

Antiferromagnetic Structures of MnS₂, MnSe₂, and MnTe₂

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garnets.³ Crystals of this type have been grown using the composition 72.7 mole % PbO, 26 mole % Ga₂O₃, and 1.3 mole % Y₂O₃. The same conditions as those for growing YIG were used.

It has also been discovered that YIG crystals may be grown from molten Bi₂O₃ using the composition 35.3 mole % Bi₂O₃, 61.7 mole % Fe₂O₃, and 3.0 mole % Y₂O₃. X-ray diffraction patterns of the crystals grown from Bi₂O₃ revealed however, that bismuth was substituted for yttrium in these crystals in varying but substantial amounts. A comparison with data obtained by M. A. Gilleo,⁴ who used polycrystalline samples, showed that the bismuth concentration in the crystals varied from about 1.5 to 17.5 mole % Bi₂O₃. Thus

³ Remeika has grown small crystals of Y₃Ga₅O₁₂; see S. Geller and M. A. Gilleo, *Acta. Cryst.* **10**, 239 (1957).

⁴ M. A. Gilleo (private communication).

Bi₂O₃ is a less satisfactory solvent than PbO, but it is interesting to note that if one considers the composition used in terms of BiO concentration, i.e., twice the mole % of Bi₂O₃, the composition is remarkably close to that for growth of garnets from PbO. This suggests that, in this case at least, the solvent action of these oxides may depend on some property of the heavy metal ion as it resides in the oxygen lattice and not on structural details of that lattice.

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Antiferromagnetic Structures of MnS₂, MnSe₂, and MnTe₂†

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The antiferromagnetic structures of MnS₂, MnSe₂, and MnTe₂ have been obtained by neutron diffraction. The disulfide exhibits ordering of the "third" kind, the ditelluride, ordering of the "first" kind, and the diselenide, an arrangement which is intermediate between the two. The structures are discussed from the viewpoint of indirect exchange.

NEUTRON diffraction studies of three polymorphic forms of MnS have shown¹ that the antiferromagnetic structures developed in these materials may be correlated with chemical binding. The observed magnetic structures indicate strong antiferromagnetic correlations between second nearest neighbors in the case of the rock-salt form of MnS and between nearest neighbors in the tetrahedral forms. Indirect exchange would thus appear to involve octahedral sulfur bonds in the first instance and tetrahedral bonds in the second. In an effort to further elucidate the role of the anion in antiferromagnetism, these studies have been extended to the homologous series consisting of MnS₂, MnSe₂, and MnTe₂.

The compounds crystallize with the pyrite structure, which is a NaCl-like arrangement of M and X₂ groups with the axes of the X₂ groups parallel to the various body diagonals. The structure is shown schematically in Fig. 1. A salient feature is the presence of somewhat distorted tetrahedra whose corner positions are occupied by three metal atoms and one member of an X₂ group, and whose center is occupied by the other member of the X₂ pair. Magnetic as well as crystal-

chemical evidence² suggest that these compounds may be regarded as essentially ionic combinations of Mn⁺⁺ and X₂⁻ groups. From this point of view, the face-centered cubic structure of manganese ions might be expected to exhibit second nearest neighbor antiferromagnetic correlations as in MnO and α-MnS. On the other hand, the existence of nearly tetrahedral Mn-X-Mn linkages between nearest neighbor manganese atoms would suggest an ordering scheme based on nearest neighbor antiferromagnetic correlations as in β-MnS.

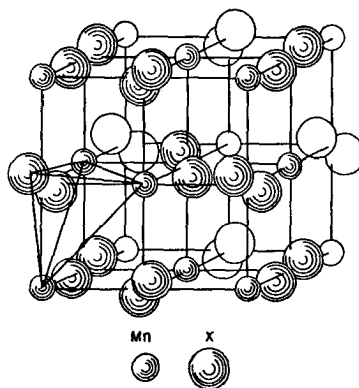


FIG. 1. The pyrite structure.

† Research performed under the auspices of the U. S. Atomic Energy Commission.

¹ Corliss, Elliott, and Hastings, *Phys. Rev.* **104**, 924 (1956).

² N. Elliott, *J. Am. Chem. Soc.* **59**, 1958 (1937); L. Néel and R. Benoit, *Compt. rend.* **237**, 444 (1953).

