Superconductivity and Localized Magnetic States in Ti-Mn Alloys*

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Evidence for superconductivity (Matthias *et al.*) and for localized magnetic states (Hake, Leslie, and Berlincourt) in the dilute hcp alloys of Ti-Mn has been given previously. In this paper, detailed studies are described which indicate that the superconductivity observed previously in the dilute (1 to 5 at.% Mn) alloys was due to retained enriched bcc inclusions and not proper to the hcp matrix itself. Curie-Weiss susceptibility behavior is observed in dilute (0.2–4 at.%) Ti-Mn confirming the existence of localized magnetic states in the hcp phase. The magnitude of the Curie constant (typically $\approx 10^{-4}$ emu/g) suggests that magnetic moments ($\mu \approx 3.5\ \mu_B$/atom) are localized at the sites of Mn atoms in the hcp (α or α') phases of the alloys. No Curie-Weiss behavior is observed in bcc (β) Ti-Mn. Annealing and quenching techniques were employed to prepare single phase hcp specimens and two-phase specimens consisting of bcc filaments in an hcp matrix. The former are *not* superconducting down to 1°K; the latter have zero resistance at the temperature coinciding with the T_c of bulk bcc specimens. It is concluded that localized magnetic states suppress superconductivity in hcp Ti-Mn, while in the bcc phase T_c is elevated commensurately with expected changes in the electronic state density $N(0)$. In consequence, the existing experimental evidence on this system should not be interpreted in support of a magnetic-interaction hypothesis for superconductivity.

INTRODUCTION

THE role of magnetic[1] impurities in superconductors has been the subject of considerable experimental study.[2–10] In most instances, the presence of the magnetic impurities in a metal or alloy serves to depress its superconducting transition temperature. Examples are Gd in La,[4] Fe in Mo,[9] and Fe in Ir.[10] Several authors[7,10–12] have sought to correlate the depression of T_c with the presence of localized magnetic states at the impurity atom sites as evidenced by a Curie-Weiss temperature dependence of the magnetic susceptibility. On the theoretical side,[13–15] consideration of the coupling between the conduction electrons and the impurity moments has given some qualitative understanding of the deleterious effect of localized spins on superconductivity.

In alloys which do *not* contain localized magnetic moments, it is generally found that the effect of alloying on T_c is governed by the resultant change in $N(0)$, the electronic density of states at the Fermi surface.[16] T_c is found to depend on $N(0)$ according to[17]

$$\ln(T_c/\theta_D) \propto 1/N(0)\,, \tag{1}$$

where θ_D is the Debye temperature. Equation (1) is predicted by the BCS[18] theory on the basis of a phonon-induced electron-pairing interaction.

In what appeared to be an exceptional case, Matthias *et al.*[5] reported that the dilute (viz., 1–5 at.%) addition of Cr, Mn, Fe, or Co to Ti *raised* T_c of Ti much more sharply [$(dT_c/dc)_{c\to 0} \approx 10$°K/at.%] than might be expected from the usual alloying effects on the density of states. Curie-Weiss susceptibility behavior was not observed[11] in dilute Ti-Fe and Ti-Co, and it was subsequently speculated[19–22] that "magnetic" impurities which do *not* carry an observable localized moment may, nevertheless, give rise to superconductivity via a magnetic interaction rather than the electron-phonon interaction of BCS.[18] On the other hand, Hake, Leslie, and Berlincourt[23] studied the electron transport properties of the dilute hcp alloys of Ti with Mn (0.02–2.0

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[1] A magnetic impurity will be defined here as an element which exhibits magnetic ordering in the bulk state, for example, Fe, Cr, Gd.

[2] W. Buckel and R. Hilsch, Z. Physik. **128**, 324 (1950).

[3] W. Opitz, Z. Physik **141**, 646 (1957).

[4] B. T. Matthias, H. Suhl, and E. Corenzwit, Phys. Rev. Letters **1**, 92 (1958).

[5] B. T. Matthias, V. B. Compton, H. Suhl, and E. Corenzwit, Phys. Rev. **115**, 1597 (1957).

[6] K. Schwidtal, Z. Physik **158**, 563 (1960).

[7] B. T. Matthias, M. Peter, H. J. Williams, A. M. Colgston E. Corenzwit, and R. C. Sherwood, Phys. Rev. Letters **5**, 542 (1960).

[8] R. Hilsch, G. v. Minnigerode, and K. Schwidtal, in Proceedings of the Eighth International Conference on Low-Temperature Physics (to be published).

[9] T. H. Geballe, B. T. Matthias, E. Corenzwit, and G. W. Hull, Jr., Phys. Rev. Letters **8**, 313 (1962).

[10] R. A. Hein, J. W. Gibson, B. T. Matthias, T. H. Geballe, and E. Corenzwit, Phys. Rev. Letters **8**, 408 (1962).

[11] B. T. Matthias, IBM J. Res. Develop. **6**, 250 (1962).

[12] A. M. Clogston, B. T. Matthias, M. Peter, H. J. Williams, E. Corenzwit, and R. C. Sherwood, Phys. Rev. **125**, 541 (1962).

