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# Calorimetric Investigation of Localized Magnetic Moments and Superconductivity in Some Alloys of Titanium with Manganese and Cobalt*

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The specific heats $C$ of arc-cast specimens of Ti and alloys of Ti with Mn and Co have been measured between 1.2 and 4.5°K. For ≈99.92 wt.% pure hcp Ti, the standard $C=\gamma T+\beta T^3$ relation is closely obeyed, with $\gamma=3.30\pm0.03$mJ/mole(°K)$^2$ and $\beta^{-1/3}\propto\theta_D=429\pm7$°K. For hcp Ti alloys containing 0.17–1.7 at.% (nominal atomic percent) Mn we observe (1) a large excess specific-heat contribution which *increases* with decrease of temperature, evidently associated with ordering of magnetic moments localized at the Mn ions, and (2) no calorimetric evidence of a standard bulk superconducting transition. Neither a large localized-moment-type specific-heat contribution nor a standard bulk superconducting transition is calorimetrically observed in hcp Ti–1 at.% Co. The absence of standard bulk superconducting transitions in dilute hcp Ti-Mn and Ti-Co is in apparent conflict with earlier magnetic evidence for elevation of the superconducting transition temperature $T_c$ above 1.2°K in such alloys. That dilute Mn addition to the hcp Group-IV transition elements Ti or Zr actually lowers $T_c$ is suggested by the observation that 0.2 at.% Mn added to the superconducting alloy hcp Ti–50 at.% Zr [$T_c=1.60$°K, $\gamma=4.2$mJ/mole(°K)$^2$,$\theta_D=304$°K] (1) induces localized-moment behavior in the magnetic susceptibility and specific heat, (2) eliminates the standard bulk calorimetric superconducting transition, and (3) results in a broad and incomplete resistance-versus-temperature superconducting transition. In contrast to the behavior of hcp Ti-Mn and Ti-Zr-Mn alloys, a predominantly bcc Ti–14 at.% Mn alloy displays (1) standard normal-state specific-heat behavior with no evidence of localized moments, and (2) a standard calorimetric superconducting transition at $T_c=2.55$°K. The formation and interaction of dilute localized moments in Ti and Ti-Zr, and the effect of the localized moments on superconductivity, are qualitatively discussed.

## I. INTRODUCTION

THE study of the formation and interaction of dilute localized magnetic moments in metals appears to be a valuable approach to the problem of metallic magnetism.[1] The effect of such moments upon superconductivity is also of interest.[2] Although there have been many observations of localized-moment behavior in the electronic, magnetic, and thermal properties of nontransition-metal base alloys such as Cu, Ag, Au, Mg, and Zn containing dilute additions of Cr, Mn, Fe, Co, and Ni,[3,4] relatively little experimental work has been done on dilute localized-moment phenomena in transition metal base alloys,[5–10] despite the

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[1] The prominent ideas regarding the formation and interaction of localized magnetic states have been recently discussed with regard to the general problem of metallic magnetism by H. Brooks, in *Electronic Structure and Alloy Chemistry of the Transition Elements*, edited by P. A. Beck (Interscience Publishers, Inc., New York, 1963), p. 3 ff.

[2] For a recent review of the relations between superconducting and magnetic properties, see P. G. de Gennes and G. Sarma, J. Appl. Phys. 34, 1380 (1963).

[3] For a recent review, see G. J. van den Berg and J. de Nobel, J. Phys. Radium 23, 665 (1962).

[4] A useful tabulation of resistive, magnetic, and thermal property results on fifteen different dilute alloy systems has been prepared by A. N. Gerritsen, Physica 25, 489 (1959).

[5] D. K. C. MacDonald, W. B. Pearson, and I. M. Templeton, Phil. Mag. 5, 867 (1960).

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

[7] R. R. Hake, D. H. Leslie, and T. G. Berlincourt, Bull. Am. Phys. Soc. 6, 146 (1961); Phys. Rev. 127, 170 (1962); T. G. Berlincourt, R. R. Hake, and A. C. Thorsen, *ibid.* 127, 710 (1962).

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

[9] B. R. Coles, Phil. Mag. 8, 335 (1963).

[10] Some studies of localized-moment behavior due to rare-earth ions in dilute solution in transition metals have been reported by R. D. Parks and W. A. Little, Phys. Rev. Letters 6, 539 (1961); T. Sugawara and I. Yamase, J. Phys. Soc. Japan 18, 1101 (1963); T. Sugawara and R. Soga, *ibid.* 18, 1102 (1963).

potential value of such work to a much needed understanding of the electronic character and magnetic interactions in metals with unfilled $d$ shells. Indeed, it has been previously emphasized[7] that the mere existence of localized magnetic moments in a transition metal alloyed with another transition metal is in apparent conflict with the simple collective band model which is often applied to such alloys.

Several years ago we presented low-temperature electron-transport property evidence[7] that localized magnetic moments were associated with Cr, Mn, and Fe ions in dilute solution in a transition metal, hcp Ti, and that the localized moments must interact with the conduction electrons. Some controversy was attached to this interpretation since Matthias *et al.*[11] had found that dilute additions of Cr, Mn, Fe, or Co to hcp Ti sharply *raised* the superconducting transition temperature $T_c$, whereas localized moments almost always *lower* $T_c$.[6,12,13] More recently we reported the observation of Curie-Weiss-type temperature dependence of the magnetic susceptibilities[14,15] and large anomalies in the low-temperature specific heats[14] of dilute hcp Ti-Mn[16] alloys, further supporting the existence of localized moments in hcp Ti-Mn. On the other hand, standard bulk calorimetric superconducting transitions were not observed above 1.2°K in dilute hcp Ti-Mn,[14] suggesting that magnetic measurements indicating[11] $T_c>1.2$°K and observations of zero electrical resistance above[7] 1.2°K in such alloys might reflect the presence of superconducting filaments which are not representative of the bulk material. Indeed, it was shown[15] that thin Ti-Mn alloy strips which had been very rapidly quenched through the two-phase hcp-bcc region, showed no trace of superconductivity down to 1.1°K even in resistivity measurements. This suggested[15] that the slower quenched arc-cast alloys of previous studies[7,11] might contain filaments of a superconducting Mn-enriched bcc phase (calorimetric[14] and susceptibility[14,15] measurements had shown bcc Ti–14 Mn to be a standard superconducting material with relatively high $T_c$), even though no such filaments could be directly observed in arc-cast alloys by standard techniques[7,14,15] (x-ray diffraction, electron microprobe x-ray analysis, light and electron microscopy). Calorimetric and susceptibility studies[17] also showed that 0.2-at.% Mn added to the superconducting alloy hcp Ti–50 Zr ($T_c=1.6$°K) produced localized-moment behavior and *lowered* the standard bulk superconducting transition below 1.24°K. On the basis of the Ti-Mn and Ti-Zr-Mn studies it was suggested[15,17] that dilute addition of Mn to hcp Ti should actually *lower* $T_c$. This prediction appears to have been verified recently by Falge[18] who found a $T_c=0.42$°K for high-purity Ti(<5 ppm Mn, <2 ppm Fe); a $T_c=0.17$°K for "pure" arc-cast "iodide-process" Ti (≈30-ppm Mn, ≈20-ppm Fe, ≈20-ppm Cr); and a $T_c<0.06$°K for arc-cast hcp Ti-Mn alloys made from "iodide-process" Ti with Mn additions of 70–6500-ppm Mn (0.007–0.65-at.% Mn).

