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SYSTEMATICS OF SUPERCONDUCTIVITY

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In these lectures I wish to present an empirical and somewhat metallurgical approach to superconductivity. New ideas about superconductors will be presented during the lectures along with a discussion of high temperature superconductors. But, as an introduction, let me talk briefly about the mentality of my approach to high transition temperatures which I think I must do in order to destroy illusions and false impressions that you may have gotten over the last fifteen years.

Ever since Fröhlich and Bardeen considered electron phonon interactions, and in particular since the publication of the BCS theory in 1957, the hope has been that their approach would lead to higher transition temperatures based, of course, on this theory. In 1950, the highest transition temperature (T_c) was reported by Justi for niobium nitride (NbN). It was 15°K. As far as high transition temperatures are concerned in superconductivity there's hardly any other field where so much false information has been distributed – distributed repeatedly to the point where like any good propaganda, people believe it. Let me start with Justi. Justi found $T_c = 15°K$ or 16°K in NbN which was good. It was much higher than anything anyone had seen before. But it was not good enough for Justi. He tried to get higher temperatures. Finally he reported in Z. Physik that he'd gotten to 20°K and in a consecutive paper he reported he'd raised the T_c to 23°K. And then he finally reported that nuclei for the superconducting state existed up to liquid nitrogen temperature. But, let me quickly describe Justi's experiment.

He filled a dewar with hydrogen; and then pumped on the hydrogen. Justi was a very good physicist, actually, and there's nothing wrong with pumping on hydrogen so when he reached 15°K, NbN became superconducting (s.c.). However, when he wanted to raise the temperature back up again, he simply put the hydrogen back in, read the temperature by the pressure on top of the hydrogen bath and completely forgot all about the temperature gradient downward. Naturally he got to 20°K and 23°K. His experiment with superconducting nuclei at nitrogen temperatures went like this. He took the sample on a string, pulled it out of the hydrogen dewar, ran to the nitrogen dewar, dumped it into the introgen dewar, came back, dumped it back in the hydrogen and if it was still cold down in the lower part of the hydrogen, of course it became superconducting. Thus he said the nuclei exist.

It took almost 15 years and the combined effort of many people, but particularly K. Mendelssohn from Oxford to unravel the errors in Justi's experiment. Mendelssohn finally insisted that Justi should perform this experiment at a meeting of the German Physical Society. Justi was unwilling to come; however, he sent an assistant who did the whole experiment. Where upon Mendelssohn got up, took the dewar and just shook it – gently, after which, of course, the superconductivity was gone.

There have been many other cases. You know, of course, about Ogg's report. Ogg found that if you dissolve alkali in liquid ammonia you suddenly get superconductivity even far above liquid nitrogen temperatures. Well, Ogg did the following. As the liquid ammonia cools, the alkali metal precipitates, forms metal bridges and gives the impression that there is a somewhat higher conductivity which Ogg confused with superconductivity. This idea, however, lasted only about two or three months until people verified that it was only higher conductivity and not superconductivity.

After that, the experiments to reach high transition temperatures gave way completely to the theory. And I'm sure that ever since the early days in 1950, you've been told that the T_c's will get higher. You've been told that the optimum T_c probably will be somewhere of the order of the Debye temperature (θ_D), judging, of course, from the famous formula

$$T_c \propto \theta_D \exp\left(-\frac{1}{g}\right)$$

Nothing happened; 15°K rose to 17° in 1953 and today to 21°K. Since 1953 – I counted them – there have been close to 300 publications on how to reach high temperatures, what to do, what the optimum temperature will be, what the mechanisms are, and so forth.

To talk about high superconducting transition temperatures – as far as the theory is concerned, I'm sorry to relate that there just have not been any temperatures.

Therefore I really want to caution you because I feel quite strongly that these theories which are being currently published ranging from Gor'kov to Little may be true--I don't know--however, at the same time let me also assure you they have been until today totally and entirely unsuccessful.

Now, you might say "You're not an organic physicist." I am now. Together with Orgel who really is a very good organic chemist, we decided--against our better knowledge--that we should look into the superconductivity of organic materials. There are many complicated ones, I don't even know the formulas, most are called T.C.N.Q.'s or something similar. We checked a large number. It's very easy to check for superconductivity, particularly if it is not there. Whenever anything becomes superconducting, you will see it if you measure the susceptibility (χ), for instance. It would give you an increased diamagnetic χ. So, if you have 10 materials you put them all in, hope, and look. If one is, you'll see it. We looked at over 100 materials and never saw a trace.

Actually, the only organic material with a T_c, or about as close to organic as they come, was discovered at Bell Labs. It consists of the formula C_8A where A stands for any alkaline atom that forms it. This is called an intercalation compound and it looks like this (see Fig. 1(a)). It doesn't matter whether A is K or Cs, T_c is always low, usually ranging from 0.5°K-0.9°K.

There's another compound, namely $C_{16}A$—today the opinions are divided as to whether it is actually $C_{16}A$ or $C_{24}A$. You can see immediately what the difference is. If it is $C_{16}A$ two graphite layers are adjacent; if it is $C_{24}A$ you have three, until the next alkalide layer comes in again. The moment you go to

$C_{16}A$ or to $C_{24}A$ there is no longer any superconductivity, at least above 10 millidegrees. (Whenever I say there is no superconductivity it means usually above 10 millidegrees). However, graphite is a hexagonal lattice which has three A axes and one C axis. The A axis is never affected because it means that these sandwiches essentially remain the same. They don't extend the graphite laterally. However, the C axis is enormously extended. Alkalides are not the only things you can put in. Actually, you can put in anything you want, $KHSO_4$, for instance, makes a well known compound. It is also well understood that organic compounds do fit into these planes between the graphite layers. My conclusion which, of course, i open to disbelief by others is that you have a superconductor in (a) because the graphite atom can now hang on to an alkali atom. Essentially what you have is a continuous chain of metal alkali and carbon atoms. If, however, this chain is broken such that you have two carbons with nothing else in between, then of course this bond is no longer as metallic as before. Then you should have what it considered a two-dimensional superconductor. I'm sure you have heard a great deal about surface superconductivity, Ginzburg's theory and so forth. There is no reason whatsoever why these two-dimensional sandwiches being unchanged and unaltered, should no longer be superconducting. However, they're not. And here is my thought on this subject. It is, of course, that there is no such thing as two-dimensional superconductivity and, also, there is no such thing as a one-dimensional superconductor. My apologies go of course from Gor'kov to Little, but I don't believe a word of this because, you see, in the past you were told that

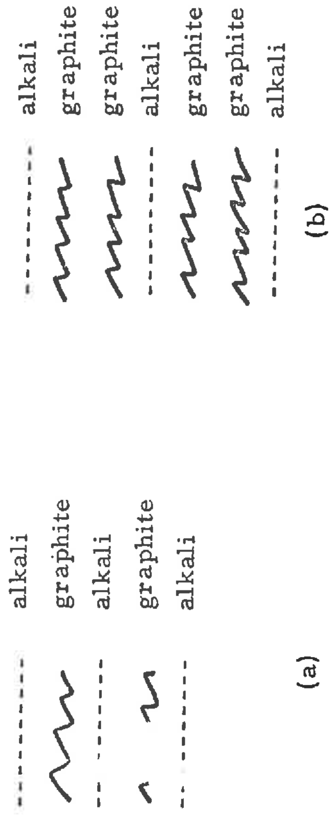


Fig. 1. Schematic diagram of (a) C_8A and (b) $C_{16}A$ where A is an alkali atom.

cooperative phenomena in linear chains, particularly, cooperative phenomena like ferromagnetism, are nonexistent. Therefore, if it is impossible, at least in this system of graphite-alkali (I don't know much about the systems that haven't been reported yet) to have two-dimensional superconductivity, then you can rest assured that there will be no one-dimensional superconductivity either.

Now the next question is, if all these things are so highly speculative, why do people talk about them incessantly? Well, the answer to this is that for the most part it's wishful thinking. There is a science fiction story called, "Four from Planet Five" you know "planet five" is the planet which suddenly disintegrated--turned into asteroids. Well, four children, apparently saved in some strange spaceship, landed on earth. Needless to say, they then transformed the earth once they landed on the north pole. The pole was made immediately inhabitable with green things and so forth. All these things were accomplished because these four children knew how to deal with superconductivity at room temperature. It was a special process done to copper which led to superconductivity at very high temperatures. However there was one thing in this book that really infuriated me, because it said "poor earthlings, they have never gotten above 18 °K." It was just like the old story all over again. That was two years ago, and it is true that the limit had been at 18 °K since 1954. Suddenly last year, when I began to take many things seriously, like melting points, suddenly it was possible to get to 20° and as of today we are at 21 °K. So if you plot the time it took and the transition temperature--clearly this does not give any room for extrapolation. When I talk about it I'm often asked, "How high will you get?" "I don't know." Because, you see, people thought that I had said there was a limit to 18°K. I was always clearcut; the limit was my own stupidity that I could not get above. I just didn't know how to get higher and whatever I did it was 18°K.

But now, let me come back to the correlation to the theory because I think that since this is a summer school, I should teach something and what I really want to teach you is that as far as high transition temperatures are concerned, and any theory (save one that hasn't been published yet by Hopfield) there is a complete and total anti-correlation. As a matter of fact, almost invariably, when a theory predicts a superconductor, and you try to make it, it won't form. The anti-correlation is so good that in fact you think there is something to it. So now, since I am sure that not all of you are theorists and some of you may be experimentalists, let me talk about the experimental approach to high T_c's.

Ever since 1953 when Hardy and Hulm published V_3Si at 17°K we got gradually higher and higher from 17° to 18° to 18.5 and then to 20°. But are you aware that today there are at least 5000 experimentalists working in the field of superconductivity and not one of them has managed to get to a higher temperatures? Now that is an exceedingly dismal record. I mean, if they would try, at least. They don't try for two reasons. Either they take the theories too seriously--then of course they are lost to begin with, since the whole effort is concentrated on verifying one theory or another and of course this is not the way to get to high temperatures. Or then they are determined to publish. You can't publish--on second thought you could, as a matter of fact, that this and that material did not get to a high temperature. I mean, it's the gamble you take. But I think the experimentalists should be a little more adventurous than they have been until now. Instead they repeat the transition of Nb_3Sn endlessly instead of attempting to do new things. Well, mind you, now and then they think they're doing new things. You heard, for instance, about thin films of aluminum getting to 5° or 6°K which of course was claimed in the most elaborate terms of a theoretical approach—surface superconductivity, dielectric effects and so on. It is too bad that most people just do not read these days. Had they read they would have know that Hilsch in 1947 had gotten to 5.7°. Not with complicated layers of aluminum and insulators and so forth—just with one poor aluminum film which was disordered, sometimes even amorphous. He got exactly the same temperature. All the things that are done on thin films today can be found easily in Hilch's work and his collaborators. He's done it all before. He has found that there was some very clearcut correlation between the increased temperature of a disordered film and the Debye temperature, θ_D. All elaborate results on thin films had been obtained by him 20 years ago in a straight forward way.

You see, what I'm trying to tell you is I know how to make superconductors but I also seem to have by now a vague clue as to what may really be the crucial variable in order to determine the transition temperature. I assure you it is not the density of states. If it's anything it is one over the density of states, which goes the other way. This crucial variable is the melting point. I know a lot of people have thought for a long time, ever since I came out with this a year or so ago, that this was just some sort of theatrics to link melting points and superconductivity because melting points are a moderately high temperature phenomena and superconductivity is an extremely low temperature phenomenon. And one may think: Good Heavens, they have really nothing in common!

But, I assure you, they do have something in common. Let me, therefore, give you another conclusion. To treat superconductivity as a pathological case of conductivity, i.e., conductivity that has gone wild, is wrong. Because conductivity, to a certain degree of accuracy, can be dealt with as shown by Bloch and many others on a one electron model. If you assume one electron is in a periodic field or in a periodic potential it gives fairly good estimates as to the behaviour of electric resistivity. However, this has nothing to do with superconductivity. As a matter of fact it is my feeling that the infinite conductivity is only a side effect. The crucial effect is the Meissner effect. And, of course, a Meissner effect requires infinite conductivity whereas infinite conductivity does not require the Meissner effect. And, you know, if German metallurgy had not been as good as it was when Meissner did this work he would, of course, have seen what today one finds in a piece of lanthanum which is a very bad metal with a flux that is a hundred per cent frozen in and nobody would ever have seen anything. As it so happened, Meissner's tin and lead sphere was perfect and so his Meissner effect was better than 99%. But what I'm trying to point out to you is that the Meissner effect is the crucial feature, not the conductivity. You couldn't have a Meissner effect with a finite conductivity but you could easily visualize an infinite conductivity without a Meissner effect. For instance if you make an extremely good, zinc disc, using zinc because zinc is a metal in which one gets the highest resistance ratio in the normal conducting state, that is, before it becomes superconducting. It is six nines, i.e., 99.9999 and gives you a resistance ratio of above half a million. Now when you induce a current in zinc just above the superconducting transition, the current will last for many minutes before it eventually disappears.