[13] C. Herring, Physica, Suppl. **24**, 184 (1958).

[14] H. Suhl and B. T. Matthias, Phys. Rev. **114**, 977 (1958).

[15] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **39**, 1781 (1960) [translation: Soviet Phys.—JETP **12**, 1243 (1961)].

[16] For extremely dilute alloys, T_c may depend on electronic mean-free-path effects [cf., E. A. Lynton, B. Serin, and M. Zucker, J. Phys. Chem. Solids **3**, 165 (1957)] of no concern to the present discussion.

[17] For an experimental survey and discussion of this "regularity" in the transition metal alloys, see F. J. Morin and J. P. Maita, Phys. Rev. **129**, 1115 (1963).

[18] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[19] A. I. Akhiezer and I. Y. Pomeranchuk, Zh. Eksperim. i Teor. Fiz. **36**, 859 (1959) [translation: Soviet Phys.—JETP **9**, 605 (1959)].

[20] B. T. Matthias, Phys. Today **16**, 21 (1963).

[21] B. T. Matthias, in *Superconductors*, edited by M. Tannenbaum and W. V. Wright (Interscience Publishers, Inc., New York, 1962).

[22] B. T. Matthias, J. Phys. Soc. Japan **17**, Suppl. B-1, 104 (1962).

[23] R. R. Hake, D. H. Leslie, and T. G. Berlincourt, Phys. Rev. **127**, 170 (1962).

at.%), Cr (1.0 at.%), Fe (1.0 at.%), and Co (1.0 at.%), and observed large *negative* magnetoresistivities (Ti-Mn), *field-dependent* Hall coefficients (Ti-Mn) and low temperature *minima* in the electrical resistivity (Ti-Cr, Ti-Mn, Ti-Fe). Recently, Coles[24] has observed a resistivity minimum in Mo-Fe where localized moments are believed to depress T_c. These electronic transport phenomena are now almost universally ascribed to the presence of localized magnetic moments.[25]

Thus an unusual and conflicting situation presents itself with regard to the dilute alloys of Ti with elements of the iron group. It therefore seemed important to examine further the question of elevated transition temperatures and localized magnetic states in these alloys. In the present paper, the magnetic susceptibilities and resistively determined transition temperatures of Ti-Mn alloys are correlated with their phase structure. The evidence supports the view that localized magnetic states occur in hcp Ti-Mn, in agreement with earlier transport property measurements,[23] while in the bcc phase of these alloys, moment localization does *not* occur, and T_c is elevated in accord with an increase in the density of states [Eq. (1)]. Moreover, from the evidence presented below, it is inferred that the elevated transition temperatures observed previously[5,23] for the hcp modification of Ti-Mn (and probably other dilute Ti alloys) were a result of retained superconducting bcc inclusions. In consequence, the data for dilute Ti alloys cannot justifiably be interpreted in support of a magnetic interaction for superconductivity.

EXPERIMENTAL PROCEDURE

The preparation of the arc-cast alloys and the resistivity measuring techniques have been described earlier.[23] Magnetic susceptibilities were measured by means of a standard Gouy technique.[26] A sample $0.1\times0.1\times1.0$ cm^3 ($m\approx0.040$ g) was suspended longitudinally from an automatic recording vacuum semimicrobalance in a nonuniform magnetic field with an approximately linear gradient 3 kG/cm at an average field of about 16 kG. The magnetic susceptibility per gram is then given in terms of the force, F, (measured by the balance) by

$$\chi=2Fl/m(H_1^2-H_2^2),$$

where l is the length, m the mass and H_1 and H_2 the field strengths at the ends of the sample. With the present apparatus, a change in χ of 1×10^{-8} ergs g^{-1} G^{-2} is easily measured. The absolute accuracy is limited mainly by uncertainty in H_1 and H_2 to conservatively $\pm5\times10^{-8}$ erg g^{-1} G^{-2}.

Temperatures were measured by means of a six-junction thermopile (three thermocouples in series) of Au+2.1 at.% Co versus Cu. The thermopile was calibrated at pumped He and pumped H_2 temperatures, at the superconducting transition of high-purity Pb (7.2°K) and high-purity single crystal Nb (9.2°K), at the boiling point of liquid N_2, and at the ice point. At temperatures above 10°K, the calibration points agreed very well with the thermoelectric data given by Powell, Bunch, and Corruccini.[27] The sensitivity of the thermopile at 4.2°K was approximately 13 μV/°K. In the present arrangement, the sample and balance were enclosed in a common chamber which was evacuated except for approximately 100-μ pressure of He gas. The He "exchange" gas served to keep the sample and thermocouple junctions at the same temperature as the immediate surroundings (a copper "bucket" filled with activated charcoal effectively surrounds the sample region) of the low-temperature Dewar. Measurements were made during warmup after cooling to liquid-He temperatures and boil-off of all helium except for that absorbed by the charcoal. On account of the large thermal mass of the helium-saturated charcoal, warmup could be controlled simply by controlling the heat leak through the vacuum space of the helium Dewar. The usual procedure was to admit heat pulses so that the sample was warmed in steps.

