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Superconductivity and Ferromagnetism†

Abstract: The close relationship between superconductivity and ferromagnetism is discussed and illustrated; it is suggested that several mechanisms cause superconductivity and also ferromagnetism. Various rare earth alloys show simultaneous superconductivity and dilute ferromagnetism. Such dilute ferromagnetism does not occur, however, in the transition-metal superconductors. Striking differences in the effects of adding magnetic elements to transition-metal superconductors are traced to the presence or absence of localized magnetic moments; such occurrences show a dependence on electron concentration similar to superconductivity. Superconductivity in the transition and non-transition elements shows a simple dependence on valence electron concentration—but when such elements are mixed they interfere drastically.

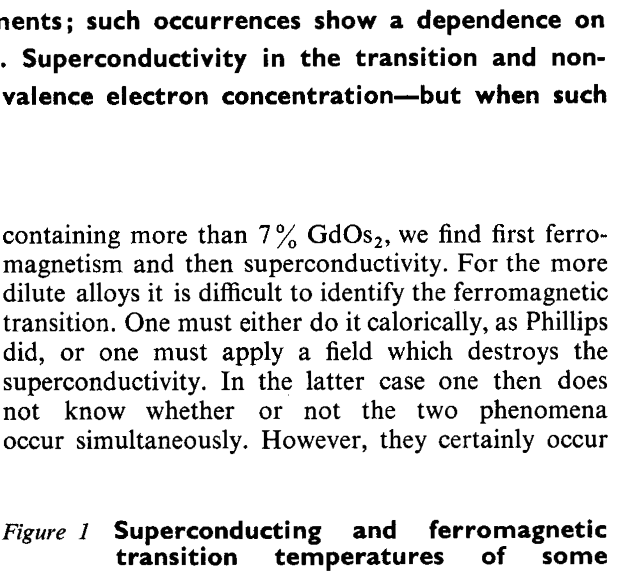
Superconductivity and ferromagnetism seem to be extremely similar in their appearance, in the nature of their occurrence, and from many other points of view. It is known that there are various kinds of ferromagnetism. A plausible deduction from this is that there may be many kinds of superconductivity. In this paper I shall now try to show why I think there are probably three, but at least two, mechanisms that cause superconductivity. The starting point for this discussion is the subject of ferromagnetic superconductors.

Rare-earth alloys

Figure 1 shows the behavior of the transition temperature (superconducting on the left and ferromagnetic on the right) when Gd is dissolved in La. The fact that Gd lowers the superconducting transition temperature, T_c, of La was expected; the part that is much more interesting is the dilute ferromagnetism which goes very far down in temperature to below 1°. In fact Phillips[1] has found by caloric measurements that some alloys could even become ferromagnetic in the superconducting state. This raises the question, how could the sample be superconducting and ferromagnetic at the same time?

Figure 2 shows the effect of adding $GdOs_2$ to the superconducting compound YOs_2. $GdOs_2$ is a ferromagnet with a transition near 100°K. On adding this as a ferromagnetic impurity, the superconducting transition of YOs_2 drops, and then the dilute ferromagnetism will occur again. On cooling samples containing more than 7% $GdOs_2$, we find first ferromagnetism and then superconductivity. For the more dilute alloys it is difficult to identify the ferromagnetic transition. One must either do it calorically, as Phillips did, or one must apply a field which destroys the superconductivity. In the latter case one then does not know whether or not the two phenomena occur simultaneously. However, they certainly occur

Figure 1 **Superconducting and ferromagnetic transition temperatures of some lanthanum-gadolinium alloys.** *Matthias and co-workers (dotted line), Hein and Matthias and their co-workers (solid line).*



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simultaneously beyond 7%, and, there is no separation of phases that can be detected by X-rays.

Figure 3 shows what happens if this mixing is not done properly. If a superconductor is mixed with a ferromagnet which does not have a sufficiently high Curie temperature, a gap appears in which there is neither superconductivity nor ferromagnetism.

