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 $MnAs_{1-x}P_x$, 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 $T_c(\text{ext}) \approx 127$°C. (2) At a $T_t \approx 127$°C, there is a second-order $B31 \rightleftarrows B8_1$ transition. There is a maximum in the magnetic susceptibility at T_t, but MnAs is not antiferromagnetic in the interval $T_c<T<T_t$. Rather there is a change in the magnitude of the manganese moment ($d\mu/dT>0$) in this interval. (3) The high-temperature ($T>T_t$) hexagonal phase exhibits a Curie-Weiss behavior with a $\mu_{\text{eff}}=4.95\mu_B$ and a $\theta_f \approx$ 10°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 $T_c(\text{ext}) \approx 127$°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[1] developed a thermodynamic theory involving "exchange inversion" to explain the antiferromagnetic$\rightleftarrows$ferrimagnetic transition in $Mn_{2-x}Cr_xSb$ and suggested it might be applicable to MnAs. The lack of antiferromagnetic order in the interval $T_c<T<T_t$ rules out this possibility. (2) Bean and Rodbell[2] 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[3] to measure T_c as a function of pressure P and applied field strength H in the ranges $15<T<65$°C, $0<P<1$ kbar, and $0<H<$ 110 kOe. They appeared to obtain a qualitative match between theory and experiment. (3) Goodenough[4] pointed out how the two transitions, $B8_1 \rightleftarrows B31$ at T_c

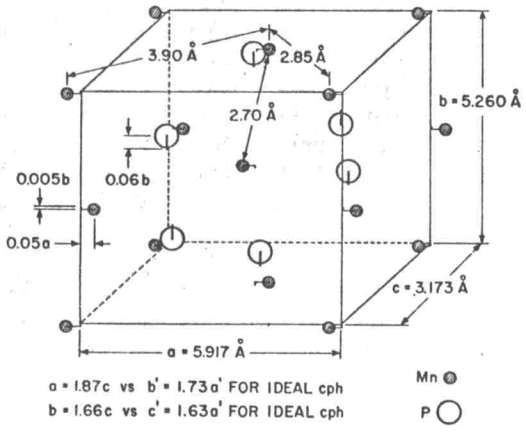

FIG. 1. The orthorhombic $B31$ structure of MnP.

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