Isotopic Shift in the Electron-Spin-Resonance Absorption Spectrum of Cr³⁺ in Magnesium Oxide*

S. A. Marshall, J. A. Hodges, and R. A. Serway

Physics Division, IIT Research Institute, Chicago, Illinois

The fine and hyperfine structure spectra of trivalent Cr^{52} $(I=0)$ and $Cr^{53}(I=\frac{3}{2})$ located substitutionally for magnesium in magnesium oxide at sites of axial symmetry, where the axial distortion is along a crystal [100] direction, have been re-examined at 3-cm wavelength. Spectral constants for both isotopes have been measured with a precision equivalent to determining absorption-line field positions to within ± 10 mOe. From measurements taken at 77°K, it is concluded that the crystalline-field splitting energy for Cr^{52} is (0.10 ± 0.01) Oe greater in magnitude than that for Cr^{53}, which corresponds to a relative shift in this parameter of 1.1×10^{-4}. In addition, the components of the spectroscopic splitting tensor for the two isotopes are found to be the same to within the limits of experimental error. From data taken over the range 4.2 through 350°K, it is found that the isotopic shift decreases with temperature while the crystalline-field splitting energy increases with temperature. The origin of the isotopic shift and its temperature dependence are discussed in terms of a dynamical crystal structure.

I. INTRODUCTION

RECENTLY, an isotope effect has been reported in the electron-spin-resonance absorption spectrum of trivalent iron located substitutionally for calcium in single-crystal calcite.[1] This effect was observed as a slight magnetic field displacement between the fine structure components of Fe^{56} and the effective fine structure components of Fe^{57}. It was found that this displacement could be attributed to a slight (roughly one part in 10^4) increase in the magnitude of the spin-Hamiltonian crystalline-field parameters of Fe^{57} relative to those of Fe^{56}.

Since trivalent iron is an S-state ion, an analysis of the isotope effect is inhibited by the fact that there may be more than one process contributing to removal of spin degeneracy by a crystalline electric field.[2-5] Therefore, it would seem advantageous to observe such an effect in a non-S-state ion whose ground orbital term under the influence of a crystalline electric field is nondegenerate. In seeking such an effect, it seems desirable that the crystal-ion system in question possess a number of specific characteristics. These are (i) that the paramagnetic ion have at least two isotopes, each in sufficient abundance to be readily detectable, and that the spectral components of the two or more isotopes be completely resolved, this being most easily achieved when one or more of the isotopes exhibits hyperfine structure; (ii) that the system have a nonzero crystalline-field splitting energy, which is the case for an ion with $S>\frac{1}{2}$ located in a noncubic crystalline electric field; and, (iii) that the crystalline-field splitting energy be sufficiently large compared to the widths of the resonance absorptions that its

magnitude may be determined to within one part in 10^4.

A system satisfying these requirements is the ^4F trivalent chromium ion located at sites of axial symmetry in magnesium oxide with the axial distortion along a crystal [100] direction.[6] In this spectrum, each fine-structure transition exhibits a quintet resonance absorption pattern due to the two principal isotopes Cr^{52} $(I=0)$ and Cr^{53} $(I=\frac{3}{2})$ of natural abundances 83.8 and 9.4%, respectively. The spectral components of this quintet pattern are well resolved because the linewidths are approximately one Oe while the Cr^{53} hyperfine-structure splitting is near 17 Oe. Also, because of the narrowness and strength of the resonance absorption lines, and since the crystalline-field splitting energy is near 900 Oe, a difference in this parameter between the two isotopes of the order of one part in 10^5 should be detectable.

The results of an investigation on this crystal-ion system are presented here and do in fact show the presence of an isotopic shift in the effective fine-structure spectrum of Cr^{53} relative to that of Cr^{52}. This shift is interpreted as a difference in the crystalline-field splitting energies between the two chromium isotopes, and is found to be of the same relative order of magnitude as that reported in the fine-structure spectrum of trivalent iron located substitutionally for calcium in single-crystal calcite.

