

Leo Merrill

## High-Pressure Study of the First-Order Phase Transition in MnAs

J. B. GOODENOUGH AND J. A. KAFALAS

Lincoln Laboratory,\* Massachusetts Institute of Technology, Lexington, Massachusetts

(Received 21 November 1966)

The first-order magnetic-transition temperature in MnAs has been measured as a function of both increasing and decreasing pressure. A critical pressure  $P_c \sim 4.6$  kbar has been obtained for the range of stability of the hexagonal phase. The pressure hysteresis increases with decreasing temperatures. Cooling to 77°K under 5 kbar and then releasing pressure gives the B31 phase at atmospheric pressure, and it remains stable on heating to 138°K, where there is an increase of magnetization of over a factor of 50. These data, together with earlier magnetic measurements on the system  $\text{MnAs}_{1-x}\text{P}_x$ , demonstrate that the origin of the first-order phase transition is a large exchange striction in the basal planes plus a volume-dependent Weiss molecular field and manganese moment. This volume dependence is due to electron rearrangements associated with a high-spin-to-low-spin transition. The sharpness of the high-spin-to-low-spin transition cannot be accounted for by variations in crystal-field splitting with volume. It is suggested that a bandwidth is increasing with decreasing volume through the maximum bandwidth for spontaneous band ferromagnetism. The critical band appears to consist of  $t_{\pm}$  orbitals, which are primarily influenced by the Mn-Mn interactions within basal planes.

## I. INTRODUCTION

THE magnetic and structural properties of MnAs are summarized in Table I. The significant features are: (1) There is a first-order phase change (latent heat 1.79 cal/g) at the ferromagnetic Curie temperature  $T_c$  from the hexagonal NiAs ( $B8_1$ ) structure at  $T < T_c$  to the orthorhombic MnP ( $B31$ ) structure at  $T > T_c$ . There is a discontinuous loss of ferromagnetism at  $T_c$ , and extrapolation to  $T > T_c$  of magnetization versus temperature with a Brillouin function gives an extrapolated Curie temperature for the low-temperature phase  $T_c(\text{ext}) \approx 127^\circ\text{C}$ . (2) At a  $T_c \approx 127^\circ\text{C}$ , there is a second-order  $B31 \rightleftharpoons B8_1$  transition. There is a maximum in the magnetic susceptibility at  $T_i$ , but MnAs is not antiferromagnetic in the interval  $T_c < T < T_i$ . Rather there is a change in the magnitude of the manganese moment ( $d\mu/dT > 0$ ) in this interval. (3) The high-temperature ( $T > T_i$ ) hexagonal phase exhibits a Curie-Weiss behavior with a  $\mu_{\text{eff}} = 4.95\mu_B$  and a  $\theta_f \approx 10^\circ\text{C}$ . Since any ferromagnetic temperature is always smaller than  $\theta_f$ , this implies that the net ferromagnetic coupling in this phase is smaller than that in the low-temperature ( $T < T_c$ ) hexagonal phase, which has a  $T_c(\text{ext}) \approx 127^\circ\text{C}$ . (4) A discontinuity of 1.86% in the density at  $T_c$  is caused by an expansion in the basal plane below  $T_c$ . (5) The  $B31$  structure is derived from the  $B8_1$  structure by a displacement of the manganese atoms out of the centers of symmetry of their arsenic interstices to make one shortest manganese-arsenic bond. Alternate  $[1\bar{1}, 0]$  rows of manganese are displaced toward one another primarily within the basal planes, and along the hexagonal  $c_h$  axis metal atoms in alternate basal planes are displaced in opposite directions, as shown in Fig. 1.

Three explanations of the first-order phase change at  $T_c$  have been suggested. (1) Kittel<sup>1</sup> developed a thermo-

dynamic theory involving "exchange inversion" to explain the antiferromagnetic  $\rightleftharpoons$  ferrimagnetic transition in  $\text{Mn}_{2-x}\text{Cr}_x\text{Sb}$  and suggested it might be applicable to MnAs. The lack of antiferromagnetic order in the interval  $T_c < T < T_i$  rules out this possibility. (2) Bean

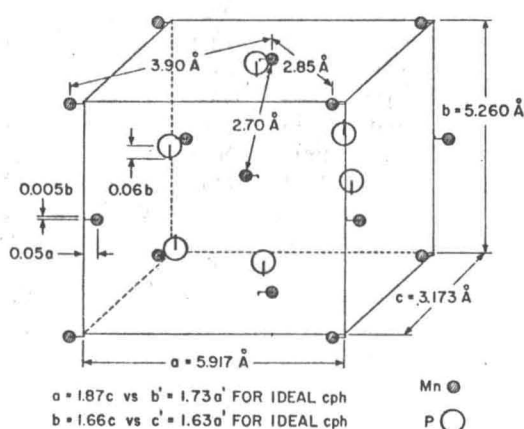


FIG. 1. The orthorhombic B31 structure of MnP.

and Rodbell<sup>2</sup> proposed a thermodynamic theory involving a net ferromagnetic exchange interaction that is sensitive to molar volume, so that

$$T_c = T_0 [1 + \beta(V - V_0)/V_0]. \quad (1)$$

This motivated DeBlois and Rodbell<sup>3</sup> to measure  $T_c$  as a function of pressure  $P$  and applied field strength  $H$  in the ranges  $15 < T < 65^\circ\text{C}$ ,  $0 < P < 1$  kbar, and  $0 < H < 110$  kOe. They appeared to obtain a qualitative match between theory and experiment. (3) Goodenough<sup>4</sup> pointed out how the two transitions,  $B8_1 \rightleftharpoons B31$  at  $T_c$

<sup>2</sup> C. P. Bean and D. S. Rodbell, Phys. Rev. 126, 104 (1962).

<sup>3</sup> R. W. DeBlois and D. W. Rodbell, Phys. Rev. 130, 1347 (1963).

