The ground-state splitting observed here is the first observation of a multihole effect for valence-electron acceptor impurities in semiconductors. This same explanation would also predict a splitting of the excited states of neutral group-I acceptors in silicon and germanium. A weak line should appear on the high-energy side of each "normal" transition. Such satellites would be very difficult to observe against the background of stronger "normal" transitions.

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[12] This notation is that of Refs. 1-3. The transitions A, B, C, D, E, and G correspond to photoexcitation transitions from the 1s ground state to various excited states with A being to the least bound excited state.

[13] This G' line is the "unidentified" line in Ref. 7.

[14] The single-hole wave function is a product of a hydrogenlike envelope function and a bandlike function. The major contribution of the band wave functions to the mercury ground state comes from the light and heavy bands ($j=\frac{3}{2}$); the spin-orbit coupling is strong in germanium and we do not need to consider the $j=\frac{1}{2}$ band which is split off by 0.29 eV.

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CONTRIBUTION TO THE HYPERFINE FIELD FROM CATION-CATION INTERACTIONS*

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Two mechanisms are reported for the change in hyperfine field at the site of a magnetic ion brought about by the presence of neighboring magnetic ions: transfer of a 3d electron from the neighboring ion to the 4s level of ion in question, and orthogonalization of the antibonding orbitals of the surrounding cations to the inner s cores of the magnetic ion. The total s-state admixture from both mechanisms results in an increase in the hyperfine field in a simple cubic antiferromagnet over that found in the dilute salt.

Heeger and Houston[1] first noted an apparent dependence of the hyperfine field at a given magnetic cation on the proximity of neighboring magnetic cations in the manganese spinels. Such a change can alter the conclusions usually reached in the determination of the zero-point reduction of $\langle\vec{S}\rangle$ in an antiferromagnet.[2] We report here two mechanisms which are responsible for an increase in the hyperfine constant A in a simple cubic antiferromagnet upon going from the dilute magnetic salt to the concentrated material. The increase will be shown to amount to approximately 4% in going from Mn^{2+}:KMgF$_3$ to KMnF$_3$. Thus, the measurements of Heeger, Portis, and Witt,[3] Witt and Portis,[4] and Montgomery, Teaney, and Walsh[5] which indicate that AS in Mn^{2+}:KMgF$_3$ is essentially equal to $A\langle\vec{S}\rangle$ in KMnF$_3$, in fact demonstrate a roughly 4% zero-point decrease in $\langle\vec{S}\rangle$ in antiferromagnetic $KMnF_3$. A similar result should obtain for other antiferromagnetic materials.

Mechanism 1.—We adopt the four-electron model displayed in Fig. 1. An electron is transferred from the $3d_{z^2}$ orbital of one Mn^{2+} ion to the empty $4s$ orbital of its neighbor. In the antiferromagnetic state, the spin of the first Mn^{2+} ion is opposite to the second. The transfer Hamiltonian is spin independent, so that the spin of the electron transferred to the $4s$ state is oppositely directed from the $3d$ spins of the second atom. This results in an enhancement of the hyperfine interaction because the $3d$ electrons give rise to a negative-spin density at the nucleus due to core polarization, whereas the $4s$ electron contributes positively.

Quantitatively, we denote the ground configuration by A, the excited configuration by B, as in Fig. 1. The perturbed ground-state wave function is written as

$$\psi = \psi^A + a\psi^B, \tag{1}$$

where

$$a = (\langle A|\mathcal{H}|B\rangle - \langle A|B\rangle\langle A|\mathcal{H}|A\rangle)/(E_A - E_B). \tag{2}$$

