PHYSICAL REVIEW B VOLUME 5, NUMBER 7 1 APRIL 1972

# Electronic Properties of $Fe^{2+}$ in Cubic $KMgF_3$ from Mössbauer Spectroscopy*

R. B. Frankel
*Francis Bitter National Magnet Laboratory,*[†] *Massachusetts Institute of Technology,*
*Cambridge, Massachusetts* 02139

and

J. Chappert and J. R. Regnard
*Centre d'Etudes Nucleaires, Grenoble, France*

and

A. Misetich
*Francis Bitter National Magnet Laboratory,*[†] *Massachusetts Institute of Technology,*
*Cambridge, Massachusetts* 02139
*and Comision Nacional de Energia Atomica, Gerencia de Investigaciones, Buenos Aires, Argentina*

and

C. R. Abeledo
*Chemistry Department, Brandeis University, Waltham, Massachusetts* 02154
(Received 5 November 1971)

Iron-doped $KMgF_3$ single crystals have been studied by Mössbauer spectroscopy of $Fe^{57}$. Single lines due to $Fe^{2+}$ and $Fe^{3+}$ are observed at room temperature. For $T < 12$ K, the $Fe^{2+}$ line splits into a quadrupole doublet with a splitting $\Delta E_Q' = 0.44 \pm 0.02$ mm/sec. Comparison with a random-strain model due to Ham yields a value of 120 $cm^{-1}$ for the position of the first excited spin-orbit split level. Magnetic hyperfine structure in external magnetic fields at low temperature is observed and analysis yields a value of $-495 \pm 30$ kOe for the core-polarization hyperfine field in $Fe^{2+}$ and a value of 4.1 a.u. for $\langle 1/r^3 \rangle$.

## I. INTRODUCTION

We have used Mössbauer spectroscopy with $Fe^{57}$ to study the electronic properties of the ground state of $Fe^{2+}$ in the cubic crystal $KMgF_3$. It is interesting to compare this system with $Fe^{2+}$ in cubic MgO, which has been well studied.[1-4] Jahn-Teller effects manifest themselves in MgO primarily as a reduction of the effective spin-orbit splitting and as a reduction of the orbital contribution to the magnetic moment. As covalency can produce similar reductions, comparison of the two systems may provide some insight into the relative importance of covalency and Jahn-Teller coupling.

Another interesting comparison of $MgO:Fe^{2+}$ and $KMgF_3:Fe^{2+}$ concerns the hyperfine-interaction parameters. The magnetic hyperfine structure can be observed by applying an external magnetic field and the external field also induces electric-quadrupole hyperfine structure. Also, as shown below, random-strain splitting of the ground state of $Fe^{2+}$ results in a quadrupole splitting at low temperature.[2] Taken together, analysis of these measurements yields the relative magnitudes of $\langle 1/r^3 \rangle$ and the core-polarization hyperfine field $H_c$ in the two systems.

In Sec. II A below, we present the experimental results; in Secs. II B–II D we review the theory of random-strain splitting due to Ham which is relevant to this work; in Sec. III we evaluate and discuss the results.

## II. EXPERIMENTAL RESULTS AND EVALUATION

### A. Experiments

Single crystals of 0.05-at.%-$Fe^{57}$-doped $KMgF_3$ were grown by the Czochralski method. Mössbauer measurements were made from 4.2 K to room temperature and in external magnetic fields up to 80 kOe, with absorbers which were 0.8-mm slices in a [100] direction. The room-temperature spectrum is shown in Fig. 1. There are two single lines with isomeric shifts (relative to sodium ferrocyanide) of 0.77 and 1.42 mm/sec which we assign to $Fe^{3+}$ and $Fe^{2+}$, respectively. At low temperature, the $Fe^{2+}$ line is split into a symmetric doublet[5] with separation of 0.44 mm/sec, as is shown in the $T = 4.2$ K spectrum in Fig. 1. On raising the temperature the splitting suddenly collapses to a single line at 12 K. At 4.2 K small values of applied magnetic field ($H_0 > 1$ kOe) induce a hyperfine field of $-110$ kOe at the nucleus (Fig. 2) which also collapses at 12 K. Measurements in fields up to 80 kOe at 4.2 K show that

