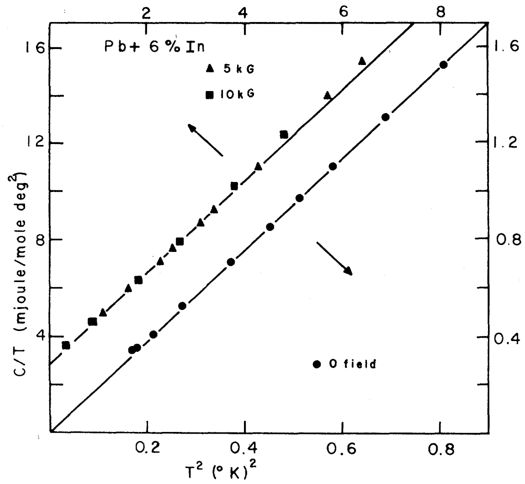

FIG. 2. Specific Heat of Pb + 6% In in zero, 5 kG and 10 kG fields.

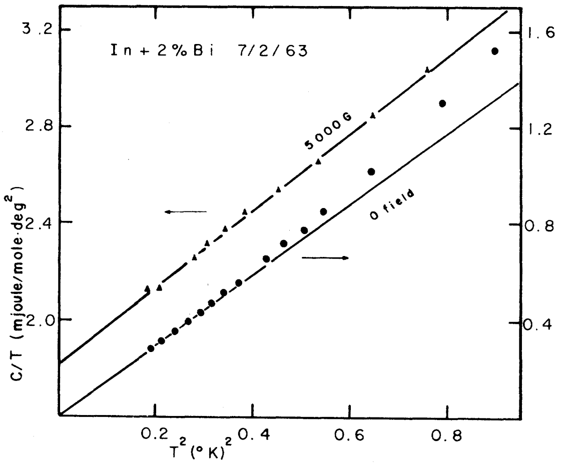

FIG. 3. Specific Heat of In + 2% Bi in zero and 5 kG fields.

# TRANSITION ELEMENTS AND ALLOYS

CHAIRMEN: *B. T. Matthias, B. S. Chandrasekhar*

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## Superconductivity in the Transition Metals

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### OCCURRENCE

The superconducting state is the most commonly occurring ground state among the metallic elements at low temperatures. If we restrict ourselves to transition metals—those having unfilled *d* shells and filled or empty *f* shells—then, at present, more than 50% out of the 26 are superconducting. The balance is split rather equally between those magnetically ordered, and those having no as yet observable low temperature condensation. Since more than 75% of the transition elements do order at low temperatures, it seems possible that the rest might also order under the proper conditions.

We have therefore focused experimental attention on elements where this ordering has not been observed. These elements are to be found in the periodic system where the *d* band is just starting to fill, Sc, Y, and Lu; a lone spot in the middle, W; and the nearly full *d*-band elements Rh, Pd, and Pt. The experimental method consists of searching for superconductivity in intermetallic systems in which the element in question is the major component, preferably the solvent in solid solutions, and then to study the effect of various physical and chemical parameters on the transition. This method has been particularly successful in the study of Mo–Re and Ir–Os solid solutions which led to the discovery of superconductivity in Mo[1] and in Ir.[2] In addition, the crucial effect of Fe on the transition temperature of Mo was first observed in Mo–Re solid solutions.[3] In several of the systems studied, the desired terminal solid so-

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[1] T. H. Geballe, B. T. Matthias, E. Corenzwit, and G. W. Hull, Jr., Phys. Rev. Letters 8, 313 (1962).

[2] R. A. Hein, J. W. Gibson, B. T. Matthias, T. H. Geballe, and E. Corenzwit, Phys. Rev. Letters 8, 408 (1962).

[3] B. T. Matthias, M. Peter, H. J. Williams, A. M. Clogston, E. Corenzwit, and R. C. Sherwood, Phys. Rev. Letters 5, 542 (1960).

lutions do not occur. However, superconducting intermediate phases which are rich in the element in question do occur and these are discussed in another paper.[4]

If the nearly empty *d*-band elements, Sc, Y, and Lu, are assumed to be superconducting, then one might ask why their transition temperatures are so low whereas that of La, which also belongs to this group, is so high. Both their electronic heat capacities and also their superconducting behavior in solid solution in Th are quite similar; and no other physical properties suggest that such a difference should occur.

