

Low-Temperature Resistivity Minima and Negative Magnetoresistivities in some Dilute Superconducting Ti Alloys*

R. R. HAKE, D. H. LESLIE, AND T. G. BERLINCOURT

Atomics International Division of North American Aviation, Inc., Canoga Park, California

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Electrical resistivities in the range 1.1 to 35°K and magneto-resistivities in the range 1.1 to 4.2°K have been measured in a number of dilute, superconducting hcp Ti alloys. Resistivity minima occurring between 14 and 18°K are observed in $\approx 99.92\%$ pure Ti, and in Ti-Mn alloys with Mn concentrations between 0.02 and 2.0 at.% (nominal atomic percent). Negative magneto-resistivities between 2.6 and 7.2% at 30 kG and 4.2°K are observed in Ti-Mn alloys with Mn concentrations between 0.1 and 2.0 at.%. The absolute magnitude of the negative magnetoresistance increases as temperature decreases for $T_s < T < 4.2^\circ\text{K}$, where T_s is the temperature at which the zero-field resistivity begins to decrease due to the onset of superconductivity. Field- and temperature-dependent Hall coefficients are observed at liquid helium

temperatures in Ti containing Mn concentrations of 1.0 and 2.0 at.%. Ti alloys containing 1.2 at.% Cr and 0.96 at.% Fe display resistivity minima at about 17°K, but, unlike Ti-Mn alloys, they have small positive magnetoresistivities and do not exhibit field-dependent Hall coefficients at 4.2°K. Neither negative magneto-resistivities nor significant resistivity minima are observed in Ti containing 1.3 at.% Co, 1.0 at.% Ni, 1.1 at.% Al, or 1.0 at.% Nb. Considered in the light of recent ideas regarding the origin of the low-temperature resistive anomalies, the data suggest that localized magnetic moments exist in dilute superconducting Ti alloys containing Cr, Mn, and Fe, and that the conduction electrons interact with these moments.

I. INTRODUCTION

OVER the past thirty years there have been many observations of "anomalous" resistance maxima and/or minima and the often associated negative magnetoresistance in certain dilute metallic alloys at temperatures below about 25°K.¹⁻³ Nearly all these observations have been confined to dilute solutions of various metals (especially transition metals) in Cu, Ag, Au, Mg, and Zn. In order to gain more insight into the problem of low-temperature resistive anomalies it would appear profitable to extend the search for such behavior to a wider variety of dilute alloys. Several years ago Berlincourt⁴ observed negative magnetoresistance at liquid helium temperatures in a single crystal of Ti thought to contain Mn as an impurity, and the similarity of the magneto-resistive behavior of Ti-Mn to that of Cu-Mn was pointed out. Since recent ideas and experiments would associate dilute alloy negative magnetoresistance with the presence of

localized magnetic moments,⁵⁻⁸ the Ti-Mn behavior⁹ is of particular interest as an apparent violation of the simple collective band model often applied to transition metals and alloys,^{10,11} and a more extensive experimental investigation seems warranted.

Although low-temperature resistive anomalies have been observed in some other impure transition metals, only fragmentary information has thus far been generated. In 1930, Meissner and Voigt¹² reported that the resistance of specimens of Co and Mo increased with decrease of temperature in the liquid helium temperature region. In 1952, Thomas and Mendoza¹³ reported a negative temperature coefficient of resistance below 4.2°K in each of five specimens of impure Mo wire. Negative magnetoresistance was observed in only one of the five specimens. Thomas and Mendoza observed no anomalous resistive behavior in specimens of Co or W between 4.2 and 0.06°K. Recently, MacDonald, Pearson, and Templeton¹⁴ have observed low-temperature thermoelectric anomalies in Pd and Pt containing dilute amounts of Fe.

Aside from the relevance of the low-temperature resistive and magnetoresistive behavior of dilute Ti

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¹ For a review of experiment and theory, see J. M. Ziman, *Electrons and Phonons* (Oxford University Press, London, 1960), p. 344. This discussion was written prior to the illuminating work of A. V. Gold, D. K. C. MacDonald, W. B. Pearson, and I. M. Templeton, *Phil. Mag.* **5**, 765 (1960), demonstrating that the resistance minimum and the associated thermoelectric power anomaly produced in Cu by dilute addition of nontransition metals such as Ga, Ge, and Sn is most probably due to the internal reduction of iron oxide by the solute, thus placing the iron in solid solution.

² For work on Au-Co and a tabulation of resistive, magnetic, and thermal property results on fifteen different dilute alloy systems (with references), see A. N. Gerritsen, *Physica* **25**, 489 (1959).

³ For the most recent and inclusive review see G. J. van den Berg, in *Proceedings of the Seventh International Conference on Low-Temperature Physics, Toronto, 1960*, edited by G. M. Graham and A. C. Hollis Hallett (University of Toronto Press, Toronto, 1961), p. 246.

⁴ T. G. Berlincourt, *Phys. Rev.* **114**, 969 (1959).

⁵ K. Yosida, *Phys. Rev.* **107**, 396 (1957).

⁶ J. M. Ziman, reference 1, p. 348.

⁷ R. W. Schmitt and I. S. Jacobs, *Can. J. Phys.* **34**, 1285 (1956); *J. Phys. Chem. Solids* **3**, 324 (1957).

⁸ I. S. Jacobs and R. W. Schmitt, *Phys. Rev.* **113**, 459 (1959).

⁹ The alloy designation *A-B* or *A-NB* will be used to designate dilute alloys in which *A* is the solvent, *B* is the solute, and *N* is a number indicating the solute concentration in atomic percent.

¹⁰ For an informal review of various ideas about the electronic character of transition metals, see C. Herring, *J. Appl. Phys.* **31**, 3S (1960).

¹¹ For some recent theories on the nature of localized moments in transition metals, see John B. Goodenough, *Phys. Rev.* **120**, 67 (1960); J. Friedel, G. Leman, and S. Olszewski, *J. Appl. Phys.* **32**, 325S (1961); and P. W. Anderson, *Phys. Rev.* **124**, 41 (1961).

¹² W. Meissner and B. Voigt, *Ann. Physik* **7**, 892 (1930).

¹³ J. G. Thomas and E. Mendoza, *Phil. Mag.* **43**, 900 (1952).

¹⁴ D. K. C. MacDonald, W. B. Pearson, and I. M. Templeton, *Phil. Mag.* **5**, 867 (1960).

alloys to the resistance minimum problem, this behavior is of interest from the superconductivity standpoint, especially in view of the recent work of Matthias *et al.*¹⁵ showing that the superconducting transition temperature of hcp Ti is markedly increased by the addition of dilute amounts of Cr, Mn, Fe, and Co. A conduction electron-localized moment exchange interaction, such as is often invoked to account for low-temperature negative magnetoresistance and associated resistive, thermal, and magnetic anomalies in dilute alloys,^{5,16-25} might instead be expected to depress the superconducting transition temperature.²⁶

In the present paper²⁷ we discuss the results of an investigation of the low-temperature resistivity and magnetoresistivity of a series of dilute hcp Ti-Mn alloys and of hcp Ti alloys containing about one at. % (atomic percent) of Al, Cr, Fe, Co, Ni, Zr, and Nb. Some Hall coefficient data on dilute Ti-Mn, Ti-Fe, and Ti-Cr are also reported. The possible significance of the observed low-temperature resistive, magnetoresistive, and Hall effect anomalies with respect to the magnetic nature of dilute Ti alloys is indicated.

