In this configuration only the Mn–As–Mn interactions via collective e_g electrons are ferromagnetic. Although these may dominate the antiferromagnetic Mn–Mn interactions within basal planes and along the c_h axis, the net ferromagnetic Weiss molecular field W must be smaller than in the low-temperature $B8_1$ phase, where β-spin t_0 electrons are present. This conclusion is consistent with a high-temperature $\theta_f = 283°K$ being smaller than the low-temperature $T_c(\text{ext}) \approx 400°K$. Equation (20) is also consistent with the molar Curie constant for $T > T_t$, which gives a $\mu_{\text{eff}} = 4.95\mu_B$, corresponding to $S = 2$.

4. *Comments on Symmetry Changes*

(a) The distortion from hexagonal $B8_1$ to orthorhombic $B31$ symmetry is in such a direction that it does not remove the $t_\pm$ orbital degeneracy, but rather stabilizes the bonding orbitals relative to the antibonding orbitals. Thus the distortion is in a direction that favors the transition of Eq. (16). (However, the driving force for the $B31$ distortion below T_t probably lies elsewhere.[10,17])

(b) The low-temperature phase is hexagonal because the Mn–Mn interactions within the basal planes are all repulsive below T_c, giving rise to the large, positive exchange striction.

IV. CONCLUSIONS

1. The existence of a critical pressure above which the $B31$ phase is stabilized shows that the critical temperature interval in $MnAs_{1-x}P_x$ is related to a critical molar volume. Since there is a high-spin⇄low-spin transition within this critical molar volume, this implies a critical bandwidth, or overlap integral, at which there is a dramatic change in the magnitude of the intra-atomic-exchange energy.

2. The critical bandwidth, or overlap integral Δ_c^f, represents the maximum value that can support spontaneous magnetization of collective electrons in bonding orbitals. Therefore the sharpness of the region of molar volumes over which $d\epsilon_{\text{ex}}/dV > 0$ indicates that Δ_c^f has a sharp empirical definition.

3. Where high-spin manganese are present, the crystal symmetry is hexagonal $B8_1$; where low-spin manganese are present, it is orthorhombic $B31$. In the intermediate state, corresponding to Eq. (17), the symmetry is orthorhombic if $T > T_c$, but becomes hexagonal if $T < T_c$ because of a large, positive exchange striction in the basal planes. This exchange striction arises from half-filled $t_\pm$ orbitals, which produce antiferromagnetic Mn–Mn interactions within a basal plane. There is no exchange striction along c_h, because β-spin t_0 electrons are present to make the Mn–Mn interactions in this direction ferromagnetic.

4. The magnitude of the atomic moment $\mu_0 = 3.1\mu_B$, of a paramagnetic Curie temperature $\theta_f < T_c(\text{ext})$, of a Weiss molecular field $W_{31} > W_8$, corresponding to $dW/dV < 0$, of an effective paramagnetic moment $\mu_{\text{eff}} = 4.95\mu_B$, corresponding to $S = 2$, and of $d\mu/dV > 0$ are all consistent with a model in which Eq. (10) applies within the small volume interval about a critical molar volume.

5. On a macroscopic, thermodynamic scale, a first-order transition at T_c occurs because of the coincidence of a large exchange striction with a volume-dependent Weiss molecular field W and manganese moment μ. The Curie temperature may be expressed by Eq. (1), where the significant parameter is $\beta \backsim 10$. Further, since the free energy of the ferromagnetic phase contains a magnetic term, T_c increases with applied magnetic field.

In addition, the $t_\pm$ electrons appear to be localized in the ferromagnetic $B8_1$ phase and collective in the $B31$ phase. Since experiments[13] on $LaCoO_3$ have shown a first-order localized-electron⇄collective-electron transition, it is possible that an electronic latent heat may also contribute to the first-order transition in MnAs. *Note added in proof*: N. P. Grazhdankina and Yu. S. Bersenev [Zh. Eksperim. i Teor. Fiz. 51, 1052 (1966)] report changes with temperature in the resistivity and magnetic state of MnAs at different pressures that are in reasonable agreement with our results above 230°K. They report a $dT_c/dP = -(16.0 \pm 0.3)$ deg/kbar with increasing temperature and a $dT_c/dP = -(34 \pm 7)$ deg/kbar with decreasing temperature. They also found a second-order magnetic transition in the high-pressure phase having $T_N \approx 230°K$ at 3 kbar, as obtained indirectly by us from the $MnAs_{1-x}P_x$ system, and a $dT_N/dP = (2.22 \pm 0.07)\ 10^{-3}$ deg/kbar. They also present magnetic data that indicate the presence, in their experiments, of mixed $B8_1$ and $B31$ phases after cooling through the magnetic transition in the hysteretic region of the P-T diagram.

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[17] J. B. Goodenough, speech presented at the Symposium on Structural Inorganic Chemistry in Halifax, Nova Scotia, 1965 (unpublished).