An interesting hypothesis has recently been suggested by Kondo[5a] and by Hamilton and Jensen[5b]. They note that since the unfilled $4f$ band in La is just above the Fermi surface it is possible for virtual $4f$ levels to be excited. Since Ce with one $4f$ electron is known to be antiferromagnetic it is possible that a magnetic interaction between virtual $4f$ electrons in La is responsible for the large attractive interaction that must exist in La. A similar situation can arise in uranium where the $5f$ level is just above the Fermi surface and which also has an unexpectedly high superconducting transition temperature. If the hypothesis is correct and the superconductivity of La is due to a special contribution of the $4f$ band then, as Hamilton and Jensen point out, there is a symmetrical distribution in the occurrence of superconductivity about $n = 6$ ($n$ = number of electrons outside filled bands), and the empirical rule of Matthias[6] concerning the dependence of $T_c$ upon $n$ must be modified.

Solid solution formation of Sc and of Y with elements to their right in the periodic table would result in an increase in $n$ and, hopefully, in the occurrence of superconductivity. This procedure has been successful for Ti and Zr and solution formation with almost every element to their right has increased their transition temperatures. However, of the elements studied, only Cr in Sc[7] and Ir in Y[4] have resulted in superconducting solid solutions. We have studied the Sc–Cr system in detail. According to the x-ray investigations of Ch. J. Raub at La Jolla, there are no intermediate phases in the system. The two terminal solutions are present when different compositions of Cr and Sc are melted together. Metallurgical work by H. Schreiber using the electron beam microprobe indicate that within the resolving power of the probe ($\sim 1\mu$), the Cr is in solution when the samples are superconducting. The conclusion that the superconductivity is due to a supersaturated solution of Cr in Sc is supported by other annealing and quenching experiments and photomicrographs. The reaon why this particular system, possibly alone among Sc solutions, shows superconductivity could be related to the enhanced effect Fe has in Ti. An enhanced attraction caused by virtual levels which can interact by a magnetic exchange has been postulated previously.[8] Another model along related lines is to be discussed in the Theoretical Session by Cohen.[9] The occurrence of superconductivity in dilute solution of Ir in Y will be discussed by Matthias.[4] The solution of Fe in Ti causes an increase in $T_c$ about 5 times greater than would normally be expected from the valence electron effect.[10] If a similar order of magnitude enhancement is to be attributed to the presence of Cr in Sc, one would expect to find superconductivity in other Sc solutions around 0.1°, and in pure Sc not much lower.

The absence of superconductivity in W is easier to explain, although it might, in the end, be more difficult to discover superconductivity in W than in Sc and Y. The explanation, of course, rests on the effect of elusive impurities such as Fe which can have a major effect in suppressing superconductivity even when present in trace quantities. When we compare alloys of W and Mo with their neighbors we find that the minimum in $T_c$, which in the $4d$ series is between Nb and Mo, is shifted to the right in the $5d$ series, i.e., towards pure W. Why this is so is a question for which at least two explanations have been offered. The first follows from Pines[11] who shows from simple BCS theory that $T_c$ should follow the density of states or the electronic heat capacity coefficient $\gamma$ in a simple exponential way. The $\gamma$ for *W* with a resistivity ratio of 20 000 has recently been measured by J. P. Maita to be 2.0 cal/mole$^{-1}$ deg$^{-2}$, the smallest of any transition metal. Hein and Gibson in a following paper[12] interpret their data on Nb–Mo alloys in this light. However, frequently $T_c$ does not follow $\gamma$, not even qualitatively, in the simple BCS manner.

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[4] B. T. Matthias, T. H. Geballe, V. B. Compton, E. Corenzwit, and G. W. Hull, Jr., Rev. Mod. Phys. **36**, 155 (1964).

