O))$ empirically and then plot f_2 as a function of Z, and hence n, for each row of the transition metals. As expected, one finds three curves, each of

which has a very broad peak in the center of the transition metal series with the curves falling off less rapidly at the right for higher masses M. Both empirically determined functions f_1 and f_2 show the expected behavior, leading to the conclusion that the observed variation of T_c in the transition metals is at least consistent with the postulate that the electron-phonon interaction is responsible for their superconductivity.

In order to go beyond the McMillan equation, one must solve the Eliashberg equations numerically to find λ and T_c. The resultant values of λ and T_c will always satisfy the generalized equation

$$T_c = \frac{\bar{\omega}}{1.2} \exp\left[-\frac{1+\lambda}{A\lambda(1-0.62\mu^*)-\mu^*}\right] .$$

Of course, this equation is of use only if one can find formulas for A and $\bar{\omega}$. As McMillan found, the phonon spectrum of niobium corresponds to $A = 0.96$ and $\bar{\omega} = \theta_D/1.2$ for all values of the coupling constants λ and μ^*. Extensive numerical calculations lead to the more general results

$$A = 0.44 + 0.74 \langle\omega^2\rangle^{1/2}/\omega_0$$

and

$$\bar{\omega} = 0.38\ \omega_0 + 0.66\ \langle\omega^2\rangle/\omega_0 ,$$

where $\langle\omega\rangle$ and $\langle\omega^2\rangle$ are defined as by McMillan,

$$\langle\omega^n\rangle = \int \omega^{n-1}\, d\omega\ \alpha^2(\omega)\, F(\omega) / \int \frac{d\omega}{\omega}\, \alpha^2(\omega)\, F(\omega) .$$

The use of this generalized McMillan equation with the attendant equations for $\bar{\omega}$ and A enables one to construct a one-parameter model for the effect of disorder on T_c in thin films. Since a later symposium will be devoted to such effects, I will only note here that this model, when fit to the enhanced transition temperature of aluminum observed experimentally, yields an amazingly good fit, as is shown in Fig. 12, to the values of T_c for all the crystalline granular films of Hilsch, for some amorphous granular films, and for bulk alloys here labelled amorphous. Furthermore, our equations give good agreement with the tunneling experiments of Leslie on amorphous bismuth and gallium films. We compare our calculated values of T_c only with the data of Hilsch because the one parameter in our model represents the degree of disorder, because films prepared by different techniques in different laboratories are characterized by different amounts of disorder, and because Hilsch prepared films of a larger number of different metals than any other experimentalist.

Finally, we wish to present one interpretation of the anomalous superconducting properties of α-uranium. From preliminary band structure calculations we estimate α-uranium to have an f-band of width approximately 5 eV. It is clear from many different band calculations that the f electrons in uranium do form a band and are not localized; this result is supported by the lack of any observable magnetic behavior which could be associated with localized electrons. We postulate the lower edge of this f-band to be slightly above the Fermi level, a model assumption which is consistent with all experimental evidence and with band structure calculations, but which is certainly not well established. Further, as is consistent with symmetry considerations and with existing

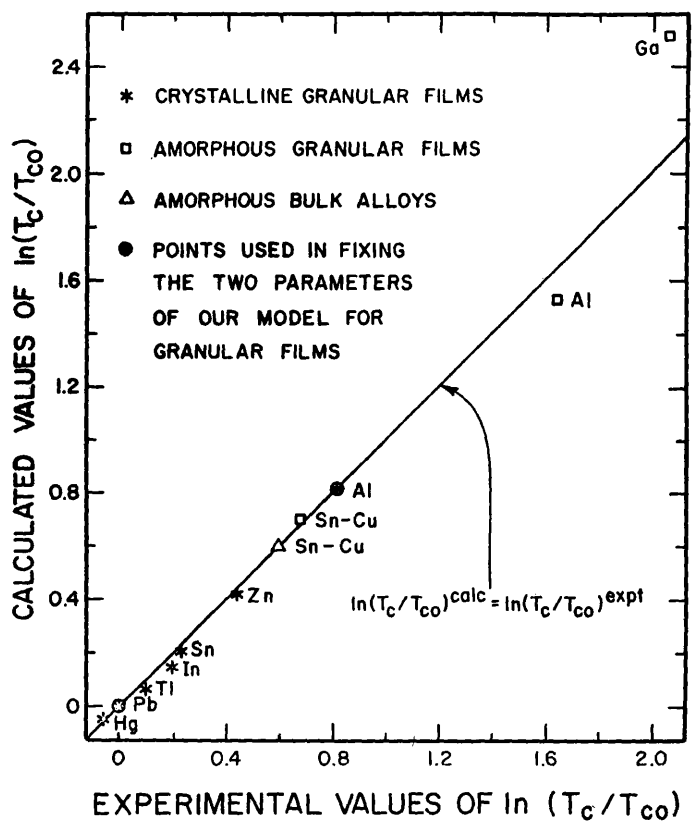

Figure 12

band structure calculations, we postulate the lower edge of the f-band to be very sharp. Finally, we assume the lower edge to move up in energy with increasing pressure, as is the case for cerium. That the lower edge should move up follows from a very general theoretical argument. Squeezing the atoms together increases the overlap between atomic potentials and thus lowers the potential between atoms relative to that in the cores. The conduction electrons spend more time in this region than the f-band electrons do; therefore, the average energy of the conduction band should be lowered relative to the energy of the f-band electron. This point of view is borne out by some transition metal optical experiments as well as by the results for cerium.