In the present paper we report in more detail the results of the calorimetric investigation of the magnetic and superconducting properties of Ti and Ti–50 Zr alloyed with Mn. This work apparently constitutes the first calorimetric study of dilute localized-moment behavior in alloys in which both solute and solvent are transition metals. We also present specific heat data on hcp Ti–1 Co. Calorimetric, magnetic-susceptibility, and electron-transport-property results are qualitatively discussed with regard to the formation and interaction of dilute localized moments in Ti and Ti-Zr and the effect of the localized moments upon superconductivity.

## II. EXPERIMENTAL RESULTS

### A. "Pure" hcp Ti

Figure 1 shows the specific heat $C$, plotted in the conventional $C/T$ versus $T^2$ form, for a 28-g arc-cast button made from nominally 99.92 wt.% pure "iodide-process" Ti supplied by the Foote Mineral Company. Typical impurities are given by the manufacturer in wt.% as: Zr–0.05; Si, Al–0.005; Mg, Mn, Ca–0.003; Cr, Fe, $O_2$, $N_2$–0.002. The calorimetric apparatus, experimental technique, and data reduction procedures

TABLE I. Specific-heat results for specimens which display standard normal-state specific-heat behavior.

| Material | $\gamma$[a] | $\theta_D$[b] (°K) | $r$(%)[c] | $p_n$[d] | $T_c$[e] (°K) | $\Delta T$[e] (°K) |
|---|---|---|---|---|---|---|
| Ti[f] | 3.305±0.002 | 429±1 | 0.26 | 68 | ··· | ··· |
| Ti–50 Zr | 4.205±0.006 | 304±1 | 0.42 | 49 | 1.60 | 0.30 |
| Ti–14 Mn | 5.528±0.008 | 372±2 | 0.22 | 30 | 2.55 | 0.30 |

[a] Electronic specific-heat coefficient in mJ/mole (°K)². Only the probable error is indicated. Estimated systematic error is ±1%.
[b] Debye temperature. Only the probable error is indicated. Estimated systematic error is ±1.5% for Ti and Ti–50 Zr and ±3% for Ti–14 Mn.
[c] Average of the absolute values of the residuals of the normal-state data points $C/T$ from the linear least-squares fit of $C/T$ to $T^2$.
[d] Number of data points taken in the normal state.
[e] The superconducting transition temperature $T_c\equiv(T_{max}+T_{min})/2$ where $T_{max}$ and $T_{min}$ are, respectively, the temperatures at maximum and minimum specific heats on the low- and high-temperature sides of the transition. The superconducting transition breadth $\Delta T\equiv T_{max}-T_{min}$.
[f] Arc-cast button made from nominally 99.92 wt.% pure "iodide process" Ti supplied by the Foote Mineral Company.

[11] B. T. Matthias, V. B. Compton, H. Suhl, and E. Corenzwit, Phys. Rev. **115**, 1597 (1959). For more recent magnetic measurements of $T_c$ for hcp Ti–Co (in agreement with those of Matthias *et al.*), see Ch. J. Raub and G. W. Hull, Jr., Phys. Rev. **133**, A932 (1964).
[12] R. Hilsch, G. V. Minnigerode, and K. Schwidtal, in *Proceedings of the Eighth International Conference on Low Temperature Physics* [Butterworths Scientific Publications Ltd., London (to be published)].
[13] B. T. Matthias, IBM J. Res. Develop. **6**, 250 (1962).
[14] J. A. Cape and R. R. Hake, Bull. Am. Phys. Soc. **8**, 192 (1963).
[15] J. A. Cape, Phys. Rev. **132**, 1486 (1963).
[16] The alloy designation $A$–$B$ or $A$–$NB$ will be used to designate alloys in which $A$ is the solvent, $B$ is the solute, and $N$ is a number indicating the nominal solute concentration in atomic percent. Crystal structure designations preceding $A$–$B$ or $A$—$NB$ will refer to the predominate phase.
[17] R. R. Hake and J. A. Cape, Bull. Am. Phys. Soc. **8**, 419 (1963).
[18] R. L. Falge, Jr., Phys. Rev. Letters **11**, 248 (1963).

are essentially the same as those previously described.[19]

The essential linearity of the $C/T$ versus $T^2$ curve for the "pure" Ti of Fig. 1 indicates that the usual relationship

$$C(T)=\gamma T+\beta T^3 \quad (1)$$

is reasonably well obeyed. Here $\gamma T$ and $\beta T^3$ are normally identified as, respectively, the electronic and lattice contribution to the specific heat with $\gamma \propto N(E_F)$, the energy density of electronic states at the Fermi surface; and $\beta^{-1/3} \propto \theta_D$, the Debye temperature. Table I shows $\gamma$, $\theta_D$, and their probable errors as determined by the method of least squares. The estimated systematic error is $\pm 1\%$ in $\gamma$ and $\pm 1.5\%$ in $\theta_D$. The present $\gamma=3.30\pm0.03$ mJ/mole (°K)$^2$, $\theta_D=429\pm7$°K values may be compared with the calorimetric values of other workers (expressed in the same units): Wolcott[20]—$\gamma=3.56$, $\theta_D=430$, Aven *et al.*[21]—$\gamma=3.38\pm0.04$, $\theta_D=421\pm2$ (errors are probable); and Kneip *et al.*[22]—$\gamma=3.346\pm0.026, \theta_D=427\pm5$; $\gamma=3.351\pm0.029, \theta_D=430\pm6$ [errors for $\gamma$ are 99% confidence limits plus estimated 0.5% systematic error; the two ($\gamma$, $\theta_D$) sets are apparently the results of two separate runs on one specimen]. A value $\gamma=3.2$ mJ/mole (°K)$^2$ has been calculated by Falge[18] from his superconducting critical-field and critical-temperature data for high-purity Ti.

Despite the fair agreement of the present ($\gamma$, $\theta_D$) values for Ti with those obtained in the recent careful measurements of Kneip *et al.*, it is possible that the present values have been slightly affected by Mn impurity. As can be seen in Fig. 1, there is a small ($\approx+1\%$) deviation from linearity in the $C/T$ versus $T^2$ curve for "pure" Ti at the lowest temperatures. (A similar deviation is apparent in the $C/T$ versus $T^2$ curve for Ti of Kneip *et al.*) That Mn concentrations $c\geq0.17$ at.% (1700 ppm) can have considerable effect on the low-temperature specific heat of Ti is shown in Fig. 1 and discussed below in Sec. IIB. If it is assumed that for $0<c\leq0.36$ at.% the elevation of the specific heat is directly proportional to $c$ with a proportionality constant determined by the data for $c=0.17$, 0.36 at.% of Fig. 1, then the nominal impurity concentration of 30-ppm Mn could result in deviation from $C/T$ versus $T^2$ linearity of the magnitude observed, and cause an overestimation of $\gamma$ and $\theta_D$ by $\approx0.5\%$ and $\approx2\%$, respectively. That very small concentrations of some impurities can affect the bulk electronic properties of Ti is also suggested by the observation of a low-temperature electrical resistivity minimum in $\approx99.92$ wt.% pure Ti,[7] and the extreme sensitivity of the superconducting transition temperature of Ti to Mn and Fe impurities.[18]

