conducting transition affects only the T^2 term. Very roughly, the electronic contribution may be represented by $1\times10^{-3}T^2$ W/(cm²-deg).

CONCLUSIONS

Between 1.1 and 2.1°K, the thermal conductance of indium-sapphire boundaries can be represented by the sum of a T^2 term and a T^3 term. For two samples the T^3 terms are, respectively, $(0.0295\pm0.0016)T^3$ and $(0.0281\pm0.0016)T^3$ W/(cm²-deg). These numbers are within the range of possible values expected on the basis of the theory of Little. For one sample the T^2 term is $0.0059T^2$ or $0.0069T^2$ W/(cm²-deg) for the indium superconducting or normal, respectively. For the second sample this term is $0.0098T^2$ or $0.0108T^2$, respectively. These values are uncertain by $\pm1\times10^{-3}T^2$, but the change caused by the superconducting transition is believed accurate to $\pm4\times10^{-4}T^2$.

ACKNOWLEDGMENTS

The authors wish to thank Professor Little for his suggestion and Professor Dransfeld and I. Ciccarello for furnishing values for the velocities of sound in sapphire.

PHYSICAL REVIEW VOLUME 135, NUMBER 4A 17 AUGUST 1964

Magnetic Properties of a Single Crystal of Manganese Phosphide

E. E. Huber, Jr.,* and D. H. Ridgley
Lincoln Laboratory,† Massachusetts Institute of Technology, Lexington, Massachusetts
(Received 17 April 1963; revised manuscript received 6 May 1964)

Magnetic measurements were made on a spherical single crystal of high-purity stoichiometric MnP with a vibrating-sample magnetometer which was modified to allow precise temperature control and temperature cycling from 4 to 500°K. Anisotropy, saturation magnetization, and susceptibility data were obtained over this temperature range. The ferromagnetic Curie temperature was found to be 291.5±0.2°K. Evidence is presented which shows that MnP is neither ferrimagnetic nor antiferromagnetic, as has been previously supposed. Strong ferromagnetic coupling between spins may be assumed from the fact that the $1/\chi$ versus T curve has strong concave-up curvature above the Curie point. A magnetic transformation, not previously reported, was observed at 50°K which may be interpreted in terms of temperature-dependent, competing antiferromagnetic-ferromagnetic interactions. Below 50°K, MnP is metamagnetic, i.e., it exhibits an antiferromagnetic-ferromagnetic transition which is a function of applied field and temperature.

I. INTRODUCTION

THE principal results of magnetic measurements on a single crystal of MnP have been reported in abbreviated form elsewhere.[1] In that report a preliminary suggestion was made that the magnetic properties of MnP could be explained on the basis of temperature-dependent, competing antiferromagnetic-ferromagnetic interactions. The experimental results led to this hypothesis on comparison of the magnetic data with the theoretical predictions made by Enz,[2] Yoshimori,[3] and others for competing-interaction models. The purpose of this paper is to present some of the magnetic data in more detail and to develop more completely an explanation in terms of temperature-dependent competing interactions.

Structural considerations, coupled with inconsistencies in the previous magnetic data, have led certain investigators to attempt to explain the magnetization of MnP on the basis of either ferrimagnetism or antiferromagnetism with weak, superimposed ferromagnetism (canted spins). MnP has an orthorhombic, slightly distorted NiAs structure,[4,5] and there is some indirect evidence to indicate that it is an intermetallic compound with a narrow range of composition.[6] The structure is shown in Fig. 1 where the displacements of the ions from their positions in an ideal NiAs structure are indicated.

Definition of the orthorhombic axes is ambiguous in the literature. The axis convention $a>b>c$ is used in this investigation. In MnP the Mn atoms form zigzag chains along the a and b axes, which allows the Mn sublattice to be separated into two sublattices. If the Mn atoms of each sublattice are similar, antiferromagnetism is possible and canting would give rise to a superimposed ferromagnetism. If the Mn atoms

* This paper is prepared from material submitted in partial fulfillment of the requirements for the degree of Sc.D., Department of Metallurgy, Massachusetts Institute of Technology, Cambridge, Massachusetts.

† Operated with support from the U. S. Army, Navy, and Air Force.

[1] E. E. Huber, Jr., and D. H. Ridgley, J. Appl. Phys. **34**, 1099 (1963).
[2] U. Enz, J. Appl. Phys. **32**, 22S (1961).
[3] A. Yoshimori, J. Phys. Soc. Japan **14**, 807 (1959).
[4] H. Nowotny, Z. Elektrochem. **49**, 254 (1943).
[5] H. Nowotny, Z. Physik, Chem. ABT **B38**, 356 (1937).
[6] K. H. Sweeny and A. B. Scott, J. Chem. Phys. **22**, 917 (1954).

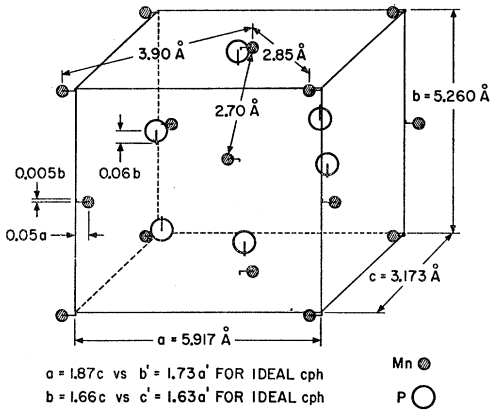

FIG. 1. The $B31$ structure of orthorhombic MnP.

of the two sublattices are different, ferrimagnetism is possible. Both of these mechanisms have been invoked by previous investigators to explain the anomalously low saturation moment of MnP.[7,8]

Early magnetic investigations on MnP have not had the benefit of single crystals, nor has the data gone any lower than 77°K. Bates[9] and Whitmore[10] did some of the first magnetic studies and found an effective paramagnetic moment $\mu_{\text{eff}}=3.69$ Bohr magnetons and a paramagnetic Curie point of $\theta_p=315$°K. Their material must not have been pure MnP, however, since it lost its ferromagnetic properties below 303°K in disagreement with the results of later investigators and the results of this investigation.