The conventional or static theory of the origin of crystalline fields is extended here to include the influence of the dynamical nature of the crystal-ion system. Such a treatment is found to explain the presence of the observed isotope shift.

II. EXPERIMENTAL PROCEDURE

Magnesium oxide single-crystal specimens used in this investigation were found to contain of the order of ten parts per million by weight of chromium ion impurities, and exhibited no optical absorptions in the visible or near infrared region. These specimens

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FIG. 1. First-derivative chart-recorder tracing of the $M=\frac{1}{2} \to \frac{3}{2}$ transition of Cr^{3+} at $\theta=0$ in the axially distorted sites of magnesium oxide.
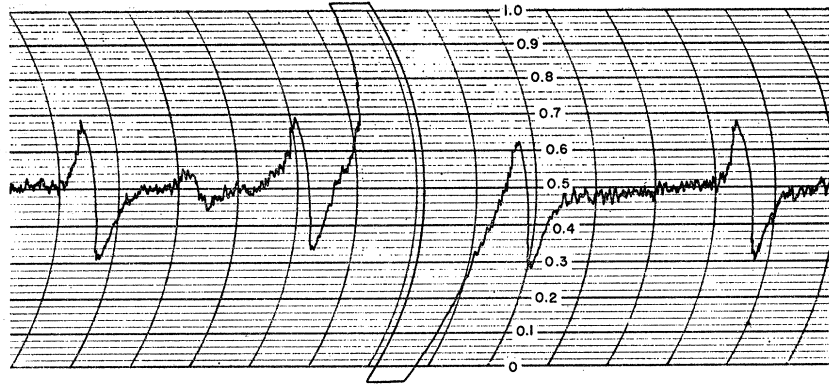
were cleaved into rectangular parallelepipeds of dimensions $0.3 \times 0.3 \times 2.0$ cm, and mounted along the axis of a 3-cm-wavelength cylindrical cavity resonator operating in the TE_{011} mode and having a loaded Q of about 7500. The spectrometer used 30-Mc/sec superheterodyne detection and was operated at microwave power levels of from one to ten μW so as to reduce saturation broadening of resonance absorption lines.

In taking data, a procedure similar to that described in the experimental section of Ref. 1 was followed. The principal feature of this procedure is the requirement of a constant monitor on the signal oscillator frequency during a run of data. For such a run, data were accepted only when the signal oscillator frequency remained constant to within ± 10 kc/sec, where, by a run is meant a sequence of measurements which determine the magnetic field strengths of the quintet components of a Cr^{3+} fine-structure resonance absorption. To achieve the precision necessary for this experiment, a magnetic-field stabilization network was used together with a phase-sensitive lock-in-type detector to establish the magnetic-field positions of the peaks of resonance-absorption lines. Typically, the resonance-absorption field strength of a particular chromium-ion-quintet component was determined to within ± 0.01 Oe.

III. RESULTS

The spin Hamiltonian used to describe the magnetic spectrum of this crystal-ion system is

$$\mathcal{K}=\beta \mathbf{H}\cdot \mathbf{g}\cdot \mathbf{S}+\tilde{D}[S_z^2-\tfrac{1}{3}S(S+1)]+\mathbf{I}\cdot \tilde{\mathbf{A}}\cdot \mathbf{S}$$
$$+\beta^n \mathbf{H}\cdot \mathbf{g}^n\cdot \mathbf{I}+eQ[I_z^2-\tfrac{1}{3}I(I+1)], \quad (1)$$

where the terms have their conventional spectroscopic meaning.[7] When the Zeeman field is directed along a crystal [100] direction, which is defined to be the z direction, the spin Hamiltonian conveniently reduces into two components, one which yields diagonal matrix elements in the electron and nuclear spin states repre-

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sentation

$$\mathcal{K}_z=g_{11}\beta H S_z+\tilde{D}[S_z^2-\tfrac{1}{3}S(S+1)]+\tilde{A}_{11}I_z S_z$$
$$+g_{11}{}^n\beta^n H I_z+eQ[I_z^2-\tfrac{1}{3}I(I+1)], \quad (2)$$

and a component

$$\mathcal{K}_z'=(\tilde{A}_1/2)[I_+S_-+I_-S_+], \quad (3)$$

which yields only off-diagonal matrix elements connecting states $|M,m\rangle$ to states $|M\pm 1, m\mp 1\rangle$, where M and m are electron and nuclear-spin quantum numbers, respectively.

