

Antiferromagnetism in the Face-Centered Cubic Lattice. III. α -MnS

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Alpha MnS is a face-centered cubic antiferromagnet which exhibits the same ferromagnetic-layer spin arrangement which is found in MnO. The Mn^{55} zero-field nuclear magnetic resonance (NMR) has been observed in the antiferromagnetic state of α -MnS and, from the temperature dependence of the resonance frequency, information is derived regarding the spin deviation as a function of temperature. The so-called anomalous temperature dependence of sublattice magnetization which has been reported for MnO is found to be essentially absent in α -MnS. The general question of the incorporation of biquadratic exchange terms $-j(\mathbf{S}_i \cdot \mathbf{S}_j)^2$ into molecular-field and spin-wave theories of magnetism is discussed, and a simple spin-wave theory is developed for α -MnS which includes both bilinear and biquadratic exchange interactions between nearest and next-nearest neighbors ($J_1, j_1; J_2, j_2$) as well as both isotropic and anisotropic magnetostrictive terms. The spin deviation is found to be an extremely sensitive function of j_1 and of distortion (anisotropic magnetostriction), but is relatively insensitive to j_2 and isotropic magnetostriction. The bilinear exchange interactions are estimated by using Lines' Green's-function theory to describe the paramagnetic properties of α -MnS, for which we find values $J_1 = 7^\circ K$ and $J_2 = 12.5^\circ K$. Comparison of theory with experiment for the temperature dependence of spin deviation allows an upper limit to be placed upon the magnitude of j_1 . The ratio j_1/J_1 is found to be less than 10^{-3} , which is at least an order of magnitude smaller than any previous estimates made for Mn^{2+} interactions.

1. INTRODUCTION

IN Parts I and II of the present series of papers,¹ the statistical problem for antiferromagnetism in the face-centered cubic lattice is treated using a random-phase Green's-function approximation, and the results are used to interpret the magnetic properties of MnO. It is found, contrary to an earlier suggestion,² that the anomalous temperature dependence of the MnO magnetization curve is not evidence for the existence of intrinsic biquadratic exchange in the MnO system. The anomalous behavior may be quantitatively explained in the complete absence of biquadratic exchange by taking account of an anisotropic magnetostrictive effect, the existence of which has been known for many years,³⁻⁵ but which has previously been studied only in a molecular-field approximation,⁵ which badly underestimates the importance of the effect.

In spite of this result, some uncertainty still remains concerning an upper limit to the size of a possible biquadratic term. The reasons for this are twofold. Firstly, the effect of introducing a biquadratic contribution to the exchange Hamiltonian in addition to the distortion (magnetostrictive) terms was never considered in detail in Parts I and II, although our general "feeling" that it would behave very much like an additional distortion term (as far as magnetization is concerned) will be shown, in the present paper, to be

correct. Secondly, although the shapes of the magnetization curves as a function of T/T_N (where T_N is the Néel temperature) are extremely sensitive to distortion for very small values of the latter, they become rather insensitive for values of distortion larger than those observed in MnO. The reason is that the Néel temperature itself becomes a function of distortion at these higher values (see Fig. 7 of Part II). Thus, for MnO, the *shape* of the magnetization curve is fairly insensitive to any biquadratic exchange which might be present in the system in addition to the distortion terms.

On the other hand, the spin arrangement which is found in MnO (the antiferromagnetic fcc type-2 order; see Fig. 1 of Parts I and II), would seem to be an ideal system for use in detecting the effects of very small magnetostrictive and/or biquadratic terms on bulk magnetic properties—far better, for example, than simple two-sublattice antiferromagnetic systems such as MnF_2 . The reasons for this are related to the breakdown of molecular-field theory for the present case (compare Figs. 6 and 7 of Part II) and will be discussed at some length in Sec. 4.

An ideal substance for use in searching for very small biquadratic effects would therefore be one which exhibits the fcc type-2 spin structure and also has small magnetostrictive effects. For simplicity, however, and in order to allow for as accurate a theoretical analysis of the problem as possible, it is also desirable that the salt should have well-isolated orbital-singlet single-ion ground states and a magnetic anisotropy which is very small compared to the isotropic exchange energy. Of the obvious candidates, viz., NiO, EuTe, and α -MnS, only the last is really suitable on all counts. Although Ni^{++} has an orbital-singlet ground state in NiO, and an isotropic exchange energy which far outweighs any dipolar anisotropy, its Néel temperature is so large

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¹ M. E. Lines, Phys. Rev. **139**, A1304 (1965); M. E. Lines and E. D. Jones, *ibid.* **139**, A1313 (1965).

² D. S. Rodbell, I. S. Jacobs, J. Owen, and E. A. Harris, Phys. Rev. Letters **11**, 10 (1963).

³ N. C. Tombs and H. P. Rooksby, Nature **165**, 442 (1950).

⁴ J. Kanamori, Progr. Theoret. Phys. (Kyoto) **17**, 197 (1957).

⁵ D. S. Rodbell and J. Owen, J. Appl. Phys. **35**, 1002 (1964).

that an analysis of the paramagnetic state necessitates the inclusion of higher energy orbital contributions which are difficult to handle in an accurate statistical treatment. EuTe, on the other hand, contains magnetic cations with well isolated orbital-singlet ground states, but the $4f$ wave functions are so localized, and the resulting superexchange so small, that the dipolar anisotropy energy is by no means small compared with the isotropic exchange. In such a case, the anisotropic effects are not well approximated by effective fields, and result in considerable theoretical complications.

For these reasons we have singled out α -MnS as being the salt most suitable for detailed study in a search for effects which might be due to biquadratic exchange. The experimental information presently available for α -MnS is, however, rather scant, and it is hoped that the work of the present paper will stimulate interest in the magnetic properties of this salt.

We have observed the Mn⁵⁵ nuclear magnetic resonance (NMR) in zero external magnetic field at temperatures between 1.5 and 20.4°K. The temperature dependence of the NMR frequency provides information concerning the temperature dependence of sublattice magnetization. We find that the so-called anomalous behavior of sublattice magnetization which was observed for MnO is essentially absent in α -MnS, indicating that the lattice distortion in α -MnS is probably rather small, and that α -MnS should therefore allow for a sensitive measurement of biquadratic exchange.

In discussing the possible interactions in α -MnS, we have allowed for both isotropic and anisotropic magnetostrictive effects and have introduced biquadratic interactions between both the nearest and next-nearest neighbors in addition to the bilinear exchange J_1 and J_2 . A spin-wave theory has been developed for the system and it is demonstrated that the deviation of magnetization from its value at $T=0$ is very sensitive indeed to anisotropic distortion Δ and to nearest-neighbor biquadratic exchange j_1 , but is fairly insensitive to isotropic magnetostriction and to next-nearest-neighbor biquadratic exchange. This allows us to describe the NMR results in terms of J_1 , J_2 , j_1 , and Δ only.

Values for the nearest- and next-nearest-neighbor bilinear exchange parameters J_1 and J_2 are estimated from a description of the paramagnetic state using the Green's function theory of Part I; we find $J_1=7^\circ\text{K}$ and $J_2=12.5^\circ\text{K}$. Using these values in the spin-wave calculation, and fitting the theory to the NMR experimental results, then provides us with information concerning j_1 and Δ . We conclude that the ratio $j_1/J_1 < 0.001$ for α -MnS; it may even be negative. All previous estimates of biquadratic exchange for Mn⁺⁺ interactions (see, for example, Joseph⁶) have indicated that j/J is positive and $\sim 0.01 \rightarrow 0.05$. Whether j_1/J_1

is positive or negative for α -MnS can be decided by a direct measurement of anisotropic distortion Δ , but the results of such a measurement are not yet available. It is important to note, however, that the result $j_1/J_1 < 0.001$ refers only to nearest neighbors (superexchange via a 90° ligand). It does not follow that an equivalent result is necessarily valid for next-nearest neighbors (superexchange via a 180° ligand).

In Sec. 2 we discuss biquadratic exchange in the molecular-field approximation, comparing the effects of biquadratic and distortion terms on sublattice magnetization in this theory. In Sec. 3 we investigate the manner in which biquadratic exchange can be included in a simple spin-wave theory. Section 4 derives an exchange Hamiltonian for α -MnS and discusses the spin-wave estimate of sublattice magnetization using this Hamiltonian. The paramagnetic properties of α -MnS are analyzed in Sec. 5 using the random-phase Green's-function theory of Part I, and estimates are obtained for the bilinear exchange parameters in this salt. In Sec. 6 we describe the measurement of the zero-field NMR in the antiferromagnetic state of α -MnS, and discuss the temperature variation of this frequency in terms of the spin-wave calculations of Sec. 4. Also discussed is the resonance linewidth and the contribution to this linewidth to be expected from indirect nuclear spin-spin interaction. Finally, Sec. 7 discusses the conclusions concerning biquadratic exchange which follow from the results of the present paper.