<sup>4</sup> J. B. Goodenough, M.I.T. Lincoln Laboratory, Lexington, Massachusetts, Technical Report No. 345, DDC 435758, 1964 (unpublished).

\* Operated with support from the U.S. Air Force.

<sup>1</sup> C. Kittel, Phys. Rev. 120, 335 (1960).

TABLE I. Some physical properties of MnAs.<sup>a</sup>

Property	$0 < T < T_c$	$T_c < T < T_t$	$T_t < T$
Magnetic order	Ferromagnetic	Paramagnetic	Paramagnetic
Molecular moment	$\mu_0 = 3.4 \mu_B$	$d\mu/dT > 0$	$\mu_{\text{eff}} = 4.95 \mu_B$
Transition temp. ( $^{\circ}\text{K}$ ) <sup>b</sup>	$T_c(\text{ext}) \approx 400$ ; $T_c \uparrow = 317$ , $T_c \downarrow = 307$	$T_t \approx 400$	$\theta_f = 283$
Structure	Hexagonal $B8_1$	Orthorhombic $B31$	Hexagonal $B8_1$
$(dV/VdT)_P$ ( $^{\circ}\text{C}^{-1}$ ) <sup>c</sup>	$< 0$ ( $295^{\circ}\text{K} < T \leq T_c$ )	$\approx 2 \times 10^{-4}$	$\approx 6 \times 10^{-5}$
$c_N/2$ ( $\text{\AA}$ )	$> 2.85$	$\approx 2.87$	$\approx 2.9$
$a_N$ ( $\text{\AA}$ )	$\approx 3.72$	3.68–3.70	$> 3.71$
Latent heat (cal/g)		1.79 at $T_c$	None at $T_t$

<sup>a</sup> T. Hirone, *Landolt-Börnstein Tabellen* (Springer-Verlag, Berlin, 1962), Vol. 6, II/9, pp. 3–14; W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon Press, Inc., New York, 1958), p. 58; R. W. DeBlois and D. S. Rodbell, *Phys. Rev.* **130**, 1347 (1963); J. B. Goodenough, D. H. Ridgley, and W. A. Newman, in *Proceedings of the International Conference*

on Magnetism, Nottingham, 1964 (The Physical Society and The Institute of Physics, London, 1965), p. 542.

<sup>b</sup> At atmospheric pressure and zero applied field  $(\partial T_c/\partial P)_H > 0$ ;  $(\partial T_c/\partial H)_P > 0$ .

<sup>c</sup> Density increases by 1.86% on heating across  $T_c$ .

and  $B31 \rightarrow B8_1$  at  $T_t$ , could reflect a high-spin manganese configuration in the  $B8_1$  phase and a low-spin manganese configuration in the  $B31$  phase. This motivated measurements<sup>5</sup> of the magnetic properties of the systems  $\text{MnAs}_{1-x}\text{P}_x$  and  $\text{MnAs}_{1-y}\text{Sb}_y$ , which demonstrated that the  $B31$  phase does contain a much smaller manganese moment (low-spin manganese configuration) and that the range of temperatures over which the high-spin configuration is converted to a low-spin configuration on cooling through  $T_t$  is only about  $125^{\circ}\text{C}$ . It was also found that a first-order phase change at  $T_c$  only occurs if  $T_c > T_t - 125^{\circ}\text{C}$ . The addition of phosphorus in the amount of only  $x > 0.04$  is able to stabilize the  $B31$  phase to lowest temperatures.

Since a temperature change is related to a volume change via the thermal expansion coefficient, the experiments on the system  $\text{MnAs}_{1-x}\text{P}_x$  indicate that there is a  $d\mu/dV > 0$  for a critical range of volume  $V$  corresponding to the  $125^{\circ}\text{C}$  temperature interval below  $T_t$ . If this is so, then there should be a critical pressure  $P_c$  above which the  $B31$  phase can be stabilized to lowest temperatures. The present study was designed to demonstrate that such a critical pressure exists and to determine its magnitude. Previous pressure studies on MnAs have been confined to  $P < 2.5$  kbar.<sup>3,6</sup>

Given a critical pressure  $P_c$ , the present study also attempts to interpret the significance of the sharpness of the high-spin  $\rightleftharpoons$  low-spin transition at a critical molar volume.

## II. EXPERIMENTAL

The pressure dependence of  $T_c$  in polycrystalline MnAs was determined by monitoring the change of electrical resistance with hydrostatic pressure at various

<sup>5</sup> J. B. Goodenough, D. H. Ridgley, and W. A. Newman, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (The Physical Society and The Institute of Physics, London, 1965), p. 542.

<sup>6</sup> G. A. Samara and A. A. Giardini, *Physics of Solids at High Pressures* (Academic Press Inc., New York, 1965), p. 308.

fixed temperatures between 77 and  $300^{\circ}\text{K}$ . This is convenient because of a discontinuity in the electrical resistance that occurs at  $T_c$ .<sup>7</sup> The resistance was monitored in the conventional four-probe manner. Two types of apparatus were used: a piston-cylinder apparatus employing isopentane liquid as the transmitting medium and, at the lowest temperatures, a high-pressure gas apparatus employing helium gas as the transmitting medium. Constant temperatures were maintained by immersing the pressure vessel in a constant-temperature bath. The room-temperature run shown in Fig. 2 is typical of the data obtained. The transition pressure was chosen as that pressure at which the large change in resistance is initiated. This point has good reproducibility.

Table II gives a summary of the data. In the interval  $200 \leq T \leq 317^{\circ}\text{K}$ , the data points for increasing pressure can be fitted by a quadratic equation:

$$P = -5.6230 + 0.1072 T_c - 0.000283 T_c^2, \quad (2)$$

where  $P$  is the pressure in kbar and  $T_c$  is in degrees

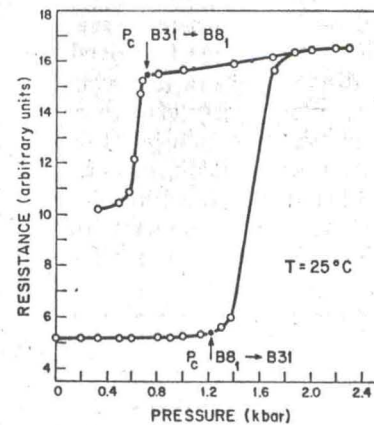


FIG. 2. Electrical resistance versus pressure at  $25^{\circ}\text{C}$  of polycrystalline MnAs.

