

Superconductivity of Zirconium Alloys

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The superconducting transition temperatures of alloys between zirconium and VIIIth column elements are substantially higher than those of zirconium. The same is true for zirconium-gold alloys. This observation confirms a rule previously established about the height of transition temperatures.

I. INTRODUCTION

IT has been shown previously¹ that a maximum in superconducting transition temperatures occurs for those elements, compounds and alloys which have an average valence electron per atom ratio near 5 or 7. This behavior seems analogous to that of γ , the electronic term of the specific heat,² which shows a maximum for elements with 3, 5, or 7 valence electrons per atom. It seemed likely, therefore, that a maximum in the superconducting transition temperature should occur simultaneously with a maximum for γ . Elements with 4 valence electrons per atom should have, therefore, minimum transition temperatures. In fact, hafnium is the lowest known superconductor at 0.32°K. The purpose of this note is to show data on zirconium alloys with electron concentrations on both sides of 4 and which show the expected minimum in the superconducting transition temperature.

II. THE VARIATION OF ELECTRON DENSITIES

Zirconium, which also has 4 valence electrons per atom, becomes superconducting at 0.75°K. Zr-Rh alloys show rather high transition temperatures,¹ presumably due to the increase in electron density. This same effect should now be shown in varying degrees by alloying Zr with the other elements in the VIIIth column of the

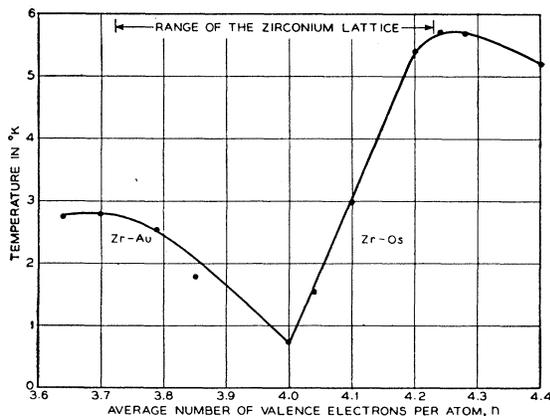


FIG. 1. Superconducting transition temperatures as function of electron concentration.

¹ B. T. Matthias, Phys. Rev. 97, 74 (1955).

² J. G. Daunt, Phys. Rev. 80, 911 (1950).

periodic system. The results confirming this assumption are given in Table I.

Table I shows the superconducting transition temperatures of alloys between Zr and 10% (atomic) of the given element. As can be seen, they all raise the transition temperature of zirconium.

In order to demonstrate the existence of a minimum, one had to find superconducting Zr alloys with an average valence electron per atom concentration below 4. These were finally discovered in the zirconium-gold system. For about 10% (atomic) Au the transition temperature is at a maximum of 2.80°K.

In Fig. 1, the variation of transition temperature with varying electron concentration is shown. To illustrate the rise in temperature for an increase of electrons, osmium alloys were chosen. Any other element in the VIIIth column would have exhibited the same behavior qualitatively. We are aware that by comparing zirconium-gold alloys on the left side to zirconium-osmium alloys on the right side, we are stretching the analogy. Our excuse is that within the indicated region we preserve essentially the same Zr lattice in both alloys. The minimum transition temperature of Zr is apparent. The maxima, however, on both sides are not those mentioned earlier and are only due to the onset of a second phase.

III. Zr ALLOYS WITH FERROMAGNETIC ELEMENTS

It seems worthwhile to point out specifically the increase in superconducting transition temperature of Zr by the ferromagnetic elements in Table I. Considering the empirical fact that superconductivity and ferromagnetism seem to be mutually incompatible, the superconductivity of these alloys suggests that most of the d shell holes have been filled.³ This again is a proof of the formerly stated hypothesis¹ that the superconducting transition temperature is primarily determined by the average electron density and not strongly affected by

TABLE I. Superconducting transition temperatures of Zr alloys with VIIIth column elements.

Fe($\sim 1^\circ$)	Co(3.9°)	Ni(1.5°)
Ru(5.7°)	Rh(9°)	Pd(7.5°)
Os(5.2°)	Ir(5.5°)	Pt(3°)

³ This is consistent with the fact that Fe, Co, and Ni dissolve substitutionally rather than interstitially in Zr.

the individual atom. (Mass and volume are of course important, but are neglected for the moment to preserve the simplicity of the picture.) Thus, an alloy containing 5% Fe and 5% Ni shows a behavior similar to that of an alloy with 10% Co. In the same way, an alloy with 5% Ru and 5% Pd duplicates the one with 10% Rh.

