



FIG. 6. Schematic representation of the meaning of the critical overlap integrals Δ_c and Δ_c' .

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

Stoner¹⁴ has pointed out that there is a maximum bandwidth, corresponding to a Δ_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 μ_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 μ_{31} . However, if Eq. (15) applies, then ϵ_{ex} does not resolve the α -spin and β -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^{11,15}: (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 B8₁ 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 $n \approx 0.45$ β -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 β -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 α -spin t_{\pm} electrons, since the α -spin t_{\pm} orbitals, bonding and antibonding, are completely filled. (If both bonding and antibonding orbitals are filled, localized and band descriptions become equivalent.¹⁶) 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

$$W_{31} = (\mu_8^*/\mu_{31}^*)^2 \frac{2}{3} \frac{3}{4} W_8 > W_8. \quad (19)$$

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 β -spin t electrons disappear because with zero β -spin t electrons the Mn-Mn interactions become antiferromagnetic.

(c) *High-temperature B8₁ phase.* The model suggests that for $T > T_c$

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

¹⁴ E. C. Stoner, *Phil. Mag.* 25, 899 (1938).

¹⁵ J. B. Goodenough, *J. Appl. Phys.* 38, 1054 (1967).

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

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