II. APPARATUS AND METHOD

The cryogenic, magnetic, and electrical equipment, as well as the measuring method employed in this experiment have, for the most part, been described elsewhere.^{4,28,29} The resistivity measurements in the temperature range above 4.2°K were made during a slow warm-up (about 1.5 h between 4.2 and 35°K) effected via the desorption of liquid helium from cotton.³⁰ Temperatures in this range were measured by means of a copper-constantan thermocouple. The primary junction

was clamped against one end of the specimen, and the reference junction was immersed in a liquid helium bath at 4.2°K. A voltage-temperature calibration curve between 4.2 and 35°K was derived from that given by Bunch, Powell, and Corruccini³¹ and temperature calibration points taken at the normal boiling points of He (4.2°K), H₂ (20.4°K), and Ne (27.1°K), and the superconducting transition of high-purity Pb (7.2°K). It is estimated that the absolute temperature values may be in error by $\pm 1^\circ\text{K}$ between 5.0 and 35°K.

Magnetoresistive, Hall, and thermocouple voltages were normally measured with a Rubicon microvolt potentiometer and photoelectric galvanometer such that readings could be made to $10^{-3} \mu\text{V}$. Magnetoresistive and Hall voltages were usually measured at 5-kG intervals between zero field (actually the residual field of the magnet ≈ 200 G) and 30 kG. A Leeds and Northrup K-3 potentiometer was normally used for the resistance measurements. Measuring currents between 0.4 and 1.2 A were usually employed, and were maintained constant to approximately 0.001% by means of a Garwin-type current regulator.³² Thermal voltages were eliminated from resistive voltage readings in the usual manner, and from the Hall voltages by a field reversing procedure. Absolute values of resistivity may be in error by $\pm 3\%$ due primarily to uncertainties in specimen dimensions, but relative values in the 1.1 to 35°K range are probably accurate to $\pm 0.2\%$.

III. SPECIMENS

The bcc (β) phase of Ti is stable from the melting point down to about 1156°K, at which point it transforms martensitically to the low-temperature stable hcp (α) phase.³³ Above the α - β boundary there is extensive solid solubility in bcc Ti of the solute elements of concern here (Al, Cr, Mn, Fe, Co, Ni, Zr, Nb). Except for Al and Zr, the maximum equilibrium solid solubility of these elements is severely restricted in the hcp phase (i.e., less than 1 at. %, except in the case of Nb). However, dilute metastable hcp solid solutions can be formed by quenching the alloys to room temperature from the bcc phase field, since at low enough solute concentrations the martensitic β to α transformation apparently goes to completion above room temperature.

Crystal bar, "iodide process" Ti, produced by the Foote Mineral Company, was used in this study. A typical purity of 99.92 wt. % (weight percent) is claimed by the manufacturer for this type of Ti. Typical impurities are given as: Zr, 0.05 wt. %; Si and Al, 0.005 wt. %; Mg, Mn, Ca, 0.003 wt. %; and Cr, Fe, O₂, and N₂, 0.002 wt. %. The solute materials used in

¹⁵ B. Matthias, V. B. Compton, H. Suhl, and E. Corenzwit, *Phys. Rev.* **115**, 1597 (1959); also B. Matthias, M. Peter, H. J. Williams, A. M. Clogston, E. Corenzwit, and R. C. Sherwood, *Phys. Rev. Letters* **5**, 542 (1960).

¹⁶ R. W. Schmitt, *Phys. Rev.* **103**, 83 (1956).

¹⁷ K. Yosida, *Phys. Rev.* **106**, 893 (1957).

¹⁸ R. E. Behringer, *J. Phys. Chem. Solids* **2**, 209 (1957).

¹⁹ A. J. Dekker, *Physica* **25**, 1244 (1959).

²⁰ A. Blandin and J. Friedel, *J. phys. radium* **20**, 160 (1959).

²¹ A. W. Overhauser, *J. Phys. Chem. Solids* **13**, 71 (1960).

²² W. Marshall, *Phys. Rev.* **118**, 1519 (1960).

²³ A. D. Brailsford and A. W. Overhauser, *J. Phys. Chem. Solids* **15**, 140 (1960).

²⁴ A. R. de Vroomen and M. L. Potters, *Physica* **27**, 657 (1961).

²⁵ M. Bailyn, Westinghouse Research Laboratories Scientific Paper 029-B000-P1 (unpublished).

²⁶ For recent reviews of the pertinent theory and experiments, see P. W. Anderson, in *Proceedings of the Seventh International Conference on Low-Temperature Physics, Toronto, 1960*, edited by G. M. Graham and A. C. Hallett (University of Toronto Press, Toronto, 1961), p. 298; also, J. Bardeen and J. R. Schrieffer, in *Progress in Low-Temperature Physics*, edited by C. J. Gorter (Interscience Publishers, Inc., New York, 1961), Vol. III, p. 275ff.

²⁷ For a brief, preliminary account of this work, see R. R. Hake, D. H. Leslie, and T. G. Berlincourt, *Bull. Am. Phys. Soc.* **6**, 146 (1961).

²⁸ T. G. Berlincourt, *Phys. Rev.* **112**, 381 (1958).

²⁹ R. R. Hake, D. H. Leslie, and T. G. Berlincourt, *J. Phys. Chem. Solids* **20**, 177 (1961).

³⁰ J. O. Linde, in *Proceedings of the Fifth International Conference on Low-Temperature Physics and Chemistry, Madison, Wisconsin, 1957*, edited by J. R. Dillinger (University of Wisconsin Press, Madison, Wisconsin, 1958), p. 402.

³¹ As quoted in R. B. Scott, *Cryogenic Engineering* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1959), p. 349.

³² R. L. Garwin, *Rev. Sci. Instr.* **29**, 223 (1958); R. L. Garwin, D. Hutchinson, S. Penman, and G. Shapiro, *Rev. Sci. Instr.* **30**, 105 (1959).

³³ For a review of the physical metallurgy of Ti and Ti alloys, see R. I. Jaffee in *Progress in Metal Physics*, edited by B. Chalmers and R. King (Pergamon Press, New York, 1958), Vol. 7, p. 65.

this study are all believed to have been greater than 99.4 wt.% pure, except for the Zr which may have contained 3 wt.% Hf. The alloys were melted under one-half atmosphere of "gettered" argon in a laboratory arc-furnace utilizing a water-cooled copper hearth and a tungsten electrode. Chips of the solute material were inserted into a narrow hole drilled in the Ti crystal bar, and the alloy was then arc-melted at least six times. The button was inverted after each melt in order to promote homogeneity. Rapid quenching of the melt (in direct contact with the water-cooled copper hearth) occurred when the arc was broken. In order to avoid possible contamination and segregation, the arc-melted buttons were not subjected to homogenizing treatments, such as cold-working and high-temperature annealing. Sections were cut directly from the arc-melted buttons and then ground and polished to a form ($\approx 1 \times 0.12 \times 0.010$ in.) suitable for resistivity and Hall coefficient measurements.

Table I shows the nominal at.% of solute for each of the alloys studied as calculated from the weights of the starting materials. The weight loss during melting of each alloy was less than 0.03% of the total weight of the starting materials, except in the case of the Ti-Mn alloys, where this loss varied from 0.03% for the Ti-0.018 Mn specimen⁹ to 0.18% for the Ti-2.01 Mn specimen. An analysis of these weight losses in relation to the starting solute weights and an estimate of the degree of inhomogeneity of the alloy buttons based upon previous experience with similarly arc-melted Ti-Mo buttons,²⁹ suggest that the actual specimen solute concentrations may differ from the nominal values listed in Table I by +5% to -15% for the Ti-Mn alloys and by +5% to -10% for the other Ti alloys. In addition to the uncertainty in the true specimen solute concen-

tration due to possible loss of solute during melting and to button inhomogeneity, there exists the possibility that some of the solute may have precipitated out of solution during the quenching. The 4.2°K resistivities of all the alloys are listed in Table I and indicate that an appreciable amount of the alloying element did go into solution in the Ti in each case.

