(g) In $BaTiO_3$ it is assumed that the unstable modes correspond to wave vectors k near $k=0$. The domain size is determined roughly by $\lambda=2\pi/k$ for the unstable modes. In addition, modes where $k=0$ correspond to tetragonal distortions with no change of the number of ions in the unit cell (rigid distortions of the inequivalent sublattices). Distortions that correspond to the increase in the number of ions in the unit cell by a small factor would come from wave vectors k near the edge of the Brillouin zone. No domain structure should be observed in this case for an unstrained crystal. This, as was said earlier, is a reasonable possibility for $SrTiO_3$. It would mean, however, that the size and shape of the region of uniform birefringence observed in $SrTiO_3$ would be determined by the strain field built into the crystal at growth. This strain causes birefringence even in cubic phase. At the phase transition the elastic constants change slightly[10] and thus the strain field changes. The change in birefringence pattern observed at the transition is a reflection of this effect.

V. CONCLUSION

The Gd^{3+} EPR spectrum has been studied in detail in the cubic and tetragonal phase of two isomorphous crystals $SrTiO_3$ and $BaTiO_3$. A birefringence experiment is reported that confirms the existence of such transition as a property of pure $SrTiO_3$. This is of some importance since previous evidence of such a transition came from EPR measurements of impurities in the crystal. The temperature of the cubic to tetragonal transition in $SrTiO_3$ has been determined to be 110 ± 2.5°K. This transition was shown to be of a different nature than that in $BaTiO_3$. It is a transition of the order of $n>1$ and probably the tetragonal phase has no permanent polarization.

VI. ACKNOWLEDGMENTS

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Pulsed Magnetic Field Studies of the Negative Magnetoresistivities of Dilute Ti-Mn and Cu-Mn Alloys at Low Temperatures*

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Measurements of the low-temperature negative magnetoresistivities of dilute Ti-Mn and Cu-Mn alloys have been extended to higher magnetic fields by means of pulsed magnetic field techniques. At 4.2°K the observed decreases of resistivity in a transverse magnetic field of 130 kG are approximately 5, 23, and 26% of the zero-field resistivity, respectively, for Ti-0.101 at.% Mn, Ti-1.00 at.% Mn, and Cu-1.00 at.% Mn. Saturation of the negative magnetoresistivity is essentially complete in Ti-0.101 at.% Mn below 100 kG. A trend toward saturation is strongly evident in Ti-1.00 at.% Mn and is less marked in Cu-1.00 at.% Mn. Close agreement between transverse and longitudinal magnetic field measurements is observed in all cases. The Ti-Mn data are in accord with earlier evidence which suggests that in these alloys there exist localized magnetic states which interact with the conduction electrons.

I. INTRODUCTION

NOBLE metal rich alloys containing dilute additions of first transition group metals have been the subject of intensive study by a number of investigators.[1,2] Perhaps the best known example of such an alloy is Cu containing up to several percent Mn. At low temperatures an alloy of this type might exhibit several (though seldom all) of the characteristic types of electron transport property behavior listed below:

1. A minimum in the resistivity vs temperature (followed in some instances by a maximum at lower temperatures).
2. A decrease of resistivity with applied magnetic field (negative magnetoresistance).
3. A strong temperature dependence of the negative magnetoresistance. (In accord with Kohler's rule[3] normal positive magnetoresistivities are in general temperature independent below 4°K.)
4. Near equality of transverse and longitudinal negative magnetoresistivities for not too dilute compositions. (In contrast normal positive magnetoresistivities of

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[1] For a tabulation of resistive, magnetic, and thermal property results on fifteen different alloy systems (with references) see A. N. Gerritsen, Physica **25**, 489 (1959).

[2] For a recent review, see G. J. van den Berg, in *Proceedings of the Seventh International Conference on Low-Temperature Physics* (University of Toronto Press, Toronto, 1961), p. 246.

[3] J. P. Jan, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 29.

polycrystalline metals are a factor of about three greater for transverse than for longitudinal fields.[4])

5. Magnetic-field-dependent Hall coefficient.

Such behavior is today almost universally attributed to the interaction of conduction electrons with localized magnetic states at the transition metal atom sites.[5–8]

That such localized magnetic states and interactions might also exist for the case of a transition metal in dilute solution in another transition metal was suggested by the observation by one of us[9] several years ago of negative magnetoresistance in a Ti single crystal containing Mn impurity. Subsequent studies by Hake *et al.*[10] on a series of quenched polycrystalline Ti-Mn alloys provided more conclusive evidence for such localized states, viz., resistivity minima, strong temperature dependence of the negative magnetoresistance, and a magnetic-field-dependent Hall coefficient. Attention was directed to the fact that such behavior is of considerable interest in relation to the superconductivity of Ti-Mn alloys.[11]

The present investigation[12] was undertaken to compare the relative magnitudes of the transverse and longitudinal negative magnetoresistivities in dilute Ti-Mn alloys, to extend to higher fields this comparison for a dilute Cu-Mn alloy, and to investigate the question of possible approach to saturation of the negative magnetoresistance at high magnetic fields. Because the results constitute new facets of a subject already discussed in considerable detail in reference 10, the present treatment is somewhat abbreviated.