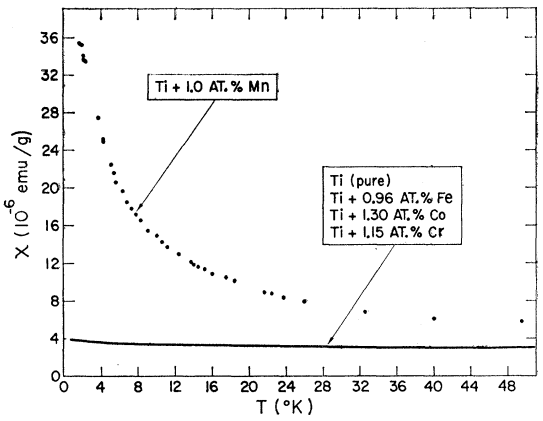

FIG. 1. Temperature dependence of the magnetic susceptibility of "pure" Ti and some dilute Ti alloys. On this scale susceptibilities for "pure" Ti and for the alloys with Fe, Co, and Cr, are so nearly alike that the results are shown as a single solid line. The measured values at room temperature were for Ti-1.0 Mn, 3.6×10^{-6} emu/g and for the others 3.3×10^{-6} emu/g.

EXPERIMENTAL RESULTS

Magnetic Susceptibility

Because a strong indication of the presence of localized magnetic states is Curie-Weiss behavior of the magnetic susceptibility, measurements of the susceptibility were made on various dilute (0.1 to 4.0 at.%) alloys of Ti with the magnetic transition elements. In Fig. 1 is shown a plot of the magnetic susceptibility χ of as-cast

[24] B. R. Coles, Phil. Mag. 8, 335 (1963).
[25] A bibliography on this subject may be found in Ref. 23.
[26] See, for example, L. F. Bates *Modern Magnetism* (Cambridge University Press, New York, 1961).
[27] R. L. Powell, M. D. Bunch, and R. J. Corruccini, Cryogenics 1, No. 3, 1 (1961).

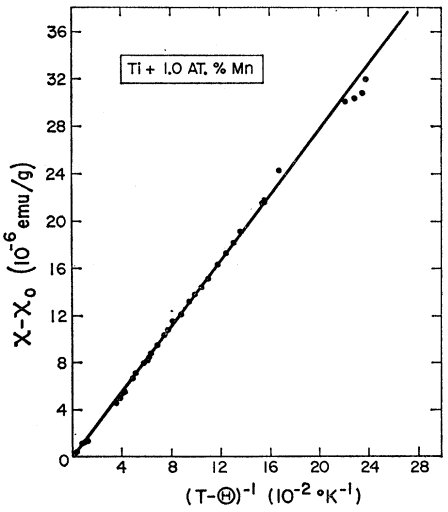

FIG. 2. Curie-Weiss plot for the susceptibility data for Ti+1.0 at.% Mn. For this plot $\chi_0+3.4\times10^{-6}$ emu/g and $\theta+-2.2$°K. From the slope of the line one finds the Curie constant $np^2\mu_B^2/3k=1.39\times10^{-4}$ in cgs units.

"pure" Ti and Ti alloyed with approximately 1.0 at.% additions of Cr, Mn, Fe, and Co, respectively.[28]

Only the Ti-Mn alloy exhibited strong temperature dependence at low temperatures. On Fig. 2, the Ti-1 Mn[29] data points are shown to fit a Curie-Weiss equation i.e.,

$$\chi-\chi_0=C(T-\theta)^{-1}. \tag{2}$$

The straight line drawn through the data points is a plot of Eq. (2) with $\chi_0=3.4\times10^{-6}$ emu/g and $\theta=-2.2$°K. Since this value of χ_0 is close to the nearly temperature independent susceptibility of the Ti matrix, and since the θ value is small, it is reasonable to consider the extra susceptibility $\chi-\chi_0$ in terms of a molecular field model for the magnetic atoms. In this model, the Curie constant is given by

$$C=nP^2_{\text{eff}}\mu_B^2/3k, \tag{3}$$

where n is the number/g of impurity atoms (Mn, Co, etc.) with associated effective magnetic moments. The effective magneton number P_{eff}, is given by $P_{\text{eff}}=g[J(J+1)]^{1/2}$, μ_B is the Bohr magneton, and k is Boltzmann's constant. If one takes the g value to be 2, then

$$P^2_{\text{eff}}=4.87\times10^{24}\,C/n, \tag{4}$$

and the saturation moment of the localized impurity state μ, is given by

$$\mu/\mu_B=gJ=(1+P^2_{\text{eff}})^{1/2}-1. \tag{5}$$

With C given by the slope of the line in Fig. 2 and n given by the nominal concentration of Mn atoms, i.e., counting all Mn atoms initially added to the Ti, Eq. (5) gives $\mu\approx1.5\,\mu_B$ per Mn atom. The reasonable magnitude of the local moment, and the excellent agreement of the susceptibility data with the Curie-Weiss equation corroborates the earlier evidence[23] from electron transport property measurements for the existance of localized magnetic states in hcp Ti-Mn. Despite this considerable evidence for moment localization, the same specimen on which the data of Fig. 2 were taken was found to have vanishing electrical resistance at 1°K in agreement with earlier resistive[23] and magnetic[5] measurements. In this instance, therefore, the alloy exhibits simultaneously a marked increase in T_c,[28] and localized magnetic states.