For convenience, the alloys will be designated in terms of the nominal solute concentrations, "at.%" will mean nominal atomic percent when used with reference to alloy composition, and the low-temperature resistive and magnetoresistive properties will be shown plotted against the nominal solute concentration values.

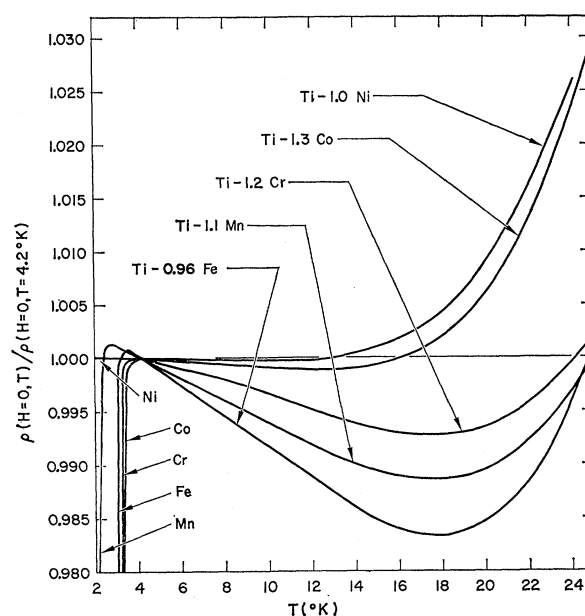


FIG. 1. Resistivity-temperature curves (normalized at 4.2°K) measured in zero magnetic field for Ti alloys containing about one at.% of various solutes, as indicated. The sharp fall of the resistivity curves below 4.2°K is due to the onset of superconductivity. Ti-NB means Ti containing *N* nominal at.% of solute *B*.

Sections of the buttons adjacent to the resistivity specimens were examined via microscopy and x-ray diffraction. No cubic material, indicative of an incomplete β to α transformation during the quench was observed in any of the microscopic or x-ray examinations. All the specimens appeared to be homogeneous under the light microscope. Samples of Ti-Mn containing up to and including 0.114 at.% Mn had a coarse α -Ti "platelet" structure, typical of pure Ti which has been quenched from the β -phase field.³⁴ Ti-Mn alloys containing 0.212 at.% Mn and above showed a progressively more striated martensitic appearance.³⁵

³⁴ H. R. Ogden and F. C. Holden, Battelle Memorial Institute TML Report No. 103 (unpublished), p. 7, Fig. 2(a). Ti-1.06 Al, Ti-1.00 Zr, and Ti-1.00 Nb also exhibit microstructures similar to that shown in Fig. 2(a).

³⁵ Reference 34, p. 26, Fig. 15(a). Ti-1.15 Cr, Ti-0.96 Fe,

TABLE I. Resistivity and resistivity minima data for dilute Ti alloys in zero magnetic field.

Solute at.% (nominal) ^a	$\rho(273^\circ\text{K})$ ($\mu\Omega\text{-cm}$)	$\rho(4.2^\circ\text{K})$ ($\mu\Omega\text{-cm}$)	$\frac{\rho(273^\circ\text{K})}{\rho(4.2^\circ\text{K})}$	$10^2 \Delta\rho_T^b$ $\rho(4.2^\circ\text{K})$	T_{\min}^c (°K)
$\approx 0^d$	42.2	1.44	29.3	0.839	14.1
0.018 Mn	42.1	1.71	24.6	0.715	14.3
0.101 Mn	43.5	3.66	11.9
0.114 Mn	42.8	2.88	14.9	1.637	16.2
0.212 Mn	46.5	5.47	8.50	1.638	18.3
0.407 Mn	47.8	6.85	6.98
1.00 Mn	49.5	7.81	6.34
1.06 Mn	50.0	8.22	6.08	1.181	17.0
2.01 Mn	54.1	10.7	5.06	1.028	17.9
1.15 Cr	48.6	7.36	6.60	0.835	16.8
0.96 Fe	44.3	3.44	12.9	1.663	17.3
1.29 Co	46.9	3.43	13.7	0.117	12.0
1.01 Ni	45.4	4.37	10.4	0.027	10.9
1.00 Nb	47.2	3.65	12.9	0.135	8.6
1.06 Al	55.9	15.2	3.68	0.028	12.5
1.00 Zr	44.1	3.22	13.7

^a Calculated from the weights of the starting materials.

^b $\Delta\rho_T = \rho(H=0, T=4.2^\circ\text{K}) - \rho(H=0, T=T_{\min})$.

^c Estimated accuracy is $\pm 1^\circ\text{K}$.

^d Nominally, 99.92 wt.% pure Foote "iodide" crystal bar Ti from lot No. 005-1.

IV. EXPERIMENTAL RESULTS

A. Resistivity in Zero Magnetic Field

1. Resistivity Minima

Figure 1 shows low-temperature resistance-temperature curves for some of the dilute alloys of this study containing about one at. % of solute. For greater clarity the data points have been omitted since the scatter barely exceeds the line widths. The points were taken about every 0.1 to 0.5°K as temperature was increased from 4.2 to 35°K, and about every 0.2° below 4.2°K. The depths of the resistivity minima for the alloys of Fig. 1 and for other alloys measured in this work are listed in Table I, expressed in terms of a percentage of the 4.2°K resistivity, i.e. $[10^3 \Delta \rho_T] / [\rho(H=0, T=4.2^\circ\text{K})]$ where $\Delta \rho_T \equiv [\rho(H=0, T=4.2^\circ\text{K}) - \rho(H=0, T=T_{\min})]$. The temperatures at which the resistance minima occurred, T_{\min} , are also listed in Table I. The Ti-1.06 Mn specimen⁹ of Fig. 1 exhibits a re-

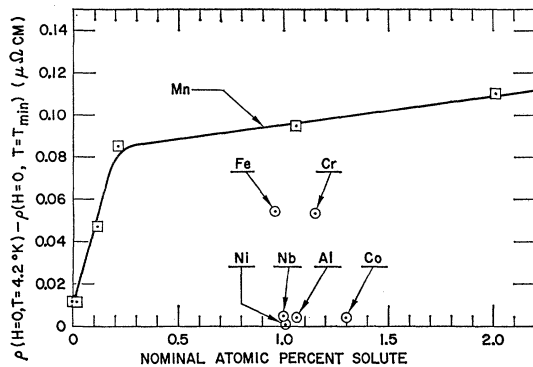


FIG. 2. The depth of the resistivity minimum in zero magnetic field, $\Delta \rho_T$, vs the nominal at. % solute concentration for various dilute Ti alloys.

sistivity minimum of 1.18%. Ti-1.15 Cr and Ti-0.96 Fe display resistivity minima of 0.83% and 1.66%, respectively. Only barely detectable resistivity minima (possibly due to Cr, Mn, and/or Fe impurities) are observed in Ti containing 1.01 at. % Ni, 1.29 at. % Co, and two other dilute alloys whose ρ vs T curves are not shown in Fig. 1: Ti-1.00 Nb and Ti-1.06 Al. The sharp decrease in the resistivities of the alloys containing Cr, Mn, Fe, and Co below 4.2°K, shown in Fig. 1, is due to the onset of superconductivity and is not to be confused with the "resistivity maximum" behavior of, for example, Cu-Mn.²

Figure 2 shows the magnitude of the resistivity minimum in zero magnetic field, $\Delta \rho_T$, vs the nominal solute concentration for various dilute Ti alloys. For Ti-Mn alloys there is a monotonic increase in $\Delta \rho_T$ with the nominal solute concentration, c , the rate of increase becoming small above 0.2 at. % Mn. The small $\Delta \rho_T$

