Canted ground states and the paramagnetic-antiferromagnetic transition in semiconductor zinc-blende antiferromagnets

Richard J. Cohen
Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556
(Received 1 March 1993; revised manuscript received 6 July 1993)

Group-theoretical techniques are used to analyze the paramagnetic-antiferromagnetic transition in β-MnS and zinc-blende MnTe, which are both thought to undergo a transition to a canted antiferromagnetic ground state. Although the canting angle itself has remained inaccessible to experiment, the magnetic transition is known to be first order. To date, canting angles of $0, \pi/2, \pi, 3\pi/2$ have been analyzed theoretically and found to exhibit first-order transitions. The theoretical analysis is, here, completed for arbitrary canting angles in the hopes of finding and then ruling out any canting angles that give rise to a second-order transition. It is found that the group representation associated with a canted ground state of arbitrary canting angle (other than $\pi/2$ or $3\pi/2$) is reducible and an argument is provided for a first-order transition to these states on a stronger basis than the usual reducibility of the order parameter. One then concludes that the first-order nature of the experimental transition provides no clue as to the actual canting angle.

The nature of the magnetically ordered phase of a zinc-blende antiferromagnet with dominant antiferromagnetic nearest- and next-nearest-neighbor interactions has been a topic of debate for more than 30 years. To date, we are aware of only two materials of this class that have been synthesized, β-MnS and an epitaxially grown zinc-blende phase of MnTe.[1] The initial experiments[2] on β-MnS showed antiferromagnetic order at the wave vector $\mathbf{k} = (2\pi/a)(\frac{1}{2}, 1, 0)$ where a is the lattice constant of the chemical unit cell. The experiments are, in fact, consistent with a continuum of magnetically ordered states distinguished by what is referred to as the canting angle. The magnetic unit cell for arbitrary canting angle, θ, is shown in Fig. 1. For $\theta = 0, \pi$ the structure is just a type-III antiferromagnet predicted long ago by Anderson[3] to be the ground state of a face centered cubic (fcc) crystal with dominant nearest- and next-nearest-neighbor antiferromagnetic interactions in the parameter range $0 < J_2/J_1 < 1/2$, where J_1 and J_2 are the nearest- and next-nearest-neighbor exchange integrals, respectively, and satisfy $J_1, J_2 < 0$. The zinc-blende structure, unlike the fcc structure, lacks inversion symmetry which then allows the existence of the Dzialoshinski-Moriya (DM) anisotropic superexchange interaction.[4,5] Taking into account both isotropic and DM superexchange as well as the magnetic dipolar energy, Keffer[6] proprosed a $\theta = \pi/2, 3\pi/2$ ground state for β-MnS which was in agreement with the known experiments and which he deemed very likely to have the lowest energy. Experiment, however, has not yet been able to probe the canting angle and thus Keffer's work remains conjecture.

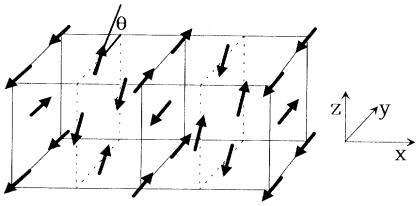

FIG. 1. Magnetic unit cell for a canted ground state with canting angle θ. Note that the magnetic unit cell size is double the chemical unit cell size along, in this case, the x direction. All spins lie in the y-z plane.

More recent attempts at characterizing the ordered state have focused on the nature of the paramagnetic-antiferromagnetic phase transition, i.e., first or second order, as a possible probe of the magnetic order. In particular both β-MnS (Ref. 7) and zinc-blende MnTe (Ref. 1) are known to undergo a first-order transition and thus one can rule out proposed ground states that exhibit a second-order transition. In this regard, Mukamel[7] has argued from renormalization-group ideas that the transition to the Keffer state should be first order. Bak and Mukamel[8] have shown that the order parameter for the $\theta = 0, \pi$ state is associated with a reducible representation of the relevant space group which then suggests, by the group-theoretical arguments of Landau,[9] that the $\theta = 0, \pi$ model also has a first-order transition. The arbitrary θ model, i.e., $\theta \neq 0, \pi/2, \pi, 3\pi/2$, has, however, not yet been explored. The purpose of this paper, then, is to complete the theoretical analysis for arbitrary canting and, in particular, to inquire as to whether or not the order of the transition depends on the canting angle.

