Electronic Structure and Superconductivity of Transition Metals and Their Alloys

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INTRODUCTION

Most of what little detailed information we have about the electronic structures of transition metals, whether experimental or theoretical in origin, comes from studies of elements of the first (3*d*) transition series, although the range of occurrence of superconductivity is greater in the second series, and still greater in the third. Fortunately, certain rather general patterns of behavior are preserved from series to series; and it seems likely that the contrasts found in any column towards the end of the series—the change, for example, from ferromagnetic cobalt to paramagnetic, nonsuperconducting rhodium, to superconducting iridium—are due to decreasing exchange effects and increasing spin–orbit interactions rather than to any major differences in band structure and occupation.

If $N(E)$, the density of states at the Fermi surface, as measured by the coefficient (γ) of the linear term in the specific heat, is plotted against atomic number, well-defined peaks are found close to the beginning and end of each transition series, with perhaps another at about 7 electrons per atom. The band structure calculations which have been made (for example, those of Fletcher and Wohlfarth,[1] Asdente and Friedel,[2] and Wood[3]) show maxima in $N(E)$ towards the bottom and top of the band, and rather general arguments in support of the likelihood of these in most transition elements can be brought. Plots of energy (E) versus wave vector (k) for different directions in the Brillouin zone will show both small values of dE/dk and degeneracies of $E - k$ branches of different symmetry at the top and bottoms of the total *d* band (see Fig. 1). If, as we suggest later, a simple-minded collective band is appropriate for alloys of neighboring elements in the Periodic Table, there are strong experimental indications that a very high density of states for the body-centered cubic structure results for alloys having a mean outer electron concentration of 6.4 per atom (see Fig. 2). Theory has yet to come forward with indications of why this should be the case, and it would be rather remarkable if midband interactions (between *d* states of different symmetry or between *d* and *s* states) gave large areas of constant energy surface with small dE/dk at *exactly* the same band occupation in each of the transition series.

A point of interest about the general form of the *d* band is that, for the first transition series, soft x-ray spectroscopy and preliminary band structure calculations[4] show only a rather slow variation in bandwidth along the series. Since we believe that *d* levels are moving to lower energy along the series, a distinct narrowing of the *d* band might have been expected, but this effect only seems to become appreciable at the very end of the series where interatomic distances begin to increase with atomic number (and contributions of the *d* electrons to cohesion diminish). It may be that earlier in the series the *decrease* of interatomic distance with atomic number brings about enough increase in the overlap of *d* functions on neighboring atoms to offset the expected narrowing of the band.

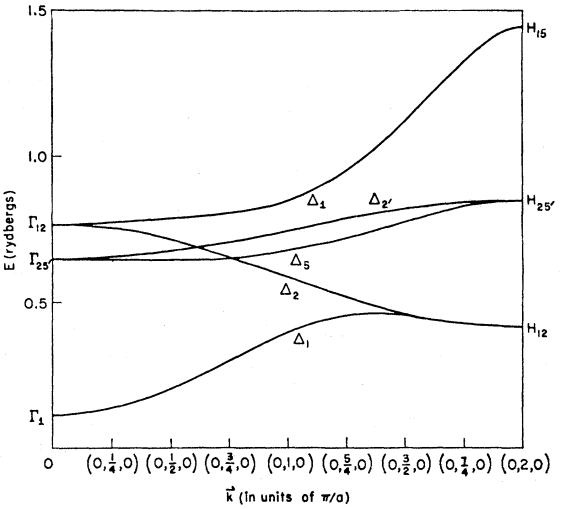

FIG. 1. Energy bands in bcc iron along the [010] direction (after Wood).