Perhaps the most controversial of these assumptions is the assumption that the f states are not localized in α-uranium. The primary reason for this is the fact that the f levels are strongly hybridized. Band structure calculations indicate approximately 40% hybridization of the s-p-d band; our interpretation of the experiments yields approximately 30% hybridization of the s-p-d band. The calculated f-band width, approximately 5 eV, is greater than the bandwidth of several transition metals. Also, note that the ratio of the radius of the f-electron atomic wave function to the interatomic distance is much larger in uranium than in the rare earths. Finally, the f-band in α-uranium either is not occupied or is so slightly occupied as not to induce enough correlation to cause localization of the f states.

Certain other assumptions are also necessary in order to study the superconducting properties of α-uranium. The s-p-d band is very broad, of the order of 20 eV; thus, we assume that the pressure dependence of its density of states should be small, of the order of the pressure dependence of the density of states of a free electron band. Thus, we attribute the very rapid increase in the total density of states $N(0)$ at the Fermi level to an increase in the f character of the electronic wave functions at the Fermi level caused by increasing hybridization. That hybridization should increase with increasing pressure follows simply from the fact that as the atoms are pressed closer together the overlap increases; it is substantiated by band structure calculations. This suggested increase in hybridization with pressure is not directly tested by observing the pressure dependence of the melting temperature as suggested by Matthias because (1) the melting temperature varies with pressure due to other effects such as the $P\Delta v$ term in the free energy change, and (2) the melting experiments were performed on a different phase. Norman Phillips has found that the linear coefficient γ of the specific heat increases rapidly with pressure; we claim that the unenhanced density of states, the band density of states, also increases with pressure due to increasing hybridization. We also find that the enhancement factor $m^*/m_b \equiv 1 + \lambda$ increases with pressure. Specifically, we assume the total band density of states at the Fermi level be the sum of two terms, $N_{s\text{-}p\text{-}d}(0)$, which is relatively insensitive to pressure, and $N_f(0)$, which arises from hybridization and increases with pressure, and assume the total $N(0)$ to be enhanced by the factor $1 + \lambda$ which increases with pressure. The s-p-d contribution $N_{s\text{-}p\text{-}d}(0)$ is furthermore assumed to be the same as in thorium since it is a very slowly varying function of energy.

A host of experimental anomalies are displayed by α-uranium, as is outlined in Fig. 13. Many of the anomalies found at and near 43°K are indicative of a high-order phase change, especially the hysteresis observed in the lattice constants of α-uranium under temperature cycling about 43°K. Also, a discontinuity in x-ray intensities at 43°K, unaccompanied by any discontinuity in lattice constants, has been observed. We tentatively ascribe these anomalies to a cooperative low-temperature distortion of the lattice induced by very-low-lying transverse phonon modes. We hypothesize that this distortion of the lattice distorts the f-band so as to cause a critical point in the f-band (presumably the lower edge) to cross the Fermi level at 43°K. This hypothesis appears to be consistent with the experimental evidence. Although it is not necessary for our discussion of superconductivity, it does show that our model is consistent with the experimental anomalies observed in the normal state.

Four previously proposed explanations of these anomalies are indicated in Fig. 14. The first explained logically and consistently the pressure dependence of the specific heat and the superconducting transition temperature T_c. However, the existence of localized 5-f levels in α-uranium, postulated in this explanation, has not been verified and is in definite contradiction to the predictions of electronic band structure theory as discussed above. The second explanation listed in Fig. 14 also postulates localized f states, is apparently in disagreement with the experiments of Gardner and Smith, gives the wrong isotope effect, and suffers from some purely theoretical flaws.

