8. J.M.E. Harper, T. H. Geballe, L. R. Newkirk, and F. A. Valencia, J. of the Less-Common Metals, 43 (1975) 5-11.

9. M. C. O'Connor, Ph.D. Dissertation, Stanford University, 1976 (unpublished).

10. J. A. Wilson, F. J. DiSalvo, and S. Mahajan, Adv. in Phys. 24, 117 (1975).

11. L. P. Gor'kov, Sov. Phys.-JETP 38, 830 (1974).

12. R. H. Hammond, IEEE Trans. Mag. MAG-11, 201 (1975).

13. A. B. Hallak, R. H. Hammond, and T. H. Geballe, to appear in Applied Physics Letters.

14. L. Kokot, R. Horyn, and N. Iliew, J. Less-Common Metals 44, 215 (1976).

15. W. L. McMillan, Phys. Rev. 167, 331 (1968).

Critical ~~[illegible]~~ Materials Problems in Energy Production
ed. Charles Stein
Academic, 1976.

Chapter 21

SUPERCONDUCTIVITY

Bernd T. Matthias

Institute for Pure and Applied Physical Sciences*
University of California, San Diego, La Jolla, California 92093

and

Bell Laboratories
Murray Hill, New Jersey 07974

I. *INTRODUCTION*

From 1921 until 1933, only one ferroelectric compound was known and thus ferroelectricity was considered one of the rarest collective phenomenon. Finally, a large number of new ferroelectrics were found and it became evident that ferroelectric was a rather general phenomenon. This suggested that the same approach be utilized in superconductivity. At that time, there were very few superconducting compounds known aside from some of the elements. Since then, the number of superconducting elements has

*Research in La Jolla sponsored by the Air Force Office of Scientific Research, Air Force Systems Command, USAF, under AFOSR Contract #AFOSR/F-44620-72-C-0017.

not only more than doubled, but the number of superconducting compounds and alloys now reaches into the thousands. Similarly, after the discovery of a great many new superconducting elements and compounds, superconductivity has gradually emerged as the normal behavior of metals at very low temperatures.

Although superconductivity was discovered in 1911 nevertheless, the transition temperature has been raised only slowly, although steadily. In 1911 it started at 4°K and the highest transition temperature known today is at ~23°K for the compound Nb_3Ge.

Why does it rise so slowly? One of the reasons is that during the last 25 years, all new superconductors with high transition temperatures have been discovered in only four laboratories throughout the world: Bell Laboratories, La Jolla, Los Alamos and Westinghouse.

At present, one recognizes one feature which is common to all superconductors — they are all metals. Contrary to what one might have heard or read or have been told, there are no superconductors today which are not real metals. To be quite specific, this author's work in the area of ferroelectricity demonstrated that ammonium sulfate was ferroelectric after almost half a century of speculations by many people. It was then realized that probably many more compounds were ferroelectric or antiferroelectric, and to a large extent, at the present time this has turned out to be true.

It may be illustrative to point out how the superconductivity of the element molybdenum was discovered. A lot of people had worked on molybdenum; in fact a paper had reported that superconductivity did not exist in molybdenum, down to 40 millidegrees. However, Geballe, Corenzwit and the present author found its superconductivity by just boiling molybdenum for a short period of time in the arc furnace. At present, molybdenum is superconducting at .98°K. What had been overlooked earlier was the

purity of the molybdenum. Now, clearly by the year 1963 or 1964, one might have expected that before the absence of superconductivi was reported down to a temperature of 40 millidegrees, one might h looked a little bit closer at the purity of the metal.

Since the time that research in superconducting compounds was started 25 years ago, we have also more than doubled the number of superconducting elements. Sometimes it was not just simply improving the purity of the element but in addition one had to subject materials to pressure in order to make them metallic. For example, phosphorous became superconducting at the respectable temperature of 5°K under a pressure of 80 kilobars. From all this one gradually comes to the conclusion that at low temperatures everything will be superconducting unless it is magnetic or ferroelectric.

Stated more directly: superconductivity is not esoteric property of materials. Most metallic elements today are superconducting and since it is the majority that defines normalcy superconductivity is now the normal property, and the so called "normal" (i.e., not superconducting) metals are anomalous because they are now in the minority. It is all really a matter of definition.