2. BIQUADRATIC EXCHANGE IN THE MOLECULAR-FIELD APPROXIMATION

Consider an exchange Hamiltonian of the form

$$\mathcal{H} = \sum_{\langle ij \rangle} [J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - j_{ij} (\mathbf{S}_i \cdot \mathbf{S}_j)^2], \quad (2.1)$$

where J_{ij} and j_{ij} are, respectively, the bilinear and biquadratic exchange parameters for interactions between spins S_i and S_j , and where $\sum_{\langle ij \rangle}$ runs over all pairs of spins in the system. In the molecular-field approximation, we reduce Eq. (2.1) to a single spin Hamiltonian \mathcal{H}_i by replacing the various spin functions of all spins $S_{j \neq i}$ by their average values, thus neglecting all correlations between the spins. If we assume that spin S_j is in an eigenstate of S_{jz} (which is self-consistent in the sense that the resulting Hamiltonian \mathcal{H}_i has stationary states which are eigenstates of S_{iz}), then we may readily replace the operators of S_j which occur in (2.1) by their average values, which can be written as functions of $\langle S_{jz} \rangle$ and $\langle S_{jz}^2 \rangle$. The resulting single spin Hamiltonian is

$$\mathcal{H}_i = \sum_{j \neq i} \{ J_{ij} S_{iz} \langle S_{jz} \rangle - j_{ij} [S_{iz}^2 \langle S_{jz}^2 \rangle + S_{ij}^2 \langle S_{jz}^2 \rangle + S_{iz}^2 \langle S_{jz}^2 \rangle - \frac{1}{2} S_{iz} \langle S_{jz} \rangle] \}, \quad (2.2)$$

where

$$\langle S_{jz}^2 \rangle = \langle S_{jy}^2 \rangle = \frac{1}{2} S(S+1) - \frac{1}{2} \langle S_{jz} \rangle^2, \quad (2.3)$$

⁶ R. I. Joseph, Phys. Rev. **138**, A1441 (1965).

and where the axis z has been singled out as the direction of spin alignment in the ordered state, so that $\langle S_{jz} \rangle = \langle S_{jy} \rangle = 0$.

The Hamiltonian (2.2) is already in diagonal form and has eigenvalues

$$E_i = \sum_{j \neq i} \{ (J_{ij} + \frac{1}{2} j_{ij}) m \langle S_{jz} \rangle - j_{ij} [S(S+1)\alpha + m^2 \beta] \}, \quad (2.4)$$

where m and m^2 are, respectively, the eigenvalues of S_{iz} and S_{iz}^2 , and where

$$\alpha = \frac{1}{2} S(S+1) - \frac{1}{2} \langle S_{iz}^2 \rangle, \quad (2.5)$$

and

$$\beta = \frac{1}{2} [3 \langle S_{iz}^2 \rangle - S(S+1)]. \quad (2.6)$$

We now introduce two sublattices; an "up" sublattice which includes the spin S_i , and a "down" sublattice, thus restricting ourselves to spin arrangements which have a single axis of spin alignment in the ordered state. Writing the average value of spin $\langle S_{jz} \rangle$ equal to $+\bar{S}$ on the "up" sublattice, and equal to $-\bar{S}$ on the "down" sublattice, and writing $\langle S_{jz}^2 \rangle = \langle S_z^2 \rangle$ for spins on both sublattices, we may calculate the thermal averages $\langle S_{iz} \rangle$ and $\langle S_{iz}^2 \rangle$ in the form

$$\langle S_{iz} \rangle = \bar{S} = \frac{\sum_m m \exp[Xm + Ym^2]/kT}{\sum_m \exp[Xm + Ym^2]/kT}, \quad (2.7)$$

and

$$\langle S_{iz}^2 \rangle = \langle S_z^2 \rangle = \frac{\sum_m m^2 \exp[Xm + Ym^2]/kT}{\sum_m \exp[Xm + Ym^2]/kT}, \quad (2.8)$$

where \sum_m runs over values $-S, -S+1, \dots, S-1, S$, and where the functions X and Y are given by

$$X = \sum_j^d (J_{ij} + \frac{1}{2} j_{ij}) \bar{S} - \sum_{j \neq i}^s (J_{ij} + \frac{1}{2} j_{ij}) \bar{S}, \quad (2.9)$$

$$Y = \sum_{j \neq i} j_{ij} \beta, \quad (2.10)$$

where \sum_j^d runs only over those values j for which S_j and S_i are on different sublattices, and where $\sum_{j \neq i}^s$ runs only over values j for which S_j and S_i are on the same sublattice. The Eqs. (2.7) and (2.8) may now be solved simultaneously to provide us with the temperature dependence of \bar{S} and $\langle S_z^2 \rangle$ in the molecular-field approximation.

The system is most easily described in the limit $\bar{S} \rightarrow 0$, $\langle S_z^2 \rangle \rightarrow \frac{1}{3} S(S+1)$, for which both X and Y go to zero. This limit will determine the Néel temperature unless j_{ij} is large enough to give a first-order transition, and we find, from Eq. (2.7)

$$\bar{S} = S(S+1)X/3kT, \quad (2.11)$$

which, on using (2.9), gives

$$3kT_N = S(S+1) \left[\sum_j^d (J_{ij} + \frac{1}{2} j_{ij}) - \sum_{j \neq i}^s (J_{ij} + \frac{1}{2} j_{ij}) \right]. \quad (2.12)$$

Solutions are also readily obtained for the paramagnetic state, where we may calculate the magnetic susceptibility in the form

$$\chi = N g^2 \mu_B^2 S(S+1)/3k(T+\theta), \quad (2.13)$$

[using conventional notation] with θ , the Curie-Weiss constant, given by

$$3k\theta = S(S+1) \sum_{j \neq i} (J_{ij} + \frac{1}{2} j_{ij}). \quad (2.14)$$

Thus, in the paramagnetic state, the biquadratic interaction $-j_{ij}(\mathbf{S}_i \cdot \mathbf{S}_j)^2$ behaves exactly as would an antiferromagnetic bilinear term $\frac{1}{2} j_{ij} \mathbf{S}_i \cdot \mathbf{S}_j$. In general, of course, this is a result which is restricted to both the paramagnetic state and to the molecular-field theory. There is one case, however, for which the result is rigorous; namely $S = \frac{1}{2}$, for which

$$(\mathbf{S}_i \cdot \mathbf{S}_j)^2 \equiv \frac{3}{16} - \frac{1}{2} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (S = \frac{1}{2}). \quad (2.15)$$

Solution of the simultaneous Eqs. (2.7) and (2.8) in the antiferromagnetic region is best carried out numerically. We have considered in detail the case $S = \frac{5}{2}$, which is the value of spin applicable to Mn^{++} salts. The results for \bar{S} and $\langle S_z^2 \rangle$ as functions of temperature are shown in Figs. 1 and 2, where the curves are plotted for different values of the parameter p , where

$$2p \left[\sum_j^d (J_{ij} + \frac{1}{2} j_{ij}) - \sum_{j \neq i}^s (J_{ij} + \frac{1}{2} j_{ij}) \right] = \sum_{j \neq i} j_{ij}. \quad (2.16)$$

The curves show the transition to become of first order for values $p \gtrsim 0.06$.

Although we expect the molecular-field result to be very poor for the fcc type-2 spin arrangement, it is interesting to compare the curves of Fig. 1 with those of Part II, Fig. 6. Consider the case where the only nonzero interactions in (2.16) are for nearest neighbors J_1, j_1 , and for next-nearest neighbors J_2, j_2 . If we put $j_2 = 0$, we have (for the MnO-type spin pattern), $p = j_1/J_2$. In this case, the system described by Fig. 6 of Part II differs from the present one only by having nearest-neighbor interactions $[J_1 \pm j(\bar{S})^2] \mathbf{S}_i \cdot \mathbf{S}_j$ in place of $J_1 \mathbf{S}_i \cdot \mathbf{S}_j - j_1 (\mathbf{S}_i \cdot \mathbf{S}_j)^2$. We see that the biquadratic exchange does behave (at least for spin $\frac{5}{2}$), very much like the distortion term which was discussed in detail in Part II. Quantitatively, however, the biquadratic terms produce a rather smaller effect on sublattice magnetization than do equivalent distortion terms (they are about $\frac{2}{3}$ effective for spin $\frac{5}{2}$). It is probable that they become progressively less effective for smaller values of spin until, in the limit of spin $\frac{1}{2}$, they have no

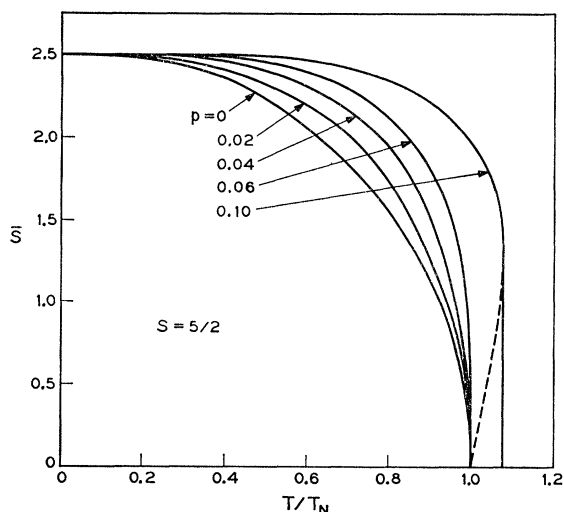


FIG. 1. Average spin per site \bar{S} as a function of temperature, calculated in the molecular-field approximation for an arbitrary uniaxial antiferromagnetic spin pattern, for spin $\frac{5}{2}$, and for various values of the "biquadratic parameter" p of Eq. (2.16). The parameter T_N in the coordinate of the abscissa is calculated from Eq. (2.12), and is the molecular-field Néel temperature as long as the magnetic transition remains of second order.

effect at all on the shape of the magnetization curves (when plotted as functions of T/T_N).

3. BIQUADRATIC EXCHANGE IN THE SIMPLE SPIN-WAVE APPROXIMATION

Since our main concern in this paper will be a description of the experimentally measured low-temperature sublattice magnetization curves of α -MnS, it is important to investigate the effect of biquadratic exchange interactions at very low temperatures. The available experimental data are all contained in a temperature region for which a simple noninteracting spin-wave theory should give an excellent approximation, so that we need consider only this simplest of spin-wave approximations.