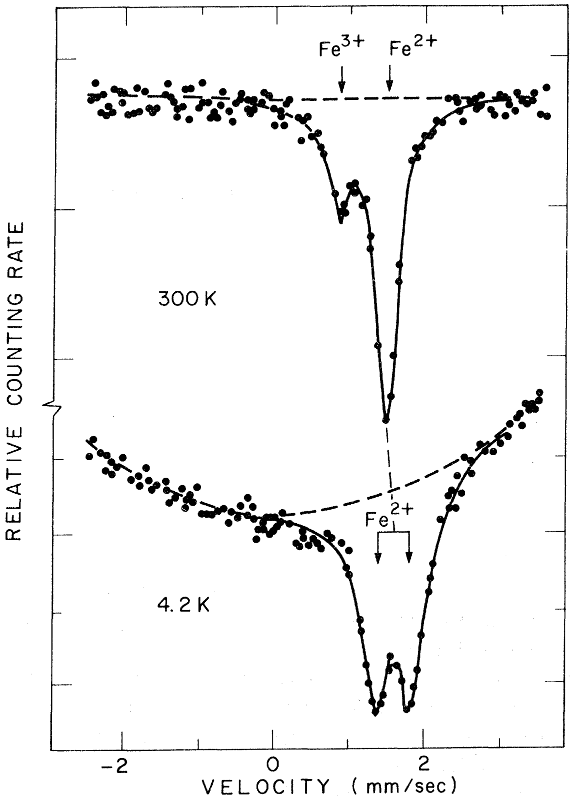

FIG. 1. Mössbauer spectra of Fe-doped $KMgF_3$ at 300 and 4.2 K showing the appearance of an $Fe^{2+}$ quadrupole doublet at low temperature. The source is $Co^{57}$ in chromium.

this is the full hyperfine field. In the larger applied fields, a quadrupole interaction of 0.44 mm/sec is observed.

These phenomena are very similar to the behavior of $Fe^{2+}$ in cubic MgO, which has been studied in detail.[2–4] In particular, the quadrupole doublet at low temperature and its narrowing at 12 K indicate that the triply degenerate $Fe^{2+}$ ground state is split by random strains in the $KMgF_3$.

### B. $Fe^{2+}$ Strain-Induced Quadrupole Interaction

The onset of $Fe^{2+}$ low-temperature quadrupole splitting observed in a cubic host in the absence of an external magnetic field was first interpreted by Ham on the basis of crystal-field theory.[2] An electric field gradient is produced at the $Fe^{57}$ nucleus by the valence electrons of $Fe^{2+}$ combined with random strains in the crystal which remove the electronic degeneracy of the ground-state triplet.

The ground state of the ferrous ion is $3d^6\,{}^5D$ with $L=2$ and $S=2$ (Fig. 3). The crystalline cubic field splits the ground term into a lower-orbital triplet and an upper-orbital doublet, separated by $10Dq \sim 10^4$ cm$^{-1}$. The orbital triplet, which behaves as an $L=1$ manifold, is further split by the spin-orbit interaction into a number of levels of which a $\Gamma_{5g}$ triplet is lowest, with an effective $J'=1$. In the presence of an arbitrary static strain (strain splitting small compared to spin-orbit coupling) the threefold degeneracy may be lifted. Each electronic eigenstate may then be written as

$$|\psi\rangle = a\,|\xi\rangle + b\,|\eta\rangle + c\,|\zeta\rangle \ , \qquad (1)$$

where $|\xi\rangle$, $|\eta\rangle$, and $|\zeta\rangle$ transform, respectively, like $yz$, $zx$, $xy$, and $a$, $b$, $c$ are real coefficients. The quadrupole splitting due to the interaction between the nuclear-quadrupole moment $Q$ of $Fe^{57}$ and the electronic state $|\psi\rangle$ was calculated by Ham[2]