In 1960 everybody was assured that everything in superconductivity was clearly defined and that there were few unsolved problems since the isotope effect had been predicted and found. At that time T. Geballe and this author decided to measure the isotope effect of ruthenium which had not been measured before Ruthenium is superconducting below .5 degrees. It was measured an then there was no isotope effect found, whatsoever. This was astonishing since a large segment of the scientific community had believed that the regular isotope effect occurred throughout the entire periodic system. When it was demonstrated that ruthenium had no isotope effect at all, there was a certain amount of astoni ment, malaise and embarrassment. However, recovery soon set in, and after two years the lack of an isotope effect was finally predicted. Several years ago M. Fowler and H. Hill, at Los Alamos, looked into the isotope effect of uranium since, if the present author's picture of superconductivity was correct, uranium should show the opposite isotope effect. Indeed, the transition temperature of α-uranium under pressure was found to be approximately proportional to the square of the mass, and not to the inverse square root of the mass. Because of these findings, the theory of transition temperatures is, at present, of not much help to us. On the contrary, it may be a hindrance to the search for high temperature superconductors. Due to the enormous success of the theory in other directions such as pairing, tunneling and ultrasonic attenuation, all efforts or almost all efforts towards finding high temperature superconductors are being directed along definite theoretical lines. Unfortunately, without a single exception, these approaches have all failed.

In like manner, efforts towards getting to higher transition temperatures have been impeded by errors due to the experimentalists as well.

For example, in 1942, Justi had found a new superconductor, niobium nitride, at 15°K. There was great joy in Germany at the time and it was thought that the transition temperature could quickly be raised to room temperature. Soon Justi reported superconducting nuclei at room temperature. What was called nuclei in 1942 is what is now called fluctuations in 1976. Needless to say, what was wrong was that Justi forgot to stir the hydrogen bath. Another example occurred about five or six years later when Ogg reported superconductivity of metal-liquid ammonia solutions. This superconductivity involved very high transition temperatures, namely in the range of 200°K or so. What had gone wrong with Ogg's experiment was that he precipitated metal bridges of sodium and had misinterpreted their high conductivity for superconductivity which he realized and admitted shortly thereafter. Justi was more difficult to convince. He persisted that his was a real effect. His

persistance lasted for 12 years until he was forced to present his experiment at a public meeting of the German Physical Societies where it failed, of course. Following these errors a great number of minor papers reported very high temperature superconductivity which, subsequently, were all proven not to be factual.

This is indeed unfortunate since there is no doubt that if one could raise the transition temperature to 30 or 60°K or even better, room temperature, it would change our whole technology, drastically.

The research effort, of searching for metals with high transition temperatures is between 5 and 10% of the total monetary and manpower effort currently directed by theoretical considerations. Of course ever since the theory came into existenc the theorists direct and lead the experimentalists. As a consequen most of the effort today directed toward superconductivity is done so without any hope of applicability in the future. This is the reason why all progress towards real high transition temperatures is so slow — too few people and little money. This has been with us for many decades. But, let me come back to the errors of experimentalists.

The latest example relating to erroneous high temperature superconducting materials pertains to work on tetrathiofulvalenium - tetracyanoquinodimethane single crystals. In three simultaneous press releases, superconducting fluctuations at 58°K were announced. The normal conductivity of TTF-TCNQ had been known and reported much earlier. In the present instance a very simple mistake had been made: on three crystals out of seventy the electrodes were painted on poorly. Consequently, when vanishin resistivity was noticed, it was due to the fact that there was actually no current to speak of. TTF-TCNQ is a highly antisotropic crystal and hence has a highly anisotropic conductivity. This has all since been shown by Gordon Thomas.(1) In addition, in a recent Physical Review there is a paper - which in solid state physics is an entirely novel event - in which 30 authors from many different laboratories together published the finding that in TTF-TCNQ there are no superconducting fluctuations or otherwise. "The high values reported for a few crystals are incorrect."(2) In reality TTF-TCNQ is an impure antiferroelectric. It has been known for many years that ferroelectrics and antiferroelectrics in the impure state have an enormously high conductivity at the Curie point (3) which drops as the temperature decreases. For instance, if barium titanate contains small amounts of lanthanum, scandium, or samarium oxide as an impurity to induce better conductivity, these values change by five orders of magnitude at the Curie point - a truly staggering effect. This effect is true not only for barium titanate, but for ice at its Curie point, for ammonium sulfate - in fact, all ferroelectrics display this same phenomenon. For that reason, when the data for TTF-TCNQ were published, this author predicted that it would be either a ferroelectric or antiferroelectric, one can never be quite sure in advance. However, when the dielectric constant was finally measured and found to be 5,000 the veracity of this argument became self evident.

