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

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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 θ_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) Kittel¹ 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

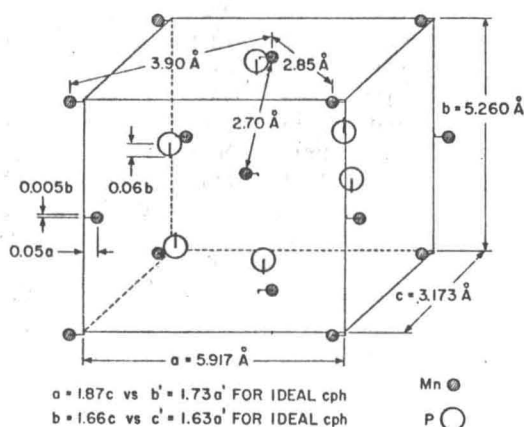


FIG. 1. The orthorhombic B31 structure of MnP.

and Rodbell² 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 Rodbell³ 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) Goodenough⁴ pointed out how the two transitions, $B8_1 \rightleftharpoons B31$ at T_c

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

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

⁴ J. B. Goodenough, M.I.T. Lincoln Laboratory, Lexington, Massachusetts, Technical Report No. 345, DDC 435758, 1964 (unpublished).

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¹ C. Kittel, Phys. Rev. 120, 335 (1960).