Guillaud,[11] in a later study than Bates, has measured the saturation moment of polycrystalline MnP down to 77°K and found an extrapolated spontaneous moment at $T=0$°K of $\mu_0=1.2$ Bohr magnetons. He pointed out that the spontaneous moment is low compared to Bates' paramagnetic moment and compared to the spin-only value of Mn^{3+} (4 Bohr magnetons). He noted that the structure permits a two-sublattice model of magnetic interactions and therefore speculated that the low moment was due to ferrimagnetism.[7] (He speculated that the two types of Mn atoms carried the electron configuration $3d^5 4s^2$ and $3d^7$.)

Krasovskii and Fakidov[8,12] have performed magnetic and caloric studies on polycrystalline MnP near the Curie temperature. Their measurements of the temperature dependence of the spontaneous magnetization gave the result $(M_s/M_0)^2=\xi(1-T/T_c)$ with $\xi=3.4$, where M_s is the spontaneous magnetization at the temperature T, M_0 is the saturation magnetization at $T=0$°K, and T_c is the Curie temperature. They cited theoretical work of Vlasov and Vonsovskii[13] which claims that $\xi>3$ for metallic, ferromagnetic substances and $\xi<3$ for ferrimagnetic substances. On this basis they conclude that MnP behaves somewhat more like a ferromagnet than a ferrimagnet. They therefore rejected Guillaud's hypothesis of ferrimagnetism and explained the reduced moment on the basis of a canted-spin model. To account for the observed moment they calculated an angle of 165° between the spins. It is to be noted, however, that the canted spin configuration is essentially an antiferromagnetic model.

To summarize, the existing knowledge of the magnetic properties of MnP is not only scanty, but also contains inconsistencies. The low μ_0 and discrepancies between μ_{eff} and μ_0 have suggested a magnetic order that is either ferrimagnetic or has strongly canted spins. Both models contain antiferromagnetic interactions, which is inconsistent with the high positive value of θ_p. A value of $\xi=3.4$ is probably also inconsistent with the canted-spin model of Fakidov and Krasovskii since parasitic ferromagnetism consists of a small ferromagnetic component superimposed on a large antiferromagnetic component.

The availability of a high-purity stoichiometric MnP crystal, coupled with the lack of much previous work on this material, suggested a reinvestigation of the problem. Magnetic investigations on a single crystal are much to be preferred over polycrystalline material because complicating effects of high anisotropy in the latter make it difficult to determine the saturation, or spontaneous, moment. Also, the measurement of anisotropy is, in itself, desirable and can serve as an indicator of crystal symmetry and, therefore, of possible changes in crystal symmetry.

II. EXPERIMENTAL TECHNIQUES

A vibrating sample magnetometer of the type first developed by Foner[14] was constructed for this investigation. The principle of this technique consists of vibrating a sample in a uniform magnetic field and measuring the ac field induced in a set of pickup coils by the moving magnetic dipole of the sample. This voltage is compared to that induced by a known nickel standard. Temperature can be varied by surrounding the sample with a Dewar such as shown in Fig. 2. The advantages of this technique over previous methods lie in the speed with which measurements can be made and the ease with which all of the crystallographic directions in a fixed plane can be studied.

One modification of the Foner technique in this investigation was in the method of temperature control and temperature measurement. Ordinarily, the sample is allowed to warm up continuously in the vapor from

[7] Ch. Guillaud, Compt. Rend. **235**, 468 (1952).
[8] V. P. Krasovskii and I. G. Fakidov, Fiz. Metal i Metalloved. **11**, 319 (1961).
[9] L. F. Bates, Phil. Mag. **8**, 714 (1929).
[10] B. G. Whitmore, Phil. Mag. **7**, 125 (1929).
[11] Ch. Guillaud and H. Creveaux, Compt. Rend. **224**, 266 (1947).
[12] I. G. Fakidov and V. P. Krasovskii, Zh. Eksperim. i Teor. Fiz. **36**, 1063 (1959) [English transl.: Soviet Phys.—JETP **9**, 755 (1959)].
[13] S. V. Vonsovskii and K. B. Vlasov, Zh. Eksperim. i Teor. Fiz. **25**, 327 (1953).
[14] S. Foner, Rev. Sci. Instr. **30**, 548 (1959).