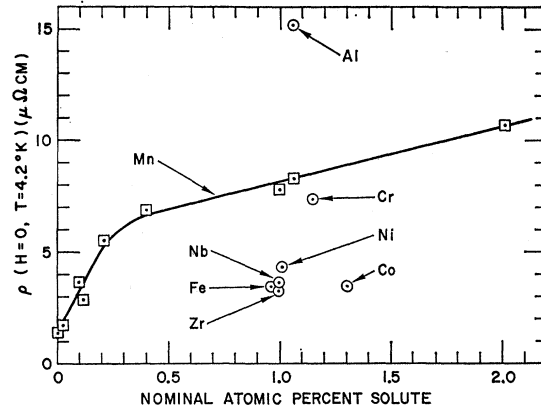


FIG. 3. Resistivity at 4.2°K and zero magnetic field vs the nominal at. % solute concentration for various dilute Ti alloys.

observed in ≈ 99.92 wt. % pure Ti (the point on the ordinate of Fig. 2) can probably be attributed to impurities. (As a rough estimate of the impurity required we take $d\Delta \rho_T/dc \approx 0.36 \mu\Omega\text{-cm}/(\text{at. \%})$ near zero solute concentration from Fig. 2. Hence the $\Delta \rho_T$ of $0.0121 \mu\Omega\text{-cm}$ observed in ≈ 99.92 wt. % pure Ti could be caused by ≈ 0.034 at. % of Mn impurity. A consideration of the magnetoresistance of the ≈ 99.92 wt. % pure Ti (Sec. IV B, 2) suggests that the Mn impurity content is actually much less than this, so that the resistance minimum is probably due primarily to Fe and/or Cr impurity.)

2. Resistivities at 4.2°K

Figure 3 shows the 4.2°K resistivities in zero magnetic field vs the nominal solute concentration for various dilute Ti alloys. For Ti-Mn alloys a break in the resistivity-solute concentration curve occurs at about 0.2 at. % Mn, just as in the $\Delta \rho_T$ vs solute concentration curve of Fig. 2. Due to the limited solid solubility of Mn in hcp Ti (0.44 at. % at 550°C)³⁶ it is possible that precipitation is responsible for the saturation effects in Figs. 2 and 3, although the magnitude of the magnetoresistivity (Fig. 5) does not saturate in this manner. The slopes of the two nearly linear sections of the $\rho(H=0, T=4.2^\circ\text{K})$ vs c curve of Fig. 3 are such that $(d\rho/dc) = 18 \mu\Omega\text{-cm}/(\text{at. \%})$ for $c < 0.2$ at. % and $(d\rho/dc) = 2.5 \mu\Omega\text{-cm}/(\text{at. \%})$ for $0.5 \leq c \leq 2.0$ at. %. Less markedly concentration-dependent values of $(d\rho/dc)$ at $c < 1$ at. % have been observed for the dilute alloys Cu-Mn,³⁷ Au-Mn,³⁷ Ag-Mn,³⁷ Au-Fe,² and Au-Ni,² for which, in each case, a range of solid solubility greater than 5 at. % exists.

Some precipitation of solute might also have occurred in the Ti alloys containing Cr, Co, Fe, and Ni. More extensive solid solubility exists for Nb, Zr, and Al in hcp Ti and for these alloys the 4.2°K resistivities are

Ti-1.29 Co and Ti-1.01 Ni exhibit microstructures more similar to the coarse, platelike "basketweave" structure shown in Fig. 15(d) although no β phase was detected.

³⁶ M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958), p. 957.

³⁷ A. N. Gerritsen and J. O. Linde, *Physica* **18**, 877 (1952).

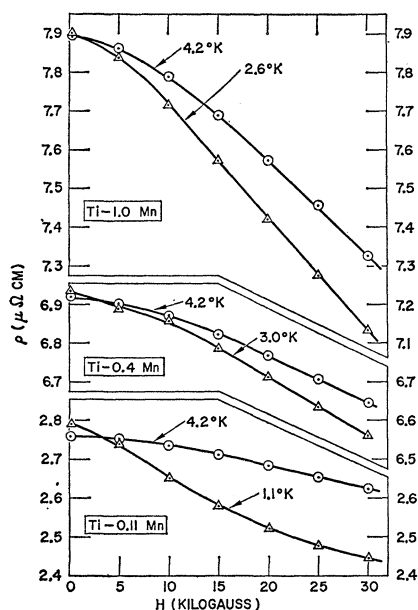


FIG. 4. Representative negative transverse magnetoresistivity data for dilute Ti-Mn alloys, containing 1.0, 0.4, and 0.11 nominal at.% of Mn.

more likely representative of random solid solutions with solute concentrations close to the nominal values. Resistivity measurements at 4.2°K on Ti-Zr and Ti-Al alloys with solute concentrations of about 2, 4, and 8 at.%³⁸ yield $\rho(4.2^\circ\text{K})$ vs concentration curves which are nearly linear and pass through the $\rho(4.2^\circ\text{K})$ values shown in Fig. 3, with slopes such that $(d\rho/dc)$ is 1.6 and $13 \mu\Omega\text{-cm/at.}\%$, respectively, for Ti-Zr and Ti-Al. These values are in good agreement with those obtained from a graph of the room temperature resistivity data of Ames and McQuillan³⁹ on one Ti-10 Zr alloy and six Ti-Al alloys with $2 \leq c \leq 8$ at.% (these workers observe linearity in the room temperature ρ vs c curve for Ti-Al up to 8 at.%).

B. Magnetoresistivity

1. Negative Magnetoresistivity of Ti-Mn

Figure 4 shows representative transverse magnetoresistivity data for dilute Ti-Mn alloy specimens in fields up to 30 kG. The application of a magnetic field has the unusual effect of decreasing the resistivity. Such behavior has previously been observed in conjunction with low-temperature resistive maxima and/or minima in alloys of Cu, Ag, Au, and Zn containing dilute concentrations of certain transition metals.¹⁻³ At 4.2°K and 30 kG the resistivity change is -7.18%, -3.95%, and -4.92% of the zero-field value for the Ti alloys of

Fig. 4 containing 1.00,⁴⁰ 0.407, and 0.114 at.% Mn, respectively. Table II shows the percentage field-induced resistivity changes for all the dilute Ti alloys measured in this study, i.e., $10^2 \Delta\rho_H/\rho(H=0)$ where $\Delta\rho_H \equiv [\rho(H, T) - \rho(H=0, T)]$ and where H and T have the values specified in the table.

The magnitude of the negative magnetoresistivity of the dilute Ti-Mn alloys of Fig. 4, as well as all other Ti-Mn alloys measured (see Table II), increases markedly as temperature is reduced. Such an effect has been found in most other dilute alloy systems which exhibit negative magnetoresistivity. (Exceptions to the normal behavior occur in the case of Cu and Ag containing above about 1 at.% of Mn,^{7,41,42} where the absolute magnitude of the negative magnetoresistivity

TABLE II. Magnetoresistivity data for dilute Ti alloys.

Solute at.% (nominal ^a)	$10^2 \Delta\rho_H^b$	$10^2 \Delta\rho_{HK}^c$	$10^2 \Delta\rho_H$	T_L^d (°K)
	$\rho(H=0)$ (30 kG, 4.2°K)	$\rho(H=0)$ (30 kG, 4.2°K)	$\rho(H=0)$ (30 kG, T_L^d)	
≈ 0 ^e	+1.39	+1.46	+ 1.31	1.1
0.018 Mn	+0.472	+1.03	- 1.01	1.3
0.101 Mn	-2.58	+0.240	- 6.26	1.1
0.114 Mn	-4.92	+0.375	-12.5	1.1
0.212 Mn	-2.91	+0.123	- 3.94	3.1
0.407 Mn	-3.95	+0.082	- 5.37	3.0
1.00 Mn	-7.18	+0.068	- 9.65	2.6
1.06 Mn	-5.15	+0.063
2.01 Mn	-6.01	+0.043	- 7.75	2.9
1.15 Cr	+0.054	+0.074
0.96 Fe	+0.550	+0.28
1.29 Co	+0.820	+0.32
1.01 Ni	+0.349	+0.18	+ 0.292	1.1
1.00 Nb	+0.396	+0.28
1.06 Al	+0.016	+0.023
1.00 Zr	+0.297	+0.32	+ 0.181	1.1

^a Calculated from the weights of the starting materials.

