ANTIFERROMAGNETIC EXCHANGE INTERACTIONS BETWEEN Mn^{2+} IONS IN MgO

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Paramagnetic resonance methods[1] have been used to investigate exchange interactions between neighboring Mn^{2+} ions present as substitutional impurities in MgO, with $Mn:Mg \approx 1:100$. These interactions are expected to be similar to those in the antiferromagnetic MnO. The crystal structure of both salts is face-centered cubic, with lattice parameter $a_0 = 4.203$ A for pure MgO and $a_0 = 4.4448$ A for pure MnO.[2] The interactions have been measured for (a) an isolated nearest neighbor (nn) pair of Mn ions, e.g., an Mn ion at 0, 0, 0 with only one close Mn neighbor at $\frac{1}{2}, \frac{1}{2}, 0$; and (b) an isolated next nearest neighbor (nnn) pair of Mn ions, e.g., an Mn ion at 0, 0, 0 with only one close Mn neighbor at 0, 0, 1. The latter type of pair has structure Mn-O-Mn and is perhaps the best known example of a pair of superexchange-coupled paramagnetic ions.[3]

The two Mn^{2+} ions of the pair are in a $^6S_{5/2}$ ground state with electronic spins $S^i = S^j = 5/2$. The main interaction between them is expected to be an isotropic exchange,

$$J\vec{S}^i\cdot\vec{S}^j = \tfrac{1}{2}J[S(S+1) - S^i(S^i+1) - S^j(S^j+1)], \qquad (1)$$

where S is the total spin which can take values $S = 0$, 1, 2, 3, 4, or 5. The relative energies of the states corresponding to these different spins thus follow a Landé interval rule and are 0, J, $3J$, $6J$, $10J$, and $15J$, respectively. The $S = 0$ state is lowest if J is positive, i.e., antiferromagnetic. The allowed magnetic resonance transitions are between the Zeeman components belonging to any one of these states, and in the present experiments we have analyzed the part of the spectrum corresponding to $S = 1$ for an nn pair, and $S = 1$ for an nnn pair, using wavelengths between 0.95 and 3.3 cm. It is found that the relative energies of the Zeeman components for these two states can be described by the spin Hamiltonian,

$$\mathcal{H} = g\beta\vec{H}\cdot\vec{S} + D[S_z^{\,2} - \tfrac{1}{3}S(S+1)] + E[S_x^{\,2} - S_y^{\,2}] + A\vec{S}\cdot(\vec{I}^i + \vec{I}^j), \qquad (2)$$

where $g = 2.00$, $S = 1$, $I^i = I^j = 5/2$ = nuclear spin of Mn^{55}, and the values of D and E are given in Table I. For nn pairs the axes x, y, z are along sets of directions such as $[1, \bar{1}, 0]$, $[0, 0, 1]$, $[1, 1, 0]$, respectively, with the z axis along the $[1, 1, 0]$ direction joining the two ions. For nnn pairs there is a fourfold symmetry axis so that $E = 0$, and z is along the $[1, 0, 0]$ direction joining the ions.

The observed hyperfine structure (Fig. 1) consists of eleven lines corresponding to the allowed values of the total nuclear magnetic quantum number $M_I = 5, 4, \cdots, -5$. The relative intensities are close to the expected ratios 1:2:3:4:5:6:5:4:3:2:1 corresponding to the different ways of building up each M_I value. The structure constant is $A = 40 \times 10^{-4}$ cm^{-1} which is half the value found for an isolated Mn^{2+} ion in MgO as is expected if $J \gg A$.

The value of J has been estimated from the temperature dependence of the signal intensity which tends to zero at very low temperatures because the higher levels become depopulated

FIG. 1. Hyperfine structure from a nearest neighbor pair of Mn^{2+} ions in the $S = 1$ state. The spacing between adjacent lines is 43 gauss.