$N(E)$ is only a very crude measure of the electronic

[1] J. Fletcher and E. P. Wohlfarth, Phil. Mag. **42**, 106 (1951).
[2] M. Asdente and J. Friedel, Phys. Rev. **124**, 384 (1961).
[3] J. H. Wood, Phys. Rev. **126**, 517 (1962).
[4] J. H. Wood (to be published).

structure of a metal, and we should not really expect to be able to explain many properties in terms of it alone. In due course, we hope for knowledge of the shape of the Fermi surface, and the variations over it of the derivatives of E with respect to k, properties which can be very approximately taken account of in

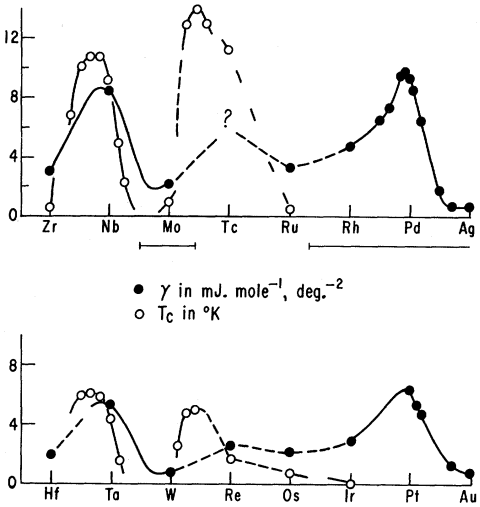

FIG. 2. Electronic specific heat coefficients (γ) and superconducting transition temperatures (T_c) for the 4d and 5d transition series.

discussions of experimental data by introducing the concepts of mobility, effective mass, and effective number of carriers. Thus for a quarter of a century it has proved useful to discuss the late members of the transition series in terms of two groups of electrons, one of s character and high mobility and the other of d character and high effective mass. Evidence from transport properties[5] and galvanomagnetic work[6] is now showing that even for palladium and nickel at the end of their respective series this separation has its limitations, but there is still justification for regarding the d electrons of palladium as being less effective current carriers than those of, say, niobium.

THE ELECTRONIC STRUCTURE OF ALLOYS

The difficulties facing any general discussion of the electronic structures of alloys of the transition metals with one another is strikingly emphasized for the 3d transition series by the Slater–Pauling curve of saturation magnetic moment as a function of mean atomic number (Fig. 3), and this has provided a central theme for many approaches to the problem.[7–9] In recent years, considerable insight into the underlying physics has been provided by the concept of the virtual bound state,[10,11] and associated discussions of how the screening of an impurity transition metal atom is to be accomplished. In alloys of two transition metals with one another, the appropriate description of the resultant electronic structure depends on, among other things, their separation in the Periodic Table and the value of $N(E)$. The dominant effect when Cr is dissolved in Ni is for empty virtual states of both spin direction to be pushed out of the top of the d band with a resultant decrease in the spin imbalance. Co atoms, on the other hand, constitute a smaller perturbation and the antiscreening required is provided by a hole in the d-band electrons, so that a collective band description of the occupation is reasonable, although neutron diffraction studies[12] show the extra spin moment to be localized around the cobalt atoms. In the absence of ferromagnetism, we have no such sensitive tool to study the fine structure of alloys of the second and third transition groups, but analogy suggests that in them also it is probably justifiable to use specific heat and other data on alloys of *neighbors* to give indications of band behavior above and below the Fermi level of a pure metal. We might also expect, by analogy with the results of Fig. 3, that virtual bound states will be of importance in alloy systems like Rh–Mo, Pd–Mo, Pd–Nb, etc. Spontaneously magnetized states do not occur in these systems, but the susceptibility of palladium has been shown[13] to be reduced by Nb or Mo additions in much the same way as the saturation moment of nickel is reduced by V or Cr additions. In fact, alloys based on palladium seem to show a greater tendency for the formation of virtual bound states than those based on nickel, for while Pd–Rh shows collective band behavior[14] Pd–Ru appears not to.[15]

The role of $N(E)$ for the solvent metal in affecting the formation and magnetization of virtual bound states about a solute atom has been strikingly demonstrated for solutions of iron in metals and