If we expand the interaction $J\mathbf{S}_i \cdot \mathbf{S}_j - j(\mathbf{S}_i \cdot \mathbf{S}_j)^2$ in terms of the operators S_i^\pm , S_i^z , S_j^\pm , and S_j^z , where $S^\pm = S_x \pm iS_y$, then the resulting expression involves the single spin operators S^\pm , S^z , $S^\pm S^\pm$, $S^\pm S^\mp$, $S^\pm S^z$, $S^z S^\pm$, and $S^z S^z$ of both spins. In spin-wave theory we describe a system in terms of the deviation of its spins from the ordered state $S^z = \pm S$ by introducing boson creation and annihilation operators in the form⁷

$$S^z = S - a^*a, \quad S^\dagger = (2S)^{1/2}a, \quad S^- = (2S)^{1/2}a^*, \quad (3.1)$$

for a spin on the "up" sublattice, and

$$S^z = -S + b^*b, \quad S^\dagger = (2S)^{1/2}b^*, \quad S^- = (2S)^{1/2}b, \quad (3.2)$$

for a spin on the "down" sublattice, where a^*a and b^*b are, respectively, the number of spin deviations on

an "up" and a "down" site (i.e., equal to zero in the ground state, and equal to one in the first excited state).

In the simplest spin-wave approximation, we write the exchange interactions in terms of the above boson operators in such a way that all the single-spin operators involved have the correct matrix elements between the ground and first excited states. Consider, for example, the operator $(S^z)^2$. In single spin states $|S\rangle$ and $|S-1\rangle$, it has eigenvalues S^2 and $(S-1)^2$, respectively. It can therefore be represented by $S^2 - (2S-1)a^*a$. Consider also the operator $S^\dagger S^z$. It has only one nonzero matrix element between the states $|S\rangle$ and $|S-1\rangle$, which is $\langle S|S^\dagger S^z|S-1\rangle = (2S)^{1/2} \times (S-1)$. It can, therefore, be represented by $(2S)^{1/2} \times (S-1)a$. We note that neither of these operator equivalents results from a direct substitution of (3.1) and subsequent neglect of terms higher than quadratic in spin deviations. A full set of the required operator equivalents is given in Table I.

If a spin S_j is on the "up" sublattice, and a spin S_k is on the "down" sublattice, then the exchange interaction $\mathcal{H}_{jk} = JS_j \cdot S_k - j(\mathbf{S}_j \cdot \mathbf{S}_k)^2$ between them may be written in terms of the boson operators (using Table I) in the form

$$\mathcal{H}_{jk} = -(J+j)S^2 - jS^4 + S[J+j(2S^2-2S+1)] \times [a_j^*a_j + b_k^*b_k + a_j b_k + a_j^* b_k^*], \quad (3.3)$$

where we have neglected terms higher than quadratic in spin deviations. As far as the thermal excitations are concerned, the interaction behaves exactly as if there were a bilinear exchange $J+j(2S^2-2S+1)$ alone.

If we now consider two spins S_j and $S_{j'}$ on the "up" sublattice, an exchange interaction $\mathcal{H}_{jj'} = JS_j \cdot S_{j'} - j(\mathbf{S}_j \cdot \mathbf{S}_{j'})^2$ may be expressed as

$$\mathcal{H}_{jj'} = JS^2 - jS^4 - S[J-j(2S^2-2S)] \times [a_j^*a_j + a_{j'}^*a_{j'} - a_j a_{j'}^* - a_j^* a_{j'}]. \quad (3.4)$$

In this case the thermal excitations are the same as one would get for a bilinear exchange $J-2jS(S-1)$. An exactly equivalent result may be obtained for a pair of spins on the "down" sublattice.

For spin $S = \frac{1}{2}$, we easily verify that the biquadratic exchange behaves as an antiferromagnetic bilinear term $+\frac{1}{2}j\mathbf{S}_i \cdot \mathbf{S}_j$ both for parallel and antiparallel spins, in agreement with the exact result (2.15). In the limit of very large spin quantum numbers, the biquadratic terms are equivalent to a bilinear *antiferromagnetic* exchange $2jS^2$ for antiparallel spin pairs and equivalent to a *ferromagnetic* exchange $2jS^2$ for parallel spin pairs. Thus, in this limit, the system behaves in the classical manner, the term $-j(\mathbf{S}_i \cdot \mathbf{S}_j)^2$ favoring parallel and antiparallel spin alignment equally. For spin $S = \frac{5}{2}$, which will be the case of interest for α -MnS, the biquadratic terms are as $+(17j/2)\mathbf{S}_i \cdot \mathbf{S}_j$ for antiparallel spin pairs, and as $(-15j/2)\mathbf{S}_i \cdot \mathbf{S}_j$ for parallel spin pairs.

It is of some interest, in passing, to note a few properties of the purely biquadratic (j positive) system,

⁷ R. Kubo, Phys. Rev. 87, 568 (1952).

TABLE I. S_j on the "up" sublattice, S_k on the "down" sublattice.

Spin operators	Equivalent Bose operators
$S_j^+ S_j^-$	$2S + (2S - 2)a_j^* a_j$
$S_j^- S_j^+$	$2S a_j^* a_j$
$(S_j^z)^2$	$S^2 - (2S - 1)a_j^* a_j$
$S_j^+ S_j^+$ and $S_j^- S_j^-$	0
$S_j^+ S_j^z$	$(2S)^{1/2}(S - 1)a_j$
$S_j^z S_j^+$	$(2S)^{1/2}S a_j$
$S_j^- S_j^z$	$(2S)^{1/2}S a_j^*$
$S_j^z S_j^-$	$(2S)^{1/2}(S - 1)a_j^*$
$S_k^+ S_k^-$	$2S b_k^* b_k$
$S_k^- S_k^+$	$2S + (2S - 2)b_k^* b_k$
$(S_k^z)^2$	$S^2 - (2S - 1)b_k^* b_k$
$S_k^+ S_k^+$ and $S_k^- S_k^-$	0
$S_k^+ S_k^z$	$-(2S)^{1/2}S b_k^*$
$S_k^z S_k^+$	$-(2S)^{1/2}(S - 1)b_k^*$
$S_k^- S_k^z$	$-(2S)^{1/2}(S - 1)b_k$
$S_k^z S_k^-$	$-(2S)^{1/2}S b_k$

for which all bilinear exchange J vanishes. Some of these properties are rather surprising. Thus, even in a molecular-field approximation, the antiferromagnetic ground state always has lower energy than the ferromagnetic one. [Compare Eqs. (3.3) and (3.4) in the absence of the spin excitations.] In the spin-wave approximation, the energy difference between the ferromagnetic and antiferromagnetic states is larger still, since the ferromagnetic state is an eigenstate of the biquadratic Hamiltonian whereas the molecular-field antiferromagnetic state is not.

For $S = \frac{1}{2}$ and $S = 1$, the ferromagnetic state is unstable in the spin-wave approximation, whereas the

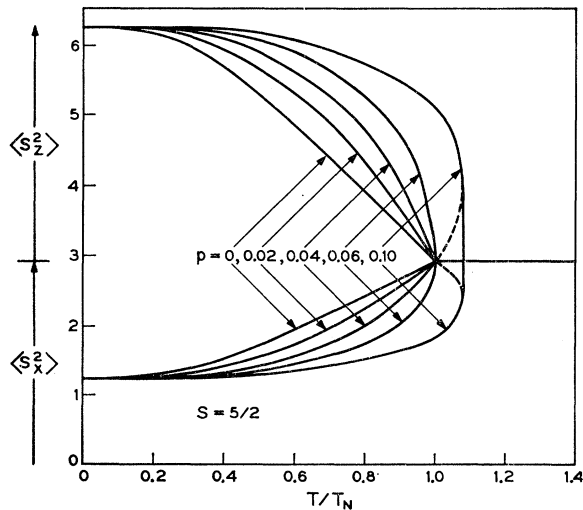


FIG. 2. The thermal average values of S_z^2 and S_x^2 (or S_y^2), calculated in the molecular-field approximation for an arbitrary uniaxial antiferromagnetic spin pattern, for spin $\frac{5}{2}$, and for various values of the "biquadratic parameter" p of Eq. (2.16).

antiferromagnetic state is stable (for three-dimensional structures) for all values of spin. For $S \geq \frac{3}{2}$, however, the ferromagnetic state is also stable in the spin-wave approximation, i.e., it is a metastable state of the system.

4. THE SPIN HAMILTONIAN FOR α -MnS

In the present section we shall write a Hamiltonian for the α -MnS spin system which includes both bilinear and biquadratic exchange interactions, and also allows for both isotropic and anisotropic magnetostrictive effects. A Hamiltonian of this nature necessarily contains quite a large number of parameters and it is unfortunate that, at the present time, little is known about many of them. In spite of this, we shall show that the shape of the magnetization curve for α -MnS is quite insensitive to a number of these unknowns, and that our lack of knowledge concerning them does not prevent us from drawing some important conclusions about the magnitude of biquadratic exchange in this salt.

The crystal structure and the antiferromagnetic spin pattern⁸ for α -MnS are exactly the same as found for MnO and discussed in some detail in Part II. We expect the dominant exchange interactions to exist between nearest neighbors and between next-nearest neighbors. We also expect the magnetic anisotropy energy to be mainly of dipolar origin, and to be very small indeed compared with the isotropic exchange energy.

We shall introduce bilinear and biquadratic exchange interactions between nearest neighbors (J_1, j_1) and between next-nearest neighbors (J_2, j_2) in the system, neglecting more remote interactions. Each of these exchange parameters will be sensitive to interspin distance. In α -MnS, however, it is possible to neglect the dependence of j_1 and j_2 on interspin distance, since terms arising from the distance dependence of biquadratic exchange are likely to be at least an order of magnitude smaller than those arising from bilinear exchange magnetostriction and from biquadratic exchange itself.