Under the selection rules $\Delta M=\pm 1$ and $\Delta m=0$, the nuclear Zeeman and quadrupole terms in Eq. (2) make no contribution to the magnetic-field positions of the hyperfine-structure resonance-absorption lines when the nuclear states are pure spin functions. However, the presence of the operator $\mathcal{K}_z'$ mixes nuclear spin functions. In the present case, the amount of such mixing is quite small, so that the nuclear Zeeman and quadrupole terms will have negligible influence on the resonance-absorption line field positions. Consequently, the zeroth-order eigenvalue expression for the Zeeman field applied along the z axis is

$$E_z^0=[g_{11}\beta H+m\tilde{A}_{11}]M+\tilde{D}[M^2-\tfrac{1}{3}S(S+1)], \quad (4)$$

from which the zeroth-order approximation to the resonance-absorption line field strength positions for the transitions $M \to M+1$, $m \to m$ are calculated to be

$$H_0(M,m)=H(\nu)-mA_{11}-D[2M+1], \quad (5)$$

where $H(\nu)=h\nu/g_{11}\beta$, $A_{11}=\tilde{A}_{11}/g_{11}\beta$ and $D=\tilde{D}/g_{11}\beta$.

An example of the quintet resonance absorption pattern associated with each fine-structure transition is shown in Fig. 1. Each such quintet pattern is characterized by a strong central field component due principally to Cr^{52} $(I=0)$ and by a hyperfine-structure quartet due solely to Cr^{53} $(I=\frac{3}{2})$. At the $\theta=0$ orientation, there are three such fine-structure quintet patterns. From the field strength position $H_0(M)$ of each of the fine-structure lines, the spin-Hamiltonian parameters g_{11} and D for Cr^{52} can be obtained by using Eq. (5) with $m=0$. For Cr^{53}, however, the same equa-
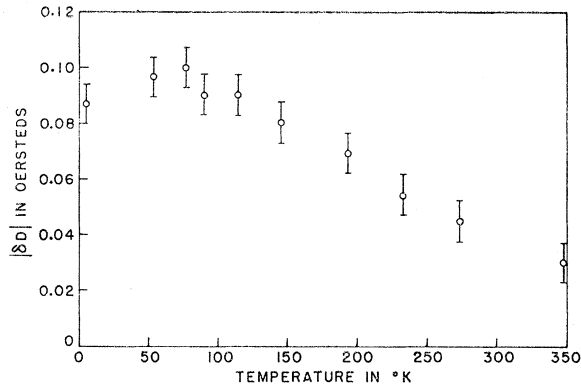
FIG. 2. Temperature dependence of the isotope shift in the crystalline-field splitting energy of Cr^{52} relative to Cr^{53}.

TABLE I. Typical values of the fine and hyperfine structure data obtained at 77°K. H_1 through H_4 are the Cr^{53} hyperfine structure field positions while H_0 is due to Cr^{52}. $\nu = [9526.58 \pm 0.01]$ Mc/sec; all field positions are determined to ± 0.01 Oe.

	$\theta=0$ $M=\frac{1}{2} \to \frac{3}{2}$ (Oe)	$\theta=0$ $M=-\frac{3}{2} \to -\frac{1}{2}$ (Oe)	$\theta=\pi/2$ $M=-\frac{3}{2} \to -\frac{1}{2}$ (Oe)
H_1	5172.32	1706.83	4275.80
H_2	5189.96	1689.42	
H_3	5207.79	1671.89	
H_4	5225.71	1654.19	4325.53
H_0	5199.32	1680.25	4299.33