<sup>7</sup> C. Guillaud, *J. Phys. Radium* **12**, 223 (1951).

Kelvin at 1 a results Giardini (DeBlois  $B31 \rightarrow B$  ment w imply t done o single c see note

The p where t interval demonstr which t tempera creases  $P > 2$  kbar to stabil fact, it i pheric p from  $P >$

The tr A specimen in the hi was cool the speci vibrating

FIG. 3. T pressure d first-order and  $B31 \rightarrow B$  tions in M  $320^{\circ}\text{K}$ .

<sup>8</sup> As quoted

TABLE II. Data for the magnetic  $B8_1$  to  $B31$  transition in MnAs.

Pressure (kbar):	0.001	1.22	2.33	3.73	4.23	4.5	4.5
$B8_1 \rightarrow B31 T_c$ ( $^{\circ}\text{K}$ ):	317	298	278	243	223	201	77
Temperature ( $^{\circ}\text{K}$ ):	307	298	283	245	240	201	138
$B31 \rightarrow B8_1 P_c$ (kbar):	0.001	0.7	0.9	2.0	1.7	1.4	0.001

Kelvin. Differentiation gives  $dT_c/dP = -13.8^{\circ}\text{C}/\text{kbar}$  at 1 atm. This is in moderate agreement with the results of Rodbell and Wilson<sup>8</sup> and of Samara and Giardini,<sup>9</sup> who report  $-12$  and  $-12.3^{\circ}\text{C}/\text{kbar}$ . (DeBlois and Rodbell<sup>8</sup> give  $-24.1^{\circ}\text{C}/\text{kbar}$  for the  $B31 \rightarrow B8_1$  transition, which is also in reasonable agreement with Table II and Fig. 3.) However, these authors imply that the slope is constant. Our experiments were done on polycrystalline samples, whereas they used single crystals and were confined to  $P < 2.5$  kbar. (Also see note added in proof at end of paper.)

The pressure dependence of  $T_c$  is displayed in Fig. 3, where the smooth curve for increasing pressure in the interval  $190 \leq T \leq 317^{\circ}\text{K}$  is Eq. (2). The data clearly demonstrate a critical pressure  $P_c \approx 4.6$  kbar above which the  $B31$  phase is indeed stable down to lowest temperatures. In addition, the pressure hysteresis increases with decreasing temperature, so that pressures  $P > 2$  kbar applied at room temperature are sufficient to stabilize the  $B31$  phase to lowest temperatures. In fact, it is possible to obtain the  $B31$  phase at atmospheric pressure below  $138^{\circ}\text{K}$  if the pressure is reduced from  $P > 4.6$  kbar at a  $T < 138^{\circ}\text{K}$ .

The transition at  $T = 138^{\circ}\text{K}$  was obtained as follows: A specimen of MnAs was placed under 5-kbar pressure in the high-pressure gas apparatus, and the apparatus was cooled to  $77^{\circ}\text{K}$ . Pressure was then released and the specimen transferred to the cold stage ( $4.2^{\circ}\text{K}$ ) of a vibrating-coil magnetometer. At no time was the speci-

men allowed to warm up more than a few degrees above  $77^{\circ}\text{K}$ . The magnetic properties were measured from  $4.2^{\circ}\text{K}$  to room temperature. Below  $138^{\circ}\text{K}$  there was a small susceptibility that decreased with increasing temperature. An abrupt transition occurred at  $138^{\circ}\text{K}$ , the magnetization increasing by over a factor of 50 to the magnetization value of the  $B8_1$  phase.

Although the low-temperature  $B31$  phase appeared to resemble the metamagnetic phase of low-temperature MnP and  $\text{MnAs}_{0.9}\text{P}_{0.1}$ , our preliminary measurements on a polycrystalline sample do not allow characterization of the magnetism of this phase. This point is significant because Rodbell and Bean<sup>9</sup> have anticipated a ferromagnetic  $\rightleftharpoons$  antiferromagnetic phase change with increasing pressure at low temperatures. A pressure bomb for further magnetic studies is under construction. Meanwhile, monitoring of the resistance at room temperature up to 12 kbar has shown only one first-order phase change. The Rodbell-Bean  $P^*-T$  phase diagram contains  $P^* = P - \alpha_1 T/K$ , where  $\alpha_1$  is the thermal expansion coefficient and  $K$  is the compressibility. Their diagram would reflect the  $P^*-T$  curve through the  $P^* = [4.6 + (\alpha_1 T/K)]$  kbar line to predict a room-temperature paramagnetic  $\rightleftharpoons$  antiferromagnetic phase change near  $[8 + (\alpha_1 T/K)]$  kbar = 11.8 kbar. If such a transition exists below 12 kbar, it is not first-order. Further, reduction in temperature under  $P = 3$  kbar from the paramagnetic  $B31$  phase at room temperature and 3 kbar gave no anomaly in the resistance down to  $90^{\circ}\text{K}$ . Since the high-pressure phase is magnetically ordered at  $90^{\circ}\text{K}$ , this means that the paramagnetic  $\rightleftharpoons$  magnetic-order transition in the high-pressure phase is not first-order. (The magnetic-order transition temperature for the high-pressure phase is not indicated in Fig. 3 since it is not clearly defined by a resistivity anomaly.) Therefore, it may be assumed that the high-pressure phase retains the  $B31$  structure in the areas so designated in Fig. 3 and that there is no crystallographic phase change associated with magnetic ordering in the high-pressure phase.