A curious feature of these mixtures is the following. If, in a superconducting compound of a rare earth element with *no* spin, the rare earth is replaced by a rare earth that has a spin, then the resulting Curie temperature is always proportional to the superconducting transition temperature of the initial compound. This is seen in Fig. 4, which gives the superconducting transition temperatures of Y compounds with Re, Os, Ir, and Pt; essentially the concentration of the valence electrons is being varied. If the same thing is done with Nd we get ferromagnets in which the Curie points follow a similar curve (note the change of scale between left and right ordinates). Ferromagnetism and superconductivity in this system behave very much alike. A situation favorable to the one is favorable to the other.

Transition-metal alloys

The question then arises: do similar phenomena occur with the transition elements? Figure 5 shows the result of dissolving Fe in Ti. The transition was not lowered, but instead was raised very steeply at low concentrations; at higher concentrations it followed exactly the valence electron concentration. If, however, the transition temperature of Ti is raised by addition of Ru (Fig. 5), the initial steep rise is not present. In either case, dilute ferromagnetism does not appear, and the transition temperature is not lowered, in contrast to the rare earth curve. Figure 6 shows Co in Ti, which gives almost identically the same effect as Fe. Again the addition of a transition element from the next row is shown; here the comparison is made with Rh, since Rh has the same number of valence electrons as Co.

These alloys, even with large concentrations of Fe

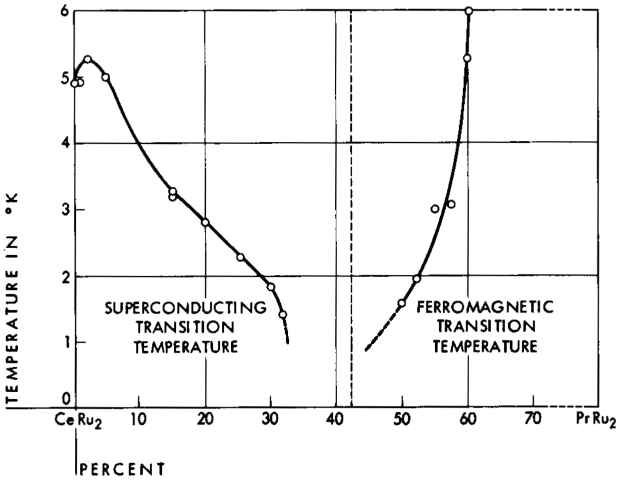


Figure 3 **Superconducting and ferromagnetic transition temperatures of (Ce, Pr) Ru_2 solid solutions.**

Figure 2 **Superconducting and ferromagnetic transition temperatures of dilute solutions of $GdOs_2$ in YOs_2.**

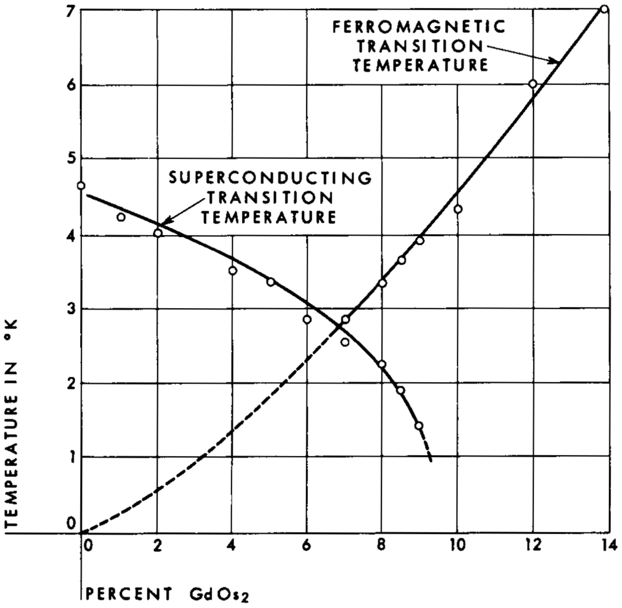
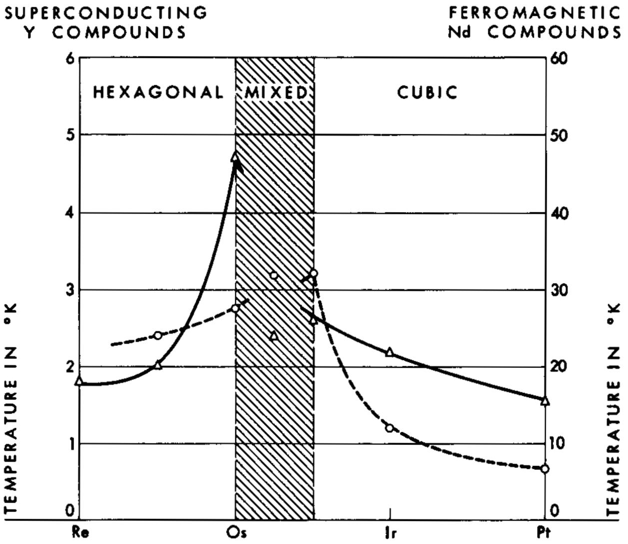