II. *EXPERIMENTAL EFFORTS TO OBTAIN HIGHER TRANSITION TEMPERATURE SUPERCONDUCTORS*

In order to achieve higher temperature superconductors one has to be cognizant of changes taking place at all temperatures in the metal. To illustrate this, see Fig. 1, in which those elements which have been found to be superconducting are shown in the periodic system. One can see immediately that the earlier statement that the majority of all metallic elements are superconducting is verified and that superconductivity in itself is a general phenomenon. Now, how does one achieve higher temperatures?

From the beginning it was realized that the only way to get to higher temperatures experimentally would be through

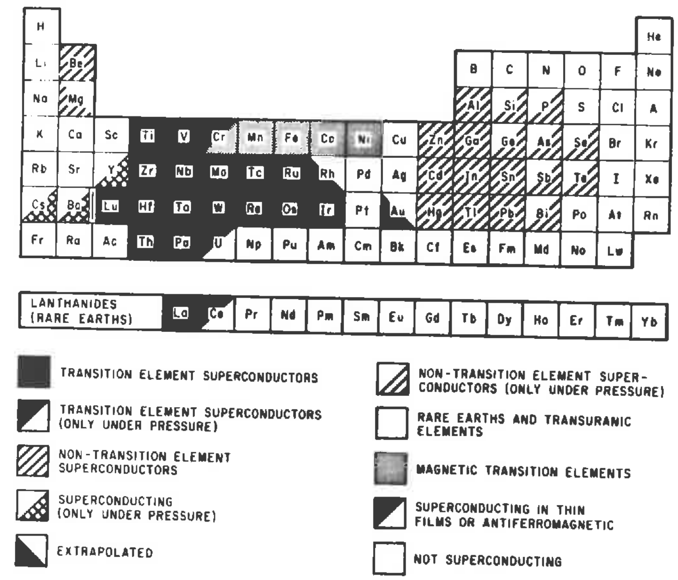

FIG. 1. The Periodic System of the Elements

a very primitive and empirical approach. In other words, one had to look at so many superconductors that a rule would be immediately apparent and obvious. At that time there was no doubt that one could get to higher temperatures. Unfortunately, superconductivity is closely related to the melting point of elemental metals, which, like superconductivity is just not understood. In fact, the melting point is more poorly understood than superconductivity as far as our ability to make predictions are concerned. The melting point is the oldest collective phenomenon known to mankind, yet even today, with all our sophistication in science, it seems no one can predict melting points.

For quite awhile measured melting points of compounds, as a function of time, went up until in 1929 - a bad year like everything else - it suddenly stopped going up. That was when

Agte and Alterthun (4) found the melting point of hafnium tantalum carbide near 4,200C. Hard as it may seem, ever since that time no one has found a material with a higher melting point. That's remarkable because if one could get to a melting point of only 5,000C our whole technology would be radically different.

In superconductivity we are more fortunate because one can make superconductors which are ternary systems. In binary systems, the melting point is sometimes at a maximum, however, in ternary systems it is always lower. Since we have more or less exhausted all binary systems in superconductivity, we have now found that ternary systems have great possibilities and that in some cases have even much higher critical temperatures. Therefore, the hope today for obtaining higher transition temperatures resides in looking at the superconductivity of ternary metallic compounds and alloys.

Unfortunately, nature, not just our scientific environment, has also raised enormous obstacles to our obtaining higher superconducting temperatures. It has been pointed out already that some of the high temperature superconductors are intrinsically unstable. As a matter of fact, it is this author's feeling that all high transition temperature superconductors are unstable, without exception. When experimenters sometimes cannot find the instabilities, it is simply due to the laboratory difficulties involved. For every crystal investigated, the introduction of a low temperature and low symmetry modification, which is thought to be its equilibrium state, has invariably resulted in a lower (5) superconducting temperature. Figure 2 shows several superconducting transition temperatures and the depression of the transition temperatures once the low temperature modification is induced. While no mathematician would be willing to fit a curve at this stage of the game, one could guess that the maximum transition temperature achievable will be somewhere between 25 and 30°K. Paul Stein has extrapolated from the time of the discovery of superconductors how

long it will take to get to 25-30°K. See Figure 3.