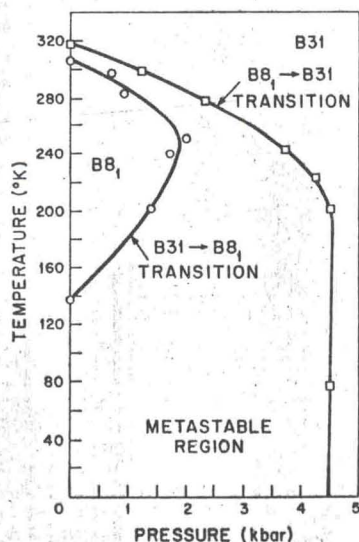
### III. DISCUSSION

#### A. Significant Observations

These results, together with the earlier study<sup>6</sup> of  $\text{MnAs}_{1-x}\text{P}_x$  and the data of Table I, establish the

<sup>9</sup> D. S. Rodbell and C. P. Bean, J. Appl. Phys. Suppl. 33, 1037 (1962).

FIG. 3. Temperature-pressure diagram for first-order  $B8_1 \rightarrow B31$  and  $B31 \rightarrow B8_1$  transitions in MnAs below  $130^{\circ}\text{K}$ .



<sup>6</sup> As quoted by Ref. 3.

The Institute of  
( $\partial T_c / \partial P$ )<sub>H</sub> > 0;

This is con-  
e electrical  
e was moni-  
anner. Two  
cylinder ap-  
transmitting  
es, a high-  
a gas as the  
atures were  
ssel in a con-  
operatu run  
obtained. The  
sure at which  
d. This point  
n the interval  
asing pressure

$33 T_c^2$ , (2)

is in degrees

FIG. 2. Electrical  
istance versus  
essure at  $25^{\circ}\text{C}$  of  
polycrystalline  
nAs.

following facts that are important for any theory of the transitions at  $T_c$  and  $T_t$  in MnAs:

1. There is a  $d\mu/dV > 0$  in the temperature interval  $T_t - \Delta T < T < T_t$ , where  $\Delta T \approx 125^\circ\text{C}$ .

2. From Table I, the thermal expansion coefficient in this temperature interval is about  $2 \times 10^{-4} \text{C}^{-1}$ , so that  $d\mu/dV > 0$  occurs in a critical molar volume range  $V_t - \Delta V < V < V_t$ , where  $V_t$  is the molar volume at  $T_t$  and

$$\Delta V/V \approx 0.025. \quad (3)$$

3. A first-order  $B8_1 \rightleftharpoons B31$  transition at  $T_c$  only occurs if the molar volume at  $T_c$  falls within the critical range  $V_t - \Delta V < V < V_t$ . Further, the fact that the low-temperature phase is hexagonal, with a discontinuous expansion of the basal planes on cooling through  $T_c$ , demonstrates that there is a large, positive exchange striction in the basal planes if  $V > V_t - \Delta V$  at  $T_c$ . This exchange striction has essentially disappeared where  $V < V_t - \Delta V$ .

**B. Contact with Thermodynamic Theory**

Since the Curie temperature is proportional to  $W\mu^{*2}$ , where  $\mu^{*2} \approx 4S(S+1)\mu_B^2$  and  $W$  is the ferromagnetic Weiss molecular field, it follows from Eq. (1) that

$$\beta = V \left( W^{-1} \frac{dW}{dV} + \frac{2}{\mu^*} \frac{d\mu^*}{dV} \right). \quad (4)$$

Bean and Rodbell<sup>2</sup> have shown that if this parameter is large enough, then the change in volume associated with the large exchange striction can produce a first-order phase change at  $T_c$ . Bean and Rodbell assumed  $d\mu^*/dV = 0$  and therefore that there is a large  $dW/dV > 0$ . The fact that  $d\mu^*/dV \neq 0$  means that this assumption must be modified.

The  $B31$  phase of  $\text{MnAs}_{0.96}\text{P}_{0.04}$  has a  $T_c \equiv T_{31} \approx 230^\circ\text{K}$  and the hexagonal  $B8_1$  phase of MnAs has a  $T_c(\text{ext}) \equiv T_8 \approx 400^\circ\text{K}$ . Since the Curie temperature is proportional to  $W\mu^{*2}$ , this gives

$$\frac{T_8 - T_{31}}{T_8} = \frac{W_8 - (\mu_{31}^*/\mu_8^*)^2 W_{31}}{W_8} \approx \frac{170}{400}. \quad (5)$$

It follows that  $dW/dV < 0$ , if  $(\mu_8^*/\mu_{31}^*)^2 > 40/23$ , and

$$\beta \approx (V/\Delta V) [1 - (\mu_8^*/\mu_{31}^*)^2 (23/40) + 2 - 2(\mu_{31}^*/\mu_8^*)] \approx 50 [3 - 0.575(\mu_8^*/\mu_{31}^*)^2 - 2(\mu_{31}^*/\mu_8^*)]. \quad (6)$$

Hence

$$\beta > 6 \text{ if } (\mu_8^*/\mu_{31}^*)^2 \leq 3. \quad (7)$$

Here  $\Delta V/V \approx 0.02$  is taken from the discontinuous volume change at  $T_c$ , and a  $\beta > 6$  could be large enough to account for the first-order phase change.<sup>3</sup> Although this places an upper limit on the change in  $\mu^*$  at  $T_c$ , it is shown below that this limit is compatible with the changes that are observed.

**C. Atomic Theory**

Thus far we have seen that the first-order transition at  $T_c$  in MnAs can be accounted for by a volume-dependent atomic moment and Weiss molecular field within a critical range of volumes  $V_t - \Delta V < V < V_t$ . We must now inquire into the atomic mechanisms responsible for such a volume dependence within a small volume interval about a critical molar volume.

