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JAHN–TELLER EFFECT OF AN ORTHORHOMBIC CENTER IN MgO

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The orthorhombic distortion of octahedral Ti^{3+} : MgO system having a three fold orbital degeneracy is discussed on a model considering covalency and the essential features of static Jahn–Teller effects. Both linear and the main second order lattice-ion interaction terms are included to explain the observed *g*-anisotropy.

1. Introduction

The EPR spectra of Ti^{3+} in MgO have been reported by Davies and Wertz [1] and the results are interpreted by these authors in terms of a static orthorhombic crystalline electric field model. The symmetry of the anisotropic EPR spectra were taken as evidence that the orthorhombic field includes in it a sizable contribution from the static Jahn–Teller (JT) distortion at low temperatures. In the present study we propose to calculate the *g*-anisotropy by considering the static orthorhombic JT interaction including the second order JT term as well as the covalency overlap between the ligand charges with the charge cloud of the central impurity ion.

2. Theory

In an octahedral coordination of symmetry O_h, the free ion $3d^1\ ^2D$ ground state of the Ti^{3+} impurity ion splits up into an orbital doublet ^2E_g higher in energy than the lower orbital triplet $^2T_{2g}$ by $10\,Dq$, where Dq is the one-electron cubic field splitting parameter. The small superimposed orthorhombic component of the ligand field lifts all orbital degeneracies of the cubic field levels. The potential for the cubic and static crystalline orthorhombic fields, including the quadratic and quartic terms but neglecting the spin-orbit (SO) interaction is of the form [2]

$$V = D(x^4+y^4+z^4-3/5r^4)+[Ax^2+By^2-(A+B)z^2]+[ax^4+by^4-(a+b)z^4 +6ay^2z^2+6bz^2x^2-6(a+b)x^2y^2], \tag{2.1}$$

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where the first term represents the cubic component and the remaining terms are due to the orthorhombicity of the static crystalline electric field.

Van Vleck [3] has shown that any combination of $Q_2 = (\varphi \sin\theta)$ and $Q_3 = (\varphi \cos\theta)$ modes of displacement will produce an equivalent splitting of the cubic field levels, Now $\theta = 90°$ and $270°$ correspond to orthorhombic x, y deformations. In our problem we describe the small x, y orthorhombic type of JT compression (dilatation) by the angle $\Delta\varphi$ which is linked with the equilibrium displacement parameter ϱ_0 for Q_2 by the expression

$$\varphi_0 = (6)^{-1/2} R_0 \sin 2\Delta\varphi,$$

where R_0 is half the space diagonal of the cube. With $\Delta\varphi > 0$ we get a x dilatation and y compression, for $\Delta\varphi = 0$, the orthorhombic JT potential becomes zero.

Using the equivalent operator formalism we obtain from Eq. (2.1) an expression for the JT orthorhombic perturbation potential in the form

$$\begin{aligned}\Delta V_{\text{ortho}} &= A_2^2(L_+^2 + L_-^2) + A_4^4[(35L_z^4 - 155L_z^2 + 72) - 7/8(L_+^4 + L_-^4)] \\ &- A_4^2[(7L_z^2 - 11)(L_+^2 + L_-^2) + (L_+^2 + L_-^2)(7L_z^2 - 11)] + (\Delta V_{\text{ortho}})^2, \end{aligned} \tag{2.2}$$

with

$$\begin{aligned} A_2^2 &= \tfrac{1}{2}(A-B)(e/R_0^3)(\sin 2\Delta\varphi), \\ A_4^2 &= \tfrac{1}{2}(a-b)(e/R_0^5)(\sin 2\Delta\varphi), \\ A_4^4 &= -\tfrac{1}{2}(a+b)(e/R_0^5)(\sin 2\Delta\varphi)^2, \end{aligned} \tag{2.3}$$

and $(\Delta V_{\text{ortho}})^2$ is the second order JT interaction operator as given by Englman [4].

Operating the total Hamiltonian $\mathscr{H} = \sum -e(V_{\text{cubic}} + \Delta V_{\text{ortho}})$ on the cubic field wavefunctions

$$d_1,\ d_{-1},\ \frac{1}{\sqrt{2}}(d_2 - d_{-2}) \quad \text{and} \quad d_0,\ \frac{1}{\sqrt{2}}(d_2 + d_{-2})$$

we get a secular matrix which gives the eigenvalues

$$\begin{aligned} E_{1,2} &= -4Dq + 12B_4^4 \mp (3B_2^2 + 2B_4^2) + \tfrac{1}{2}(K_e \mp K_t)\delta^2, \\ E_3 &= -4Dq - 24B_4^4 - K_e\delta^2, \\ E_{4,5} &= 6Dq \mp [324(B_4^4)^2 + 3(2B_2^2 - B_4^2)^2]^{1/2}, \\ (\delta &= \sqrt{2}\,qi, \quad i = x, y) \end{aligned} \tag{2.4}$$