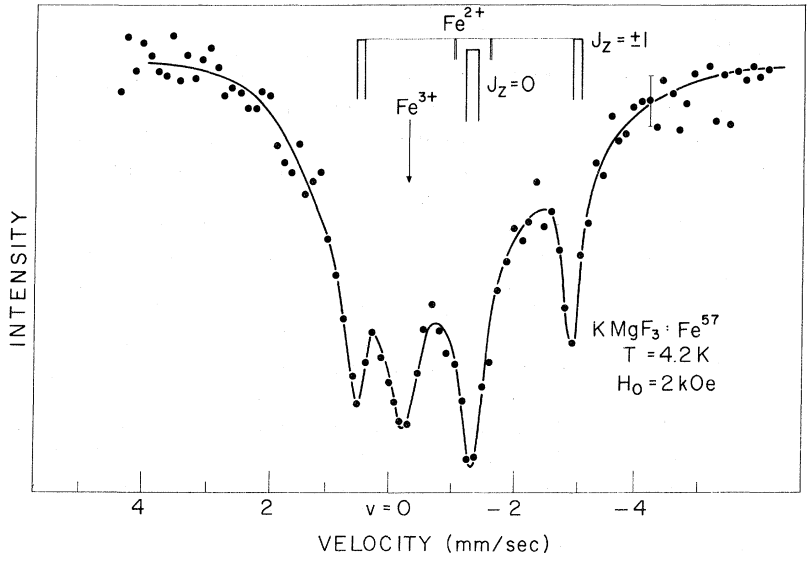

FIG. 2. Mössbauer spectrum of Fe-doped $KMgF_3$ at 4.2 K and in a longitudinal magnetic field of 2 kOe. The stick diagrams indicate the lines due to the $J_z = \pm 1$ and $J_z = 0$ states, respectively, all of which are appreciably populated at this field and temperature.

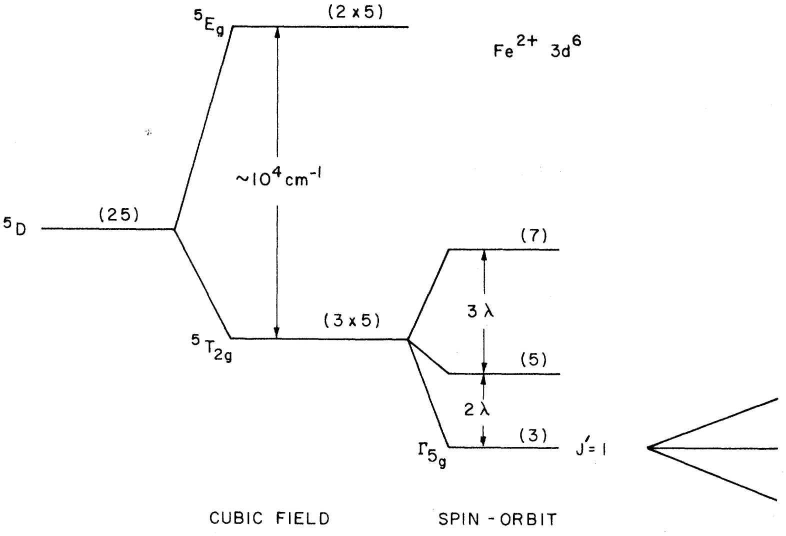

FIG. 3. Energy level diagram of the $Fe^{3+}$ $^5D$ term.

and is given by

$$\Delta E_q = 3[c_3^2 + \tfrac{1}{3}(16c_5^2 - 9c_3^2)(a^2b^2 + b^2c^2 + c^2a^2)]^{1/2} , \tag{2}$$

where $c_3$ and $c_5$ are coefficients of the electric-quadrupole-interaction operator. Using a point-charge crystal-field model, $c_3$ and $c_5$ are shown by Ham to be related,

$$-3c_3 = 4c_5 = +(3/35)\langle 1/r^3\rangle(1-R)e^2Q/I(2I-1), \tag{3}$$

where $\langle 1/r^3 \rangle$ refers to the expectation value using one-electron $d$ orbitals, $1-R$ represents Sternheimer shielding, and $I$ is the $Fe^{57}$ 14.4-keV excited-state nuclear spin. Inserting this into Eq. (2), we get

$$\Delta E_Q = (1/35)\langle 1/r^3\rangle(1-R)e^2Q \tag{4}$$

for $I = \frac{3}{2}$. Since Eq. (4) is independent of the coefficients $a, b, c$, the magnitude of $\Delta E_Q$ is the same for the three $|\psi\rangle$ states, i.e., the $\Delta E_Q$ is independent of the magnitude of the strain splitting. Therefor a unique quadrupole splitting will be observed at temperatures sufficiently low that the relaxation time $\tau$ for transitions among the three electronic states $|\psi\rangle$ is long compared to $\hbar/\Delta E_Q$.