The analysis of the paramagnetic-antiferromagnetic transition presented below is based on Landau theory.[9] In particular, the paramagnetic space group for both β-MnS and zinc-blende MnTe is $F\bar{4}3m$. The canted ground state of Fig. 1 is associated with the wave vector $\mathbf{k}_1 = (2\pi/a)(\frac{1}{2}, 1, 0)$. The star of $\mathbf{k}_1$ consists of the six vectors $\mathbf{k}_1 = (2\pi/a)(\frac{1}{2}, 1, 0)$, $\mathbf{k}_{\bar{1}} = (2\pi/a)(-\frac{1}{2}, 1, 0)$, $\mathbf{k}_2 = (2\pi/a)(0, \frac{1}{2}, 1)$, $\mathbf{k}_{\bar{2}} = (2\pi/a)(0, -\frac{1}{2}, 1)$, $\mathbf{k}_3 = (2\pi/a)(1, 0, \frac{1}{2})$, $\mathbf{k}_{\bar{3}} = (2\pi/a)(1, 0, -\frac{1}{2})$. The group of $\mathbf{k}_1$ is S_4 which has both one- and two-dimensional repre-

sentations, implying that the magnetic order parameter associated with this wave vector is either 6- or 12-dimensional. By applying the symmetry operations of $F\bar{4}3m$ to the magnetic structure of Fig. 1, one finds that both the $\theta = \pi/2$, and $3\pi/2$ states are described by a six-dimensional order parameter and all other angles by a 12-dimensional order parameter. A schematic of the magnetic structures associated with the order parameter components for arbitrary canting angle is shown in Fig 2. For brevity, only the four structures associated with $\mathbf{k}_1$ and $\mathbf{k}_{\bar{1}}$ are shown. The eight remaining structures are obtained by applying rotations around the threefold axis [111]. To make clear the notation used in Fig. 2, the number 1 in $(1y)$, for example, refers to the fact that this structure has a magnetic unit cell doubled in the x direction (2 refers to the y direction and 3 to the z direction) and y refers to the fact that the leftmost plane of spins is oriented along the y axis. Note that the structure $(\overline{1y})$ differs from $(1y)$ in that the canted spins in the middle plane are rotated by an angle $(\pi - 2\theta)$ from the canted spins in the middle plane of structure $(1y)$. The eight structures not shown are $(2x)$, $(\overline{2x})$, $(2z)$, $(\overline{2z})$, $(3x)$, $(\overline{3x})$, $(3y)$, $(\overline{3y})$. The 12 order parameter components associated with these 12 structures are denoted $\phi_{i\mu}, \bar{\phi}_{i\mu}$ where $i = 1, 2, 3$ refers to the direction in which the unit cell is doubled and $\mu = x, y, z$ refers to the axis of spin orientation as described for $(1y)$ above. One then finds that the order parameter components transform under the generators of the symmorphic group $F\bar{4}3m$ in the following way:

$$
\begin{aligned}
C_3([111]) &: \phi_{1y} \to \phi_{2z},\ \bar{\phi}_{1y} \to \bar{\phi}_{2z},\\
&\quad \phi_{1z} \to \phi_{2x},\ \bar{\phi}_{1z} \to \bar{\phi}_{2x},\\
&\quad \phi_{2x} \to \phi_{3y},\ \bar{\phi}_{2x} \to \bar{\phi}_{3y},\\
&\quad \phi_{2z} \to \phi_{3x},\ \bar{\phi}_{2z} \to \bar{\phi}_{3x},\\
&\quad \phi_{3x} \to \phi_{1y},\ \bar{\phi}_{3x} \to \bar{\phi}_{1y},\\
&\quad \phi_{3y} \to \phi_{1z},\ \bar{\phi}_{3y} \to \bar{\phi}_{1z},\\
i \times C_4([001]) &: \phi_{1y} \to -\phi_{2x},\ \bar{\phi}_{1y} \to -\bar{\phi}_{2x},\\
&\quad \phi_{1z} \to \phi_{2z},\ \bar{\phi}_{1z} \to \bar{\phi}_{2z},\\
&\quad \phi_{2x} \to -\bar{\phi}_{1y},\ \bar{\phi}_{2x} \to -\phi_{1y},\\
&\quad \phi_{2z} \to -\bar{\phi}_{1z},\ \bar{\phi}_{2z} \to -\phi_{1z},\\
&\quad \phi_{3x} \to \phi_{3y},\ \bar{\phi}_{3x} \to \bar{\phi}_{3y},\\
&\quad \phi_{3y} \to -\phi_{3x},\ \bar{\phi}_{3y} \to -\bar{\phi}_{3x},\\
C_2([100]) &: \phi_{1y} \to -\phi_{1y},\ \bar{\phi}_{1y} \to -\bar{\phi}_{1y},\\
&\quad \phi_{1z} \to -\phi_{1z},\ \bar{\phi}_{1z} \to -\bar{\phi}_{1z},\\
&\quad \phi_{2x} \to -\bar{\phi}_{2x},\ \bar{\phi}_{2x} \to -\phi_{2x},\\
&\quad \phi_{2z} \to \bar{\phi}_{2z},\ \bar{\phi}_{2z} \to \phi_{2z},\\
&\quad \phi_{3x} \to -\bar{\phi}_{3x},\ \bar{\phi}_{3x} \to -\phi_{3x},\\
&\quad \phi_{3y} \to \bar{\phi}_{3y},\ \bar{\phi}_{3y} \to \phi_{3y},\\
t([\tfrac{1}{2}0\tfrac{1}{2}]) &: \phi_{1y} \to \sin(\theta)\bar{\phi}_{1z} - \cos(\theta)\bar{\phi}_{1y},\\
&\quad \bar{\phi}_{1y} \to \cos(\theta)\phi_{1y} + \sin(\theta)\phi_{1z},\\
&\quad \phi_{1z} \to -\sin(\theta)\bar{\phi}_{1y} - \cos(\theta)\bar{\phi}_{1z},\\
&\quad \bar{\phi}_{1z} \to \cos(\theta)\phi_{1z} - \sin(\theta)\phi_{1y},\\
&\quad \phi_{2x} \to -\phi_{2x},\ \bar{\phi}_{2x} \to -\bar{\phi}_{2x},\\
&\quad \phi_{2z} \to -\phi_{2z},\ \bar{\phi}_{2z} \to -\bar{\phi}_{2z},\\
&\quad \phi_{3x} \to \cos(\theta)\bar{\phi}_{3x} - \sin(\theta)\bar{\phi}_{3y},\\
&\quad \bar{\phi}_{3x} \to -\cos(\theta)\phi_{3x} - \sin(\theta)\phi_{3y},\\
&\quad \phi_{3y} \to \sin(\theta)\bar{\phi}_{3x} + \cos(\theta)\bar{\phi}_{3y},\\
&\quad \bar{\phi}_{3y} \to \sin(\theta)\phi_{3x} - \cos(\theta)\phi_{3y},
\end{aligned}
\tag{1}
$$

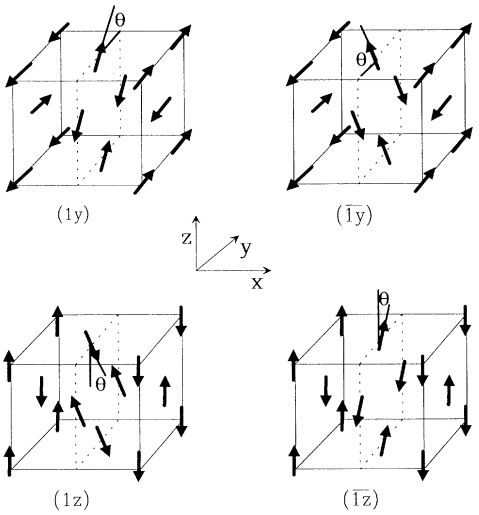

FIG. 2. Schematic of the spin arrangements corresponding to the 12 components of the order parameter. There are four structures for each of the three cubic axes; only those with magnetic unit cell doubled along the x direction are shown. The four structures $(2x)$, $(\overline{2x})$, $(2z)$, $(\overline{2z})$ with magnetic unit cell doubled along the y direction have spins lying only in the x-z plane and the four structures $(3x)$, $(\overline{3x})$, $(3y)$, $(\overline{3y})$ with magnetic unit cell doubled along the z direction have spins lying only in the x-y plane.

where $C_l([\cdots])$ is an l-fold rotation axis along the $[\cdots]$ direction, i is the inversion operation, $t([\frac{1}{2}0\frac{1}{2}])$ is a translation of $[\frac{1}{2}0\frac{1}{2}]a$, and θ is the canting angle. For example, the transformation of ϕ_{1y} under $t([\frac{1}{2}0\frac{1}{2}])$ is found by applying a translation of $[\frac{1}{2}0\frac{1}{2}]a$ to the structure $(1y)$ of Fig. 2 and expressing the resulting spin configuration as a linear combination of $(1y)$, $(\overline{1y})$, $(1z)$, $(\overline{1z})$ (all spins have unit magnitude).