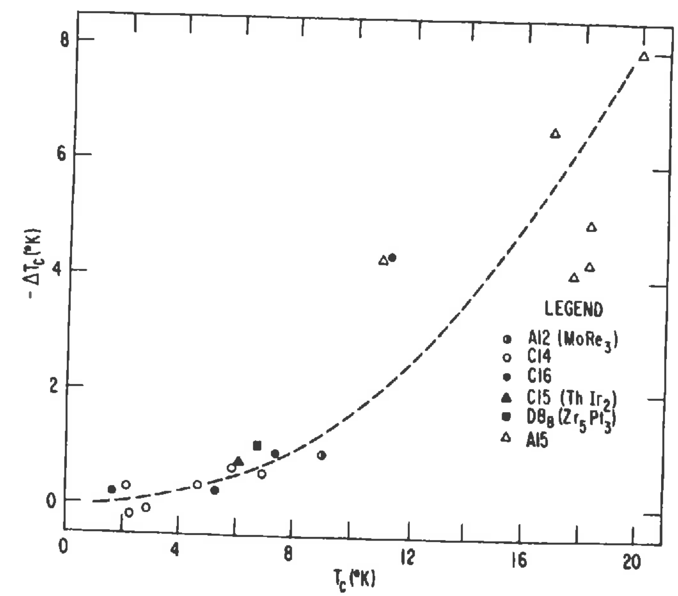

FIG. 2. Depression of the Superconducting Transition Temperature for the Low Temperature Modification

Not only must these instabilities be overcome, but one must also overcome anisotropies because cubic crystals, isotropic crystals or high symmetry crystals are the ones which have the highest transition temperatures. When the symmetry is lowered, the transition temperature will also go down. That is the reason why all two-dimensional crystals never get much above 5 or 6 degrees, and why pseudo one-dimensional crystals, such as $(SN)_x$ do not get above .5°K. One can immediately see the importanc of cubic symmetry in Figure 4 (6). This is the beta-wolfram crystallographic morphology. Nb_3Si usually crystallizes in the tetragonal form which has a c/a_o ratio of exactly 2. A great deal

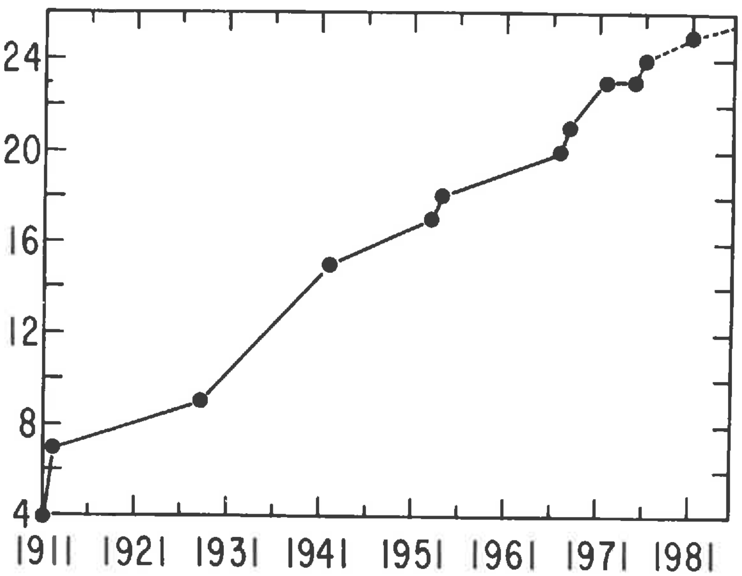

FIG. 3. Superconducting Transition Temperature as a Function of Time

of experimental work has been expended in attempts to change this structure into cubic beta wolfram. However, even though they are so closely related, with a_o being exactly what it should be in beta-wolfram, success, as yet, has not been achieved. It would seem that nature has an aversion to cubic Nb_3Si. Now it is true, some groups have claimed to have made "Nb_3Si." But it turns out to be about the most nonstoichiometric and poorest compound there is. While silicon is smaller than germanium yet the lattice constant of the reported Nb_3Si is a good deal larger than that of Nb_3Ge. If one could make it properly, if one could overcome the visicitudes of nature, one would easily raise the superconducting transition temperature somewhat above 25°K. Alas, this has yet to be accomplished.