The Meissner effect is my most primitive way of looking at superconductivity and corresponds to London's picture of the macroscopic quantum state. What superconductivity involves, in my opinion, are all the electrons. Namely, the valence electrons and all the electrons which are outside of a filled shell. Now, there is no convention about that. You know, you have heard about many metallurgical rules where one defines atoms as having zero valence electrons. Hume-Rothery did this in iron, cobalt, and nickel. When you use valence electrons as they appear in the periodic table you have to be honest. That is to say, for the alkalis it's 1, for the alkaline earths it's 2, and so you go on all the way until you get to platinum where you have 10 and a filled d shell. You start again with the noble metals with copper, silver, gold, you have 1 and you go on again to 8 (Fig. 2).

Now I will show you how this number is another one of the crucial variables for making superconductors. As a matter of fact it has produced several thousands of superconductors. However, what really are valence electrons? The valence electrons, being outside of filled shells, affect other things than just cause superconductivity. Let me stress one point: they may hold the lattice together but they are not

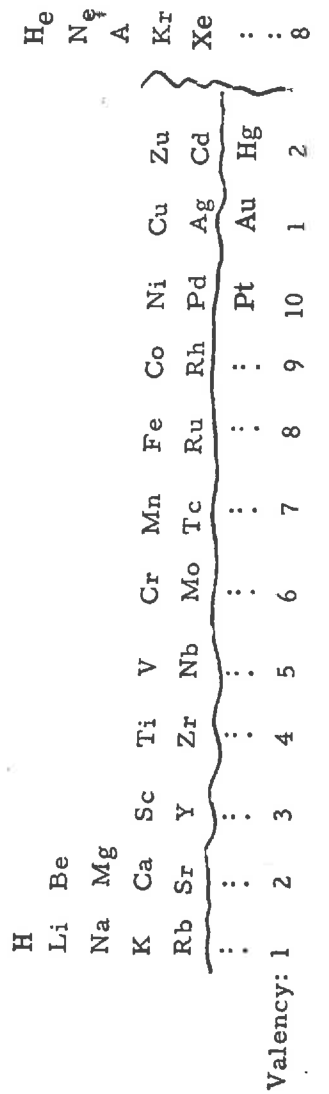


Fig. 2. Valency in the periodic table.

synonymous with bonding strength. You see, so often people confuse bonding strength and melting temperature as being the same. They are not. Only the boiling point is determined by the bonding strength. It's very simple. By the time the atoms fly apart, the bond is gone. But the melting point is a much more complicated phenomenon. As a matter of act, if I seem to express a dim view as to the achievement for superconducting transition temperatures, I assure you I take a much dimmer view about the understanding of melting temperatures. While most people make an effort to calculate superconducting T_c's, as far as melting temperatures (T_m) are concerned, they have completely given up. It's the oldest cooperative phenomena which we know and it's the least understood. Today there is no theory of the melting point (m.p.) and I was intrigued when I found that there was some extremely close correlation. In a cubic lattice your bonds form along directions which are anisotropic. The moment, however, that it melts you have almost complete isotropy. You still have more or less the same coordination as you had in the original cubic crystal. It's a little bit lower, its' about 11 instead of 12 or 14. But basically the material is still together. So it is only that difference between complete isotropy and incomplete isotropy that determines the melting point and that again involves all the electrons outside the filled shells. And this is where the connection comes in. It is this number of electrons that determines the superconductivity. It's also this number that determines the melting point and the moment you change this number you will change the melting point very rapidly and I'm going to show you how the melting point and the superconducting behaviour really go beautifully hand in hand. It's always the same feature. You cannot consider these things as a one particle problem. After all, the bond strength can be calculated (bond between two particles) but the melting point cannot be calculated. You have to consider all the electrons in many atoms and it's exactly the identical situation in superconductivity. Now I'm going to show you how these things look throughout the periodic system.

The superconducting behaviour shows a distinctive pattern throughout the periodic system. What I'm telling you now is true for all superconductors with the exception of 5, no--with the exception of 7 or 8 superconductors altogether. The reason for this exception is the following: today there are many ways that a metal can become a superconductor. In other words, it is my feeling there are many different mechanisms which lead to superconductivity. The electron-phonon interaction is one of them. You know of course that for years electron-phonon interactions have been considered the only mechanism leading to superconductivity and with determination people refused to believe that there could be any other mechanisms. And yet, look at other cooperative phenomena. The closest to superconductivity of course is ferromagnetism (fm). There are today at least 7 different kinds of fm. For instance in Fe, Co, and Ni where one has the d-spin alignment. In gadolinium there is a half filled shell of seven 4f electrons or in europium oxide where you have super exchange between the f electron. The garnets, or things like silver fluoride are different again. There are many, many different ways to get ferromagnetism. The external behaviour is of course always the same except when sometimes they are insulators; usually they are conductors. But when they're ferromagnetic they always have a magnetic moment. Take ferroelectricity which is an electric analogue to ferromagnetism. There are many similarities actually between the development of ferroelectricity and the development of superconductivity, again in different mechanisms.

When I started on ferroelectricity, there was something very strange. There was Rochelle salt which is a complicated crystal, a tartrate with two Curie points and it was a very interesting crystal. Kurtschatov in Russia, and Sawyer and Tover in the United States both discovered the ferroelectric properties at the same time and everybody was very much intrigued. In those days it was not called ferroelectricity, it was called Seignette electricity. Very soon the theories followed. I remember when I was a student there were numerous theories which amounted to many hundreds of papers. They explained ferroelectricity in contrast to iron—why there had to be here a lower Curie point, i.e., a temperature below which the whole cooperative phenomena disappears—the formulas went on and on and on. And yet it turned out that Rochelle salt was one of the very rare exceptions. I will spare you all the comedy of errors that came afterwards when ferroelectricity was considered as one of nature's extreme accidents. They culminated in 1956 or 57 after having found so many new ferroelectrics I decided something was wrong with the field.

For instance, at that time one of the crystals about which there had been 400 or 500 articles written was ammonium sulphate. Everyone had been completely puzzled by its behavior. You know, ammonium sulphate is a fertilizer. It's an extremely simple crystal. It's one of the most simple crystals known today. Simon and Fowler in 1916 saw a transition and decided it must be some kind of a transition connected with the non-spherical symmetry of the ammonium radical, that it rotates or showed hindered rotation or something like this – so they decided that it is an interesting transition. For instance, later there were papers that invoked 9 different relaxation times to explain the dielectric phenomena of that crystal. Until one day I realized could all this be wrong and all that happened to ammonium sulphate was that it was ferroelectric. As a matter of fact it was, and this was the end. After that I left the field because that had been too much.

Can you imagine hundreds and hundreds of people overlooking it, just plotting away – and now you see I came to that conclusion because by this time there were all indications that just about everything was ferroelectric that went through a dielectric transition. Any dielectric that shows something is probably ferroelectric and if it isn't ferroelectric, it's antiferroelectric. Like C. Kittel who once said something very wise when a student came to show him something that he didn't care too much about, "It's true, there must be forces at work." Now surely, there are electric forces at work, there is not doubt about that. You know, the number of mechanisms today in ferroelectricity is unbelieveable. They go from ammonium sulphate to thiourea to potassium dihydrogen phosphate. But the latest ferroelectric that has intrigued me is HBr, bromic acid. However, because of the fact that people started out with Rochelle salt it took 25 years just to overcome the mental block that there does not necessarily have to be a lower Curie point, that in fact

not only the hydrogen bond is a crucial feature of ferroelectricity. It is one of the crucial features but there are many others also and the result of all the other mechanisms is always the same – it's ferroelectric. And this same situation in my opinion exists in superconductivity.

But due to the excellent and formidable support by the theory and since it was once decided on the electron-phonon interaction in 1950, you can't change the outlook. However, I will show you now why I think this is such an oversimplification. If you plot the T_c's versus these numbers of electrons (valence electrons), then you will find the behaviour in Fig. 3 and those cases which don't fit (7 or 8 exceptions) are just very representative of these other mechanisms. The transition temperature goes like this: it's a beautifully symmetric function throughout the periodic system. As a matter of fact whenever anything is not symmetric in the periodic system, watch out, because the periodic system, as far as I am concerned, is still one of the primary tools and the one crutch you can lean on that won't fail you. If it's symmetric within the periodic table you can be sure that it's right.

The minimum is at 6 electrons and the maxima are near 5 and 7. There is no superconductivity further to the right until you get to the sp elements where again everything is superconducting. Whatever you do (with one exception – you have to have a metal; if you don't have a metal, you're not going to get superconductivity) in the sp range, you will get superconductivity invariably. For sd elements in the range from 4-8 electrons it matters immensely whatever you do (transition temperature and otherwise) while in the sp region whatever you do doesn't matter at all to

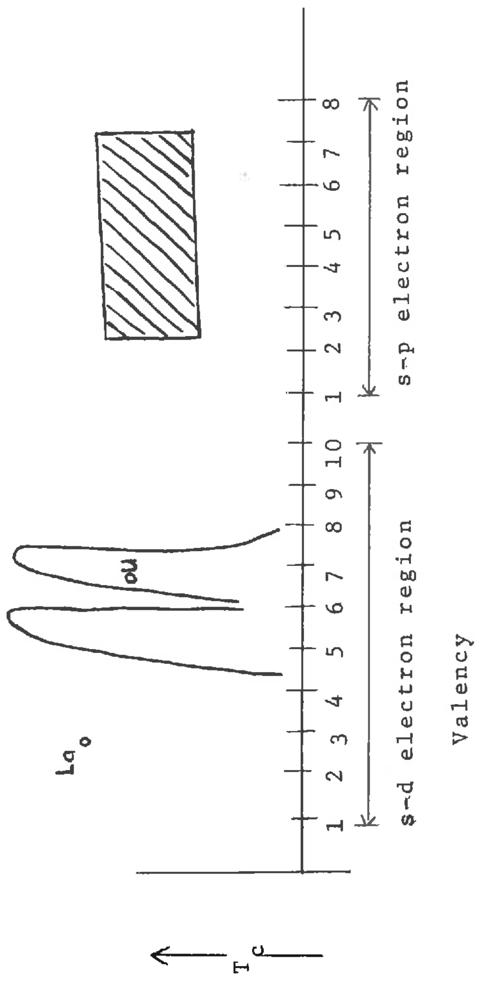


Fig. 3. Transition temperature versus periodic system valency. The s-p electron region is on the right and the s-d region on the left. The values on the curve are $\alpha (T_c \propto M^\alpha)$.

superconductivity. I came to the conclusion that there must be a different cause for the superconductivity. In the sp region the isotope effect, $T_c \sim M^\alpha$ where $\alpha = -0.5$ was a beautiful proof for an electron-phonon interaction. Our first attempt to show that this was not universal was extremely lucky, we just chose ruthenium for metallurgical reason (it's one of the metals one can obtain that is really clean). We looked for the isotope effect in ruthenium just to show that the mechanisms would be different. There was no isotope effect. α was completely zero.

Zirconium which in the periodic system is an element symmetric to Ru with respect to the half filled shell has also a zero isotope effect. As you go toward the center of the periodic system α is -0.3, -0.4, etc. We're trying to measure the isotope effect of tungsten directly now. That is difficult because the T_c is only 10 millidegrees. But you know Black and Wheatley will get it and this isotope effect will be -0.5. So you see there is an entirely different mechanism here and only the very low temperature elements, W, etc., will correspond somewhat to the sp behaviour.

Thus I have tried to show by these deviations from the normal isotope effect that the mechanisms are quite different as well as the different behavior of T_c.

But now let me show you a few diagrams so you can see what I'm trying to talk about. Fig. 4 is an old plot out of a few hundred alloys to illustrate the sd behaviour. It was done a few years ago in order to see just how well it fits. Already you can see in this plot some of the exceptions that I am going to talk about. La is a big exception. U is way too high like La. As such they are very drastic exceptions from this picture; however, later I will come to this in detail.