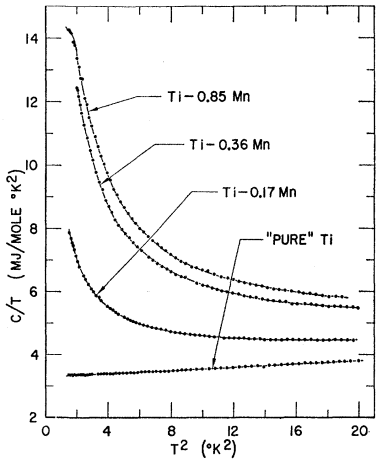


FIG. 1. $C/T$ versus $T^2$ for $\approx99.92$ wt.% pure Ti and various arc-cast dilute hcp Ti–Mn alloys. Ti–$N$ Mn means Ti containing $N$ nominal at.% of Mn.

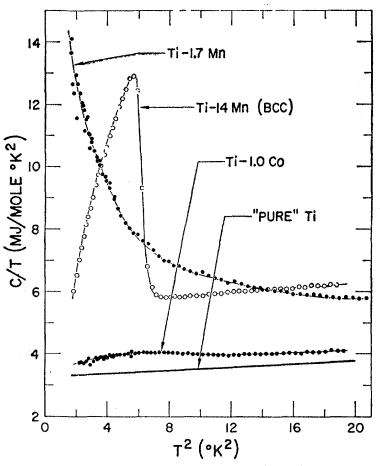


FIG. 2. $C/T$ versus $T^2$ for Ti alloys. All are hcp except Ti–14 Mn which is predominantly bcc. The "pure" Ti curve of Fig. 1 is shown for comparison. Ti–$N$ B means Ti containing $N$ nominal at.% of B.

## B. Dilute hcp Ti-Mn Alloys

Figures 1 and 2 show $C/T$ versus $T^2$ curves for arc-cast hcp Ti alloys containing 0.17, 0.36, 0.85, and 1.7 nominal at.% Mn. The specimen preparation techniques have been previously described.[7,19] The Mn concentrations have been calculated from the weights of the starting materials with a correction for weight loss during melting. The pronounced effect of small concentrations of Mn on the specific heat of Ti is noteworthy, and is evidently due to the ordering of localized moments whose existence in hcp Ti-Mn has previously been inferred from electron transport[7] and magnetic susceptibility[14,15] studies. The $C(T)/T$ values for the three most concentrated alloys are not widely different. A similar saturation of electronic and magnetic properties as functions of dilute Mn concentration in Ti has previously been observed[7,15] and may be due in part to phase segregation. The restricted equilibrium solid solubility of Mn as well as Cr, Fe, Co, and Ni in the hcp phase of Ti (a maximum of $\approx0.5$ at.% for

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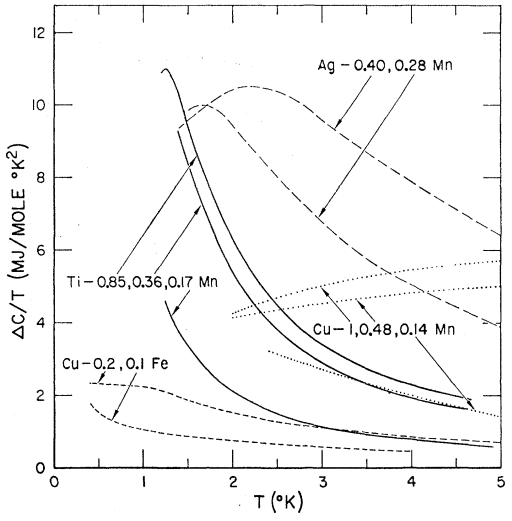


FIG. 3. $\Delta C/T$ versus $T$ for the more dilute hcp Ti-Mn alloys of this study and the Ag-Mn (Ref. 25), Cu-Mn (Ref. 26), and Cu-Fe (Ref. 27) of other investigations. Here $\Delta C \equiv C(\text{alloy}) - C(\text{solvent})$, so that $\Delta C$ represents approximately the "anomalous" specific-heat contribution, and the areas under the curves represent the "anomalous" entropy contributions. The numbers represent the nominal atomic percentages of the solutes.

Mn) and the resultant possibility of metallurgical complication is martensitically transformed hcp Ti alloys which have been quenched from the solid-solution bcc region (and which contain more than a few tenths percent of Cr, Mn, Fe, Co, or Ni addition) has been previously discussed in some detail.[7,15]

### 1. *Absence of Standard Bulk Superconductivity*

The $C/T$ versus $T^2$ curves for Ti–0.85 Mn and Ti–1.7 Mn show no sharp increase in slope at $T^2 \approx 1.7$, 4(°K)², respectively, as might be expected if standard bulk superconducting transitions took place at the $T_c \approx 1.3$, 2°K, respectively, suggested by the magnetic measurements of Matthias *et al.*[11] [Assuming $\gamma$ (alloy) $\approx \gamma$(Ti), one might expect a specific-heat jump $\delta C/T \approx \gamma \approx 3.3$ mJ/mole (°K)² centered at $T_c^2$ and spread over $\approx 1$(°K)².] However, in two separate runs on Ti–1.7 Mn, erratic thermal drifts were encountered at $T^2 \lesssim 4$(°K)² with consequent scatter in the data as apparent in Fig. 2. Similar data scatter is apparent in the $C/T$ versus $T^2$ curves for Ti–1.0 Co (Fig. 2) and Ti–49.9 Zr–0.2 Mn (Fig. 4) at $T^2 \lesssim 6$ (°K)², and may be characteristic of specimens containing a small volume fraction of inclusions which undergo superconducting transitions, especially if the localized superconducting transitions occur in the presence of localized-moment-induced effective internal fields. As indicated above, recent susceptibility and resistivity results[15] indicate that the superconductivity observed in magnetic[11] and resistive[7] measurements on arc-cast hcp Ti-Mn may be due to filaments of metastable Mn-enriched bcc material. Since efforts[7,14,15] to detect such filaments in the hcp matrix of arc-cast Ti-Mn by standard techniques have not been successful, it is probable that such filaments (if they exist) occupy less than $\approx 2\%$ of the specimen volume, consistent with the absence of prominent calorimetric evidence for superconductivity.