^b $\Delta\rho_H \equiv [\rho(H, T) - \rho(H=0, T)]$.

^c An estimate of the normal positive "Kohler" component of the magnetoresistivity as indicated in the text, see Eq. (2).

^d T_L is the lowest temperature at which magnetoresistivity data were taken.

^e Nominally, 99.92 wt.% pure Foote "iodide" crystal bar Ti from lot No. 005-1.

decreases as temperature is lowered below 4.2°K, an effect presumably associated with the apparent antiferromagnetism occurring in these alloys.^{7,43,44} In Fig. 4 and in Table II the lowest temperature at which magnetoresistivity data were taken, T_L , was determined by the experimental requirement that $T_L > T_s$, where T_s is

⁴⁰ Preliminary pulsed field measurements on Ti-1.00 Mn by Berlincourt indicate that the resistance is decreased about 25% by a field of 135 kG at 1.1°K. The transverse and longitudinal magnetoresistivities are nearly the same, as has previously been observed in other dilute alloys which display negative magnetoresistivity.

⁴¹ A. N. Gerritsen, *Physica* **19**, 61 (1953).

⁴² A. N. Gerritsen and J. O. Linde, *Physica* **17**, 584 (1951).

⁴³ J. Owen, M. Browne, W. D. Knight, and C. Kittel, *Phys. Rev.* **102**, 1501 (1956); J. Owen, M. Browne, V. Arp, and A. F. Kip, *J. Phys. Chem. Solids* **2**, 85 (1957).

⁴⁴ A. van Itterbeck, W. Peelaers, and F. Steffens, *Appl. Sci. Research* **B8**, 337 (1961).

³⁸ R. R. Hake, D. H. Leslie, and T. G. Berlincourt, (unpublished).

³⁹ S. L. Ames and A. D. McQuillan, *Acta Met.* **4**, 619 (1956).

the temperature at which the zero-field resistivity began to decrease due to the onset of superconductivity. In the case of the more dilute Ti-Mn alloys, such as Ti-0.114 Mn of Fig. 4, superconductivity did not occur down to 1.1°K. The negative magnetoresistivity at this low temperature in Ti-0.114 Mn is large (12.5% at 30 kG) and shows a tendency to saturate at the higher fields. Similar saturation effects were observed in Ti-0.101 Mn at 1.1°K and in Ti-0.018 Mn at 1.34°K. These effects could be due to the influence of the ordinary positive component of the magnetoresistivity {which should be larger for the more dilute, lower resistivity alloys [see the discussion following Eq. (2)]}, and/or a saturation tendency of the localized moment magnetization [see Sec. IV C, and Eq. (4)].

The ρ vs H curves for the Ti-0.114 Mn specimen indicate that the temperature coefficient of resistivity at constant field shifts from negative to positive as the field is increased. This crossover of the ρ vs H curves for

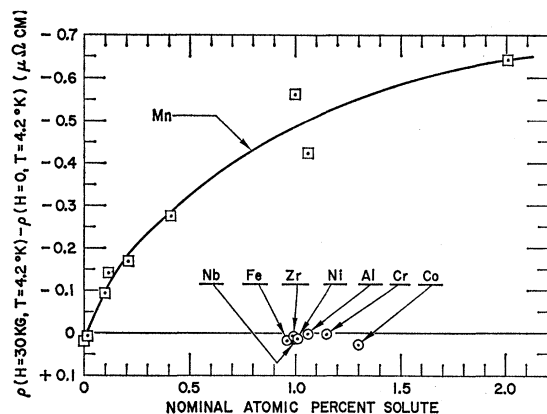


FIG. 5. The magnitude of the transverse magnetoresistivity, $\Delta\rho_H$, at 30 kG and 4.2°K, vs the nominal at.% solute concentration for various dilute Ti alloys.

different temperatures is present but less apparent in all the other Ti-Mn alloys measured.

The shapes of the ρ vs H curves shown in Fig. 4, as well as all others obtained for Ti-Mn in this study, are generally similar to those measured in fields up to about 20 kG at comparable temperatures and solute concentrations for Cu-Mn,⁴¹ Ag-Mn,⁴² Au-Mn,⁴¹ Au-Fe,⁴⁵ and Zn-Mn^{46,47}; the ρ - H curves appear to be approximately parabolic at low fields, becoming nearly linear at fields above 10-15 kG. At the lowest solute concentrations and highest fields, saturation effects similar to those observed in the ρ - H curve of Ti-0.114 Mn at 1.1°K (Fig. 4) have been seen in the ρ - H curves of Au-Mn,⁴¹ Au-Fe,⁴⁵ and Zn-Mn.⁴⁷

Hysteretic behavior in the field dependence of the magnetoresistivity, associated with small ferromagnetic

remanences, has been observed by Schmitt and Jacobs^{7,8} in Cu-Mn with Mn concentrations equal to or greater than 0.4 at.%, but not in Cu-Co.⁸ Schmitt and Jacobs observed a maximum field hysteresis in $\Delta\rho_H$ (4.2°K) of about 7% of $\Delta\rho_H$ (7.1 kG, 4.2°K). A search was made for similar hysteresis in the Ti-2.01 Mn specimen at 4.2 and at 3.2°K. It was found that any such hysteresis must be less than 1.3% of $\Delta\rho_H$ (30 kG).

Figure 5 shows the magnitude of the magnetoresistivity, $\Delta\rho_H$, at 30 kG and 4.2°K, plotted against the nominal at.% of solute for Ti-Mn alloys, as well as for the other dilute Ti alloys of this study. In the case of Ti-Mn, the value of $\Delta\rho_H$ (30 kG, 4.2°K) is essentially a monotonically increasing function of the nominal Mn concentration.

2. Positive Magnetoresistivities of Various Dilute Ti Alloys

As shown in Fig. 5 and also in Table II, dilute Ti alloys containing about one at.% of Cr, Fe, Co, and Ni do not display negative magnetoresistance but only a relatively small positive magnetoresistance, much the same as that observed in Ti containing about one at.% of the "nonmagnetic" solutes Nb, Zr, and Al. In Fig. 6 some of the positive transverse magnetoresistance data taken at 4.2°K are shown in the usual Kohler-type plot. For comparison the negative magnetoresistance data have been plotted for the Ti-1.0 Mn specimen on the same figure. The magnetoresistivity of "pure" Ti measured in this study at 4.2°K can be represented to

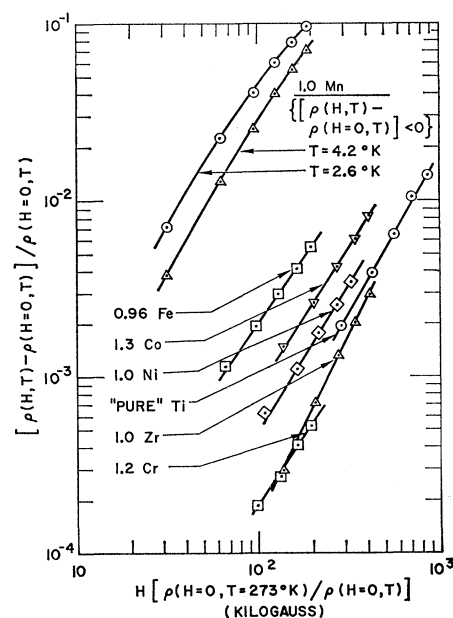


FIG. 6. A Kohler-type plot of the transverse magnetoresistivity data for various dilute Ti alloys at a temperature of 4.2°K (except where indicated). Ti-NB means Ti containing N nominal at.% of solute B .