The third explanation, which is related only to the anomalous dependence of T_c on pressure and isotopic mass, is that superconductivity is induced by the virtual polarization of ions by the excitation of largely localized electronic states. This mechanism for superconductivity is also invoked by Matthias and others for the transition metals. It is certainly a possible mechanism, since the electronic wave functions at the Fermi level have appreciable f character and since localized states are not necessary for such a virtual polarization. It was originally proposed independently by Kondo, Peretti, Adler, and Nordvedt, and myself for the transition metals, but was largely abandoned because in

MECHANISMS FOR SUPERCONDUCTIVITY

Experimental Anomalies Found in α-Uranium

A) Superconductivity

1) Pressure induced superconductivity (Gardner & Smith, Ho & Phillips).
2) Positive isotope effect $T_c \propto M^2$ (Fowler, Lindsay, White, Hill & Matthias)

B) Low Temperature Anomalies

1) $\partial v/\partial T < 0$ (Andres).
2) Extreme anisotropy.
3) Electronic specific heat increases with pressure. (Ho, Phillips, & Smith)

C) Anomalies at 43°K

1) Negative cusp in elastic constants (Fisher & McSkimin)
2) Minimum in $\theta_D(T)$ from c_v (Flotow & Osborne)
3) Sharp maximum in c_p/T (Flotow and Lohr)
4) Positive cusp in resistivity (Berlincourt)
5) Hall coefficient increases by factor 3.5 from 14° to 43° (Berlincourt)
6) Change in x-ray intensities
7) Hysteresis in xtal structure (Fisher), but no evidence of localized magnetic moments (Lam & Fradin, Gardner & Knapp) or change in lattice constants.

Figure 13

Previous Explanations of Those Anomalies

1) Geballe, Matthias, Andres, Fisher, Smith and Zachariasen (1966) -- Transfer of valence electrons from s-p-d band to localized 5f levels lowers volume at low temperatures and suppresses T_c; pressure drives these electrons back into s-p-d band (calculated .04 f-electron/atom at 4°K). (c.f. Ho, Phillips & Smith)

2) Kuper, Jensen and Hamilton (1964) -- Superconductivity induced by virtual excitation of localized f-levels with a strong attractive exchange interaction between localized states on nearest neighbor atoms.

3) Fowler, Lindsay, White, Hill and Matthias (1967) -- Superconductivity induced by virtual excitation of polarons. (Proposed earlier by Kondo, Peretti, Adler & Nordvedt, & Garland for transition metals, where it was less appropriate)

4) Smith and Gardner (1966) -- Superconductivity aided by hybridization of s-p-d band with f-band above Fermi level. (Not consistent with superconductivity of Th and γ-U). T_c at p = 0 due to strain fields in grain boundaries. Suggest low temperature, p = 0 spin density wave.

Figure 14

its original formulation it yielded much too small values for the free energy and critical field in the superconducting state and because it could be destroyed by impurity scattering, in contradiction to experiment. However, this mechanism does not suffer from these objections when applied to α-uranium because, for α-uranium, one considers virtual excitations to f states significantly above the Fermi level, not to other states about at the Fermi level. On the other hand, according to the calculations of Schrieffer and Cappelman, such a mechanism by itself is incapable of yielding the observed anomalous isotope effect. Also, this mechanism would be destroyed by hybridization even half as large as that indicated by band structure calculations.

The last explanation appears to be inconsistent with the observed superconductivity of thorium, which has much less hybridization than does uranium. Also, it offers no explanation of the anomalous isotope effect in α-uranium. The suggested low-temperature $p = 0$ spin wave cannot be ruled out, but appears extremely unlikely.

Figures 15 through 18 illustrate certain features pertinent to our discussion of the electronic band structure of α-uranium. Although the band density of states $N(E)$ has not been computed for uranium, the lower edge of the f-band should be qualitatively similar to that in plutonium, which is shown in Fig. 15 to be very sharp with a width certainly less than 0.02 eV. Figures 16 and 18 show the computed atomic charge densities and atomic levels of uranium. Note that a slight change in the assumed atomic configuration shifts the position of the f levels by 6 volts; this shows the inadequacy of any band calculation for determining the position of the f band. Obviously, its position must be treated as a parameter to be fit to experiment. Figure 18 shows the extreme anisotropy in the α crystal structure, which we associate with the f character of the wave functions at the Fermi level induced by hybridization. The interatomic distances are much shorter along distorted chains in the z direction than in any other direction.