Metallurgy and Microstructure

In lieu of the possibility that localized magnetic states and elevated T_c can coexist in a given microscopic region of the alloy, it is possible to assume that more than one metallurgical phase is present in the specimen and that the superconductivity and localized magnetic states occur in different phases. An understanding of how such phase separation might occur during casting of the alloy is provided by a study of their phase diagrams. Shown in Fig. 3 is a partial phase diagram for the system Ti-Mn.[30] From Fig. 3 one may note that the solid solubility of Mn in α Ti is very limited. An accurate $\alpha/(\alpha+\beta)$ phase boundary has not been determined but it is known that the maximum solubility is in the neighborhood of 0.5 at.% at 600°C.[30] At higher solute

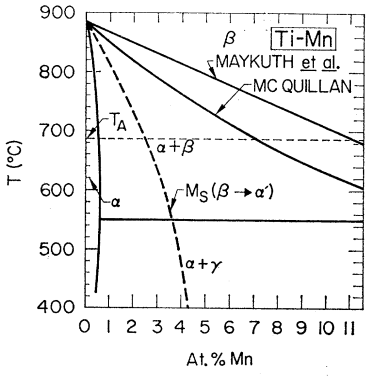

FIG. 3. Phase diagram for the Ti-rich region of the Ti-Mn system. Note two $\beta/(\alpha+\beta)$ boundaries are shown, one after Maykuth *et al.* (Ref. 34), the other after McQuillan (Ref. 34). Because the $\alpha/(\alpha+\beta)$ boundary has not been determined with any precision, the boundary shown is only approximate. The M_s martensitic transformation of $\beta\rightarrow\alpha'$ curve shown is after M_s. Duwez (Ref. 31).

[28] Iodide process (Foote Mineral Company) crystal bar Ti nominally 99.92 at.% pure, with residual resistivity ratio $\rho(273)/\rho(4.2)\approx30$–40. See Ref. 23. Most alloy specimens used in this investigation were cut from the same ingots used in Ref. 23. The transition temperature of one lot of starting material Ti (lot No. 005-1) was 0.14°K. We are indebted to R. Falge for this measurement.

[29] In the remainder of this paper the notation A-MB will denote a dilute solution of M at.% of element B in element A.

[30] R. I. Jaffee, Progr. Metal. Phys. 7, 65 (1958).

additions, the resultant alloy obtained upon cooling from above the $\beta/(\alpha+\beta)$ boundary will depend predominantly on the cooling rate and will not, in general, be a homogeneous equilibrium structure. This is so becasue in the $\alpha+\beta$ region of temperatures and concentrations, the alloy tends to separate into Mn-poor ($\approx 0.5\%$) α phase and Mn rich (value given by the $\beta/(\alpha+\beta)$ boundary at temperature) β phase. Moreover, the β-phase portions of the alloy undergo martensitic transformations to the hcp "martensite" structure (denoted by α') at the concentrations and temperatures defined by the line M_s.[31] This is best illustrated by considering two extreme cases. Figure 4 is an optical micrograph of a Ti-2 Mn specimen which has been quenched from 1000°C (within the β field) to −190°C. The initial cooling rate was approximately 3000°C/sec.[32] Electron and x-ray microscopy studies confirm the expectation that the specimen consists entirely (no detectable α or β) of

FIG. 4. Optical micrograph of Ti-2 Mn annealed at 1000°C and quenched rapidly (≈ 0.6 sec) to −190°C. This structure is characteristic of the α' martensite phase. Fiducial marks indicate 10 μ.

a homogeneous martensitically formed hcp (α') solid solution. In contrast, Fig. 5 shows a specimen of Ti-1 Mn which was initially quenched from the β field to establish a homogeneous α' matrix (similar to that of Fig. 4), then annealed for 8 h at 690°C (in the $\alpha+\beta$ region of Fig. 3) and finally quenched rapidly to −190°C. One now sees, immeshed in the host hcp matrix, the filament-like structure of precipitated enriched β phase. This specimen probably[30,33] consists very nearly of equilibrium $\alpha+\beta$ at concentrations of approxi-

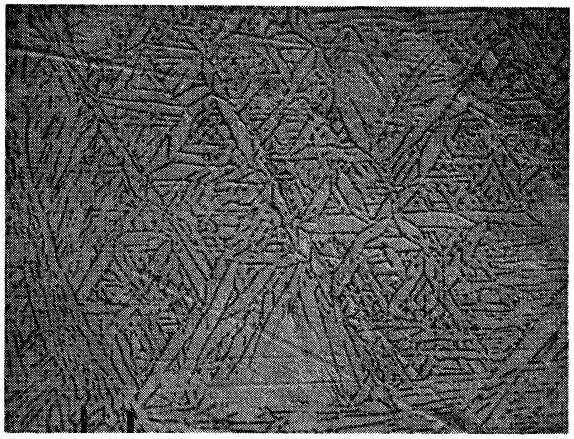

FIG. 5. Optical micrograph of Ti-1 Mn after first quenching from 1000°C (Fig. 4), then annealing for 8 h at 690°C and quenching to −190°C. Note mesh-like array of β phase filaments in α-phase matrix. Fiducial marks indicate 10 μ.