### 2. *"Anomalous" Specific Heat Contribution*

Figure 3 shows $\Delta C/T$ versus $T$ curves for the alloys Ti–0.17, 0.36, 0.85 Mn where $\Delta C \equiv C(\text{alloy}) - C(\text{solvent})$. If one makes the plausible assumption that the normal electronic $\gamma T$ and lattice $\beta T^3$ specific-heat components for these dilute alloys are nearly the same as for the "pure" solvent Ti, then the $\Delta C/T$ versus T curves of Fig. 3 represent the "anomalous" specific-heat-over-temperature contribution due to the Mn addition. A $\log(\Delta C/T)$ versus $\log T$ plot of the data of Fig. 3 shows that the curves for Ti–0.17, 0.36 Mn can be approximated to within 2% by: $\Delta C/T \propto T^{-x}$; $x(T<T_b)=1.56$, $x(T>T_b)=1.35$; $T_b$(Ti–0.17 Mn) $=2.7$°K, $T_b$(Ti–0.36 Mn) $=3.3$°K. Thus, for $1.2<T<4.5$°K, $\Delta C(T)$ *increases* with decrease of temperature, and does not obey the $\Delta C/T \propto 1/T^3$ characteristic of a nuclear hyperfine interaction[23] nor the $\Delta C/T \propto 1/T$ ascribed[24] to superparamagnetic clusters in more concentrated alloys.

The areas under the curves of Fig. 3 approximately represent the anomalous contribution to the entropy. If we assume that the anomalous contribution is due to localized-moment ordering, then numerical integration of the Ti–0.17 Mn and Ti–0.36 Mn curves indicates that in each case 27% of the total spin entropy.

$$S = cR \ln(2s+1) \tag{2}$$

is removed in going from 4.5°K to the lowest temperature of measurement. Thus, the magnitudes of the anomalous specific-heat contributions are not inconsistent with a localized-moment-ordering interpretation. In Eq. (2), $c$ is the atomic fractional concentration of Mn, $R$ is the gas constant, and a temperature-independent spin state $s=\frac{3}{2}$ is assumed to be associated with the Mn atoms, reasonably consistent with the $\mu = 3.5 - 3\mu_B$/(Mn ion) indicated by a Curie-Weiss analysis (assuming negligible orbital contributions) of the 4–300°K susceptibility results[15] on Ti alloyed with $\approx 0.2$–0.4 at.% Mn. The calculation of total spin entropy by means of Eq. (2) becomes more doubtful for the higher Mn concentration alloys due to uncertainty as to the amount of Mn in solution in the hcp phase.[7,15]

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### 3. Comparison with Ag- and Cu-Base Alloys

Figure 3 also shows, for comparison, $\Delta C/T$ versus $T$ curves for Ag-Mn,[25] Cu-Mn,[26] and Cu-Fe.[27] The curves for Ag-Mn and Cu-Mn have been constructed from published small-scale plots and are thus accurate to only about 10%. The spin states suggested for the magnetic additions by the Curie constants which characterize the high-temperature magnetic susceptibility data and by the entropies associated with the low-temperature specific-heat anomalies are: Ag-Mn, $s=\frac{5}{2}$; Cu-Mn, $s=2$ or $\frac{5}{2}$; and Cu-Fe, $s=\frac{1}{2}$. These alloys, like Ti-Mn,[7] all display low-temperature anomalies in their electron transport properties,[4] presumably due to the interaction of localized moments with the conduction electrons.

It is noteworthy that the $\Delta C/T$ versus $T$ curves for the transition metal base Ti-Mn alloys are qualitatively similar to those for the filled-$d$-shell base Cu–0.14 Mn; Ag–0.28, 0.40 Mn; and Cu–0.1, 0.2 Fe. For Cu-Mn, it has been shown[26] that at high enough Mn concentration and/or low enough temperature (e.g., Cu–0.48, 1 Mn at $T<4.5$°K as in Fig. 3), the $\Delta C/T$ is approximately independent of Mn concentration and temperature. Franck *et al.*[27] have speculated that measurements at still lower temperatures than indicated in Fig. 3 might reveal Cu-Mn-type specific-heat behavior in Cu-Fe. Liu[28] has pointed out the similarity of the specific-heat behavior of[29] La-Gd to that of Cu-Mn. The peaks in $\Delta C/T$ versus $T$ at lower temperatures in Ti–0.85 Mn and Ag–0.28, 0.48 Mn may then mark the onset of roughly temperature and concentration independent $\Delta C/T$ versus $T$ regions. (Measurements on Ag-Mn and Ti-Mn at lower temperatures would be of interest but interpretation may be complicated by nuclear contributions.[23]) Thus, the (non-nuclear) specific-heat anomalies in dilute Cu-Mn, Ag-Mn, Cu-Fe, La-Gd, and Ti-Mn may all fit the same general pattern.

## C. Dilute hcp Ti-Co

Figure 2 shows $C/T$ versus $T^2$ for an arc-cast hcp Ti–1.0 Co alloy. As in the case of hcp Ti-Mn *there is no evidence of a standard bulk superconducting transition*, although magnetic measurements[11] on arc-cast alloys would suggest $T_c\approx 2.2$°K for hcp Ti–1 Co, while resistivity measurements[7] indicated a broad resistance versus temperature transition with $T_r\approx 2.3$°K for arc-cast hcp Ti–1.3 Co. Here $T_r$ is defined[7] as the intercept of the steep linear portion of the resistance versus temperature curve with the zero-resistance axis. The Ti–1 Co specific-heat bump at $2<T^2<12(°K)^2$ in Fig. 2 may be associated with superconductivity (probably of a filamentary type) and/or a very weak localized-moment-ordering contribution to the specific heat. (There is no definite evidence of localized moments in the low-temperature electron transport[7] or 4–300°K susceptibility measurements[15] on arc-cast hcp Ti–1.3 Co.) It is of interest that the $C/T$ versus $T^2$ curve as measured for arc-cast hcp Ti–1 Fe by Morin and Maita[30] is somewhat similar to that shown in Fig. 2 for arc-cast Ti–1 Co, showing no evidence of a standard bulk superconducting transition. Similar to the Ti-Co case, magnetic measurements[11] on arc-cast Ti-Fe suggest a relatively high $T_c\approx 2.6$°K for hcp Ti–1 Fe, and a broad resistance versus temperature transition was observed[7] in arc-cast hcp Ti–0.96 Fe with a relatively high $T_r\approx 2.4$°K. (Recent measurements by Strongin *et al.*[31] using a complex-ac-susceptibility technique indicate a filamentary character for the above-1°K superconductivity in arc-cast hcp Ti–1 Fe, as might be expected from the calorimetric results.)

## D. Ti–50 Zr and Ti–49.9 Zr–0.2 Mn

In view of the body of evidence[6,12,13] indicating that localized moments generally lower $T_c$, it seemed reasonable to suspect[15,17] that Mn might actually *lower* the $T_c\approx 0.42$°K[18] of pure Ti. Since localized-moment behavior is also observed in the electron-transport[32] and magnetic-susceptibility[33] characteristics of dilute hcp Zr-Mn, one also suspects that Mn might lower the $T_c\approx 0.55$°K of pure Zr. In order to investigate the possibility of $T_c$ depression by Mn in hcp Group-IV transition metals and yet avoid the complications of measurements below 1°K, we studied[17] the effect of Mn on the superconducting transition of the hcp alloy Ti–50 Zr. This alloy displays a relatively high $T_c\approx 1.57$°K, according to the measurements of Hulm and Blaugher,[34] and, judging from the behavior of its constituents, might be expected to provide a moment-localizing environment for Mn. Of course, the fact that the superconducting state electronic "coherence distance" $\xi$[35] should be much smaller in the Ti–50 Zr alloy than in pure Ti or Zr suggests that the addition of dilute localized moments might affect $T_c$ somewhat differently in the two cases, although qualitatively similar effects might be expected.