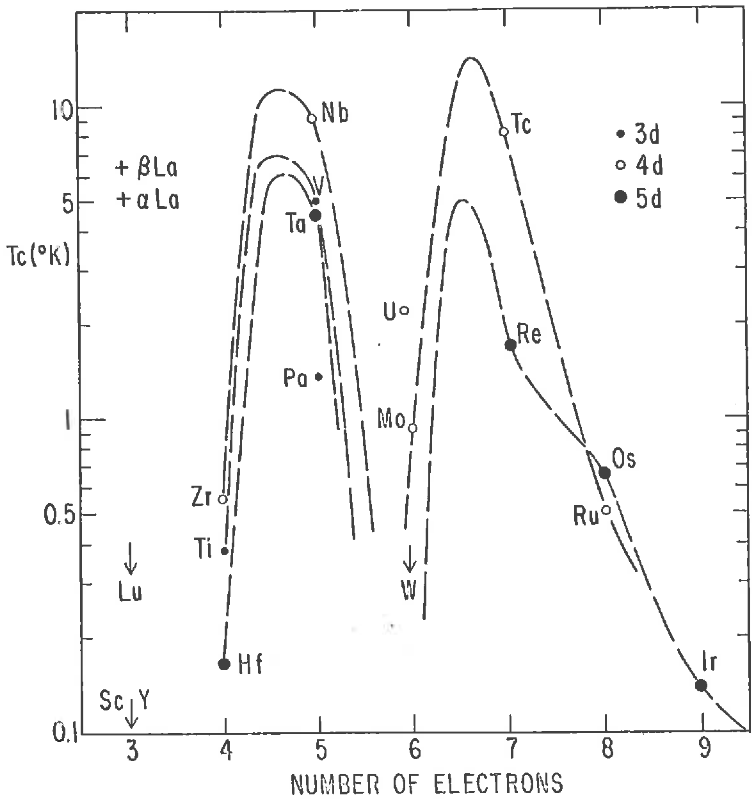


Fig. 4

Now let me show you what the periodic system looks like in Fig. 5. Some of the sp elements are not really metals (they are semimetals) and only once they have become real metals do they then become superconducting. There are several ways in which you can do this. You can do it by compound formation; it's the easiest way. You can do it by condensing thin films at low temperatures in order to get a different crystallographic modification; it's a good way. You can also do it by applying high pressures, that's the cleanest way. Bismuth can be done in both ways. Antimony can be made superconducting only by pressures; also tellurium, selenium, germanium, silicon; and during the last three weeks (we were really determined to show this behaviour), we made phosphorous superconducting with high pressures. It's easy enough; you just squeeze it to 80 or 90 kilobars and it becomes a very good superconductor at a very accessible T_c of 6.5°K. Arsenic isn't superconducting yet because technically the pressures aren't high enough. There will be 3 more superconductors during the next year—arsenic, sulphur, and iodine (lowest pressure between 200-300 kilobars). These will all become superconducting and thus complete the picture of the general behaviour of superconductivity in this range—again absolutely in contrast to the very specific behaviour in the sd region.

Now, at present, this looks moderately homogeneous. Let me point out, however, that we made some changes in the periodic system. Here is Lu; all of your text books show La in its place. We just shifted the whole thing over and started La near Ba then all the rare earths, and finally Lu under Y. From all points of view, a crystallographic, metallurgical,

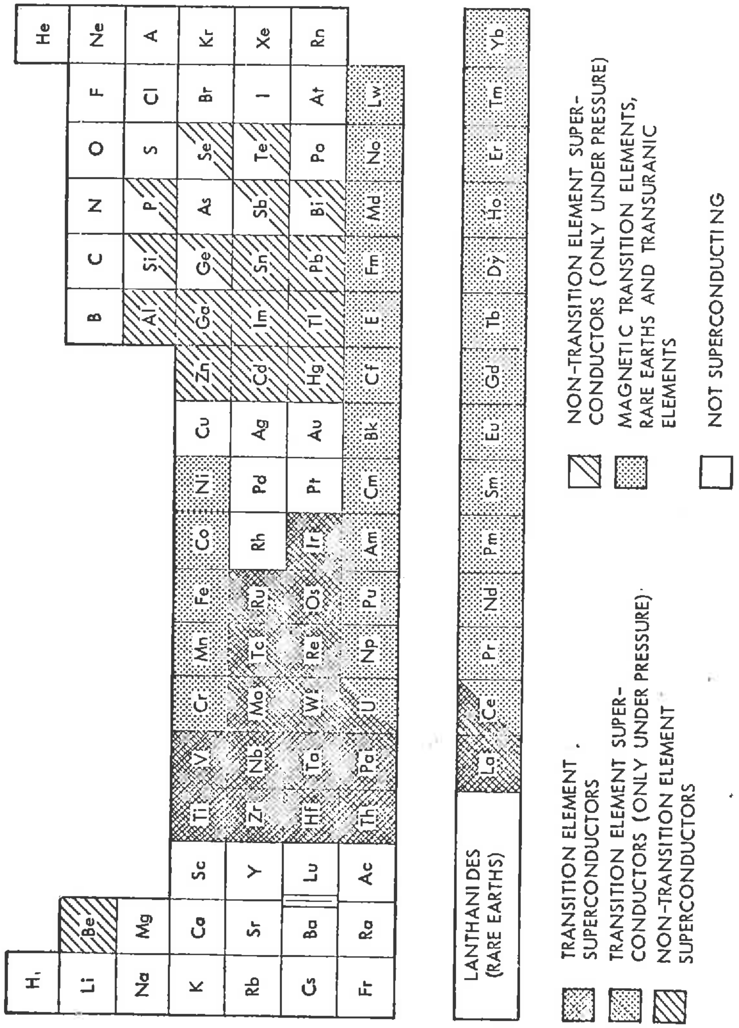


Fig. 5

superconducting, melting point in particular – this is the proper way to do it. And it was a mistake in the periodic system – unfortunately mostly propagated by the Welsh Company, that La was here and again, everybody copied it. When we published that there was a mistake in the periodic system and La should be where Lu is and vice-versa, we were extremely proud of it until we found it in the Landau Lifschitz book where they had previously mentioned it. In subsequent papers we gave them credit but we didn't know it at the time we came to this conclusion. Uranium, about which I will talk at length, is both antiferromagnetic and superconducting. Uranium will do just about anything you want it to do.

You have been told, I'm sure, that the transition temperature is determined by the density of states. Let me show you quickly how the behaviour of the density of states looks in the periodic system. It really requires some fantastic optimism to assume that this one coincidence should be crucial for the superconducting behaviour. What is really (at least, sort of) reminiscent of the T_c curve in the periodic system is the melting point (Fig. 6). As you go from left to right unfortunately in the first series ferromagnetism begins: it's always the same. If you don't get superconductivity where you should, you get ferromagnetism instead. And for that matter, vice versa. Something else is very elegant. The number of valence electrons does not only determine superconductivity and the melting point, at the same time it relates intimately to a phenomena like ferromagnetism. This is why the melting points of Fe, Co, Ni are also completely anomalous. But basically the same type of symmetry throughout the periodic system for the melting point

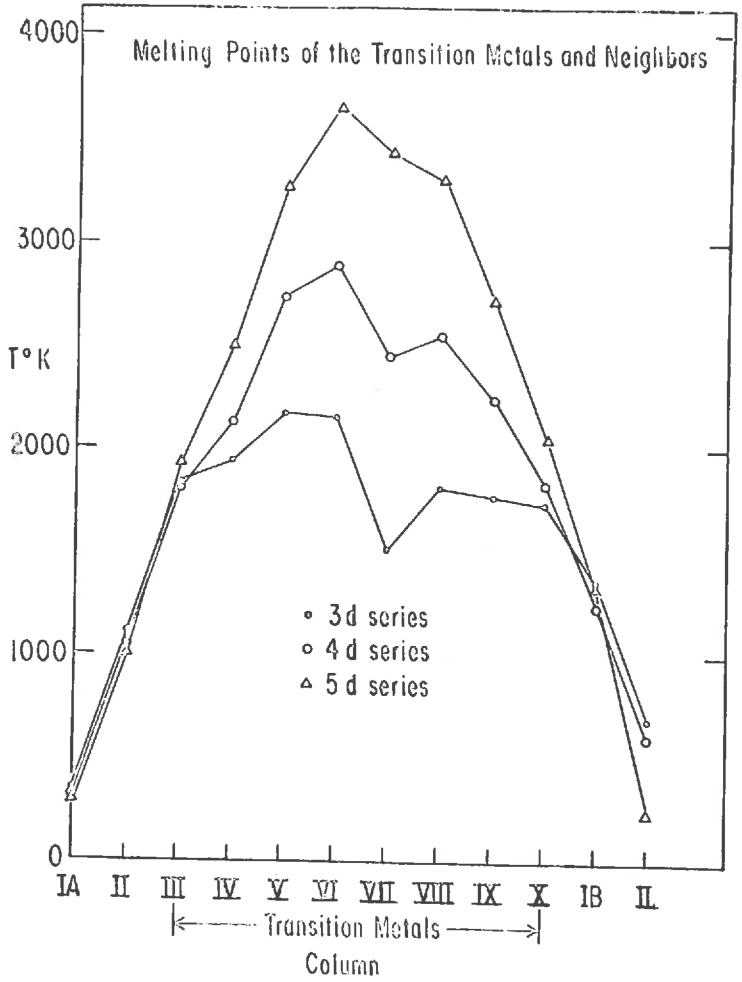


Fig. 6

is evident. A few years ago, I realized this only by looking at the properties in the periodic system to see what coincides with the T_c's. The only thing I knew was that the density of states did not. But I didn't know what would until one of my students said "let's plot the latest data in all detail." Now let me show you these points, scandium, yttrium and lutetium, none of which are superconducting. La has a melting point far below that of the other three elements--we didn't put it in because it would have marred the picture. So you see it not only does not fit the usual pattern of superconductivity, it also does not fit the usual pattern of melting points.

Let me now come back to the systematics of T_c. There are two cases on which I want to concentrate for a time. One is Sc, Y, Lu, La. Now, how do these elements differ from one another? If you believe superconductivity has something to do with resistivity (ρ) chemical valence (V), number of carriers (n), boiling point (b.p.), χ density of state (N), θ_D, then we write

$$T_c = T_c(\rho, V, n, (\text{b.p.}), \chi, N, \theta_D)$$

If you do this there is no distinction between these 4 elements. But Sc, Y, Lu are not superconducting and La is at 6°K. Because it is superconducting, obviously there is something different. Now what is it? The largest difference is in the melting point since this temperature is radically different from what it should be. It is 500°K too low. And those are the only two pronounced features in which La differs but of course if we are trying to explain superconductivity we cannot use superconductivity as a criterion--this is like calculating the interaction constant by measuring the T_c. And only the melting point is the other independent parameter that makes La different from all the other three.

A while ago we found that Mo was a superconductor at 0.9°K by cleaning, which was a rather unexpected feature. So we decided that maybe Sc, Y and Lu were also dirty. We tried to purify, and then we tried to extrapolate from alloys. There was no hope for Y to become superconducting above 10^{-2}°K. That is when I realized that something was really wrong, because all these elements are identical and the one quantity in which they were not was the melting point.

The reason for this turned out to be in the character of the electron configuration. As I showed you before, La is the last element before the rare earths begin, before the f electrons are actually localized. So in La you have the f electrons just about to appear (I am talking in pictures) but are not yet quite there; this is the cause for the superconductivity of La. And I will show you how analogous La and U are, strictly from every point of view--melting point, superconductivity, all other behaviours. The similarity between the two is actually quite astonishing.

I can't give you an explanation for superconductivity, I can only give you the critical conditions for the occurrence of superconductivity in relation to metallurgy in particular, and the periodic system in general.

In conclusion, of course, an enormous amount of metallurgy is involved in superconductivity. I'm sort of sorry to say that in the next lecture I will bore you with some metallurgy in which I'm sure you are not interested but which is necessary for you to see the

approach to get superconductivity first and to get the high T_c's second. While I wouldn't usually subscribe that the end justifies the means, as far as superconductivity and metallurgy are concerned, I think it does. As a matter of fact today's situation has reversed this. Today it is much easier to do metallurgy through superconductivity. For example AuMo showed complete immiscibility until we made some AuMo alloys and checked them. There was superconductivity and hence the phase diagram was wrong. You see, it's so easy to check for superconductivity. Every one of the other metallic properties, except χ, is a major job to measure. To measure superconductivity is a cinch. It can be done--I used to do it when I was young--40-50 samples a day. It is really the easiest measurement and it is possible to do metallurgy on a scale that is really quite unprecedented. They use superconductivity today for all sorts of metallurgical approaches because it's a non-denstructive test, a quick test, and you get three parameters: T_c gives the composition, the width gives the homogeneity, and the Meissner effect gives the quality. All this in one easy measurement. So the metallurgy, while at first it was indispensable for superconductivity, is now benefitted by superconductivity.