[5] B. R. Coles and J. C. Taylor, Proc. Roy. Soc. (London) **267**, 139 (1962).
[6] E. Fawcett and W. A. Reed, Phys. Rev. **131**, 2463 (1963).
[7] J. E. Goldman, Rev. Mod. Phys. **25**, 108 (1953).
[8] W. Hume-Rothery and B. R. Coles, Advan. Phys. **3**, 149 (1954).
[9] W. M. Lomer and W. Marshall, Phil. Mag. **3**, 185 (1958).
[10] J. Friedel, Nuovo Cimento Suppl. **7**, 287 (1958).
[11] W. M. Lomer, J. Phys. Radium **23**, 716 (1962).
[12] M. S. Collins and D. A. Wheeler, Proc. Phys Soc. (London) **82**, 633 (1963).
[13] E. Kudielka-Artner and B. B. Argent, Proc. Phys. Soc. (London) **80**, 1143 (1962).
[14] D. W. Budworth, F. E. Hoare, and J. Preston, Proc. Roy. Soc. (London) **A257**, 250 (1960).
[15] E. Vögt and E. Oehler, Ann. Physik (to be published).

alloys of the 4*d* transition series.[16] The local perturbation would be expected to be larger for a niobium matrix than for a molybdenum one; but the higher $N(E)$ for Nb provides more states to resonate with *d* states localized on the iron atoms, so that the resultant virtual bound state broadens and loses its moment for **Nb**–Fe but not for **Mo**–Fe. This difference in behavior has, as emphasized by Matthias *et al.*[17] very important consequences for the effect of iron on the superconductivity of these metals. It also leads to low temperature resistivity anomalies for **Mo**–Fe which are absent in **Nb**–Fe.[18] It seems possible therefore that, even for the small differences in group number occurring in **Mo**–Tc and **W**–Re alloys, the presence of rather narrow virtual bound states may have to be considered. Empirically it seems that the high $N(E)$ values of Pd and Pt are less effective in suppressing the occurrence of narrow virtual states on solute iron atoms, just as they are less effective in promoting the occurrence of superconductivity.[19] One can fairly confidently predict noncollective behavior therefore for **Pt**–W and **Pt**–Ta alloys.

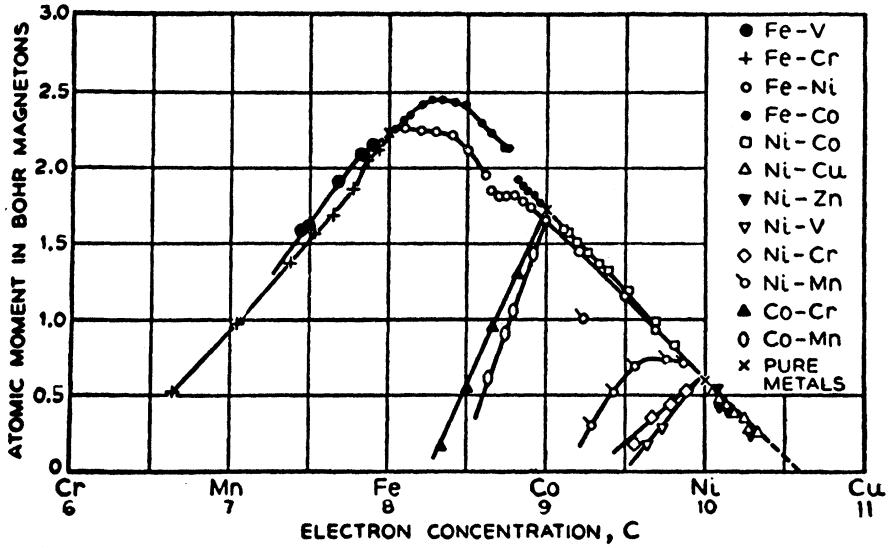

FIG. 3. Average atomic moments of binary alloys in the 3*d* transition series.

SUPERCONDUCTIVITY OF TRANSITION METALS

The Pure Elements

It would be rash to pretend that all the experimental data on the superconductivity fall neatly into place in the light of the above remarks. It is still not clear, for example, whether different metals have the same basic superconductivity-inducing interaction, since in a multiband situation attractive interactions other than the electron–phonon one have been shown to be possible.[20,21] In recent work, Garland[22] has shown that phonon-induced superconductivity and the various peculiar features of transition metal superconductivity (especially the absence or reduction of the isotope effect) are not necessarily inconsistent, and he is of the opinion that in most transition metals for which data are available a virtual phonon interaction is the dominant one. However, the possibility of variations, from metal to metal, in the sensitivity of T_c to θ_D means that the use of the BCS expression for T_c and experimental data for θ_D and $N(E)$ to derive values of V, the interaction parameter, will not be particularly meaningful. On the other hand, direct comparisons of T_c and γ (the experimental source of $N(E)$ values) do suggest some sort of systematic variation, as pointed out by Matthias in a well-known paper.[23] Correlations between T_c and γ seem to exist for transition metals of up to 7 or 8 outer electrons per atom (see Fig. 1), but attention has been drawn[24,19] to the failure of the end members of the 4*d* and 5*d* series to be supercon-

