[4]J. K. Hulm and R. D. Blaugher (private communication).
[5]D. Pines, Phys. Rev. 109, 280 (1958).
[6]E. Mendoza, Experimental Cryophysics, edited by F. E. Hoove, L. C. Jackson, and N. Kurti (Butterworths Scientific Publications, Ltd., London, 1961), p. 172.
[7]J. M. Daniels and N. Kurti, Proc. Roy Soc. (London) A221, 243 (1954).
[8]Reference 6, p. 191.
[9]D. A. Spohr, thesis, Oxford University, Oxford, England, 1958 (unpublished).
[10]J. C. Wheatley, D. F. Griffing, and T. C. Estle, Rev. Sci. Instr. 27, 1070 (1956).
[11]R. A. Hein and R. L. Falge, Jr., Phys. Rev. 123, 407 (1961).

BIQUADRATIC EXCHANGE BETWEEN Mn^{2+} IONS IN MgO

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Paramagnetic resonance measurements[1] on pairs of Mn^{2+} ions in MgO have indicated values for the isotropic Mn-Mn exchange interactions which are surprisingly large compared with those estimated from bulk measurements on MnO. We have therefore made a more detailed investigation of the pair spectrum. The results suggest that there is an appreciable biquadratic contribution to the exchange of the form $-j(\vec{S}^a\cdot\vec{S}^b)^2$ in addition to the usual bilinear term, $J(\vec{S}^a\cdot\vec{S}^b)$. This not only helps to explain the discrepancy, but may also have significant effects on the magnetic properties of MnO.

The measurements have been made on crystals of MgO containing about 1 at.% Mn using wavelengths 0.85 and 1.25 cm in the temperature range 4 to 200°K. Only nearest-neighbor pairs have been examined in the present experiments, i.e., Mn^{2+} ions occupying lattice sites such as (0, 0, 0) and (1/2, 1/2, 0). Following previous work,[1,2] we first assume that the isotropic exchange is of the usual form, $J(\vec{S}^a\cdot\vec{S}^b)$, where $S^a = S^b = 5/2$ for Mn^{2+} and J is positive (antiferromagnetic). This gives total spin states $S = 0,1,2,3,4,5$, and the interval rule describing the spacing between adjacent states is

$$W_{S,S-1} = JS, \qquad (1)$$

where S is the spin of the higher state.

We have confirmed previous results[1] on the $S = 1$ state and have also identified all the expected transitions belonging to $S = 2$, 3, and 4 from the positions and anisotropies of the lines in the spectrum. (The spectrum from $S = 5$ is obscured by stronger absorption due to lower S states and due to isolated Mn^{2+} ions.) These positions are found to be accurately predicted by anisotropic interaction parameters of the expected form.[2] Having identified the transitions in this way, the energy intervals predicted by Eq. (1) have been investigated by measuring, as a function of temperature, the intensity of transitions belonging to different total spin states both relative to each other and relative to standard comparison substances. The results are given in the first two columns of Table I. It can be seen that the expected interval rule [Eq. (1)] is not obeyed. Much better agreement with experiment would be obtained if the isotropic exchange were of the form

$$\mathcal{H}_{ex} = J(\vec{S}^a\cdot\vec{S}^b)^2 - j(\vec{S}^a\cdot\vec{S}^b)^2, \qquad (2)$$

which gives a modified interval rule

$$W_{S,S-1} = JS - jS[S^2 - S^a(S^a+1) - S^b(S^b+1)]. \qquad (3)$$

Table I. Comparison between predicted and observed Landé intervals.

Measured interval	Experimental energy (°K)	Modified interval rule	Calculated for $j/J = 0.05$ ($J/k = 14.6$°K, $j/k = 0.73$°K)
$\frac{1}{4}\times W_{4,3}$	17.5 ± 3	$J + 1.5j$	15.7
$\frac{1}{3}\times W_{3,2}$	20.0 ± 3	$J + 8.5j$	20.8
$\frac{1}{2}\times W_{2,1}$	24.5 ± 2	$J + 13.5j$	24.5
$1\times W_{1,0}$	28.0 ± 3	$J + 16.5j$	26.7

The intervals appropriate to the experiments are then as given in the third column of the table. A reasonable fit to the results can be made by choosing $j/J = +0.05 \pm 0.03$ as is indicated in the fourth column. Though the errors are quite large, the results thus suggest that j is positive and of order a few percent of J.