⁴⁵ A. N. Gerritsen, *Physica* **23**, 1087 (1957).

⁴⁶ Y. Muto, Y. Tawara, Y. Shibuya, and T. Fukuroi, *J. Phys. Soc. Japan* **14**, 380 (1959).

⁴⁷ Y. Muto, *Sci. Repts. Tôhoku University* **13**, 1 (1961).

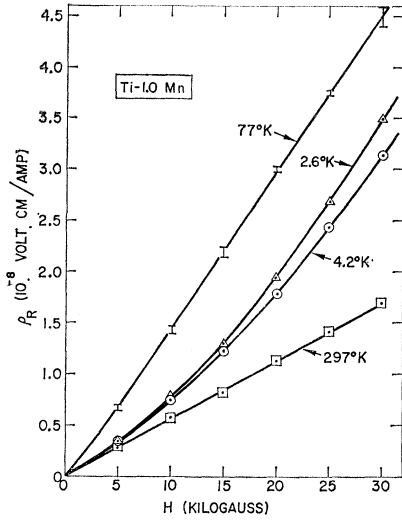


FIG. 7. Hall-effect data for Ti containing 1.00 nominal at.% Mn. ρ_R is the Hall resistivity (the transverse, isothermal Hall field per unit current density). The Hall coefficient, R , is just (ρ_R/H) .

within $\pm 5\%$ as

$$\begin{aligned} \Delta\rho_H/\rho(H=0) &= +1.62 \times 10^{-11} H^2 \\ &= +1.89 \times 10^{-14} \{[\rho(273^\circ\text{K})/\rho(4.2^\circ\text{K})]H\}^2, \end{aligned} \quad (1)$$

where H is in gauss. The coefficient of H^2 in Eq. (1) is 7% larger than that observed by Berlincourt⁴ in another Ti specimen, "T3", with an ice point to 4.2°K resistivity ratio of 30.8, although the 7% difference is within the combined error limits of the two measurements. As can be seen in Fig. 6, there is a rather wide variation in the magnetoresistive characteristics of dilute Ti alloys. As a check that the positive magnetoresistivity at 4.2°K of Ti containing Fe, Co, Cr, Ni, and Zr was not caused or magnified by possible magnetic field-quenching of superconducting inclusions, a search was made for current-dependent resistance in zero magnetic field at 4.2°K. The resistance of each of the alloy specimens was found to be current-independent to within the limits of error (0.05%) over the current range employed, 0.1 to 1.0 A.

As a rough estimate of the size of the ordinary positive "Kohler" component of magnetoresistivity to be expected, $\Delta\rho_{HK}$, in Ti-Mn, we have listed in Table II the magnetoresistivities at 30 kG as calculated from a Kohler-type relationship of the form suggested by Eq. (1) for "pure" Ti:

$$\Delta\rho_{HK}/\rho(4.2^\circ\text{K}) = K \{[\rho(273^\circ\text{K})/\rho(4.2^\circ\text{K})]H\}^2. \quad (2)$$

As an approximation K and α are assumed to have the same values as for the "pure" Ti of this study [Eq. (1)]. In Table II, intercomparison of the measured magnetoresistivities, $\Delta\rho_H/\rho(H=0)$, with those calculated from Eq. (2), $\Delta\rho_{HK}/\rho(H=0)$, suggests that the Kohler component is only a few percent, at most, of the total magnetoresistivity at 30 kG for alloys containing

above 0.2 at.% Mn, and that the positive Kohler component and the "anomalous" negative component are comparable in the Ti-0.018 Mn alloy. The latter is also suggested by the fact that for Ti-0.018 Mn, $\Delta\rho_H$ (30 kG, 4.2°K) is positive whereas $\Delta\rho_H$ (30 kG, 1.34°K) is negative, and at 1.34°K the sign of $(d\rho/dH)$ changes from negative to positive at about 25 kG.

Since Ti-1.01 Ni and Ti-1.00 Zr did not become superconducting at 1.1°K, their magnetoresistivities were measured at this temperature. For each of these alloys a deviation from Kohler's rule was observed in that $[\Delta\rho_H/\rho(H=0)]$ did not appear to be only a function of $[H/\rho(H=0)]$, since the 1.1°K data did not fall on the same curve on Fig. 6 as did the 4.2°K data. At the highest reduced field values, the positive magnetoresistivity $[\Delta\rho_H/\rho(H=0)]$ was 16% and 39% less at 1.1°K than at 4.2°K for Ti-1.01 Ni and Ti-1.00 Zr, respectively. This suggests that an "anomalous" negative component of magnetoresistivity, $\Delta\rho_{HA}$, exists in these alloys which increases in magnitude as temperature is lowered. An analysis along lines similar to that given at the end of Sec. IV A, 1 [assuming that $|\Delta\rho_{HA}| \propto (1/T)$, as appears to be very roughly the case for $\Delta\rho_H$ in Ti-Mn, and that $d(\Delta\rho_H)/dc \approx 1.1 \mu\Omega\text{-cm}/(\text{at.}\%)$ near the zero solute concentration from Fig. 5] suggests that the deviations from Kohler's rule in these alloys could be due to only about 0.001 at.% of Mn impurity. A deviation from Kohler's rule of the same type as in Ti-1.01 Ni and Ti-1.00 Zr and probably also due to impurities is observed in the "pure" Ti specimen (see Table II). Since a rough calculation as above suggests that only ≈ 0.0004 at.% Mn could cause the observed deviation from Kohler's rule in "pure" Ti, we assume that the zero-field resistance minimum in the "pure" Ti must be caused by Fe and/or Cr impurity (see Sec. IV A, 1).

C. Hall Coefficients

Figure 7 shows the Hall resistivity, ρ_R (the Hall field per unit current density), vs the field strength, H , for the Ti-1.00 Mn specimen. The linearity of the ρ_R - H curves taken at room temperature ($\approx 297^\circ\text{K}$) and at 77°K indicate field-independent Hall coefficients, R , at these temperatures since $R \equiv (\rho_R/H)$. The nonlinearity of the helium temperature ρ_R - H curves and their marked temperature dependence are probably associated with the low-temperature resistivity minimum and the negative magnetoresistivity. Very similar temperature and nonlinear magnetic field dependencies of ρ_R were observed in Ti-2.01 Mn at 4.2 and at 2.87°K, but not in "pure" Ti, Ti-0.96 Fe, or Ti-1.15 Cr. Although ρ_R was linear in magnetic field at helium temperatures for Ti-0.114 Mn, a sizable temperature dependence of ρ_R was observed between 1.1 and 4.2°K. The values of the non-field-dependent Hall coefficients measured for these various alloys, as well as values from

TABLE III. Hall coefficients R for some dilute Ti alloys.

Specimen	$\rho(273^\circ\text{K})$	$T(^{\circ}\text{K})$	R ($10^{-5} \text{ cm}^3/\text{C}$)
	$\rho(4.2^\circ\text{K})$		
"pure" Ti ^a	29.3	297	- 3.59
		77	- 4.78
		4.2	- 11.9
"pure" Ti ^b	30.8	297	- 3.55
		77	- 4.58
		4.2	- 10.5
Ti-0.114 Mn ^c	14.9	297	- 6.76
		77	- 12.2
		4.2	- 15.3
		1.1	- 16.0
Ti-1.00 Mn	6.34	297	- 5.67
		77	- 15.1
		4.2	$R(H)$ ^d
		2.6	$R(H)$
Ti-2.01 Mn	5.06	297	- 5.37
		77	- 15.8
		4.2	$R(H)$
		2.87	$R(H)$
Ti-0.96 Fe	12.9	297	- 4.17
		77	- 6.19
		4.2	- 10.6
Ti-1.15 Cr	6.60	297	- 3.01
		77	+ 2.90
		4.2	+ 10.3

^a Nominally, 99.92 wt.% pure Foote "iodide" crystal bar Ti from lot No. 005-1.

