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 $n\approx0.45$ 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

$$-\epsilon_s<(\epsilon_{ex}-\epsilon_{cf})\leq0, \qquad d(\epsilon_{ex}-\epsilon_{cf})/dV>0. \qquad (10)$$

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

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

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[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 $\mu_0=3.4$ μ_B. This would change n of Eq. (8) to $n\approx0.3$, but does not alter the argument that follows because for either value $0<n<0.5$.
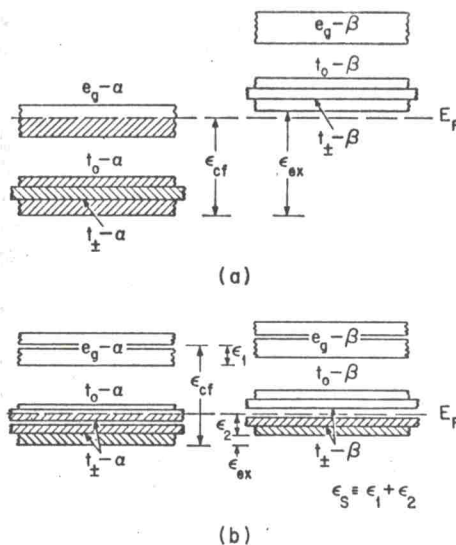

FIG. 5. Schematic one-electron energies for $3d$ electrons in MnAs, given collective $t_\pm$ electrons: (a) high-spin manganese ($\epsilon_{ex}>\epsilon_{cf}$ and $\Delta_b{}^t<\Delta_c{}^t$) and (b) low-spin manganese ($\Delta_{ob}^t<\Delta_c{}^t<\Delta_b{}^t$). Splittings of bands of low-spin phase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

where an $\epsilon_s\geq0.1$ eV can be anticipated. Now ϵ_{cf} is proportional to $V^{-1/3}$, so that

$$\Delta(-\epsilon_{cf})\approx\tfrac{1}{3}\epsilon_{cf}\Delta V/V\approx0.01 \text{ eV}, \qquad (12)$$

where $\Delta V/V\approx0.025$ from Eq. (3) and $\epsilon_{cf}\approx1-2$ eV is known from spectroscopic data. The fact that $\Delta(-\epsilon_{cf})<kT$ in the critical temperature interval shows that the low-spin⇌high-spin transition cannot be due $d(-\epsilon_{cf})/dV$ alone, and we are forced to assume that

$$\Delta\epsilon_{ex}=<d\epsilon_{ex}/dV>\Delta V\geq0.1 \text{ eV} \qquad (13)$$

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 $\mu_8=3.1\mu_B$, $\mu_8{}^{*2}\approx17\mu_B{}^2$. Therefore Eq. (7) requires $\mu_{31}{}^{*2}\geq5.3\mu_B{}^2$, 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

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