Bulk Superconductivity in Dilute Hexagonal Titanium Alloys

F. HEINIGER* AND J. MULLER*

Department of Solid State Physics, Federal Institute of Technology, Zurich, Switzerland

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The superconductivity, the low-temperature specific heat, and the paramagnetic susceptibility have been investigated in a series of dilute hexagonal titanium alloys. In the solid solutions with V or Nb, both the transition temperature and the density of states are strongly increased and the entire volume exhibits superconductivity. A similar study of Ti-Fe alloys suggests either an incomplete volume transition or a different entropy variation in the superconducting state.

INTRODUCTION

THE significance of the enhancement of the superconducting critical temperature, which is observed in dilute alloys of titanium with other transition elements, has been subject to considerable controversy.[1-7] Matthias et al. interpreted the behavior of these alloys as evidence of the existence of a mechanism of a different type from that provided by the electron-phonon interaction,[1,8] while recent work by Cape[6] on Ti-Mn alloys suggested that the high transition temperatures might simply be due to filamentary cubic precipitations in the hexagonal matrix. The experiments to be described indicate (a) that in dilute solid solutions of Ti with V or Nb, in which cases the hexagonal phase extends to the highest solute concentrations, the enhancement of superconductivity is a real bulk effect; and (b) that the substantial increase of the transition temperature is accompanied by a marked increase of both the electronic specific heat and the magnetic sus-

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* Present address: Institut de Physique Expérimentale, Université de Genève, Geneva, Switzerland.

[1] B. T. Matthias, V. B. Compton, H. Suhl, and E. Corenzwit, Phys. Rev. 115, 1597 (1959).

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[3] W. Buckel, G. Dummer, and W. Gey, Z. Angew. Phys. 14, 703 (1962).

[4] C. J. Raub and C. A. Andersen, Z. Physik 175, 105 (1963).

[5] J. A. Cape and R. R. Hake, Bull. Am. Phys. Soc. 8, 192 (1963); R. R. Hake and J. A. Cape, ibid. 8, 419 (1963).

[6] J. A. Cape, Phys. Rev. 132, 1486 (1963).

[7] R. L. Falge, Phys. Rev. Letters 11, 248 (1963).

[8] See, for example, B. T. Matthias, in Proceedings of the Eighth International Conference on Low Temperature Physics, London, 1962 (Butterworths Scientific Publications Ltd., London, 1963), p. 135.

ceptibility. On the other hand, dilute alloys of Ti with Fe show a different calorimetric behavior at the temperature of the diamagnetic transition, and the normal electronic specific heat remains essentially unchanged.

HEXAGONAL ALLOYS OF Ti WITH V AND Nb

The structure of Ti-rich alloys is goverened by the $\alpha-\beta$ phase transition and the Martensite-type diffusionless transformation. The hexagonal alloys containing V or Nb were obtained by quenching after repeated melting in the argon arc. According to x-ray examination, the quenched specimens were single phase up to more than 10 at.% in both cases. The initial slope of the superconducting transition temperature T_c versus solute concentration is practically identical in the V and Nb series, the increase near pure Ti being approximately 1°K per at.%. The observation that very rapid quenching yields somewhat higher transition temperatures has to be interpreted in terms of the state of internal strains or a high concentration of defects, since we have found that Ti-Zr alloys show a similar effect.

Bearing in mind that even a complete diamagnetic transition may not unambiguously indicate a volume effect, we have to rely on the calorimetric transition which is insensitive to possible partial screening. The specific heat of representative samples weighing 3–10 g (small specimens are essential for efficient quenching[9])
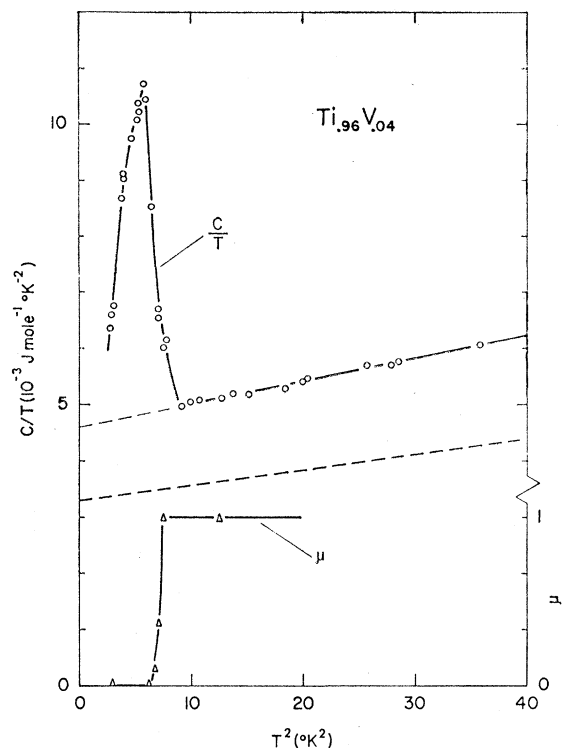
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FIG. 1. Specific heat $(C/T$ versus $T^2)$ and magnetic permeability μ of hexagonal $Ti_{0.96} V_{0.04}$. Lower broken line indicates C/T versus T^2 of pure Ti. For T_c versus concentration, see Ref. 2.