Carrying this concept further, it was possible to ob-

tain a superconducting compound which seemed comparable to CoSi_2 , which becomes superconducting at 1.4°K. It is CoZr_2 which becomes superconducting at 6.3°K. We found also that NiZr_2 becomes superconducting at 1.52°K.

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Magnetic Moment Arrangements and Magnetocrystalline Deformations in Antiferromagnetic Compounds*

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The neutron diffraction data of Shull *et al.* on the powder specimens of MnO, FeO, CoO, etc., are re-examined. It is found that except for FeO the observed Debye-Scherrer patterns may be produced by a number of magnetic moment arrangements with the same antiparallel coupling among the moments on the next nearest neighboring ions, but with different sublattice correlations and different orientations of magnetic axis (or axes). The symmetry change observed at the Néel point is interpreted as a strong effect of spontaneous anisotropy magnetostriction. As a consequence the uniaxial direction of the modified symmetry must coincide with that of the magnetic axis. Assignments of antiferromagnetic arrangements for the compounds are reached. Our prescription does not agree with that of Shull *et al.* except in the case of FeO. The sharp readjustment of lattice parameters at the transition temperature and the orientation of spin axis in other antiferromagnetic compounds are discussed from the viewpoint of the anisotropy magnetostriction approach.

I. INTRODUCTION

IN this note we intend to give a close re-examination of the neutron diffraction data obtained by Shull *et al.*¹ on MnO, FeO, CoO, NiO, MnS, and MnSe in powder form. This study is of interest in view of the fact that whereas FeO, MnO, NiO, and MnS are distorted slightly from the cubic to rhombohedral symmetry and CoO becomes tetragonal at temperatures below the Néel point, yet the arrangements of moments on magnetic ions assigned by Shull *et al.* to MnO, NiO, MnS, and CoO are all the same, both as to the configuration of + and - spins and the direction of spin axis.² It should be remarked that the symmetry changes stated above are established results of more than one author^{3,4} using x-ray techniques. The explanation of this magnetocrystalline effect put forward by Smart and Greenwald⁵ is not consistent with the same discrepancy.

From our analysis of the neutron diffraction data and the hypothesis of anisotropy magnetostriction we prescribe for these compounds (except FeO) antiferromagnetic arrangements different from those assigned previously. We shall also discuss the crystallographic position of the magnetic axis in other antiferromagnetics such as Cr_2O_3 , MnF_2 , etc.

The neutron diffraction patterns of MnO, MnS, MnSe, CoO, and NiO below their respective Néel points are alike. The pattern of FeO is slightly different with the singular absence of a certain magnetic diffraction line. Shull *et al.* find that the magnetic unit cell dimensions are twice as large as the dimensions of a chemical unit cell and that the *next nearest* neighboring magnetic ions must have the spins opposite. These statements are conclusive and can be verified with little effort. However, there are two types of spin arrangements, both consistent with the next nearest antiparallel coupling, but different in the coupling among the *nearest* neighboring magnetic ions. They are illustrated in Fig. 1. In type *A* the four face-centered cubic (f.c.c.) sublattices of antiparallel spins are correlated such that on each (111) plane the spins are parallel and the spins on two neighboring (111) planes opposite; in type *B* this particular coupling among the nearest spins is absent. The four f.c.c. sublattices divide the full f.c.c. lattice in such a way that no two *nearest* neighboring ions are in the same sublattice. Shull *et al.* have shown that a satisfactory agreement is obtained between the

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¹ Shull, Strauser, and Wollan, *Phys. Rev.* **83**, 333 (1951).

² Since we do have in some cases orbital contributions to the magnetic moment, it is preferable to use the terms "antiferromagnetic axis" or "magnetic axis" instead of "spin axis." We shall use them alternatively with the same meaning. Similarly, "spins" and "magnetic moments" are used interchangeably.

³ H. P. Rooksby, *Acta Cryst.* **1**, 226 (1948); N. C. Tombs and H. P. Rooksby, *Nature* **165**, 442 (1950); H. P. Rooksby and N. C. Tombs, *Nature* **167**, 364 (1951).

⁴ S. Greenwald and J. S. Smart, *Nature* **166**, 523 (1950); S. Greenwald, *Acta Cryst.* **6**, 396 (1953).

⁵ J. S. Smart and S. Greenwald, *Phys. Rev.* **82**, 113 (1951).