orbitals,[10] so their energies are distributed over a narrow bandwidth. Similarly the short (<2.9 Å) Mn–Mn separation along c_h means the t_0 orbitals are collective, band orbitals.[11] The larger (≈ 3.7 Å) Mn–Mn separations within basal planes, on the other hand, are compatible with $t_\pm$ orbitals that are either localized or, if collective, very narrow-band. These are shown as localized orbitals in Fig. 4, as narrow-band orbitals in Fig. 5.

The fact that low-temperature MnAs has a saturation moment of $\mu_0 = 3.1\mu_B$[3] indicates that the partially filled $t_\pm$ orbitals are either localized or sufficiently narrow-band to support a spontaneous magnetization of the bonding as well as the antibonding orbitals.[12] This spontaneous magnetization creates an intra-atomic-exchange interaction with the other d-band electrons so as to lift the spin degeneracy of all the d orbitals. We shall define ϵ_{ex} as the intra-atomic-exchange splitting of the bottom of the d bands and ϵ_{cf} as the crystal-field splitting from the bottom of the α-spin t_0 band to the density-of-states minimum near the middle of the α-spin e_g bands. (A density-of-states minimum separates cation-sublattice bonding versus antibonding e_g orbitals, even though all e_g orbitals are antibonding with respect to the anion sublattice.)

Figures 4(a) and 5(a) correspond to $\epsilon_{ex} > \epsilon_{cf}$, which gives a high-spin manganese moment $\mu_8 = 4\mu_B$. If $-\epsilon_s < (\epsilon_{ex} - \epsilon_{cf}) < 0$, where $\epsilon_s = \epsilon_1 + \epsilon_2$ is the energy shown in Fig. 4(b) or 5(b), then there are $0 < n < 1$ electrons per atom in the β-spin t_0 orbitals, and the high-spin manganese atomic moment is somewhat reduced to

$$\mu_8 = (4 - 2n)\mu_B, \qquad (8)$$

where n increases towards $n = 1$ as $(\epsilon_{ex} - \epsilon_{cf})$ decreases towards $-\epsilon_s$. A $\mu_0 = 3.1\mu_B$ would correspond to $n \approx 0.45$ in low-temperature MnAs.

Figures 4(b) and 5(b) correspond to $(\epsilon_{ex} - \epsilon_{cf}) < -\epsilon_s$ and a low-spin atomic moment μ_{31}, where

$$1\mu_B < \mu_{31} < 2\mu_B. \qquad (9)$$

The maximum spin-only moment is $2\mu_B$. The minimum moment of $1\mu_B$ corresponds to a spontaneous magnetization of only antibonding t_{2g} electrons.

From these considerations, it follows that the condition for a $d\mu/dV > 0$ is

$$-\epsilon_s < (\epsilon_{ex} - \epsilon_{cf}) \leq 0, \qquad d(\epsilon_{ex} - \epsilon_{cf})/dV > 0. \qquad (10)$$

Since a $d\mu/dV > 0$ is restricted to a critical volume interval, this requires that over this interval

$$\Delta(\epsilon_{ex} - \epsilon_{cf}) \geq \epsilon_s, \qquad (11)$$

[10] J. B. Goodenough, J. Appl. Phys. 37, 1415 (1966); and speech presented at Colloque International sur les Dérives Semimétalliques, University of Paris, 1965 (unpublished).
[11] J. B. Goodenough, *Magnetism and the Chemical Bond* (John Wiley & Sons, Inc., New York, 1963).
[12] C. Guillaud [thesis, University of Strasbourg, 1943 (unpublished)] reports $\mu_0 = 3.4 \mu_B$. This would change n of Eq. (8) to $n \approx 0.3$, but does not alter the argument that follows because for either value $0 < n < 0.5$.
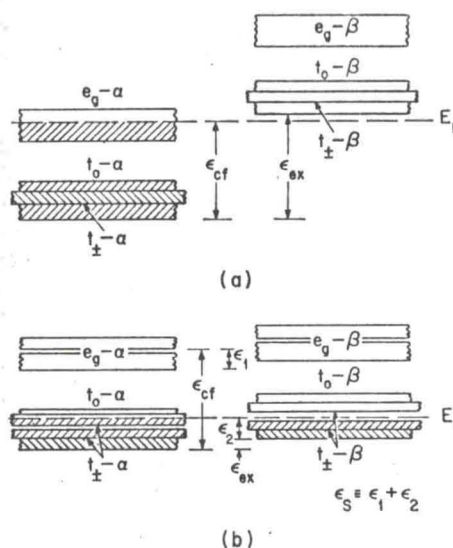

FIG. 5. Schematic one-electron energies for $3d$ electrons in MnAs, given collective $t_\pm$ electrons: (a) high-spin manganese ($\epsilon_{ex} > \epsilon_{cf}$ and $\Delta_b{}^t < \Delta_c{}^l$) and (b) low-spin manganese ($\Delta{}^t_{ab} < \Delta_c{}^l < \Delta_b{}^t$). Splittings of bands of low-spin phase is due to orthorhombic symmetry of B31 structures.

where an $\epsilon_s \geq 0.1$ eV can be anticipated. Now ϵ_{cf} is proportional to $V^{-1/3}$, so that

$$\Delta(-\epsilon_{cf}) \approx \tfrac{1}{3}\epsilon_{cf}\Delta V/V \approx 0.01 \text{ eV}, \qquad (12)$$

where $\Delta V/V \approx 0.025$ from Eq. (3) and $\epsilon_{cf} \approx 1-2$ eV is known from spectroscopic data. The fact that $\Delta(-\epsilon_{cf}) < kT$ in the critical temperature interval shows that the low-spin$\rightleftharpoons$high-spin transition cannot be due $d(-\epsilon_{cf})/dV$ alone, and we are forced to assume that

$$\Delta\epsilon_{ex} = <d\epsilon_{ex}/dV>\Delta V \geq 0.1 \text{ eV} \qquad (13)$$

within the small, critical volume interval. This, in turn, implies that there is a critical molar volume, and hence a critical bandwidth for the $t_\pm$ electrons, at which there is a sharp change in the magnitude of the intra-atomic-exchange splitting responsible for a spontaneous atomic moment.

Note that with $\mu_8 = 3.1\mu_B$, $\mu_8{}^{*2} \approx 17\mu_B{}^2$. Therefore Eq. (7) requires $\mu_{31}{}^{*2} \geq 5.3\mu_B{}^2$, which from Eq. (9) is satisfied so long as $\mu_{31}{}^*$ refers to the intermediate state of Eq. (10).

2. Origin of a Sharp Change in ϵ_{ex} with Bandwidth

Spontaneous atomic moments may occur if the d electrons are localized. Measurements[13] on LaCoO$_3$ appear to have demonstrated that, in this compound at least, a localized-electron and a collective-electron state correspond to two thermodynamically different electronic phases and that there is a first-order phase change from one to the other at some critical overlap integral Δ_c. In a tight-binding approximation, the

[13] P. M. Raccah and J. B. Goodenough, Phys. Rev. 155, 932 (1967).