[16] A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, and R. Sherwood, Phys. Rev. **125**, 541 (1962).
[17] B. T. Matthias, M. Peter, H. J. Williams, A. M. Clogston, E. Corenzwit, and R. C. Sherwood, Phys. Rev. Letters **5**, 542 (1960).
[18] B. R. Coles, Phil. Mag. **8**, 335 (1963).
[19] B. R. Coles, Solid State Comms. **1**, 5 (1963).
[20] H. Suhl, B. T. Matthias, and L. R. Walker, Phys. Rev. Letters **3**, 552 (1959).
[21] J. Kondo, Progr. Theoret. Phys. (Kyoto) **29**, 1 (1963).
[22] J. W. Garland, Phys. Rev. Letters **11**, 111, 114 (1963).
[23] B. T. Matthias, *Progress in Low Temperature Physics* (North-Holland Publishing Company, Amsterdam, 1957), Vol. 2.
[24] J. K. Hulm and R. D. Blaugher, Phys. Rev. **123**, 1569 (1961).

ductors in spite of high values of $N(E)$. It has been suggested[19] that this emphasizes the inadequacy of $N(E)$ as a complete description of the electronic structure and the importance of taking into account the higher effective masses and more localized character of the d electrons in these elements. It should also be remembered that exchange effects will be playing a larger part, as they clearly do in the $3d$ series, towards the end of a series. In view of indications[8] that the change in character of the wave functions takes place further towards the end of the series in the $5d$ group, it is not surprising that iridium is a superconductor while rhodium is not. What is perhaps more surprising is that scandium and tungsten have not yet been shown to be superconducting in the pure state; tungsten has a comparatively low $N(E)$, but that of molybdenum whose T_c is about 1°K is not very much larger.

Alloys of Transition Metals with One Another

It has been pointed out above that a simple collective band model for the d electrons of an alloy of two transition metals (as used by Hulm and Blaugher[24]) is likely to be a reasonable one for elements that are neighbors in the Periodic Table. Data for such alloys are included in Fig. 1; where, for example the T_c variation in Nb–Zr and Nb–Mo alloys reflects the variations in $N(E)$ suggested by specific heat and magnetic susceptibility results. For later elements, where correlations between T_c and $N(E)$ break down for the pure metals, the validity of such a model cannot yet be tested. Thus, for the Os–Ir alloys the behavior of T_c is dominated by the changing character of the d wave functions, but if these can be taken into account by future theories, a comparatively straightforward account of the band structure will probably be found to be appropriate.

When the component metals are more widely separated in the Periodic Table the superconducting behavior will depend critically on the character of the virtual bound states associated with the atoms of the added element; and these, in turn, will depend on the electronic structure of the matrix. An extreme example of this is provided by the **Mo**–Fe alloys mentioned above, but for alloys where a fairly narrow but not magnetized virtual state exists near the Fermi level the enhanced $N(E)$ is likely to lead to an *increase* in T_c. There are not yet sufficient detailed data for dilute alloys of selected metals for it to be clear whether or not the increase of T_c can be understood purely in terms of the enhanced $N(E)$ or whether special types of interaction mechanism come into play in such circumstances. [A theoretical analysis of possibilities of this type is given in the paper presented at this conference by M. H. Cohen.] The fine balance between the occurrence of a moment and depression of superconductivity and nonoccurrence of a moment and elevation of T_c is vividly demonstrated by work on **Ti**–Mn and **Ti**–**Zr**–Mn by Hake and Cape,[25,26] but the situation is unfortunately complicated for these group IV solvents by the presence of two crystal structures. The close connection between magnetic and superconductive behavior for these and other solvents has been frequently emphasized by Matthias.[27,28]