LECTURE II

Now let me go on from yesterday where I said the melting point of La is too low because of the f electrons or the impending f electrons. Obviously the impending f electrons will interfere with the melting point. Everything in the periodic system always varies in a monotonic and symmetric fashion. For example, when you go from left to right the melting point goes as in Fig. 6. However if you go vertically, the melting point is again a monotonic function. So in order to evaluate what the melting point of a certain element does we interpolate vertically and then horizontally and by doing this you get extremely precise data as to what you should have. For most of the elements this fits extremely well. They all lie on smooth curves. And when I say to you La is too low then it is the fact that we get a melting point of 920° and we should get a melting point of from 1500-1600°. Why is this so?

Well, as I told you before, all the electrons that contribute to superconductivity, to forming the crystal lattice, are the electrons outside the filled shells. However, there is one exception–f electrons which will not contribute because the f electrons are too far inside the electron shell and too close to the nucleus. For instance, the average radius of s and d electrons in La is 1.8Å; the f electrons of the following elements (Ce---) have a radius of only about 0.9Å or less. So they no longer contribute to the formation of the crystal lattice. And what we say is this: while the normal

trivalent element will have 3 valence electrons, namely s and d electrons, in the case of La it may look like this, $(sd)^{3-x}(4f)^{x}$, where x may even be time dependent if it's a virtual state. This mechanism is responsible for inhibiting the contribution to the formation of the crystal lattice and thus lessening its rigidity hence lowering its melting point. Clearly as we go on to the rare earths this effect will disappear as once there are no more f electrons because of the filled shell then everything should be just as before and we should get the correct melting point. Now in Fig. 7 let me show you how this is born out. Everything again is monotonic, La and Ce have the lowest melting point. Then the depression begins to disappear. The tendency to fill half-filled or filled shells is enormous. Therefore what happens in europium is that you pull one electron from the d range and turn it into an f electron. One is left with a divalent metal and one extrapolates to get the correct melting point for europium. In the case of Yb the same thing is repeated. Instead of the 13 f electrons according to the periodic system, you have 14 by making it a divalent element. This is the reason for the dips in the melting point at europium and Yb. As we begin to fill up the f electrons the melting points became more and more normal and by the time we arrive at Lu everything is normal again, just as Sc and Y. So this so-called hybridization between s and d and f electrons is in my opinion the cause of the reduction in the melting point of La and the consecutive rare earths as Ce. Always remember whether you have a virtual f electron or an f electron that is localized; they will never contribute to the rigidity of the crystal lattice whatever you may find in the literature.

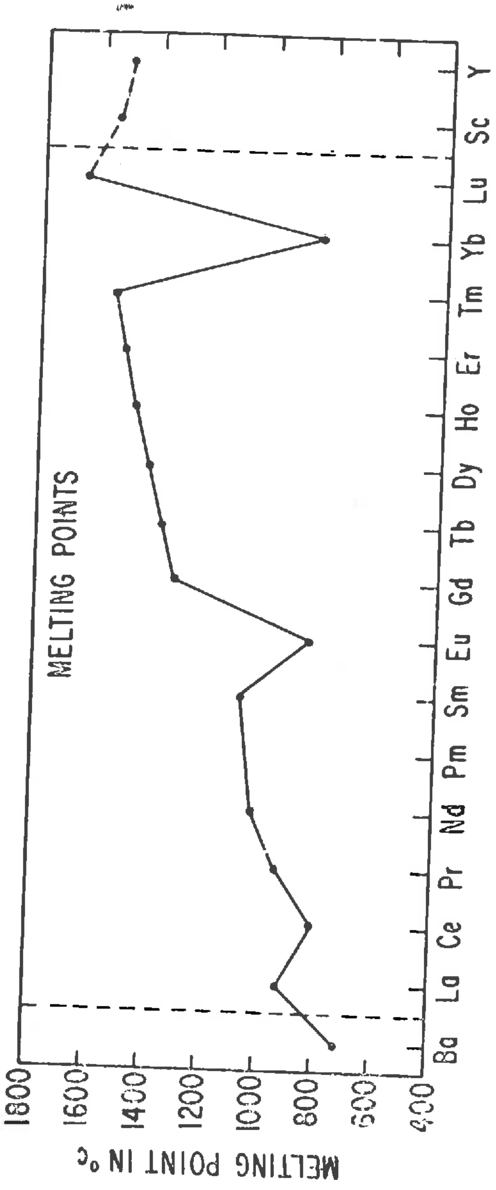


Fig. 7

Basically, there are no exceptions in the periodic system or in nature. As I've shown you in the periodic system before, the 4 f's eventually repeat themselves in the 5 f's, namely from U on. Now the 5 f and 6 d levels are much closer together than the 4 f and 5 d levels and this close proximity interferes more. That is one of the reasons, but essentially the 5 f's will be more active because they are closer to the binding electrons, to the valence electrons. They will be more active in changing the behaviour from that which would normally be expected by extrapolation or interpolation. The results are in Fig. 8. This is just where I show you the discrepancies. The line is what you should get for clean cut trivalency in the rare earths and you see how the discrepancy (the length of the line) vanishes. In Fig. 9 you see the same thing for the 5 f's, and you see it is very intriguing. The same behaviour repeats itself only much more so. In protactinium the f character begins and gets more and more pronounced towards larger atomic numbers. You see now that the elements that follow thorium should have a quadrivalent or trivalent character. The depression of the melting point is even more than anything ever expected before--it's huge. U in the periodic system is a 6-valence element. W has a melting point of 3300°C. U is below in the periodic system and melts around 1200°. It gets even more drastic with neptunium and plutonium, both of which are around 600°C. Neptunium, which is the same column, corresponds to rhenium which is about 3000°C. So we now get a discrepancy which is much, much larger yet. The discrepancy due to the 5 f hybridization is just stunning and that, of course, is the explanation for why these elements--Np, Pu and also U--have these extremely low melting

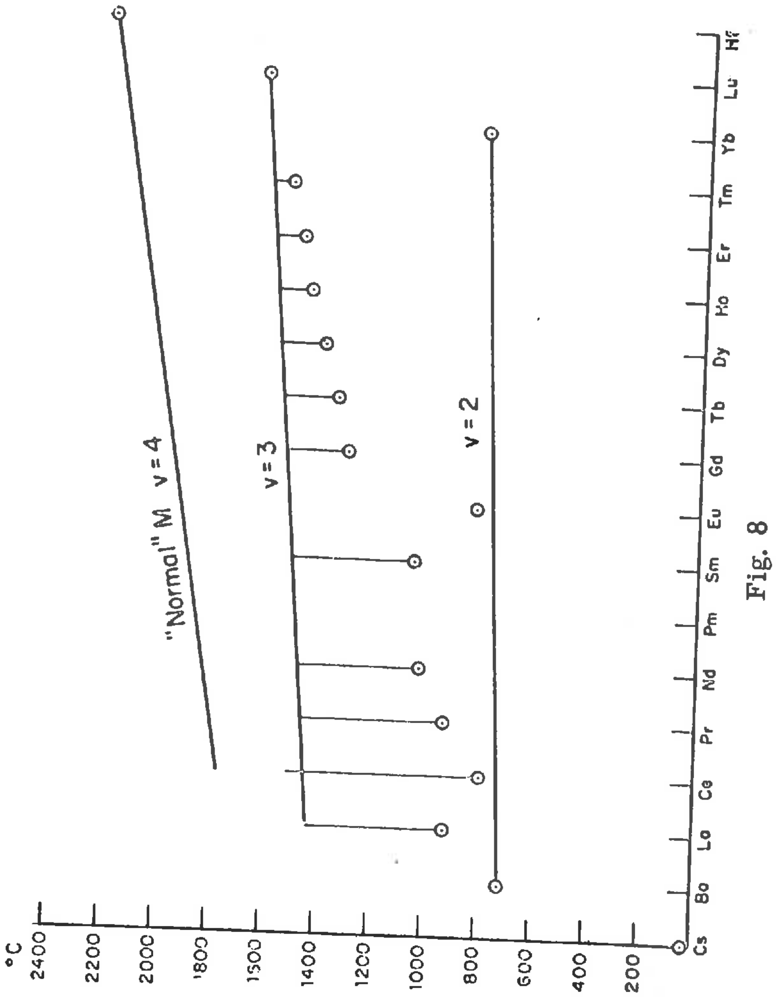

°C
2400
2200
2000
1800
1500
1400
1200
1000
800
600
400
200
Cs
Ba
La
Ce
Pr
Nd
Pm
Sm
Eu
Gd
Tb
Dy
Ho
Er
Tm
Yb
Lu
Hf
"Normal" M v = 4
v = 3
v = 2

Fig. 8

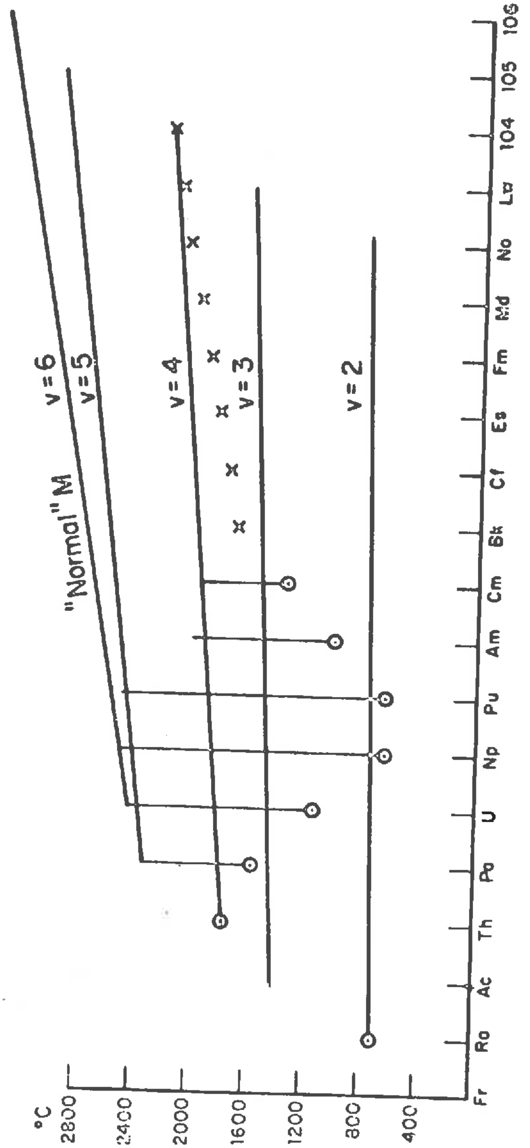

°C
2800
2400
2000
1600
1200
800
400
Fr
Ra
Ac
Th
Pa
U
Np
Pu
Am
Cm
Bk
Cf
Es
Fm
Md
No
Lw
104
105
106
"Normal" M
v = 6
v = 5
v = 4
v = 3
v = 2

Fig. 9

points whereas from their position in the periodic system you would think they would have had a high melting point.

Now you can see right away why thorium, superconductivity wise, still behaves in a perfectly normal manner. Pa and U already have the f-character and are very difficult. Now let me make a few comments about Pa. The work on this element was done in Los Alamos because nobody else could handle it. The T_c is unfortunately too low but we know why it is too low again by considering the f-electron argument. Due to the f character, Pa forms a crystal structure that is exceedingly complicated–because it's so simple. It's a tetragonal lattice with a c/a ratio close to 1. It's really very complicated because many of the atoms are non-equivalent but basically it is still cubic. I can't explain it to you, you'd better read it and then you won't understand it either. The structure of Pa is exceedingly difficult. We've removed this complication of structure by alloying. We made it cubic and then of course it's T_c is where it should have been, at 4°K. By itself it is near 1.3° or so.

The rest of this lecture I would like to dedicate to uranium. U is symptomatic for an enormous number of things–from superconductivity to the short comings of some experimentalists. Now let me explain this to you in detail.

