are completely different from those furnished by naive quasiparticle theory. Thus it is of real interest to work out these consequences and to subject them to as complete an experimental check as possible.

There is no clear inconsistency between theory and experiment, and in some cases it would be very hard to explain the data with other forms of singularity. We can claim a large number, then, of small but not conclusive checks on the theoretical predictions. In addition, the singularity analysis furnishes additional and quite precise information on the location and nature of the Van Hove singularities, which may be of value in analysis of phonon spectra of various metals.

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Superconductivity of Solid Solutions of Ti and Zr with Co, Rh, and Ir

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A detailed investigation of superconductivity in α and β-Ti and Zr solid solutions with Co, Rh, and Ir showed that T_c rises with increasing valence electron concentration n. Small amounts of Co, Rh, and Ir dissolved in α-Ti, or α-Zr increase T_c by a factor of 2 to 4. In the bcc phase region of the β-Ti alloys T_c goes through a maximum of $4°K$ at 90 at.% Ti, which is explained by Matthias' rule.

I. INTRODUCTION

IT has been shown by Matthias and co-workers that the transition temperature of α-Ti is increased more by the addition of Fe than by the addition of an equal amount of Ru.[1] Since both elements have the same number of valence electrons, the phenomenon was explained by a magnetic interaction. It therefore seemed interesting to investigate the effect of the Co-group elements, Co, Rh, and Ir, on the transition temperatures of Ti and Zr.

Previous superconducting studies include the Ti and the Zr solid solutions with Co and Rh. Since the superconductivity of[1] Ti-Co solid solutions had been investigated thoroughly, only a few alloys in the Ti hcp and bcc regions were prepared in the current study. The previous results are confirmed. The transition temperature of a Zr alloy containing 10 at.% Co has been reported as 3.9°K.[2] Recently, the superconductivity of Ti-Rh and Zr-Rh solid solutions in the α and β regions has been investigated.[3,4]

Since there is no information in the literature about the superconducting properties of Ti and of Zr solid solutions with Ir and only limited data for Zr-Co solid solutions, we concentrated our investigations on these systems. A few additional solid solutions in the Ti-Rh system were also studied.

II. EXPERIMENTS

Of greatest importance in working with Ti and Zr alloys is the purity. Not only metallic impurities, but also oxygen and nitrogen contaminations, change the behavior of these alloys in various ways, as shown by Raub and Röschl[5] for the Ti-Ru and Zr-Ru alloys. They may influence T_c directly or change the thermodynamic stabilities of the different modifications. Most dilute Ti and Zr alloys show a martensitic transformation of the bcc β modification into a hcp α' form, which has the same crystal structure and lattice constant as the low-temperature α modification, but different concentration. During appropriate heat treatment α' transforms into the stable α modification. The yields of the β, α, α' phases depend not only on the concentration or rate of cooling, but also on the purity of the components, e.g., it is well known that oxygen and nitrogen contaminations tend to stabilize the α-Zr modification. In general, one can predict that if the eutectoid is much lower than the $\beta \rightarrow \alpha$ transformation temperature of the pure

[1] B. T. Matthias, V. B. Compton, H. Suhl, and E. Corenzwit, Phys. Rev. 115, 1597 (1959).
[2] B. T. Matthias and E. Corenzwit, Phys. Rev. 100, 626 (1955).
[3] Ch. J. Raub and C. A. Andersen, Z. Physik 175, 105 (1963).
[4] W. Buckel, G. Dummer, and W. Gey, Z. Angew. Physik 14, 703 (1962); Phys. Kondens Materie 1, 66 (1963).
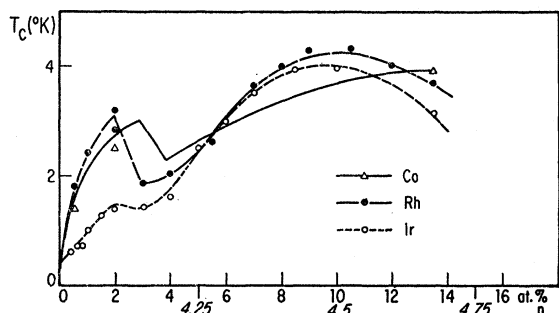[5] E. Raub and E. Röschl, Z. Metallk. 54, 455 (1963).