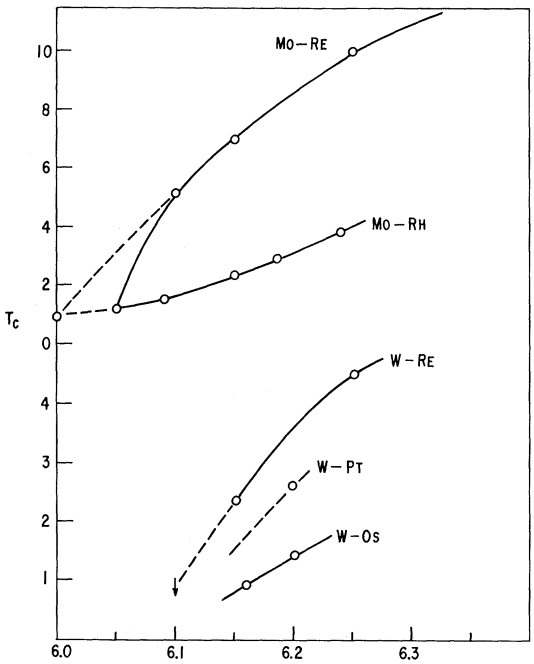

FIG. 4. Transition temperatures of solid solutions in Mo and W as a function of the average number of outer electrons per atom.

In alloys of widely separated members of the $4d$ and $5d$ series magnetic moments are less likely, but virtual bound states are almost certainly occurring, and it is probably to them that we may ascribe the behavior (illustrated in Fig. 4) of solid solutions in Mo and W of the elements that follow them.[29] Thus T_c rises with solute concentration in the **W**–Re, **W**–Os, and **W**–Pt systems, but no detailed correlation

[25] R. R. Hake and J. A. Cape, Bull. Am. Phys. Soc. **8**, 419 (1963).
[26] J. A. Cape and R. R. Hake, Bull. Am. Phys. Soc. **8**, 192 (1963).
[27] B. T. Matthias, V. B. Compton, H. Suhl, and E. Corenzwit, Phys. Rev. **115**, 1597 (1959).
[28] B. T. Matthias, IBM J. Res. Develop. **6**, 250 (1962).
[29] B. T. Matthias, T. Geballe, and V. B. Compton. Rev. Mod. Phys. **35**, 1 (1963).

of T_c with mean electron concentration (of the sort one would expect for a collective band model) is found. Another clear-cut instance is provided by alloys of V with the elements that follow it in the Periodic Table. The change of T_c with composition[30] does not show a simple dependence on electron concentration, although susceptibility data[31] show that no moments are present. For most of these alloys (except **V**–Cr where the smallness of the perturbation, the fine structure effects in the susceptibility, and the similarities to the **Nb**–Mo and **Ta**–W systems suggest a collective band) virtual states should probably be invoked.

It was suggested above that even in the nearest-neighbor systems **Mo**–Tc and **W**–Re virtual bound states are of importance because of the low $N(E)$ of the matrix. Such states would certainly account for the striking variations of T_c with composition in these systems; but because of the great sensitivity of T_c to iron impurities this suggestion must be made cautiously until extremely pure alloys have been examined. In the iso-electronic **Cr**–Mn alloys a moment on the Mn atoms and a steep rise in Néel temperature are found,[32] and even in **Cr**–Re an increase of Néel temperature has been observed.[33]

Intermediate Phases

In the above section the alloys under consideration were all primary solid solutions. A large amount of information (summarized by Matthias, Geballe, and Compton[29]) is also available about intermediate phases, both random solid solutions with structures different from the parent metals (secondary solid solutions), and phases of limited composition range based on particular atomic ratios and usually ordered (intermetallic compounds). When both components are transition metals intermediate phases of both types are often superconductors. It is not yet clear how important a role a particular crystal structure plays in affecting the superconductivity of such alloys, but Matthias *et al.*[29] suggest that the sigma phase structure, the α-manganese structure, and the β–W structure are particularly favorable for superconductivity.

