SUPERCONDUCTIVITY and FERROMAGNETISM

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SUPERCONDUCTIVITY and ferromagnetism were considered exclusive phenomena for many decades. Ever since Kamerlingh Onnes' discovery that strong magnetic fields will destroy superconductivity it had been assumed that the large internal, or Weiss field, in a ferromagnet would never permit the occurrence of superconductivity. In the case of the magnetic elements, chromium, manganese, iron, cobalt, and nickel, this point of view certainly seems justified, as none of them has as yet been shown to be superconducting. And yet, whenever two phenomena seem to exclude one another so entirely, it is frequently because similar, if not identical, mechanisms are responsible.

It has been found during the last few years that there may indeed be a strong similarity between magnetic and superconducting interactions, and in the following we want to show just this.

One feature common to both superconductivity and ferromagnetism is the absence of any theory which predicts the critical temperature. Hence there is no theoretical criterion for the occurrence of either phenomenon. Experimentally, the situation is quite different, because it has been possible to develop empirical rules, based on the number of valence electrons per atom, which give a necessary criterion for the occurrence of superconductivity and a better than qualitative prediction of the transition temperature. It has not been possible until now to find similar rules for the occurrence of ferromagnetism. Here, with the exception of the ferromagnetism among the rare earths and actinides, which is rather well understood, there is at present no way to predict ferromagnetism not tied to one of the five elements, Cr, Mn, Fe, Co, or Ni, these being the only known ferromagnetic transition elements.

Since the occurrence of superconductivity is now so much better understood, let us at first go into more detail on our experimental approach to gain some insight into superconductivity. From it we may also reach, more or less through the back door, some insight into the nature of ferromagnetism.

In contrast to ferromagnetism, superconductivity is an extremely general phenomenon. While there were 24 superconducting elements a while ago,

more have been discovered recently, and one conclusion of Geballe's and my experiments is that perhaps most metals, once their purity is sufficiently high and their temperature sufficiently low, will eventually become superconducting. There are many hundreds of superconducting compounds which often contain only elements not yet found to be superconducting; in fact the constituent elements can be nonmetallic or even ferromagnetic. An example is $CoSi_2$, which is superconducting at 1.4°K.

The most recent theory of superconductivity is that of Bardeen, Cooper, and Schrieffer (BCS).[1,2] It originally described and explained superconductivity through an electron-phonon interaction though the theory does not seem to be limited to this mechanism. At present it is not possible for BCS to predict any transition temperature, or give any criterion for the occurrence of superconductivity.

In the beginning, the isotope effect, according to which the transition temperature varied with the isotopic mass as $T_c \backsim M^{-x}$, $0.45 < x < 0.50$, appeared to be a universal phenomenon. Thus it served to support the hypothesis of an electron-lattice interaction.

The basis for all this optimism had been largely the observed occurrence of superconductivity amongst the nontransition elements, coupled with the rather wishful thinking that the transition elements would follow the same pattern and show a more or less similar behavior. Empirically obtained rules stating the necessary conditions for the occurrence of superconductivity had shown long before, however, that the assumption of one mechanism was not justified. While the appearance of superconductivity among the nontransition elements was almost universal, the transition elements had always been quite a different problem. Just the same, until early 1961, the assumption of different mechanisms had seemed quite unfounded from a theoretical point of view. The only possibility for us to prove this was to show that the isotope effect, which at that time was considered universal, essential, and crucial for any electron-phonon theory, was going to be different for the transition elements. This experiment turned out to be successful. Since then the study of superconductivity of the transition elements has given new insight and results, including new superconducting elements. There has been a change in thinking as to the generality of the phenomenon, and an element of suspicion as to the finality of any theoretical solution has been introduced.

An empirical relation [9] based on the number of valence electrons in a metal mentioned above, permits a rough estimate of where and when to find superconductivity. If one defines n as the number of valence electrons, i.e., all those electrons which are outside a filled shell, then the occurrence of superconductivity can be described and predicted in a consistent way. For the transition elements, the critical temperature is a strongly oscillatory function of n, with maximum temperatures near 3, 5, and 7 valence electrons—and no superconductivity above 1°K for less than two and more than eight electrons per atom. For the nontransition elements there is always superconductivity once n is appreciably larger than one. For these elements the transition temperature itself does not seem to vary very much with n, and superconductivity of the nontransition elements and their compounds seems to be equally insensitive to variations of crystal structure.