Above the Néel point ($T_N = 147^\circ\text{K}$), α -MnS possesses the cubic rocksalt structure. In the ordered state, the spin systems form ferromagnetic [111] layers which are stacked antiferromagnetically.⁸ The distortion which accompanies this type of ordering has been described by Rodbell and Owen.⁵ It may be considered as the sum of two separate parts, the first being an isotropic contraction of all cube edges by an amount $\delta a/a$, and the second a deformation along the (111) axis (i.e., normal to the ferromagnetic sheets) with the length of the cube edges fixed. In the latter deformation, the cube corner angles become $\frac{1}{2}\pi \pm \Delta$.

If the nearest- and next-nearest-neighbor distances are, respectively, d_1^0 and d_2^0 in the cubic state, then in

⁸ L. Corliss, N. Elliott, and J. Hastings, Phys. Rev. **104**, 924 (1956).

the ordered state they become d_1^\pm and d_2 , where d_1^+ refers to nearest-neighbor parallel pairs of spins and d_1^- refers to nearest-neighbor antiparallel pairs, and where

$$(d_1^\pm - d_1^0)/d_1^0 = \pm \frac{1}{2}\Delta - \delta a/a, \quad (4.1)$$

$$(d_2 - d_2^0)/d_2^0 = -\delta a/a. \quad (4.2)$$

If we write the dependence of the exchange J_i ($i=1, 2$) on small variations δr of interspin distance from the (cubic) equilibrium separations in the form

$$J_i(r+\delta r) = J_i(r) + [\partial J_i(r)/\partial r]\delta r \\ = J_i(r)[1 - \epsilon_i \delta r/r], \quad (4.3)$$

thus defining the dimensionless parameters ϵ_i as

$$\epsilon_i = (-r/J_i)\partial J_i/\partial r, \quad (4.4)$$

then we may represent the exchange part of the α -MnS energy by the Hamiltonian

$$\mathcal{H} = \sum_{nn}^a [J_1^+ \mathbf{S}_i \cdot \mathbf{S}_j - j_1 (\mathbf{S}_i \cdot \mathbf{S}_j)^2] \\ + \sum_{nn}^p [J_1^- \mathbf{S}_i \cdot \mathbf{S}_j - j_1 (\mathbf{S}_i \cdot \mathbf{S}_j)^2] \\ + \sum_{nnn} [J_2^+ \mathbf{S}_i \cdot \mathbf{S}_j - j_2 (\mathbf{S}_i \cdot \mathbf{S}_j)^2], \quad (4.5)$$

where \sum_{nn}^a refers to a sum over antiparallel pairs of nearest neighbors, \sum_{nn}^p refers to a sum over parallel pairs of nearest neighbors, and where

$$J_1^\pm = J_1 [1 + \epsilon_1 (\delta a/a) \pm \frac{1}{2}\epsilon_1 \Delta], \quad (4.6)$$

$$J_2^+ = J_2 [1 + \epsilon_2 (\delta a/a)]. \quad (4.7)$$

In the latter equations, J_1 and J_2 refer to the exchange parameters in the paramagnetic state, and $\delta a/a$ and Δ refer to the equilibrium values of these quantities. Throughout this analysis we shall neglect any spin-separation dependence due to thermal expansion of the lattice, since it is extremely small indeed in the temperature region $\lesssim T_N$.

In this approximation, the free energy of the system is made up of an exchange part F_{ex} [see Part II, Eq. (3.3)] and an elastic part. The latter,⁵ may be expressed as

$$F_{\text{el}} = \frac{1}{2}C_\Delta \Delta^2 + \frac{1}{2}C_a (3\delta a/a)^2, \quad (4.8)$$

thus defining a pair of elastic constants C_Δ and C_a for the system. The equilibrium values of Δ and δa are obtained by minimizing the total free energy (exchange plus elastic) with respect to Δ and δa , when we obtain

$$\langle \partial \mathcal{H} / \partial \Delta \rangle + C_\Delta \Delta = 0, \quad (4.9)$$

$$a \langle \partial \mathcal{H} / \partial (\delta a) \rangle + 9C_a \delta a/a = 0, \quad (4.10)$$

where the pointed brackets represent thermal averages.

The resulting equilibrium values are given by

$$8C_\Delta \Delta_{\text{eq}} = N z_1 J_1 \epsilon_1 [\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle_{nn}^p - \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle_{nn}^a], \quad (4.11)$$

$$-9C_a (\delta a/a)_{\text{eq}} = \frac{1}{4} N z_1 J_1 \epsilon_1 [\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle_{nn}^p + \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle_{nn}^a] \\ + \frac{1}{2} N z_2 J_2 \epsilon_2 \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle_{nnn}, \quad (4.12)$$

where $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle_{nn}^a$ and $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle_{nn}^p$ refer, respectively, to thermal averages over antiparallel and parallel nearest neighbors, where $z_1 (=12)$ and $z_2 (=6)$ are the numbers of nearest and next-nearest neighbors of any particular spin, and where N is the total number of spins in the lattice.

In the following section, from an analysis of the paramagnetic properties of α -MnS, we find values $J_1 = 7^\circ\text{K}$, and $J_2 = 12.5^\circ\text{K}$. For this ratio $J_2/J_1 \approx 1.8$, Fig. 7 of Part I shows that the nearest-neighbor spin correlations are very small at the Néel point. It is quite likely, therefore, that the molecular-field estimate $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle_{nn}^p = -\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle_{nn}^a = (\bar{S})^2$ is a good approximation in the ordered state. The same is not likely to be true for next-nearest neighbors where (Fig. 8 of Part I) the magnitude of $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle_{nnn}$ at T_N is $\sim 0.3S(S+1)$. With this simplification, Eqs. (4.11) and (4.12) reduce to

$$\Delta_{\text{eq}} = N z_1 J_1 \epsilon_1 (\bar{S})^2 / 4C_\Delta, \quad (4.13)$$

$$(\delta a/a)_{\text{eq}} = -N z_2 J_2 \epsilon_2 \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle_{nnn} / 18C_a. \quad (4.14)$$

We note that, whereas the distortion Δ is absent in the paramagnetic region (see also Sec. 6 of Part II), the isotropic contraction $\delta a/a$ will not set in suddenly at the Néel point but will be a continuous function of temperature varying closely as $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle_{nnn}$ near T_N . Equation (4.14) will, however, be valid only for $T \lesssim T_N$; the temperature variation of $\delta a/a$ (still neglecting thermal expansion) in the paramagnetic region should be determined from (4.12).

Our main concern in the present paper is the interpretation of magnetic data obtained in the spin-wave region. Using the results of Sec. 3 for biquadratic exchange in the spin-wave approximation, and considering specifically the case $S = \frac{5}{2}$, we may make the following substitutions in Hamiltonian (4.5):

$$\sum_{nn}^a -j_1 (\mathbf{S}_i \cdot \mathbf{S}_j)^2 \rightarrow \sum_{nn}^a \left(\frac{17j_1}{2} \right) \mathbf{S}_i \cdot \mathbf{S}_j, \\ \sum_{nn}^p -j_1 (\mathbf{S}_i \cdot \mathbf{S}_j)^2 \rightarrow \sum_{nn}^p \left(\frac{-15j_1}{2} \right) \mathbf{S}_i \cdot \mathbf{S}_j, \quad (4.15) \\ \sum_{nnn} -j_2 (\mathbf{S}_i \cdot \mathbf{S}_j)^2 \rightarrow \sum_{nnn} \left(\frac{17j_2}{2} \right) \mathbf{S}_i \cdot \mathbf{S}_j.$$

Substituting for C_Δ and C_a [using (4.13) and (4.14)] in Eq. (4.8), the full spin-wave Hamiltonian for the α -MnS system, including strain and anisotropy, may now be written, and takes exactly the form which was used for describing MnO [Eq. (4.1) of Part II] but

with rather more complex expressions for the "effective" exchange parameters. Thus, we write

$$\mathcal{H} = \sum_{nn}^a g_1^+ \mathbf{S}_i \cdot \mathbf{S}_j + \sum_{nn}^b g_1^- \mathbf{S}_i \cdot \mathbf{S}_j + \sum_{nnn} g_2 \mathbf{S}_i \cdot \mathbf{S}_j + \sum_n D_1 S_{iz}^2 + \sum_n D_2 S_{iy}^2, \quad (4.16)$$

where D_1 and D_2 are parameters describing, respectively, the anisotropy which restricts the spins to the [111] plane, and the anisotropy which constrains the spins to a particular direction z within this plane, and where

$$g_1^+ = J_1 [1 + \epsilon_1 (\delta a/a)_{\text{eq}} + \frac{1}{4} \epsilon_1 \Delta_{\text{eq}}] + (17/2) j_1, \quad (4.17)$$

$$g_1^- = J_1 [1 + \epsilon_1 (\delta a/a)_{\text{eq}} - \frac{1}{4} \epsilon_1 \Delta_{\text{eq}}] - (15/2) j_1, \quad (4.18)$$

$$g_2 = J_2 [1 + \frac{1}{2} \epsilon_2 (\delta a/a)_{\text{eq}}] + (17/2) j_2, \quad (4.19)$$

with $(\delta a/a)_{\text{eq}}$ and Δ_{eq} given by Eqs. (4.13) and (4.14).