tion yields only approximate results for $H_0(M)$, the mean-field position of a hyperfine quartet, since off-diagonal matrix elements due to the perturbations of Eq. (3) now appear in the energy matrix. As long as the hyperfine-interaction energy is small compared to the Zeeman interaction and crystalline-field splitting energies, the contribution of these off-diagonal elements to the resonance-absorption field strength positions may be calculated using conventional perturbation theory. The mean field position of a hyperfine quartet, that is, the equivalent fine-structure field position for Cr^{53}, is then given by

$$H_0(M)=\frac{1}{2}[H(M,-m)+H(M,m)]$$
$$+\frac{1}{4}A_\perp^2[I(I+1)-m^2]\left\{2\frac{(S-M)(S+M+1)}{H+D(2M+1)}\right.$$
$$-\frac{(S+M+2)(S-M-1)}{H+D(2M+3)}$$
$$\left.-\frac{(S-M+1)(S+M)}{H+D(2M-1)}\right\}, \quad (6)$$

where $H(M,m)$ is the magnetic-field position corresponding to the transition $M \to M+1$, $m \to m$, and where H in the denominators is the mean of $H(M,m)$ and $H(M,-m)$. In this expression, the perturbations are taken to second order in the parameter $A_\perp$. Such perturbations have, in fact, been calculated out to fourth and sixth order in $A_\perp$, and these higher order terms have been found to contribute cumulatively less than one mOe to $H_0(M)$ and consequently can be neglected.

Using Eqs. (5) and (6), the fine-structure spin Hamiltonian parameters $g_{||}$ and D for Cr^{53} can be obtained. In practice, both $g_{||}$ and D were obtained from data taken on the $M=\frac{1}{2} \to \frac{3}{2}$, and $M=-\frac{3}{2} \to -\frac{1}{2}$ transitions. The $M=-\frac{1}{2} \to \frac{1}{2}$ transition could not be used to determine $g_{||}$ because it was obscured by other resonance-absorption lines in the central field region. Some typical data obtained from runs taken at 77°K

are given in Table I. Analysis of these data obtained in the manner outlined in the foregoing section shows that for the $M=\frac{1}{2} \to \frac{3}{2}$ transition, $H_0(M)$ of Cr^{52} is greater than $H_0(M)$ of Cr^{53} by approximately 0.20 Oe. Analogous data for the low-field $M=-\frac{3}{2} \to -\frac{1}{2}$ transition shows that $H_0(M)$ of Cr^{52} is less than $H_0(M)$ of Cr^{53} by nearly 0.20 Oe. This indicates that $D(Cr^{52})$ is numerically greater than $D(Cr^{53})$ by (0.10 ± 0.01) Oe, and that there is no measurable difference in the value of $g_{||}$ for the two isotopes.

The temperature dependence of the isotopic shift in the crystalline-field splitting energy between Cr^{52} and Cr^{53} was measured over a range of 4.2 to 350°K and is shown in Fig. 2. This shift is seen to increase in magnitude with decreasing temperature, reaching a maximum of (0.10 ± 0.01) Oe at low temperatures. Measurements of the isotope shift could not be made to the desired precision above 350°K owing to the increased uncertainty in determining resonance absorption line peak field positions as a consequence of increasing linewidths. At liquid helium temperatures, slight line broadening due to saturation effects also contributed to the uncertainty in determining the isotope shift.

To obtain the hyperfine splitting tensor component $A_{||}$, a perturbation correction similar to that carried out for Eq. (6) was applied, giving

$$A_{||}=\frac{1}{2m}[H(M,-m)-H(M,m)]$$
$$+\frac{1}{4}A_\perp^2\left\{\frac{(S+M+2)(S-M-1)}{H+D(2M+3)}\right.$$
$$\left.-\frac{(S-M+1)(S+M)}{H+D(2M-1)}\right\}, \quad (7)$$

where the terms have the same meaning as in Eq. (6).

At 77°K, the best value of $A_{||}$ was found to be (17.73 ± 0.02) Oe, with the positive value determined relative to the negative value of the crystalline-field splitting energy. $A_{||}$ showed no temperature dependence over the range 4.2 to 350°K.