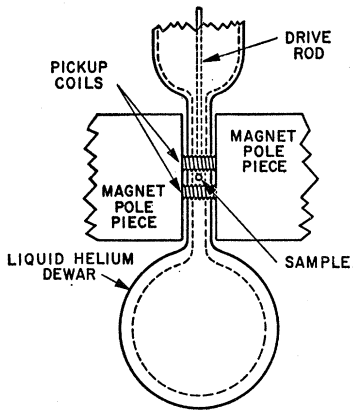

FIG. 2. Temperature control.

the evaporating liquid helium or liquid nitrogen. It was deemed desirable to study the magnetization processes at a fixed temperature, and so this technique was changed to permit stable temperature control by placing heaters on the sample holder and in the liquid bath. Heat from the sample heater could be balanced against increased cold vapor evolution caused by the heater in the liquid bath. The sample could thus be cycled over the whole temperature range of 500 to 4°K. Stable control was achieved to within $\pm 0.04°$ at high ($T>200$°K) temperatures, and within $\pm 0.2°$ at low (4.2°K) temperatures by an automatic control feeding current into one of the heaters. Temperatures were measured by a gold-cobalt thermocouple which had no detectable magnetic moment and which was in *direct* contact with the sample. The thermocouple was calibrated against premium grade copper-constantan wire from the Thermoelectric Company using their reference tables, which are based on NBS measurements. The absolute accuracy is probably better than ± 1°K, but the Curie point accuracy in this report is ± 0.2°K due to a separate calibration.

A further modification of the Foner technique consisted of using sample pickup coils parallel to the field direction instead of perpendicular as shown in Fig. 2. This geometry has the advantage of permitting smaller gaps and hence higher fields, but has the disadvantages of producing a slight change in slope in the magnetization curves due to a magnetic-pole image effect and also of causing an increased spurious signal due to vibrational pickup in the coils. The first effect is of negligible importance for the purposes of this investigation, but the vibrational pickup limited the sensitivity of the magnetometer to a magnetic moment of about 3×10^{-4} emu, which corresponds to a difference in susceptibility of $\Delta\chi=3\times10^{-8}$ for a 1-g sample in a field of 10 000 G. This sensitivity is sufficient, however, to permit measurements on most paramagnetic materials with good accuracy for a 1-g sample. The small sample size in this investigation (about 80 mg) caused a 20% uncertainty in the determination of μ_{eff}.

The method of measuring the spontaneous moment calls for special comment. The classic method due to Weiss and Forrer is basically a high-field extrapolation method which is more applicable to a polycrystal than to a single crystal. The method followed here is one which has been developed by Smith.[15] He pointed out that the M-H curve, measured in the easy direction on a single crystal, breaks away from its demagnetizing slope at a value of M exactly equal to M_s.

For low values of M and $T<T_c$, the magnetization curves in the easy direction are all linear with the applied field H and have an initial slope $1/N$, where N is the demagnetizing constant. If $M\geq M_s$, it is no longer possible for changes in M to compensate H to give an internal field $H_i=0$, and there is an abrupt change in the M-H curve. The breakaway point from this slope, which gives $M_s=H/N$, occurs for different temperatures at different critical values of the external field. A plot of $M_s(T)$ extrapolated to zero magnetization yields the ferromagnetic Curie point T_c.

Anisotropy is measured in a variety of ways, one of the best techniques being the torque magnetometer. Following Néel *et al.*,[16] however, it is possible to describe, by simple formulas, the magnetization curves measured in different crystallographic directions on a good spherical single crystal having uniaxial anisotropy. The anisotropy constant can be obtained as a parameter in the fitting process. For an orthorhombic crystal, such as MnP, the anisotropy energy to first order is given by $E=K_1\alpha_1^2+K_2\alpha_2^2$. If the measurements are confined to a principal crystallographic plane, then $E=K_1\alpha_1^2$ and $E=K_2\alpha_2^2$ for $\alpha_2=0$ and $\alpha_1=0$, respectively. The theory of Néel *et al.* applies for these special cases since the latter equations are equivalent to uniaxial anisotropy. In MnP the c axis is easy and the direction cosines α_1 and α_2 are measured relative to the a and b axes, respectively. The method of Néel *et al.* has a self-check between the low-field, multidomain region, where one set of equations applies, and the high-field, single-domain region, where another set of equations applies. This check was used for K_2 in the bc plane for MnP, but could not be used for K_1 in the ac plane because the anisotropy was prohibitively large.

III. PREPARATION OF MnP SINGLE CRYSTAL

Spectroscopically pure manganese metal was placed in a high-purity alumina crucible, which was supported at the upper end of a quartz tube. Phosphorus was placed at the lower end, and the tube was evacuated and sealed. The upper end of the tube was heated with a resistance furnace to approximately 1150°C. The lower end was heated initially to 450°C, and after 24 h to 500°C. The center portion of the tube was maintained at intermediate temperatures. After five days

[15] D. O. Smith, Phys. Rev. **102**, 959 (1956).
[16] L. Néel, R. Pauthenet, G. Rinet, and V. X. Giron, J. Appl. Phys. **31**, 27S (1960).

the manganese zone was slow-cooled. (The temperatures indicated are only approximate since a thermocouple could not be placed inside the sealed tube.)

A single crystal was obtained from the product, part of which was ground into a 0.118-in.-diam sphere by glass ball milling, the remainder being used for analyses. The principal crystallographic directions of the sphere were located by standard x-ray methods.

The stoichiometry of the crystal was established by analysis for the manganese content, which showed $100\pm0.2\%$ of theoretical Mn for MnP. Spectroscopic analysis of a portion of the crystal showed the following impurities: Mg 0.001%, Si 0.001%, Pb 0.001%, Fe $<0.0001\%$. X-ray powder diffraction data agreed with published data.

IV. RESULTS

With decreasing temperature MnP goes from paramagnetic to ferromagnetic at a Curie temperature which was measured to be 291.5 ± 0.2°K. With continued decrease of temperature, a transition from ferromagnetism to metamagnetism occurs at 50 ± 1°K. These properties will be discussed in the order of decreasing temperature.