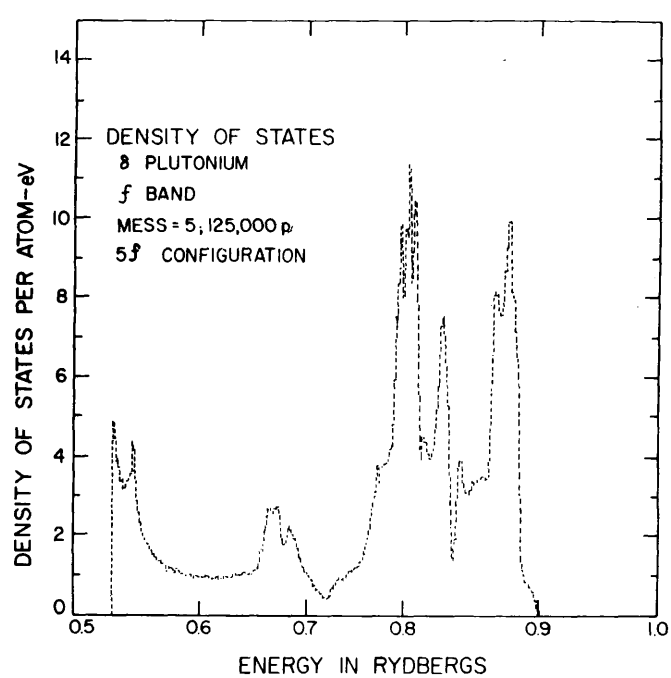

Figure 15

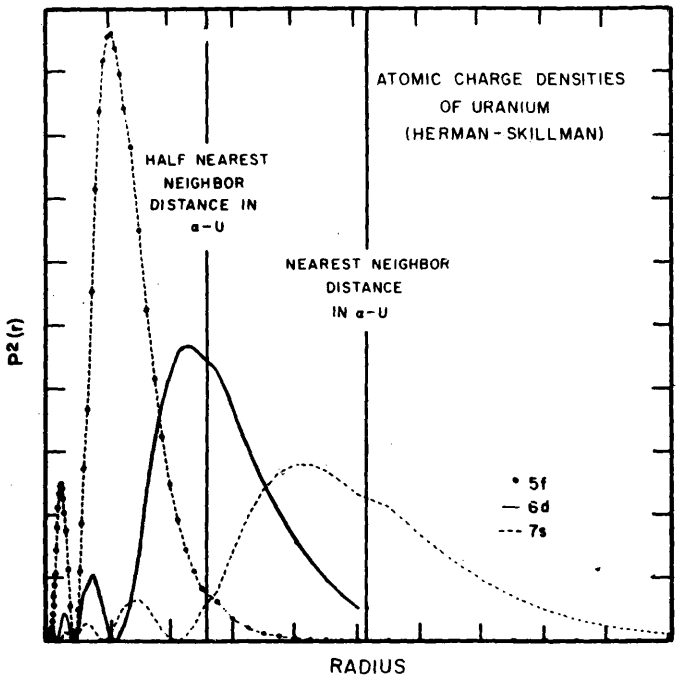

Figure 16

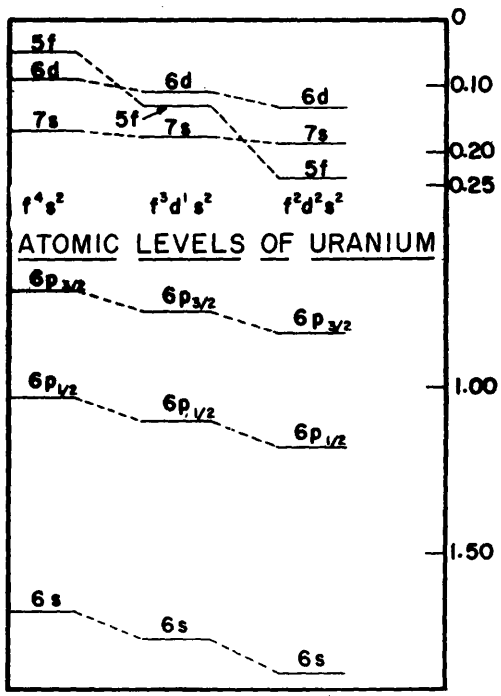

Figure 17

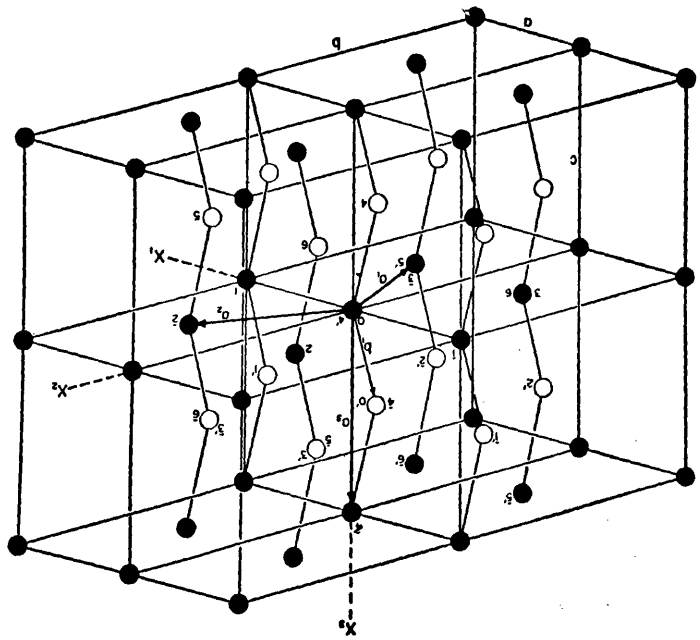

Figure 18

Thorium is a bulk superconductor at zero pressure with no obvious anomalies. Also, it is the presence of an f-band near the Fermi level which distinguishes the electronic structure of α-uranium from that of thorium and which presumably is responsible for the many normal state anomalies found in α-uranium. Thus, we shall assume that it is the presence of the f-band near the Fermi level which suppresses superconductivity at zero pressure in α-uranium when compared to that found in thorium, and shall investigate whether the f-band could lead to the anomalous positive isotope effect $T_c \propto M^{2.0}$ found in α-uranium.