FIG. 1. The T_c versus composition curves for the Ti alloys. The Ti-Co curve was obtained from Ref. 1; the additional points found by us are marked as triangles. Plotted are the mid-transition points.

elements, the β phase will be retained in alloys of higher concentrations during quenching, and impurities will affect its stability very little.

The alloys were prepared in an arc furnace in a Zr-gettered argon atmosphere. They were cast in a small groove in a water-cooled Cu hearth, assuring good quenching after the arc was turned off. The iodide Ti and Zr (99.9% purity) was obtained from Foote Mineral Company. The other metals were at least of 99.8% purity.

Superconductivity above 1.2°K was determined in an apparatus similar to that described by Hardy and Hulm.[6] Below 1.2°K we used the Schawlow and Devlin[7] resonance frequency shift technique and a He³ bath.

The phases present and their lattice constants were determined by the x-ray powder technique using a GE XRD-5 diffractometer and Cu $K\alpha$ radiation. Sometimes filings of the alloys had to be annealed at 1000°C for $\frac{1}{2}$ h in order to obtain better patterns.

III. RESULTS AND DISCUSSION

The transition temperatures of the Ti and Zr alloys are plotted as a function of composition and valence electron concentration in Figs. 1 and 2. The transitions of the Ti alloys were fairly sharp (0.10–0.20°K in width), while those of the Zr alloys were, in general, broader (up to 1°K in width). This can be caused by the high sensitivity of Zr to contamination by oxygen or nitrogen.

All curves show nearly the same behavior. Up to 2 or 3 at.% additions we find a pronounced increase in T_c, then the curves drop or flatten out until they increase again and after passing through a maximum drop. The increase of T_c with composition is explained by Matthias' rule. When elements of group VIII of the periodic system are added to Ti or Zr, the valence electron concentration n is increased to a more favorable value for the occurrence of superconductivity, namely, closer to $n=5$. When this value is exceeded a subsequent decrease in T_c occurs.

[6] G. F. Hardy and J. K. Hulm, Phys. Rev. 93, 1004 (1954).
[7] A. L. Schawlow and G. E. Devlin, Phys. Rev. 113, 120 (1959).

At high Ti concentrations little difference in superconductivity between Ti-Co and Ti-Rh alloys was found. Even the slope of the T_c versus composition curve is the same in both systems. This means that a magnetic interaction, purported to cause an additional increase in T_c for Ti-Fe alloys,[1] does not exist in the Ti-Co solid solution. On the other hand, it cannot be explained why the influence of Ir is much less than that of Rh.

For the Zr alloys the slope of the T_c versus composition curve is, in general, appreciably higher. Again Rh increases T_c most. But this time the roles of Co and Ir are changed, Co having the smaller influence on T_c.

According to x-ray investigations the phase with 97 or more at.% Ti or Zr is the hcp α or α' phase. Since no change in the lattice constants of the pure α phase upon the addition of 2 or 3 at.% Rh or Ir could be detected, we used another method to show that the α phase really dissolves small amounts of other metals. This was done by annealing a homogeneous sample $Ti_{0.96} Rh_{0.04}$ (bcc, $a=3.24$ Å) for 200 h at 700°C.[3] According to Fig. 3, which is a schematic of a part of the Ti-Rh phase diagram, the β phase decomposes into 2 phases, hcp α component and a bcc β component, with a little higher Rh concentration.

The compositions of the two phases were determined by the x-ray fluorescence microprobe as 2–3 at.% Rh, the boundary concentration of α phase, and 5–6 at.% Rh, the concentration of the β modification. X-ray investigations also showed that the concentration of the bcc phase was only slightly changed, since the lattice constant of the bcc phase was the same before and after annealing.

The same kind of detailed investigation was not made for all the alloys, since it seemed very likely from superconductivity measurements that the α modification dissolves small amounts of noble metals.