The oscillation among the transition elements and the uniform behavior for the nontransition elements could be checked in further detail by forming solid solutions between the elements. However, they had to belong to the same group to give reproducible results. Solutions of the transition elements in the nontransition elements, or vice versa, invariably lead to destruction of superconductivity. Consider, for example, solutions of a four-valent element in niobium. Both Zr and Sn are four valent, but when dissolved in niobium, Zr raises the temperature and Sn lowers it, because the latter is not a transition element. Thus, from these rules about the occurrence of superconductivity, it soon became very evident that there seemed to be at least two different mechanisms causing the same phenomenon—and there may be a third one for compounds between elements of the two groups. The electron-phonon interaction of Fröhlich and Bardeen had predicted an isotope effect for the transition temperature according to which the temperature would be inversely proportional to the square root of the mass. For all nontransition elements checked thus far, this effect has indeed been found. However, as expected from the rules mentioned before indicating different kinds of superconductivity for transition and nontransition elements, the isotope effect is quite different for the transition elements. Ruthenium and osmium do not show any isotope effect.[3] The isotope effect of Mo is roughly [4] $T_c \backsim M^{-\frac{1}{3}}$. In compounds the isotope effect has been measured for Sn in Nb_3Sn[5] and found to be 1/6 of the theoretical value and again $-\frac{1}{3}$ for Mo in Mo_3Ir.[4] Here the same dependence as in Mo metal has been

noticed provided the total mass is considered. Otherwise it would be smaller by almost a factor of two. As can be seen, in none of the five systems measured thus far have we obtained the inverse square root dependence postulated by the theory. Lately, Swihart [6] and Morel and Anderson [7] have given a modification of the theory that would explain the intermediate values observed, except for Ru and Os where the predicted exponent is close to 0.25 and not zero as observed.

On the other hand, for the nontransition elements, none of these deviations for the isotope effect have been observed, thus again stressing the assumption of a different mechanism.

The BCS theory gives a formula for the transition temperature $T_c \backsim C \exp[-1/N(0)V]$. In this formula C is essentially proportional to the Debye temperature while the exponent $N(0)V$ is the product of the density of states and an interaction constant. $N(0)V$ will determine in a dominant way the transition temperature. It is hard to prove or disprove this factor with the nontransition elements as here T_c never varies very much, and the crystal structure changes quite frequently, thus making any statement concerning the constancy or variability of V rather difficult.

But for the transition elements where extended regions of solid solubility of one element in the other exist, there is the possibility of a check for the validity of $N(0)V$ in determining the transition temperature.

In the middle of the periodic system on either side of the fifth column of vanadium and niobium T_c seems to depend on $N(0)$ (or the electronic specific heat) in a form given by the above equation. This is under the assumption that V remains rather constant. This is in agreement with Pines who had stated this expectation previously.[8] However, on either side of the periodic system as well as going from the $4d$ to the $5d$ elements, the dependence of T_c on $N(0)$ changes its sign. From Ti to Sc, and from Zr to Y, $N(0)$ increases while T_c drops at least an order of magnitude. Thus far their superconductivity has not yet been found. In a similar way, from the seventh column of technetium and rhenium to the tenth column of palladium and platinum, $N(0)$ rises continuously to reach a maximum value at a thus far vanishing transition temperature for Pd and Pt. In the face-centered cubic part of the Os-Ir system T_c and $N(0)$ go, even over a narrow range of composition, in a way opposite from that predicted by the equation. The same discrepancy is observed in going from Ru to Os, Rh to Ir, and Y to La. These are always pairs of isoelectronic elements in which T_c and $N(0)$ do not obey the equation but do go the opposite way. We want to show now why these difficulties seem to point towards a new mechanism for the occurrence of superconductivity, different from the electron-phonon interaction.

While our speculations with regard to this mechanism should be deferred until later, let me say right now that the mechanism must be a spin exchange between the conduction electrons and the metal ions. Thus it must be a *magnetic interaction.* A strong indication in this direction was obtained several years ago when the necessary conditions for the occurrence of superconductivity were found in the number of valence electrons.[9] The fact that maximum transition temperatures always occurred near an odd number of electrons and maxima and minima were separated by one valence electron was an indication of the possibility of a net spin.