Figure 4 **Superconducting transition temperatures of Y compounds with Re, Os, Ir, and Pt—solid line. Ferromagnetic transition temperatures of Nd compounds with Re, Os, Ir, and Pt—dotted line.**



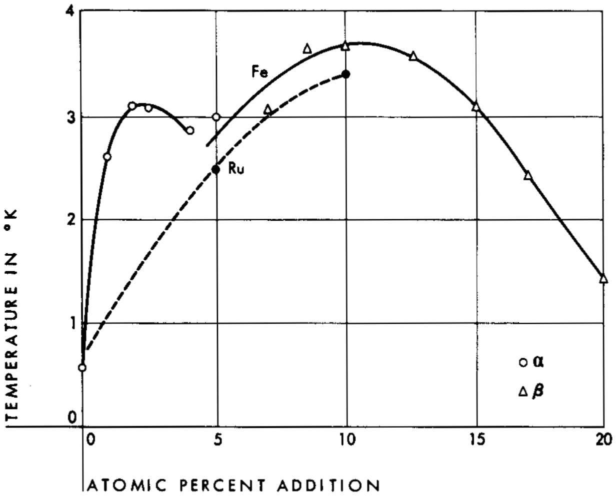


Figure 5 **Superconducting transition temperatures of Fe or Ru solid solutions in Ti.**

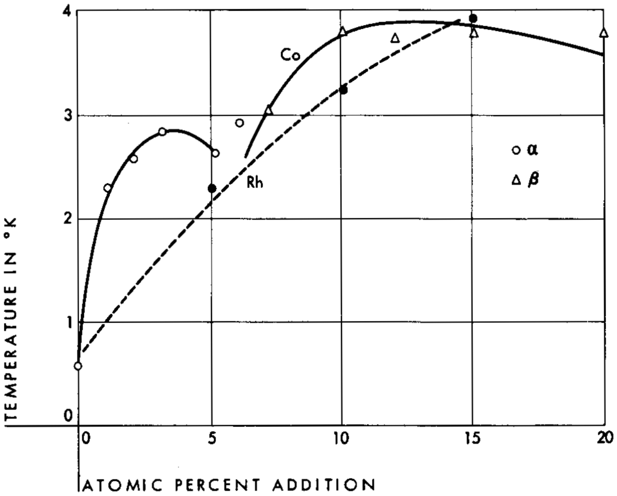


Figure 6 **Superconducting transition temperatures of Co or Rh solid solutions in Ti.**

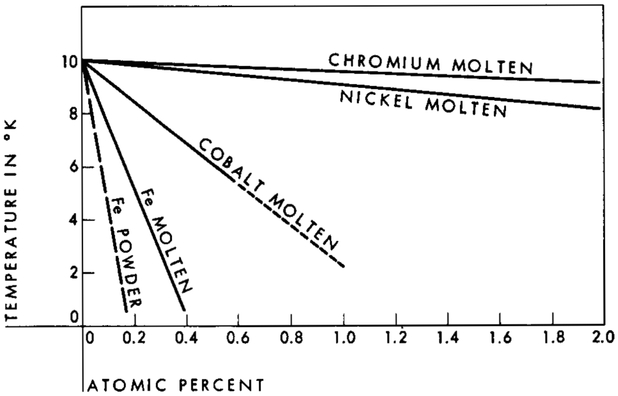


Figure 7 **Superconducting transition temperatures of an 80% Mo-20% Re alloy with addition of Fe, Co, Ni or Cr.**

or Co, did not show dilute ferromagnetism. In fact there was not even a temperature-dependent magnetism. The alloys showed strictly the temperature-independent Pauli paramagnetism. In other words, not even a localized moment was detectable.