The disappearance of the $Fe^{2+}$ quadrupole doublet above[5] 12 K is due to motional narrowing resulting from rapid transitions among the three strain-split electron states of each $Fe^{2+}$ ion. Ruling out a direct process for phonon-induced transitions [because of the small strain splitting ($\sim 10^{-2}$ $cm^{-1}$)] Ham proposed that in MgO : $Fe^{2+}$ relaxation occurs by an Orbach mechanism involving the next $Fe^{2+}$ spin-orbit level. In the case of $Fe^{2+}$ in MgO the motional narrowing occurs at 14 K, and Ham calculated that the energy separation between the spin-orbit-split levels was reduced from the free-ion value of $2\lambda = 200$ to 95 $cm^{-1}$ and pointed out that covalent bonding or Jahn-Teller coupling could be responsible for such a reduction. This calculation of the energy separation in $Fe^{2+}$ in MgO was later confirmed by far-infrared spectroscopy[6] and spin resonance,[7] and the Orbach mechanism was confirmed by measurements of the exact temperature dependence of the collapse of the quadrupole splitting.[4]

Using the same theory, we can obtain an estimate of the energy separation of the first spin-orbit-split level in $Fe^{2+}$ in $KMgF_3$. At 12 K, where the motional narrowing occurs, $\tau_1$, the electronic relaxation time, is equal to $\hbar/\Delta E_Q$ with $\Delta E_Q = 0.44$ mm/sec, i.e., $\tau_1 = 3.0\times 10^{-8}$ sec. For an Orbach-type relaxation process, the temperature dependence of $\tau_1$ is given by[2]

$$\frac{1}{\tau_1} = \frac{6G_{44}^2\Delta^3}{\pi\rho\hbar^4V_T^5}\left[1 + \frac{2}{3}\left(\frac{V_T}{V_L}\right)^5\right]e^{-\Delta/kT}, \tag{5}$$

where $\Delta = 2|\lambda|$, $\rho$ (= 3.15 $g/cm^3$) is the density of $KMgF_3$, $V_T$ and $V_L$ are the velocities of propagation of transverse and longitudinal sound waves, and $G_{44}$ is the strain-coupling coefficient for $Fe^{2+}$ in $KMgF_3$. Taking $V_L = 6.47\times 10^5$ cm/sec, $V_T = 3.94\times 10^5$ cm/sec,[8] and $G_{44} = 1000$ $cm^{-1}$,[9] we find $\Delta \approx 120$ $cm^{-1}$. This value is somewhat higher than the value calculated by Ham[2] and observed by Wong[6] for MgO:$Fe^{2+}$ (105 $cm^{-1}$), but still is significantly reduced from the free-ion value of 200 $cm^{-1}$. As the strain-coupling coefficients $G_{11}$ and $G_{44}$ are nearly twice as large in $KMgF_3$:$Fe^{2+}$ as in MgO:$Fe^{2+}$ and since the Jahn-Teller energy is proportional to the square of the coupling coefficients, larger Jahn-Teller effects are expected in $KMgF_3$:$Fe^{2+}$ than in MgO:$Fe^{2+}$ which would manifest themselves as a larger reduction of the spin-orbit coupling in $KMgF_3$.

### C. $Fe^{2+}$ Magnetic Hyperfine Interaction

We shall now discuss the $Fe^{2+}$ magnetic hyperfine interaction induced at the iron nucleus by an external magnetic field. For paramagnets we may write the observed field at the nucleus $H_n$ as

$$\vec{H}_n = \vec{H}_0 \pm \vec{H}_{hf} \ , \tag{6}$$

where $H_0$ is the external applied field and $H_{hf}$ is the field at the nucleus due to the hyperfine interaction. The observed hyperfine spectrum will depend on whether the relaxation rate among the three electron states $J'_\alpha = +1, 0, -1$ is fast or slow compared with the Larmor precession time of the nucleus. In the former case, fast relaxation, the hyperfine field seen by the nucleus is the thermal average of the contributions of the three levels,