Further data concerning the isotope shift were obtained by studying the $\theta=\pi/2$ spectrum. For this study, it was found unnecessary to alter the Zeeman

field direction relative to the specimen, since this spectrum is provided at the same crystal-to-Zeeman-field orientation by trivalent chromium ions having axial distortion along either a crystal [010] or [001] direction. In addition to obtaining perpendicular quantities, there are a sufficient number of transitions at this orientation to give an independent measure of the crystalline field splitting energy and its isotopic shift. The spin Hamiltonian at $\theta = \pi/2$ and $\phi = 0$ takes the form

$$\mathcal{H}_z = g_1 \beta H S_z - \tfrac{1}{2}\tilde{D}[S_z^2 - \tfrac{1}{3}S(S+1)] + \tfrac{1}{4}\tilde{D}[S_+^2 + S_-^2]$$
$$+ \tilde{A}_1 I_z S_z + \tfrac{1}{2}\tilde{A}_{11}[I_+S_- + I_-S_+], \qquad (8)$$

which can be obtained from Eqs. (2) and (3) by first defining the Zeeman field direction to be the z axis and then rotating the crystal coordinates through the polar angle $\theta = \pi/2$. An inspection of this spin Hamiltonian shows that it can, except for the term $\tfrac{1}{4}\tilde{D}[S_+^2 + S_-^2]$, be obtained from Eqs. (2) and (3) by substituting $-\tfrac{1}{2}\tilde{D}$ for $\tilde{D}$ and perpendicular quantities for parallel quantities. If, in addition to these substitutions, $-(M+1)$ is substituted for M in the eigenvalue expression, Eqs. (6) and (7) can, except for one modification, be used to obtain the Cr⁵³ equivalent of a fine-structure field position and its hyperfine-structure constant at $\theta = \pi/2$. This substitution of $-(M+1)$ for M is due to the fact that the crystalline-field splitting energy effectively changes sign under this change in orientation. This modification is a consequence of the term $\tfrac{1}{4}\tilde{D}[S_+^2 + S_-^2]$ in the spin Hamiltonian Eq. (8) which mixes states $|M\rangle$ with states $|M\pm 2\rangle$. As a result of this mixing, the term $\tilde{A}_1 I_z S_z$ of the $\theta = \pi/2$ spin Hamiltonian does not operate on pure electronic spin states, but upon mixed states which are eigenvectors of the $\theta = \pi/2$ fine-structure spin Hamiltonian. The expectation values of S_z evaluated in these eigenvector states $\psi(M)$ are given by

$$\langle \psi(M) | S_z | \psi(M) \rangle$$
$$= \frac{1}{1 + \Gamma_+^2 + \Gamma_-^2}\{M + (M+2)\Gamma_+^2 + (M-2)\Gamma_-^2\}, \quad (9)$$

where

$$\Gamma_\pm = \tfrac{1}{4}D \sum_{K \neq M} \frac{\langle M | S_\pm^2 | K \rangle}{E(M) - E(K)}. \qquad (10)$$

On using these expectation values for S_z, it becomes necessary to correct numerically the value of A_1 obtained from Eq. (7) by making appropriate substitutions because of this spin-state mixing. This correction amounts to dividing the value of A_1 as obtained from Eq. (7) by the expression $[1 + F(M+1) - F(M)]$, where

$$F(M) = 2\frac{\Gamma_+^2 - \Gamma_-^2}{1 + \Gamma_+^2 + \Gamma_-^2}. \qquad (11)$$

As a result of the sign change in the effective crystalline-field splitting energy on going from $\theta = 0$ to $\pi/2$,

TABLE II. Constants in the spin Hamiltonian at 77°K.