The sigma phase, which is a secondary solid solution, is an especially interesting case; for it is found only in transition metal systems, and invariably the associated primary solid solution is one for which we have suggested that virtual bound state treatment is appropriate. It seems likely, therefore, that it should be regarded as a Hume–Rothery type electron compound, although a detailed explanation of how it is stabilized is likely to prove difficult. Since alloys with this structure have at least 20% of the minor component it cannot be appropriate to discuss them in terms of noninteracting virtual states, and the interactions between neighbors must give rise to a broadening over and above that caused by the original resonance of a bound state on an isolated atom with the Bloch states of the matrix. In many cases, however, the values of T_c for sigma and α-manganese phases are not very different from those of neighboring primary solid solutions, and high values are found for a mean number of outer electrons close to 6.4 or 6.8 per atom.[34a,34b]

Occurrence of the β–W structure seems to depend on a particular ratio of atomic sizes to make the required stoichiometry (A_3B) possible; and when both A and B are transition metals they are from different series. For these ordered phases it may prove rather easier to construct a satisfactory model for their electronic structures.

Alloys of Transition Metals with Nontransition Metals

There is, as yet, very little detailed information on the electronic properties and electronic structures of the many superconducting alloys in this group. All the ones of interest because of their high transition temperatures are intermediate phases (generally intermetallic compounds) since, as Matthias *et al.*[29] have emphasized, additions of nontransition metals in solid solution always lower the T_c of transition metals.

It is perhaps worth pointing out that in alloys of the end members of the transition series certain regularities occur which can be correlated with what might be expected to be appropriate descriptions of their electronic structures.

On adding Zn to Ni or Cd to Pd one may naively picture the extra electrons of the group II element as filling the d-band holes of the transition metal, thereby producing a fall in one case of the saturation moment and in the other of the magnetic susceptibility. If the filling of the d-band goes to completion

[30] J. Müller, Helv. Phys. Acta **32**, 141 (1959).
[31] B. G. Child, W. E. Gardner, and J. Penfold, Phil. Mag. **8**, 419 (1963).
[32] G. de Vries, J. Phys. Radium **20**, 438 (1959).
[33] W. E. Gardner and J. Müller (private communication), See also Fig. 5 of the paper at this conference by Bucher, Heiniger, Muheim, and Müller [Rev. Mod. Phys. **36**, 146 (1964)].
[34] (a) R. D. Blaugher and J. K. Hulm. J. Phys. Chem. Solids. **19**, 134 (1961). (b) L. Bucher, F. Heiniger, and J. Müller. *Proceedings of the Eighth International Conference no Low Temperature Physics* (Butterworths Scientific Publications, Ltd., London, 1962). Paper 4.5.

one would then expect to find the primary solid solution succeeded by a series of Hume–Rothery phases; and, at least in Pd–Cd, this is what seems to happen. As the added element moves along the series Cd–In–Sn–Sb–Te one would expect the filling of the d band and the phase changes to take place more rapidly as the valence of the added element increased. Such an expectation does not, however, take into account the change in the contrast of electronegativity between solvent and solute along the series. (For compounds of Ni or Pd with Group VI elements empty d states are certainly associated with the transition element, and reveal themselves by their magnetic properties for the nickel compounds.) The observed behavior shows a regular change in the type of phase diagram along the series Pd–Cd, Pd–In, Pd–Sn, Pd–Sb and the appearance of superconducting compounds towards the end of the series.

Thus, Pd–Cd shows a straightforward series of Hume–Rothery α, β, γ phases occurring at compositions which suggest a full d band for the palladium; Pd–In has β and γ phases at slightly displaced compositions but with no reported superconducting phases; Pd–Sn has no β or γ phases but shows superconductivity in the Pd_2 Sn, Pd_3 Sn_2, and Pd Sn phases[35]; Pd–Sb shows superconductivity with a rather higher T_c than the Pd–Sn alloys, and Pd Te and Pd Te_2 have higher T_c values again. (It may be remarked that the electron concentration of Pd_2 Sn would be 1.33 if the d band of the Pd were full.) This behavior could be ascribed either to the presence of a partly filled high $N(E)$ d band, or to a conduction band enriched by the extra electrons given up by the palladium under the influence of its electronegative partner.