The temperature dependence of sublattice magnetization in the spin-wave region has been calculated, for the antiferromagnetic fcc type-2 spin arrangement and a Hamiltonian of the form (4.16), in Part II. The result is

$$\bar{S} = S + \frac{1}{2} - \frac{1}{4} \left\langle \frac{\beta_1 + \beta_2}{[(\beta_1 + \gamma)(\beta_2 - \gamma)]^{1/2}} \times \coth \left[\frac{S [(\beta_1 + \gamma)(\beta_2 - \gamma)]^{1/2}}{2kT} \right] \right\rangle_{\kappa}, \quad (4.20)$$

where

$$\beta_1 + \gamma = 2(g_1^+ + g_1^-)(c_1 c_2 + c_2 c_3 + c_3 c_1) + 4g_2(c_1^2 + c_2^2 + c_3^2) + 2(g_1^+ - g_1^-) \times (3 - s_1 s_2 - s_2 s_3 - s_3 s_1) + 2D_1, \quad (4.21)$$

$$\beta_2 - \gamma = 2(g_1^+ - g_1^-)(s_1 s_2 + s_2 s_3 + s_3 s_1) + 4g_2(s_1^2 + s_2^2 + s_3^2) + 2(g_1^+ - g_1^-) \times (3 - c_1 c_2 - c_2 c_3 - c_3 c_1) + 2D_2, \quad (4.22)$$

and where c_i and s_i ($i = 1, 2, 3$) are the cosines and sines of three arguments which, in the average $\langle \dots \rangle_{\kappa}$, run independently between $-\pi$ and π . If we suppose the anisotropy parameters D_1 and D_2 to be known, then the spin deviation $\bar{S}(0) - \bar{S}(T)$ is a function of the three variables $g_1^+ + g_1^-$, $g_1^+ - g_1^-$, and g_2 . In the case of no magnetostriction and no biquadratic exchange, these variables are, respectively, $2J_1$, 0, and J_2 . Numerical evaluation of (4.20) reveals the very important result that the spin deviation $\bar{S}(0) - \bar{S}(T)$ is many times more sensitive to $g_1^+ - g_1^-$ than it is to deviations of $g_1^+ + g_1^-$ from $2J_1$ and g_2 from J_2 . For α -MnS, for which the effects of magnetostriction and biquadratic exchange are quite small, this result is very significant, allowing us to describe the system to a good approximation in terms of J_1 , J_2 , and $g_1^+ - g_1^-$ only, where

$$g_1^+ - g_1^- = \frac{1}{2} J_1 \epsilon_1 \Delta_{\text{eq}} + 16 j_1, \quad (4.23)$$

thus eliminating the "unknowns" j_2 and $(\delta a)_{\text{eq}}$ from the problem.

The large sensitivity of spin deviation to $g_1^+ - g_1^-$ is readily understood by considering the spin-wave energies of the system, which are proportional to $[(\beta_1 + \gamma)(\beta_2 - \gamma)]^{1/2}$. We see from (4.21) and (4.22) that, in the limit $g_1^+ - g_1^- \rightarrow 0$, there are a number of regions in the reciprocal lattice space where the excitation energies go to zero in the absence of anisotropy. Thus, for systems with small anisotropy, very little energy is required to excite spin-waves with wave vectors close to these values. It follows that for low temperatures nearly all the spin waves in the lattice are of this type. The thermal average $\bar{S}(0) - \bar{S}(T)$ of the system is therefore very greatly reduced if these particular spin-wave energies are increased. Examination of the spin-wave energy expression shows that contributions from g_2 and from $g_1^+ + g_1^-$ are very inefficient in this respect. The $g_1^+ - g_1^-$ terms, on the other hand, are very much more effective, making the system ultrasensitive to distortion Δ and to nearest-neighbor biquadratic exchange. The effect is most pronounced at low temperatures and for small distortion (or nearest-neighbor biquadratic) terms, when the latter terms are more than ten times as effective at reducing spin deviation than are equivalent contributions to g_2 or $g_1^+ + g_1^-$. Such an effect is describable only in terms of collective oscillations and will be overlooked by molecular-field or cluster approximations.

Physically, such a supersensitivity is only likely to arise for systems which contain "unfavorably oriented" spins, where we use the latter expression to denote pairs of spins which are aligned ferromagnetically in the ordered state but which have an antiferromagnetic exchange interaction between them (or vice versa). The fcc type-2 order has six unfavorably oriented nearest neighbors and provides perhaps the best example of this supersensitivity to lattice distortion and biquadratic exchange which is presently known.

5. THE PARAMAGNETIC STATE AND THE DETERMINATION OF J_1 AND J_2

In the paramagnetic state, we shall assume that the α -MnS system can be described in terms of bilinear nearest- and next-nearest-neighbor exchange parameters J_1 and J_2 alone, i.e., in the complete absence of magnetostrictive and biquadratic terms. In this approximation we may use the results of random-phase Green's-function theory (Part I) and we shall be able to estimate J_1 and J_2 with a probable accuracy of better than 10%. We assume, therefore, that the effects of magnetostriction and biquadratic exchange in the paramagnetic state are small compared with the effects produced by a variation $\sim \pm 10\%$ in bilinear exchange. Since anisotropic magnetostriction is almost certainly completely absent for $T > T_N$ (see Part II, Sec. 6) and, to a first approximation, biquadratic exchange $-j(\mathbf{S}_i \cdot \mathbf{S}_j)^2$ be-

has as a bilinear term $\frac{1}{2}j(\mathbf{S}_i \cdot \mathbf{S}_j)$ at high temperatures (see Sec. 2), such a situation is extremely likely, and will prove consistent with the low-temperature findings of the following section.

Experimental measurements of magnetic susceptibility in the paramagnetic state have been published for α -MnS by several authors,⁹⁻¹⁶ who report a very wide range of values for both the Curie constant C_M and the Curie-Weiss temperature θ . The widely differing results undoubtedly arise in part from differences in sample composition, but equally responsible, one suspects, are the errors incurred by fitting the results to a simple Curie-Weiss law in temperature regions where such a law is not valid. The most recent, and the most extensive, measurements are those of Banewicz and Lindsay,¹⁴⁻¹⁶ who find that the situation for α -MnS is very similar to the one found for MnO and discussed in Part II. They find that if experiments are carried out at temperatures $T > 5T_N$, for which short-range order effects should be negligible, then the measured Curie constant C_M is some 10% smaller than the value appropriate for a spin $\frac{5}{2}$ system. This would indicate that the system deviates significantly from a Mn^{++} and S^{--} ionic description at these elevated temperatures. We shall prefer to interpret the lower temperature ($T_N < T \lesssim 2T_N$) data in terms of the Green's-function theory of Part I. In Fig. 3 we compare the data of Lindsay and Banewicz¹⁵ with the theoretical estimates from Part I (Fig. 2), and we find that good agreement can be obtained for a value of Curie-Weiss constant $\theta = 465^\circ\text{K}$. Some additional information is furnished by the slope of the curves concerning the ratio J_2/J_1 , indicating that for α -MnS this ratio is certainly greater than 1 and less than 3, and is probably close to 1.5.

The value of magnetic susceptibility at the Néel point as measured by Lindsay and Banewicz¹⁵ is $\sim 6260 \times 10^{-6}$ emu/g, and allows a value to be derived for $J_1 + J_2$ [by use of the Green's-function result $\chi(T_N) = Ng^2\mu_B^2/12(J_1 + J_2)$]. We are using, throughout, the results obtained for the sintered-rod sample of Ref. 15 which differ by a few percent from those obtained for the powder specimen of Ref. 14. We find a value $J_1 + J_2 = 20.0^\circ\text{K}$.

The final piece of information concerns the transition temperature T_N . It can be measured quite accurately by observing the temperature for which the manganese NMR in the paramagnetic region disappear. We have found this to occur quite suddenly and reproducibly at $147 \pm 1^\circ\text{K}$.¹⁷ This is in exact agreement with the dis-

continuity in the specific heat,¹⁸ and is, as expected,¹⁹ a few degrees below the temperature where the maximum in the magnetic susceptibility is found. We note that the random-phase Green's-function theory is not sufficiently accurate in the immediate vicinity of T_N to indicate the latter effect. The double cusp feature of the specific-heat curve¹⁸ is puzzling, but a possible explanation is put forward in Sec. 7.

We have used the theoretical estimate for T_N which we considered (in Part II) to be the best presently available for the fcc type-2 spin structure and spin $\frac{5}{2}$, viz., the random-phase Green's-function result plus 10%. Within the range $1.0 < J_2/J_1 < 3.0$, this result may be expressed in the form $KT/J_2 = 12.6 - 2.3/x^2$, where $x = J_2/J_1$.

Our findings may be summarized as follows:

- (i) from $\chi(T > T_N)$; $2J_1 + J_2 = 26.6^\circ\text{K}$,
- (ii) from $\chi(T_N)$; $J_1 + J_2 = 20.0^\circ\text{K}$,
- (iii) from T_N ; $12.6J_2 - 2.3J_1^2/J_2 = 147^\circ\text{K}$, (5.1)
- (iv) from $\chi(T > T_N)$; $1.0 < J_2/J_1 < 3.0$.

As was the case for MnO, the first three results should certainly be good to better than 10%. We are easily able to find values J_1 and J_2 which very closely satisfy the conditions (i) to (iii) and which fall within the limits set by (iv). The best values are very close to

$$J_1 = 7.0^\circ\text{K}, \quad J_2 = 12.5^\circ\text{K}, \quad (5.2)$$

giving a ratio $J_2/J_1 \approx 1.8$. They may be compared with our findings for MnO, which were $J_1 = 10^\circ\text{K}$, $J_2 = 11^\circ\text{K}$.

6. Mn⁵⁵ ZERO-FIELD NMR IN THE ANTI-FERROMAGNETIC STATE OF α -MnS

In this section, we present the results and interpretations of the observation of the Mn⁵⁵ zero-field NMR in the antiferromagnetic state of α -MnS. We find that the determination of the average value of sublattice spin \bar{S} for the antiferromagnetic ground state at 0°K is not possible for α -MnS because of an apparent increase in the value of the hyperfine coupling constant in α -MnS over the value determined by electron paramagnetic resonance (EPR) on the Mn²⁺ ion in an appropriate nonmagnetic host lattice. A similar situation for the isomorph MnO has been noted in Part II.

The observed temperature dependence of the Mn⁵⁵ zero-field NMR frequency provides the only measurements, to date, yielding information regarding the temperature dependence of the sublattice magnetization in α -MnS. From these measurements we are able to compare the experimental results with the noninteracting spin-wave theory developed in Sec. 4.