II. SPECIMENS AND EXPERIMENTAL METHOD

The quenched metastable hcp Ti-1.00 at.% Mn and Ti-0.101 at.% Mn specimens used in this investigation were strips $\approx 0.025 \times 0.025 \times 1.4$ cm sheared from the $\approx 0.025 \times 0.30 \times 2.5$-cm specimens studied at lower fields in reference 10. Detailed characteristics of and preparation techniques for these specimens are given in that paper.

The Cu-1.00 at.% Mn alloy was prepared from American Smelting and Refining Company Cu of nominal purity greater than 99.999% and Electro Manganese Corporation Mn of 99.9% purity. The material was induction melted six times under high vacuum in a graphite mold and was inverted in the mold following each melting. The final experimental specimen was drawn to wire of 0.025-cm diam and was annealed under high vacuum at 550°C for 2 h. For this specimen $\rho\,(300°\mathrm{K}) = 4.36\ \mu\Omega$ cm and $\rho(4.2°\mathrm{K}) = 2.81\ \mu\Omega$ in good accord with the results of Schmitt and Jacobs[7] for the same composition.

The measurements were carried out at liquid helium temperatures in pulsed magnetic fields up to 135 kG. A standard four-probe resistivity measurement technique was used. Current leads were soldered to the ends of the specimens, which, in the case of Ti-Mn, were first copper plated. Potential probes separated by approx 0.5 cm were securely clamped to the specimens, and great care was taken to avoid loops which could give rise to induced voltages during the magnetic field pulse. A measuring current of 2.5 A was used for the Ti-0.101 at.% Mn and Cu-1.00 at.% Mn specimens, and a current of 1.0 A was used for the Ti-1.00 at.% Mn specimen.

Data were recorded on an oscilloscope as illustrated in Fig. 1, where the magnetic field is shown rising sinusoidally from zero to 135 kG in 6.2 msec. Shortly after attainment of the maximum field the magnet is shorted, and the field decays exponentially thereafter. The lower and upper oscillating traces represent, respectively, the voltage on the potential probes with and without current through the specimen for two successive magnetic field pulses. Thus, the upper oscillating trace represents the induced voltage, and the distance between the two oscillating traces is proportional to the specimen resistivity. The oscillations are apparently instrumental in origin and are not yet understood. Although a nui-

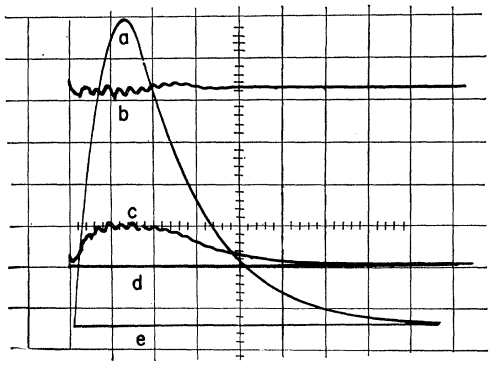

FIG. 1. Typical oscilloscope recording of transverse magnetoresistance data for Ti-1.00 at. % Mn at 3.0°K. (a) magnetic field, (b) and (c) specimen voltage without current and with current for two successive magnetic field pulses, (d) and (e) base lines. Time base: 5 msec/cm. Specimen voltage deflection sensitivity: 2 mV/cm.

[4] For comparisons of transverse and longitudinal magnetoresistance data see reference 15 (Cu, Ag, Au) and bibliography of reference 3.

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

[6] J. Owen, M. E. Browne, V. Arp, and A. F. Kip, J. Phys. Chem. Solids **2**, 85 (1957).

[7] R. W. Schmitt and I. S. Jacobs, J. Phys. Chem. Solids **3**, 324 (1957).

[8] A. V. Gold, D. K. C. MacDonald, W. B. Pearson, and I. M. Templeton, Phil. Mag. **5**, 765 (1960). It is noteworthy that this study demonstrated that the resistance minimum and 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.

[9] T. G. Berlincourt, Phys. Rev. **114**, 696 (1959).

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

[11] B. T. Matthias, V. B. Compton, H. Suhl, and E. Corenzwit, Phys. Rev. **115**, 1957 (1959), also B. T. Matthias, M. Peter, H. J. Williams, A. M. Clogston, E. Corenzwit, and R. C. Sherwood, Phys. Rev. Letters **5**, 542 (1960).