mately 0.5 at.% Mn and 11 at.% Mn,[34] respectively. It is therefore clear that sufficiently slow cooling through the $\alpha+\beta$ field will result in a partial and inhomogeneous separation into α and β phases so that the final state of the specimen in a given instance will consist of α, α', and β. This is believed to be true of the as-cast state of these arc-melted alloys and those with alloying additions above about 0.4 at.% discussed previously.[5,23] An optical micrograph of an as-cast sample of Ti-1 Mn is shown in Fig. 6 for comparison with Figs. 4 and 5. In this instance it is clear that some inhomogeneity exists since the structure appears to be a mixture of α' martensite and nucleation and growth α.[33] Best esti-

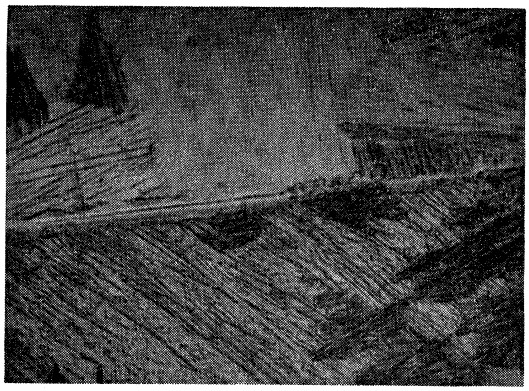

FIG. 6. Optical micrograph of as-cast (argon arc melted) Ti-1 Mn. This is probably a mixture of α, α', and β phases. See Refs. 30 and 31. Note grain boundary of parent β phase. Fiducial marks indicate 10 μ.

[31] The M_s shown in Fig. 3. is after P. Duwez, Trans. Am. Soc. Metals. **45**, 934 (1953).

[32] The specimens were cold-rolled to 0.005-in. thickness after which annealing and quenching were accomplished by the technique described by L. J. Cuddy and E. S. Machlin, Phil. Mag. **7**, 745 (1962). Quench rates (determined by observing the resistivity) were roughly exponential in time, requiring about 0.6–0.8 sec to reach room temperature.

[33] H. R. Ogden and F. C. Holden, TML Report No. 103, Battelle Memorial Institute, 1958 (unpublished).

[34] See Fig. 3. This is the value given by the Maykuth *et al.* diagram [D. J. Maykuth, H. R. Ogden, and R. I. Jaffe, Trans. AIME **197**, 225 (1953)]. According to the McQuillan diagram [A. C. McQuillan, J. Inst. Metals **80**, 363 (1952)], 7 at.% would be the Mn concentration in the β phase. In the following it will be observed that the present data appear to agree with the results of Maykuth *et al.*

mates, based on x-ray and electron microscopy are that at least 97 to 98% of the as-cast Ti-1 Mn is hcp α and α'. Judging from the structure of Fig. 5, it is expected that the retained β phase material exists in a mesh-like acicular distribution of extremely fine layers or filaments separating α platelets or along parent grain boundaries. With such a structure, the alloy might be expected to exhibit zero resistance at the bulk transition temperature of the Mn-enriched retained β phase. Thus, in the dilute-as-cast material, the apparent transition to superconductivity (i.e., onset of zero resistance) would be due to a small fraction of the entire specimen. This conclusion is in good accord with the calorimetric measurements of Morin and Maita[35] on Ti-1 Fe and of Hake[36] on various dilute Ti-Mn alloys. In the case of Ti-Fe, Morin observed a very small specific heat jump ($\approx 5\%$) at the apparent T_c. This would be expected if only a small fraction of the specimen were superconducting. Moreover, below T_c, the specific-heat values tended closely to those of pure Ti again suggesting a preponderance of normal material. In the case of Ti-1 Mn and Ti-2 Mn, Hake observed what appeared to be a large magnetic contribution to the heat capacity similar to that observed in Cu-Co by Crane and Zimmerman.[37] There appeared only slight indication of a specific heat jump at the "T_c" indicated by the resistive[23] or magnetic[5] measurements, apparently because a very small contribution from the superconducting material was nearly overshadowed by the large magnetic contribution to the specific heat.

In summary of the preceding discussion, it seems reasonable to put forth the hypothesis that in the β (bcc) phase alloys of Ti-Mn the superconducting transition temperature is raised in accord with Eq. (1) while in hcp Ti-Mn the formation of localized magnetic states is favored in agreement with the transport property results.[23] As a consequence, one may expect that T_c is actually depressed[38] in hcp Ti-Mn.