An extrapolation of the data for α-Ti-Ir solid solutions gives a T_c of about 0.4°K for pure Ti which is in good
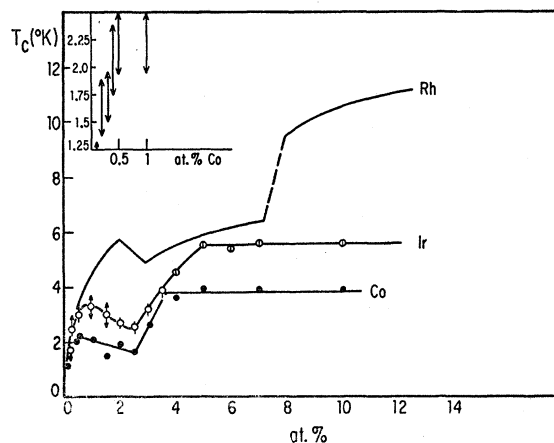

FIG. 2. The T_c versus composition curves for the Zr alloys. The Zr-Rh curve was obtained from Ref. 3. The arrows indicate the width of the superconducting transition.
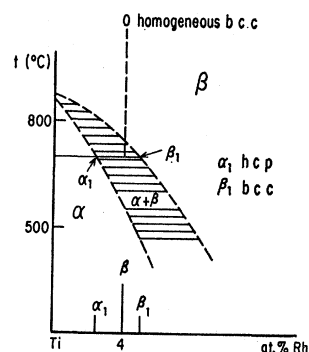
FIG. 3. A schematic of the Ti-rich side of the Ti-Rh phase diagram.

agreement with the recently reported value of $0.42°K$.[8] It does not seem probable, therefore, that the superconductivity in these alloys is caused by filaments of β phase in a superconducting α matrix. Specific-heat measurements might give a definite answer.

In the Zr-Co solid solutions it seems unlikely too that the superconductivity in the α phase is caused by filaments of the β phase, since we were unable to retain the bcc β-Zr-Co solid solution by quenching, even at concentrations above 5 at.% Co, where the β phase could be expected to be fairly stable.

The T_c versus composition curves for bcc Ti-Rh and Ti-Ir alloys show maxima at 90 at.% Ti. This composition is well within the β range, since the phase boundary for β-Ti-Rh alloys is between[9] 12 and 25 at.% Rh[10] and Croeni, Armantrout, and Kato[10] determined the maximum solubility of Ir in β-Ti as 10 to 15 at.% Ir. According to our own investigations it is closer to 15 at.% Ir.

In both systems we observed the decrease of the lattice constant with decreasing Ti concentration; which is typical for the β-Ti solid solutions:

	Å	$T_c,°K$
$Ti_{0.96} Rh_{0.04}$	3.24	2.0
$Ti_{0.88} Rh_{0.12}$	3.22	4.0
$Ti_{0.96} Ir_{0.04}$	3.25	1.6
$Ti_{0.90} Ir_{0.10}$	3.22	4.3

[8] R. L. Falge, Phys. Rev. Letters 11, 248 (1963).
[9] According to E. Raub (private communication) the phase boundary is close to 25 at.% Rh.
[10] I. G. Croeni, C. E. Armantrout, and H. Kato, U. S. Bur. Mines, Rept. Invest. No. 6079, 1962 (unpublished).

The nearly identical lattice constants of the Rh and Ir alloys are understandable if one keeps in mind that the atomic radii of Rh and Ir are nearly the same (1.34 and 1.36 Å).

In other Ti systems a maximum in T_c is very often observed at compositions of about 90 at.% Ti. This means that going to the right side of the periodic system the optimum value of n shifts to higher values.

System	Maximum at (at.%)	n	$T_c{}_{max}°K$	Reference
Ti-Mo	10	4.2	3.9	11
Ti-Mn(Re)	10	4.3	3.0	1
Ti-Fe	10	4.4	3.7	1
Ti-Co	12	4.5	3.8	1

There is no appreciable change in $T_c{}_{max}$ for Mo, Fe, or Co additions. Only the value for Mn and Re alloys is lower, which up to now cannot be explained, since apparently even Mn is not localized in β-Ti alloys.[12] It shows that for the elements of the VIIB group of the periodic system not *only* the valence electron concentration is of influence on T_c.

Unfortunately, the homogeneity range of the bcc solid solutions of β-Zr is so small that no T_c maxima could be observed within this phase.

Since there are no specific-heat data or magnetic measurements available for these alloys, no definite statements can be made why the various elements have a different effect on the α and β modifications or if these maxima in the β region are associated with variations of other electronic properties.

ACKNOWLEDGMENTS

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