with

$$\begin{aligned} B_2^2 &= -eA_2^2\alpha\langle r^2\rangle_{\text{av}}, \qquad B_4^2 = 8/3\pi^{1/2}kA_4^2\langle r^4\rangle_{\text{av}}, \\ B_4^4 &= -eA_4^4\beta\langle r^2\rangle_{\text{av}}, \\ Dq &= -3/5eD\beta\langle r^4\rangle_{\text{av}}, \quad (\alpha = -2/21,\ \beta = 2/63) \end{aligned} \tag{2.5}$$

where k is a numerical factor arising from the Wigner coefficient relations. The effect of the second order JT interaction in the excited orbital doublet state has not been considered in the present problem as this causes a very small additional displacement in these levels at $\sim 20000\ \mathrm{cm}^{-1}$ above the fundamental level.

The corresponding eigenfunctions are

$$\psi_1 \equiv |\varphi_{xz}\rangle \equiv \frac{1}{\sqrt{2}}(d_1-d_{-1}), \quad \psi_4 \equiv a_1\phi_{3z^2-r^2}+b_1\phi_{x^2-y^2} \equiv a_1 d_0+\frac{b_1}{\sqrt{2}}(d_2+d_{-2}),$$

$$\psi_2 \equiv |\varphi_{yz}\rangle \equiv \frac{1}{\sqrt{2}}(d_1+d_{-1}), \quad \psi_5 \equiv b_1\varphi_{3z^2-r^2}-a_1\varphi_{x^2-y^2} \equiv b_1 d_0-\frac{a_1}{\sqrt{2}}(d_2+d_{-2}),$$

$$\psi_3 \equiv |\varphi_{xy}\rangle \equiv \frac{1}{\sqrt{2}}(d_2-d_{-2}), \tag{2.6}$$

where $|\varphi_{xy}\rangle$ etc. are the molecular orbital wavefunctions as modified by the appropriate combinations of ligand σ and π orbitals. In Eq (2.4) K_e and K_t are the second order JT coupling coefficients.

3. *Calculation of g values*

The spin orbit interaction has no effect in the first order on the lowest orbital singlet state φ_{xz} and hence for the calculation of g values we adopt Pryce's spin Hamiltonian technique [5]. The spin Hamiltonian is

$$\mathcal{H}_S = \langle\psi_1|\mathcal{H}'|\psi_1\rangle - \sum_{n\neq 1}\frac{\langle\psi_1|\mathcal{H}'|\psi_n\rangle\langle\psi_n|\mathcal{H}'|\psi_1\rangle}{E_n-E_1}$$

$$+\sum_{m\neq 1}\sum_{n\neq 1}\frac{\langle\psi_1|\mathcal{H}'|\psi_m\rangle\langle\psi_m|\mathcal{H}'|\psi_n\rangle\langle\psi_n|\mathcal{H}'|\psi_1\rangle}{(E_m-E_1)(E_n-E_1)}$$

$$-\sum_{n\neq 1}\frac{\langle\psi_1|\mathcal{H}'|\psi_n\rangle\langle\psi_n|\mathcal{H}'|\psi_1\rangle\langle\psi_1|\mathcal{H}'|\psi_1\rangle}{(E_n-E_1)^2}, \tag{3.1}$$

where the perturbation Hamiltonian is of the form

$$\mathcal{H}' = \lambda \boldsymbol{L}\cdot\boldsymbol{S}+\beta\boldsymbol{H}\cdot(\boldsymbol{L}+2\boldsymbol{S}). \tag{3.2}$$

For $\boldsymbol{H}||z$, the spin Hamiltonian reduces to the form

$$\mathcal{H}_S^{(z)} = \beta H[2S_z(1-u_1\lambda_z\chi_z)-iS_xS_y(p_1+p_2)+p_3S_x^2+p_4S_y^2+p_5S_z^2]. \tag{3.3a}$$

For $\boldsymbol{H}||x$, it becomes

$$\mathcal{H}_S^{(x)} = \beta H[2S_x(1-v_1\lambda_x\chi_x)+iS_yS_z(q_1-q_2)], \tag{3.3b}$$

and for $\boldsymbol{H}\|y$, it is approximated as

$$\mathscr{H}_S^{(y)} = \beta H[2S_y\{1-(w_1+w_2)\lambda_y\chi_y\}-S_xS_z(\gamma_1+\gamma_2)]. \tag{3.3c}$$