Measurements on Annealed and Quenched Alloys

In the following are presented the results of a group of measurements designed to test the hypothesis that it is only in the β phase of Ti-Mn that T_c is raised by Mn additions while in hcp (α or α') Ti-Mn T_c is not raised but localized magnetic states are formed. Two groups of samples, each consisting of various solute additions of Mn, were prepared. One group was annealed at 1000°C (in the β field) and quenched rapidly to liquid-nitrogen temperature. These samples appeared to be pure α' martensite under metallographic examination

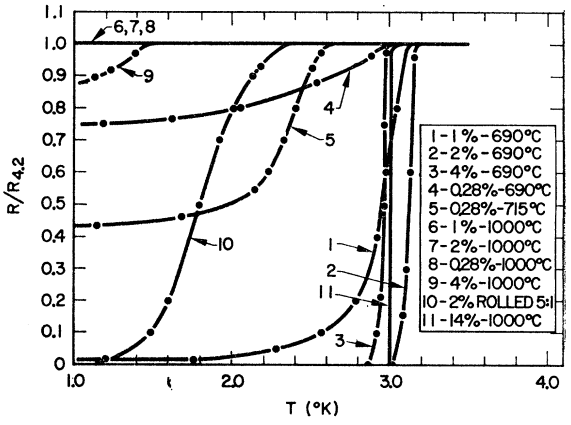

FIG. 7. Resistive superconducting transitions for various Ti-Mn alloys. Resistances (ordinate) are normalized to resistance at 4.2°K. Note that alloys quenched from β field (1000°C) remain normal to 1°K, while those annealed in $\alpha+\beta$ field (690°C) all begin to lose their resistance at approximately 3°K. Curve 10 illustrates the adverse effects of cold-work.

(see Fig. 4). The second group annealed at 690°C for 8 h and quenched as above were similar in structure to Fig. 5. They were found to be pure α plus pure β as expected from the phase diagram, Fig. 3. On Fig. 7 are shown the resistive superconducting transitions for these annealed and quenched alloys. Note that the alloys annealed at 690°C all start to lose their resistance at the same temperature, approximately 3°K, curves 1–4. According to the Maykuth[34] diagram, Fig. 3, the β phase portion of each of these alloys contains about 11 at.% Mn. This is in excellent agreement with the atomic concentrations (10–12 at.%) reported by Matthias *et al.*[5] for a transition temperature of 3°K in bcc Ti-Mn. Bulk β phase Ti-Mn exhibtis no Curie-Weiss behavior[39] and its transition temperature appears to be governed by $N(0)$[36] in accord with the BCS prediction, Eq. (1). It is to be expected that 0.28 at.% Mn (curve 4) is insufficient concentration to cause the precipitation of more than the minutest traces of β-phase strands. Thus the incomplete transition is not surprising. Likewise Ti-1 Mn, curve 1, does not become entirely superconducting, again, we believe because of incomplete connectivity of the β-phase precipitates.[40]

Increasing the annealing temperature would be expected to decrease the Mn concentration in both the final α and β phases. Consequently, the relative volume fraction of β phase material should be greater, and its T_c should be lower. This tendency is exemplified by curve 5 for Ti-0.28 Mn annealed at 715°C which is to be compared with curve 4 for annealing at 690°C.

In marked contrast to the above results and to

[35] F. J. Morin (private communication).
[36] R. R. Hake (to be published). See also J. A. Cape and R. R. Hake, Bull. Am. Phys. Soc. 8, 192 (1963).
[37] L. T. Crane and J. E. Zimmerman, Phys. Rev. 123 113 (1961).
[38] Preliminary measurements by R. Falge appear to support this conclusion (private communication).
[39] The susceptibility of Ti+14% Mn, for example, is virtually constant at 4.5×10^{-6} emu/g from 4.2 to 80°K after which it rises gradually to about 5.5×10^{-6} emu/g at room temperature.
[40] Assuming the value for the limit of solubility in α Ti, to be 0.5%, the Maykuth diagram predicts the equilibrium volume fraction of β phase for Ti-1 Mn at 690°C to be $\approx 4\%$.

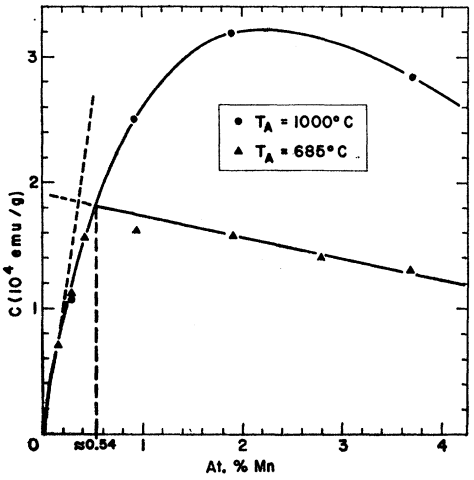

FIG. 8. Plot of the Curie constant (slope of the Curie-Weiss line) $nP^2_{\text{eff}}\mu_B^2/3k$ versus at.% Mn for various Ti-Mn alloys after annealing and quenching from 1000°C (solid circles) and 690°C (triangles). The initial slope at the origin gives the value $\mu \approx 3.5$ μ_B/Mn atom.

earlier[5] data for the superconductivity of hcp Ti-Mn, are the results for the group of alloys quenched from the β field. None of these alloys from 0.28 at.% to 4 at.% became superconducting down to 1.1°K. There is some indication that in the 4% sample (curve 9) small portions of enriched β phase were precipitated or else there was incomplete transformation of nonenriched material.