If we just go to Schrieffer's book on superconductivity and look at the energy dependence of the energy gap function $\Delta(\omega)$, as is shown for lead in Fig. 19, we immediately see how the f-band could suppress superconductivity. The energy gap is large and negative in the region of energy just above the maximum phonon frequency ω_0, yet the kernel $K(\Delta_0, \omega)$ connecting the energy gap Δ_0 at the Fermi level with the states in this region is, in general, positive. Thus, the excitation of virtual electronic states in this region leads to an effective electron-electron interaction out of phase with that which induces superconductivity. The introduction of an f-band with its lower edge in this energy region thus suppresses superconductivity. The coupling constant $\alpha^2(\omega)F(\omega)$ calculated from a model phonon density of states for α-uranium and shown in Fig. 20 is rather different from that for the simple metals because of the extreme anisotropy of the crystal structure and hence of the phonon spectra. The calculated real and imaginary parts of the energy gap function shown in Fig. 21, however, are rather similar to those found for simple metals. The region of energy in which the product $ReK(\Delta_0, \omega)\ Re\Delta(\omega)$ goes negative is shown in Fig. 22; adding states in that region suppresses superconductivity. Also, the addition of states in that region reduces superconductivity by increasing renormalization, as shown in Fig. 23, and thus increasing the factor $1 + \lambda$ in the McMillan equation. The lower

