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Ferromagnetic Solutes in Superconductors

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Solid solutions of chromium, manganese, iron, or cobalt in titanium raise its superconducting transition temperature by almost an order of magnitude. At very small concentrations this is much more than could be expected from a variation of electron concentration.

IT has been assumed for a long time that "ferromagnetic impurities" lower the transition temperature in superconductors. Impurities or small amounts of the magnetic transition elements from chromium to nickel dissolved in superconductors would on the basis of this assumption be expected to lower the superconducting transition temperatures. Until recently no systematic data have been available. Recent results[1] for solid solutions of rare earth metals in lanthanum showed that rare earth atoms with magnetic moments did depress the superconducting transition temperature very strongly.

One would have expected this depression to be proportional to the effective moment if the magnetic field due to this moment would have been responsible for lowering the superconducting transition temperature in the same way as an external magnetic field would have done. But it turned out that the depression of the superconducting transition temperature was essentially proportional to the projection of the electronic spin on the lowest J-state and not related to the total magnetic moment. This led to the conclusion that it was an exchange interaction between the conduction electrons and the rare earth spins which caused the depression. This idea then suggested the possibility that the transition elements, especially those with a large electronic spin, would act in a way similar to the rare earths in superconductors.

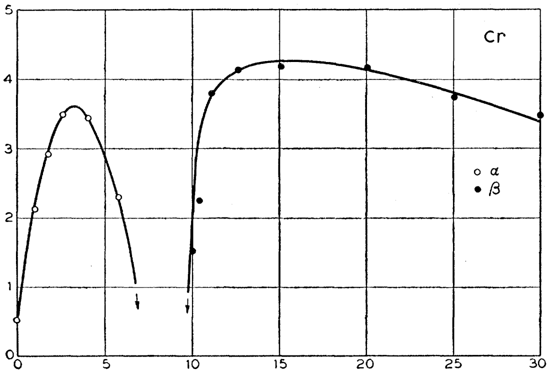

FIG. 1. Superconducting transition temperatures of chromium solid solutions in titanium.

We have now carried out experiments which show that this conclusion is not borne out. We had shown previously that alloys of zirconium with iron, cobalt, or nickel had higher superconducting transition temperatures than pure zirconium.[2] We have now observed the superconducting behavior of the solid solutions of chromium, manganese, iron, and cobalt in titanium, and have again shown that the transiton temperatures in every case is raised, and not lowered, by dissolving these magnetic impurities. Solid solutions were prepared by melting the elements together in an argon arc furnace. Each sample was remelted at least six times. While liquid the melts were rolled around to insure homogeneity. In order to avoid precipitation, the samples were not annealed. It was found that cold working changed the superconducting transition temperature, particularly of those solid solutions with compositions close to the α-β transition region. For this reason considerable care was used in preparing the samples for measurement. The width of the superconducting transitions ranged between 0.1° and 0.25°, which indicated that no new or additional strains except those of quenching were introduced. In these solid solutions the body-centered cubic β phase of titanium was stabilized at room temperature if the concentration of the transition element exceeded values that ranged from 5 atomic percent to 8 atomic percent.

Superconductivity was observed by mutual inductance measurements. The most significant result is that in every case the superconducting transition tempera-

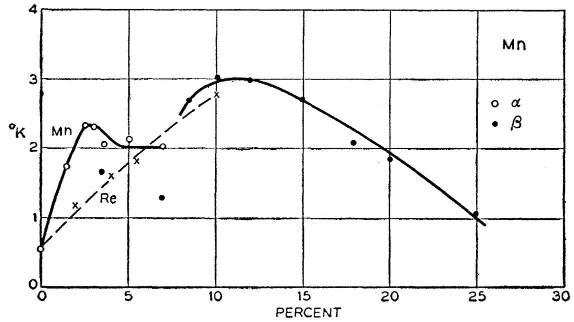

FIG. 2. Superconducting transition temperatures of manganese or rhenium solid solutions in titanium. The β values of 3.5 and 7 at% Mn are isolated and unreproducible points.

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[1] Matthias, Suhl, and Corenzwit, Phys. Rev. Letters **1**, 92 (1958).