Just as we can raise the valence electron concentration in Ti by adding Rh, we can do the same in Mo. The valence electron concentration of Mo does not need to be raised much to make it superconducting. This was done by adding Rh—we did not want to use another superconductor—with Rh only small percentages are needed. With 16% Rh solid solution in Mo a superconducting transition occurs at 8°K, while with 1% addition the transition is near 0.3°K, as determined by Daunt.[2] Here the variation of temperature with the number of valence electrons is really quite drastic. If this occurs with Rh, why doesn't this occur with Fe? The experiment was carried out with Fe repeatedly but no superconductivity at all was found.

However, when Hulm[3] dissolved Re in Mo he found an immediate steep rise in the superconducting transition; thus with 20% Re in Mo, T_c is almost 8° or 9°K. This suggested that if the change in T_c in Mo on adding Fe could not be seen, one could use what appears to be the closest thing to Mo, namely Hulm's Mo-Re. The 80%-20% combination with T_c near 9° was chosen. Figure 7 shows the result when Fe was dissolved in alloy. With only 0.4% of molten Fe,* T_c dropped below 1°K. This drop per Bohr magneton is 20 times larger than the drop produced by Gd in La. Thus we do find an effect of iron on the superconducting transition temperature. The experiment was also done in a solid from the elements by powder metallurgy, in which case there was almost a factor of 50 compared to Gd in La; this effect is enormous. The effects on adding Co in arc-melted specimens were much less; Ni and Cr have almost no effect. Finally, if we put Rh or Ru in Mo-Re the transition temperature rises.

Localized moments

We thus see that adding Fe to Mo-Re produces a very different effect from the Ti case. A. M. Clogston[4] immediately suggested that we measure the susceptibility of this alloy. It turned out that it behaved quite differently from the alloy of Fe in Ti. The reciprocal of the susceptibility showed a very large temperature dependence, indicating a localized moment of about two Bohr magnetons. Unfortunately, the intersection was always at negative temperatures, indicating antiferromagnetism, but at least a localized moment was indicated; there was still no dilute ferromagnetism. The drop in the superconducting transition of Mo-Re makes it obvious we shall never get any ferromagnetic superconductors among the transition elements.

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* The alloy was prepared in an arc furnace. Since the boiling point of Fe is very close to the melting point of Mo-Re, the composition may be too high.

This magnetic effect, namely that we never get dilute ferromagnetism among the transition elements, appears to be almost universally true, with two exceptions. If you dissolve iron group elements in Pd or Pt, then you *do* get dilute ferromagnetism; but of course there you have the polarization of the matrix, and this is quite a special case. Because, apart from Pd or Pt, there is no dilute ferromagnetism, it appears convincing that there are two kinds of ferromagnetism: one for the transition elements and one for the rare earths.

Thus the superconducting transition was not depressed in Ti because in Ti we did not get a localized moment. If we put Fe in Nb we find the same effect: the superconducting transition is practically unchanged. However, in the case of Nb-Mo alloys the results are otherwise. The dashed curve in Fig. 8 shows the values of T_c for pure Nb-Mo (i.e., without added Fe); it fits well with Hulm's[5] and Pippard's[6] data. Then 1% of Fe was dissolved. Recall that previously, with between 0.2% and 0.4% Fe, the superconducting transition was lowered by 10°. Here with 1% addition of Fe nothing much happened (the solid line of Fig. 8). So it is obvious that something drastic happens between Nb and Mo, even though these two elements are so much alike—the one has only one more *d* electron than the other.

Figure 9 shows the results of susceptibility measurements in the Mo-Nb alloys. The dashed curve is the susceptibility of the matrix, which does not change very much. The solid curve is the effective localized moment determined from the susceptibility data; it shows that the moment begins to appear in quite a small range.

Now we understand (or at least we can describe) why iron group impurities sometimes have a large effect but at other times no effect. It is strictly due to the fact that either we have a localized moment—then the effect on superconductivity is enormous—or we do not have a localized moment and we do not see anything, except sometimes a rise of T_c. But as far as dilute ferromagnetism is concerned, there is no hope whatsoever. While, with the exception of Pd and Pt, there has never been a case of dilute ferromagnetism for the transition elements, with the rare earths there are many cases of dilute ferromagnetism. Therefore, we can say there are two different kinds of ferromagnetism. And since superconductivity behaves so much like ferromagnetism, or at least so much like localized moments, there must be two different kinds of superconductivity.