We seem to be fighting against nature. However,

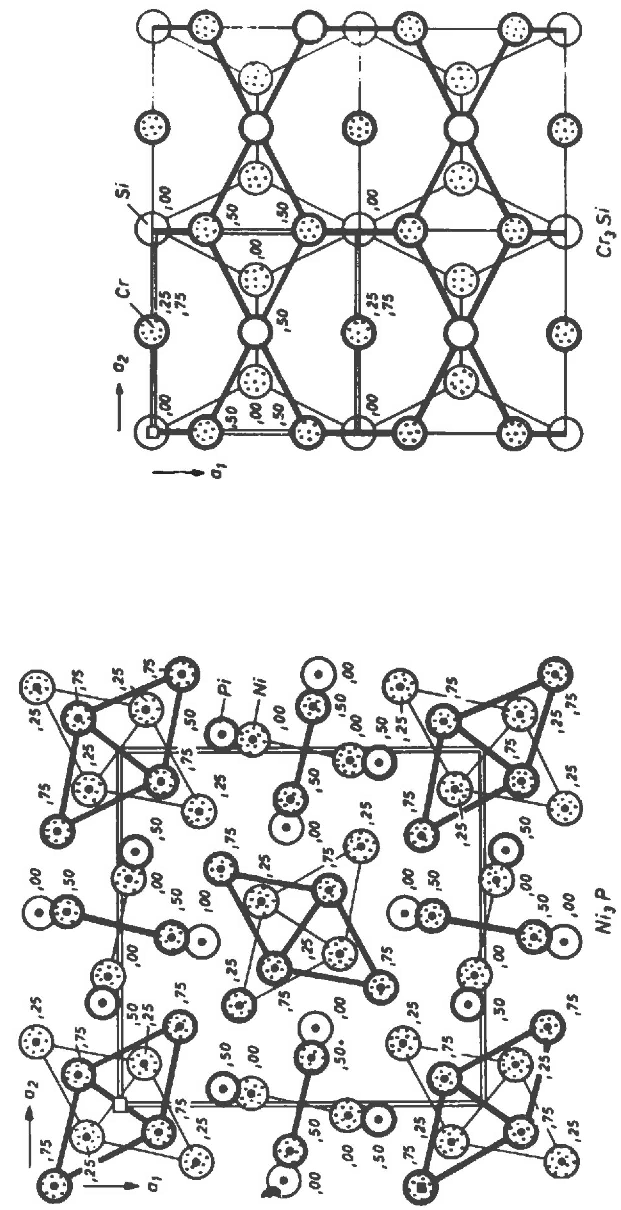

FIG. 4. A_3B: Tetragonal vs. Cubic Symmetries

it has been demonstrated that if one has a cubic metallic crystal, it will usually be superconducting if one addresses the problem correctly.

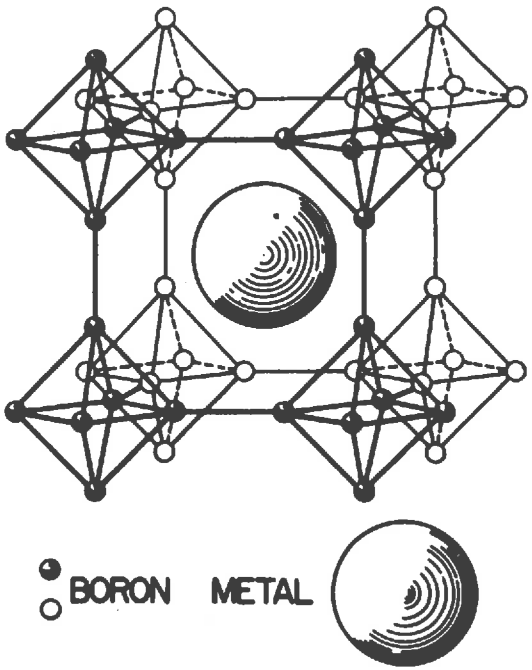

FIG. 5. Cubic Hexaboride Compounds

Take, for example, the XB_6 compounds all of which have been found to be superconducting. It really doesn't matter what the metallic atom X is. As long as the compound has cubic symmetry and is metallic, it will either be superconducting or magnetic. As another example, consider the B_{12} compounds. Here, again, the actual chemistry of the compound doesn't matter; provided crystallographically they are cubic and metallic they are always found to be superconducting. Unfortunately, these are not

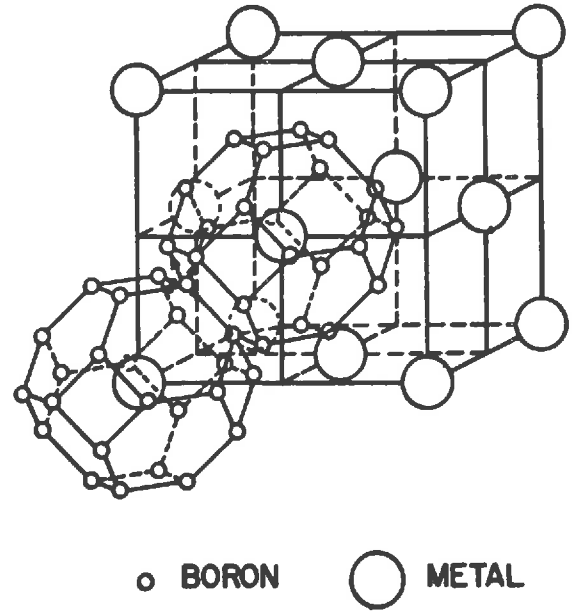

FIG. 6. Cubic Dodecaboride Compounds

very high temperature superconductors and sadly, we were never abl to get the transition temperature above 7 degrees.