Such a value of j does not seem inconsistent with Anderson's theory of superexchange[3] which predicts that there will be fourth-order terms of the form $(\vec{S}^a \cdot \vec{S}^b)^2$ with magnitude ~1% of the second-order terms, $(\vec{S}^a \cdot \vec{S}^b)$. An effective biquadratic exchange term can also arise via a mechanism[4,5] in which a balance is set up between elastic and exchange forces. Using the elastic constants for MnO, it would appear that this gives too small an effect to account for the present results.

Finally, we will briefly consider MnO. The Curie-Weiss θ depends almost entirely on bilinear exchange and suggests that for first and second neighbors the average interaction is $\frac{1}{2}(J_1 + J_2) \approx 11°\mathrm{K}$. This was previously[1] compared with the pair splitting $(W_{1,0})_1 \approx (W_{1,0})_2 \approx 28°\mathrm{K}$, but the present work indicates that about half of this splitting is due to biquadratic exchange and that $J_1 \approx J_2 \approx 15°\mathrm{K}$ for the pair, assuming $j_1 = j_2$. Hence, $J(\mathrm{pair})/J(\mathrm{MnO}) \approx 1.4$, which is now in reasonable agreement with estimates allowing for the small decrease in lattice spacing from MnO to MgO.

For many properties other than θ, j is important. For example, in MnO at $T = 0$, the exchange field appropriate to antiferromagnetic resonance or to the transverse susceptibility is proportional to $J + 12.5j$, while the total exchange field seen by any Mn^{2+} ion is proportional to $J + 37.5j$, assuming $J_1 = J_2$ and $j_1 = j_2$. Effects such as these are discussed in the following Letter[6] and indicate that $j/J \approx 0.01$ to 0.02 for MnO. This result is roughly consistent with the pair measurement, expecially when it is noted that if $J(\mathrm{pair})/J(\mathrm{MnO}) \approx 1.4$, one might expect[3] that $j(\mathrm{pair})/j(\mathrm{MnO}) \gtrsim (1.4)^2$. All of the results thus appear to support the hypothesis that there is appreciable biquadratic exchange between neighboring Mn^{2+} ions.

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[1]B. A. Coles, J. W. Orton, and J. Owen, Phys. Rev. Letters 4, 116 (1960).

[2]J. Owen, Suppl. J. Appl. Phys. 32, 213 (1961).

[3]P. W. Anderson, Phys. Rev. 115, 2 (1959); Solid State Physics, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1963), Vol. 14, p. 99.

[4]C. Kittel, Phys. Rev. 120, 335 (1960).

[5]C. P. Bean and D. S. Rodbell, Phys. Rev. 126, 104 (1962).

[6]D. S. Rodbell, I. S. Jacobs, J. Owen, and E. A. Harris, following Letter [Phys. Rev. Letters 11, 10 (1963)].

BIQUADRATIC EXCHANGE AND THE BEHAVIOR OF SOME ANTIFERROMAGNETIC SUBSTANCES*

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In the previous Letter,[1] Harris and Owen have described the electron spin resonance spectrum of nearest-neighbor Mn^{2+} ion pairs in MgO. Their analysis suggests that there is a biquadratic contribution to the isotropic Mn-Mn exchange interaction in addition to the usual bilinear term, i.e., the interaction is of the form

$$J\vec{S}^a \cdot \vec{S}^b - j(\vec{S}^a \cdot \vec{S}^b)^2, \qquad (1)$$

where $S^a = S^b = 5/2$ for Mn^{2+} ions, $J > 0$ (antiferromagnetic) and $j/J \approx 0.05$. The magnitude of j is consistent with Anderson's theory of superexchange.[2] The only other mechanism that could be considered is that of exchange-induced distortion of the crystal,[3,4] but this is an order of magnitude too small to be responsible here. The purpose of this Letter is to show that a similar exchange interaction in antiferromagnetic MnO