Quantity	Value
g_{11}	1.97854 ± 0.00005
g_1	1.98171 ± 0.00005
A_{11}	$[17.73 \pm 0.02]$ Oe
A_1	$[17.67 \pm 0.02]$ Oe
D^{52}	$[-879.76 \pm 0.04]$ Oe
$D^{53} - D^{52}$	$[0.10 \pm 0.01]$ Oe

the perturbation correction of Eq. (7) for A_1 at $\theta = \pi/2$ must have its sign changed, assuming A_{11} and A_1 to be of the same sign, which seems reasonable for an atomic ion. The best value obtained for A_1 at $T = 77°$K is given by 17.67 ± 0.02 Oe; see Table II. As was the case for A_{11}, the parameter A_1 is found to be temperature-independent from 4.2 to 300°K. Finally, at 77°K, $H_0(M)$ of Cr⁵² is found to be 0.09 ± 0.02 Oe greater than that of Cr⁵³ for the high-field $\theta = \pi/2$ transitions; see Table I. This result is, to within first-order approximation, in agreement with the data obtained at $\theta = 0$. That is, since D goes over to $-\tfrac{1}{2}D$ as $\theta = 0$ goes over to $\pi/2$, the isotope shift in $H_0(M)$ should diminish in magnitude by 50%.

IV. DISCUSSION AND CONCLUSION

To develop a satisfactory interpretation of the isotope effect in the electron-spin-resonance absorption spectrum of a crystal-ion system, it would be advantageous if there existed a well-established theory to account for spectral parameters. In the present case, however, there seems to be no single interaction process which adequately accounts for $2D$, the spin multiplicity splitting of the $^4A_2$ ground term of trivalent chromium located at an axially distorted octahedral site. Consider for example the simple crystal-field theory applied to trivalent chromium located substitutionally for aluminum in α-Al₂O₃.[8,9] This theory considers interactions with only those terms which issue from the ^4F free-ion ground term and predicts a $^4A_2$ spin multiplicity splitting of 0.01 cm⁻¹ with the $\pm\tfrac{1}{2}$ doublet lying lowest, while both optical and electron-spin-resonance absorption spectra yield a splitting of 0.38 cm⁻¹ with the $\pm\tfrac{3}{2}$ doublet lying lowest.[6,10,11] The inadequacy of the crystal-field theory in dealing with this specific problem, as well as problems related to the optical spectra, has led to considerable work in this area. Such work has involved application of configuration mixing and covalency,[12] reduction of local symmetry,[13] introduction

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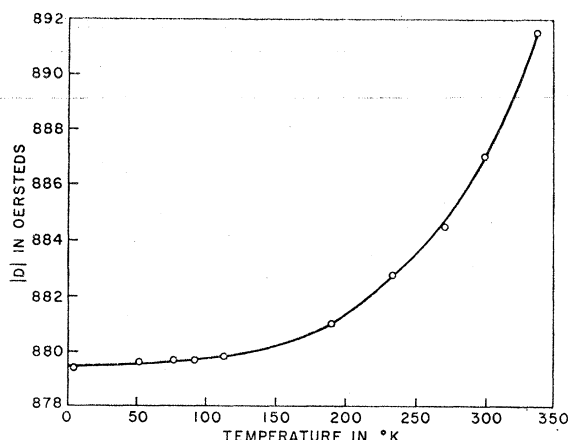
FIG. 3. Temperature dependence of the crystalline-
field splitting energy.

of anisotropic spin-orbit coupling,[14] as well as the use of molecular-orbital-theory computer programs.[15] Although these theoretical treatments deal primarily with optical properties of the crystal-ion system, they also provide information on the splitting of the $^4A_2$ ground term. However, none of the interactions of these theories are presently considered to be the sole contributor to $2D$. Consequently, rather than attempting to incorporate all interactions in a theory and then deriving the isotope effect, a simpler approach will be adopted. In this approach, an attempt is made at an interpretation of the isotope effect which is specific to the extent that it assumes the splitting in question arises from some interactions which, in second order, connect the $^4A_2$ ground term with other noncubic terms of this ion. The form for such a splitting is taken to be

$$2D = \sum_{p \neq 0} \frac{V^2(p)}{E(p) - E(0)}, \qquad (12)$$

where $V(p)$ is a matrix element which connects $|p\rangle$, an excited noncubic term of the ion, with $|0\rangle$, the ground term. This formalism, which considers a static crystal-ion system, enjoys the advantage of being adaptable to take account of the fact that the paramagnetic ion along with its host is a dynamical system. Such an adaptation is effected by first noting that each electronic level is, in fact, a manifold potential well, with each sheet of the manifold associated with a specific oscillational mode of the crystal-ion system. As a consequence, each virtual transition of the second-order perturbation expression in Eq. (12) will take place between electron-vibration states rather than between pure electronic states. Furthermore, there will be associated with each mode of oscillation a given set of such virtual transitions, and because of the differences