It now seemed useful to determine where in the periodic system localized moments are encountered. Figure 10 gives the localized moment of iron in different elements. These are the only elements we could find which would dissolve the iron. This curve is vaguely reminiscent of the curve for the transition temperature in superconductors. If that is true, we should be able to use averages too. Accordingly an alloy of V and Ru

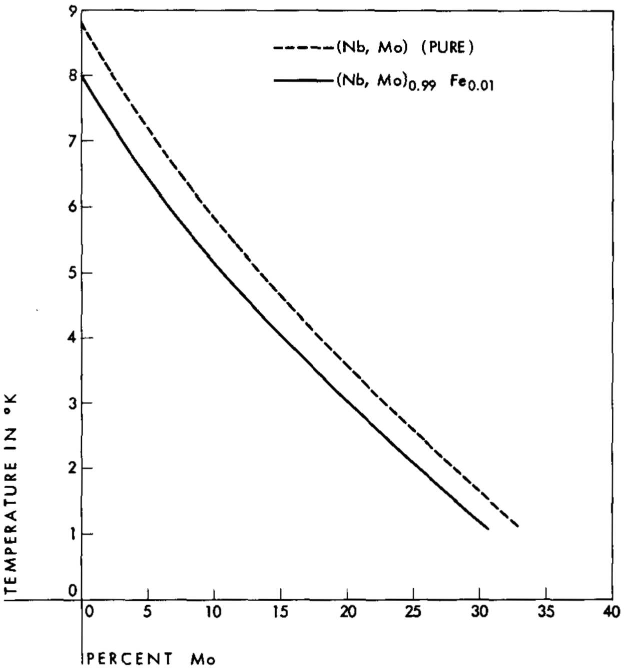
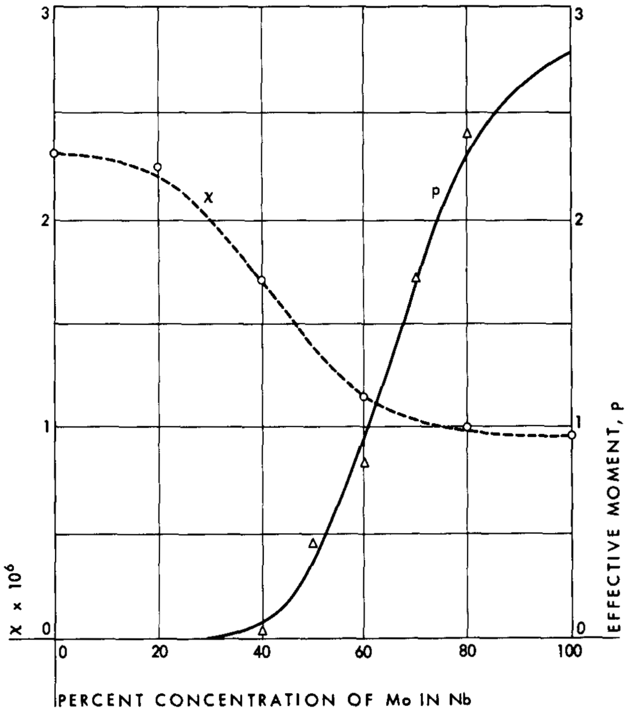


Figure 8 **Transition temperature of Nb-Mo solutions with and without addition of 1 at. % Fe impurity.**
(Nb, Mo) pure (dotted line), (Nb, Mo)$_{0.99}$ *Fe*$_{0.01}$ *(solid line).*

Figure 9 **Effective magnetic moment per iron atom, *p*, in Nb-Mo solutions containing 1 atomic percent Fe (full line), and susceptibility, χ, at 300°K in the absence of Fe.**