^b Specimen "T3" of reference 4, Mallory-Sharon "iodide" crystal bar Ti.

^c Ti containing 0.114 at.% Mn.

^d Hall coefficient was field dependent.

some earlier measurements on "pure" Ti by Berlincourt,⁴ are listed in Table III.

Field-dependent Hall coefficients have previously been observed in conjunction with low-temperature resistive anomalies in impure Au by Alekseevski and Gaidukov⁴⁸ and in dilute Ag-Mn alloys by Franken and van den Berg.⁴⁹ The latter workers have pointed out the likely connection here with the "extraordinary Hall effect" in ferromagnetics⁵⁰ where ρ_R is commonly written as

$$\rho_R = R_0[H + \alpha I], \quad (3)$$

where R_0 is the "ordinary" Hall coefficient, I is the magnetization, and α is the so-called "field parameter." Schmitt and Jacobs^{7,8} found that the absolute magnitude of the negative magnetoresistivity in Cu-Mn and Cu-Co alloys was just proportional to the square of the measured magnetization:

$$|\Delta\rho_H| = bI^2, \quad (4)$$

⁴⁸ N. E. Alekseevski and I. U. P. Gaidukov, Soviet Phys.—JETP **5**, 1301 (1957).

⁴⁹ B. Franken and G. J. van den Berg, in *Proceedings of the Seventh International Conference on Low-Temperature Physics, Toronto, 1960*, edited by G. M. Graham and A. C. Hollis Hallett (University of Toronto Press, Toronto, 1961), p. 261.

⁵⁰ For a review, see J. P. Jan in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 74.

where b was found to be solute concentration dependent and, in the case of Cu-Mn, to be also temperature dependent. In Ti-Mn (unlike Cu-Mn and Cu-Co) the ordinary "Pauli" susceptibility, χ_p , might well result in a magnetization in any given field, $I_p(H)$, which is comparable with the localized moment magnetization, $I_L(H)$, if such does indeed exist. Assuming that this latter term is related to $|\Delta\rho_H|$ as in Eq. (4), one might write the total magnetization, I , as

$$I = I_p + I_L = \chi_p H + (|\Delta\rho_H|/b)^{1/2}. \quad (5)$$

Insertion of Eq. (5) into Eq. (3) yields

$$\rho_R/H = R_0(1 + \alpha\chi_p) + R_0\alpha b^{-1/2} \rho^{1/2} (|\Delta\rho_H|/\rho)^{1/2} H^{-1}, \quad (6)$$

where ρ is the zero-field resistivity. As did Franken and van den Berg, we have plotted measured values of (ρ_R/H) vs $[(|\Delta\rho_H|/\rho)^{1/2}/H^{-1}]$ in order to derive values of $[R_0(1 + \alpha\chi_p)]$. The curves would indicate that $(\alpha b^{-1/2})$ is dependent on temperature, solute concentration, and field (below ≈ 15 kG). Extrapolation of the high-field linear curves yields values of $[R_0(1 + \alpha\chi_p)]$ of approximately $-20 \times 10^{-5} \text{ cm}^3/\text{C}$ for both Ti-1.00 Mn and Ti-2.01 Mn at $T \leq 4.2^\circ\text{K}$.

The data listed in Table III show that the Hall coefficient of Ti is greatly affected by the addition of Mn and Cr. The Hall coefficients of dilute Ti-Mn alloys are even more temperature dependent than the Hall coefficient of nominally "pure" Ti. Concentration and temperature-dependent values of $[\alpha I(H)]$ could be responsible for strongly concentration- and temperature-dependent Hall coefficients in Ti and in Ti alloys according to Eq. (3). It is also possible that the sensitivity of the Hall coefficient to alloying and temperature reflects an extremely sensitive electronic structure condition affecting R_0 directly. Such a condition might also account for the low-temperature resistive anomalies⁵¹ (as well as the highly concentration-dependent superconducting transition temperatures) without invoking the presence of localized magnetic moments. However, for the case of Ti-Mn it is difficult to see how any such electronic structure condition could give rise to negative magnetoresistivity and field-dependent Hall coefficients in such high residual resistivity alloys.

D. Superconductivity

Figure 8 shows resistive superconducting transitions for various dilute Ti alloys measured in this study. The transitions are very broad and are doubtless of a filamentary type, the bulk of the specimen being in the normal state during most of the resistive transition. The measuring current density, J , for all the transitions shown in Fig. 8 was about $100 \text{ A}/\text{cm}^2$ except in the case of Ti-0.96 Fe, where $J = 132 \text{ A}/\text{cm}^2$. If a resistive tran-

⁵¹ Possibly along the lines indicated by F. Blatt, J. Phys. Chem. Solids **17**, 177 (1961) for the case of the high-temperature resistivity minima in nondilute bcc U-Mo alloys. Similar high-temperature resistance minima have been observed in non-dilute bcc Ti-Mo, Ti-V, and Ti-Fe (see reference 29).

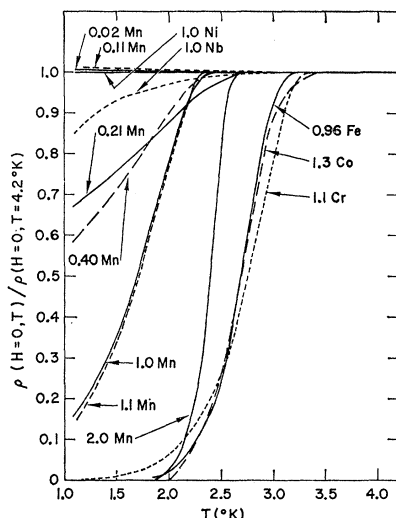


FIG. 8. Resistive superconducting transitions for dilute Ti alloys containing various atomic percentages of solute, as indicated. The measuring current density, J , was in each case about 100 A/cm², except for Ti-0.96 Fe where $J=132$ A/cm².

sition temperature, T_r , is defined as the intercept of the steep linear portion of the curves shown in Fig. 8 with the abscissa, then these T_r values agree reasonably well with the superconducting transition temperatures, T_c , as measured magnetically by Matthias *et al.*¹⁵ The observation that Ti-1.01 Ni does not become superconducting down to 1.1°K is also in agreement with the results of Matthias *et al.* The alloys Ti-1.06 Al and Ti-1.00 Zr were also found to be nonsuperconducting at 1.1°K. The tendency of T_r to increase rapidly with dilute addition of Mn is apparent in Fig. 8, and is again in harmony with the T_c vs solute concentration results of Matthias *et al.* (The most dilute Ti-Mn alloy of that study was Ti- ≈ 1.5 Mn with $T_c \approx 1.7^\circ K$.)

V. DISCUSSION

A comparison of the present results with earlier data¹⁻³ shows that, except for the generally somewhat larger absolute magnitudes of the negative magnetoresistivities, $|\Delta\rho_H/\rho(H=0)|$, the resistive and magnetoresistive behavior of Ti-Mn is fairly typical of that observed in a number of nontransition metal base alloys which exhibit resistivity *minima* and negative magnetoresistivities (the latter sometimes only at the lowest temperatures and highest solute concentrations) but in which resistivity *maxima* have not been observed, e.g., Cu-Co,⁸ Cu-Ni,⁵² Au-Co,² Zn-Mn,^{46,47} and Au-Mo.⁵³ Although other explanations are possible,^{1,3,51} it appears probable in the light of current ideas^{5,16-25} that localized moments exist in Ti-Mn, as in other dilute alloys ex-

hibiting low-temperature resistance and magnetoresistance anomalies, and that these moments interact with the conduction electrons.