**1. Origin of  $d\mu/dV > 0$**

The electronegativity difference between manganese and arsenic is sufficiently large that there is an energy gap between the bonding and antibonding  $s$  and  $p$  orbitals. It is reasonable to assume that, as in the semiconductor GaAs, the Fermi energy lies in the gap, so that the bonding orbitals form a filled valence band and the antibonding orbitals form an empty conduction band. This leaves four electrons per molecule to be placed in the manganese  $3d$  orbitals.

Schematic one-electron energies for the  $3d$  orbitals are shown in Fig. 4. The cubic component of the crystalline fields at an octahedral-site manganese atom splits the orbitally fivefold-degenerate  $3d$  level in two: a less stable level for the two  $e_g$  orbitals directed toward the anions and a more stable level for the remaining three  $t_{2g}$  orbitals. The  $t_{2g}$  level is split by the positive trigonal component of the field into a more stable level for the  $t_0$  orbital directed along the hexagonal  $c_A$  axis and a less stable level for two  $t_{\pm}$  orbitals primarily directed within basal planes. In addition, covalent mixing between manganese  $e_g$  orbitals and arsenic  $s$  and  $p$  orbitals is large enough to make the  $e_g$  orbitals collective, band

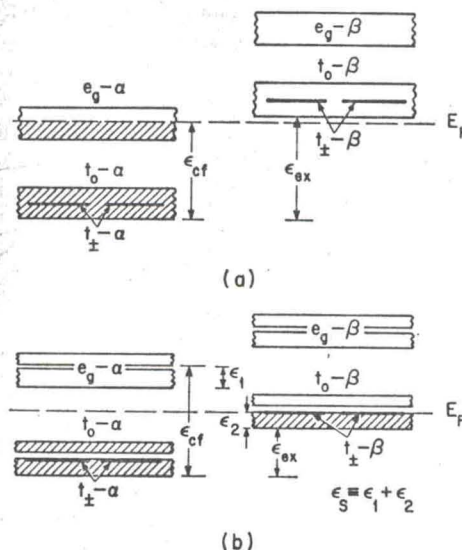


FIG. 4. Schematic one-electron energies for  $3d$  electrons in MnAs, given localized  $t_{\pm}$  electrons: (a) high-spin manganese ( $\epsilon_{\text{ex}} > \epsilon_{\text{cf}}$ ) and (b) low-spin manganese ( $\epsilon_{\text{cf}} > \epsilon_{\text{ex}} + \epsilon_{\text{s}}$ ). Splittings of  $t_{\pm}$  and  $e_g$  bands of low-spin phase is due to orthorhombic symmetry of  $B31$  structure.

ori  
ba  
sep  
ban  
tio  
pat  
col  
loc  
in J  
T  
tion  
fille  
nar  
of t  
Thi  
ator  
elec  
orbi  
split  
crys  
band  
of th  
sepa  
 $e_g$  or  
with  
Fi  
gives  
 $-\epsilon_s <$   
in Fi  
per a  
mang  
  
where  
towar  
in low  
Fig  
and a  
  
The m  
mome  
tion o  
Fron  
tion fo  
  
 $-\epsilon$   
Since a  
terval,  
  
<sup>10</sup> J. B.  
presente  
liques, U  
<sup>11</sup> J. B.  
Wiley &  
<sup>12</sup> C. G  
lished) ]  
 $n \approx 0.3$ ,  
either va

orbitals,<sup>10</sup> so their energies are distributed over a narrow bandwidth. Similarly the short ( $<2.9 \text{ \AA}$ ) Mn-Mn separation along  $c_h$  means the  $t_0$  orbitals are collective, band orbitals.<sup>11</sup> The larger ( $\approx 3.7 \text{ \AA}$ ) Mn-Mn separations within basal planes, on the other hand, are compatible with  $t_{\pm}$  orbitals that are either localized or, if collective, very narrow-band. These are shown as localized orbitals in Fig. 4, as narrow-band orbitals in Fig. 5.

The fact that low-temperature MnAs has a saturation moment of  $\mu_0 = 3.1\mu_B$  indicates that the partially filled  $t_{\pm}$  orbitals are either localized or sufficiently narrow-band to support a spontaneous magnetization of the bonding as well as the antibonding orbitals.<sup>12</sup> This spontaneous magnetization creates an intra-atomic-exchange interaction with the other  $d$ -band electrons so as to lift the spin degeneracy of all the  $d$  orbitals. We shall define  $\epsilon_{ex}$  as the intra-atomic-exchange splitting of the bottom of the  $d$  bands and  $\epsilon_{cf}$  as the crystal-field splitting from the bottom of the  $\alpha$ -spin  $t_0$  band to the density-of-states minimum near the middle of the  $\alpha$ -spin  $e_g$  bands. (A density-of-states minimum separates cation-sublattice bonding versus antibonding  $e_g$  orbitals, even though all  $e_g$  orbitals are antibonding with respect to the anion sublattice.)

Figures 4(a) and 5(a) correspond to  $\epsilon_{ex} > \epsilon_{cf}$ , which gives a high-spin manganese moment  $\mu_8 = 4\mu_B$ . If  $-\epsilon_s < (\epsilon_{ex} - \epsilon_{cf}) < 0$ , where  $\epsilon_s = \epsilon_1 + \epsilon_2$  is the energy shown in Fig. 4(b) or 5(b), then there are  $0 < n < 1$  electrons per atom in the  $\beta$ -spin  $t_0$  orbitals, and the high-spin manganese atomic moment is somewhat reduced to

$$\mu_8 = (4 - 2n)\mu_B, \quad (8)$$

where  $n$  increases towards  $n=1$  as  $(\epsilon_{ex} - \epsilon_{cf})$  decreases towards  $-\epsilon_s$ . A  $\mu_0 = 3.1\mu_B$  would correspond to  $n \approx 0.45$  in low-temperature MnAs.

Figures 4(b) and 5(b) correspond to  $(\epsilon_{ex} - \epsilon_{cf}) < -\epsilon_s$  and a low-spin atomic moment  $\mu_{31}$ , where

$$1\mu_B < \mu_{31} < 2\mu_B. \quad (9)$$

The maximum spin-only moment is  $2\mu_B$ . The minimum moment of  $1\mu_B$  corresponds to a spontaneous magnetization of only antibonding  $t_{2g}$  electrons.