For the high T_c, high H_c alloys between group V transition metals and nontransition metals of groups III and IV a narrow d band with a high $N(E)$ has been suggested[36] to account for a number of the electronic properties. It is not yet clear whether this follows from the reduced overlap of d functions on, say, V atoms, or whether the particular (β-W) structure plays a special role.

ACKNOWLEDGMENTS

The author's thanks are due to Dr. B. T. Matthias and Dr. W. M. Lomer for many helpful and stimulating discussions on the subject of this paper.

[35] C. J. Raub, W. H. Zachariasen, T. H. Geballe, and B. T. Matthias, J. Phys. Chem. Solids (to be published).
[36] A. M. Clogston and V. Jaccarino, Phys. Rev. 121, 1357 (1961).

Discussion 20

MENDELSSOHN: In the last few weeks we have cooled neptunium and plutonium down to 0.4 degrees and this adds a little more information to the end of the series of Dr. Geballe's table. Neither of these elements becomes superconductive down to that temperature, and this doesn't seem surprising in view of what we know from the resistance curves. Their behavior is indicative of some cooperative effect, possibly some sort of helical antiferromagnetism. In fact, the very beginning of this extra configurational resistance appears in uranium. It is not there in thorium—it appears in uranium and becomes progressively stronger in going from there to neptunium and to plutonium. We hope to get, in the near future, the real cornerstone to the whole question, that is, metallic protoactinum, which nobody has yet seen. It may be superconductive rather than antiferromagnetic.

BERLINCOURT: This so-called enhancement of the superconductivity of Ti by the addition of small quantities of Fe has often been sighted as evidence for an interaction mechanism other than the phonon mechanism. I would like to point out that Dr. Cape of our Laboratory has obtained information which is very pertinent to this point. For alpha Ti 1% Fe, he was able to deduce, from gamma- and from normal-state resistivity, a kappa value of the order of 2. This leads to an upper field, according to the Abrikosov mechanism, of roughly 200 G. For beta Ti–Fe, the kappa value is of the order of 80, which leads to a predicted upper critical field of about 50kG. Experimentally, traces of superconductivity persist in Ti containing 1% Fe to roughly 40 kG. We cite this as extremely convincing evidence that beta-phase filaments are present in Ti containing 1% Fe. Consequently, with such powerful superconducting beta filaments present, a meaningful determination of the transition temperature of alpha Ti 1% Fe is not possible.

GORTER: The chairman suggested I should just mention a recent measurement of which we are not 100% sure. If small amounts of Fe of about 0.1% are added to Al, the transition temperature goes considerably upward. It has been reported by Mr. Du Chatenier that the transition temperature goes up to about 1.5°. In this case we do not have localized moments because the specific heat and the susceptibility show no effect of this kind.

E. MAXWELL, *Massachusetts Institute of Technology:* I would like to comment further on this point and another point. We have made some measurements on Fe dissolved in Ti that Dr. Strongin will talk about later this morning. We have made magnetic measurements, but in general they reinforce what Dr. Berlincourt has said, namely that superconductivity, we think, is due to a precipitated beta phase. The other point I would like to make is in connection with the mechanism of the interaction in some of the transition metals. We've recently completed measurements on the isotope effect in rhenium and we find a rather substantial isotope effect; it's the order of 0.38 to 0.4. These specimens were arc-melted several times until no further change in transition temperature was noted. The samples are rather small, about 200 mg or less, which makes them quite homogeneous when arc-melted. The transitions are rather

sharp, on the order of a couple of mdeg, so the metallurgy doesn't seem to be too bad in this case. This is at least consistent with Garland's prediction for rhenium, which as I recall, predicts something like a range of 0.2 to 0.4, so that we just about meet his outermost limit.