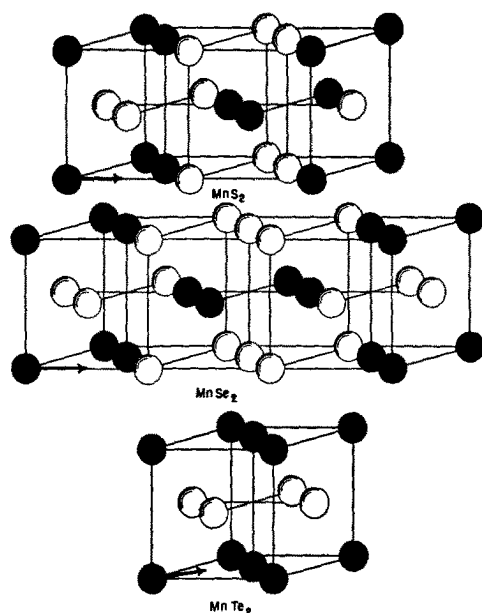


FIG. 2. Magnetic structure of MnS_2 (ordering of the "third" kind), MnSe_2 , and MnTe_2 (ordering of the "first" kind). Positive and negative orientations of the dipoles are shown by black and white spheres. The direction of the magnetic axis relative to the crystallographic axes is shown by an arrow. In the case of MnTe_2 the spin direction lies in the ferromagnetic sheets, but orientation within the plane is unspecified.

All three compounds become antiferromagnetic in the neighborhood of liquid nitrogen temperatures or below. Neutron diffraction patterns obtained at liquid helium temperatures show well developed superstructure lines and indicate the appearance of three distinct antiferromagnetic structures. The structures deduced from the magnetic peak intensities and extinctions are shown in Fig. 2. The magnetic ordering scheme for MnS_2 is that of the "third" kind and for MnTe_2 , that of the "first" kind. The structure exhibited by MnSe_2 , on the other hand, is not homogeneous, but is intermediate between these two. The spin direction in both the disulfide and diselenide is parallel to the axis along which the chemical unit cell is enlarged and in the ditelluride it lies within the ferromagnetic sheets.

Despite the differences in antiferromagnetic structure, the three arrangements are, in some significant respects, similar. This can best be seen by considering the distribution of parallel and antiparallel neighbors. In

all three compounds the Mn atoms have eight nearest neighbors with antiparallel spin and four nearest neighbors with parallel spin. This is the maximum antiferromagnetic nearest neighbor correlation that can be uniformly propagated in the face-centered cubic structure and corresponds to the arrangement observed in the zinc blende form of MnS . This strongly suggests that the Mn-X-Mn tetrahedral linkage provides the important path for indirect exchange. The differences in the various antiferromagnetic structures manifest themselves in the second nearest neighbor arrangements. In the case of the ditelluride (ordering of the first kind), all six second nearest neighbors are parallel to the central atom. In the disulfide (ordering of the third kind), each Mn atom has four parallel and two antiparallel second nearest neighbors. In the case of the diselenide, which does not develop a homogeneously ordered structure, the second nearest neighbor distribution is intermediate between the disulfide and ditelluride. Thus in all cases the second nearest neighbor interaction is ferromagnetic, with the strength of the interaction increasing in the order MnS_2 , MnSe_2 , and MnTe_2 .

Keffer and O'Sullivan³ have computed the magnetic dipolar energy for arrays of spins corresponding to ordering of the third kind. They find that the energy is a minimum when all dipoles point parallel to the direction in which the chemical unit cell is enlarged. Furthermore, they point out that this result is in disagreement with the moment direction obtained for the zinc blende form of MnS from neutron diffraction data, which place the dipoles at right angles to this direction. In MnS_2 , as the present work shows, the spin direction is in agreement with the predictions of Keffer and O'Sullivan. However, the two results taken together indicate that the agreement may be fortuitous and that there are indeed important contributions to the anisotropy which have not been considered in the calculations.

A comprehensive report of this work, including an account of sample preparation, magnetic measurements, neutron diffraction data, and computations relating to both magnetic and chemical structure, will be published elsewhere.

³ F. Keffer and W. O'Sullivan, *Phys. Rev.* **108**, 637 (1957). T. Nagamiya, Osaka University, Japan (private communication) confirms these calculations for ordering of the third kind.