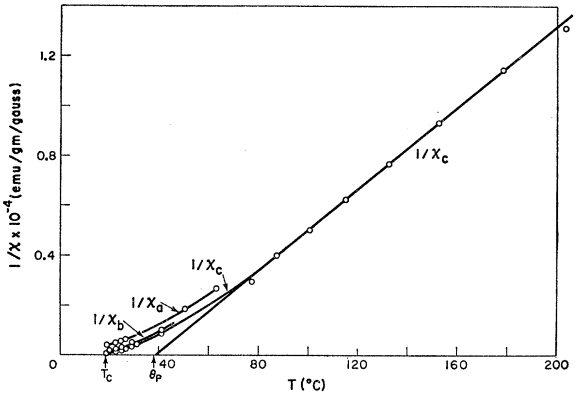

FIG. 3. $1/\chi$ versus T along the a, b, and c axes.

The paramagnetic susceptibility of MnP as a function of temperature is shown in Fig. 3. χ_a, χ_b, and χ_c refer to susceptibilities along the a, b, and c axes, respectively, given the axis convention $a>b>c$. No attempt was made to measure χ_a and χ_b any higher than shown, since their relative magnitudes converged toward χ_c at higher temperatures. The differences, however, between the reciprocal susceptibilities, namely $(1/\chi_a-1/\chi_c)$ and $(1/\chi_b-1/\chi_c)$, were observed to be approximately constant with temperature above the Curie point. No correction has been made for the demagnetizing field in Fig. 3, but the difference between any two values of $1/\chi$ is not sensitive to this effect.

From the Weiss[17] theory of ferromagnetism above the Curie point, the data of Fig. 3 fits the expression $\chi_g=C_g/(T-\theta_p)$, with $C_g=1.23\times10^{-2}$, where χ_g refers to the susceptibility in emu/g and $\theta_p=39°\pm1°C=312°\pm1°K$. Converting to C_A and χ_A (susceptibility per gram atom) and use of the expression[18] $\mu_{\text{eff}}=(8C_A)^{\frac{1}{2}}\beta$ for the effective paramagnetic moment, gives $\mu_{\text{eff}}=2.9\pm0.6$ Bohr magnetons.

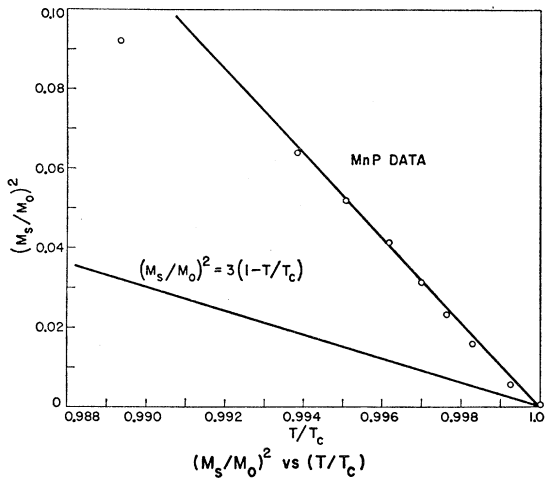

FIG. 4. $(M_s/M_0)^2$ versus (T/T_c) near the Curie point. The point at $(M_s/M_0)^2\cong0.092$ shows the beginning of the deviation from linearity.

In the ferromagnetic region, the spontaneous moment M_s was measured as a function of temperature, and the extrapolation to $M_s=0$ to yield the Curie point was done by the previously described method due to Smith.[15] A plot of $(M_s/M_0)^2$ versus (T/T_c) is shown in Fig. 4 for the sake of comparison with the results of Krasovskii and Fakidov. It is seen that near the Curie point $(M_s/M_0)^2=\xi(1-T/T_c)$ with $\xi=10.8$. The ferromagnetic Curie point was found to be 291.5 ± 0.2°K.

Values of (M_s/M_0) are plotted in Fig. 5 versus

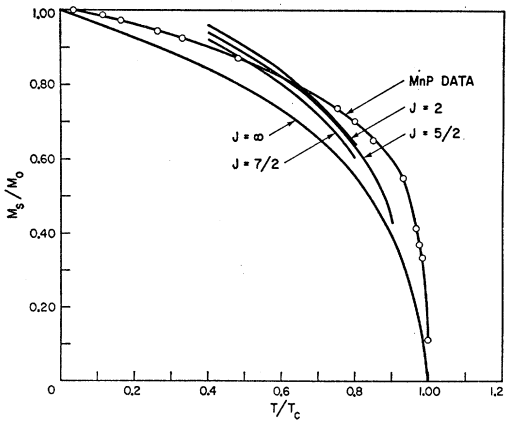

FIG. 5. (M_s/M_0) versus (T/T_c). Comparison of MnP data with Brillouin curves.

[17] P. Weiss, J. Phys. **6**, 661 (1907).

[18] R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand Company, Inc., Princeton, New Jersey, 1956).