III. *FUTURE HIGH TRANSITION TEMPERATURE SUPERCONDUCTORS*

It may be instructive to speculate here about a those structures which show promise for future high transition temperature superconductivity. In the first instance are those structures of the sodium chloride form, such as NbN and NbC, whic were discovered by Justi many years ago. Then there is the beta wolfram structure which Hardy and Hulm first found for V_3Si in 19 Following this came the plutonium sesquioxide structure, which Giorgi, Szklarz and Krikorian found in 1968 through the synthesis of $(Y,Th)_2C_3$.(7) More recently, the first ternary phases were found which gave transition temperatures up to 16 degrees. Some examples of these are the cubic spinel compound $LiTi_2O_4$ (8) and the rhombohedral XMo_6S_8 and Mo_6Se_8 (9) phases where X includes many elements from Mg to Ag to La to Pb and many more.

It should also be pointed out that during the last few years hydrides of the noble metal palladium have become superconducting at temperatures as high as 17°K. (10) The reason for this high transition temperature is not quite understood, but it is a very interesting phenomenon indicating, once again, the role of instabilities. Since in contrast to Pd, the metals Cu, Ag and Au have little affinity for hydrogen, their lattices become quite unstable and thus the transition temperatures will rise. The effect may also be due to metallic hydrogen which, according to some speculation, has been predicted to be superconducting at room temperature. This is unlikely, and if it is ever made, it will probably be superconducting in the range between 15 and 20°K.

Instabilities can sometimes be overcome either by rapidly quenching the crystal lattice or by imposing high hydrostatic pressures. Instabilities can always be enhanced by uniaxial pressure, whereas hydrostatic pressures tend to keep the lattice deformation symmetrical. Consequently, at Bell Labs when instabilities were observed at lower temperatures in the lanthanum sulfides, it was immediately suggested that the application of large hydrostatic pressures would directly effect these instabilities and their superconducting transition temperatures. While both expectations were verified, the polymorphic transition which occurs more or less in parallel with the superconducting transition temperature, was different from what had been expected. Since the crystal is less isotropic below the phase transition than above it, this seemed to be a contradiction to our assumption. After all, the higher the transition temperature, the higher the anisotropy at low temperatures. But something had to happen to make them more isotropic as their transition temperature increased. What

happened under pressure at these high temperatures is that an increasingly smaller phase change occurs. Consequently, with high hydrostatic pressures one would expect to achieve higher transition temperatures. This proved to be correct. Lanthanum sulfide rose from 8 degrees to 12 degrees and lanthanum selenide shows more or less the same behavior (see Figure 7a).

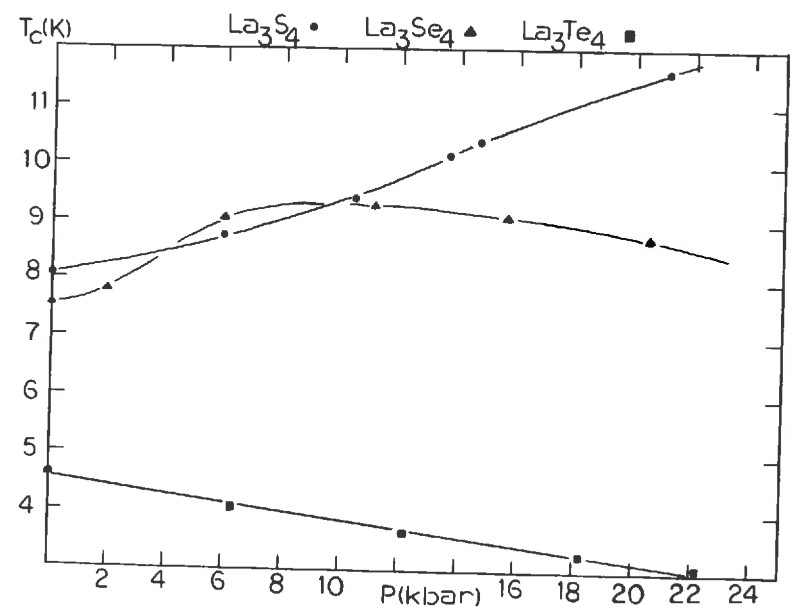

FIG. 7a. Superconducting Transition Temperature of Lanthanum Chalcogenides

This is a beautiful demonstration which shows how instabilities correlate closely with the corresponding superconductivity. Instabilities are the real, and major obstacle to high temperature superconductivity. Unfortunately, as pointed out before, they are very difficult to overcome.