TABLE I. Variation of electronic specific heat γ, Debye temperature θ, and magnetic susceptibility χ, of hexagonal alloys of Ti with V and Nb.

	Ti	$Ti_{0.96} V_{0.04}$	$Ti_{0.96} Nb_{0.04}$
γ $(10^{-3}$ J mole^{-1} °K$^{-2})$	3.3	4.6	4.3
θ_0 (°K)	415	365	340
χ_{at}/χ_{at} (Ti)	(1)	1.09	1.05
χ_{at} (10°K)/χ_{at} (300°K)	0.92	0.92	0.92

portance of the effective Coulomb interaction is not known and no information on the isotope effect in group IV transition elements is available.

In fact, a knowledge of the isotope effect from experiment would permit separation of the interaction into a Coulomb and a phonon part.[12] Unfortunately, attempts of determining the isotopic shift of the transition temperature in[13] Ti and[14] Zr have been unsuccessful due to the difficulties of the sample preparation.

DILUTE Ti-Fe ALLOYS

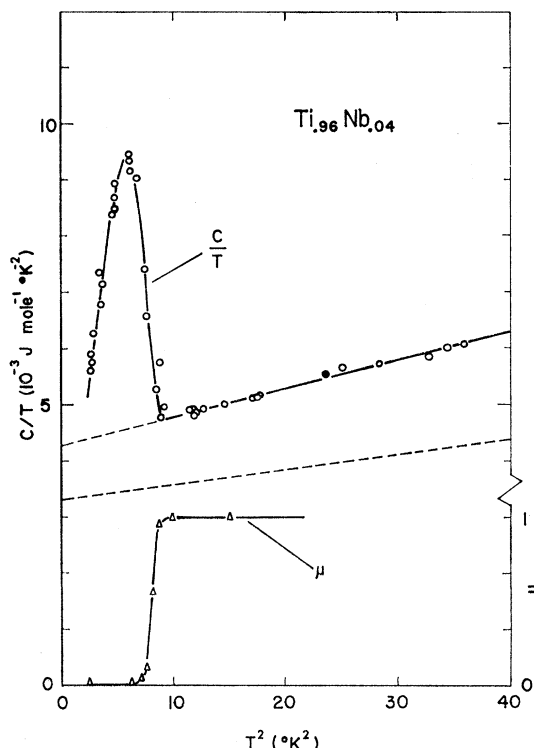For comparison, several dilute Ti-Fe alloys with iron content up to 1.5 at.% have been prepared in the same

have been determined with an absolute accuracy of $\pm 2\%$.[10] Figures 1 and 2 show the results for two alloys (single-phase hcp) containing 4 at.% V or Nb, respectively. Considering the discontinuity at the superconducting transition $[(C_s - C_n)/\gamma T]_{T=T_c}$, we conclude that the bulk of the material is superconducting below the temperature of complete diamagnetic shielding. Therefore, the marked increase of the magnetically observed transition temperature,[2] compared to T_c of pure Ti, is characteristic of the solid solution and is not due to precipitations. Furthermore, as it is seen from Table I, the V and Nb solutes significantly affect the normal electronic specific heat. We also note that the change of γ is much more pronounced than the change of χ. It is reasonable to assume the presence of a large paramagnetic contribution in addition to the spin susceptibility, although in regard to different interaction corrections, γ and χ_{spin} alone need not vary similarly upon alloying. A plot of $\ln(T_c/\theta)$ versus $1/\gamma$ reveals that the data for dilute Ti-V and Ti-Nb essentially agree with those obtained with the isoelectronic Ti-Zr system.[11] Such a relationship is expected qualitatively on the basis of the BCS theory. For the time being, a more detailed interpretation is of little use since the relative im-

FIG. 2. Specific heat and permeability of hexagonal $Ti_{0.96} Nb_{0.04}$.

[10] Jean Muller, Helv. Phys. Acta 33, 514 (1960).

[11] E. Bucher, F. Heiniger, J. Muheim, and J. Muller, Rev. Mod. Phys. 36, 146 (1964).