We use the Dirac-Van Vleck-Serber spin-operator-expansion technique to evaluate the numerator of (2). We find

$$\begin{aligned}\langle A|\mathcal{H}|A\rangle &= \mathcal{H}_I^{AA} - \mathcal{H}_{13}^{AA} - \mathcal{H}_{14}^{AA} \\ &\quad + \mathcal{H}_{34}^{AA} - \mathcal{H}_{134}^{AA} + 2\mathcal{H}_{13,24}^{AA}, \\ \langle A|\mathcal{H}|B\rangle &= \mathcal{H}_I^{AB} - \mathcal{H}_{13}^{AB} - \mathcal{H}_{14}^{AB} + \mathcal{H}_{34}^{AB} \\ &\quad - \mathcal{H}_{134}^{AB} - \mathcal{H}_{143}^{AB} + 2\mathcal{H}_{13,24}^{AB}, \end{aligned} \tag{3}$$

where

$$\mathcal{H}_P^{AA} = \langle Pa_1a_2a_3a_4|\mathcal{H}|a_1a_2a_3a_4\rangle,$$

$$\mathcal{H}_P^{AB} = \langle Pa_1a_2a_3a_4|\mathcal{H}|b_1b_2b_3b_4\rangle.$$

Denoting the overlap integrals by

$$S = \langle a_1|a_4\rangle = -\langle a_1|a_3\rangle, \quad T = \langle a_3|a_4\rangle,$$

$$S' = \langle b_1|b_3\rangle, \qquad T' = \langle a_3|b_3\rangle,$$

we find, to a good degree of approximation,

$$a = \frac{(\mathcal{H}_I^{AB} - T'\mathcal{H}_I^{AA} - \mathcal{H}_{13}^{AB} - SS'\mathcal{H}_I^{AA})}{(E_A - E_B)}. \tag{4}$$

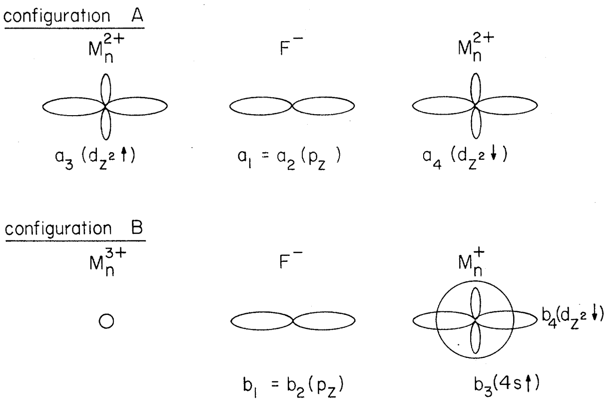

FIG. 1. Orbitals considered in the four-electron model. Configuration A is the ionic configuration. Configuration B is the excited configuration corresponding to a transfer of a d_{z^2} orbital of a Mn^{2+} ion to the $4s$ orbital of the nearest neighboring Mn ion.

We use Watson's[6] wave functions for Mn^{2+} and F^-, and Rimmer's[7] wave function for $Mn^+(4s)$ to evaluate (4). We find $a = 3\times10^{-2}$, which leads to a net increase of the hyperfine field (after summing over the contribution from the six antiparallel nearest Mn^{2+} neighbors) of

$$\Delta H_{\text{hyp}} = +12.7 \text{ kG}. \tag{5}$$

Mechanism 2.—The second important contribution to ΔH_{hyp} arises from the orthogonalization of the antibonding orbitals of the surrounding cations to the inner $1s$, $2s$, and $3s$ core orbitals. We construct the σ antibonding molecular orbital

$$\psi_{z^2} = N(d_{z^2} - \lambda_\sigma P_z - \sum_n \mu_{ns}\varphi_{ns}), \tag{6}$$

where φ_{ns} are the $1s$, $2s$, and $3s$ core orbitals of the Mn^{2+} ion for which ΔH_{hyp} is to be calculated. The orthogonality requirement between ψ_{z^2} and φ_{ns} gives

$$\mu_{ns} = \langle d_{z^2}|\varphi_{ns}\rangle - \lambda_\sigma\langle P_z|\varphi_{ns}\rangle. \tag{7}$$