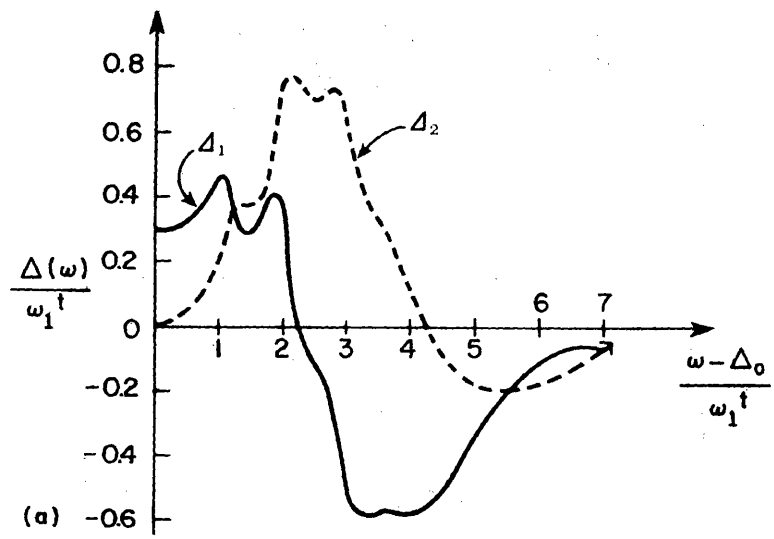

Figure 19

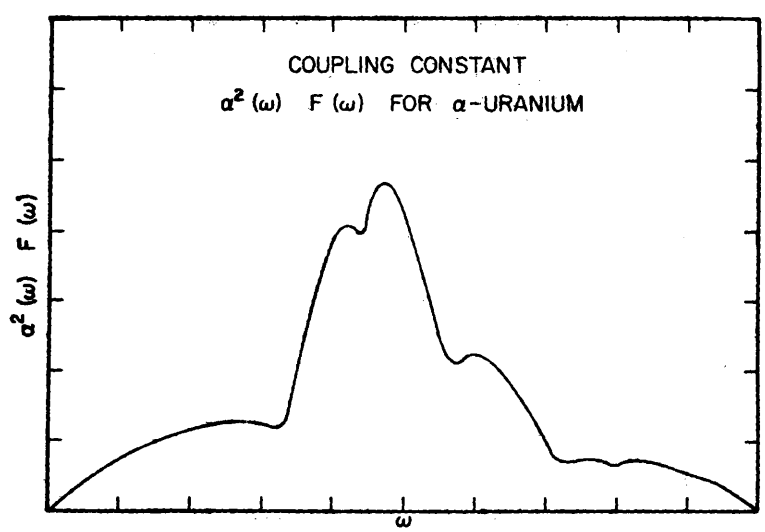

Figure 20

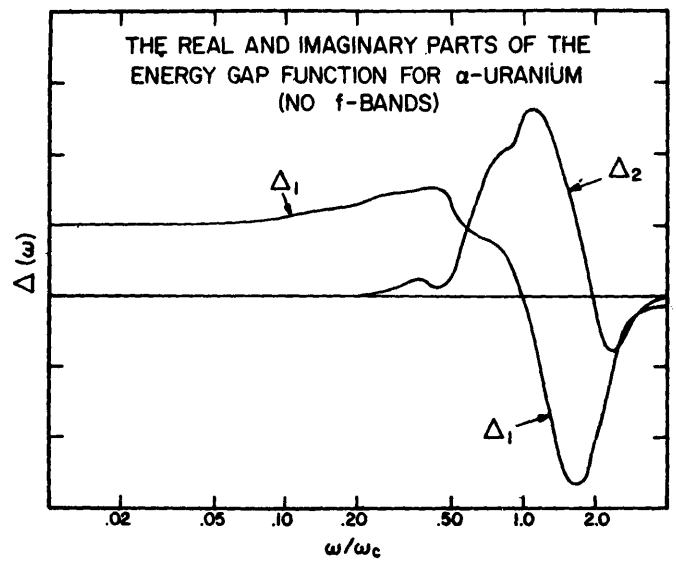

Figure 21

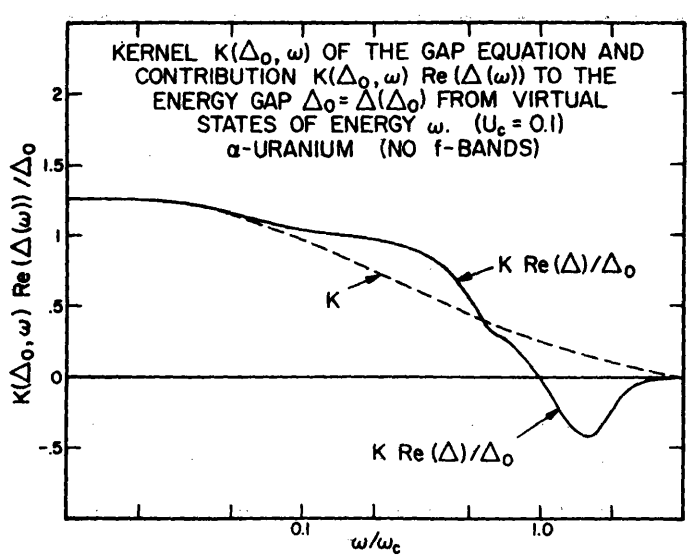

Figure 22

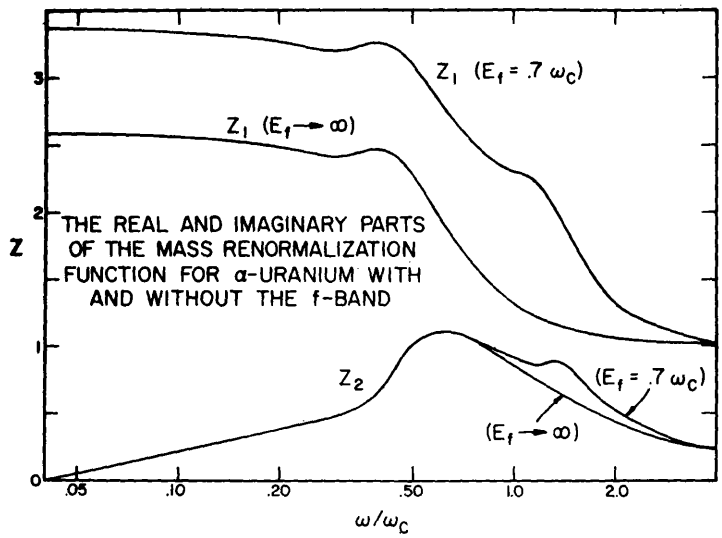

Figure 23

curves in Fig. 23 were computed assuming no f-band, and the top lines assuming an f-band with lower edge an energy 0.7 ω_0 above the Fermi level.

In order to calculate the isotope effect in α-uranium, it is necessary to make the preceding discussion more specific by choosing a simple model for the band structure of α-uranium. The new assumptions made from this point on do not affect our results qualitatively and are not easily justified except that some such assumptions are necessary to obtain numerical results and that our final results depend only weakly on these assumptions. The f-band is chosen to have a sharp square lower edge and estimated to have a density of states of 5 states/atom-eV near its lower edge. Later we shall investigate the effect of smearing this lower edge. The s-p-d band density of states is chosen to be the same as that of thorium, and averages $\langle |M|^2 \rangle$ of the matrix elements of $\exp(i\underset{\sim}{q} \cdot \underset{\sim}{r})$ between different bands are estimated. Then, using these estimates the hybridization of the states at the Fermi level and the phonon-induced mass renormalization are calculated self-consistently for $p = 0$ and $p = 10$ kbars from the known specific heat. The resultant parameters are shown in Fig. 24.

Using this model, we then calculated T_c as a function of the energy E_f of the lower edge of the f-band. As is shown in Fig. 25, we obtained much too large a variation in T_c as a function of E_f because the lower edge of the f-band, of course, is not square. We found T_c varying from a temperature $T < 10^{-5}$ up to $T \simeq 12°$K. A rough estimate indicates that smearing of the edge of the f-band could reduce the maximum T_c to 1° or 2°K. If one were to use only this curve to calculate the isotope effect one could obtain any result from $\zeta = 10$ ($T_c \propto M^{4.5}$) to $\zeta = -2.5$ ($T_c \propto M^{-1.75}$), depending on the choice of E_f. Clearly, a choice of E_f corresponding to that pressure which gives a maximum T_c would give some positive value of ζ substantially less than 10. But, such a calculation certainly can give only a rather large range of allowed values of ζ. The variation of T_c as a function of E_f depends much too sensitively upon the choice of a model for the band structure of α-uranium to yield any useful direct conclusions about the isotope effect.