[12] A preliminary report has already appeared. T. G. Berlincourt, R. R. Hake, and A. C. Thorsen, Bull. Am. Phys. Soc. **6**, 502 (1961).

sance, they are reproducible to better than one-half the trace thickness and do not therefore constitute a serious source of error. The high reproducibility of the magnetic field pulse is evident in Fig. 1 where the traces for two successive pulses are indistinguishable.

The reduction of data was confined to decreasing magnetic fields only, because the correspondingly smaller rate of change of field insured smaller induced voltages, better thermal conditions, and hence higher accuracy. This should be kept in mind in referring to the results on Cu-1.00 at.% Mn, which, as shown by Schmitt and Jacobs,[7,13] exhibits hysteretic behavior amounting to a percent or so. Over-all accuracy in the determination of relative resistivity, $\rho(H,T)/\rho(H=0, T=4.2°K)$, is estimated as $\pm 1.5\%$. Consequently, most conclusions to be drawn from the data are only semiquantitative, and changes of relative resistivity with temperature are to be taken only as indicative of trends.

III. EXPERIMENTAL RESULTS

In Fig. 2 relative resistivity is plotted as a function of magnetic field strength at 4.2 and 1.2°K for Ti-1.00 at.% Mn. Data below about 10 kG have been omitted for $T=1.2$°K, because under these conditions the specimen was superconducting. The solid and dashed curves represent respectively the transverse and longitudinal results, and the points represent transverse magnetoresistance data obtained in steady fields up to 30 kG. The

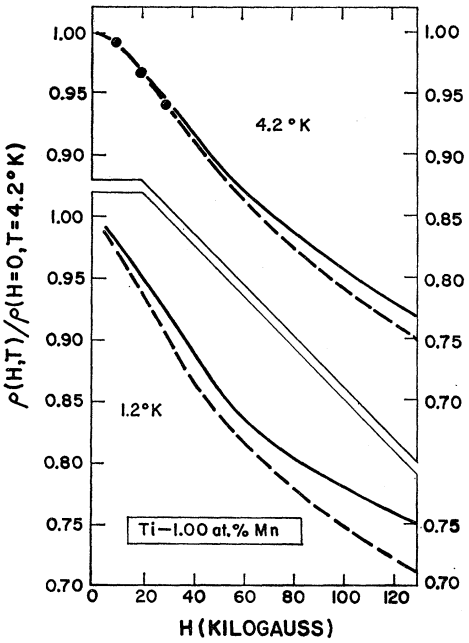

FIG. 2. Relative resistivity vs magnetic field for Ti–1.00 at.% Mn at 4.2 and 1.2°K. The solid and dashed curves correspond, respectively, to transverse and longitudinal results, and the points represent steady field transverse magnetoresistance data.

[13] R. W. Schmitt and I. S. Jacobs, Can. J. Phys. **34**, 1285 (1956).

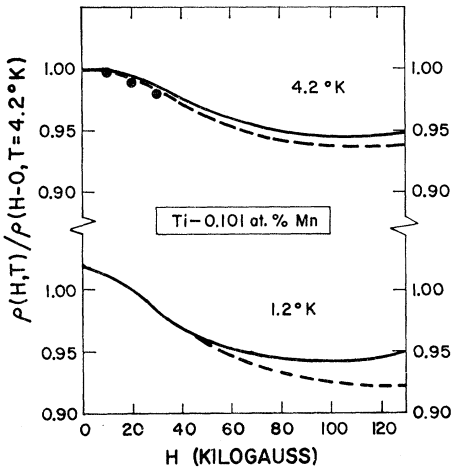

FIG. 3. Relative resistivity vs magnetic field for Ti–0.101 at.% Mn at 4.2 and 1.2°K. The solid and dashed curves correspond, respectively, to transverse and longitudinal results, and the points represent steady field transverse magnetoresistance data.

relatively good accord between the steady and pulsed field measurements engenders confidence in the pulsed measurements. The agreement between transverse and longitudinal results may be considered as quite good, especially when it is recalled that normal positive transverse and longitudinal magnetoresistivities ordinarily differ by a factor of about three. A tendency toward saturation of the negative magnetoresistance is evident particularly at the lower temperature. This could be largely a consequence of partial alignment of localized moments by the applied magnetic field, since the normal positive or Kohler component of transverse magnetoresistance for this case[14] should amount to only 1.3% at 130 kG.