[5] (a) J. Kondo, Progr. Theoret. Phys. **29**, 1 (1963). (b) D. C. Hamilton and M. Anthony Jensen, Phys. Rev. Letters **11**, 205 (1963).

[6] B. T. Matthias, "Superconductivity in the Periodic System," *Progress in Low-Temperature Physics*, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, 1957), Vol. II, p. 138; Phys. Rev. **97**, 74 (1955).

[7] O. Arrhenius, T. H. Geballe, and B. T. Matthias, Bull. Am. Phys. Soc. **8**, 294 (1963).

[8] B. T. Matthias, T. H. Geballe, E. Corenzwit, and G. W. Hull, Jr., Phys. Rev. **129**, 1025 (1963).

[9] M. H. Cohen, Rev. Mod. Phys. **36**, 243 (1964).

[10] B. T. Matthias, V. B. Compton, H. Suhl, and E. Corenzwit, Phys. Rev. **115**, 1597 (1959).

[11] D. Pines, Phys. Rev. **109**, 280 (1958).

[12] R. A. Hein, J. W. Gibson, and R. D. Blaugher, Rev. Mod. Phys. **36**, 149 (1964).

Apparently Bucher *et al.* report new cases where this is so in a following paper.[13] It seems unwise therefore to attach significance to cases where $T_c$ and $\gamma$ do follow each other. A second explanation has been offered by Matthias who suggests that the dip in superconductivity is caused by the varying effectiveness of a dilute and relatively constant background of impurities in suppressing the transition temperature. We have found that Fe is much more effective in suppressing superconductivity in Mo than in Mo–Re solid solutions. Recent work by Sarachik is perhaps significant in this respect.[14] She has studied the resistivity of a series of 4*d* alloys in which *n* is varied by making near neighbor solutions Nb, Mo, and Re with and without additions of 1% iron. This procedure isolates the scattering due to the iron. Her results show that the resonant scattering of an iron impurity reaches a maximum in alloys containing between 15 to 20% Nb in Mo. The superconducting minimum and magnetic scattering maximum are found therefore in the same concentration range. Since one would expect to find the effectiveness in depressing $T_c$ to be a maximum where the magnetic scattering is a maximum, the above results are in harmony with the second suggestion. The magnetic scattering is related to the density of states, and therefore should be greater in W than in Mo. From a rough analogy with the behavior of Mo solutions we suspect that Fe concentrations in W may have to be reduced to the order of 1 part in $10^8$ before superconductivity can be observed. Considering that the $T_c$ of the 5*d* elements is normally lower than that of the corresponding 4*d* elements when the band is $\lesssim$ one-half full, one can only estimate that the $T_c$ of sufficiently pure W will be well below 1°K.

In the remaining not-yet-superconducting nonmagnetic *d*-band metals, Rh, Pd, and Pt, we are at the other extremity of the *d* band and have the option of adding elements to the right and thus filling it or adding those to the left and depleting it. A group at La Jolla, Bell Laboratories, and the University of Chicago headed by Raub[15] employed the former method and studied the superconductivity of systems containing Si, P, and S and the eight other elements which are below them in the periodic system with the Pt-metal elements. While there are too many details to go into, the number of superconducting phases is summarized in Fig. 1. It can be seen that Rh and Pd can easily fill their *d* bands in such a way as to average over the periodic table and become superconducting. This behavior is, of course, similar to the superconductivity of CuS which was discovered by Meissner[16] almost 35 years ago. When one starts with a less full *d* shell as in Ru the averaging no longer results in superconductivity. The nearly filled 5*d* band, which itself has stronger superconducting interactions, is less able to produce superconductivity when the *d* band is filled than the 4*d*. Recently, we reported on superconducting solutions of W in Pt[17] and in collaboration with Hein are extending the study to include Ir in Pt. More data are needed before we can extrapolate to pure Pt. Rh and Pd have been more difficult and no terminal solid solutions have been discovered. Intermediate phases of Rh will be discussed separately.[4] Pd is known to develop giant magnetic moments when magnetic impurities are dissolved in it. Trace amounts of such impurities could easily have a devastating effect on superconductivity.

