ORIGIN OF THE F^{19} HYPERFINE STRUCTURE IN TRANSITION ELEMENT FLUORIDES*

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(Received February 21, 1961)

The F^{19} hyperfine structure has now been observed in many iron series fluorides[1] by both electron paramagnetic resonance[2] and nuclear magnetic resonance.[3] In a new theoretical investigation of the origin of this effect we have found that all previous phenomenological interpretations and theoretical analyses have neglected terms which are important for understanding the magnetic interactions and for determining the electron distributions in these materials.

The large internal magnetic fields that have been found to exist at the nucleus of normally diamagnetic ions, like F^-, have been interpreted as arising from unpaired electron spins in the fluoride ion orbitals. Since the origin of the unpairing lies in the interaction of these electrons with the $3d$ magnetic electrons of the iron series atoms, the experiments have been shown to yield valuable information about the distribution of the magnetic electrons and have greatly increased our understanding of the behavior of these materials. Very briefly, the theoretical interpretations of the hfs observations have followed several distinct models which describe the unpairing as being the result of (1) an admixture of covalent bonding into the purely ionic configuration[2,4] (i.e., the metal ion $3d$ wave functions have been augmented by small amounts of fluorine functions of the proper symmetry), or (2) the unpairing action of the Pauli principle (on the wholly ionic configuration) which affects those fluoride orbitals which have the same spin as the cation $3d$ orbital differently from those orbitals which have opposite spin.[5] In either method the unpaired fluorine s electrons produce an isotropic hfs (from the contact part of the Fermi interaction) whereas the $2p$ electrons are responsible for the anisotropic interaction. For lack of space we shall only discuss the isotropic shifts, but our findings are applicable to a lesser degree to the anisotropic interaction as well.

In the covalent bonding scheme [(1) above], the degree of unpairing is measured by the fraction f_s of $2s$ ligand wave function admixed into the $3d$ wave function and is given by $(S+\lambda)^2$, where S is the overlap integral between the $3d$ (metal ion) and the $2s$ (ligand) wave functions and λ is the covalent mixing parameter. {In the ionic model [(2) above], the mixing is determined by S^2 (plus several other small terms) and by definition the degree of covalency λ is zero.} If the measurements are interpreted on this basis, then the degree of covalency λ is determined and this important information about the electron densities has already been put to use in a variety of ways.[6]

Let us consider these theories in some detail now. For simplicity we follow the usual procedure and reduce the problem to a consideration of the diatomic system, say Mn^{++}-F^-. The antibonding molecular orbitals (i.e., the augmented Mn^{++} $3d$ wave functions) may be written as

$$\Phi = N[\psi_{3d}(Mn^{++}) - (S_{2s}+\lambda)\phi_{2s}(F^-)], \tag{1}$$

where S_{2s} is the overlap integral

$$\int \psi_{3d}^*(Mn^{++})\phi_{2s}(F^-)dv,$$

and the normalization factor is

$$N = (1+\lambda^2 - S_{2s}^2)^{-1/2} \tag{2}$$

if ψ_{3d} and ϕ_{2s} are normalized. (The ionic model gives a similar result, but with $\lambda = 0$, if one-electron functions in the Slater determinant are transformed to an orthogonal set.)

The unpaired, augmented $3d$ orbital interacts with the magnetic moment of the nucleus, via the Fermi contact term, to give an isotropic hfs which depends on the electron's spin density at the fluorine nucleus. In general this spin density is written as being due solely to the fractional $2s$ admixed into the wave function. It produces an effective field at the fluorine nucleus which is 4π times this spin density, or

$$H_e = 4\pi N^2 (S_{2s}+\lambda)^2 |\phi_{2s}(0)|^2, \tag{3}$$

in atomic units (i.e., 1 a.u. $= 4.2\times 10^4$ gauss). No other terms are included as these are thought to be of little importance. In particular the unpairing action of the 1s electrons is disregarded on the grounds that S_{1s} is much smaller than S_{2s} (and this is certainly true). On the other hand, $|\phi_{1s}(0)|^2$ is appreciably larger than $|\phi_{2s}(0)|^2$ and this physical fact has important consequences which have been overlooked.