From these considerations, it follows that the condition for a  $d\mu/dV > 0$  is

$$-\epsilon_s < (\epsilon_{ex} - \epsilon_{cf}) \leq 0, \quad d(\epsilon_{ex} - \epsilon_{cf})/dV > 0. \quad (10)$$

Since a  $d\mu/dV > 0$  is restricted to a critical volume interval, this requires that over this interval

$$\Delta(\epsilon_{ex} - \epsilon_{cf}) \geq \epsilon_s, \quad (11)$$

<sup>10</sup> J. B. Goodenough, *J. Appl. Phys.* **37**, 1415 (1966); and speech presented at Colloque International sur les Dérives Semimétalliques, University of Paris, 1965 (unpublished).

<sup>11</sup> J. B. Goodenough, *Magnetism and the Chemical Bond* (John Wiley & Sons, Inc., New York, 1963).

<sup>12</sup> C. Guillaud [thesis, University of Strasbourg, 1943 (unpublished)] reports  $\mu_0 = 3.4\mu_B$ . This would change  $n$  of Eq. (8) to  $n \approx 0.3$ , but does not alter the argument that follows because for either value  $0 < n < 0.5$ .

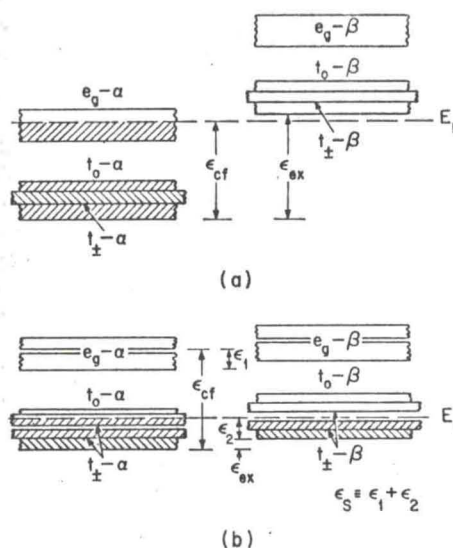


FIG. 5. Schematic one-electron energies for  $3d$  electrons in MnAs, given collective  $t_{\pm}$  electrons: (a) high-spin manganese ( $\epsilon_{ex} > \epsilon_{cf}$  and  $\Delta_b^t < \Delta_c^f$ ) and (b) low-spin manganese ( $\Delta_c^f < \Delta_b^t$ ). Splittings of bands of low-spin phase is due to orthorhombic symmetry of B31 structures.

where an  $\epsilon_s \geq 0.1$  eV can be anticipated. Now  $\epsilon_{cf}$  is proportional to  $V^{-1/3}$ , so that

$$\Delta(-\epsilon_{cf}) \approx \frac{1}{3}\epsilon_{cf}\Delta V/V \approx 0.01 \text{ eV}, \quad (12)$$

where  $\Delta V/V \approx 0.025$  from Eq. (3) and  $\epsilon_{cf} \approx 1-2$  eV is known from spectroscopic data. The fact that  $\Delta(-\epsilon_{cf}) < kT$  in the critical temperature interval shows that the low-spin  $\rightleftharpoons$  high-spin transition cannot be due to  $d(-\epsilon_{cf})/dV$  alone, and we are forced to assume that

$$\Delta\epsilon_{ex} = \langle d\epsilon_{ex}/dV \rangle \Delta V \geq 0.1 \text{ eV} \quad (13)$$

within the small, critical volume interval. This, in turn, implies that there is a critical molar volume, and hence a critical bandwidth for the  $t_{\pm}$  electrons, at which there is a sharp change in the magnitude of the intra-atomic-exchange splitting responsible for a spontaneous atomic moment.

Note that with  $\mu_8 = 3.1\mu_B$ ,  $\mu_8^{*2} \approx 17\mu_B^2$ . Therefore Eq. (7) requires  $\mu_{31}^{*2} \geq 5.3\mu_B^2$ , which from Eq. (9) is satisfied so long as  $\mu_{31}^*$  refers to the intermediate state of Eq. (10).

## 2. Origin of a Sharp Change in $\epsilon_{ex}$ with Bandwidth

Spontaneous atomic moments may occur if the  $d$  electrons are localized. Measurements<sup>13</sup> on  $\text{LaCoO}_3$  appear to have demonstrated that, in this compound at least, a localized-electron and a collective-electron state correspond to two thermodynamically different electronic phases and that there is a first-order phase change from one to the other at some critical overlap integral  $\Delta_c$ . In a tight-binding approximation, the

<sup>13</sup> P. M. Raccach and J. B. Goodenough, *Phys. Rev.* **155**, 932 (1967).

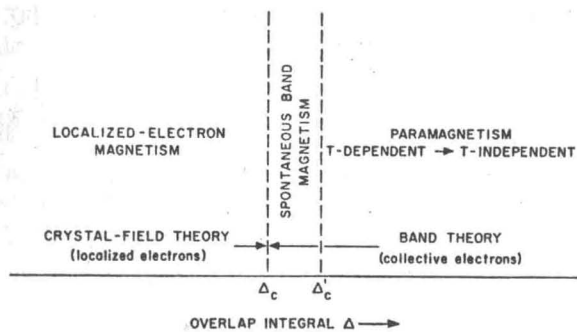


FIG. 6. Schematic representation of the meaning of the critical overlap integrals  $\Delta_c$  and  $\Delta_c'$ .

bandwidth is proportional to a transfer integral, which is in turn proportional to an overlap integral  $\Delta$ . Figure 6 shows schematically the localized-electron and collective-electron domains separated by a sharply defined  $\Delta_c$ , corresponding to a critical bandwidth.