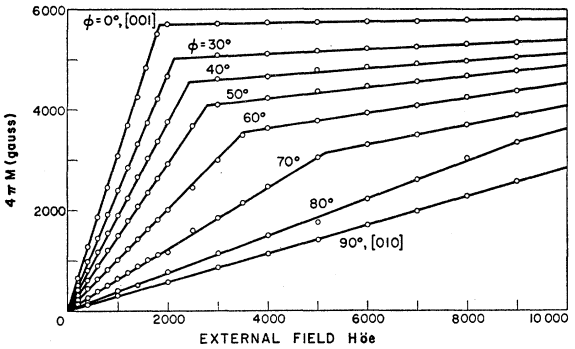

FIG. 6. Magnetization curves at 77°K in the *bc* plane. φ is the angle between H and the c axis and is 0° for the [001] direction and 90° for the [010] direction.

(T/T_c) in comparison with portions of Brillouin curves for different values of J. It is seen that no Brillouin curve can fit the observed data, but it is also noted that (M_s/M_0) is a smooth, monotonically decreasing function of (T/T_c). Extrapolation of $M_s(T)$ from $T=4.2$ to 0°K gives $4\pi M_0=6000$ G, or $\mu_0=1.29\pm0.04$ Bohr magnetons. (In high fields along the easy direction, the complicated metamagnetic effects reported below do not appear.) This is in good agreement with Guillaud's result[11] of 1.2 Bohr magnetons, despite the fact that his extrapolation was made from 77°K.

The ferromagnetic data are typified by the *M-H* curves shown in Figs. 6 and 7 for different directions in the *bc* and *ac* planes, respectively, at 77°K. It is noted that the crystal axes have a magnetic "hardness" of the same order as their respective lengths: c is easy, b intermediate, and a hard; and $c<b<a$. Moreover, this relative hardness is preserved throughout the entire ferromagnetic and paramagnetic regions. The possibility of other axes becoming easier than the c axis at lower temperatures resulting in a metastable "easy" axis was checked by a magnetic anneal. That is, the crystal was cycled from above room temperature to the liquid-helium range of temperatures in the presence of an applied field along different directions. No temperature or magnetic hysteresis effects were noticeable anywhere in the entire temperature range.

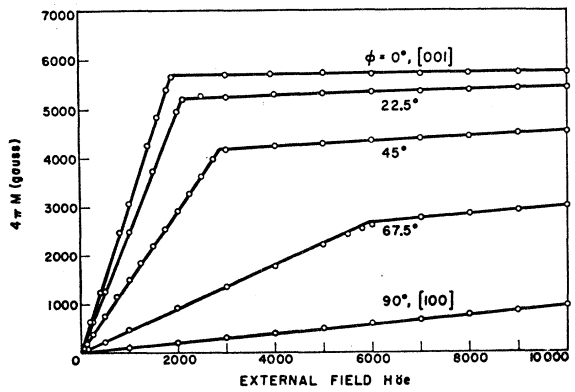

FIG. 7. Magnetization curves at 77°K in the *ac* plane. φ is the angle between H and the c axis and is 0° along the [001] direction and 90° along the [100] direction.

Curves very similar to the ones in Figs. 6 and 7 were obtained at other temperatures between 50 and 291.5°K with modifications coming in 3 ways: (1) The saturation magnetization dropped with increasing T as discussed in the previous section. (2) A strong curvature develops in $M(H)$ near the Curie point, and (3) the slope of *M-H* curves measured at angles to the c axis become larger as $T\rightarrow T_c$ due to the temperature dependence of anisotropy.

The shapes of the various magnetization curves in Figs. 6 and 7 are readily explained on the basis of the magnetization laws derived by Néel *et al.*[16] for the case of a single crystal having uniaxial anisotropy within a principal crystallographic plane. As mentioned in the preceding section, the anisotropy constants K_1 and K_2 were derived by this method and their temperature dependence in terms of the normalized parameters $(2K_1/M_s^2)$ and $(2K_2/M_s^2)$ is plotted in Fig. 8. Note

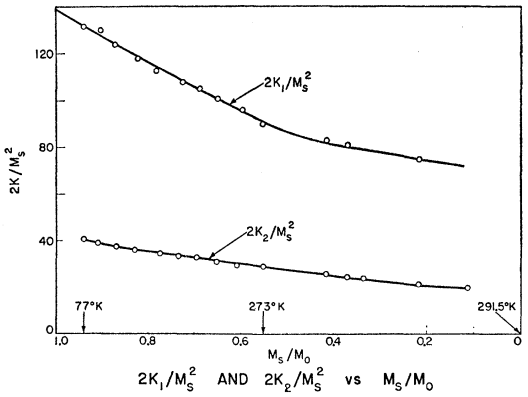

FIG. 8. $2K_1/M_s^2$ and $2K_2/M_s^2$ versus M_s/M_0.

that K_1 and K_2 do not vanish as $(M_s)^3$ near the Curie temperature, but more like $(M_s)^2$. This is consistent with the paramagnetic measurements described above. Also note that $K_1>K_2$ throughout the entire temperature range.

At 50°K an abrupt change occurs in the low-field properties of MnP. The consistent trend of properties mentioned above is broken, all the magnetization curves begin to shift to the right along the H axis, and a small initial susceptibility is observed. The start of this process is shown in Figs. 9 and 10 for the *bc* and *ac* planes at 47.5°K. The shift has become quite large, by contrast, at 7.3°K as shown in Figs. 11 and 12 for the *bc* and *ac* planes, respectively.