$$H_{hf} = H^s_{hf} B_{J'}(g\mu_B H_0/kT) \ , \tag{7}$$

where $H^s_{hf}$ is the saturation hyperfine field, $B_{J'}$ is a Brillouin function for an effective spin $J'$, and $g$ is the electron $g$ factor. The spectrum should then consist of four lines ($\gamma$ rays observed along the field direction) with a splitting corresponding to $|\vec{H}_0 - \vec{H}_{hf}|$. On the other hand, if the relaxation rate is slow there is no average over the three states and each contribution is seen separately. The states $J'_\alpha = \pm 1$ give rise to hyperfine fields of equal magnitude but with opposite signs, and the state $J'_\alpha = \pm 0$ gives only a central quadrupole-split doublet. Therefore we expect the spectrum to be the superposition of the three patterns, the outermost lines of the $J'_\alpha = +1$ and $J'_\alpha = -1$ states being now separated by $H^s_{hf} + H_0$ and $H^s_{hf} - H_0$, respectively. As $H_0$ increases, the splitting between the electronic levels becomes greater and the relative line intensities vary due to changes in the Boltzmann distribution.

As in MgO:$Fe^{2+}$, we find the latter case, slow relaxation, to be appropriate for $Fe^{2+}$ in $KMgF_3$. Thus the full hyperfine splitting of $-110$ kOe is observed in magnetic fields such that the magnetic field splitting is large with respect to the random-strain splitting; this occurs for $H_0 \sim 1$ kOe, which gives us a rough upper limit of the random-strain splitting of $1.5 \times 10^{-1}$ $cm^{-1}$, using the known $g$ factor in $KMgF_3$, $g = 3.37$.[1] Above 12 K, the spectrum motionally narrows as in the zero-field case to the fast relaxation regime.

The hyperfine field at the nucleus may be written as a sum of terms

$$H_{hf} = H_C + H_{ORB} + H_{DIP} \ , \tag{8}$$

where $H_C$, $H_{ORB}$, and $H_{DIP}$ are the core-polarization, orbital, and dipolar contributions. In terms of the electronic state,

$$H_{hf} = 2[H_C/2\langle S_\alpha\rangle]\langle S_\alpha\rangle + 2\mu_B k_{hf}\langle 1/r^3\rangle\langle L_\alpha\rangle + \tfrac{1}{2}\mu_B k_{hf}\langle 1/r^3\rangle\,[3\langle L^2_\alpha\rangle - L(L+1)\langle S_\alpha\rangle] \ , \tag{9}$$

where $H_C/2\langle S_\alpha\rangle$ is the core-polarization field per spin and $k_{hf}$ is an orbital hyperfine reduction factor. For $J'_\alpha = \pm 1$, $\langle L_\alpha\rangle$ and $\langle S_\alpha\rangle$ are $\pm\frac{1}{2}$ and $\pm\frac{3}{2}$, respectively, and for $J'_\alpha = 0$, both are zero.

Values for $\langle 1/r^3\rangle$ have been calculated by Watson and Freeman[10] and it is possible to use the measured EPR reduction factor $k_{ze}$ to obtain the hyperfine reduction factor $k_{hf}$, allowing the calculation of the dipolar and orbital terms. This procedure, however, only yields an estimate of $H_C$ because as discussed in Ref. 3 there are uncertainties in $k_{hf}$ and calculated values of $\langle 1/r^3\rangle$. Another approach is to take the value of $\langle 1/r^3\rangle$ from the calculation of the electric field gradient, Eq. (4), because as shown by Freeman and Watson[10] the $\langle 1/r^3\rangle$ appropriate to magnetic interactions only differs by at most 10% from that appropriate to electric interactions. Such a procedure also allows a more self-consistent comparison of the hyperfine parameters for $Fe^{2+}$ in MgO and in $KMgF_3$.

### D. Magnetic-Field-Induced Quadrupole Interaction

The origin of the magnetic-field-induced quadrupole interaction is completely independent of the strain-induced coupling mentioned above. The theory has been explicated by Ham in his discussion of $Fe^{2+}$ in MgO.[2] In large applied fields (~ 50kOe) at 4.2 K, the Zeeman splitting (~ 9 $cm^{-1}$) is much larger than the strain splitting (~ $1.5 \times 10^{-1}$ $cm^{-1}$), and the ground-state wave functions are the eigenstates of $J'_\alpha$ with $\alpha$ in the direction of $H_0$. Using crystal-field theory, Ham showed that for $H_0$ along [100] or [111], $\Delta E_Q$ is proportional to $+3C_3$ or $+4C_5$, respectively, i.e., $\Delta E_Q$ will have the same magnitude but opposite signs in the two cases. This was observed in $Fe^{2+}$ in MgO.[4,5] In $Fe^{2+}$ in $KMgF_3$ at 50 kOe and 4.2 K only the $J'_\alpha = -1$ state is populated and for $H_0$ parallel to [100], we observed $\Delta E_Q = 0.44$ mm/sec, and the interaction is negative, in agreement with Ham's theory and confirming the value of the electric-quadrupole splitting obtained from the random-strain split regime.