Stoner<sup>14</sup> has pointed out that there is a maximum bandwidth, corresponding to a  $\Delta_c'$ , that will support spontaneous band ferromagnetism. Therefore Fig. 6 also separates schematically the domain of spontaneous band ferromagnetism from the domain of band paramagnetism.

Finally, it is also known that bonding orbitals have a greater bandwidth than the corresponding antibonding orbitals, or  $\Delta_b > \Delta_{ab}$ . This distinction is meaningful in the present context, since the  $t_{2g}$  orbitals may be bonding or antibonding with respect to Mn-Mn interactions even though they are only antibonding with respect to the arsenic array. Since  $\Delta_c \leq \Delta_c'$ , the conditions for spontaneous ferromagnetism in MnAs include

$$\Delta_b^t < \Delta_c', \quad (14)$$

or

$$\Delta_{ab}^t < \Delta_c' < \Delta_b^t. \quad (15)$$

Equation (14) must be satisfied if the atomic moments are high-spin  $\mu_8$ , since this requires spontaneous magnetization of bonding as well as antibonding orbitals. Either Eqs. (14) or (15) may be satisfied if the atomic moments are low-spin  $\mu_{31}$ . However, if Eq. (15) applies, then  $\epsilon_{ex}$  does not resolve the  $\alpha$ -spin and  $\beta$ -spin  $t_{2g}$  energies, and the manganese atoms are necessarily low-spin ( $\mu \approx 1\mu_B$ ), as shown in Fig. 5(b). In this case, three of the four  $d$  electrons are spin-paired in bonding  $t_{2g}$  orbitals and only the remaining antibonding electron is spontaneously magnetized. Thus a sharp  $d\epsilon_{ex}/dV > 0$  at a critical volume implies

$$\Delta_b^t < \Delta_c' \rightarrow \Delta_{ab}^t < \Delta_c' < \Delta_b^t. \quad (16)$$

### 3. Origin of the Exchange Striction and $dW/dV$

The sign of the magnetic coupling depends upon the occupancy of the orbitals<sup>11,15</sup>: (a) Half-filled localized-

electron orbitals couple antiferromagnetically and half-filled bands would stabilize an antiferromagnetic spin-density wave rather than spontaneous ferromagnetism. (b) Orbitals more than half-filled, localized or collective, may exhibit spontaneous ferromagnetism. (c) Localized electrons coupled via conduction electrons in a band less than one-quarter filled exhibit ferromagnetism.

With these rules for the signs of the magnetic couplings, we now inquire about the nature of the magnetic couplings within the three phases of MnAs.

(a) *Low-temperature B8<sub>1</sub> phase.* According to our analysis and the reduced moment  $\mu_8 = (4 - 2n)\mu_B = 3.1\mu_B$ , this phase has

$$-\epsilon_s < (\epsilon_{ex} - \epsilon_{of}) < 0, \quad (17)$$

and  $n \approx 0.45$   $\beta$ -spin  $t_0$  electrons per atom. This means that the  $t_0$  orbitals are more than half-filled and so support ferromagnetic coupling. (Note that so long as  $n < 0.5$ , only bonding  $\beta$ -spin orbitals are occupied.) The  $t_{\pm}$  orbitals, on the other hand, are only half-filled. Therefore forced ferromagnetic coupling reduces the Mn-Mn bonding in the basal planes, thus introducing a large, positive exchange striction below  $T_c$ . It simultaneously localizes the  $\alpha$ -spin  $t_{\pm}$  electrons, since the  $\alpha$ -spin  $t_{\pm}$  orbitals, bonding and antibonding, are completely filled. (If both bonding and antibonding orbitals are filled, localized and band descriptions become equivalent.<sup>16</sup>) The ferromagnetic coupling can be forced by the coupling via collective  $e_g$  electrons. However, the Weiss molecular field  $W_8$  contains a negative contribution from the Mn-Mn interactions in basal planes, which tends to reduce it.

(b) *The B31 phase.* A low-temperature, high-pressure B31 phase has low-spin manganese and

$$(\epsilon_{ex} - \epsilon_{of}) < -\epsilon_s, \quad (18)$$

corresponding to Figs. 4(b) and 5(b). The  $e_g$  bands are empty and the  $t_{2g}$  bands are two-thirds filled. Therefore all the Mn-Mn interactions are potentially ferromagnetic and spontaneous ferromagnetism occurs as long as  $\Delta_{ab}^t < \Delta_c'$ . This means there is no anomalous exchange striction at  $T_c$  and no negative component in the Weiss molecular field  $W_{31}$ . This is consistent with Eq. (5), or

$$W_{31} = (\mu_8^*/\mu_{31}^*)^2 \frac{2}{3} W_8 > W_8. \quad (19)$$

At intermediate temperatures, where Eq. (17) applies, the electron distribution amongst the  $d$  bands is changing rapidly with temperature, so that  $d\mu/dV > 0$  and  $dW/dV < 0$ , the Weiss molecular-field constant  $W$  decreasing as the  $\beta$ -spin  $t$  electrons disappear because with zero  $\beta$ -spin  $t$  electrons the Mn-Mn interactions become antiferromagnetic.

(c) *High-temperature B8<sub>1</sub> phase.* The model suggests that for  $T > T_c$

$$\epsilon_{ex} - \epsilon_{of} > 0. \quad (20)$$

<sup>14</sup> E. C. Stoner, *Phil. Mag.* 25, 899 (1938).

<sup>15</sup> J. B. Goodenough, *J. Appl. Phys.* 38, 1054 (1967).

<sup>16</sup> F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Company, Inc., New York, 1940), p. 301.