Uranium for the last 25 years was reported as being a superconductor. Uranium has three forms. Just below the melting point it is b.c.c. and as the temperature is lowered it takes on a tetragonal and then an orthorhombic structure successively. This latter structure is unique to U because of the f character. According to various experimentalists, T_c

varied from 0.7-1.8°K. About 3 or 4 years ago various people also measured the anomaly of the specific heat. When a metal becomes superconducting you get an anomaly in the specific heat. (Fig. 10) The area under the anomaly is proportional to the difference in free energy between the superconductivity and normal states. When they measured uranium they did not find this anomaly. The superconducting state has a lower free energy than the normal state, otherwise it wouldn't become superconducting. To say that this is the first gapless superconductor that doesn't show an anomaly in specific heat is unbelievable, but it was said for awhile.

After looking through all these things and wondering about it, I suddenly came to the conclusion, maybe it is always α-uranium that isn't even a superconductor. What have all these people measured from 0.7-1.8°K? Many of them measured magnetically, you may say measuring magnetically is an absolutely foolproof method. Let me quickly demonstrate to you, as was illustrated several years ago by Giorgi and Szklarz, again at Los Alamos, that one can have a metallurgical system in which the impurities are in such a state that the metal appears magnetically as a perfect superconductor. Take a wooden sphere and make a very thin film of Sn around it. Then there are only two ways to find out whether it is a superconductor because magnetically it will behave as a superconductor. The two ways are the specific heat and the Meissner effect. The Meissner effect more often than not does not show up becuase the metal is poor, but the specific heat has to be there. In conclusion though, it is a very difficult measurement and unless you see an anomaly in the specific heat, there just won't be any superconductivity.

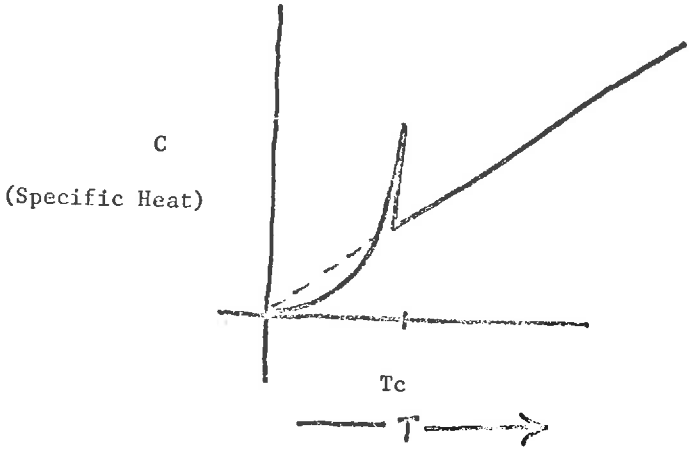


Fig. 10. Anomaly in the specific heat of s.c. near $T = T_c$.

So what do we have in U? The metal has spun a network of several phases in such a fashion that the whole appears to be a superconductor even though in fact these phases are a minute fraction of the whole sample. How do you verify this? Simply powder it and the effect should be gone.

We started with a piece of U at 1.5°. We broke it up, filed it and ground it. Right away we got to 0.7° and so we kept grinding. Eventually, we got rid of all the superconductivity. In other words α-uranium was never a superconductor and what people were measuring were impurities. Pictures were than taken with an electron microscope and they showed these filaments. What were those misleading impurities? (Fig. 11). Many years ago J. Hulm had stabilized the body centered phase by making alloys. He then got a T_c of 1.8°K; Hulm and Chandrasekhar measured the specific heat and found a beautiful anomaly as had to be expected at 1.8°. Well, I suddenly realized that these filaments must have been just stabilized regions of the cubic phase and those people who measured 0.7° might have been measuring the T_c of traces of the tetragonal phase. So we came to the conclusion that if we could stabilize the tetragonal phase it should have a T_c of 0.7° and it should also show a cleancut specific heat anomaly. And in Fig. 12 you see the results of the measurements: nothing gapless; the T_c was where we thought it should be, a little higher. We stabilized it with 1.2% of platinum or chromium. Stabilization is a dirty business but it always works and the anomaly of specific heat as measured by Norman Phillips was just beautiful. There was no longer any doubt that impurities formed a network which had stabilized some of the cubic and some of the tetragonal phases

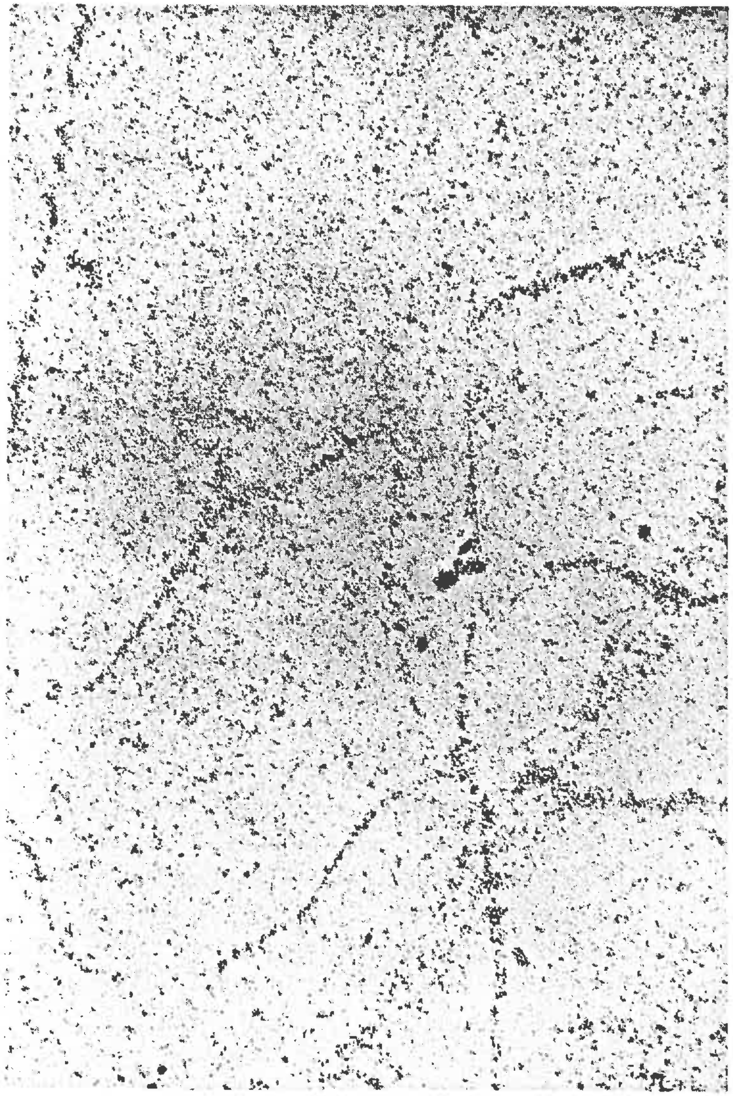
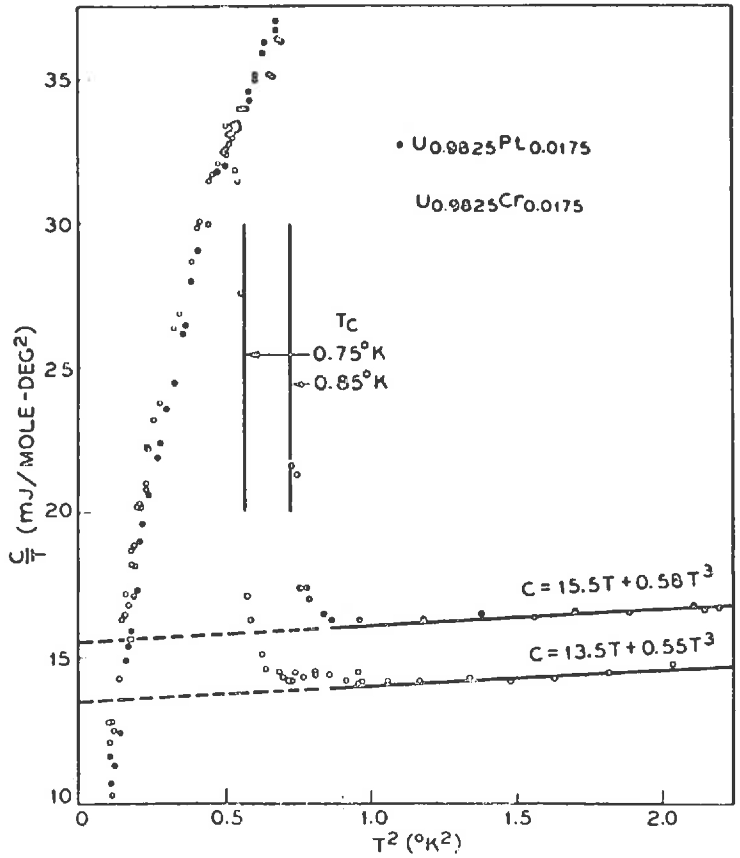


Fig. 11



35
30
25
20
15
10
$\frac{C}{T}$ (mJ/MOLE-DEG^2)
0
0.5
1.0
1.5
2.0
T^2 (°K^2)
• $U_{0.9825}Pt_{0.0175}$
$U_{0.9825}Cr_{0.0175}$
T_C
0.75°K
0.85°K
$C = 15.5T + 0.58T^3$
$C = 13.5T + 0.55T^3$

Fig. 12

and that the orthorhombic phase was not superconducting above 0.1°. Later on, Geballe got some perfect single crystals and then the transition was at 0.2°. It was still so high for a very funny reason. At these temperatures one has to use vaseline to get heat exchange. Naturally all these things became very hard and squeeze the metal. T.F. Smith had found previously that pressures might do some very drastic things to U.

It has been known for a long time that the f electron, particularly in the initial state—that is when they are not quite localized, are extremely sensitive to pressure for the simple reason that the size of the lattice depends upon the bonding electrons. If you change the size of the lattice, you change the number of bonding electrons, i.e., you change the number of f electrons. So we thought that by squeezing one could do some drastic things to U, particularly because U does something very weird at 43°. In two directions it begins to expand rapidly, and the third shrinks a little bit (orthorhombic). This was shown by measurements with neutrons by Barrett. In Fig. 13 you see what the effective volume does; it suddenly begins to increase! This is quite exciting because metals usually shrink when they get colder—there are exceptions like Si, Ge but these are not really metals. Why does it expand? The answer came to some of us as quite obvious. As the temperature drops, some of the s-d electrons become more f like in character; the moment they become more f in character the crystal lattice would have fewer lattice forming electrons and therefore the lattice would expand and it was our feeling that orthorhombic uranium was not superconducting because the f character has just gotten out of hand.

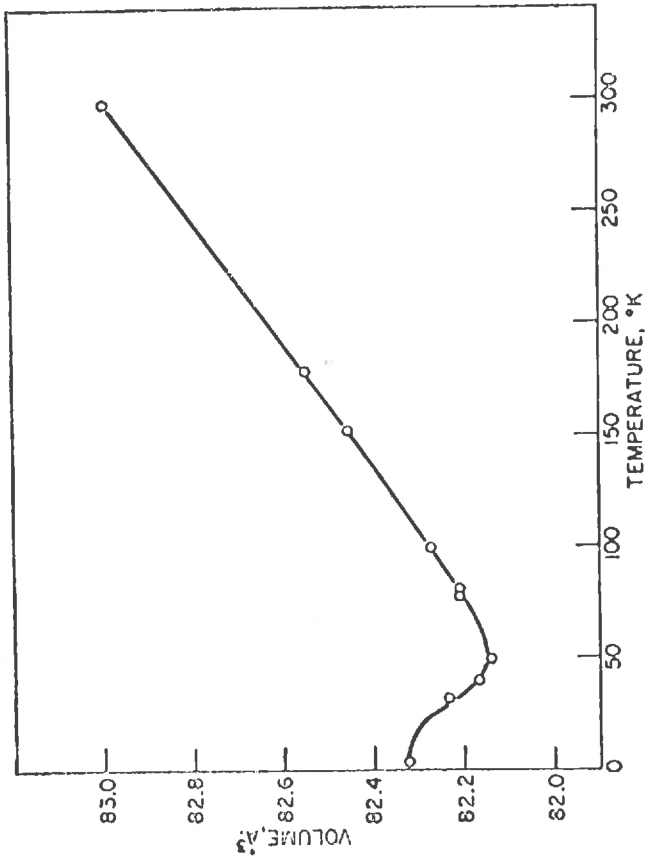


Fig. 13. Volume change for alpha uranium as determined from the lattice constants.

Smith squeezed U that had been made as clean as possible and the T_c suddenly went to 2°K. (Fig. 14) "This is a bulk effect," he said. Phillips in Berkeley was kind enough to measure the specific heat of this U under pressure which is quite a feat. It was a bulk superconductor!