In Eqs (3.3a), (3.3b), (3.3c) terms independent of H and those involving β^2H^2 are not retained as they are not important in the calculation of g-values. Operating the spin Hamiltonians $\mathscr{H}_s^{(i)}$, $(i = x, y. z)$ on the spin states $|1/2\rangle$ and $|-1/2\rangle$, we get a secular matrix which finally gives the g values

$$\begin{aligned} g_x &= g_0[(1-v_1\lambda_x\chi_x)-(q_1-q_2)], \\ g_y &= g_0[\{1-(w_1+w_2)\lambda_y\kappa_y\}-(r_1+r_2)], \\ g_z &= g_0[(1-u_1\lambda_z\kappa_z)-(p_1+p_2-p_3-p_4-p_5)], \end{aligned} \tag{3.4}$$

where

$$u_1 = \frac{1}{E_2-E_1}, \quad v_1 = \frac{1}{E_3-E_1}, \quad w_1 = \frac{(\sqrt{3}\,a_1-b_1)}{E_4-E_1}, \quad w_2 = \frac{(\sqrt{3}\,b_1+a_1)}{E_5-E_1},$$

$$p_1 = \frac{\lambda_x\lambda_y\kappa_x\kappa_y}{(E_2-E_1)(E_3-E_1)}, \quad p_2 = \frac{\lambda_x\lambda_y\kappa_x\kappa_y b_1(b_1-\sqrt{3}\,a_1)}{(E_3-E_1)(E_4-E_1)}, \quad p_3 = \frac{\lambda_x^2\kappa_x^2}{(E_3-E_1)^2},$$

$$p_4 = \frac{\lambda_y^2\kappa_y^2(\sqrt{3}\,a_1-b_1)^2}{(E_4-E_1)^2}, \quad p_5 = \frac{\lambda_y^2\kappa_y^2(a_1+\sqrt{3}\,b_1)^2}{(E_5-E_1)^2},$$

$$q_1 = \frac{\lambda_y\lambda_z\kappa_y\kappa_z}{(E_2-E_1)(E_3-E_1)}, \quad q_2 = \frac{2\lambda_y\lambda_z\kappa_y\kappa_z b_1(b_1-\sqrt{3}\,a_1)}{(E_3-E_1)(E_4-E_1)},$$

$$r_1 = \frac{\lambda_x\lambda_z\kappa_x\kappa_z}{(E_2-E_1)(E_3-E_1)}, \quad r_2 = \frac{2\lambda_x\lambda_z\kappa_x\kappa_z b_1(\sqrt{3}\,a_1-b_1)}{(E_3-E_1)(E_4-E_1)}. \tag{3.5}$$

With the molecular orbitals of Eq. (2.6) the reduced matrix elements for the orbital and spin orbit (SO) interaction are defined as follows

$$\begin{aligned} \langle T_2\|\boldsymbol{L}\|T_2\rangle &= \kappa_i, \quad \langle T_2\|\lambda\boldsymbol{L}\|T_2\rangle = \lambda_i, \\ \langle T_2\|\boldsymbol{L}\|E\rangle &= \kappa_i', \quad \langle T_2\|\lambda\boldsymbol{L}\|E\rangle = \lambda_i'. \end{aligned} \tag{3.6}$$

In the present problem we have considered $\kappa_i = \kappa_i'$ and $\lambda_i = \lambda_i'$.

4. Results

The parameters appearing in the calculation of g values are the cubic field splitting constant Dq, the JT field coefficients B_2^2, B_4^2, B_4^4, $K_e\delta^2$ and $K_t\delta^2$, and the covalency reduction factors κ_i and $\lambda_i(i = x, y, z)$. The cubic and JT field parameters are obtained by comparing the transitions [1] with our Eq. (2.4). The covalency parameters are then adjusted by trial and error computations so as to get the best fit between the theoretical and observed g

values at 20 K. The agreement between the calculated and experimental g values [1] are shown in Table I. Comparison with the experimental results indicates that in the orthorhombic JT center there is an appreciable covalency overlap of the ligand charges with the charge cloud of the central impurity ion.

TABLE I

Field parameters and g-values

Field parameters

$10\,Dq = 20\,000$, $B_2^2 = 3784.5$, $B_4^2 = -5031.7$, $B_4^4 = -54.5$,
$\lambda_x = 132.4$, $\lambda_y = 126.3$, $\lambda_z = 138.6$, $\lambda = 154$, (free ion value)
(all in cm^{-1})
$K_e\delta^2 = 29.9\ cm^{-1}$, $K_t\delta^2 = 32.6\ cm^{-1}$,
$\varkappa_x = 0.860$, $\varkappa_y = 0.820$, $\varkappa_z = 0.880$

g-values

	present calculation JT model		on static crystal field model	experimental results [1]
	20 K	4 K	20 K	
g_x	1.8484	1.8483	1.8782	1.8487+0.0007
g_y	1.9461	1.9455	1.9463	1.9464+0.0007
g_z	1.7669	1.9680	1.7654	1.7670+0.0007

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