As mentioned above, it is known from the work of Bak and Mukamel[8] that the representation associated with the $\theta = 0, \pi$ model is reducible and, as such, is expected to exhibit a first-order transition according to Landau's rules for continuous transitions.[9,10] Given the above transformation rules for the order parameter one can now address the question of reducibility for arbitrary canting. One finds, in fact, that the 12-dimensional representation presented above reduces to two inequivalent six-dimensional representations. The order parameters of the two six-dimensional representations are related to the order parameter of the original 12-dimensional representation in the following way:

$$\begin{aligned}
&\psi_1 \equiv \xi_{1y} - \alpha(\theta)\bar{\xi}_{1z}, \quad \eta_1 \equiv \xi_{1y} + \beta(\theta)\bar{\xi}_{1z}, \\
&\bar{\psi}_1 \equiv \xi_{1z} + \alpha(\theta)\bar{\xi}_{1y}, \quad \bar{\eta}_1 \equiv \xi_{1z} - \beta(\theta)\bar{\xi}_{1y}, \\
&\psi_2 \equiv \xi_{2z} - \alpha(\theta)\bar{\xi}_{2x}, \quad \eta_2 \equiv \xi_{2z} + \beta(\theta)\bar{\xi}_{2x}, \\
&\bar{\psi}_2 \equiv \xi_{2x} + \alpha(\theta)\bar{\xi}_{2z}, \quad \bar{\eta}_2 \equiv \xi_{2x} - \beta(\theta)\bar{\xi}_{2z}, \\
&\psi_3 \equiv \xi_{3x} - \alpha(\theta)\bar{\xi}_{3y}, \quad \eta_3 \equiv \xi_{3x} + \beta(\theta)\bar{\xi}_{3y}, \\
&\bar{\psi}_3 \equiv \xi_{3y} + \alpha(\theta)\bar{\xi}_{3x}, \quad \bar{\eta}_3 \equiv \xi_{3y} - \beta(\theta)\bar{\xi}_{3x},
\end{aligned} \tag{2}$$

where one of the six-dimensional representations is specified with ψ and the other with η and where the following notation has been introduced: $\xi_{i\mu} \equiv (\phi_{i\mu} + \bar{\phi}_{i\mu})/2$, $\bar{\xi}_{i\mu} \equiv (\phi_{i\mu} - \bar{\phi}_{i\mu})/2$, $\alpha(\theta) \equiv [1 - \sin(\theta)]/\cos(\theta)$, and $\beta(\theta) \equiv [1 + \sin(\theta)]/\cos(\theta)$. In fact, both the ψ and η representations exhibit the Keffer ordering discussed in the Introduction. In particular, the spin structure associated with ψ_1 is obtained from $(1y)$ of Fig. 2 when $\theta = \pi/2$, and the spin structure associated with η_1 is obtained when $\theta = 3\pi/2$. Thus ψ_1 and η_1 differ from each other only in their handedness (the difference in handedness for the ψ and η representations is true for each pair of corresponding components such as ψ_1 and η_1) if one considers the handedness implied by the rotation of the spins on adjacent planes along the x direction. One can then view the spin configurations of the η and ψ representations as right-handed and left-handed Keffer ordering, respectively.

Although the above demonstration of reducibility of the order parameter would usually be sufficient for ruling out a second-order transition, this question is probed a bit further in the light of the nature of the two irreducible components ψ and η. In particular, the above-mentioned reducibility implies that the quadratic term in the free energy for general canting will have the form

$$\sum_{i=1}^{3} \left[r_1(P,T) \left(\psi_i^2 + \bar{\psi}_i^2 \right) + r_2(P,T) \left(\eta_i^2 + \bar{\eta}_i^2 \right) \right] \tag{3}$$