[2] B. T. Matthias and E. Corenzwit, Phys. Rev. **100**, 626 (1955).

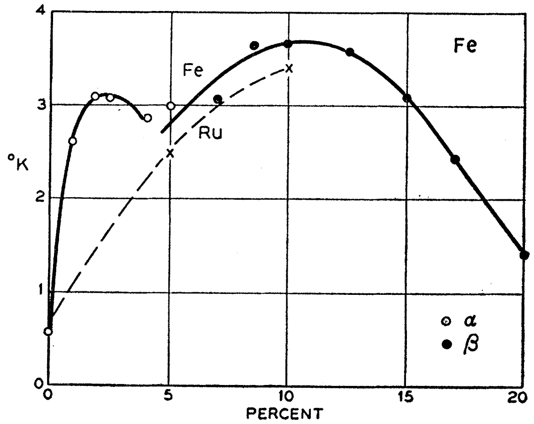

FIG. 3. Superconducting transition temperatures of iron or ruthenium solid solutions in titanium.

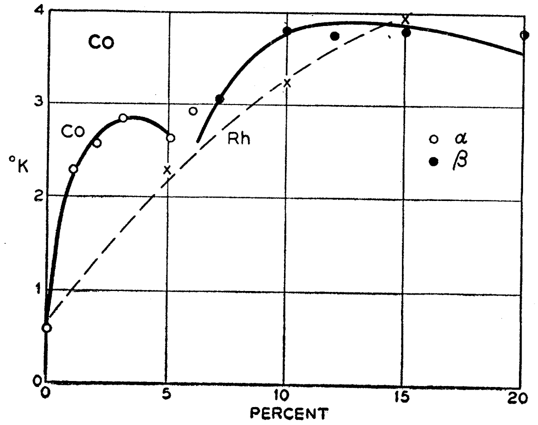

FIG. 4. Superconducting transition temperatures of cobalt or rhodium solid solutions in titanium.

ture of titanium is greatly increased by dissolving small amounts of the transition elements in it. In the case of nickel additions, at least 9 atomic percent Ni was necessary to raise the superconducting transition point above 1°K, and such melts are still hexagonal.

The superconducting transition temperatures of the various solid solutions in titanium are shown in Figs. 1 to 4. For comparison, the superconducting transition temperatures of solid solutions in titanium of transition elements from the 4*d* and 5*d* shells of the periodic system are also shown. Although these other solute elements have the same number of valence electrons, they do not have the magnetic moments of the corresponding elements in the 3*d* row.

At large percentages, the results are the same for atoms with and without magnetic moments. The maximum transition temperatures range between 3.5° and 4.5°K; at the compositions where the maxima occur the average number of valence electrons per atom lies between 4.4 and 4.7. In this range of concentration, it seems to be quite irrelevant whether these valence electrons are contributed by atoms like manganese, or by atoms of ferromagnetic elements like iron or cobalt, or by atoms of superconducting elements like rhenium.

The rare earth elements had the opposite effect.[1] One or two percent of a rare earth in solution lowered the superconducting transition temperature of lanthanum from close to 6°K to below 1°K; slightly larger concentrations caused ferromagnetism to occur.[3] As mentioned above, these effects of the rare earth ions are almost certainly due to the interaction of the 4*f* spins with the conduction electrons.[1] Since no such effects seem to occur with the spins of the 3*d* electrons, it seems probable that either (1) the $s-d$ interaction is much weaker, or (2) it is always such as to give antiferromagnetic coupling, or (3) some other interaction, always antiferromagnetic, overrides the $s-d$ exchange.

Unlike the rare-earth case, small percentages (<3 atomic percent) of the transition elements with a magnetic moment *raise* the superconducting transition temperature of titanium when dissolved in it, *much more* than would correspond to the same number of valence electrons but with negligible magnetic moment. This is illustrated by comparison with the elements of the second and third row of the periodic system that contribute the same number of valence electrons but no magnetic moment to speak of. From the experimental data it appears that *no* dilute solution ferromagnetism occurs in any case of the transition elements below 30 atomic percent.

ACKNOWLEDGMENTS

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[3] We would like to thank J. K. Galt for pointing out and impressing on us the significance of this ferromagnetism in dilute solution.