R. L. Falge, Jr., *U. S. Naval Research Laboratory:* I have a slide showing the results of some recent work I have done on Ti–Mn alloys (Fig. 4). In this slide, the concentra-

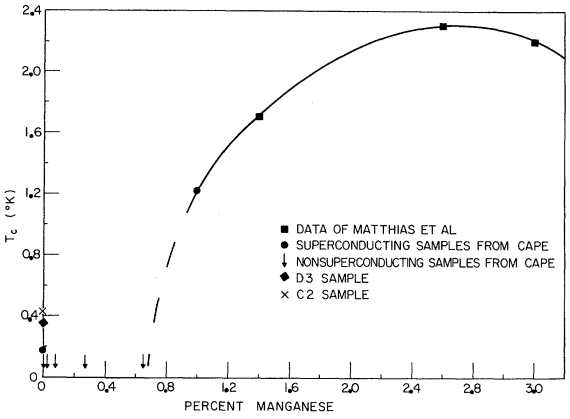

Fig. 4. Critical temperatures for Ti–Mn alloys.

tion of manganese increases as we go to the right. A considerable enlargement of the left axis would show that the slightest addition of Mn (as a matter of fact, 100 parts per million Mn) to Ti decreases the transition temperature to temperatures below that which we can produce. Then at about 0.7% Mn, the transition temperature increased in agreement with earlier data. My interpretation of this would be that Mn does have a magnetic moment when dissolved in Ti which lowers the transition temperature. The subsequent increasing portion would then be at least tentatively ascribed to the formation of filaments of the beta phase.

Blatt: I would like to suggest that perhaps there is a difference of point of view here concerning the interactions to be considered and the wavefunction. Let me make an anology. In atoms, the shell model of an atom is exceedingly successful; it classifies atoms according to whether certain shells are filled, empty, half filled, or what have you. In nuclear physics, for many years, people said that because the forces are very different, everything must be different. In fact, however, the nuclear-shell model works well and there seems to be more sense in talking about the structure of the wavefunction without worrying in too much detail about the force which produces that wavefunction. In spite of a very appreciable difference between atomic forces and nuclear forces, there is a great deal of analogy between the two shell models. Now I would like to suggest that also in superconductivity, the eventual thing to look at is the nature of the wavefunction rather than the nature of the force. I do not see any tremendous difficulty in having, in different regions of the periodic table, quite different forces produce what are substantially identical effects, once you see that the essential thing is an attractive pair coupling. I don't see any tremendous difficulty in having the force be an electron–phonon coupling in one region of the periodic table and some other sort of coupling in a different region. The essential part is the effect of the force rather than the detailed nature of the force.

Gaulé: With respect to the previous discussions on transition metals, I would like to emphasize the influence of the atomic volume via the density of states of the *d* band. I have a slide which demonstrates how the atomic distance in a typical transition metal is determined by the minimum of the bottom of the *s*-band (Fig. 5). We see that nature is not very cooperative in giving us good superconductors, since the atomic distance is too short to give us a *d* band which is as narrow as we would like. It was pointed out long ago by Matthias that the transition temperature increases with atomic volume as the fifth to tenth power, when similar materials are compared. High pressure work, for example, by Swenson, confirms this. Thus, from a 10% increase in atomic volume, we would expect a 100% increase in transition temperatures. For bulk material, the odds are very much against such an experiment because of the enormous concurrent changes in cohesive energy, as indicated on the slide. Thin films may have somewhat more promise here.

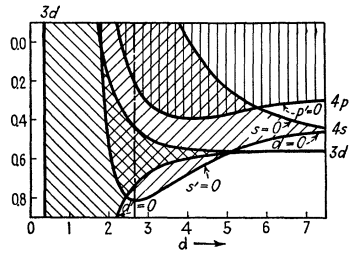

Fig. 5. Electron energy levels as a function of interatomic distance for a transition metal.

B. R. Coles, *Imperial College:* If I can just reply to that particular point. The whole point is that, at palladium and platinum, at the end of the transition series, one of the important things causing a narrowing of the *d* band is the atomic volume which is beginning to increase. This gives us a narrow *d* band, and, as we have seen, a higher density of states. But these are just the regions where we do not get superconductivity, and this emphasizes very strongly Professor Blatt's point that we have to take into account a character of the wavefunctions. Without recognizing this, a simple account of the density of states will not work at all.