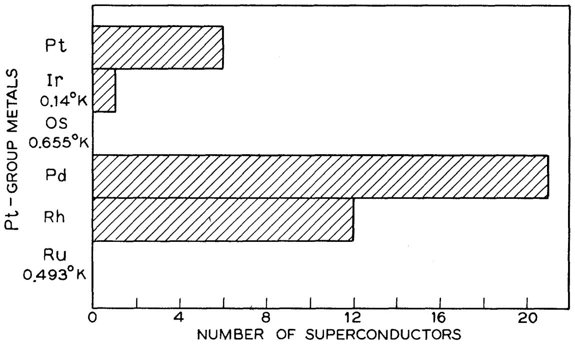

FIG. 1. Number of binary superconducting compounds of Pt-group metals with elements of groups IVA, VA, and VIA.

## MECHANISMS

Recent theoretical calculations, particularly of the isotope effect, by Garland[18] have led him and others to conclude that superconductivity is universally caused by the phonon-mediated electron interaction. Our original stimulus in studying the isotope effect in transition metals was provided by the thought that this is not so. The evidence then rested primarily on the behavior of magnetic impurities such as Fe and Cr which often either enhance or depress the transition temperature in large amounts. More

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[13] E. Bucher, F. Heiniger, J. Muheim, and J. Müller, Rev. Mod. Phys. **36**, 146 (1964).

[14] M. Sarachik (to be published).

[15] Ch. J. Raub, W. H. Zachariasen, T. H. Geballe, and B. T. Matthias, J. Phys. Chem. Solids **24**, 1093 (1963).

[16] W. Meissner, Z. Physik **58**, 570 (1929).

[17] T. H. Geballe, B. T. Matthias, V. B. Compton, E. Corenzwit, and G. W. Hull, Jr., Phys. Rev. **129**, 182 (1963).

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

such evidence is still being accumulated. The careful study of De Sorbo[19] who studied dilute solutions of 4th, 5th, or 6th group elements in Nb provides a good system in which regular behavior has been thoroughly demonstrated. We have extended the study to Fe, Ru, and Os solutions in Nb. Here again, Fe abnormally enhances the superconductivity in a way which is consistent with an interaction through virtual states. De Sorbo found, in addition to the usual valence–electron effect on the transition temperature of solutions in Nb, an explicit dependence on the volume difference between Nb and the solute atom. The smaller solute atoms, in effect, gain elecelectrons from the Nb matrix. A rough correction whereby volume changes are converted into changes in electron density gives quite reasonable results for the solutions he studied. As can be seen in Fig. 2 quite the opposite is true for Fe, Ru, and Os in Nb. Not only are the Fe solution transitions already high with respect to Ru and Os, but the De Sorbo volume correction would make them even higher.

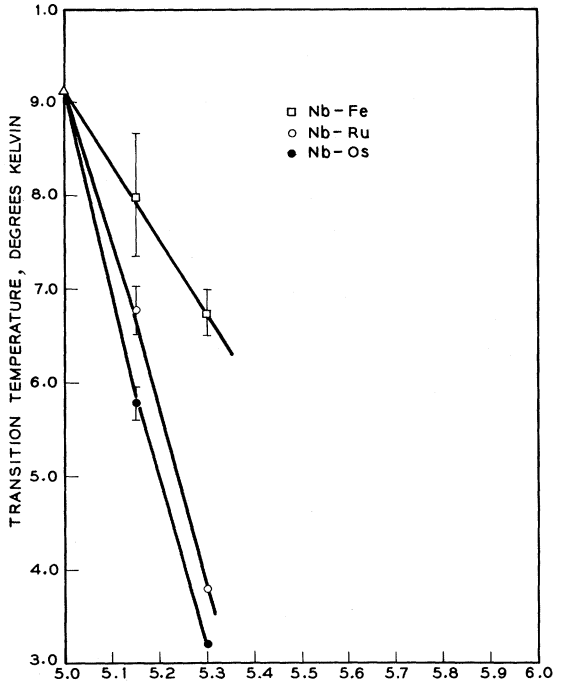

FIG. 2. Superconductivity of dilute solutions of Fe, Ru, and Os in Nb.