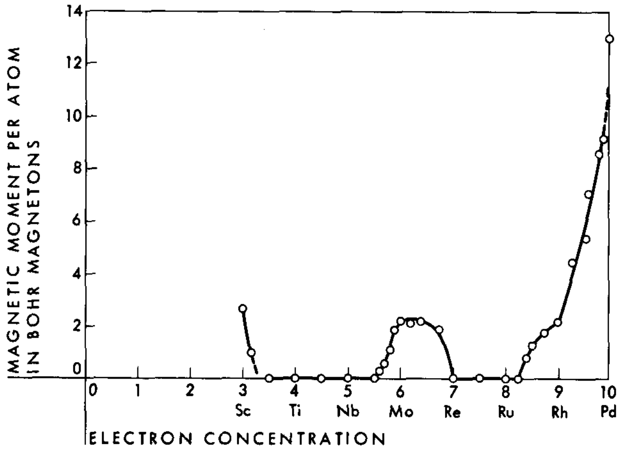


Figure 10 **Magnetic moment in Bohr magneton of an iron atom dissolved in various second-row transition metals and alloys.**

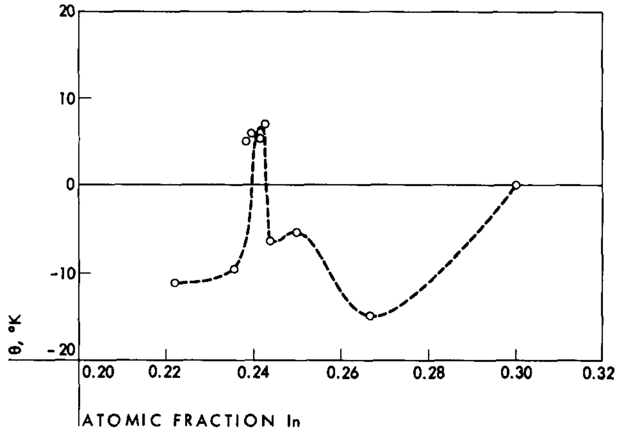
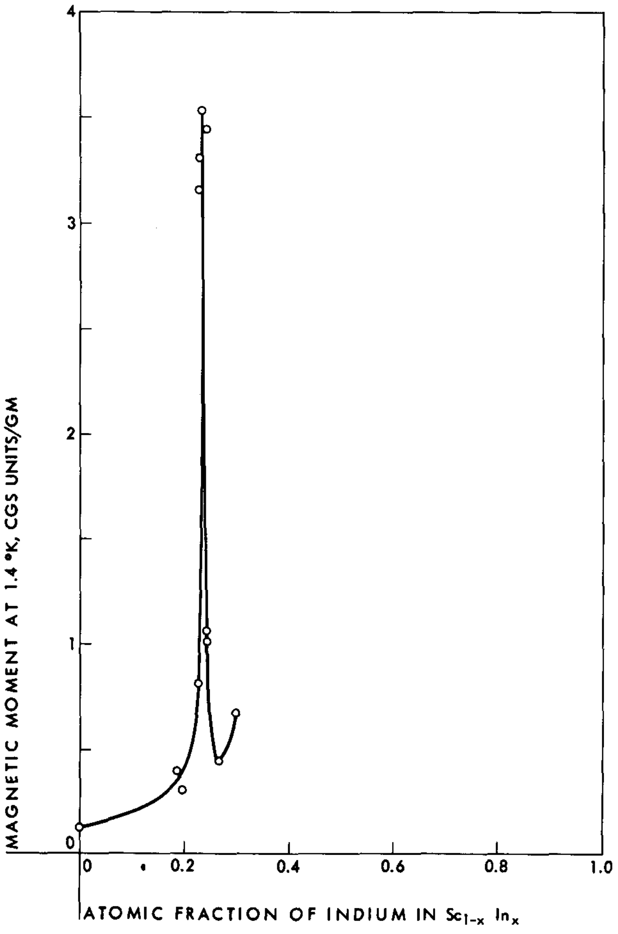


Figure 12 **Curie-Weiss constant θ of Sc-In alloys as a function of In concentration.**
The Curie point of the ferromagnetic state is about 6°K.

Figure 11 **Magnetic moment of scandium-indium alloys as a function of concentration, showing a narrow ferromagnetic peak at about 0.24 at. % In. Measured in a field of 14,000 gauss.**



was made (Fe is not localized in either of the pure elements) in which the concentration was adjusted to fall near that of Mo; again we got two Bohr magnetons for the localized moment. So the condition for localization of the magnetic moment seemed to follow the same pattern as the superconducting transition temperature. This is why it is so convincing that there are related mechanisms for magnetism and superconductivity.