Let us come back to lanthanum. He squeezed lanthanum and raised T_c from 6° to 10.5°. If La and U are so much alike when cooled, why isn't there a similar effect in La for the thermal expansion? We were told that La shrank as the temperature was lowered (20°-1°). Now Andres got the same curve as for U, that is, at 39°K there was expansion as it was cooled. It is quite astonishing that strictly from superconductivity analogies one can predict what metallurgical data will be. You can see why superconductivity has become so vital for metallurgy.

Knowing this whole story we wondered what the isotope effect for U would be. We know that for other transition elements it ranged from $\alpha = -0.5$ to $\alpha = 0$ ($T_c \sim M^{\alpha}$). A simple picture tells you immediately that in U it should be positive, i.e., inverted. Let me tell you why I think this should be so. You have heard and probably know a great deal about electron-phonon interactions. Now the electron-phonon interaction is based upon the deformation potential of moving ions apart or closer together. As one moves them, however, regardless of how one defines the interaction constant, these atoms were considered to be rigid spheres. This is called ionic polarization. There is, however, another kind of polarization going on in a crystal lattice which has been known for many years and that is the electronic polarization. Electronic polarization is of course the distortion from spherical

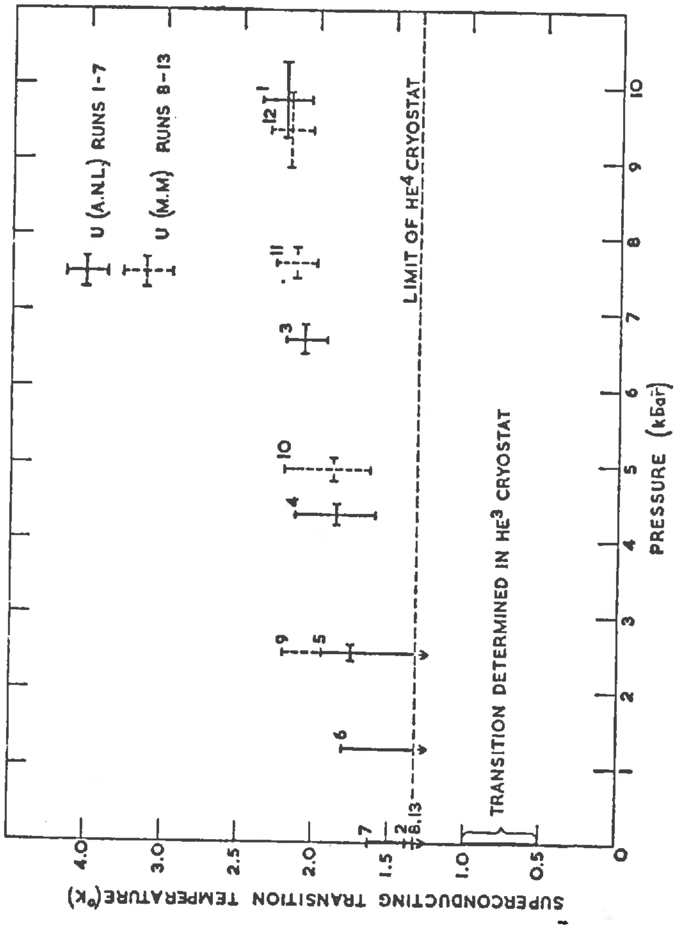


Fig. 14

symmetry when you induce a moment in the shell by a displacement with respect to the nucleus. This distortion was not taken very seriously by the electron-phonon interaction people. However it had, many years ago, worried Born and Mayer a great deal. Also, for another effect called the piezoelectric effect, i.e., one distorts a lattice and gets an electric charge or upon applying a field a mechanical distortion, and Born and Mayer tried to calculate it. A lot of other people tried and finally all came to the conclusion it was impossible to calculate because a piezoelectric effect can be obtained from an ionic polarization as well as from an electronic polarization. The crucial point is, however, that the signs are opposite, so one can't really decide since any observation could be the sum of the two effects. That all took place in the 1960's and electronic polarization has never really been considered in an isolated fashion since. Let us look at it completely and isolated.

What happens to the electronic polarization if the ions are infinitely light (just to get the sign). In this case there will be no electronic polarization because the atoms will just move away, or the lattice vibrations would be such that any net electronic polarization would be wiped out. Now assume the ions are infinitely heavy. Then the moment induced by electron scattering will be a maximum because the ions cannot move out of the way. So the magnitude of this effect increases with mass and thus we must have the opposite effect. Fowler at Los Alamos who believed this four years ago decided to do the experiment. I assure you it is one of the most difficult experiments ever done as far as I am concerned because there isn't any really clean U and in addition the U had to be under pressure to get a bulk effect.

So they had to work under hydrostatic pressure of about 12 kilobars. People might say you couldn't possibly say what the isotope effect was because the pressure might vary. The pressures were calibrated with Sn and Pb where the T_c's are well known. In addition to this, if one plots T_c against pressure for U it goes as in Fig. 14. This is a range where the first derivative is zero. So at first, the U had to be clean and then one had to work under pressure and the radio active heating of U^{235} had to be considered. All this was done in He^2 and took almost four years. Finally it was found that $T_c \sim M^2$. The absolute value of 2 is not significant but we knew it had to be positive (the exponent will probably be something other than 2 for 6 f elements if people ever find them). M^2 comes from two isotopes U^{235} and U^{238} and to decide an exponential law from these two is, to say the least, arbitrary. But at least the sign is positive!

U is fairly dirty. When all the results of all the lots were taken, the points were scattered and it was decided to calibrate with respect to impurities. Impurities affect the residual resistivity; residual resistivity will affect the skin effect and that is easy to measure. However, the skin effect depends upon the volume; the volume depends upon the mass so the skin effect was normalized by the mass. Now we finally saw that we could resolve the scattering; the cleaner the sample the higher the temperature. Unless the curves were strictly parallel the experiment had failed. The 10 samples do really lie on a smooth curve and do illustrate the positive isotope effect (Fig. 15).

F electrons interact with the d electrons in a peculiar way; they are usually antiparallel; that is one of nature's safeguards for otherwise one could

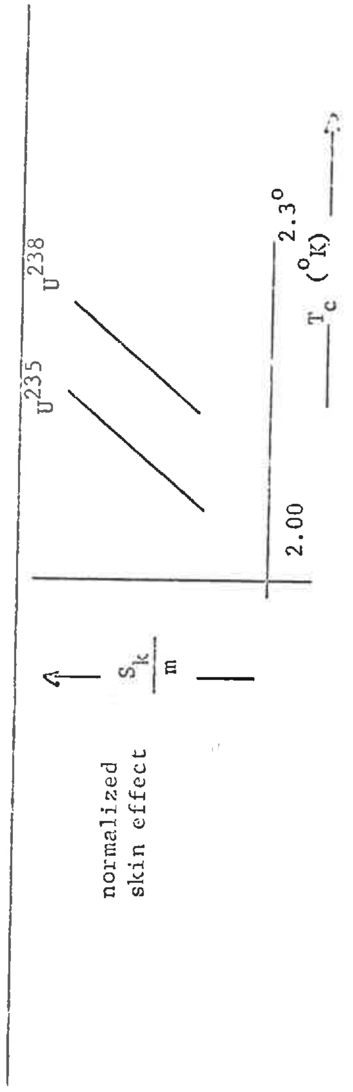


Fig. 15. Isotope effect of U. The mass normalized skin effect is plotted against critical temperature.

make fantastic magnets by combining, for instance Gd and Fe. If one asks what will U compounds do, one will find a fascinating thing. Compounds between U and any of the elements H, P. N, C, O, Bi, Si or any of the non-transition elements will cause ferromagnetism or antiferromagnetism. Everything one does in this region will result in magnetic compounds. Everything one does in the s-d region will result in nothing except combinations between ferromagnetic or antiferromagnetic elements and uranium which will result in superconducting compounds.

If we plot transition temperature and μ effective versus the periodic table in Fig. 16 we get identical curves (on different scales). μ effective is the magnetic moment of an individual ion (effective). This must be due to the interaction of the f electrons of U with the spins of the magnetic element. U is completely ambivalent; it can turn into a very good ferromagnet or it can also turn into a superconductor depending on what happens to the f electrons. The magnetic effect becomes immediately evident if the T_c is considered as a function of the μ effective.

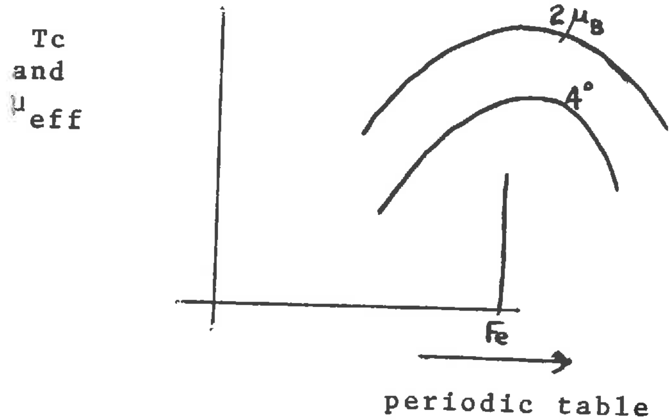


Fig. 16. T_c and μ_{eff} versus the periodic table.

LECTURE III

Let me start now on the last two topics. The first is a fourth mechanism and the second is how to get to somewhat higher T_c's.

The fourth mechanism one could have realized a long time ago with a certain amount of intelligence because it had been observed first in Be a long time ago. Be is in an extremely unusual position in the periodic table for a superconducting element. Normal Be is not superconducting if measured down to 1 °K; it certainly has no d electrons.

The Russians condensed Be on cold substrates; they found superconductivity in the order of $T_c = 8$ °K and that is a very high temperature. If warmed up, the superconductivity disappears and never returns. Obviously it's an unstable phase. Then, since the same thing happened with Bi and several other materials, we thought that maybe this was a high pressure modification, that it is just another crystallographic modification and many people tried to apply pressure to Be. There was no superconductivity; they couldn't get it under pressure. And yet these films as reported by the Russians were beautifully reproducible. The story of Be is not a complete story because there are pieces missing for the reason that Be is extremely poisonous and quite deadly to work with.

There are two forms of Be as in many metallic elements. When it first melts it becomes cubic and later becomes hexagonal. It is the identical transition that you find in many elements like Ti, Zr and so forth;

this is body centered cubic to hexagonal close-packed. A few years ago Heiniger, Bucher and Müller in Switzerland, being courageous, started with a large number of Be compounds and found something very intriguing. It is simply that Be compounds of the form X Be_{13-22} where X is essentially any transition element, are superconducting--sometimes at extremely high temperatures. The Be concentrations ranged from 13-22; in other words it was essentially Be. All these crystals were cubic and were in a superstructure off the b.c.c. form and very closely related to b.c.c. Be. It didn't matter whether it was 13 or 22 and the T_c was essentially determined by the X.

Now in the curve of T_c versus valency, La was off but Be is way off the curve! If you go to the other side of the periodic table and consider a non-transition element, also even then it has an extremely high T_c. Now when all these compounds became superconducting at varying T_c's regardless more or less of whether it was 13 or 22 and being at the boundary where things usually do become superconducting, people were amazed to say the least. Then one day Olsen, Hill and I at Los Almos thought "well maybe what the Russians had accomplished was to stabilize the cubic form. You can't make it by pressure but you can stabilize it. You can stabilize many of the elements in the cubic form with impurities. And the funny thing is that the impurities by which you can stabilize this form are always transition elements. So we started stabilizing as I told you yesterday--it's a very easy thing to do and one can stabilize forever. We made Be superconducting with things like Fe, Co, Ni, it really didn't matter; whatever we put in, even copper, it always was superconducting. Now the question arose as to whether

these things were superconducting because they were reminiscent of the stablized cubic form. Recently, Hein published the superconductivity of hexagonal Be at 26 millidegrees. It may be true and it may not because if you consider how much it takes to get temperatures as we got between 8° and 9° then in order to get to 26 millidegrees the combined amount of his transition metal impurities would have to be 5 ppm. This is a small amount that will undoubtedly be found in Be. It can be checked however by looking at various samples from different sources, zone refined, etc.

Now why are all these Be compounds so easily superconducting and furthermore was the whole amount of the Be superconducting? To make a specific heat measurement at 26 millidegrees is out of the question because technically it cannot be done yet. The specific heat of the cubic form compounds was exceedingly small (measured by Bucher and Müller) and it was a volume effect; the density of states was a little higher than that of Be.