### 1. Specific Heat

Figure 4 shows $C/T$ versus $T^2$ curves for arc-cast Ti–50 Zr and Ti–49.9 Zr–0.2 Mn. Ti–50 Zr exhibits

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[34] J. K. Hulm and R. D. Blaugher, Phys. Rev. **123**, 1569 (1961).
[35] See for example T. E. Faber and A. B. Pippard in *Progress in Low Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1955), Vol. I, p. 159.

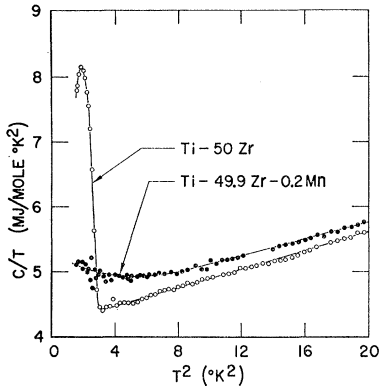


FIG. 4. $C/T$ versus $T^2$ for the hcp alloys Ti–50 at.% Zr and Ti–49.9 at.% Zr–0.2 at.% Mn.

standard normal-state behavior, Eq. (1), and a standard bulk superconducting transition. The midpoint of the negative slope portion of a $C$ versus $T$ curve defines a $T_c = 1.60$°K in reasonable agreement with the measurements of Hulm and Blaugher.[34] The values of $\gamma$ and $\theta_D$ characterizing the normal-state specific heat are listed in Table I. In sharp contrast to Ti–50 Zr, the $C/T$ versus $T^2$ curve for Ti–49.9 Zr–0.2 Mn is not linear for $T^2 \lesssim 8$(°K)$^2$ and does not indicate a standard superconducting transition. The shape of the curve for Ti–49.9 Zr–0.2 Mn is similar to that for Ti–0.17 Mn but is closer to the curve for the relatively Mn-free solvent, suggesting a reduced spin state for the Mn in Ti–49.9 Zr–0.2 Mn, as is also indicated by the magnetic susceptibility measurements discussed below. Thus, it appears that the addition of 0.2 at.% Mn to Ti–50 Zr induces localized-moment behavior and lowers the standard bulk superconducting transition from 1.6°K to below 1.24°K.

The marked increase in $T_c$ for Ti–50 Zr ($T_c = 1.6$°K) over that in pure Ti ($T_c \approx 0.42$°K) or Zr ($T_c \approx 0.55$°K) may be associated with the larger $\gamma$ value for Ti–50 Zr ($\gamma = 4.2$) than for Ti ($\gamma = 3.3$) or Zr[22] ($\gamma = 2.8$), where $\gamma$ values are in mJ/mole (°K)$^2$. A rough correlation of $\gamma$ (proportional to the electronic-state density) and $T_c$ might be expected for "nonmagnetic" transition metals on the basis of the BCS theory[36] as discussed by Pines[37] and as investigated experimentally by several workers.[19,38–40] The correlation of $\gamma$ and $T_c$ in the Ti-Zr system has also recently been observed independently by Bucher *et al.*[40] and by Betterton and Scarbrough.[41] The values for Ti–50 Zr [$\gamma = 4.1$ mJ/mole (°K)$^2$, $\theta_D = 290$°K, and $T_c = 1.5$°K], as read from a graph of the data of Bucher *et al.*, are in fair agreement with the values reported here. (Bucher *et al.* report that for Ti-Zr alloys, the $T_c$, unlike the normal-state specific heat depends markedly on the heat treatment. Possibly $T_c$ for Ti-Zr is somewhat different for the quenched martensitic $\alpha'$ and annealed equilibrium $\alpha$ structures.)

### 2. *Phase Structure and Electrical Resistivity Values*

After completion of the specific-heat measurements the Ti–50 Zr and Ti–49.9 Zr–0.2 Mn specimens were cut into sections for metallographic, x-ray, electrical-resistivity, and magnetic-susceptibility investigation. Both alloys displayed a striated martensitic hcp ($\alpha'$) structure with an expansion of unit-cell dimensions $\approx 5\%$ over those of hcp Ti, consistent with x-ray observations on Ti–50 Zr by Duwez.[42] A small amount (less than 1% of the specimen volume) of second-phase material was detected under the light microscope in both alloys. One or two cubic lines were present in the x-ray diffraction patterns of both alloys. The electrical resistivity values in $\mu\Omega$-cm for Ti–50 Zr and Ti–49.9 Zr–0.2 Mn were respectively: $\rho(273\text{°K}) = 97$, 98; $\rho(77\text{°K}) = 60$, 62, $\rho(4.2\text{°K}) = 51$, 53. The values quoted for Ti–49.9 Zr–0.2 Mn represent the average of determinations differing by $\approx 3\%$ on resistivity specimens cut from different parts of the calorimetric specimen.

### 3. *Magnetic Susceptibility*

Figure 5 shows the magnetic susceptibility $\chi$ versus temperature for specimens of Ti–50 Zr and Ti–49.9 Zr–0.2 Mn which were cut from the calorimetric

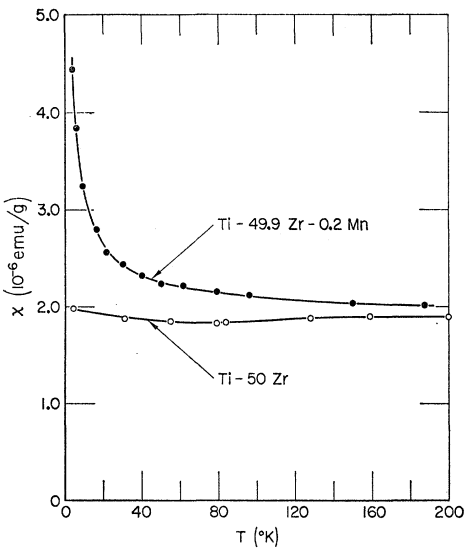


FIG. 5. Magnetic susceptibility $\chi$ versus temperature for the hcp alloys Ti–50 at.% Zr and Ti–49.9 at.% Zr–0.2 at.% Mn.

[36] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).
[37] D. Pines, Phys. Rev. **109**, 280 (1958).
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[39] C. H. Cheng, K. P. Gupta, E. C. van Reuth, and P. A. Beck, Phys. Rev. **126**, 2030 (1962).
[40] E. Bucher, F. Heiniger, J. Muheim, and J. Müller, Rev. Mod. Phys. **36**, 146 (1964).
[41] J. O. Betterton, Jr. and J. O. Scarbrough, J. Metals **15**, 686 (1963).
[42] P. Duwez, J. Inst. Metals. **80**, 525 (1952).

specimens. The susceptibility apparatus and experimental techniques have been previously described.[15] The susceptibility of Ti–50 Zr is only slightly temperature-dependent. In contrast, the susceptibility of Ti–49.9 Zr–0.2 Mn rises rapidly with decrease of temperature. In Fig. 6 the Ti–49.9 Zr–0.2 Mn data points for $10<T<100$°K are shown to fit a Curie-Weiss equation

$$\chi-\chi_0=\mathbf{C}/(T-\Theta), \qquad (3)$$

with $\Theta\approx 0$. The Curie constant $\mathbf{C}$ yields a magnetic moment value $\mu=1.1\ \mu_B$/(Mn ion), using the standard relationships[15] and assuming negligible orbital contributions.