Consider the augmented 3*d* function of Eq. (1) only augmented by $\phi_{1s}(\mathrm{F}^-)$ and limit the covalency to the 2*s* electrons.

$$\Phi = (1+\lambda^2 - S_{2s}^{\;2} - S_{1s}^{\;2})^{-1/2} \times[\psi_{3d}(\mathrm{Mn}^{++}) - (S_{2s}+\lambda)\phi_{2s}(\mathrm{F}^-) - S_{1s}\phi_{1s}(\mathrm{F}^-)], \tag{4}$$

and the spin density at the F^- nucleus due to the 2*s* <u>and</u> 1*s* electrons gives an effective field

$$H_e = N'^2\{(S_{2s}+\lambda)^2|\phi_{2s}(0)|^2 + S_{1s}^{\;2}|\phi_{1s}(0)|^2 + 2(S_{2s}+\lambda)S_{1s}\phi_{2s}(0)\phi_{1s}(0)\}. \tag{5}$$

(The same terms also occur in the ionic model, but with $\lambda = 0$.)

$\mathrm{KMnF_3}$ will be used to indicate the magnitude of the effect of using Eq. (5) instead of the usual Eq. (3). Values for $4\pi|\phi_i(0)|^2$ and S_i (appropriate for an F^--Mn^{++} distance of 3.95 a.u.) appear in Table I. These were calculated using recently obtained Hartree-Fock functions for[7] Mn^{++} and for[8] F^- which we believe to be more exact Hartree-Fock functions than the ones used in previous investigations.[3-5] The 2*s* parameters used here are rather different from the values [$S_{2s} = 0.05$ and $4\pi|\phi_{2s}(0)|^2 = 145.2$ a.u.] used previously—an indication that such parametrizations will be sensitive to the wave functions used.

Shulman and Knox[9] have observed an H_e of +0.753 a.u. for $\mathrm{KMnF_3}$. Setting $\lambda = 0$ and using the parameters of Table I, Eq. (3) predicts an H_e of 0.509 a.u. in fair agreement with experiment. The three terms of Eq. (5), however, are 0.509, 0.055, and -0.334 a.u., respectively, yielding an H_e of 0.230 a.u. in rather poor agreement with experiment. This difference is due to the large <u>negative</u> cross term—a term which is always of opposite sign to the other terms because ϕ_{2s} has a node and ϕ_{1s} does not. We could instead take the observed H_e of 0.753 and solve the equations for λ. Doing this, one obtains λ's of 0.013 from Eq. (3) and 0.033 from Eq. (5). Inclusion of the unpairing of the 1*s* electrons has altered the estimate of covalency by a factor of three, while it has increased the value of $(S+\lambda)$ by 27%.

Table I. $4\pi|\phi_i(0)|^2$ for F^- and overlap integrals, S_i, appropriate for an F^--Mn^{++} distance of 3.95 a.u.

$S_{1s} = 0.00453$	$4\pi\lvert\phi_{1s}(0)\rvert^2 = 2672.6$
$S_{2s} = 0.06166$	$4\pi\lvert\phi_{2s}(0)\rvert^2 = 136.58$

Further, it is clear from Eq. (4) that there are three other terms which contribute to the spin density and hence an H_e at the F^- nucleus (these terms also appear in the ionic model via a different mechanism). While two of these have been discussed,[5] they have, in general, not been included into covalent analyses of experiments. These terms are $|\psi_{3d}(r_\mathrm{F})|^2$, $-2(S_{2s}+\lambda)\psi_{3d}(r_\mathrm{F}) \times\phi_{2s}(0)$, and $-2S_{1s}\psi_{3d}(r_\mathrm{F})\phi_{1s}(0)$, where $\psi_{3d}(r_\mathrm{F})$ is the magnitude of the Mn^{++} free atom 3*d* function evaluated at the F^- nucleus. The first of these is 0.0005 a.u., the second +0.104 a.u. (with $\lambda = 0$), and the last -0.035 a.u. Their sum, 0.069 a.u., is indeed not negligible since it is 14% of the result using Eq. (3) and 30% of the result using Eq. (5).