In thi  
via co  
these  
intera  
the ne  
smalle  
 $\beta$ -spin  
sisten  
than  
(20)  
for  $T$   
to  $S$

(a)  
rhomb  
not re  
bilizes  
orbita  
the t  
force  
elsewh  
(b)  
the M  
all rep  
excha

1.  
the B  
peratu  
molar  
transi  
a criti  
is a c  
atomi  
2.  
repre  
taneor  
orbita  
volum  
sharp

3. V  
crysta  
mang  
intern  
symm  
hexag  
stricti

<sup>17</sup> J.  
Structu  
(unpul

In this configuration only the Mn-As-Mn interactions via collective  $e_g$  electrons are ferromagnetic. Although these may dominate the antiferromagnetic Mn-Mn interactions within basal planes and along the  $c_h$  axis, the net ferromagnetic Weiss molecular field  $W$  must be smaller than in the low-temperature  $B8_1$  phase, where  $\beta$ -spin  $t_0$  electrons are present. This conclusion is consistent with a high-temperature  $\theta_f = 283^\circ\text{K}$  being smaller than the low-temperature  $T_c(\text{ext}) \approx 400^\circ\text{K}$ . Equation (20) is also consistent with the molar Curie constant for  $T > T_i$ , which gives a  $\mu_{\text{eff}} = 4.95\mu_B$ , corresponding to  $S = 2$ .

#### 4. Comments on Symmetry Changes

(a) The distortion from hexagonal  $B8_1$  to orthorhombic  $B31$  symmetry is in such a direction that it does not remove the  $t_{\pm}$  orbital degeneracy, but rather stabilizes the bonding orbitals relative to the antibonding orbitals. Thus the distortion is in a direction that favors the transition of Eq. (16). (However, the driving force for the  $B31$  distortion below  $T_i$  probably lies elsewhere.<sup>10,17</sup>)

(b) The low-temperature phase is hexagonal because the Mn-Mn interactions within the basal planes are all repulsive below  $T_c$ , giving rise to the large, positive exchange striction.

### IV. CONCLUSIONS

1. The existence of a critical pressure above which the  $B31$  phase is stabilized shows that the critical temperature interval in  $\text{MnAs}_{1-x}\text{P}_x$  is related to a critical molar volume. Since there is a high-spin  $\rightleftharpoons$  low-spin transition within this critical molar volume, this implies a critical bandwidth, or overlap integral, at which there is a dramatic change in the magnitude of the intratomic-exchange energy.

2. The critical bandwidth, or overlap integral  $\Delta_c^f$ , represents the maximum value that can support spontaneous magnetization of collective electrons in bonding orbitals. Therefore the sharpness of the region of molar volumes over which  $d\epsilon_{\text{ex}}/dV > 0$  indicates that  $\Delta_c^f$  has a sharp empirical definition.

3. Where high-spin manganese are present, the crystal symmetry is hexagonal  $B8_1$ ; where low-spin manganese are present, it is orthorhombic  $B31$ . In the intermediate state, corresponding to Eq. (17), the symmetry is orthorhombic if  $T > T_c$ , but becomes hexagonal if  $T < T_c$  because of a large, positive exchange striction in the basal planes. This exchange striction

<sup>17</sup> J. B. Goodenough, speech presented at the Symposium on Structural Inorganic Chemistry in Halifax, Nova Scotia, 1965 (unpublished).

arises from half-filled  $t_{\pm}$  orbitals, which produce anti-ferromagnetic Mn-Mn interactions within a basal plane. There is no exchange striction along  $c_h$ , because  $\beta$ -spin  $t_0$  electrons are present to make the Mn-Mn interactions in this direction ferromagnetic.

4. The magnitude of the atomic moment  $\mu_0 = 3.1\mu_B$ , of a paramagnetic Curie temperature  $\theta_f < T_c(\text{ext})$ , of a Weiss molecular field  $W_{31} > W_8$ , corresponding to  $dW/dV < 0$ , of an effective paramagnetic moment  $\mu_{\text{eff}} = 4.95\mu_B$ , corresponding to  $S = 2$ , and of  $d\mu/dV > 0$  are all consistent with a model in which Eq. (10) applies within the small volume interval about a critical molar volume.

5. On a macroscopic, thermodynamic scale, a first-order transition at  $T_c$  occurs because of the coincidence of a large exchange striction with a volume-dependent Weiss molecular field  $W$  and manganese moment  $\mu$ . The Curie temperature may be expressed by Eq. (1), where the significant parameter is  $\beta \sim 10$ . Further, since the free energy of the ferromagnetic phase contains a magnetic term,  $T_c$  increases with applied magnetic field.

In addition, the  $t_{\pm}$  electrons appear to be localized in the ferromagnetic  $B8_1$  phase and collective in the  $B31$  phase. Since experiments<sup>18</sup> on  $\text{LaCoO}_3$  have shown a first-order localized-electron  $\rightleftharpoons$  collective-electron transition, it is possible that an electronic latent heat may also contribute to the first-order transition in MnAs. *Note added in proof:* N. P. Grazhdankina and Yu. S. Bersenev [Zh. Eksperim. i Teor. Fiz. 51, 1052 (1966)] report changes with temperature in the resistivity and magnetic state of MnAs at different pressures that are in reasonable agreement with our results above  $230^\circ\text{K}$ . They report a  $dT_c/dP = -(16.0 \pm 0.3)$  deg/kbar with increasing temperature and a  $dT_c/dP = -(34 \pm 7)$  deg/kbar with decreasing temperature. They also found a second-order magnetic transition in the high-pressure phase having  $T_N \approx 230^\circ\text{K}$  at 3 kbar, as obtained indirectly by us from the  $\text{MnAs}_{1-x}\text{P}_x$  system, and a  $dT_N/dP = (2.22 \pm 0.07) 10^{-3}$  deg/kbar. They also present magnetic data that indicate the presence, in their experiments, of mixed  $B8_1$  and  $B31$  phases after cooling through the magnetic transition in the hysteretic region of the  $P$ - $T$  diagram.

### ACKNOWLEDGMENTS

We would like to thank W. A. Newman for supplying the samples of stoichiometric (wet analysis and x-rays) MnAs and for his enthusiastic interest in this study. We would also like to thank N. Menyuk and K. Dwight for monitoring the magnetization-versus-temperature study cited.