Be has an extremely small density of states but as pointed out at the beginning, the density of states has really nothing to do with T_c. What is important however is something quite different; Be is the metal with by far the highest Debye temperature (θ_D). It is in the order of 1100°. For Be the θ_p is higher than almost anything, and the melting point is only about 1200°K which is rather low indicating again the tendency towards superconductivity.

About a half a year ago we discovered a system that was almost analogous. This time it had nothing to do with Be--it was boron. Boron is the element next to Be and there are two reasons why this is very intriguing. B is no longer a metal, but B again has an extremely high θ_D. For a long time the borides which had been recorded to be superconducting were always of the form: a metal with a little bit of boron; XB or X_2B where X was a transition metal. They were all superconducting at an average T_c between 2 and 4°K. There are many compounds of this form. Hulm and I had looked at many of them and had come to the conclusion that the moment there is too much B one cannot any longer have superconductivity. The B forms covalent zig-zag chains and begins to resemble (even though these things are metals) little by little a covalent bond and superconductivity does not exist any longer until suddenly one day we found again that in compounds XB_{6-12} just about everything was superconducting with a few exceptions which either were ferromagnetic, antiferromagnetic or insulating. Unless it was one of these three it was invariably superconducting just like the Be compounds.

Let me show you what the borides look like, because they're easier to understand than the Be compounds. In Fig. 17 are the B_6 octahedra. The metal is at the center with the boron octahedra on the side. In Fig. 18 we see the surrounding of the metal ion. Let me point out that the structure is essentially that of a cubic lattice in which the B's form a network--a three dimensional network. The B_2 and most of the B_4's do not form 3-dimensional networks and while they are extremely good metals, they do not superconduct; however once we have the 3-dimensional network, they are superconducting.

Again you see in the plot of T_c vs n that there should not have been any superconductivity because the number of valence electrons is essentially only three. With ZrB_{12} we got to 6°, with YB_6 we got to 7° and

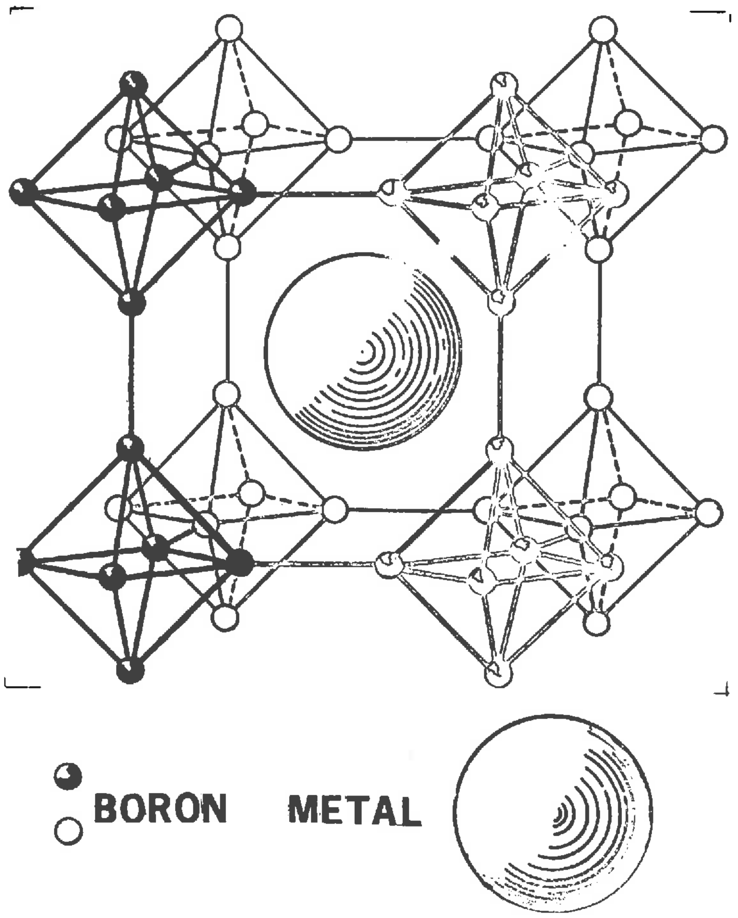


Fig. 17

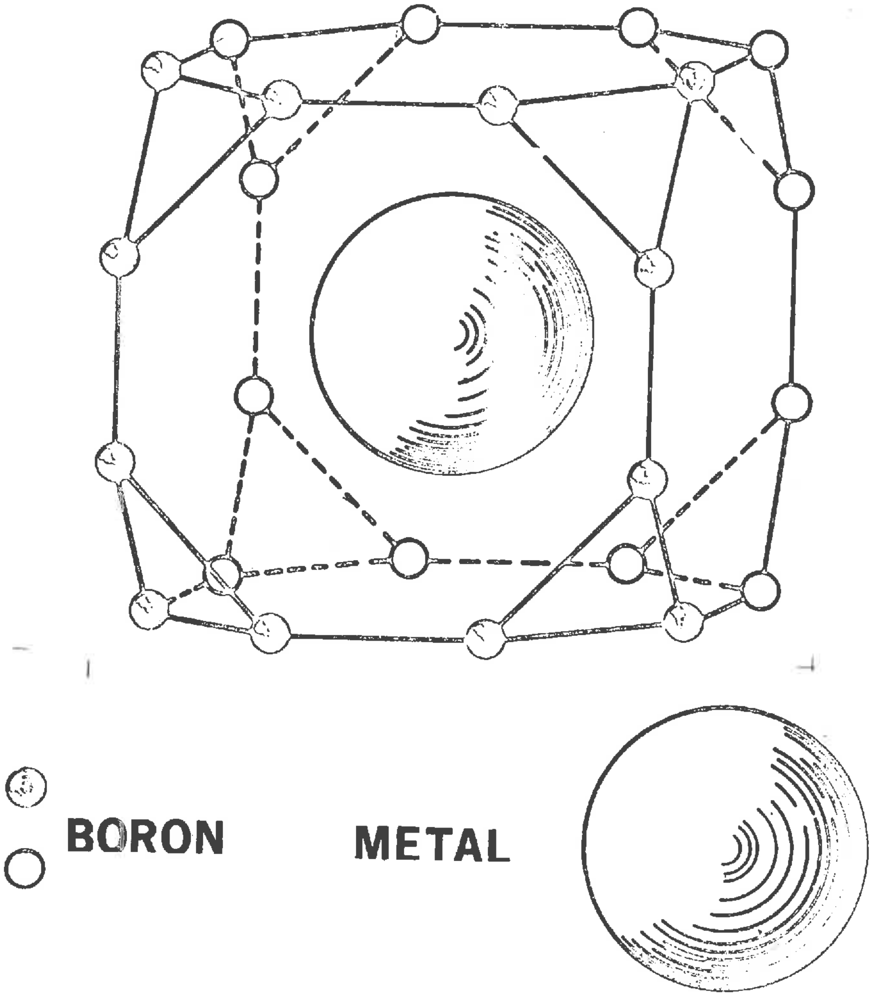


Fig. 18

again everything depended on the metal ion, the transition metal ion. As I mentioned before there are many possibilities. If the transition metal ion is not a divalent ion like Ca, Sr, Ba, or Eu then the compound is either antiferromagnetic or superconducting. That is to say, if it is not divalent and has no magnetic moment then whatever you do--and I'm not going to give you the long list of superconducting compounds which we found this way--they are all superconducting without exception--6 or 12 it doesn't make a bit of difference. If X is a divalent atom like Ca, Sr, Ba, or Eu invariably the thing is a semiconductor. Longuet-Higgins had developed a theory long ago that explains this; according to which the B octahedra correspond to divalent radicals. Thus there is a covalent bond between the metal ion and these octahedra. If X is a magnetic ion that is trivalent, antiferromagnetism results; if it's a magnetic ion, i.e., divalent like Eu you get ferromagnetism. EuB_6 if ferromagnetic; all the others with magnetic moments are antiferromagnetic. EuB_6 is at the same time semiconducting and like all the other divalent ones it is not a metal. Obviously there must be a connection between the divalency and the ferromagnetism as compared to the antiferromagnetism, but I will not speculate on this right now. The magnetic transitions however, are very reminiscent of the superconducting transition because the resistivity drops so abruptly below the Neel temperature. Let me show you what the EuB_6 look like. In Fig. 19 we have plotted ths susceptibility (χ) and resistivity (ρ) (in arbitrary units) versus the temperature. Though in superconductivity the ρ drops just as abruptly, there is really no immediate correlation to superconductivity since what happens is the cessation of the

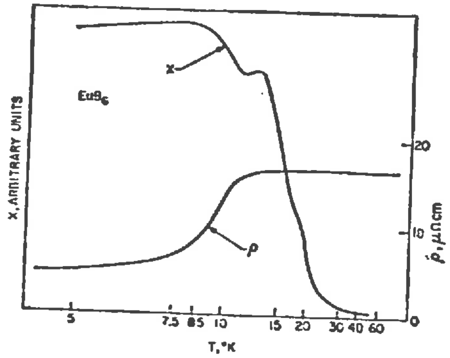


Fig. 19. Initial susceptibility (χ) and resistivity (ρ) for EuB_6.

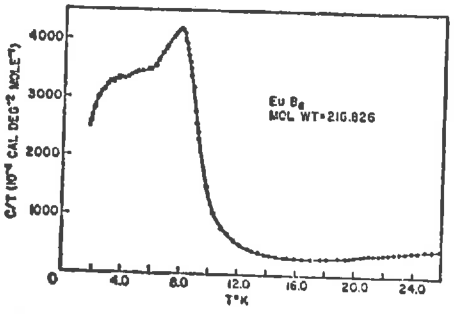


Fig. 20. Heat capacity of EuB_6.

spin disorder scattering and that is all. In Fig. 20 the specific heat is shown. Whenever you have a transition always measure the specific heat to be sure you have something. Obviously this is a kind of magnetism that people have not been accustomed to; as a matter of fact yesterday somebody asked me how one could distinguish between a magnetic transition and a superconducting transition with specific heat. It's quite simple: you apply a field and the specific heat doesn't change one bit as for example in $SrTiO_3$.

When we find that also the superconducting behaviour here is different from the general superconducting behaviour and the ferromagnetic behaviour for EuB_6 is so strange we might come to the conclusion that maybe the whole behaviour is something completely different and new. So we went throughout the whole periodic system making all the rare earth B_6 compounds (sometimes B_{12}) and measured the ordering temperature, the Curie point when it's ferromagnetic, the Neel point when it's antiferromagnetic and what we got is in Fig. 21. The magnetic ordering in fact is also quite different from all other rare earth magnets. For the first time one gets a relation where the ordering temperature is no longer connected with the spin only but also for the first time it depends only on the effective dipole moment as given by the Van Vleck curve. Throughout, the rare earths, usually whether alloys, solid solutions, or anything that becomes magnetic, follow a pattern with a maximum at Gd because the spin here is a maximum. The effective moment is measured by temperature dependent susceptibility, or any other way, and never affects directly the ordering temperature (naturally) because one would not expect that dipole forces are really crucial–

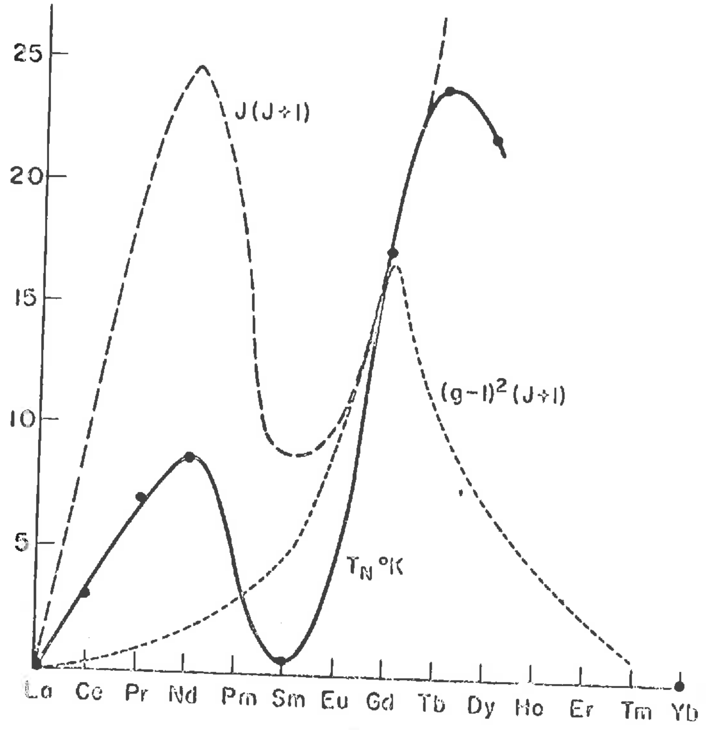


Fig. 21

it's usually spinexchange that gives you the magnetic ordering. However, in the B_6 and B_{12} compounds for the first time we now get an ordering temperature that really follows the effective moments in a beautiful way. In Fig. 22 we see how well it follows the effective moment because we plot the ordering temperature versus the effective moment and it's a beautiful one to one correlation.