Other arguments for two kinds of superconductivity

There is other evidence for these two different kinds of superconductivity. It is no problem to make superconductors among the transition elements—we can average over the periodic system; we can make compounds; we can make solid solutions; everything works like a charm! The same ideas work with the nontransition elements. We can trace peaks and use averages of electron concentrations. We know the number of valence electrons and can understand what happens. For instance, if we put a little Ti, which has four valence electrons, in V we raise the transition because the peak is in between. If, however, instead of Ti, we use a four-valent *nontransition* element, superconductivity disappears entirely. Or, if we do the opposite, if we dissolve a little V in Ti, the transition goes up. But if we do the same with Sb in Ti (both V and Sb have five valence electrons) we again lose the superconductivity completely.

Superconductivity amongst the transition elements and superconductivity amongst the nontransition elements do not mix in a simple way. These two classes will not react with one another except to disturb one another. There seems to be just one way out and that is to form a compound. Of course, if we form a compound something drastic happens. We lose partly the

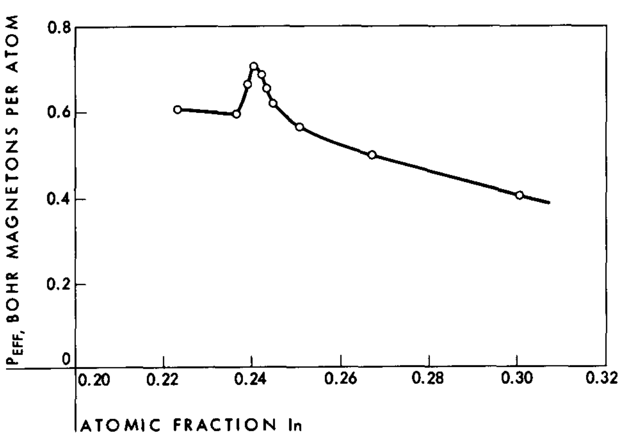


Figure 13 **Effective magnetic moment of Sc-In alloys in Bohr magnetons per atom as a function of In concentration, determined by fitting observed susceptibilities to a Curie-Weiss law.**

nature of the metallic bond. We get compounds which have practically no homogeneity ranges, i.e., they are essentially stoichiometric. They are then both *p* and *d* superconductors, but their properties are different. When you look through all of the superconductors known today, you will find that most are *d-d* combinations or *p-p* combinations. But the *p-d* combinations are extremely few, and these are limited to the β-wolfram structure and a few other selected structures. This is probably the best proof of how difficult it is to get superconductivity between the *p* and *d* elements.

This can be illustrated further. In looking through La compounds, it is found that La_3In is the lanthanum superconductor with the highest T_c, 10.4°K. Yttrium indium could not be made. Scandium indium, however, could be, and Fig. 11 shows what happened. Sc has a substantial susceptibility, but of course it is paramagnetic, not ferromagnetic. But as we add In, suddenly the susceptibility and the magnetic moment rise incredibly. This transition to ferromagnetism takes place near the composition Sc_3In. The Curie point is near 6° (Fig. 12), and the moment is 0.7 of a Bohr magneton as determined from the Curie-Weiss law (Fig. 13). The width is only 0.4 atomic percent, so it takes a really close look at those compounds which are not superconducting to find out whether they are ferromagnetic or antiferromagnetic.[7] In all likelihood they will be one or the other—or then they should become superconducting.

References

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2. J. G. Daunt, private communication.
3. J. Hulm, *Phys. Rev.* **98**, 1539(A) (1955).
4. *Note added in proof:* See Clogston, Matthias, Peter, Williams, Corenzwit, and Sherwood, *Phys. Rev.* **125**, 541 (1962).
5. J. K. Hulm and R. D. Blaugher, *Phys. Rev.* **123**, 1569 (1961).
6. A. B. Pippard, this Conference (unpublished).
7. Matthias, Clogston, Williams, Corenzwit, and Sherwood, *Phys. Rev. Letters*, **7**, 7 (1961).

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