## III. DISCUSSION

From Eq. (4) we see that the difference in $\Delta E_Q$ for $Fe^{2+}$ in $KMgF_3$ and in MgO is due to a change in $\langle 1/r^3\rangle$. Both Ingalls[11] and Hazony[12] have proposed correlations between $\Delta E_Q$ and $\langle 1/r^3\rangle$ for ferrous compounds. Ingalls[11] uses susceptibility data and hyperfine-interaction measurements in $FeSiF_6 \cdot 6H_2O$ to obtain $\Delta E_0 = 4.1$ mm/sec and $\langle 1/r^3\rangle = 3.5$ a.u., where $\Delta E_0$ is a "bare" electric-quadrupole-coupling constant which is obtained from the measured low-temperature quadrupole splitting (3.6 mm/sec at 4.2 K) by calculating the effect of the mixing of the ground state with higher-lying states by the crystal field and by the spin-orbit coupling. Johnson and Ingalls then obtain $\langle 1/r^3\rangle = 3.0 \pm 0.3$ a.u. for $FeF_2$,[13] from $\Delta E_0 = 3.5$ mm/sec, and use this value of $\langle 1/r^3\rangle$ to calculate $H_{DIP}$ and $H_{ORB}$ for $FeF_2$ and are then able to obtain $H_C = -518 \pm 25$ kOe. In MgO : $Fe^{2+}$, Ham estimates[11] that the observed quadrupole splitting at low temperature is about 9% of the bare quadrupole splitting yielding $\Delta E_0 = 3.5$ mm/sec from which $\langle 1/r^3\rangle \approx 3.0$ a.u. If we take the effects of dynamic quenching and covalency to be roughly the same for $Fe^{2+}$ in MgO and for $Fe^{2+}$ in $KMgF_3$, we obtain for the latter case $\Delta E_0 = 4.8$ mm/sec and $\langle 1/r^3\rangle_{eff} = 4.1$ a.u. Using these values we now calculate the $H_{DIP}$ and $H_{ORB}$ terms in Eq. (9) (Table I) and obtain $H_C = -344$ kOe and $H_C = -372$ for $Fe^{2+}$ in MgO and $Fe^{2+}$ in $KMgF_3$, respectively. These values refer to $\langle S_\alpha\rangle = \frac{3}{2}$. The values of the core-polarization field in various compounds generally quoted in the literature refer to $\langle S_\alpha\rangle = 2$ and these values for the two systems at hand are

$$H_C = -460 \text{ kOe for } Fe^{2+} \text{ in MgO} ,$$

$$H_C = -495 \text{ kOe for } Fe^{2+} \text{ in } KMgF_3 .$$

It is difficult to assign errors for these values, but roughly 5% is probably appropriate. The largest error concerns the normalization for $\langle 1/r^3\rangle$. This was calculated by Ingalls[11] from hyperfine parameters obtained by Johnson[14] which were extrapolations from incomplete magnetization and could involve some error, especially if the hyperfine field is not strictly proportional to the magnetization (in the case of relaxation effects, for example).