Curve 10 of Fig. 7 shows the effect of cold work on a Ti-Mn alloy. In this case, the same specimen used for the data of curve 2, was afterwards cold rolled until its thickness had been reduced five-fold. The subsequent resistive transition, curve 10, is both lowered and broadened in temperature. With further cold-rolling (not shown) the transition was lowered to below 1.1°K.[41] A reasonable explanation is that the result of cold working is to destroy the continuity of the β-phase filaments. For example, the superconductivity would be quenched by destruction of portions of the β-phase network by strain-induced martensitic conversion to the ω phase. There is considerable evidence that such a transformation does occur as a result of cold deformation in Ti-rich Ti-V[42] and Ti-Cr[43,44] alloys.

In Fig. 8 the Curie constant, i.e., the slope of the Curie-Weiss line, is plotted as a function of initial solute addition of Mn for the two groups of alloys described above. At the most dilute concentrations, presumably within the limit of solubility in α-Ti, annealing has no effect on the observed Curie constant. This may be interpreted to mean that all Mn atoms in hcp Ti-Mn carry associated magnetic moments. The magnitude of an isolated moment may be determined from the initial slope of the dashed line representing C as a function of concentration for hcp Ti-Mn. From the slope of the straight line passing through the origin, one finds $\mu \approx 3.5$ μ_B/Mn atom. The saturation effect at higher concentrations may be due to enhanced interaction among the localized moments not envisaged in the Curie-Weiss molecular-field treatment.

The solid line drawn through the measured C values for the two phase specimens is *predicted* by the Maykuth[34] phase diagram in the following sense. The equilibrium volume fraction of α phase at 690°C is unity until the maximum solubility in α Ti (intersection of the solid lines) is reached after which it decreases *linearly* to zero at 11 at.% (7 at.% if the McQuillan diagram is correct, see Fig. 3). The line passing through the 690°C data points, is, in this case the best straight line through the experimental points which passes through zero at 11 at.%. Consequently, this procedure may be regarded as a technique for *measuring* the limit of solubility of Mn in α Ti (intersection of the two solid lines) and in the present case the result is seen to be approximately 0.54 at.% at 690°C.

TITANIUM ALLOYED WITH Cr, Fe, OR Co

Unlike Ti-Mn, the transport properties and magnetic susceptibilities (Fig. 1) of the dilute hcp alloys of Ti with Cr, Fe, and Co suggest little moment localization. The slight upward curvature of χ at low temperatures permits, at best, an estimate of an upper limit for the magnitude of a localized moment on these solute atoms. One finds $\mu \leq 0.1\mu_B$/atom. Matthias[11] has reported a temperature-independent susceptibility for Ti-Fe, and Ti-Co, and Clogston *et al.*[12] reported no evident moment localization in Zr-1 Fe whereas we have observed strong Curie-Weiss behavior in hcp Zr-Mn. These results suggest that Fe, unlike Mn, has little tendency to form localized magnetic states in a transition element of the fourth column. The dilute alloys of Ti with Cr, Fe, or Co have very similar phase diagrams to Ti-Mn, and, in the as-cast state exhibit structures similar to Fig. 6, characteristic of initial stage $\alpha+\beta$ precipitation in the martensite matrix. While more work needs to be done on these impurities, it appears that they either give rise to very weakly magnetized localized states in Ti (which may inhibit superconductivity), or, while forming no local moment, nevertheless, do not give rise to anomalously high T_c in the *bulk* of as-cast specimens as suggested earlier.[5] Rather, like Ti-Mn, the observed elevated transition temperatures may be the result of enriched β phase inclusions. Preliminary results indicate that Ti-Cr, like Ti-Mn, when rapidly quenched from the β field is *not* superconducting to 1.1°K.

[41] The adverse effect of cold work on the superconductivity of Ti-Mn has also been noted by Matthias—remarks found in Proceedings of the Eighth International Conference on Low-Temperature Physics (to be published).

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SUMMARY

In the preceding, we have presented experimental data which relate, in an unambiguous way, the superconductivity of the Ti-rich Ti-Mn alloys to their metallurgical microstructure. The data establish (1) the existence of localized magnetic states in hcp Ti-Mn, (2) that there is *not* an anomalously large elevation of T_c by dissolved Mn in hcp Ti-Mn, and (3) the superconductivity of the as-cast dilute ($\lesssim$4 at.%) Ti-Mn is due to a precipitated filamentary structure of enriched β-phase Ti-Mn. The retained β phase is nonmagnetic and sufficiently rich in Mn that the observed T_c can be understood on the basis of Eq. (1) and a reasonable variation of $N(0)$ as a result of alloying. One may conclude, therefore, that the superconductivity of dilute Ti-Mn is not anomalous and ought not be to construed as evidence for a magnetic interaction for the superconducting state.

