E. HIGH-PRESSURE STUDY OF MnAs

The effect of pressure in reducing the transition temperature T_c for the first-order $B8_1 \rightarrow B31$ transformation in MnAs has been reported previously.[10] It was found that above a critical pressure of 4.5 kbar the B31 phase was stable at all temperatures. It was also observed that the phase transformation was marked by an increasing degree of hysteresis as the temperature was decreased.

The pressure-temperature hysteresis curve for the reverse $B31 \rightarrow B8_1$ transformation has now been determined. The results are shown in Fig. III-2, together with those reported earlier for the $B8_1 \rightarrow B31$ transition. For temperatures down to 200°K, the hysteresis data were obtained by observing the discontinuity in resistivity due to the reverse transformation which occurred as the pressure was reduced at constant temperature. The point at atmospheric pressure and 138°K was obtained by magnetic susceptibility measurements. In this case, a specimen was converted to the B31 phase by applying 5 kbar and then cooled to 77°K. The pressure was released, the specimen was transferred without warming up to the cold stage (at 4.2°K) of a vibrating-coil magnetometer, and the magnetization was monitored as the sample was allowed to warm up to room temperature. Initially the susceptibility was small and decreased with increasing temperature, but at 138°K the magnetization increased abruptly by a factor of more than 50 to the value characteristic of the $B8_1$ phase.

The results shown in Fig. III-2, together with those obtained in an earlier study[11] of $MnAs_{1-x}P_x$, establish the following:

(1) There is a $d\mu/dV > 0$ in the temperature interval $T_t - \Delta T < T < T_t$, where $T_t = 130°C$ is the temperature of the second-order $B31 \rightleftarrows B8_1$ transformation, $\Delta T \approx 125°C$ and μ is a manganese atomic moment. Since the thermal expansion coefficient is $\sim 2 \times 10^{-4}°C^{-1}$, this

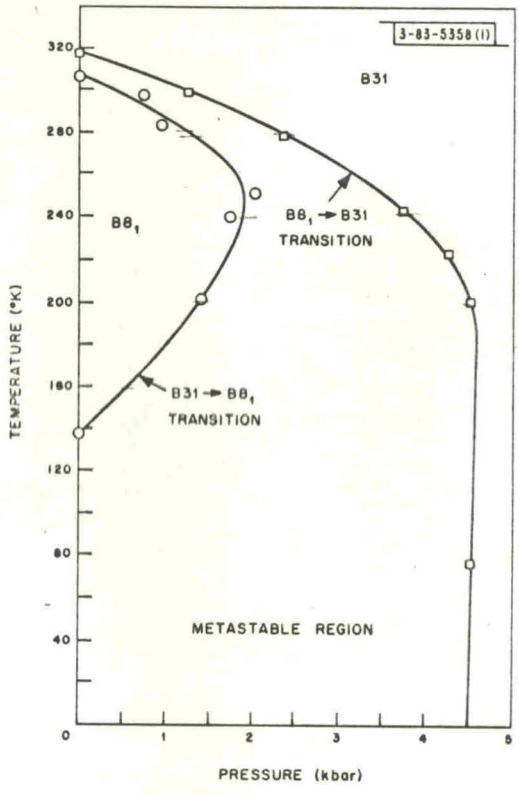

Fig. III-2. Hysteresis of $B8_1 \rightleftarrows B31$ transition in MnAs.

implies a $d\mu/dV > 0$ in a critical molar volume range $V_t - \Delta V < V < V_t$, where V_t is the molar volume at T_t and $\Delta V/V \approx 0.025$.

(2) A first-order $B8_1 \rightleftarrows B31$ transition at T_c occurs only if the molar volume at T_c falls within the critical range. 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 $V < V_t - \Delta V$.

Bean and Rodbell[12] have shown that a first-order transition can occur at T_c if

$$T_c = T_o\,[1 + \beta(V - V_o)/V_o] \quad ,$$

both the coefficient β and the compressibility are large, and there is a large ΔV at T_c due to exchange striction. Since T_c is proportional to $W\mu^{*2}$, where W is the Weiss molecular field and $\mu^{*2} \approx 4S(S+1)\,\mu_B^2$, it follows that

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

Bean and Rodbell assumed $d\mu^*/dV = 0$, and therefore required a large $dW/dV > 0$. However, analysis of available data gives $dW/dV < 0$ and

$$6 < \beta < 22 \quad \text{for} \quad 3 \geqslant (\mu_8^*/\mu_{31}^*)^2 \geqslant 2$$

where μ_8^* and μ_{31}^* are the atomic moments in the low-temperature $B8_1$ and the intermediate temperature B31 phases respectively. Interpretation of the first-order phase change appears to require[13] a $\beta \sim 10$.

A $d\mu/dV > 0$ requires a high-spin $\rightleftarrows$ low-spin transition in the critical molar volume interval, and hence

$$\langle d(\epsilon_{ex} - \epsilon_{cf})/dV \rangle \, \Delta V > 0.1 \text{ eV}$$

within this interval ΔV. Here ϵ_{ex} and ϵ_{cf} are intra-atomic exchange and crystal-field splittings, respectively, and 0.1 eV is taken as the lower limit of the d-band width for orbitals of e_g symmetry. Since

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

it follows that the sharp transition requires

$$\Delta\epsilon_{ex} = \langle d\epsilon_{ex}/dV \rangle \, \Delta V \geqslant 0.1 \text{ eV} \quad .$$

Stoner[14] has pointed out that there is a maximum bandwidth, and hence a maximum overlap integral Δ_c^f for orbitals on neighboring cations, that will support spontaneous band ferromagnetism. Further, the bandwidth for bonding orbitals is greater than that for antibonding orbitals, so that $\Delta_{ab} < \Delta_b$, where the subscripts refer to antibonding and bonding orbitals, respectively. Thus the two conditions for spontaneous band ferromagnetism are

$$\Delta_b < \Delta_c^f \quad \text{and} \quad \Delta_{ab} < \Delta_c^f < \Delta_b \quad ,$$

where high-spin manganese requires the first and low-spin manganese implies the second. It is concluded that the unusual occurrence of a $d\mu/dV > 0$ over a small volume interval ΔV manifests the transition

$$\Delta_b < \Delta_c^f \rightarrow \Delta_{ab} < \Delta_c^f < \Delta_b$$

and demonstrates that Δ_c^f is quite sharply defined.

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