A new indication for a magnetic interaction was obtained about two years ago when we investigated systematically the role of iron impurities in superconductors and normal metals.[10] It was found then that the influence of iron depended upon the magnetization of the iron in the solvent metal, i.e., whether it had a localized moment or not. Our criterion for this was whether the magnetic susceptibility obeyed a Curie-Weiss law or was temperature independent. We could then show that the localization of iron throughout the periodic system depended again on the number of valence electrons —similar to the way the superconductivity did. The regions of the periodic system where it was not localized coincided roughly with those of the superconducting elements. For some areas like Mo-Re alloys we managed to have them overlap, and thus we found that when the iron is localized, and only then, its influence on the superconducting transition temperature is very large. Thus only after molybdenum and iridium were properly purified were they suddenly found to become superconducting elements.[11,12]

While the depression of the superconducting transition temperature in $Mo_{0.8}Re_{0.2}$ alloy was about 30°/1% Fe, it was already close to 200°/1% Fe in pure Mo. This influence of impurities is now in a range where the following conclusion can be reached. In the case of an electron-phonon interaction this effect of magnetic impurities is orders of magnitude too large; thus the mechanism of superconductivity for the transition elements must be a magnetic one. Furthermore, as this iron localization does not occur for the nontransition elements, the same conclusion of different mechanisms is again evident.

Presumably the fact also again enters into the explanation of why the *sp* and *sd* elements (nontransition and transition elements) do not interact in solid solution, as pointed out much earlier.

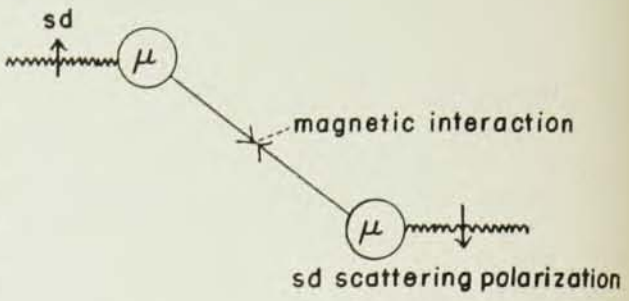
A further indication of magnetic interaction leading to superconductivity is the role of iron in those regions of the transition elements where it is *not* localized. Here, provided it is in the right range of electron concentration, iron will raise the transition temperature much faster than what would correspond to a variation of this number of valence electrons. If the two isoelectronic elements Fe and Ru are dissolved in Ti, both raise T_c of Ti, but iron does it almost four times more rapidly. Needless to say $N(0)$ again does not reflect at all the large change in transition temperature.

The nonexistence of superconductivity on either side of the transition-element regions could thus be traced to the strong localization of iron impurities in elements like yttrium or platinum. If one manages, however, to avoid the range where iron has a maximum effect on the depression of superconductivity, then it becomes possible by variation of valence electrons to cause superconductivity in usually nonsuperconducting elements. This can best be demonstrated in the W-Pt system. Neither W nor Pt has as yet become superconducting by itself but upon dissolving one in the other, superconductivity results immediately. Extrapolation thus gives good reason for supposing that both metals will become superconducting if the purity can be raised and the temperature lowered—more than has been possible in the past.

This raises the question whether or not most metallic elements, provided their purity would be high enough and their temperature low enough, eventually will become superconducting.

Clearly, the large number of superconducting compounds that were discovered above 1°K and the increase of new superconductors below 1°K now being found suggest that superconductivity is not a rare phenomenon or the result of some delicate balance between different interactions. It should be stated again that superconductivity is perhaps always the final state of a metal, provided its purity is high enough and its temperature low enough. However, this may not be the only solution. It is conceivable that ferromagnetism or antiferromagnetism might result instead. As a matter of fact, two compounds that had been expected to become superconducting became ferromagnetic instead: $ZrZn_2$ at 35°K and Sc_3In at 6°K. This ferromagnetism may be due to the parallel alignment of the conduction electrons, as compared to the opposite one in superconductors, thus again pointing out a magnetic interaction leading to superconductivity.

Such a mechanism could be actually visualized in the following way: *



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Upon collision of a conduction electron with an atom, the latter will be temporarily polarized by an *sd* scattering. This polarization will in turn induce a moment in the nearest-neighbor atoms, which then in their turn will again interact with other conduction electrons. Thus a magnetic polarization would play a role similar to that of the deformation potential in the nontransition element superconductors. What the mechanism is in superconducting compounds, formed by transition and nontransition elements, is not clear at present. It may be a mixture of elastic and magnetic interactions or it may be quite different. But whatever it is, it has become quite obvious that superconductivity seems to be an extremely general phenomenon, much more so than ferromagnetism. It may be that superconductivity is always the ground state for very pure metals at very low temperatures, unless they become ferromagnetic or take on the properties of insulators.

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