and thus given the ψ and η representations differ only in their handedness one may suspect that $r_1(P,T) = r_2(P,T)$. If such is the case, then the transition is actually second order even though the order parameter corresponds to a reducible representation. In this regard, note that reducibility, by itself, does not imply a first-order transition. A first-order transition occurs when $r_1(P,T)$ and $r_2(P,T)$ do not simultaneously vanish at the transition point. To date, all experimentally realizable reducible representations decompose into sufficiently different irreducible parts that simultaneous vanishing of the quadratic coefficients does not occur. It would, of course, be quite interesting to find a system with a reducible order parameter which exhibits a second-order transition due to simultaneous vanishing of the quadratic coefficients. The above arguments regarding the spin configurations of β-MnS and zinc-blende MnTe are sufficiently inviting in this regard to warrant further discussion.

The goal is to prove or disprove the simultaneous vanishing of $r_1(P,T)$ and $r_2(P,T)$. By appealing to the microscopic spin Hamiltonian known to be appropriate for both β-MnS and zinc-blende MnTe,[6] one can actually construct a convincing argument against simultaneous vanishing. In particular, the appropriate spin Hamiltonian has the form

$$-\sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \sum_{k,l} \mathbf{D}_{kl} \cdot (\mathbf{S}_k \times \mathbf{S}_l), \tag{4}$$

where i and j range over both first- and second-nearest neighbors, k and l over only first-nearest neighbors, and where J_{ij} is the isotropic Heisenberg coupling and $\mathbf{D}_{kl}$ the anisotropic DM coupling. By inspection of the $(1y)$ configuration of Fig. 2, one can see that the isotropic part cannot distinguish the ψ representation from the η one (recall ψ corresponds to $\theta = \pi/2$ and η to $\theta = 3\pi/2$). As pointed out by Keffer,[6] however, the DM interaction can distinguish between the two representations, i.e., either ψ or η is lower in energy but exactly which one is lower cannot be determined from the symmetry argument used by Keffer.[11] From the point of view of a phase transition it is then clear that the ψ and η representations will be associated with different transition temperatures, i.e., the lower in energy of the two will have the higher transition temperature, and thus simultaneous vanishing of $r_1(P,T)$ and $r_2(P,T)$ will not occur. One thus concludes, from a stronger position than reducibility of the order parameter, that the paramagnetic-antiferromagnetic transition to a canted ground state of arbitrary canting angle (other than $\theta = \pi/2, 3\pi/2$) is first order.

The above arguments coupled with Mukamel's renormalization-group arguments for the special case of $\theta = \pi/2, 3\pi/2$ then lead to the conclusion that the paramagnetic-antiferromagnetic transition in β-MnS and zinc-blende MnTe will be first-order regardless of the canting angle. The experimental result of a first-order transition implies that all canting angles are consistent with experiment and that the nature of the transition cannot be used to distinguish the canting angle in these systems.

I would like to thank K. E. Newman both for introducing me to the subject of ordering in magnetic semiconductors and for useful discussions regarding this work. This work was supported by ONR Grant No. N00014-91-J-1062.

[1] P. Klosowski, T.M. Giebultowicz, N. Samarth, H. Luo, J.K. Furdyna, and J.J. Rhyne, J. Magn. Magn. Mater. **104-107**, 1795 (1992).
[2] L.M. Corliss, N. Elliott, and J. Hastings, Phys. Rev. **104**, 924 (1956).
[3] P.W. Anderson, Phys. Rev. **115**, 2 (1959).
[4] I. Dzialoshinski, J. Phys. Chem. Solids **4**, 241 (1958).
[5] T. Moriya, Phys. Rev. **120**, 91 (1960).
[6] F. Keffer, Phys. Rev. **126**, 896 (1962).
[7] J.M. Hastings, L.M. Corliss, W. Kunmann, and D.

Mukamel, Phys. Rev. B **24**, 1388 (1981).
[8]P. Bak and D. Mukamel, Phys. Rev. B **13**, 5086 (1976).
[9]L.D. Landau and E.M. Lifshitz, *Statistical Physics*, 3rd ed. (Pergamon, New York, 1980), Chap. XIV, Part I.
[10]P. Bak, S. Krinsky, and D. Mukamel, Phys. Rev. Lett. **36**, 52 (1976).

[11]The lifting of the degeneracy by the DM interaction is unaffacted by inclusion of the leading order symmetric anisotropy as it can be shown that the symmetric anisotropy cannot distinguish the ψ representation from the η representation.