Note added in proof. Recent measurements by Falge [R. Falge, Phys. Rev. Letters **11**, 248 (1963)], have confirmed the suggestion presented herein that very small additions ($\lesssim$0.8 at.%) of Mn to Ti *lowers* the superconducting transition temperature of the as-cast alloys. This is in general accord with the solubility limit for Mn in α Ti and may be regarded as substantiating evidence that localized magnetic states in hcp Ti-Mn act to inhibit the superconducting state.

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Far-Infrared Spectra of Two Cerium Double Nitrate Salts*

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Far-infrared transmission experiments have been carried out on cerium magnesium nitrate and cerium zinc nitrate. The energies of the first excited doublets were found to be 36.25 and 30.2k, respectively. The frequencies of the longest wavelength lattice absorptions have also been determined.

CERIUM magnesium double nitrate (CMN) is well known to the low-temperature physicist for its useful magnetic properties. All magnetic ions are equivalent, the interactions between the ions are very small and the g tensor in the ground Kramers doublet is highly anisotropic. These properties make the crystal very suitable for use in adiabatic demagnetization and as a magnetic thermometer.

In recent years there have been several estimates of the splitting Δ_1 between the two lowest Kramers doublets. Relaxation measurements[1–3] all give $\Delta_1 = 34k$. Finn *et al.*[1] perform their experiments on pure CMN whereas Ruby *et al.*[2] and Cowan and Kaplan[3] use CMN diluted with LaMN. The analyses of magnetic susceptibility data[4–6] give values of Δ_1 in the range 33 to 43k. Estimates of the energy Δ_2 of the second excited doublet vary even more widely and lie roughly in the range 80-290k. In view of the lack of agreement prevailing and the interest that many physicists have in CMN, far-infrared transmission experiments have been carried out in an attempt to measure both Δ_1 and Δ_2 directly. The techniques used were standard.[7] Experiments were also carried out on cerium zinc double nitrate (CZN) which is isomorphous with CMN. The observed spectra were very similar as would be expected, and only that for CZN is given in Fig. 1. The data are summarized in Table I.

The absorption at Δ_1 (the following remarks apply to both salts) has the expected temperature behavior: Its

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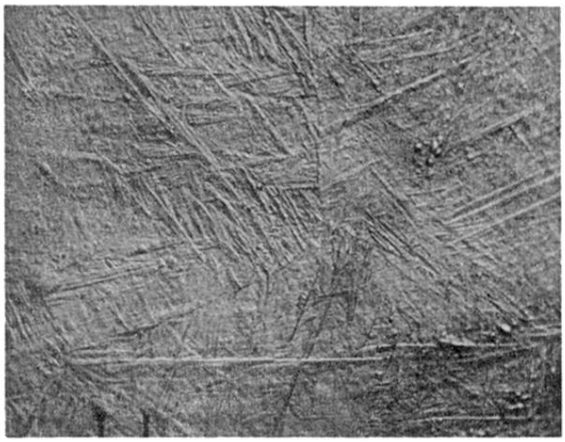

FIG. 4. Optical micrograph of Ti-2 Mn annealed at 1000°C and quenched rapidly (≈0.6 sec) to −190°C. This structure is characteristic of the α' martensite phase. Fiducial marks indicate 10 μ.

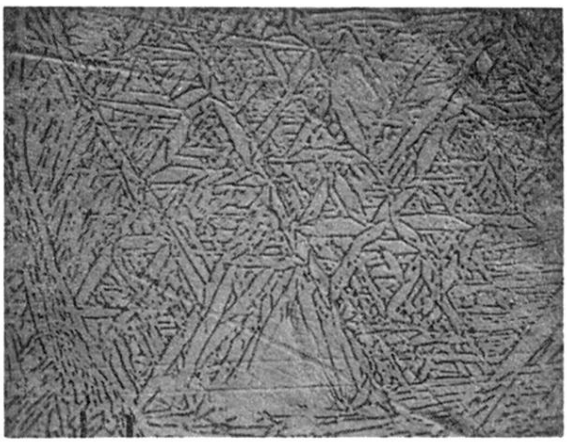

FIG. 5. Optical micrograph of Ti-1 Mn after first quenching from 1000°C (Fig. 4), then annealing for 8 h at 690°C and quenching to −190°C. Note mesh-like array of β phase filaments in α-phase matrix. Fiducial marks indicate 10 μ.

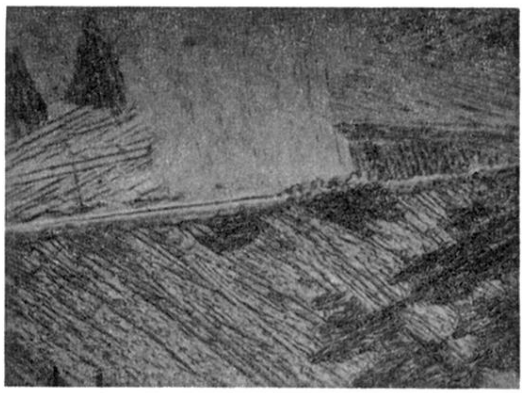

FIG. 6. Optical micrograph of as-cast (argon arc melted) Ti-1 Mn. This is probably a mixture of α, α', and β phases. See Refs. 30 and 31. Note grain boundary of parent β phase. Fiducial marks indicate 10 μ.