Hazony[12] has recently noted the correlations between $H_C$, $\langle 1/r^3\rangle$, and the isomer shift for various ferrous compounds. His schema differ from that of Ingalls in that he uses the low-temperature quadrupole splittings instead of the "bare" values defined by Ingalls.[11] Still, he fortuitously obtains the same value of $\langle 1/r^3\rangle$ for $FeF_2$ as Johnson and Ingalls[13] (see above), but he estimates $\langle 1/r^3\rangle = 3.8$ a.u. for $FeSiF_6 \cdot 6H_2O$. This is a point that clearly needs further study. In any case, Hazony notes that $H_C \sim -500$ kOe for ferrous compounds with large quadrupole splittings (= large values of $\langle 1/r^3\rangle$) and large isomer shifts (IS) (relative to iron metal). Covalency effects manifest themselves as a reduction in IS, $\Delta E_Q$, and $H_C$. Our results are in qualitative agreement with this trend. Chappert *et al.*[15] have recently reconsidered the IS scale for $Fe^{57}$ based on the isomer shifts of $Fe^{2+}$ and $Fe^{3+}$ in $KMgF_3$ and concluded that $Fe^{2+}$ in $KMgF_3$ is almost purely ionic. The isomeric shift in $Fe^{2+}$ in MgO indicates some covalency, and this reflects itself in the smaller quadrupole splitting and $H_C$.

TABLE I. Hyperfine parameters for MgO : $Fe^{2+}$ and $KMgF_3$ : $Fe^{2+}$.

| | MgO : $Fe^{2+}$[a] | $KMgF_3$ : $Fe^{2+}$ |
|---|---|---|
| $g$ | 3.428 | 3.37[b] |
| $\langle 1/r^3\rangle$ | 3.0 a.u. | 4.1 a.u. |
| $\Delta E_Q$ | 0.32 mm/sec | 0.44 mm/sec |
| $H_C(\langle S\rangle = 2)$ | −460 kOe | −495 kOe |
| $H_{DIP}$ | +6 kOe | +7 kOe |
| $H_{ORB}$ | +218 kOe | +255 kOe |
| $H^s_{hf}$ | −120 kOe | −110 kOe |
| IS | −1.06 mm/sec | −1.46 mm/sec |

[a] Reference 3. [The values quoted here differ from those in Table III of Ref. 3 because here we have taken a different value of $\langle 1/r^3\rangle$ (see text).]

[b] J. T. Vallin and W. W. Piper, quoted in Ref. 1.

In conclusion, we have found using Mössbauer spectroscopy that $Fe^{2+}$ in $KMgF_3$ behaves very similarly to $Fe^{2+}$ in MgO, in that the threefold degenerate ground state expected from simple crystal-field theory is split by random strains into three close-lying singlet states and that a quadrupole splitting is observed at low $T$ because, as in MgO, relaxation processes between the strain-split levels are very slow. From a comparison of the hyperfine parameters, we find that covalency effects play a role in reducing the value of $\langle 1/r^3\rangle$ and $H_C$ in MgO : $Fe^{2+}$, whereas these parameters approach the free-ion values for $KMgF_3$:$Fe^{2+}$. As in MgO:$Fe^{2+}$, we find that in $KMgF_3$:$Fe^{2+}$ the spin-orbit-coupling constant is considerably reduced from the free-ion value. In fact, the values of the spin-orbit-coupling constants in the two systems are remarkably similar. Ham *et al.*[1] estimated that in MgO:$Fe^{2+}$ covalency effects could account for at most 10% of the reduction in the spin-orbit-coupling constant. Above we found that covalency in MgO:$Fe^{2+}$ reduced the hyperfine-coupling parameters relative to $KMgF_3$:$Fe^{2+}$, which suggests that the difference in the values of $\Delta$ in the two systems (120 $cm^{-1}$ in $KMgF_3$:$Fe^{2+}$, 105 $cm^{-1}$ in MgO:$Fe^{2+}$) is due to covalency. If the remaining reduction is due to Jahn-Teller effects, then we find that these effects are roughly the same in the two systems, even though the value of $G_{44}$ in $KMgF_3$ is twice as large as in MgO. However, this may be simply coincidental and perhaps ascribable to different details of the phonon spectrum in the two systems. As Ham *et al.* have noted[1] the $g$ factors in the two systems differ and suggest larger Jahn-Teller effects in $KMgF_3$:$Fe^{2+}$.

---

*Work supported by the Air Force Office of Scientific Research.

†Now supported by the National Science Foundation.

[1] F. S. Ham, W. M. Schwarz, and M. C. M. O'Brien,

Phys. Rev. 185, 548 (1969).

[2] F. S. Ham, Phys. Rev. 160, 328 (1967).

[3] J. Chappert, R. B. Frankel, A. Misetich, and N. A. Blum, Phys. Rev. 179, 578 (1969).

[4] H. R. Leider and D. N. Pipkorn, Phys. Rev. 165, 494 (1968).