The important features brought out by the low-temperature data are these: (1) At 50°K there is an abrupt decrease in the initial susceptibility in the c and b directions of the crystal. This is further shown by Fig. 13, which is a plot of χ_a, χ_b, and χ_c in the low-

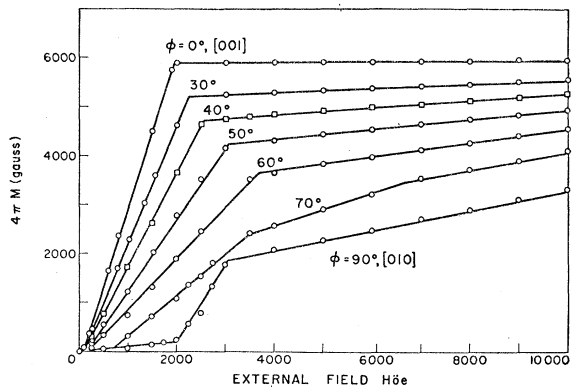

FIG. 9. Magnetization curves at 47.5°K in the *bc* plane. φ is the angle between H and the [001] direction and is 90° for H along the [010] direction.

temperature region. It is seen that χ_a stays relatively constant. The ratio $\chi_a/\chi_c \rightarrow 1$ as $T \rightarrow 0$°K, and within experimental accuracy all susceptibilities in the *ac* plane are equal at 4.2°K. The ratio $\chi_c/\chi_b = 1.65 \pm 0.05$ at that temperature. (2) There is a critical field H_c for the *c* axis at which ferromagnetism is restored. It varies from 0 Oe at $T = 50$°K to almost 2500 Oe at 4°K. This interpretation is based on the fact that M versus H changes abruptly at H_c and thereafter follows a straight line exactly parallel to the demagnetizing slope until saturation is reached. The temperature dependence of H_c is shown in Fig. 14. There is no anomaly in the saturation moment on passing through 50°K, as can be seen from Fig. 5. (3) There is also a critical field effect for the *b* axis of the crystal (and, therefore, for all directions in the *bc* plane), as can be seen from Fig. 11. At high enough field strengths, all of the curves of Fig. 11 tend to show an abrupt increase in magnetization as the field is increased. Although the abruptly rising portion of the curve along the *b* axis in Fig. 11 indicates a critical field, the slope of the step is not equal to $(1/N)$, so that it is not possible to make a straightforward correction for the demagnetizing factor, as in the case of the *c* axis.

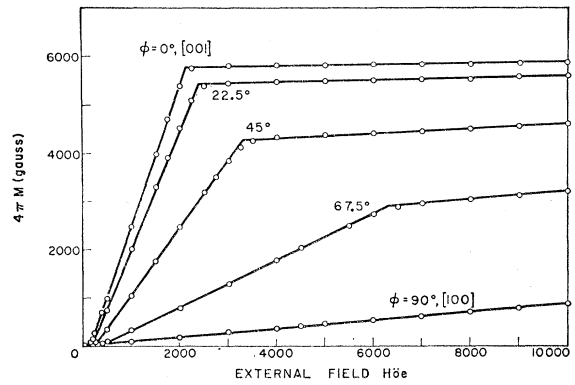

FIG. 10. Magnetization curves at 47.5°K in the *ac* plane. φ is the angle between H and the [001] direction and is 90° when H is along the [100] direction.

The interpretation of this data is that the material has become metamagnetic, i.e., it exhibits an antiferromagnetic-ferromagnetic transformation which is a function of the direction and magnitude of the applied field and of the temperature. The previously described anisotropy measurements and the lack of hysteresis effects rule out an alternate mechanism, viz., some axis other than the *c* axis becoming easy at low temperatures, thereby causing a spin-axis jump as the temperature is lowered or the field increased.

V. DISCUSSION OF RESULTS

A. High-Temperature Data

The salient feature of the high-temperature results is that MnP has strong ferromagnetic interactions. This can be inferred from the fact that the paramagnetic

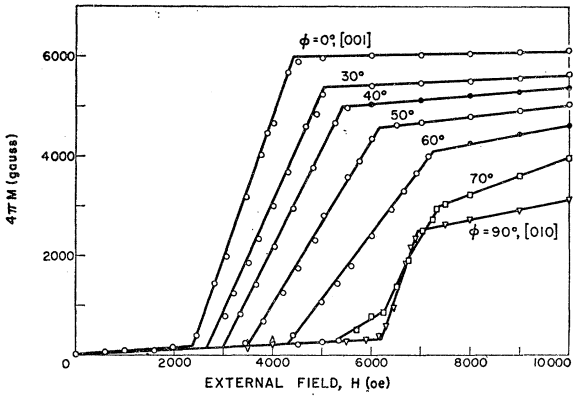

FIG. 11. Magnetization curves at 7.3°K in the *bc* plane. φ is the angle between H and the [001] direction and is 90° when H is along the [010] direction.

Curie temperature is relatively high and from the fact that the curvature of the $1/\chi$ versus T curve is concave up near the Curie point, which gives rise to $\theta_p > T_c$. From Néel's two-sublattice theory of ferrimagnetism,[19] a concave down behavior is predicted for the $1/\chi$ versus T curve and a low or negative paramagnetic Curie temperature ($\theta_p < T_c$). The value of the Curie or Néel temperature extrapolated from the $1/\chi$ versus T curve is a measure of the average value of the strength of the interactions, and a change in sign occurs from negative to positive when antiferromagnetic exchange dominates ferromagnetic exchange.