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¹³ A. Serres, J. Phys. Rad. **8**, 146 (1947).

¹⁴ J. J. Banewicz and R. Lindsay, Phys. Rev. **104**, 318 (1956).

¹⁵ R. Lindsay and J. J. Banewicz, Phys. Rev. **110**, 634 (1958).

¹⁶ J. J. Banewicz, R. F. Heidelberg, and R. Lindsay, Phys. Rev. **117**, 736 (1960).

¹⁷ E. D. Jones (to be published).

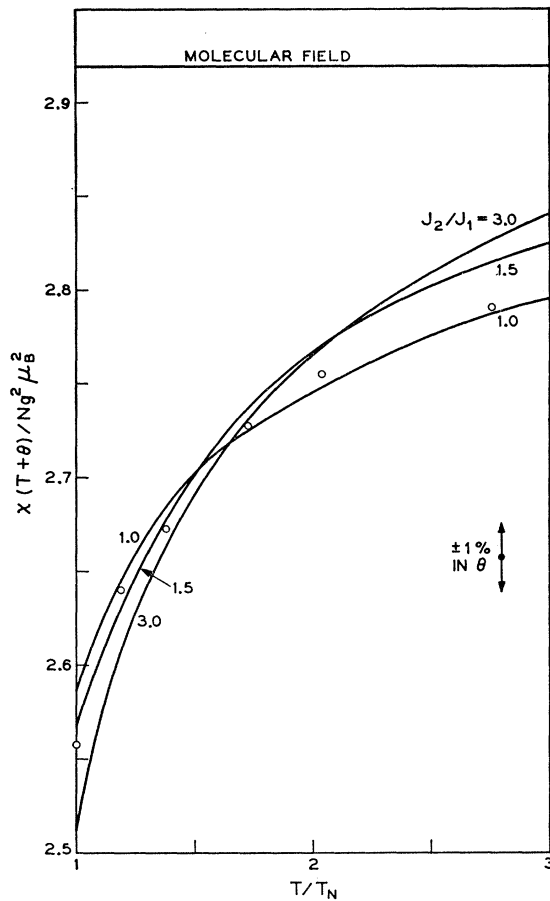


FIG. 3. Curves of magnetic susceptibility, as calculated in the random-phase Green's-function approximation, are plotted as a function of temperature and compared with the experimental data of Lindsay and Banewicz (Ref. 15) for the case $\theta=465^\circ\text{K}$ [θ is the Curie-Weiss constant].

Experimental

The Mn^{55} zero-field NMR was observed in powdered samples of α -MnS in the frequency range 575–580 Mc/sec between 1.5 and 20.4°K . The NMR spectrometer used to detect the Mn^{55} resonance was a super-regenerative uhf oscillator previously described.²⁰ Attempts to observe the Mn^{55} NMR using cw techniques have thus far proved unsuccessful. We attribute this failure to an expected increase in Mn^{55} NMR linewidth in α -MnS as compared to MnO (see discussion on linewidths). An experimental estimate for the linewidth $(\delta H)^{55}$ can be made with the super-regenerative oscillator in the following manner. The method consists of varying the self-quench frequency of the oscillator and noting the value of the quench frequency for which the sideband responses on the recorder are just resolved from each other. Thus, for α -MnS, we estimate that $(\delta H)^{55} \approx 900$ Oe.

²⁰ K. B. Jefferts and E. D. Jones, Rev. Sci. Instr. 36, 983 (1965).

Mn^{55} NMR in Antiferromagnetic α -MnS

The measured temperature dependence of the Mn^{55} zero-field NMR frequency is shown in Fig. 4. A smooth curve has been drawn through the data and extrapolated to 0°K , yielding a value $\nu^{55}(0) = 577.5 \pm 0.1$ Mc/sec. In Fig. 5, we show a comparison of the data obtained for α -MnS with those measured for MnO (see Part II). The so-called anomalous behavior of MnO, i.e., the very slow decrease in $\nu^{55}(T)$ as a function of T/T_N , is essentially absent in α -MnS. This is an early indication that the effects of lattice distortion and/or biquadratic exchange are probably small in α -MnS. The situation will be discussed in detail at the end of the present section, when a comparison between spin-wave theory and experiment is made.

The zero-field time-independent Hamiltonian for a Mn^{55} nucleus in antiferromagnetic α -MnS is written as

$$\mathcal{H} = A_z^{55} \langle S_z \rangle I_z + \gamma^{55} \hbar I_z \sum_i D_z^i \langle S_z^i \rangle, \quad (6.1)$$

where the z axis is the direction of antiferromagnetic spin alignment in the ordered state. The first term on the right-hand side of (6.1) results from core polarization of the inner s -shell electrons by the outer $3d$ electrons, where $\langle S_z \rangle = \bar{S}$ is the time-averaged electron spin polarization per Mn^{2+} ion, A_z^{55} the hyperfine coupling constant, and I the nuclear spin ($I = \frac{5}{2}$). The second term in (6.1) is the magnetic interaction between the Mn^{55} nuclear moment and the dipolar field due to neighboring electronic spins, with γ^{55} the nuclear gyromagnetic ratio, and $H_{\text{dip}} = \sum_i D_z^i \langle S_z^i \rangle$,

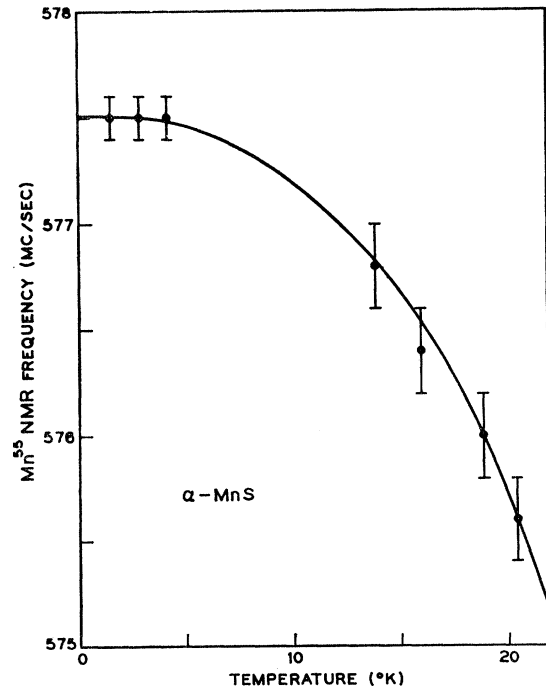


FIG. 4. Temperature dependence of the zero-field Mn^{55} NMR frequency in antiferromagnetic α -MnS.

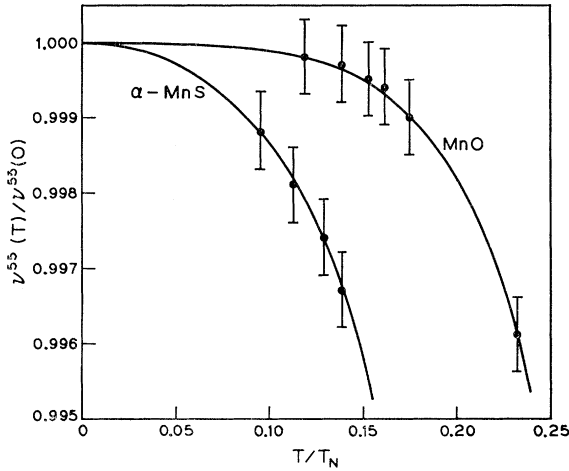


FIG. 5. Comparison of the temperature dependence of Mn^{55} NMR frequency as measured for MnO (Part II) and α -MnS.

where i is summed over all lattice sites. The dipolar field is nonzero in the cubic state and is fairly insensitive to the small distortions which lower the cubic symmetry of the lattice for $T < T_N$. We have calculated the components of the D tensor for the cubic state of α -MnS, with the result $H_{\text{dip}} = +4.78$ kOe (for $\bar{S} = \frac{5}{2}$), where the plus sign indicates that H_{dip} is in the same direction as the sublattice magnetization.

The zero-field NMR frequency $\nu^{55}(T)$ is derived from the Hamiltonian (6.1) with the result

$$\nu^{55}(T) = \left[\left(\frac{5}{2} \right) |A^{55}/h| - (\gamma^{55}/2\pi) H_{\text{dip}} \right] \bar{S}/S, \quad (6.2)$$

where we have assumed that A^{55} is negative and larger than $\gamma^{55} h H_{\text{dip}}$. Furthermore, we make the not unreasonable assumption that the temperature dependence of A^{55} between 1.5 and 20.4°K is negligible, so that the temperature dependence of \bar{S} is measured by $\nu^{55}(T)$, i.e., $\nu(T) \propto \bar{S}$.

As mentioned in Part II, it is customary at this juncture to calculate the value of \bar{S} at absolute zero, and thereby to investigate the effect of zero-point spin fluctuations upon the antiferromagnetic ground-state spin alignment at 0°K. Such a calculation can be made from (6.2) only if the value of A^{55} for α -MnS is known. It has been common practice²¹⁻²³ to assume that a good estimate for the hyperfine coupling constant of an S state magnetic ion in an antiferromagnetic salt is given by the value measured (by EPR) for the same magnetic ion in a diamagnetic isomorph. With such an assumption, the results of NMR experiments have invariably indicated zero-point spin deviations which are much smaller than those calculated by spin-wave theory, and have been considered by some to cast a doubt on the validity of simple spin-wave theory for the antiferromagnetic state. In Part II, however, we noted that

a similar calculation on MnO indicated that the zero-point spin deviation was of the wrong sign (a zero-point increment). This would indicate that the fault is more likely to be found in the assumptions made about the hyperfine constant than in the approximations of spin-wave theory.