Garland has shown that, given a number of parameters, the range of observed isotope and pressure dependences can be obtained using the model of phonon-induced superconductivity. Before one can gain confidence in his model, the input parameters should be examined. These parameters are associated with fine structure in the *d* band, namely, the width, density of states, and distance from the Fermi surface of a particular subband. It is not clear how these subband parameters are related to observables such as the electronic specific heat coefficient.

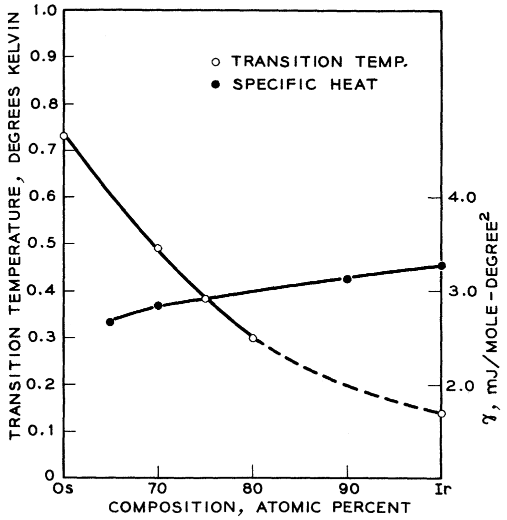

FIG. 3. Superconductivity and specific heat of fcc alloys in the Os–Ir system.

If there is another mechanism operative that is independent of the phonon interaction one would expect it to be most prominent where the observed mass dependences of $T_c$ are small or nonexistent. We have studied the behavior of solid solutions between Ru, Os, Ir, and Rh in order to see if, and how, a nonisotope effect correlates with other properties. In all six solutions made by studying the possible horizontal, vertical, and diagonal neighbor solid solutions of the above elements the density of states and $T_c$ go in opposite directions, i.e., an increase in $\gamma$ means a decrease in $T_c$. On the other hand, the four solid solutions made by melting the elements from different columns do follow the simple valence electron rule and slope to the right. The results for Os–Ir can be seen in Fig. 3. The measurements of $\gamma$ in the fcc region of the system have been made by J. P. Maita. He also finds a constant Debye temperature $=410 \pm 3\%$ for all four samples. The results for Ru–Os are shown in Figs. 4(a) and 4(b). This system is completely homogeneous and the lattice constants for the alloys have been published.[20] Starting with

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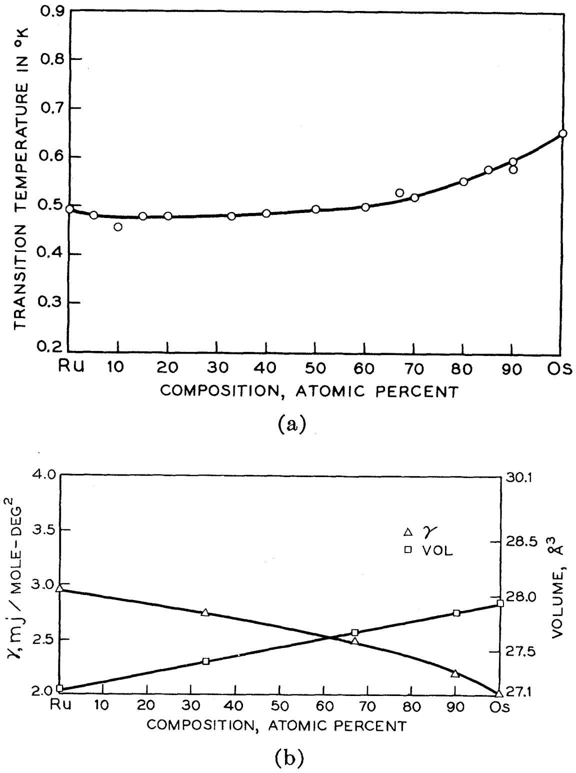
[19] W. De Sorbo, Phys. Rev. **130**, 2177 (1963).

