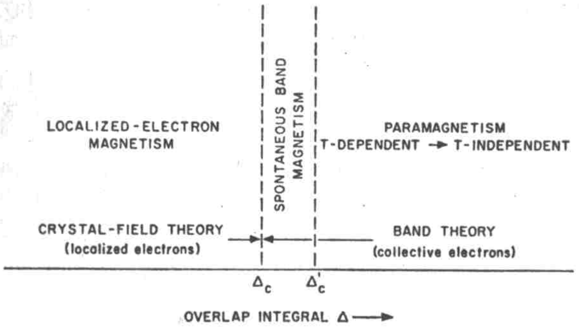

FIG. 6. Schematic representation of the meaning of the critical overlap integrals Δ_c and $\Delta_c{}^f$.

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.

Stoner[14] has pointed out that there is a maximum bandwidth, corresponding to a $\Delta_c{}^f$, 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 $\Delta_c \leq \Delta_c{}^f$, the conditions for spontaneous ferromagnetism in MnAs include

$$\Delta_b{}^t < \Delta_c{}^f, \tag{14}$$

or

$$\Delta_{ab}{}^t < \Delta_c{}^f < \Delta_b{}^t. \tag{15}$$

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

$$\Delta_b{}^t < \Delta_c{}^f \rightarrow \Delta_{ab}{}^t < \Delta_c{}^f < \Delta_b{}^t. \tag{16}$$

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* $B8_1$ *phase.* According to our analysis and the reduced moment $\mu_8 = (4-2n)\mu_B = 3.1\mu_B$, this phase has

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

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

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

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 $\Delta_{ab}{}^t < \Delta_c{}^f$. 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

$$W_{31} = (\mu_8{}^*/\mu_{31}{}^*)^2\, \tfrac{23}{40}\, W_8 > W_8. \tag{19}$$

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* $B8_1$ *phase.* The model suggests that for $T > T_t$

$$\epsilon_{ex} - \epsilon_{of} > 0. \tag{20}$$

---

[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.