For α -MnS, we experience the same difficulties as were found for MnO. For example, let us assume that at 0°K the value of $\bar{S} = S = \frac{5}{2}$, and solve Eq. (6.2) for A^{55} . Using $\nu^{55}(0) = 577.5 \pm 0.1$ Mc/sec, $H_{\text{dip}} = +4.78$ kOe, and $\gamma^{55}/2\pi = 1.0553 \times 10^8$ cycles/G, the result is $A^{55} = -(77.72 \pm 0.03) 10^{-4} \text{ cm}^{-1}$. Listed in Table II are

TABLE II. Mn^{2+} hyperfine coupling constants (sixfold cubic sulfur coordination).

Lattice	Lattice constant (\AA)	A^{55} (units of $\text{cm}^{-1} \times 10^{-4}$)		
		4.2°K	77°K	300°K
MgS	5.19	-75.23 ^a	-74.8 ^b	-74.68 ^a
CaS	5.68	...	-76.8 ^b	-75.7 ^c
SrS	5.87	-77.44 ^a	-76.8 ^b	-75.56 ^a
α -MnS	5.21			

^a S. Geschwind (private communication) (estimated accuracy $\pm 0.07 \times 10^{-4} \text{ cm}^{-1}$).

^b P. Auzins, J. W. Orton, and J. W. Wertz, *Proceedings of the First International Conference on Paramagnetic Resonance*, edited by W. Low (Academic Press Inc., New York, 1963).

^c O. Matumura, *J. Phys. Soc. Japan* **14**, 108 (1958).

various values of A^{55} determined by EPR for the Mn^{2+} ion in the nonmagnetic isomorphs of α -MnS. The isomorph corresponding most closely to α -MnS, at least in terms of lattice constant, is MgS. For this case, our value is $\sim 3\%$ larger than the equivalent low-temperature EPR result. This discrepancy is increased if one assumes a zero-point spin deviation $\sim 3.2\%$ as calculated below, from spin-wave theory. The assumption of the equivalence of the A^{55} hyperfine constants for α -MnS and for Mn^{2+} in the various nonmagnetic isomorphs again leads us to the singularly unlikely result that $\bar{S}_{T=0} > \frac{5}{2}$. We conclude that this assumption is probably suspect, and that we can make no experimental conclusions regarding the magnitude of zero-point spin reduction until the questions concerning the A^{55} value have been resolved.

Comparison with the Results of Spin-Wave Theory

The temperature dependence of sublattice magnetization in the spin-wave region may be computed from Eq. (4.20) provided that we have some knowledge of the relevant parameters which are contained in the equation. These parameters are $g_1^+ \pm g_1^-$, g_2 [see Eqs. (4.17) to (4.19)], and the anisotropy constants D_1 and D_2 . As described in Sec. 4, we may replace $g_1^+ + g_1^-$ by $2J_1$ and g_2 by J_2 , where J_1 and J_2 are the nearest- and next-nearest-neighbor bilinear exchange parameters (which have been estimated in Sec. 5 to be $J_1 = 7.0^\circ\text{K}$ and $J_2 = 12.5^\circ\text{K}$). The parameter D_2 represents the in-plane anisotropy. An idea of its magnitude is best

²¹ E. D. Jones and K. B. Jefferts, *Phys. Rev.* **135**, A1277 (1964).

²² G. L. Witt and A. M. Portis, *Phys. Rev.* **135**, A1616 (1964).

²³ P. R. Locher and S. Geschwind, *Phys. Rev.* **139**, A991 (1965).

obtained from a comparison of theory and experiment for NMR linewidth (see Part II) for the equivalent calculation for MnO), when we find $D_2 \sim 0.001^\circ\text{K}$. For the calculation of \bar{S} , it may safely be taken as zero.

The parameter D_1 describes the "out-of-plane" anisotropy which we expect, for α -MnS, to be dominantly of dipolar origin. We can evaluate it from a knowledge of the antiferromagnetic resonance frequency ω_{afmr} through the equation

$$\hbar\omega_{\text{afmr}} = S[24D_1(J_1 + J_2)]^{1/2}, \quad (6.3)$$

where $S = \frac{5}{2}$. The resonance frequency for α -MnS has been measured by Richards²⁴ and is 19.8 cm^{-1} . Using the values for J_1 and J_2 which have already been evaluated, we find a value $D_1 = 0.28^\circ\text{K}$. A calculation which assumes that D_1 is entirely of dipolar origin gives (when an allowance is made for a deviation of spin $\sim 3\%$ from $\frac{5}{2}$) the result $D_1^{\text{dip}} = 0.36^\circ\text{K}$. The total "out-of-plane" anisotropy would therefore appear to contain a nondipolar contribution which reduces D_1^{dip} by about 20%. This is exactly the situation which we found for MnO in Part II.

With the above information, it is now possible to compute the temperature variation of sublattice magnetization as a function of the single "unknown" $g_1^+ - g_1^-$. As mentioned in Sec. 4, the spin deviation is very sensitive indeed to this parameter. We may, therefore, estimate its value for α -MnS by comparing the theoretical and experimental spin-deviation results. This, in turn, by use of Eq. (4.23), will furnish us with information concerning the magnitude of distortion and biquadratic effects in this salt.

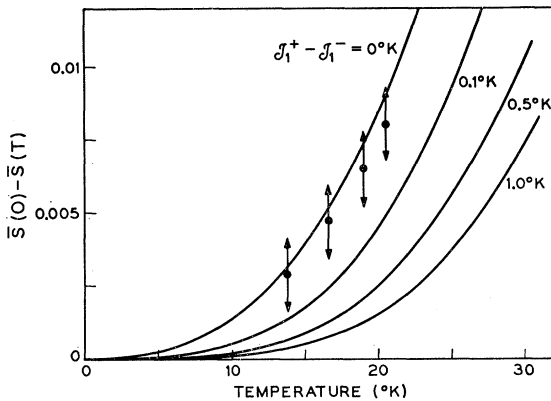


FIG. 6. Theoretical spin-deviation curves, as calculated in the simple spin-wave approximation of Sec. 4 with $J_1 = 7^\circ\text{K}$, $J_2 = 12.5^\circ\text{K}$, $D_1 = 0.28^\circ\text{K}$, and $D_2 = 0$ (which are the values which we find for α -MnS), and for various values of the parameter $g_1^+ - g_1^-$ of Eq. (4.23), are compared with the experimental temperature dependence of Mn⁵⁵ NMR frequency. The error in the experimental measurements is given by the brackets on the data. An equivalent error in the theoretical curves is produced by an uncertainty of $\pm 5\%$ in J_2 at 20°K and of $+10\%$ in J_2 at 15°K .

²⁴ P. L. Richards (private communication).

From Eq. (6.2), it is evident that $[\nu(0) - \nu(T)]/\nu(0) = [\bar{S}(0) - \bar{S}(T)]/\bar{S}(0)$. The experimental data are shown in Fig. 6, where $\bar{S}(0) - \bar{S}(T)$ is plotted as a function of temperature. The error in the experimental measurements is given by the brackets on the data. Also shown in Fig. 6 are the computed spin-wave results obtained by use of Eq. (4.20). We have computed the spin deviation as a function of temperature for several positive values of the parameter $g_1^+ - g_1^-$ (negative values would destroy the stability of our basic spin pattern, which is the spin arrangement reported⁸ from low-temperature neutron-diffraction experiments; i.e., the fcc type-2 order with spins aligned in ferromagnetic $[111]$ sheets). Also noted in the caption to Fig. 6 is the sensitivity of the curves to variations of J_2 about its estimated value of 12.5°K (the curves are much less sensitive to variations of J_1). Since our estimate for J_2 should be good to better than 10%, we see from Fig. 6 that $g_1^+ - g_1^- < \sim 0.1^\circ\text{K}$. We may also note that the presence of magnetostrictive and biquadratic next-nearest-neighbor effects (which modify J_2 in the spin-wave region by possibly a percent or two) are completely negligible when compared with the sensitivity of the curves to $g_1^+ - g_1^-$. Using Eq. (4.23), we conclude that, for α -MnS,

$$\frac{1}{2}J_1\epsilon_1\Delta_{\text{eq}} + 16j_1 < \sim 0.1^\circ\text{K}, \quad (6.4)$$

compared with a value $\sim 1.2^\circ\text{K}$ for MnO. Unfortunately, there has been no information published to date concerning the magnitude of the distortion parameter Δ_{eq} . Nevertheless, using Eqs. (4.4) and (4.13), we find

$$J_1\epsilon_1\Delta_{\text{eq}} = 3N(r\partial J_1/\partial r)^2(\bar{S})^2/C_\Delta, \quad (6.5)$$

which indicates that the first term in (6.4) is necessarily a positive quantity. We have, therefore, two possibilities:

(i) that j_1 is positive, in which case we find

$$\begin{aligned} J_1\epsilon_1\Delta_{\text{eq}} &< \sim 0.2^\circ\text{K} \\ j_1 &< \sim 0.006^\circ\text{K}, \end{aligned} \quad (6.6)$$

(ii) that j_1 is negative, in which case both $J_1\epsilon_1\Delta_{\text{eq}}$ and j_1 could have somewhat larger magnitudes but be opposite in sign. These two possibilities will be discussed in more detail in Sec. 7.

Using the result that $g_1^+ - g_1^-$ is very small in α -MnS allows us now to compute $\bar{S}(0)$, the average spin value per site at $T = 0^\circ\text{K}$. We find the result $\bar{S}(0) \approx 2.420$, a zero-point spin deviation of 3.2%.