which exist in the transformation properties between the various modes of oscillation, no transitions will take place which connect the levels of one mode in the ground electronic state with the levels of different modes in an excited electronic state. With each virtual transition, there is associated a crystalline-field-splitting, energy-dependent magnetic resonance absorption whose relative strength will depend upon the thermal population of the initial vibration state. At the temperatures over the range 4.2 to 350°K, the excited electronic states are nearly unpopulated. Thus, a given magnetic resonance absorption line will appear as the superposition of all such individual absorptions, and its mean-field position will be determined by a Boltzman averaging of the crystalline-field splitting energy.

The procedure followed in obtaining the average of the crystalline-field splitting energy parallels that used by Benedek, Englman, and Armstrong in calculating the temperature dependence of the paramagnetic chemical shift,[16] and by Englman in calculating the temperature dependence of the transition energy of an optical absorption.[17] As a consequence, the treatment presented here will not contain calculational details.

On taking into consideration the dynamical nature of the crystal-ion system and upon properly augmenting electronic wave functions with vibration wave functions, the mean crystalline-field splitting energy for a given mode of oscillation is given by

$$2\bar{D} = \{\sum_n \exp[-n(\hbar\omega/kt)]\}^{-1} \sum_{p \neq 0} \sum_{r,n} |\langle r | n \rangle|^2$$

$$\times \exp[-n(\hbar\omega/kt)]\left[\frac{V^2(p)}{\Delta E(p) + \delta E}\right], \qquad (13)$$

where $\Delta E(p) = E(p) - E(0)$, $\delta E = (r + \frac{1}{2})\hbar\omega' - (n + \frac{1}{2})\hbar\omega$, ω and ω' are the frequencies characteristic of the given mode of oscillation in the ground and excited electronic states, respectively, and the $|n\rangle$ and $|r\rangle$ refer to oscillator wavefunctions of the ground and excited electronic states, respectively. By expanding the denominator of the right-hand side of Eq. (13) and rearranging terms, the following expression is obtained:

$$2\bar{D} = \sum_{p \neq 0} \frac{V^2(p)}{\Delta E(p)}(\{\sum_n \exp[-n(\hbar\omega/kt)]\}^{-1}\sum_{r,n} |\langle r | n \rangle|^2$$

$$\times \exp[-n(\hbar\omega/kt)][1 - \delta E/\Delta E(p)]). \qquad (14)$$

If Eq. (14) is to be further reduced, some specific assumptions must be made regarding the nature of the potential wells associated with the ground and excited electronic levels. Following Ref. 17, three assumptions are made: (i) that the $^4A_2$ and connecting wells are quadratic, having different characteristic frequencies, (ii) that the excited electronic wells are horizontally

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displaced from the ground electronic well by an amount $2aQ_0$, where Q_0 is the zero-point oscillation amplitude, and (iii) that for each of the wells, the potential function contains a term λQ^3. In the last two cases, which are treated simultaneously, each of the potential wells is taken to have the same characteristic frequency and the specific departures from the quadratic potential problem are treated by approximation methods. The final result for the temperature-dependent average of the crystalline-field splitting energy is given by

$$\frac{\bar{D}}{D_0}=1+\hbar\omega\left\langle 4\frac{(\lambda-\lambda')^2Q_0^6}{\hbar^2\omega^2\Delta E}-a^2\right\rangle_{\text{av}}$$
$$+\hbar\omega\left\langle\frac{(\lambda-\lambda')aQ_0^6}{\hbar\omega\Delta E}-\frac{\omega^2-\omega'^2}{2\omega^2\Delta E}\right\rangle_{\text{av}}$$
$$\times\left[\frac{1}{2}+\frac{1}{\exp(\hbar\omega/kt)-1}\right]-\hbar\omega\left\langle\frac{60(\lambda-\lambda')^2Q_0^6}{\hbar^2\omega^2\Delta E}\right\rangle_{\text{av}}$$
$$\times\left[\frac{1}{2}+\frac{1}{\exp(\hbar\omega/kt)-1}\right]^2, \quad (15)$$

where $2D_0=\sum_{p\neq 0}V^2(p)/\Delta E(p)$ and where the averaging is performed with respect to the weighting function $V^2(p)/\Delta E(p)$ over the excited states $|p\rangle$ of the ion.