Thus, a proper treatment of the problem, either phenomenologically or theoretically, requires the simultaneous inclusion of all the terms discussed in this Letter. These matters, the role of exchange polarization, and the expansion of the cation (and the contraction of the anion) wave functions will be reported on in a future paper.

We are grateful to A. C. Switendick and F. J. Corbató for the use of their programs.

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*The work done by one of the authors (R. E. W.) was supported in part by the Ordnance Materials Research Office.

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[1] An attempt to list all pertinent references is beyond the scope of this Letter; only original references or those papers of immediate concern will be referred to when appropriate.

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DIRECTION OF INTERNAL MAGNETIC FIELDS IN RARE EARTH IONS*

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(Received March 10, 1961)

It has recently been reported[1,2] that the effective magnetic field acting at the nuclei of Fe atoms in ferromagnetic iron has a direction opposite to that expected for the uncompensated spins of the electrons in the 3*d* shell. It has been suggested[3] that this fact may be explained by taking into account the exchange interaction between the *d* and inner core *s* electrons. This interaction leads to a difference in the wave functions of the *s* electrons which have their spins parallel or antiparallel to the direction of the uncompensated *d*-electron spins. In Fe this results in a contribution to the magnetic field at the nucleus opposite to that expected without this effect and presumably larger than all other contributions to the internal field.

It is the purpose of this note to report on the signs of magnetic fields acting at the nuclei of rare earth ions in rare earth iron garnets.[4] We have used the technique previously described,[5] of measuring the rotation of the angular correlation pattern obtained in $1^+ \rightarrow 2^+ \rightarrow 0^+$ transitions in rare earth nuclei in magnetic materials. This rotation is measured relative to the direction of a weak magnetizing field applied to the garnet samples perpendicular to the plane of the two gamma-ray detectors used to measure the angular correlation pattern. Because the *g* factors of 2^+ rotational states are known to be positive, the sign of the internal field is given uniquely by the sense of rotation. We have measured the sense of rotation for $2^+ \rightarrow 0^+$ transitions in Sm^{152}, Gd^{154}, and Dy^{160} following the decay of Eu^{152}, Eu^{154}, and Tb^{160}, respectively, in polycrystalline samples of rare earth iron garnets. We find positive rotations for Sm^{152} and Gd^{154} and a negative rotation for Dy^{160}, where a positive rotation is defined to be one which would be obtained if the nucleus were precessing in the applied magnetizing field alone. These measurements were carried out at room temperature.

To interpret these results we make use of the following: (1) The direction of magnetization of the sample is given by that of the uncompensated spins, $\vec{S}_{Fe}$, of the iron sublattices. (This is true for Eu and Sm iron garnet over the whole temperature range and for Tb and Gd iron garnets above their compensation temperatures, e.g., at room temperature.[6] (2) The orbital angular momentum $\vec{L}$ of the rare earth ions is not quenched[6] in the garnets at room temperature and the relative orientation of $\vec{L}$ and $\vec{S}$ is given by Hund's rule. (3) The spins, $\vec{S}$, of the rare earth ions are antiferromagnetically oriented with respect to the uncompensated spins, $\vec{S}_{Fe}$, of the iron sublattices.

Dy^{160}: In both the parent Tb($^7F_6$) and the daughter Dy($^6H_{15}$), Hund's rule requires that $\vec{L}$ and hence $\vec{J}$ are parallel to $\vec{S}$. Thus, $\vec{J}$ is oriented opposite to $\vec{S}_{Fe}$ and hence opposite to the direction it *alone* would possess in the applied magnetizing field. Hence, we expect a negative rotation if the internal magnetic field is produced mainly by the *f*-shell electrons in the rare earth ion. This prediction agrees with experiment. [To check our picture we have also measured the sign of rotation of the Dy^{160} below the compensation temperature of the host Tb crystal. In this case we predict and find a positive rotation.]

Sm^{152}: Because Sm($^6H_{5/2}$) has less than a half-filled shell, Hund's rule requires that $\vec{L}$ be antiparallel to $\vec{S}$ and hence parallel to $\vec{S}_{Fe}$. Since $|\vec{L}| > |\vec{S}|$, $\vec{J}$ is oriented in the direction of $\vec{S}_{Fe}$, and we expect a positive rotation. This predic-