[5] J. Chappert, R. B. Frankel, A. Misetich, and N. A. Blum, J. Phys. Suppl. C 1, 941 (1971).

[6] J. Y. Wong, Phys. Rev. 168, 337 (1968).

[7] R. L. Hartman, E. L. Wilkinson, and J. G. Castle, Bull. Am. Phys. Soc. 12, 642 (1967).

[8] H. M. Rosenberg and J. K. Wigmore, Phys. Letters 24A, 317 (1967).

[9] J. K. Wigmore, H. M. Rosenberg, and D. K. Garrod, J. Appl. Phys. 39, 682 (1968).

[10] R. E. Watson and A. J. Freeman, Phys. Rev. 123, 2027 (1961).

[11] R. Ingalls, Phys. Rev. 188, 1045 (1969).

[12] Y. Hazony, Phys. Rev. B 3, 711 (1971).

[13] D. P. Johnson and R. Ingalls, Phys. Rev. B 1, 1013 (1970).

[14] C. E. Johnson, Proc. Phys. Soc. (London) 92, 748 (1967).

[15] J. Chappert, J. R. Regnard, and J. Danon, Compt. Rend. 272, 1070 (1971).

---

PHYSICAL REVIEW B VOLUME 5, NUMBER 7 1 APRIL 1972

# Temperature Dependence of the Spin-Lattice Interaction for $Gd^{3+}$ in $ThO_2$ and $CeO_2$[†]

S. B. Oseroff and R. Calvo[*]

*Centro Atômico Bariloche, Comisión Nacional de Energía Atômica,*
*Instituto de Física "Dr. José A. Balseiro," Universidad Nacional de Cuyo,*
*San Carlos de Bariloche, Argentina*

(Received 21 July 1971)

The second- and fourth-order spin-lattice coefficients of $Gd^{3+}$ in cubic positions of $ThO_2$ and $CeO_2$ crystals have been measured as a function of temperature between 4 and 360 °K by electron-paramagnetic-resonance experiments in uniaxially stressed crystals. The second-order coefficients are considerably different for the two crystals, and these coefficients show a large variation with temperature. A detailed theoretical calculation of these coefficients has not been carried out; however, it is possible to qualitatively interpret the observed temperature variation in terms of effects due to the modulation of the orbit-lattice interaction by the lattice vibrations. The temperature-variation curves are explained using an Einstein model for the vibrations of the oxygen ligands of the paramagnetic ions. The fourth-order coefficients are similar for the two crystals and are temperature independent in the range studied. The effect of a hydrostatic strain on the energy levels of the ion is used to explain the observed temperature variation of the cubic field parameter in terms of the thermal expansion of the crystal.

## I. INTRODUCTION

The interpretation of the crystal-field splittings of ions with a half-filled shell of electrons, $Cr^{+}$, $Mn^{2+}$, and $Fe^{3+}$ of the $3d$ group and $Eu^{2+}$, $Gd^{3+}$, and $Tb^{4+}$ of the rare-earth group, has involved serious difficulties. The crystalline electric field acting alone cannot remove the degeneracy of the ground level of these $S$-state ions and it is necessary to consider high-order processes involving spin-dependent interactions together with the crystalline field. A great deal of experimental information obtained by electron-paramagnetic-resonance (EPR) techniques exists for these ions and many theoretical papers dealing with this problem are found in the literature. The reader is referred to Refs. 1 and 2, where an important part of the theoretical work done on this problem until 1966 is quoted.

Important progress has been made in the understanding of the $S$-state iron-group ions and, even though a good fit between theory and experiment does not yet exist, an order of magnitude agreement has been found.[2] However, less progress has been made in the explanation of the splittings of the ground state of the rare-earth $S$-state ions, even though experimental data exist for several cubic crystals[3] and for many lattices of lower symmetry.

An attempt to estimate the ionic contributions to the ground-state splitting of trivalent gadolinium in lanthanum ethyl sulphate has been made by Wybourne.[1] Wybourne considers the contributions coming from several mechanisms involving the crystal field with other interactions in different orders of perturbation and also relativistic effects, configuration mixing, and nonlinear electrostatically correlated crystal-field interactions. The result of the calculation does not agree with the experimental values and Wybourne suggests that the correct explanation should involve the details of the interaction of the gadolinium ion with the lig-