In Ti-Cr and Ti-Fe, which display resistivity minima and *positive* magnetoresistivities at 4.2°K, it is possible that the degree of moment localization and temperature (or field) sensitive conduction electron-localized moment interaction is sufficient to produce a resistivity minimum but is not sufficient to result in an anomalous negative magnetoresistivity component, $\Delta\rho_{HA}$, large enough to dominate the ordinary positive Kohler component, $\Delta\rho_{HK}$, nor to cause field-dependent Hall coefficients at 4.2°K. A similar situation probably exists for other dilute alloys for which resistivity minima have been observed together with positive magnetoresistivities.² Evidence for a relatively small but highly temperature-dependent $\Delta\rho_{HA}$ component can sometimes be adduced from the temperature dependence of $\Delta\rho_H$ at liquid helium temperatures in such alloys^{2,52,54} (as was done for Ti-Ni and Ti-Zr in Sec. IV B, 2). In the case of the Ti-Cr and Ti-Fe alloys such a search for a $\Delta\rho_{HA}$ component was prohibited by the onset of superconductivity at about 3.3°K.

According to recent studies by Matthias and co-workers, Curie-Weiss behavior is not observed in the magnetic susceptibility of Ti containing about one at.% Fe,⁵⁵ again indicative of weak localized moment behavior. However, some caution is required in any attempt to discern the degree of moment localization in dilute transition metal base alloys from susceptibility results. For example, localized moments might exist in dilute solution in a transition metal base alloy but be locked in position by effective internal fields to an extent that Curie-Weiss type susceptibility behavior is not observed.⁵⁶ Conversely, Curie-Weiss type susceptibility behavior might be observed in a dilute transition metal base alloy where no localized moments exist, since Curie-Weiss behavior is explicable on the basis of a collective band model.⁵⁷

As in the case of the theoretically more tractable non-transition metal base alloys, the detailed interaction mechanisms responsible for low-temperature resistive

⁵⁴ R. T. Webber, Phys. Rev. **105**, 1437 (1957).

⁵⁵ B. T. Matthias, IBM J. Research Develop. **6**, 250 (1962).

⁵⁶ See, for example, the discussion of the susceptibility behavior of dilute solutions of Fe and Co in antiferromagnetic Cr by W. M. Lomer, Australian J. Phys. **13**, 451 (1960). In this regard it is possible to interpret the electrical resistivity-temperature curve of pure Ti [S. L. Ames and A. D. McQuillan, Acta Met. **2**, 831 (1954)], the magnetic susceptibility-temperature curve of pure Ti [H. Kojima, R. S. Tebble, and D. E. G. Williams, Proc. Roy. Soc. (London) A **260**, 237 (1961)], and the quasi-spin-disorder resistive characteristics of nondilute bcc Ti alloys (see ref. 29), by assuming that pure Ti is antiferromagnetic with a Néel point near the α - β phase transformation temperature. A case has recently been made for antiferromagnetism in V, which lies next to Ti in the periodic table and like Ti is a superconductor and is normally considered to be "nonmagnetic": J. Burger and M. A. Taylor, Phys. Rev. Letters **6**, 185 (1961).

⁵⁷ See, for example, E. W. Elcock, P. Rhodes, and A. Teviotdale, Proc. Roy. Soc. (London) A **221**, 53 (1954).

⁵² G. J. Los and A. N. Gerritsen, Physica **23**, 633 (1957).

⁵³ B. Knook and G. J. van den Berg, in *Proceedings of the Seventh International Conference on Low-Temperature Physics, Toronto, 1960*, edited by G. M. Graham and A. C. Hallett (University of Toronto Press, Toronto, 1961), p. 257.

anomalies in dilute Ti alloys are uncertain. With reference to the former alloys, Brailsford and Overhauser²³ have suggested that resistivity minima are due to temperature-dependent, elastic *s-d* exchange scattering, where the temperature dependence results from a progressive ferromagnetic ordering of nearest-neighbor pairs of paramagnetic ions as temperature is reduced. Bailyn²⁵ has suggested that a resistance minimum will occur if a ferromagnetic to antiferromagnetic transition of the localized moments takes place. Yosida⁵ has shown that cross terms in the expression for the elastic scattering potential, arising from the spin-dependent exchange interaction and the ordinary spin-independent Coulomb interaction between conduction electrons and localized moments, will give rise to a negative magnetoresistivity which is just proportional to the square of the magnetization, as has been observed experimentally in Cu-Mn⁷ and Cu-Co.⁸ The applicability of these ideas to the case of dilute Ti alloys might be tested by low-temperature susceptibility, specific heat, electron spin resonance, and neutron scattering experiments.

The relationship of the presently indicated magnetic interactions to the unusual alloying dependence of the superconducting transition temperature of Ti is also somewhat obscure. Investigations to see if the usual superconducting isotope effect exists⁵⁸ in pure Ti and specific heat measurements to determine the alloying dependence of the electronic density of states in dilute Ti alloys⁵⁹ would be of interest.

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⁵⁸ The usual superconducting isotope effect appears to be absent in the case of the transition metal Ru: T. H. Geballe, B. T. Matthias, G. W. Hull, Jr., and E. Corenzwit, *Phys. Rev. Letters* **6**, 275 (1961).

⁵⁹ For such measurements on nondilute bcc Ti-Mo alloys and a discussion of the results with regard to the strong alloying dependence of the superconducting transition temperature in this system see R. R. Hake, *Phys. Rev.* **123**, 1986 (1961).

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Electrical Resistivity and Thermoelectric Power of Palladium after Hydrogen Desorption

R. J. SMITH

Lewis Research Center, National Aeronautics and Space Administration, Cleveland, Ohio

AND

A. I. SCHINDLER AND E. W. KAMMER

Naval Research Laboratory, Washington, D. C.

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The electrical resistivity and thermoelectric power of desorbed palladium-hydrogen samples have been measured as functions of temperature from 4.2 to 300°K, and 77 to 273°K, respectively. The thermoelectric power of the desorbed specimens lies intermediate between the values of annealed and cold-worked palladium. An increase in the residual resistivity and a decrease in the value of $d\rho/dT$ is found for the desorbed samples. The results are explained in terms of an experimentally observed expanded lattice.

INTRODUCTION

IT is well known that palladium can absorb large amounts of hydrogen. In order to accommodate the hydrogen in interstitial octahedral sites,¹ the palladium lattice expands linearly by approximately 3%. For H/Pd atom ratios up to 0.03 the cube edge of the unit cell expands continuously from 3.88 to 3.89 Å (α phase). For ratios greater than 0.03 a lattice constant of 4.02 Å is observed (β phase). These two phases coexist up to a H/Pd atom ratio of 0.57; above this concentration, only the β phase is observable.² Some investigators² have reported complete recovery of the expanded

lattice after desorption and others³ have reported some residual expansion.

In an earlier investigation by the present authors,⁴ measurements were made of the effects of hydrogen absorption on the resistivity of annealed 99.995 at.% Pd, 90 at.% Pd–10 at.% Ni, and 83 at.% Pd–17 at.% Ni. After measurement, the hydrogen was removed from the specimens by heating them between 300 and 800°C for several minutes in vacuum. Two room temperature resistivity measurements were made, ρ_i (initial resistivity after annealing and prior to absorp-

³ G. Chaudron, A. Portevin, and L. Moreau, *Compt. rend.* **207**, 235 (1938).

⁴ A. I. Schindler, R. J. Smith, and E. W. Kammer, *Proceedings of the Tenth International Congress of Refrigeration, Copenhagen, 1959* (Pergamon Press, New York, 1960), Vol. 1, p. 74.

¹ J. E. Worsham, M. K. Wilkinson, and C. G. Shull, *J. Phys. Chem. Solids* **3**, 303 (1957).

² F. A. Lewis, *Metals Rev.* **4**, 132 (1960).