Parameters for α-Uranium

$M_b(\alpha\text{-U})/M_b(\text{Th})$	1.36	1.44
$N_f(0)/N(0)$	0.30	0.34
$N_f(E_f + \epsilon)$	5 states/atom-eV	5 states/atom-eV
$\langle\lvert M\rvert^2\rangle_{E,E'<E_f}$	0.42	0.39
$\langle\lvert M\rvert^2\rangle_{E<E_f,E'>E_f}$	0.68	0.69
$\langle\lvert M\rvert^2\rangle_{E,E'>E_f}$	0.27	0.28

Figure 24

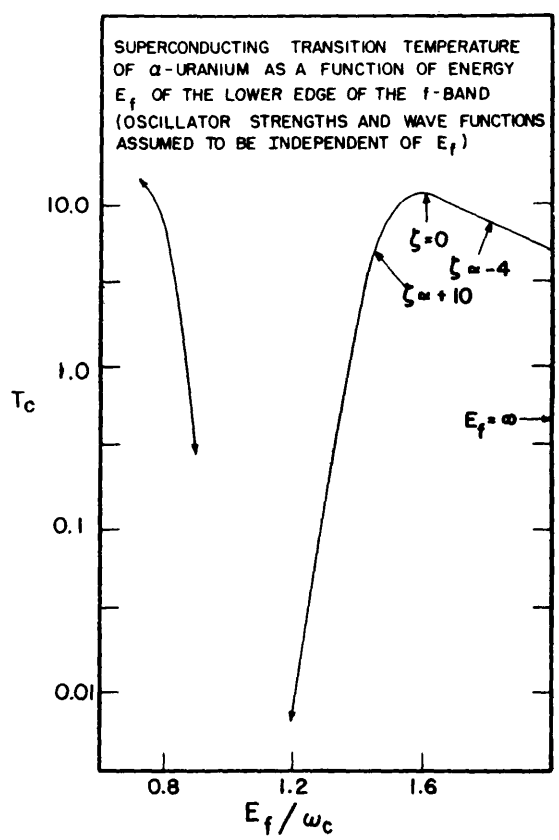

Figure 25

How, then, can one calculate the isotope effect? One must make use of the experimentally known volume dependence of T_c. Using the generalized McMillan equation introduced earlier, the volume dependence of the parameter A can be calculated as a function of the known volume dependence of T_c and the volume dependence of λ and μ^*. Noting that the isotope effect was measured at that pressure at which $\partial T_c/\partial v = 0$, one finds

$$\frac{\partial A}{\partial \ln v} = -\left[\frac{\partial \ln T_c}{\partial \ln \mu^*}\frac{\partial \ln \mu^*}{\partial \ln v} + \frac{\partial \ln T_c}{\partial \ln \lambda}\frac{\partial \ln \lambda}{\partial \ln v}\right]\Bigg/\frac{\partial \ln T_c}{\partial A} ,$$

where

$$\frac{\partial \ln T_c}{\partial \ln \mu^*}\frac{\partial \ln \mu^*}{\partial \ln v} \simeq 0 ,$$

$$\frac{\partial \ln T_c}{\partial \ln \lambda} = \ln\left(\frac{\bar{\omega}}{1.2\,T_c}\right)\frac{A + \mu^*(1 + \langle\omega\rangle\,\lambda)}{(1+\lambda)(A - \langle\omega\rangle\,\mu^*)\lambda - \mu^*} \simeq 4 ,$$

and

$$\frac{\partial \ln T_c}{\partial A} = \ln\left(\frac{\bar{\omega}}{1.2\,T_c}\right)\frac{\lambda}{(A - \langle\omega\rangle\,\mu^*)\lambda - \mu^*} \simeq 10 ,$$

giving

$$\frac{\partial A}{\partial \ln v} = \simeq -\,0.4\,\frac{\partial \ln \lambda}{\partial \ln v} .$$