### 4. *Electrical Resistivity versus Temperature*

Figure 7 shows normalized electrical resistivity versus temperature curves for Ti–50 Zr and Ti–49.9 Zr–0.2 Mn specimens which were cut from the calorimetric specimens. For Ti–50 Zr a relatively sharp resistive transition at $T_r\approx 1.6$°K is observed, as might be expected

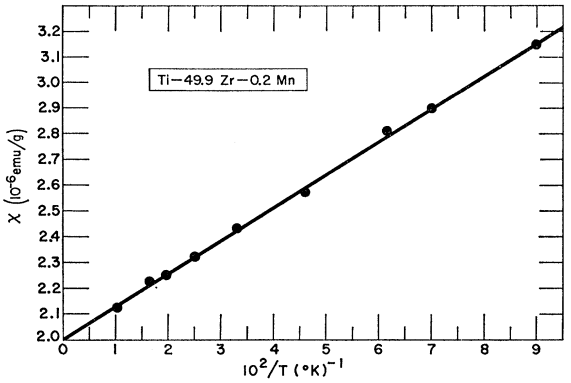


FIG. 6. Curie-Weiss-type plot of the susceptibility data for the hcp alloy Ti–49.9 at.% Zr–0.2 at.% Mn. The slope of the line determines the Curie constant $1.28\times10^{-5}$ emu °K/g.

from the calorimetric measurements. In contrast, Ti–49.9 Zr–0.2 Mn exhibits a very broad and incomplete resistance versus temperature transition characteristic of nonbulk superconductivity. It is noteworthy that some superconductivity exists at temperatures above the $T_c$ of the relatively Mn-free Ti–50 Zr alloy, possibly due to bcc inclusions, just as hypothesized[15] for dilute arc-cast Ti-Mn. Alternatively, regions of dimension $d\gtrsim\xi$ which are subjected to relatively low effective internal fields $H_e$ could become superconducting at local transition temperatures elevated by a density-of-states effect. According to some analyses of the random dilute localized-moment problem,[43–46] the probability of zero or near-zero $H_e$ at any given ion site is relatively high. A somewhat similar suggestion has been made by de Gennes and Sarma[2] with regard to dilute hcp Ti-Fe.

[43] W. Marshall, Phys. Rev. **118**, 1519 (1960).
[44] J. Friedel, J. Phys. Radium **23**, 692 (1962).
[45] M. W. Klein and R. Brout, Phys. Rev. **132**, 2412 (1963).
[46] M. W. Klein, Phys. Rev. Letters **11**, 408 (1963).

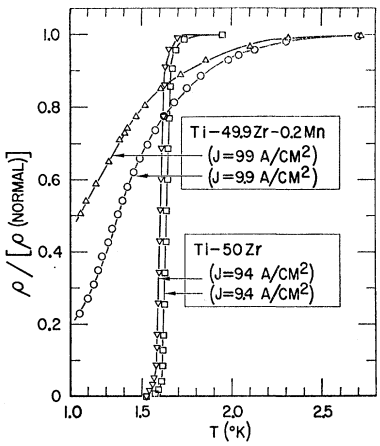


FIG. 7. Normalized electrical resistivity versus temperature $T$ for the hcp alloys Ti–50 at.% Zr and Ti–49.9 at.% Zr–0.2 at.% Mn for two different measuring current densities $J$.

### 5. *Electrical Resistivity versus Magnetic Field*

Figure 8 shows normalized resistivity as a function of transverse magnetic field ($H\perp J$) at $T=1.17$°K for Ti–50 Zr and Ti–49.9 Zr–0.2 Mn. For Ti–50 Zr, a relatively sharp $\rho$ versus $H$ transition is observed at $3<H<5$ kG. The resistive onset field at a current density $J=10$ A/cm², $H_r(J=10,\ T=1.17\text{°K})=3$–4 kG, is in agreement with the upper critical field $H_{c2}(T=1.17\text{°K})=3.3$ kG of the Ginzburg-Landau-Abrikosov-Gor'kov theory of type II superconductors as calculated from the Gor'kov-Goodman formula using the measured values of $\gamma$, $\rho(4.2\text{°K})$, and $T_c$.[47] The approximate equality of the observed $H_r(J=10)$ and the calculated $H_{c2}$ has been observed in other transition-metal alloys.[48]

In contrast, the field-induced restoration of normal resistance in Ti–49.9 Zr–0.2 Mn is spread over a very

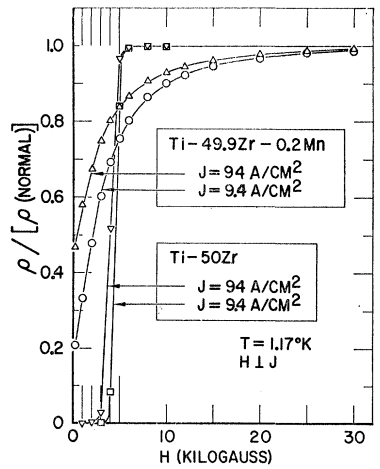


FIG. 8. Normalized electrical resistivity versus transverse magnetic field $H$ for the hcp alloys Ti–50 at.% Zr and Ti–49.9 at.% Zr–0.2 at.% Mn for two different measuring current densities $J$ at a temperature $T=1.17$°K.

[47] For the pertinent references, see the bibliography in Ref. (48). In the present $H_{c2}$ calculation we have used the approximate Eq. (3) of T. G. Berlincourt and R. R. Hake, Phys. Rev. Letters **9**, 293 (1962).
[48] T. G. Berlincourt and R. R. Hake, Phys. Rev. **131**, 140 (1963).

broad field region. The normal resistance is 99% restored at the maximum field of 30 kG, a factor 9 greater than the calculated $H_{c2}$(1.17°K) of the Ti-Zr solvent. The persistence of some superconductivity at such high fields in Ti–49.9 Zr–0.2 Mn could be due to one or a combination of several factors: (a) small dimensions (comparable to the superconducting penetration depth $\lambda$) of localized superconducting regions, (b) high $H_{c2}$ of localized superconducting regions, (c) cancellation by the external field of internal effective fields associated with localized moments.[49,50]

### E. Concentrated bcc Ti-Mn

The high-temperature-stable bcc phase of Ti-Mn is reported to be completely retained at room temperature in rapidly quenched alloys containing Mn concentrations greater than about 5.6 at.%.[51] Previous work[34,48,52] on similar metastable bcc Ti-rich binary alloys has indicated that if the addition element concentration is somewhat greater than the minimum required for bcc retention at room temperature, then the bcc structure will be retained at liquid-helium temperatures. Figure 2 shows $C/T$ versus $T^2$ for such a metastable bcc arc-cast alloy, Ti–14 Mn. After completion of the specific-heat measurements the Ti–14 Mn specimen was cut into sections for metallographic, x-ray, and electrical-resistivity studies. A relatively large amount of an undetermined second phase ($\approx$10% by volume) was observed to exist in a bcc matrix. However, the qualitative features of the calorimetric results are probably not seriously affected. The electrical-resistivity measurements indicated the following values in $\mu\Omega$-cm: $\rho(273°\text{K})=175$, $\rho(77°\text{K})=180$, $\rho(4.2°\text{K})=182$. The relatively high electrical resistivity and the anomalous negative temperature coefficients of resistivity are typical of binary bcc Ti-rich alloys.[52]

In contrast to the localized-moment, nonbulk-superconducting behavior of hcp Ti-Mn and Ti-Zr-Mn alloys, predominantly bcc Ti–14 Mn exhibits (1) standard normal-state specific-heat behavior, Eq. (1), with no evidence of localized moments, and (2) a standard, bulk, calorimetric superconducting transition.