Direct computation shows that the first term in (7) is small compared with the second. Defining $S_{p,ns} = \langle p_z|\varphi_{ns}\rangle$, we find

$$\mu_{ns} = -\lambda_\sigma S_{p,ns}. \tag{8}$$

The cation-cation transfer (mechanism 1) can be incorporated into the molecular orbital (6) so that the resulting molecular orbital of one of the surrounding cations becomes

$$\psi_{z^2} = N'(d_{z^2} - \lambda_\sigma p_z - \sum_n \mu_{ns}\varphi_{ns} + a\varphi_{4s}). \tag{9}$$

Table I. Changes in the hyperfine field (in kG) at Mn^{2+} site upon going from Mn^{2+}:KMgF$_3$ to KMnF$_3$. Diagonal terms are given by $\Delta H_{ns,ns} = (8\pi/3)g\beta_e S\mu_{ns}^2 \times |\varphi_{ns}(0)|^2$, and $\Delta H_{4s,4s} = (8\pi/3)g\beta_e S a^2 |\varphi_{4s}(0)|^2$. Cross terms are given by $\Delta H_{ns,ms} = (16\pi/3)g\beta_e S\mu_{ns}\mu_{ms}\varphi_{ns}(0) \times \varphi_{ms}(0)$, and $\Delta H_{ns,4s} = -(16\pi/3)g\beta_e S\mu_{ns}a\varphi_{ns}(0)\varphi_{4s}(0)$. Here $n \neq m = 1$, 2, and 3.

Term	Change in field (kG)
$\Delta H_{1s,1s}$	0.7
$\Delta H_{2s,2s}$	3.7
$\Delta H_{3s,3s}$	13.3
$\Delta H_{4s,4s}$	12.7
$\Delta H_{1s,2s}$	−3.2
$\Delta H_{1s,3s}$	6.1
$\Delta H_{2s,3s}$	−14.0
$\Delta H_{1s,4s}$	3.4
$\Delta H_{2s,4s}$	−7.9
$\Delta H_{3s,4s}$	15.0
ΔH_{hyp}	29.8

The main contribution to the contact hyperfine field comes from the last two terms in Eq. (9). We use Watson's[6] free-ion wave functions for evaluating $\varphi_{ns}(0)$, $\varphi_{4s}(0)$, and $S_{p,ns}$. The value of λ_σ is related to the $3d$-$2p$ covalence whereas the experimental value $f_\sigma = 1.2\%$ contains both $3d$-$2p$ and $4s$-$2p$ contributions. By using the *a priori* calculations of Hubbard, Rimmer, and Hopgood,[8] we estimate $\lambda_\sigma = 0.219$.

Summing the contributions from the six independent cations, we obtain the final result that the hyperfine field at a Mn^{2+} site in KMnF$_3$ exceeds that in Mn^{2+}:KMgF$_3$ by

$$\Delta H_{\text{hyp}} = +29.8\ \text{kG}, \tag{10}$$

or, equivalently,

$$\Delta A = 4.0 \times 10^{-4}\ \text{cm}^{-1}.$$

In Table I the diagonal contributions and the cross terms of different shells are listed. Montgomery, Teaney, and Walsh[5] extrapolate a value of $A = 91.64 \times 10^{-4}$ cm^{-1} for KMnF$_3$. Thus the fractional change in the hyperfine field is about

$$\left.\frac{\Delta A}{A}\right|_{\text{KMnF}_3} = 4\%. \tag{11}$$

This value implies that a *four*-percent zero-point spin deviation exists in KMnF$_3$, rather than the nearly zero value which would be obtained by neglecting the effects of the neighboring magnetic ions as discussed in this Letter.

Note added in proof.—After completing the manuscript we found that J. Owen and D. R. Taylor worked on the same problem. They considered only the diagonal contribution to the change in hyperfine field arising from the unpaired spin density in $3s$ core orbital only.

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