Mn⁵⁵ NMR Linewidth in α -MnS

The contribution to the NMR linewidth from the indirect nuclear spin-spin interaction has been treated in detail for MnO in Part II. Since we have not made a direct experimental observation of the linewidth for α -MnS, we shall only perform an order-of-magnitude calculation for α -MnS at the present time. If we assume

that the ratio of "in-plane" to "out-of-plane" anisotropy D_2/D_1 is the same for α -MnS as it is for MnO, i.e., $D_2/D_1 \sim 10^{-2}$ to 10^{-3} , then it is easy to show from Part II that, for small anisotropies,

$$\delta H \propto A^2/J_1 D^{1/2}. \quad (6.7)$$

Thus it follows that

$$(\delta H)_{\alpha\text{-MnS}} \approx \left[\frac{A_{\alpha\text{-MnS}}}{A_{\text{MnO}}} \right]^2 \left[\frac{J_{1\text{MnO}}}{J_{1\alpha\text{-MnS}}} \right] \times \left[\frac{D_{\text{MnO}}}{D_{\alpha\text{-MnS}}} \right]^{1/2} (\delta H)_{\text{MnO}}. \quad (6.8)$$

Using the values of A , J_1 , and D appropriate for α -MnS and MnO, and putting $(\delta H)_{\text{MnO}} \approx 500$ Oe, gives $(\delta H)_{\alpha\text{-MnS}} \approx 850$ Oe. In this estimate, however, we have ignored the effect on linewidth δH of the lattice distortion terms, which appear to be very much smaller in α -MnS than in MnO. Including such an effect increases $(\delta H)_{\alpha\text{-MnS}}$ further (probably by about 20 or 30%), giving us a final estimate

$$(\delta H)_{\alpha\text{-MnS}} \sim 1000 \text{ Oe},$$

and therefore probably accounts for our failure, thus far, to observe the Mn⁵⁵ zero-field NMR in α -MnS using cw techniques. Such a value is also consistent with our experimental estimate obtained from the sideband responses of the super-regenerative uhf oscillation.

7. DISCUSSION

The comparison of spin-wave theory with experimental measurements of the temperature dependence of sublattice magnetization in α -MnS has led to the conclusion that the parameter $g_1^+ - g_1^-$ [Eq. (4.23)] is very small indeed for this salt. This parameter is made up of the sum of two parts, one representing the effects of anisotropic distortion [$\frac{1}{2}J_1\epsilon_1\Delta_{\text{eq}}$] and the other the effects of nearest-neighbor biquadratic exchange j_1 . The fact that this parameter is so small would seem to rule out the possibility of a magnetic first-order transition at the Néel point, of the type that is expected to occur in MnO (see Part II). It would also suggest that the sublattice magnetization deviates very little from the molecular-field $B_{5/2}$ curve.

As was pointed out in the previous section, very little experimental work has been reported to date on α -MnS. This is unfortunate, because a knowledge of the magnitude of the lattice-distortion parameter Δ_{eq} at low temperatures, coupled with a measurement of the elastic constant C_Δ , would allow us to calculate $J_1\epsilon_1\Delta_{\text{eq}}$ and hence to obtain a value for j_1 from (6.4). In the absence of this information, we are left with two possibilities depending on the sign of j_1 .

If j_1 is positive, which has been the assumption made by all previous authors who have discussed the sta-

tistical problem of biquadratic exchange in the fcc antiferromagnets, then the results $J_1\epsilon_1\Delta_{\text{eq}} < \sim 0.2^\circ\text{K}$ and $j_1 < \sim 0.006^\circ\text{K}$ follow. This would indicate a value j_1/J_1 for α -MnS of less than 10^{-3} , which is at least an order of magnitude smaller than any previous estimate of such a ratio. It would also mean that $(r\partial J_1/\partial r)^2/C_\Delta$ is at least an order of magnitude smaller in α -MnS than in MnO (where the derivative is taken for r equal to the nearest-neighbor distance).

Neither of these results is impossible, or even particularly unlikely, since most of the larger estimates^{2,25} for biquadratic exchange have resulted from use of the molecular-field approximation which is highly suspect (see Part II) when applied to the fcc antiferromagnets. Even so, we think that some thought should be given to the possibility of j_1 being negative in α -MnS. In this case, the very small value found for $g_1^+ - g_1^-$ in the spin-wave region could result from a cancellation of somewhat larger distortion and biquadratic terms which are of different signs. If this is the case, a tentative explanation can be put forward for the peculiar double-cusped nature of the heat-capacity curve found for α -MnS by Anderson.¹⁸ He observes that the heat capacity reaches a cusped peak at 139°K , after which the downward part of the curve flattens off to about 147°K , at which point it drops discontinuously to a lower value. Since we have found that the NMR in the paramagnetic region disappears as the temperature is lowered through 147°K , it would seem that this is the temperature at which long-range order sets in, i.e., the Néel point. It is possible that the cusp at 139°K marks the change from one type of antiferromagnetic fcc type-2 order to another.

It was pointed out in Part II that the single-axis fcc type-2 order, which is observed by neutron diffraction in α -MnS, is not stable in the absence of distortion and biquadratic terms. The stability of this single-axis order depends, in fact, on the sign of $g_1^+ - g_1^-$, being stable for positive values of this parameter. The Eq. (4.23) for $g_1^+ - g_1^-$ has been derived for the very low temperature region only. At higher temperatures, both the distortion and the biquadratic contributions to this parameter will be temperature-dependent. The distortion term is known to vary closely as $(\bar{S})^2$. The behavior of the biquadratic contribution is less well known because of the difficulty of treating such terms in any but the simplest of molecular-field approximations. The work of Sec. 2 however, suggests that this term might also vary fairly closely as $(\bar{S})^2$. It is unlikely, however, that these terms would have *exactly* the same temperature dependence, and it is quite possible that for the case of j_1 negative there could be a temperature for which $g_1^+ - g_1^-$ changes sign. This is most likely to occur at a temperature for which \bar{S} is considerably removed from its value in the spin-wave region, i.e., a

²⁵ G. Will, S. J. Pickart, H. A. Alperin, and R. Nathans, J. Phys. Chem. Solids 24, 1679 (1963).

temperature not too far below the Néel point. If such a transition does indeed take place at 139°K, the type-2 order in the 139 → 147°K temperature region will most likely be a multiaxial one, since a negative j_1 would tend to favor such a structure.

In the light of the results obtained in the present series of papers on MnO and α -MnS, it is possibly worthwhile to re-examine the evidence available for the existence of biquadratic exchange in ordered magnetic systems. The major piece of evidence has been cited^{2,25} to be the anomalous temperature dependence of sublattice magnetization in MnO, NiO, and EuTe. A certain temperature variation of perpendicular susceptibility for $T < T_N$ in MnO and NiO has also been mentioned.² It is interesting to note that all of these salts have the same crystal structure and spin pattern, namely the fcc type-2 antiferromagnetic order. This is probably significant since we have shown that this particular order is likely to be far more sensitive to small distortions and biquadratic terms than most others. Previous authors have made a molecular-field analysis with various simplifying assumptions, e.g., putting nearest- and next-nearest-neighbor biquadratic terms equal, and calculated ratios j/J which are typically of the order 0.015 to 0.05.

The calculations of Part II and Part III of the present series of papers have shown that the molecular-field theory almost certainly seriously underestimates the effect of distortion and biquadratic terms on sublattice magnetization. An important result is that the shape of the magnetization curves is very sensitive to anisotropic distortion and nearest-neighbor biquadratic terms j_1 , but is rather insensitive to an isotropic variation of lattice parameters and to next-nearest-neighbor biquadratic exchange j_2 . We find, in particular, that the reported anomalies of magnetization and of perpendicular susceptibility in MnO may both be adequately explained by the presence of anisotropic distortion alone. The published measurements²⁶ of sublattice magnetization in MnO, however, do not extend over the entire antiferromagnetic temperature range, and more complete experimental information is required in order to determine more precisely whether any biquadratic exchange is possibly present in addition to the distortion. The existing experimental evidence

therefore provides no evidence for the existence of biquadratic exchange.

It seems quite possible that the observed anomalies in NiO are also very largely due to the anisotropic distortion. The case of EuTe is a little more puzzling since Rodbell *et al.*²⁷ have failed to observe a rhombohedral distortion in this salt for $T < T_N$, although their comment²⁷ that this lack of distortion is to be expected because of the small value of J_1 in EuTe is not correct, since Δ_{eq} depends on exchange only as $\partial J_1/\partial r$, and this derivative does not necessarily become vanishingly small in the limit of small J_1 . The theoretical problem for EuTe, however, is complicated by the fact that the dipolar anisotropy for this salt is comparable in magnitude to the isotropic exchange energy. Such a large dipolar anisotropy could conceivably give rise itself to a magnetization anomaly of the type observed in EuTe and, in the absence of quantitative calculations for this more complicated situation, it would be hasty to conclude that there is evidence for biquadratic exchange in this particular magnetic property of EuTe. Indeed, it would be surprising if the first experimental evidence for the existence of biquadratic exchange in magnetically ordered systems should be found in a rare-earth salt, since the ratio j/J is surely very much smaller in the rare earths than it is for salts of the transition-metal ions.

Perhaps the most significant result concerning biquadratic exchange, therefore, is the one obtained in the present paper concerning the nearest-neighbor interactions in α -MnS. For this case, $j_1/J_1 \lesssim 10^{-3}$ and is at least an order of magnitude smaller than any previous estimates made for Mn^{++} . This result does not necessarily tell us anything about the situation for other Mn^{++} salts or even about j_2/J_2 in α -MnS, but it is an indication that the importance of biquadratic exchange in magnetically ordered systems could be considerably less than has previously been supposed.

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²⁶ C. G. Shull, W. A. Strausser, and E. O. Wollan, Phys. Rev. **83**, 333 (1951).

²⁷ D. S. Rodbell, L. M. Osika, and P. E. Lawrence, J. Appl. Phys. **36**, 666 (1965).