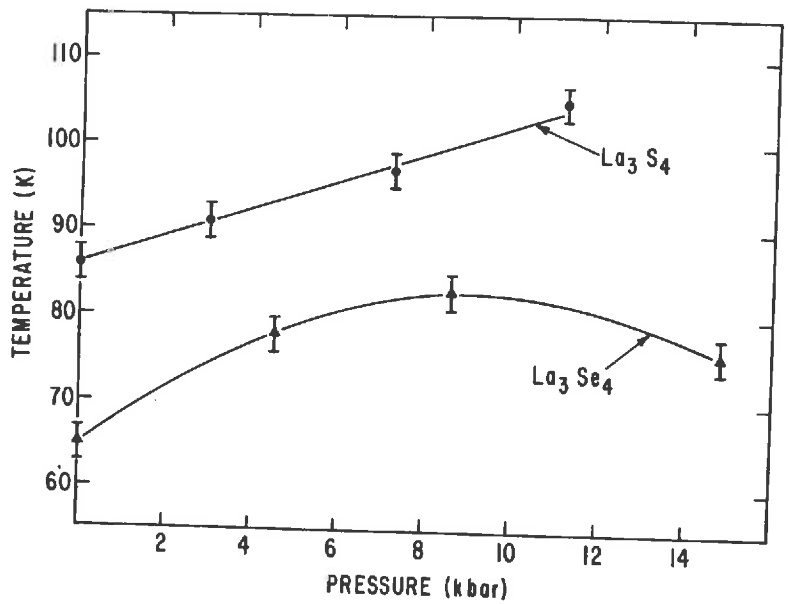

FIG. 7b. Polymorphic Transition Temperatures of Lanthanum Chalcogenides

IV. TERNARY COMPOUNDS

At present, ternary compounds seem to offer attractive superconducting possibilities. Of these the most promising system is that of the molybdenum sulfides. Experimenting with this system is very exciting because this type of behavior has never been encountered before and one can see through its use the possibility of attaining higher transition temperatures. Mo_3Se_4 is superconducting somewhat above 6°K, while, as stated before, all compounds of $X_{0.5}Mo_3S_4$, with X covering the range from Cu to Pb, are also superconducting. The transition temperatures range from 2-3°K when substituting divalent elements but up to 16°K for the four valent ones.

The crystal structure of these compounds is also

very interesting. The Mo-S or Mo-Se cubes are slightly canted and are arranged in such a way so that there are three channels of voids running through the crystal in a three-dimensional arrangement. This three dimensionality - even though it is only voids - is of primary importance, since the additional X elements are located here. The systematic occurrence of superconductivity in this system is a very unusual one. The total number of valenc electrons, which is always very close to 6, hardly varies through out this system and yet the transition temperatures cover a very wide range. It has been demonstrated that the only elements from which X can be chosen in order to get superconductivity, are thos which are both immiscible with Mo and form no compounds with Mo in binary systems. This can be seen particularly well when X is a trivalent metal. Al, Ga and In react with Mo in binary systems and consequently do not form these phases. The trivalent transition elements, from Sc to Lu all form the rhombohedral phase, bei inert with Mo in binary systems. This tendency is very strong, s much so that even many of the magnetic rare earths such as Pr, Nd or Gd form superconductors with temperatures as high as 9°K. This phenomenon is radically new and will lead to the first truly magnetic superconductivity of single compounds, where superconductivity will <u>not</u> occur <u>without</u> the presence of a strongly magne element.