From this expression and from the fact that vibrational frequencies are related to the oscillator mass by $\omega=(K/M)^{1/2}$, which gives $\delta\omega=-\frac{1}{2}\omega(\delta M/M)$, it can be seen that a variation in $\bar{D}$ with respect to the effective mass of the crystal-ion oscillator does exist, and furthermore that such a variation should be temperature-dependent.

As it stands, the expression given by Eq. (15) is overly complex in that the temperature-dependent component of the crystalline-field splitting energy associated with a given mode of oscillation is a function of five parameters. The complexity of the situation is further compounded on taking the variation in $\bar{D}$ with respect to oscillator mass. In an effort to reduce this complexity, it is now assumed that the anharmonicities in the potential functions of the ground and connecting electronic states are the same. This assumption seems not too unreasonable and enjoys the advantage of yielding a result which can readily be summed over all the modes of the crystal-ion system. On setting $\lambda=\lambda'$, Eq. (15) greatly simplifies and yields the following approximate result:

$$\delta\bar{D}/D_0\approx-\frac{1}{2}\{(\bar{D}-D_0)/D_0\}(\delta M/M). \quad (16)$$

This expression provides three predictions; (i) that the isotopic shift in $\bar{D}$ should be proportional to the change in nuclear mass; (ii) that the temperature dependence of $\delta\bar{D}$ should be similar but of opposite sign to the

temperature dependence of $\bar{D}$; and (iii) that a reasonable estimate of $(\delta\bar{D}/D_0)$ should be obtainable from data on the temperature dependence of $\bar{D}$. The first prediction is reasonably well born out by data previously obtained for the isotopic shift of Fe^{3+} in calcite.[1] In this case, it was found that the shift in the crystalline-field parameters of Fe^{57} with respect to Fe^{56} is of opposite sign and half that of the shift for Fe^{54}. The second prediction is seen to be qualitatively fulfilled by comparing the data of Fig. 2 with the data of Fig. 3, which gives values for $\bar{D}$ from 4.2°K through to 350°K. Finally, using Eq. (6) and the experimental data for $\bar{D}$ given in Fig. 3, a relative isotope shift in $\bar{D}$ is calculated to be of the order of 1 part in 10^4, which is the shift experimentally observed.

Although the actual distribution of local modes is not well known, the foregoing simplified equations, taken together with the experimental data, enable a value to be obtained for the average difference in the vibrational frequencies of the ground and excited orbital states. With the average ground-state vibrational frequency ω taken as 300 cm⁻¹, a value of $\omega'=0.8\omega$ is obtained for the average excited-state vibrational frequency. This difference in vibrational frequencies is close to those found in aqueous transition-metal ion complexes.[16]

An extension of a static theory of the $^4A_2$ ground term splitting to include dynamical properties is seen to provide a reasonable interpretation of the observed isotope shift and its temperature dependence in relation to the temperature dependence of the crystalline-field splitting energy. Two other possible sources of an isotope effect exist. The first arises from the specific mass dependence of the spin-orbit coupling parameter λ.[18,19] Here, the mass of the nucleus is included by considering the reduced mass of the electron. The relative size of such an effect, which is temperature-independent, on an isotopic shift in $2D$ is calculated to be about two orders of magnitude below the observed effect. The other possibility is that the radial potential function of the paramagnetic ion is sensitive to the ionic mass. This possibility cannot be readily evaluated, but it does seem that it would be small and that its magnitude would be insensitive to temperature.

ACKNOWLEDGMENTS

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