

Spin Arrangement in the Pyrite, MnTe_2 [†]J. M. HASTINGS, L. M. CORLISS, AND M. BLUME
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An inconsistency between Mössbauer and neutron-diffraction measurements on MnTe_2 is resolved. A new generalization of magnetic ordering of the first kind preserves the characteristic neighbor relationships of that scheme and at the same time accounts for the Mössbauer results.

RECENT Mössbauer measurements¹ on MnTe_2 have shown that the collinear spin arrangement originally proposed² for this compound on the basis of neutron-diffraction data is inconsistent with the computed angle between the internal magnetic field and the principal axis of the electric field gradient. In the present paper we show that the original model, ordering of the first kind, can be generalized in a way which preserves the characteristic neighbor relationships of the ordering scheme and at the same time accounts for the Mössbauer results.

MnTe_2 has the pyrite structure (Fig. 1), which is a NaCl-like arrangement of Mn and Te_2 "molecules" with the axes of the Te_2 "molecules" parallel to the various body diagonals, as given in Table I. In ordering of the first kind, the manganese moments are arranged in ferromagnetic (100) sheets which alternate in sign in a direction perpendicular to the sheets. For this

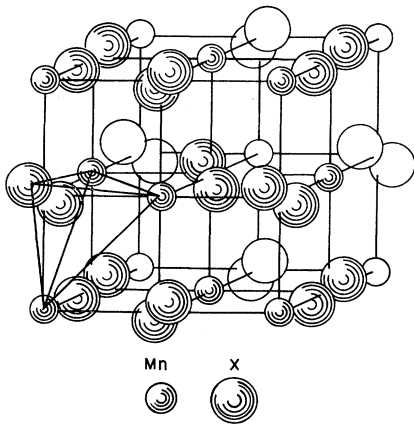


FIG. 1. Pyrite structure. The heavy lines outline a nearly regular tetrahedron whose corner positions are occupied by three metal atoms and one member of a Te_2 group, and whose center is occupied by the other member of the Te_2 pair.

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¹ M. Pasternak and A. L. Spijkervet, Phys. Rev. **181**, 574 (1969).

² J. M. Hastings, N. Elliott, and L. M. Corliss, Phys. Rev. **115**, 13 (1959).

collinear model, the observed neutron intensities require the spin direction to lie in the ferromagnetic sheet.

The Mössbauer spectra, as analyzed in Ref. 1, indicate the presence at each Te nucleus of an electric field gradient, q_{zz} , produced by the intramolecular (Te_2) bonding, and also a magnetic field produced by the magnetically ordered Mn ions. The key point found by analysis of the spectra is that the magnetic field at each Te nucleus makes a constant angle θ with the electric field gradient at that nucleus. There is no evidence for spectra corresponding to a number of different angles. The angle θ appears to vary with temperature, but this point is not as firmly established by the data as is the uniqueness of θ . Just below the Néel temperature the best value of θ is 0° , while at very low temperatures theoretical spectra assuming an angle of 30° seem to give the best fit to the data.

At a given Te site, symmetry requires that the electric field gradient lie along the local Te-Te "molecular" axis. The magnetic field is produced primarily by an isotropic transferred hyperfine interaction due to overlap of the spin density of the neighboring Mn ions. A dipolar contribution is also present but this is expected to be small compared with the isotropic term. The direction of the magnetic field at a given Te nucleus can then be determined to a very good approximation by adding vectorially the directions of the three neighboring Mn spins. With these assumptions the collinear model of Ref. 2 will produce different angles with the field gradient at different Te sites except when the spins are all parallel to a cube edge. In this case $\theta = 55^\circ$, which, however, lies outside the analyzed values of Ref. 1.

TABLE I. Structural information for MnTe_2 .

Center of Te_2 "molecule"	Direction of molecular axis	Positions of nearest Mn neighbors of Te ^a
$(\frac{1}{2}00)$	$[\bar{1}\bar{1}1]$	000 $\frac{1}{2}\frac{1}{2}0$ $\frac{1}{2}0\frac{1}{2}$
$(0\frac{1}{2}0)$	$[1\bar{1}\bar{1}]$	000 $\frac{1}{2}\frac{1}{2}0$ $0\frac{1}{2}\frac{1}{2}$
$(00\frac{1}{2})$	$[\bar{1}1\bar{1}]$	000 $0\frac{1}{2}\frac{1}{2}$ $\frac{1}{2}0\frac{1}{2}$
$(\frac{1}{2}\frac{1}{2}\frac{1}{2})$	$[111]$	$\frac{1}{2}\frac{1}{2}0$ $0\frac{1}{2}\frac{1}{2}$ $\frac{1}{2}0\frac{1}{2}$

^a Neighbors of one member of a Te_2 "molecule" are crystallographically equivalent to the neighbors of the second member.