V. CONCLUSIONS

It was once thought that all high temperature superconductivity could be characterized by the number of valence electrons - the electrons outside of the filled shell, per atom. That is to say, the more electrons there are, the better is the possibility for superconductivity. As indicated for ternary compounds, this idea doesn't seem to be correct and yet in the past it was so very applicable for structures such as beta wolfra After all, using the criteria of the number of valence electrons

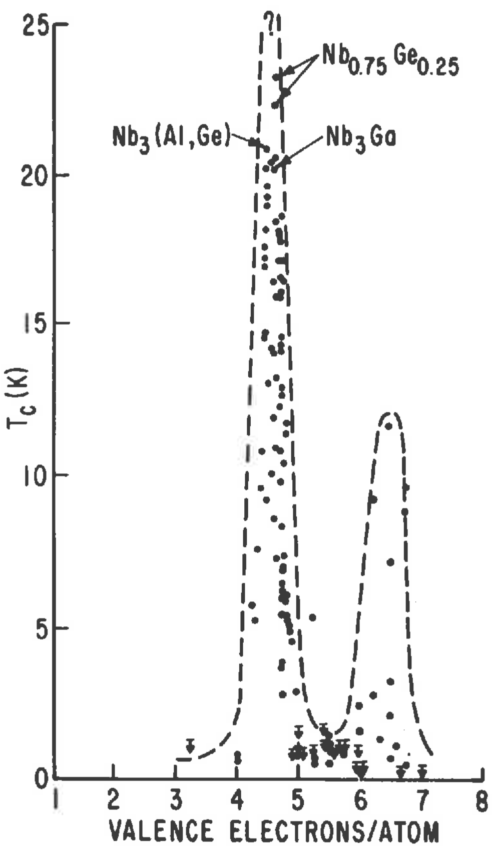

FIG. 8. Superconducting Transition Temperature in the β-W Structure as a Function of Valence Electrons/Atom

made it possible even 10 years ago for us to predict higher transition temperatures for Nb_3Ge. (11) It was already then quite obvious from this criteron that the transition temperature of Nb_3Ge should be much higher than 17 or 18°K. One conclusion becomes evident. Namely that the number of electrons is crucial as long as one is dealing with a binary system; however, with regard to these new Mo sulfides and selenides, the number of valence electrons is totally irrelevant. The reason for this change with

valency electrons from binary to ternary systems is not understoo at present.

The ternary systems are attractive from another viewpoint: many of the binary systems which exist, have been tried. But, when the number of ternary systems is considered the is, at present, no real limit. Consequently, today the most promising way to get to higher transition temperatures seems to be just to read the literature, and look for new ternary systems.

Eventually superconducting transition temperatu are expected to reach the vicinity of 25°K. This would be a trul significant achievement because hydrogen will be used without the need to pump on it.

The exciting possibility to explore a situation where there are many unanswered questions and to discover new, high transition temperature superconductors will attract, I hope, many new people to this field which should help accelerate progre toward this goal.

REFERENCES

1. D. E. Schafer, F. Wudl, G. A. Thomas, J. P. Ferraris and D. O. Cowan, Sol. St. Commun. 14, 347 (1974).

2. G. A. Thomas, D. E. Schafer, F. Wudl, P. M. Horn, D. Rimai, J. W. Cook, D. A. Glocker, M. J. Skove, C. W. Chu, R. P. Groff, J. L. Gillson, R. C. Wheland, L. R. Melby, M. B. Salamon, R. A. Craven, G. De Pasquali, A. N. Bloch, D. O. Cowan, V. V. Walatka, R. E. Pyle, R. Gemmer, T. O. Poehler, G. R. Johnson, M. G. Miles, J. D. Wilson, J. P. Ferraris, T. F. Finnegan, R. J. Warmack, V. F. Raaen and D. Jerome, Phys. Rev. 13B 5105 (1976).

3. V. M. Guervich, Electric Conductivity of Ferroelectrics, Izdatel' stvo Komiteta Standartov, Mer i Izmeritel'nykh Priborov pri Sovete Ministrov SSSR (translated from Russian, 1971).

4. C. Agte and H. Alterthum. Zschr. J. Tech. Physik 11, 182 (1930).

5. S. L. McCarthy, Jrl. of Low Temp. Physics 4, 669 (1971); A. C. Lawson and R. N. Shelton, Ferroelectrics (in press).

6. W. Rossteutscher and K. Schubert, Z. Metallk. 56, 820 (1965).

7. A. L. Giorgi, E. G. Szklarz, M. C. Krupka, T. C. Wallace and N. J. Krikorian, J. Less-Common Metals 14, 247 (1968).

8. D. C. Johnston, H. Prakash, W. H. Zachariasen and R. Viswanathan, Mat. Res. Bull. 8, 777 (1973).

9. R. N. Shelton, R. W. McCallum and H. Adrian, Phys. Letters 56A, 213 (1976).

10. W. Buckel and B. Stritzker, Physics Letters 43A, 403 (1973).

11. B. T. Matthias, T. H. Geballe, R. H. Willens, E. Corenzwit and G. W. Hull, Jr., Phys. Rev. 139, A1501 (1965).