Now, pressure affects λ by changing the ratio E_f/ω_0, by increasing hybridization, thus increasing $N(0)$, decreasing the average oscillator strength for transitions at the Fermi level, and increasing the average oscillator strength for transitions from the Fermi level to the f-band, and finally by changing the screening of the electron-ion matrix element and hence changing $\alpha^2(\omega)$. Using the parameters of our model, one obtains the approximate result

$$\frac{\partial \ln \lambda}{\partial \ln v} \simeq \left[\frac{\partial \ln \lambda}{\partial \ln E_f}\left(\frac{\partial \ln E_f}{\partial \ln v} - \gamma_G\right) + 2\gamma_G + 13\text{-}3\right] ,$$

where γ_G is the Gruneisen constant. The isotope effect is given by the equation

$$\frac{\partial \ln T_c}{\partial \ln M} = -\,\frac{1}{2}(1 - \zeta_e) + \frac{\partial \ln T_c}{\partial A}\,\frac{\partial A}{\partial \ln E_f} ,$$

where $\zeta_e \simeq 0.4$ is the value of ζ which one would calculate from McMillan's equations. In order to calculate $\partial A/\partial \ln E_f$, note that A depends on volume both through the dependence of E_f/ω_0 on volume and through the dependence of hybridization on volume. Again using the parameters of our model, one finds the approximate results

$$\frac{\partial A}{\partial \ln v} \simeq \left[\frac{\partial A}{\partial \ln E_f}\left(\frac{\partial \ln E_f}{\partial \ln v} - \gamma_G\right) + 8\right],$$

$$\frac{\partial A}{\partial \ln E_f} \simeq \left(\frac{\partial A}{\partial \ln v} - 8\right)\left(\frac{\partial \ln E_f}{\partial \ln v} - \gamma_G\right)^{-1},$$

and

$$\frac{\partial \ln T_c}{\partial \ln M} \simeq -0.3 + \left[\frac{\partial \ln T_c}{\partial \ln \lambda}\frac{\partial \ln \lambda}{\partial \ln v} + 8\frac{\partial \ln T_c}{\partial A}\right]\left(\gamma_G - \frac{\partial \ln E_f}{\partial \ln v}\right)^{-1}$$

$$\simeq -0.3 - 4\frac{\partial \ln \lambda}{\partial \ln E_f} + (4(2\gamma_G + 10) + 80)\left(\gamma_G - \frac{\partial \ln E_f}{\partial \ln v}\right)^{-1}$$

$$\simeq -0.3 - 0.6 + 136/(\gamma_G - \partial \ln E_f/\partial \ln v) .$$

The calculated isotope effect $\alpha \equiv \partial \ln T_c/\partial \ln M$ is shown in Fig. 26 as a function of the volume dependence of the energy E_f of the lower edge of the f-band. The value of α can vary from three down to zero as the value of $\partial \ln E_f/\partial \ln v$ varies from -33 to -150. An estimate of $\partial \ln E_f/\partial \ln v$ chosen to fit the observed volume dependence of T_c yields $\alpha \simeq 2.5$. However, this estimate of $|\partial \ln E_f/\partial \ln v|$ is undoubtedly too small, as it was made on the basis of our calculated too rapid dependence of T_c on E_f. A more reasonable estimate, taking account of the smearing of the bottom edge of the f-band, yields a value closer to 1.0 for α. Although the numbers -0.3, -0.6, and 136 occurring in our formula for α are not known very precisely and although we do not know the volume

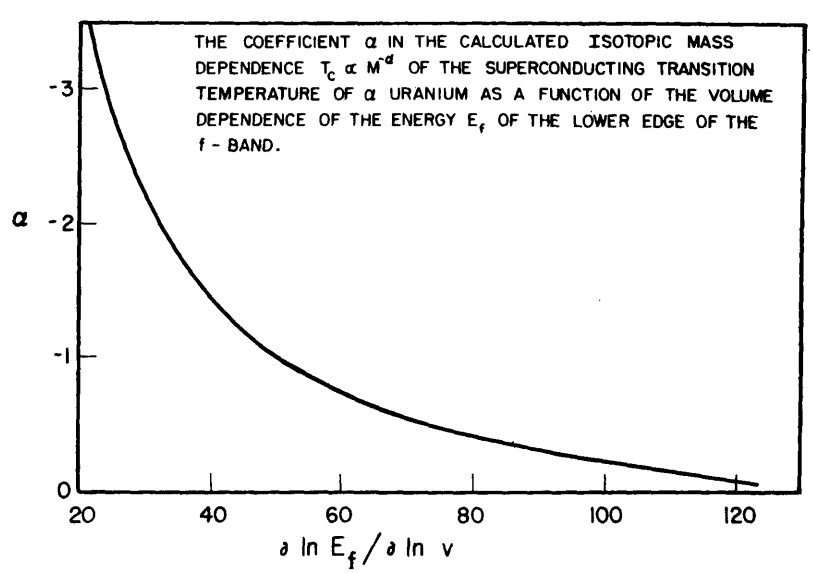

Figure 26

dependence of E_f very well, our calculation of the exponent α of the isotope effect is sufficient to unambiguously give it a positive sign and to bracket its value roughly between 0.5 and 2.5.

It is planned to fit the position of the lower edge of the f-band in a one-parameter band structure calculation so as to give the best fit to the pressure dependence of T_c. This will allow the fairly accurate calculation of the isotope effect so as to more definitively test the model discussed above. It will also allow the testing of the model by looking at the various normal-state anomalies.