[20] E. Raub, J. Less-Common Metals **1**, 3 (1959); M. A. Tylkina, V. P. Polyakova, and E. M. Savitskii, Russ. J. Inorg. Chem. **7**, 754 (1962).

pure Ru we find the zero-isotope effect result mirrored in the lack of change of $T_c$ as Os is added. By the time 90% Os is added $T_c$ has increased only $\frac{1}{2}$ of the way from Ru to Os. The volume calculated from x-ray diffraction measurements changes uniformly from Ru to Os. One would expect the phonon spectrum and perhaps phonon-induced superconductivity to do likewise rather than in the asymmetrical manner that is found. The lack of correlation with $\gamma$ is equally apparent. It not only decreases as $T_c$ increases, but again it does so in a much more symmetrical manner. There is no evidence of any subband structure.



(a)

(b)

Fig. 4(a). Superconductivity in the Ru–Os system. 4(b). Specific heat and volume of Ru–Os alloys. [The value of the heat capacity of elemental Ru is taken from R. H. Batt and N. E. Phillips (to be published), and that of elemental Os is taken from R. A. Hein and J. W. Gibson, Phys. Rev. **131**, 1105 (1963). All samples including the elements were prepared in our laboratory by arc melting on a water-cooled copper hearth.]

Finally, there is an experimental discrepancy in the magnitude of the isotope effect in Os in that our original results gave a smaller mass dependence than is now reported by Hein and Gibson.[21] The results are not as clear-cut as in Ru where the effect is zero within the experimental accuracy of ourselves[22] and of Finnemore and Mapother.[23] Nature is not so kind in the case of Os. Not only is the percentage mass-variation smaller, but the transition is quite strain sensitive. In fact, as received from Oak Ridge, the Os isotopes we studied were only partially superconducting above 0.3°K. Only after a series of eight or nine meltings did we arrive at a procedure which we felt gave representative and reproducible (upon remelting) transitions. The results were given at the IBM Conference.[24] The transition temperature of the heaviest isotope was between 0.001° and 0.002° lower than the others even after repeating our standard melting and annealing procedures. Since the isotope effect was zero for Ru and the lighter isotopes of Os had the same transition within 0.001°, we concluded that there was no isotope effect in Os. These Os samples were then sent to Hein and Gibson who made careful measurements of the transitions in magnetic fields. Presumably the samples were in the same well-annealed condition as during our final melting and annealing procedure. They find an isotope effect of $T_c \propto M^{-0.2}$ on which they report later. Since the completion of their measurements, we have remeasured the samples in zero ($\lesssim 0.01$ G) field and now find results in essential agreement with theirs. Either the transition temperature of light isotope has increased relative to the others by 1.3 mdeg or our original measurements were in error by that much. Further annealing is required.

In conclusion I would like to emphasize that we have been able to find superconductivity in phases which are rich in every nonmagnetic transition element which itself is not superconducting. This speaks strongly for the universality of the phenomenon. However, it is not yet possible to relate the appearance of superconductivity in these phases in a quantitative way to other physical properties of the alloys and therefore conclusions as to the mechanisms causing the superconductivity are open to question.

## ACKNOWLEDGMENTS

I would like to acknowledge the devoted efforts of Mrs. V. B. Compton, E. Corenzwit, G. W. Hull, Jr., L. D. Longinotti, and Ch. J. Raub, who, along with B. T. Matthias and myself are responsible for the work presented here.

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[21] R. A. Hein and J. W. Gibson, Phys. Rev. **131**, 1105 (1963).

[22] T. H. Geballe, B. T. Matthias, G. W. Hull, Jr., and E. Corenzwit, Phys. Rev. Letters **6**, 275 (1961).

[23] D. K. Finnemore and D. E. Mapother, Phys. Rev. Letters **9**, 288 (1962).

[24] T. H. Geballe and B. T. Matthias, IBM J. Res. Develop. **6**, 256 (1962).