The results for Ti-0.101 at.% Mn are presented in Fig. 3. Comparison with the earlier lower field data[10] on Ti-0.101 at.% Mn reveals some discrepancies which might presumably be attributed to the shearing and subsequent soldering of the metastable specimen. The agreement between transverse and longitudinal results is still fairly good, although for such a dilute concentration the normal positive component of magnetoresistance (which, as already pointed out, differs markedly for transverse and longitudinal cases) makes a much larger relative contribution. For this case the transverse Kohler component[14] is estimated as 4.5% at 130 kG. Saturation of the negative magnetoresistance in Fig. 3 appears to be complete below 100 kG, and for fields two to three times greater the Kohler component might be expected to dominate.

The results for Cu-1.00 at.% Mn are indicated in Fig. 4. Earlier comparisons of the transverse and longitudi-

[14] Normal positive magnetoresistance components were calculated assuming (without justification) that Kohler's rule (reference 3) holds and that the normal and negative magnetoresistance effects are additive. Transverse magnetoresistance data for pure Ti and Cu given, respectively, by Hake *et al.* (reference 10) and G. B. Yntema [Phys. Rev. **91**, 1388 (1953)] were used.

nal magnetoresistivities of dilute Cu-Mn alloys[15] have been confined to steady magnetic fields not exceeding 20 kG, so it is noteworthy that close agreement persists to the higher fields. Some tendency toward saturation is detectable at 1.2°K, but it is much weaker than in the case of the Ti-Mn alloys and in fact appears to be just comparable with the estimated Kohler component[14] of 1%. A somewhat more marked tendency toward saturation was noted by Muto[16] for Cu-5.4 at.% Mn at 4.2°K in fields up to 76 kG.

It is of interest to speculate on the Cu-1.00 at.% Mn data in terms of the predictions of Yosida's theory[5] which considers the effect on the magnetoresistance of the *s-d* exchange interaction between conduction electrons and Mn ions. Assuming $S=2$ for the spin state of the Mn ion and taking the resistivity values 2.75 and 3.02 $\mu\Omega$ cm, respectively, for the resistivities at 0°K and the so called Néel point for Cu-1.00 at.% Mn (from the work of Schmitt and Jacobs[7]), the theory predicts an infinite magnetic field resistivity value equal to 0.37 $\rho(H=0, T=0)$. In terms of this calculation (which neglects the Kohler component) a strong trend toward saturation would not yet be expected at fields (130 kG) where the observed resistivity has only reached the value 0.7 $\rho(H=0, T=0)$ (see Fig. 4).

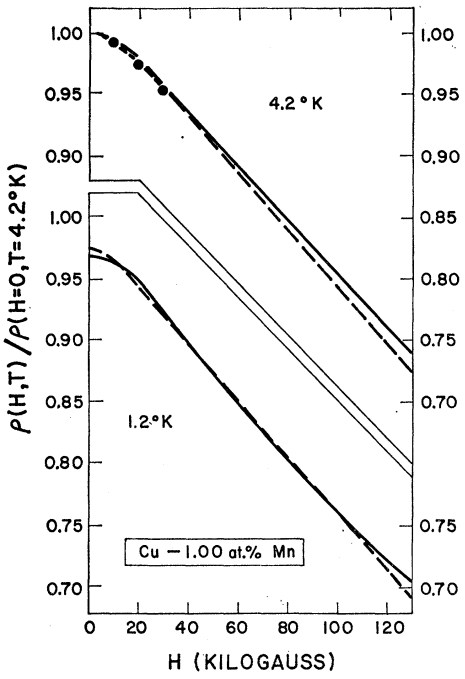

FIG. 4. Relative resistivity vs magnetic field for Cu–1.00 at.% Mn at 4.2 and 1.2°K. The solid and dashed curves correspond, respectively, to transverse and longitudinal results, and the points represent steady field transverse magnetoresistance data.

IV. DISCUSSION

This investigation has shown that, for dilute Ti-Mn alloys, as well as for dilute Cu-Mn alloys, the transverse and longitudinal negative magnetoresistivities at low temperatures are quite comparable in magnetic fields up to 130 kG. Furthermore, marked saturation effects have been observed in the negative magnetoresistance of the dilute Ti-Mn alloys. Two factors which might contribute to this saturation are the partial alignment of localized moments by the applied magnetic field and the increased relative value of the normal positive component of magnetoresistance at high fields. A less marked tendency toward saturation in the case of Cu-1.00 at.% Mn has been shown to be not inconsistent with the predictions of Yosida's theory.

The Ti-Mn data thus add weight to the body of evidence already cited[10] which suggests that localized magnetic states exist and interact with the conduction electrons in these alloys much the same as in the case of dilute noble metal-transition metal alloys.

ACKNOWLEDGMENTS

We wish to thank D. M. Sellman and D. H. Leslie for the preparation of samples and the acquisition of steady field data.

[15] A. N. Gerritsen, Physica **19**, 61 (1953).
[16] Y. Muto, Sci. Rep. Research Insts. Tohoku Univ. **13**, 1 (1961).