Table I. Interaction parameters for nearest neighbor and next nearest neighbor pairs. The calculated dipole-dipole interaction for the $S = 1$ state is $D_d = 111g^2\beta^2/(10r_{ij}^3)$, where r_{ij} = Mn-Mn separation, $g = 2.00$, and β = Bohr magneton. The values of r_{ij} for the corresponding Mg-Mg separations in MgO have been used here; the actual Mn-Mn spacings in the mixed crystal may be slightly larger.

Pair	J/k (°K)	D (cm^{-1})	E (cm^{-1})	D_d (cm^{-1})
nn Mn-Mn	28 ± 4	0.776 ± 0.01	0.149 ± 0.005	0.730
nnn Mn-O-Mn	28 ± 4	0.261 ± 0.01	0.00 ± 0.01	0.258

in favor of the singlet ($S=0$) ground state. Assuming the Landé interval rule given by Eq. (1), the intensity of transitions belonging to the $S=1$ state is proportional to $[\exp(-J/kT)]/(TZ)$, where Z is the partition function for the six spin states. Comparison of the experimental intensities over a range of temperature with this expression gives the value 28 ± 4°K for both J_{nn}/k and J_{nnn}/k. A direct comparison of the temperature dependence of the intensities of nn, $S=1$ and nnn, $S=1$ transitions yields $J_{\mathrm{nnn}}/J_{\mathrm{nn}}=1.0\pm 0.1$.

When comparing these results with the bulk properties of MnO we first assume that the value found above for the important ratio $r=J_{\mathrm{nnn}}/J_{\mathrm{nn}}$ is approximately applicable to MnO, despite the small change in lattice spacing in the mixed crystal. A value of 11.3°K for J_{nn}/k and J_{nnn}/k can then be derived for MnO by using the measured Curie-Weiss constant, $\theta=610$°K,[4] in the relation $\theta=4J_{\mathrm{nn}}(1+r/2)S(S+1)/k$ with $S=5/2$ and $r=1$. The value of about 28°K found in the present experiments is surprisingly large compared with this susceptibility value. The discrepancy may be due to the Mn-Mn separation being slightly smaller in the mixed Mn:MgO crystal. It also seems possible that the true (high temperature) value of θ may be larger than 610°K, since this experimental value appears to refer to the small temperature range 120 to 300°K just above the antiferromagnetic transition at $T_N=116$°K. Finally, concerning the values found for the anisotropic interaction parameters D and E, that for D can be mainly accounted for by the expected dipole-dipole interaction as can be seen from Table I. The value found for E(nn), on the other hand, is unexpectedly large, and may be partly due to crystal field effects arising from distortion in the mixed crystal.

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ELECTRONIC STRUCTURE OF THE "ANTIMORPH" OF THE *F* CENTER

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The electronic structure of the *F* center in alkali halides has been investigated extensively in the past, and a well-founded model has emerged from that work. The *F* center can be described as an electron trapped at a halide vacancy, and it has the symmetry appropriate to the vacancy.[1] Seitz[2] proposed in 1946 the existence of a center which should consist of a hole trapped at an alkali vacancy and thus would be the counterpart of the *F* center. He called it the "antimorph" of the *F* center.[3] In this Letter we report on the observation of a paramagnetic resonance spectrum in x-rayed LiF that is probably due to such a center, namely to a hole trapped at a Li^+ vacancy. The analogy with the *F* center, however, does not go any further as the symmetry of the new center differs considerably from that of the *F* center.

The total spread of the hyperfine spectrum is what one expects for a hole on fluoride ions.[4] The basic hyperfine spectrum consists of four equally intense lines, and for specialized orientations of the crystals in the dc magnetic field it degenerates into a three-line pattern with the intensity ratio 1:2:1. This indicates that the hole is localized on but two fluoride ions which are nonequivalent with respect to a general orientation of the applied dc magnetic field, but become equivalent for particular orientations. Thus this center can be regarded as a F_2^- molecule-ion, just as the previously investigated self-trapped hole.[4] One principal difference consists therein