[12] E. Bucher, F. Heiniger, and J. Muller, Phys. Kondens. Materie 2, 210 (1964).

[13] R. G. Netzel and J. R. Dillinger, Proceedings of the 7th International Conference on Low Temperature Physics and Chemistry, Toronto, 1960 (University of Toronto Press, Toronto, 1961), p. 389.

[14] E. Bucher, J. Muller, and J. L. Olsen (unpublished).

way as the Ti-V and Ti-Nb specimens. X-ray diffraction showed only hexagonal lines in the quenched state. Optical micrographs closely resembled the one obtained by Cape[6] for as-cast $Ti_{0.99}Mn_{0.01}$. No evidence of a pronounced precipitation of the β phase could be detected. From 0.6 to 1.5 at.% Fe, the midpoint temperature of the change in permeability, observed ballistically in a field of 1 Oe, was found to increase linearly with concentration, in agreement with the earlier data.[1] However, in contrast to the complete diamagnetic transition, the specific heat shows only a slight anomaly (Fig. 3). Similar discrepancies between the amount of flux exclusion and the calorimetric transition have been observed in a number of cases as, e.g., in the σ phase of the Nb-Ir system.[12] A smaller than expected calorimetric anomaly has also been noted by Morin[15] at the apparent T_c of $Ti_{0.99}Fe_{0.01}$. According to the arguments given below, the hypothesis that the observed effect is caused by minor body-centered cubic inclusions seems very improbable, although we cannot rule out completely that traces of the latter may be present. Rather, we are left with two possible interpretations assuming that the transitions do occur in the hexagonal phases (α and α'). Unlike the behavior of Mn in α-Ti,[5–7] the present specific heat data and susceptibility measurements[6] indicate no localized moments on the iron solute.

If we assume a normalized distribution function $f(T_c)$ of the actual volume fraction undergoing a transition at T_c, the observed electronic specific heat will be given by

$$C(T) = \int_T^{T_c\,\text{max}} C_s(T,T_c)f(T_c)dT_c + \int_0^T \gamma(T_c)Tf(T_c)dT_c,$$

where

$$\int_0^{T_c\,\text{max}} f(T_c)dT_c = 1.$$

For simplicity, we define

$$x = \int_{T_1}^{T_2} f(T_c)dT_c,$$

with T_2 representing the upper onset of the transition, and $T_1 = T_2/2$. Further, we insert the value for $C_s(T,T_c)$ provided by the two-fluid model

$$C_s(T,T_c) = [3\gamma(T_c)/T_c^2]T^3,$$

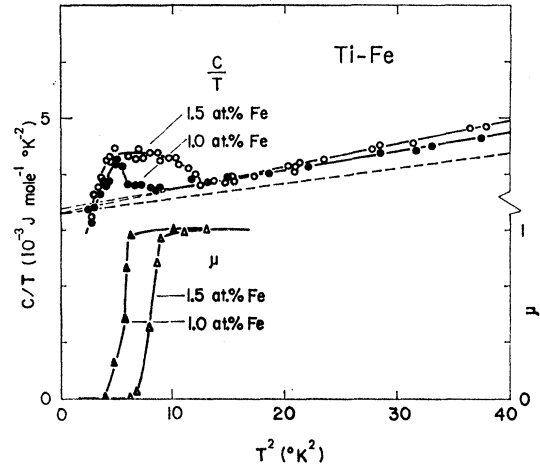---

[15] F. J. Morin (unpublished), quoted in Ref. 6.

FIG. 3. Specific heat of dilute Ti-Fe alloys. Note complete magnetic transition (μ).

since in the region between T_c and $T_c/2$ this is, for many superconductors, a better approximation than the corresponding BCS function. By the use of a numerical trial and error analysis, we obtain reliably $0.95 < x < 1$ for the V and Nb alloys, but $0.3 < x < 0.35$ for Ti$+1.5$ at.% Fe. If, in fact, only 30% of the volume were superconducting in the latter, a core structure with appreciable microscopic concentration gradients would be required to explain the magnetic transition. On the other hand, this figure almost excludes the possibility of a transition just due to cubic precipitations which are not detected in the x-ray patterns, unless induced superconductivity in the environment of such precipitations were important.

An alternative interpretation of the reduced calorimetric anomaly would have to be based on the assumption that the entropy of the superconducting state is lowered much less than usual, with a corresponding different temperature variation of the energy gap. But if so, it would be difficult to understand why isostructural and isoelectronic dilute Ti-V and Ti-Fe solid solutions, both without localized magnetic states, should exhibit a different kind of superconducting transition.