Obviously we have a magnetism that is different. We have superconductivity that is invariably there but at the same time is different from the other superconducting mechanisms. The superconductivity doesn't follow the valence electrons; the ferromagnetism doesn't follow the spin. Generally we have an entirely new behaviour. What is this behaviour? What, for instance, links these compounds to the previous ones? Again, just the high θ_D, nothing else. We measured the specific heat of many of these; again the θ_D is around 1000 °K. Obviously, if we have such a high θ_D and have a metal, then it doesn't really matter what we do for we will get superconductivity or magnetism, one way or the other.

How does this come about? Again, let's look at the isotope effect. Bucher and Müller looked at the isotope effect of $MoBe_{22}$. Be has no isotopes, alas, and Mo shows the isotope effect of $\alpha = -0.3$. In this compound he varied only the Mo through its isotopes and got a similar isotope effect, namely $\alpha = 0.2$. For the borides (ZrB_{12}) we did a similar experiment. We haven't changed the Zr at all but we have changed the B isotope (for B one can change the mass by 10% which is a very large effect, particularly if you consider that $T_c = 6$ °K). We expected a shift of something

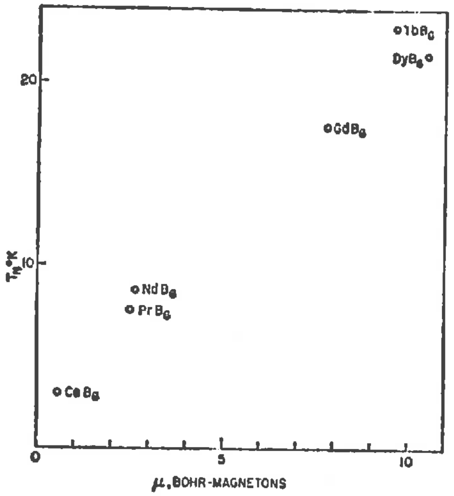


Fig. 22. Ordering temperature for antiferromagnetic hexaborides as deduced from alternating-current susceptibility and resistivity as a function of calculated effective moment, except for cerium hexaboride where the saturated (measured) moment of low temperatures is used.

like half a degree if $\alpha = 0.5$. There was no shift. The transition is extremely sharp and less than 2 millidegrees. In other words there is not a trace of an isotope effect as far as the B is concerned. Yet we knew that there was a strong isotope effect in Mo and so we finally came to the picture of what causes the superconductivity of all these things and why the behaviour is so unusual. Transition ions are metals interacting now without disturbances of any kind, electron gases or anything like this-- sort of like springs in a vacuum. And what we really have here is a matrix that doesn't scatter. The θ_D is so high that by the time we get to 1° (or 10°) the thermal scattering has virtually disappeared; what we really have is sort of a fantastic long range interaction between the transition metal ions. That is why we get superconductivity determined exclusively by the transition metals, why they give the isotope effect and why the matrix doesn't really care if it is 6, 12, 13 or 22–it is just there to keep the lattice in existence.

And so the fourth mechanism is when you have a matrix of an extremely high θ_D in which you have transition metals (it doesn't work with non-transition metals; I don't know why, probably because the lattices don't form in a clear cut cubic fashion) and atoms that can interact in a cubic lattice; one will then get superconductivity without fail. If not there is either no metal or antiferromagnetism.

What about the phonons? I assure you there are phonons. But I really don't think they have much to do with the whole thing. What they really have to do with is that they don't seem to bother the transition metal ions and their interactions with one another through conduction electrons. Now one of the crucial conditions for all this was, of course, a cubic lattice. And now this brings us to the last topic, namely high transition temperatures.

First of all let me assure you we have looked every where as you may guess and out of more than 8,000 compounds the only high T_c compounds are all cubic. We have never found anything above 12 or 13°K which is not cubic. Everything that superconducts with a high transition temperature is cubic. And there are only two lattices--for completely obscure reasons--which are particularly favourable. One of them is the NaCl lattice. It is superconducting only when you have transition metal ions in one simple cubic lattice and non-transition metal ions which are small enough to be interstitial in the other simple cubic lattice—e.g., carbon, oxygen or nitrogen. Most of these compounds are superconducting, and one knows their arrangement; from yttrium carbide to molybdenum nitride. However as soon as the non-transition metal ion is too large (e.g. P while still forming the NaCl lattice, superconductivity will no longer occur.

The first superconductor to be known was NbN. We tried to raise the T_c of NbN which is about 15°K; and replaced some of the nitrogen by C. We got to 17.8°K. At the time we thought it was the valence electron concentration because the maximum near 5 electrons/atom is a little bit wide; we no longer believe that because when we then tried to change the valency by putting in zirconium or titanium the T_c did not increase. Usually the T_c went down and it didn't follow the valence electron concentration; the T_c went down instead of going through a maximum, so it didn't follow the electron concentration very well. One day, in Los Alamos, Giorgi and Szklarz did an experiment.

They took niobium carbide which was reported to superconduct at temperatures near 6-9°. They then tried to make it very stoichiometric but only got to $NbC_{.985}$ and now T_c was at 13°K. As the carbon concentration went lower T_c dropped steeply (Fig. 23) and whether carbide or nitride it was only the C or N concentration which was sensitive while the metal really did not seem to matter. It was only the non-metal that was decisive for superconductivity. Thus we had the superconductivity of N and C in a metallic modification. Only very high pressures can cause this and in these compounds it was the crystal lattice that was effective for these drastic changes.

There is an easy check for this hypothesis. If you remember the transition elements have a high γ; while the non-transition elements have low $\gamma (C = \gamma T)$. So we measured the density of states from specific heats and found that they were very small. Since the transition temperatures were so high (18°) and the densities of states are far below those of the transition metal elements we must have the dominant interaction between N and C in these lattices. The lattices are cubic and we can get these only with transition elements. In fact all combinations we know of today with high T_c's are those of combinations by transitions with non-transition elements. There is one exception in Mo-Tc alloys.

What I'm trying to say to you is you must have the s-p-d interaction to get to high T_c elements. We have a scheme which predicts that a given crystal should be superconducting. If we predict a T_c of 30°K, this compound will not form. High T_c's seem to occur in unstable lattices and if the T_c is too high, the lattice will be too unstable. This brings us to the martensitic

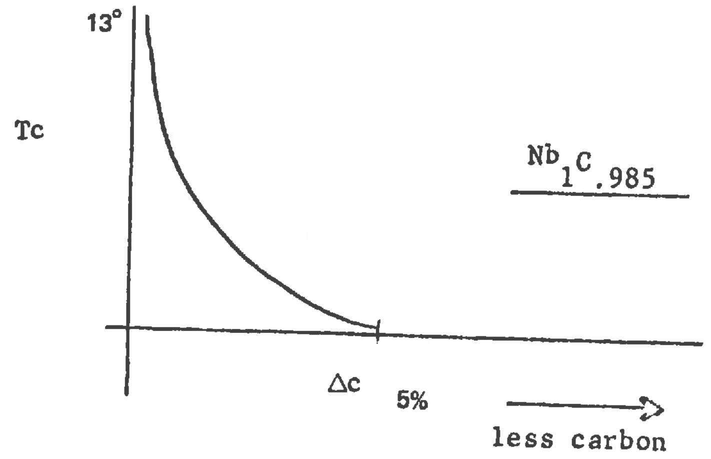


Fig. 23. Drop of T_c in $Nb_1C_{.985}$ as concentration of C is lowered.

transition which is observed in high temperature superconducting compounds. These β-W compounds go through a transition before they become superconducting. They're cubic. Before becoming superconducting there is a transition at which they undergo a distortion of less than 1%. This change from cubic symmetries implies a lattice instability; and thus we were interested to know if these crystals with a high T_c show lattice instabilities. We looked for the martensitic transition in niobium carbide and found there was also a transition. This was done by measuring the χ. In NbN the transition is higher and the discontinuity is higher yet (Fig. 24). For a while people thought they had superconductivity at high T_c's really it was only a lattice instability which seems to appear in all high temperature superconductors.

This was an ominous sign. We may decide that at a high temperature we may superconduct but that the lattice will not be stable unless we find tricks.

Let me talk some more about the very high T_c's which occur in the β-W structure; over the years this structure has been better for superconductivity than anything else. The structure is simple. It is a cubic lattice in which the B ion and A ion are as shown in Fig. 24. One has strings of A ions (transition metals) that do not intersect and extend throughout the crystal. This 3-dimensional array of strings may be responsible for superconductivity. Why this is favourable to superconductivity, I don't know. The CsCl structure, which is also cubic, and is in a way somewhat similar but hardly any of the compounds are ever superconducting.

The reason may be that most of the CsCl structures occur at 6 electrons/atom which is right at the

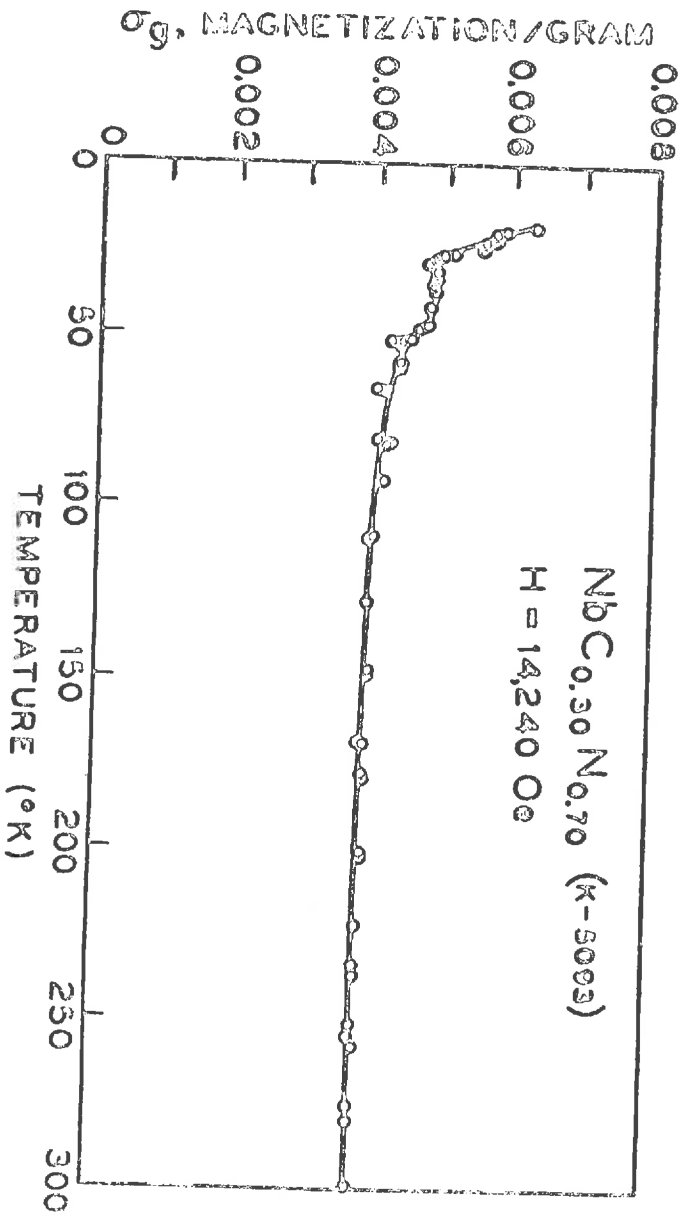


Fig. 24

minimum of T_c. The trouble is when we try to make higher T_c crystals the lattice seems to be unstable. The instabilities will occur before T_c, and the higher the T_c the more pronounced the instability.

The highest superconductor known at present, a pseudobinary compound of NbAlGe with a T_c of 21°, will deteriorate completely at higher temperatures or upon mechanical stresses. 21°K is not the limit to superconducting T_c's but somewhere in this neighborhood, there will be a limit for these systems.