From these considerations it can be concluded that MnP does not fit either a ferrimagnetic model as Guillaud[7] has proposed or a model of antiferromagnetism with weak superimposed ferromagnetism as Krasovskii and Fakidov[8] have suggested. Further support for this comes from measurement of the temperature de-

[19] L. Néel, Ann. Phys. (N. Y.) 3, 137 (1948).

pendence of the spontaneous moment $M_s(T)$. The data of Fig. 4 show that $(M_s/M_0)^2=\xi[1-T/T_0]$ if $\xi=10.8$, in contrast to Krasovskii and Fakidov's[12] result of $\xi=3.4$. As mentioned in the Introduction, a value of $\xi>3$ can be taken as indicative of ferromagnetic coupling according to a theory of Vlasov and Vonsovskii.[13] The value of 10.8 observed here is consistent with the *strong* ferromagnetic coupling inferred from the paramagnetic data. The large difference between this value of ξ and the value of Krasovskii and Fakidov[8,12] may merely be due to the fact that use of a single crystal has removed the complicating effects of anisotropy in the determination of $M_s(T)$.

A mechanism other than that of Vlasov and Vonsovskii may be operating to distort the $M_s(T)$ curve from a Brillouin function, however. Smart[20] has shown that a modification of the molecular field theory to include competing temperature-dependent interactions will cause such a distortion. Furthermore, this mechanism gives a consistent explanation of the low-temperature measurements, as described in the next section.

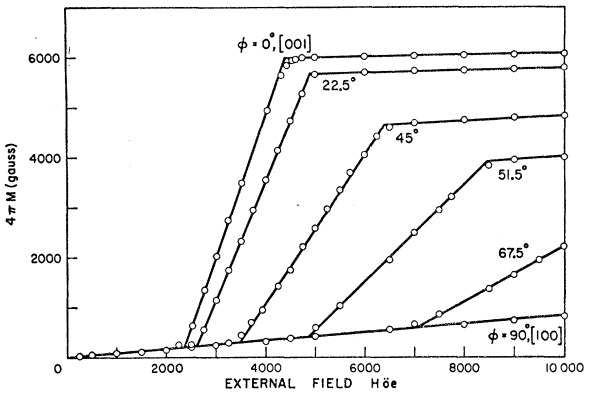

FIG. 12. Magnetization curves at 7.3°K in the *ac* plane. φ is the angle between H and the [001] direction and is 90° when H is along the [100] direction.

The measured paramagnetic moment $\mu_{\text{eff}}=2.9$ Bohr magnetons, although significantly lower than Bates'[9] result of 3.69 Bohr magnetons, is nevertheless quite a bit larger than the spontaneous moment of $\mu_0=1.29$ Bohr magnetons at $T=0$°K, and one must reckon with this in attempting to explain the properties of MnP on the basis of strong ferromagnetic coupling. The magnitude of the discrepancy is revealed by a calculation of the effective angular momentum quantum numbers from the formulas $\mu_0=gJ\beta$ and $\mu_{\text{eff}}=g[J(J+1)]^{\frac{1}{2}}\beta$. Given $g=2$, one obtains $J=0.65$ and $J=1.0$ from the ferromagnetic and paramagnetic data, respectively. The difference can be partially attributed to the experimental inaccuracy of $\pm 20\%$ in μ_{eff} and to the fact that 2.9 Bohr magnetons is actually an upper limit for μ_{eff} since the $1/\chi$ versus T curve may still have some con-

[20] J. S. Smart, Phys. Rev. **90**, 55 (1952).

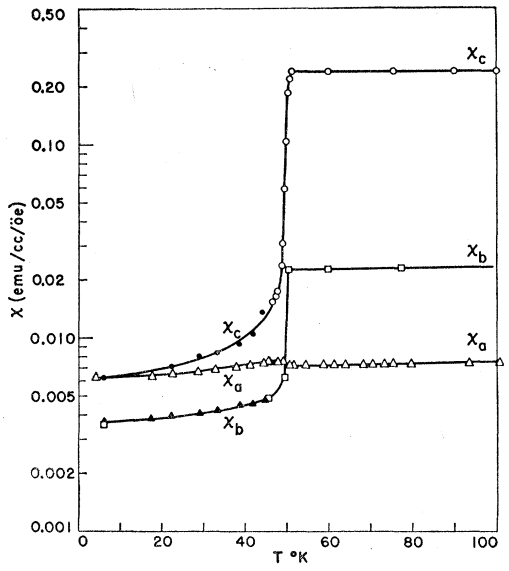

FIG. 13. Initial susceptibility vs temperature along the *a*, *b*, and *c* axes. χ_c is not infinite above 50°K because these are *effective* susceptibilities, $\chi=M/H_e$ where H_e is the external field, and no correction has been made for the demagnetizing field.

cave curvature even at 200°C. Although one cannot completely rule out the presence of angles between the spins, all of the above arguments would imply that any angle or spiraling of the spins in the ferromagnetic state would necessarily be restricted to small cone angles. Goodenough[21,22] has pointed out that Mn^{3+} is

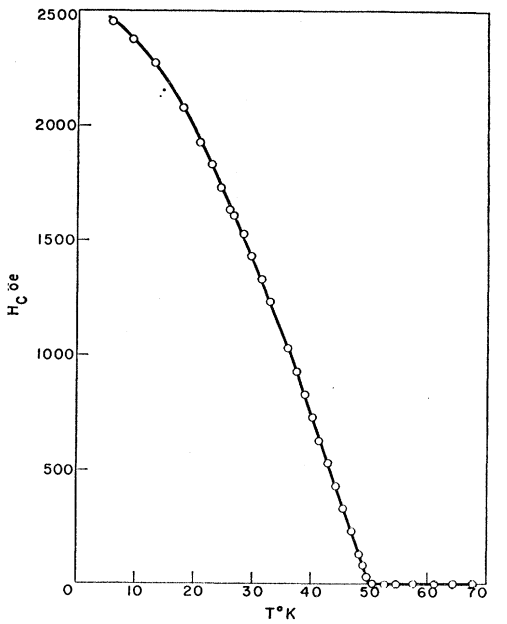

FIG. 14. Critical field for the *c* axis versus temperature.