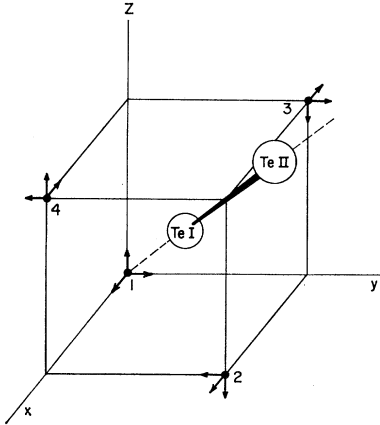


FIG. 2. One octant of the MnTe_2 unit cell. Arrows represent spin components of manganese atoms for proposed high-temperature structure. Nearest neighbor of Te I are manganese atoms 2, 3, and 4. The nearest neighbors of Te II are atoms one lattice spacing away from each of atoms 2, 3, and 4. Te_2 groups centered at the unoccupied corners in the above diagram have been omitted.

To overcome this difficulty, the neutron data were reanalyzed in terms of the most general noncollinear model consistent with an antiferromagnetic unit cell of the same size as the chemical cell. Assuming unit magnitude for the spins, the structure factor for an hkl reflection is given by

$$F_{hkl}^2 = K^2 - (\mathbf{e} \cdot \mathbf{K})^2,$$

$$\mathbf{K}_{hkl} = \sum_i \mathbf{u}_i e^{2\pi i(hx_i + ky_i + lz_i)},$$

where \mathbf{e} is the unit scattering vector and \mathbf{u}_i is the unit magnetic moment of the manganese atom at (x_i, y_i, z_i) . For the first two magnetic reflections, the structure factors, averaged over members of the crystallographic form, are

$$\langle F^2 \rangle_{100} = (8/3)(1 - \frac{1}{2}A),$$

$$\langle F^2 \rangle_{110} = 4(1 + \frac{1}{6}A),$$

where A is given by

$$A = \mu_{1x}\mu_{3x} + \mu_{2x}\mu_{4x} + \mu_{1y}\mu_{4y} + \mu_{2y}\mu_{3y} + \mu_{1z}\mu_{2z} + \mu_{3z}\mu_{4z},$$

and the subscripts 1-4 refer to the Mn positions 000 , $\frac{1}{2}\frac{1}{2}0$, $0\frac{1}{2}\frac{1}{2}$, and $\frac{1}{2}0\frac{1}{2}$, respectively, in the chemical unit cell (see Fig. 2). The experimental observation that $\langle F^2 \rangle_{100} = 2\langle F^2 \rangle_{110}$ implies that $A = -2$ and the following relations among the various spin components:

$$\begin{aligned} \mu_{1x} &= -\mu_{3x} = \pm\mu_{2x} = \mp\mu_{4x}, \\ \mu_{1y} &= -\mu_{4y} = \mp\mu_{2y} = \pm\mu_{3y}, \\ \mu_{1z} &= -\mu_{2z} = \mp\mu_{3z} = \pm\mu_{4z}. \end{aligned} \quad (1)$$

The eight allowed structures given by these relations can be generated by alternating the x component of the spin each half-unit-cell translation in the z or y directions, the y component correspondingly in the x or z directions, and similarly for the z component in the y or x directions. In the original collinear model for ordering of the first kind, the x and y components of the spin alternate in the z direction and the z component is zero. For the noncollinear models, just as in the collinear case, the sum of the moments of the twelve nearest neighbors of the i th Mn atom is $-4\mathbf{u}_i$ and the corresponding sum for next-nearest neighbors is $+6\mathbf{u}_i$.

The requirement of a constant angle θ between the internal magnetic field (contact term only) and q_{zz} , for all Te sites, reduces the choice of possible structures to the one given by the upper signs in Eq. (1). This may be seen by direct calculation of the angles using the information in Table I and Eq. (1). With this choice of signs in (1) the angle θ is determined by

$$\cos\theta = (\mu_{1x} + \mu_{1y} + \mu_{1z})/\sqrt{3} \quad (2)$$

with

$$\mu_{1x}^2 + \mu_{1y}^2 + \mu_{1z}^2 = 1.$$

The Mössbauer result that $\theta \sim 0^\circ$ just below the Néel point then requires that the x , y , and z components of the spins be equal in magnitude. This structure is shown in Fig. 2. The resulting magnetic structure belongs to space group $Pa3$, the chemical space group for the pyrite structure. In this space group, each Te_2 "molecular" axis coincides with a threefold rotation axis and hence the *total* internal magnetic field at a given Te nucleus must be parallel to q_{zz} at that site. The less certain low-temperature Mössbauer result that $\theta \sim 30^\circ$ does not determine a unique structure. A simple choice is to set one of the components, say μ_z , equal to zero, which leads to a $\theta \sim 35^\circ$.

It should be noted that the neutron-diffraction patterns obtained either from powders or from multi-domain single crystals cannot distinguish between the collinear model and the noncollinear structure proposed here. Neutron-scattering experiments provide complete and unequivocal information on magnetic structures in principle only when single-domain single crystals are used and when a polarized neutron beam is employed. In the absence of this complete information it is possible, as in the present example, for ambiguities in the structure to remain. The Mössbauer data have in this case provided essential information for the determination of the structure. Our analysis illustrates one way in which the Mössbauer effect can be used in conjunction with neutron diffraction in the study of magnetic structures.