The midpoint of the negative slope portion of a $C$ versus $T$ curve for Ti–14 Mn determines the superconducting transition temperature $T_c=2.55°\text{K}$. This is somewhat lower than the 2.7°K expected on the basis of the magnetic measurements of Matthias *et al.*[11] on a series of bcc Ti-Mn alloys. The elevation of $T_c$ in bcc Ti–14 Mn over that in pure hcp Ti is probably related to the higher $\gamma$ value in the bcc alloy. The standard bulk superconductivity of the Ti-Mn bcc phase is consistent with the view[15] that filaments of such material are responsible for the superconductivity observed in arc-cast dilute Ti-Mn alloys.

The $\gamma$ and $\theta_D$ values characterizing the normal-state specific heat are listed in Table I but are probably only of qualitative value due to the poor physical state of the present alloy. The absence of calorimetric localized-moment behavior in the normal state is consistent with the appearance of standard bulk superconductivity and with the absence[14,15] of Curie-Weiss susceptibility behavior.

Below $T_c$, the $C/T$ versus $T^2$ curve of Ti–14 Mn drops sharply in accord with the usual superconducting state energy-gap behavior. The usual plot of $\log(C_{es}/\gamma T_c)$ versus $T_c/T$, where $C_{es}$ is the electronic contribution to the superconducting state specific heat, shows very close agreement with the BCS prediction[36] as calculated by Muhlschlegel,[53] over the measured range $1.1<(T_c/T)<1.9°\text{K}$. Considering the poor physical state of the present alloy the quantitative agreement of $C_{es}(T)$ with theory may be only fortuitous. However, the qualitative behavior of $C_{es}(T)$ does reinforce the view that the bcc phase of Ti-Mn is standard "nonmagnetic" superconducting material.

## III. DISCUSSION

### A. Localized Magnetic Moments

#### 1. Formation

The present observation of large low-temperature specific-heat anomalies in dilute hcp Ti-Mn supports the view that the 4–300°K Curie-Weiss-type temperature dependence of the magnetic susceptibility[14,15] and the low-temperature electron-transport-property anomalies[7] (*minima* is the electrical resistivity versus temperature curves, *negative* magnetoresistivities, *field-dependent* Hall coefficients) observed in dilute hcp Ti-Mn are a result of the formation of localized magnetic moments. Although it has been shown by Elcock *et al.*[54] that a Curie-Weiss-type temperature dependence of the high-temperature magnetic susceptibility is explicable on the basis of a collective band model, such a model will not yield a specific heat which increases with decrease of temperature in the liquid-helium temperature region, as observed for hcp Ti-Mn, except possibly for the rather

[49] We assume here that in an alloy containing dilute localized moments in random solid solution there may exist regions of dimension $d\gtrsim\xi$ (the superconducting state electronic "coherence distance") where the spatial average of localized-moment-induced effective internal fields $H_e$ is of similar magnitude but opposite in direction to the applied field, so that the net effective field impressed upon the conduction electrons is small and superconductivity may exist. A similar idea has been discussed for the case of ferromagnets with negative conduction electron polarization by V. Jaccarino and M. Peter, Phys. Rev. Letters **9**, 290 (1962). Mechanisms for negative conduction electron polarization also exist in the dilute alloy case (Refs. 50, 56, 61–64) where (in zero applied field) a continuous spectrum of $H_e$ values ranging in magnitude from zero to very high values may exist (Refs. 43–46).

[50] P. W. Anderson and A. M. Clogston, Bull. Am. Phys. Soc. **6**, 124 (1961).

[51] D. J. Maykuth, H. R. Ogden, and R. I. Jaffee, Trans. AIME **197**, 225 (1953).

[52] R. R. Hake, D. H. Leslie, and T. G. Berlincourt, Phys. Chem. Solids **20**, 177 (1961).

[53] B. Muhlschlegel, Z. Physik. **155**, 313 (1959).

[54] E. W. Elcock, P. Rodes, and A. Teviotdale, Proc. Roy. Soc. (London) **A221**, 53 (1954).

unlikely case of an extremely narrow "critical point" peak in the electronic-state density at or very near the Fermi energy.[55] From the localized-impurity-state point of view, Anderson[56] has suggested that *nonmagnetic* localized virtual $d$ states might produce a large, slightly temperature-dependent susceptibility in a dilute alloy while increasing only slightly (no more than 20–30%) the coefficient of the standard linear-in-temperature specific-heat term. Thus the present observation (Figs. 1 and 3) of a very large and nonlinear-in-temperature specific-heat excess would argue against nonmagnetic localized-state explanations of the properties of dilute hcp Ti-Mn. In the remainder of the discussion we shall assume that localized magnetic moments do exist in hcp Ti-Mn.

The theory of localized moment formation has recently been discussed by a number of authors[8,44,56–59] from somewhat different viewpoints. Experimentally, the work of Matthias *et al.*[6] and Clogston *et al.*[8] seems to indicate that the degree of moment localization of Fe ions in dilute solution in various 4*d* transition-metal and alloy solvents is inversely correlated with the electronic specific-heat coefficient $\gamma$ of the solvent (except for solvents near the end of the 4*d* series). The present work, although not intended as a systematic investigation of such regularity, is at least consistent with those results. The degree of moment localization associated with each Mn ion goes from $\approx 3.5\mu_B$ in hcp Ti ($\gamma=3.3$), to $\approx 1\mu_B$ in hcp Ti–50 Zr ($\gamma=4.2$), to $\approx 0\mu_B$ in a predominantly bcc Ti–14 Mn alloy ($\gamma=5.5$) where all $\gamma$ values are in mJ/mole (°K)$^2$.

An important aspect of the present results, taken together with previous investigations on dilute Ti alloys,[7,15,30] is the demonstration of the crucial importance of the electronic character of the *solute* in determining localized-impurity-state characteristics. Of all the "magnetic" transition elements (Cr, Mn, Fe, Co, Ni) *only Mn displays strong localized-moment behavior in dilute solution in hcp Ti.* The elements Cr and Fe, on either side of Mn in the periodic table, do give rise to low-temperature electrical-resistivity minima[7] when in dilute ($\approx 1$ at.%) solution in hcp Ti (whereas Co and Ni do not), and Fe appears to lower the superconducting transition temperature of hcp Ti.[18] However, for $\approx 1$ at.% additions of Cr, Fe, Co, or Ni to hcp Ti no other prominent localized-moment indications are observed in (1) the 4.2°K magnetoresistivities[7] (Ti-Cr, Ti-Fe, Ti-Co, Ti-Ni), (2) the 4.2°K Hall coefficients[7] [Ti-Fe, Ti-Cr (although the sign is anomalously positive here)], (3) the 4–300°K magnetic susceptibilities[15] (Ti-Cr, Ti-Fe, Ti-Co,) or (4) the low-temperature specific heats (Ti-Fe,[30] Ti-Co). It is possible that Cr and Fe form localized states in hcp Ti which only verge on a pronounced localized-moment condition.