[21] J. B. Goodenough, J. Appl. Phys. **35**, 1083 (1964).
[22] J. B. Goodenough, MIT Lincoln Laboratory Technical Report No. TR 345, 1964 (unpublished).

probably in a low-spin state, which calls for a spin-only moment of 2 Bohr magnetons ($J=1.0$) rather than the 4 Bohr magnetons expected for high-spin-state Mn^{+++}.

B. Low-Temperature Data

The Weiss molecular field theory of magnetism cannot explain an antiferromagnetic-ferromagnetic transition, as has been discussed by Anderson[23] and Pratt.[24] Such transformations have been explained in the rare earths[3,25–27] and in MnAs and MnBi [20] (the first-order transitions at T_c now appear to be ferromagnetic-paramagnetic transitions) on the basis of competing interactions. The metamagnetism and the spiral spin structures in such compounds have also received successful interpretations on this basis. The metamagnetism of MnP makes it a logical candidate for explanation in terms of competing interactions.

The critical field for the onset of ferromagnetism is too low to represent spin flipping in a collinear antiferromagnet, since the spin-flip field is on the order of the exchange field (i.e., $\approx 10^6$ Oe or more), whereas the critical field for MnP ranges from 0 to 2500 Oe. Enz[2] has shown that a competing interaction model accounts in a natural way for the low critical field (compared to the spin-flip field for a classical collinear antiferromagnet) observed in the antiferromagnetic-ferromagnetic transition in Dy, and such may well be the mechanism in MnP. Enz has also shown that the monotonic decrease of the critical field towards zero as the critical temperature is approached can be explained on the basis of *temperature-dependent* competing interactions.

A further requirement of the Enz model is that the antiferromagnetic phase should have a spiral spin configuration. Evidence that antiferromagnetic MnP cannot have a simple collinear spin model comes from the observation of the initial susceptibilities at low temperatures. The normal collinear antiferromagnet would have symmetry about its spin axis and the susceptibility along the axis would tend to zero at $T=0°K$. Although all the susceptibilities are the same in the *ac* plane as $T \rightarrow 0°K$, and this implies a symmetric structure of spins about the *b* axis, no susceptibility approaches zero as $T \rightarrow 0°K$. It would be fortuitous for the magnetic anisotropy due to exchange to exactly balance out the crystalline anisotropy. Therefore, it is expected that MnP has a symmetric but *complex* spin configuration at $T=0°K$. A spiral configuration is a possibility, since all susceptibilities would be finite at $T=0°K$, but another argument shows the situation to be more complicated. It is expected from calculations of Yoshimori,[3] Enz,[2] and others that the susceptibility perpendicular to the planes of the spins of a spiral would be greater than any susceptibility within the plane. In MnP, $\chi_b < (\chi_a \text{ or } \chi_c)$ and one would expect the reverse for a spiral.

Goodenough[21,22] has considered the magnetic interactions in detail in MnP and has arrived at a specific model which explains the above susceptibility data as well as the metamagnetic transformation and the low ferromagnetic moment. The low-temperature spin configuration is predicted to be a strongly distorted spiral propagating along the orthorhombic *c* axis with spins lying in the *bc* plane. A neutron diffraction experiment should be done, however, to provide a definitive description of the spin structure. Smart[20] has shown that a ferromagnetic-antiferromagnetic phase change due to competing interactions ought to be first order, but Goodenough[28] has pointed out that a spiral which gradually collapses into a cone might well be second order. In this regard there are four important points to be noted: (1) There is a complete lack of temperature and field hysteresis (<5 Oe and $<0.2°K$). (2) The saturation moment (at 10 000 G) is continuous and smooth as a function of temperature through the transition region. (3) The magnetic symmetry in the ferromagnetic state below 50°K is the same as above 50°K. (4) The magnetic symmetry in the antiferromagnetic state is also orthorhombic below 50°K, but approaches cylindrical symmetry about the *b* axis at $T=4.2°K$. These facts indicate that there is probably no change in crystal symmetry at 50°K.

ACKNOWLEDGMENTS

The authors are grateful for the advice of Professor John T. Norton who supervised one of us (E.E.H.) in this research. They are especially indebted to Dr. John B. Goodenough for making available the facilities of Group 53 at Lincoln Laboratory and for his comments on the manuscript. The chemical analysis for Mn content was carried out by Earl Whipple.

Thanks also go to Norman Menyuk, Kirby Dwight, and Dr. Thomas Kaplan for many discussions on the interpretation of the magnetic data.

[23] P. W. Anderson, Phys. Rev. **79**, 705 (1950).
[24] G. W. Pratt, Phys. Rev. **108**, 1233 (1957); J. Appl. Phys. **29**, 520 (1958).
[25] T. Nagamiya, J. Phys. Radium **20**, 70 (1959).
[26] J. Villain, Phys. Chem. Solids **11**, 303 (1959).
[27] T. A. Kaplan, Phys. Rev. **116**, 888 (1959).
[28] J. B. Goodenough (private communication).