As previously indicated,[15] the solute-sensitive nature of moment localization is also apparent in hcp Zr. Here $\approx 1$ at.% additions of Mn[32] (but not Cr or Fe[60]) produce 4.2°K negative magnetoresistance; and $\approx 1$ at.% additions of Mn[33] (but not Fe[8]) produce Curie-Weiss-type temperature dependence of the 4–300°K magnetic susceptibility. For the case of hcp Hf,[60] dilute additions of Mn and Cr (but not Fe) produce 4.2°K negative magnetoresistance, suggesting more prevalent moment localization in Hf than in Ti or Zr. Negative magnetoresistance *is* observed[60] at 1.2°K in dilute hcp Zr-Cr and Hf-Fe.

### 2. *Interaction*

The nature of the interactions which occur once localized moments have formed is of interest. An interaction of the type derived by Ruderman and Kittle,[61] Kasuya,[62] Yosida,[63] and Blandin and Friedel[64] (essentially an indirect exchange between localized moments via a spatially oscillating conduction-electron-spin polarization) has been invoked by Marshall[43] and Klein and Brout[45] to explain the low-temperature specific-heat anomalies in dilute Cu-Mn.[26] More recently Klein[46] has argued that a Ruderman-Kittel type interaction (RK) will also serve to explain the specific-heat anomalies observed in dilute Cu-Fe by Franck *et al.*[27] and in dilute Cu-Co by Crane and Zimmerman.[65] Considering the rough similarity of the specific-heat anomalies (Fig. 3), RK might also occur in dilute hcp Ti-Mn. That the localized moments in hcp Ti-Mn do interact with the conduction electrons is shown experimentally by the low-temperature anomalies in the electron transport properties[7] and by the Mn-induced lowering of the superconducting transition temperature of hcp Ti observed by Falge.[18] However, considerable uncertainty exists as to the nature of magnetic interactions in metals, and other long-range coupling mechanisms for dilute localized moments in a transition metal base alloy may be important[1]: e.g., (1) coupling via a static spin density wave in the conduction electron gas,[66] (2) coupling via hybridization of localized and conduction-electron wave functions,[50,56] (3) coupling via a spatially oscillating spin polarization of $d$ electrons in a nearly empty or nearly full band.[67] Indeed, even assuming that RK dominates, there is disagreement as to the type of

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[56] P. W. Anderson, Phys. Rev. **124**, 41 (1961).
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[62] T. Kasuya, Progr. Theoret. Phys. (Kyoto) **16**, 45 (1956).
[63] K. Yosida, Phys. Rev. **106**, 893 (1957); **107**, 396 (1957).
[64] A. Blandin and J. Friedel, J. Phys. Radium **20**, 160 (1959).
[65] L. T. Crane and J. E. Zimmerman, Phys. Rev. **123**, 113 (1961). See also R. Tournier, J. J. Veyssié, and L. Weil, J. Phys. Radium **23**, 672 (1962).
[66] A. W. Overhauser, Phys. Chem. Solids **13**, 71 (1960); J. Appl. Phys. 34, 1019 (1963).
[67] J. Friedel, G. Leman, and S. Olszewski, J. Appl. Phys. Suppl. **32**, 325S (1961).

localized-moment ordering to be expected at low temperature in the dilute random alloy case. Blandin and Friedel,[64] and Klein and Brout[45] suggest a complex antiferromagnetic type of short-range ordering which seems to be consistent with much of the experimental data. On the other hand, Abrikosov and Gor'kov[68] suggest that the RK interaction should lead to homogeneous polarization of the conduction-electron spin and consequent ferromagnetic ordering of localized moments. If their argument is correct, then the experimental indications[69] of a more complex type of ordering in dilute localized moment alloys would suggest that interactions other than RK may be important. More experimental and theoretical work seems needed in this area.

### B. Superconductivity

The present calorimetric measurements do not reveal standard bulk superconducting transitions in arc-cast hcp Ti–0.85 Mn, Ti–1.7 Mn, or Ti–1 Co. These calorimetric results can be reconciled with earlier magnetic measurements indicating[11] $T_c > 1.2$°K and with earlier observations of zero electrical resistance above[7] 1.2°K in such arc-cast alloys in several ways: (1) The magnetic and resistive measurements may reflect only a localized type of superconductivity, (2) standard bulk superconductivity may exist but the standard bulk superconducting calorimetric transitions may be obscured by localized-moment ordering contributions to the specific heat, or (3) bulk superconductivity of some unusual type which does not show up prominently in a calorimetric measurement may exist (e.g., zero-gap superconductivity[70–72] induced by localized magnetic moments). However, the absence of any trace of superconductivity in resistivity measurements[15] down to 1.1°K in hcp Ti–1 Mn and Ti–2 Mn alloys which were very rapidly quenched through the two phase hcp-bcc region strongly suggests that the superconductivity observed[7,11] in arc-cast hcp Ti-Mn is a localized type atypical of the bulk specimen, and that no bulk superconductivity of any kind exists above 1.2°K in dilute hcp Ti-Mn alloys. Similarly, the incompleteness of the resistance versus temperature transition in hcp Ti–49.9 Zr–0.2 Mn (Fig. 7) indicates that no bulk superconductivity of any kind exists above 1.2°K in that alloy. As for hcp Ti–1 Co, the possibility of bulk superconductivity above 1.2°K seems remote but cannot be entirely dismissed.

The general rule[6,12,13] that localized moments depress $T_c$ seems to be borne out in the present work. The bulk $T_c$ of Ti–50 Zr drops from 1.6°K to less than 1.2°K with the addition of 0.2 at.% Mn (i.e., $|dT_c/dc| \geq 2$°K/at.%), presumably due to the localized moments whose existence is suggested by the susceptibility and specific-heat results. Similarly, the localized moments associated with the Mn ions in hcp Ti apparently result in the lowering of the superconducting transition temperature of "iodide-process" Ti from 0.17°K to below 0.06°K with the addition of $\approx$70-ppm Mn (i.e., $|dT_c/dc| \gtrsim 15$°K/at.%).[18] On the other hand, the predominantly bcc Ti–14 Mn alloy, which displays no evidence of localized moments, appears to be a conventional bulk superconductor with a relatively high $T_c = 2.55$°K. The lowering of $T_c$ by dilute localized moments is generally considered[2,28,70,73–75] to be due to an exchange interaction between conduction electrons and localized moments. However, the present uncertainty as to the detailed nature of localized moments, of conduction electron-localized moment interactions, and of dilute localized moment ordering prevents any really satisfactory understanding of dilute "magnetic" superconductors.

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