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Dynamical Jahn-Teller effects in the ground $^4T_{1g}$ and the excited $^4T_{2g}$ orbital triplets of Co^{2+} ion in a MgO crystal

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In the background of the failure of the simple crystal field theory to explain the spin-orbit splitting and the Zeeman effect of the ground ($^4T_{1g}$) and the excited ($^4T_{2g}$) levels of MgO:Co^{2+}, the dynamical Jahn-Teller effects—or, in other words, the vibronic interactions—are shown to explain consistently and satisfactorily all the experimental observables. The theory is worked out in the approximation of the cluster model. Because of the difference in the relative imporance of the Jahn-Teller energy (E_{JT}) and the spin-orbit coupling strength for the two levels, a numerical solution of the problem is necessary for $^4T_{1g}$, and for $^4T_{2g}$ one can use Ham's theory directly. Besides showing the importance of the vibronic interactions, this analysis brings out two features: First, the effective frequency (ω_E) of the E_g mode of vibration of the cluster interacting with the electron orbital is same for the ground and the excited states; second, the effect due to covalency is less important than assumed earlier. The analysis is extended to compare the results on $KMgF_3$:Co^{2+}. Conclusions that are arrived at regarding the values of ω_E and E_{JT} and covalency effects are physically justified for MgO as well as for $KMgF_3$.

I. INTRODUCTION

A considerable amount of experimental work has been done on the triplet orbital level of paramagnetic ions in octahedral crystals which confirms the importance of the dynamical Jahn-Teller (JT) effects as developed by Ham in such systems.[1–15] In the present work we are interested in studying the importance of the vibronic interactions in both the ground and the excited orbital levels, $^4T_{1g}$ and $^4T_{2g}$, respectively, of MgO : Co^{2+}. The study is made within the limitations of the molecular-cluster model, where a localized mode of vibrations with a definite frequency is assumed to be effective in the orbit-lattice interactions of the impurity ion. In fact, the studies of the dynamical JT effects which have been undertaken so far amount principally to a quantitative assessment of the JT energy (E_{JT}) and the effective frequency (ω) of the particular mode of vibration of the molecular cluster which interacts with the orbital motions of the impurity electron. In actual calculations attempts have been made to interpret the experimental results, considering at most two effective frequencies of vibration[14] of the molecular cluster instead of one particular frequency. Only recently, when the fruitfulness and success of the cluster model are generally accepted, is interest taken in explaining the effective frequencies of vibration of the molecular cluster in terms of the vibrational modes of the lattice.[13,16] The present study of the vibronic interactions in the ground and excited orbitals of Co^{2+} in the same lattice permits us to see if the effective frequency of the localized mode of vibration of the cluster changes for the two orbital states, which might arise from changes in the force constants induced by the second-order term of the orbit-lattice interaction. This is interesting because for the ground orbital triplet $^4T_{1g}$ the vibronic interaction is expected to be small,[17] whereas optical results and their qualitative analysis by Ralph and Townsend[4] indicate rather strong vibronic effects for the excited orbital triplet $^4T_{2g}$.

In Sec. II we shall first show that the static crystal field model with an effective spin-orbit interaction parameter cannot explain consistently the experimental results of the g value[18] and the shift in the g value of the lowest doublet Γ_6, using uniaxial strain,[19] the magnetic susceptibility,[20] and the optical-absorption[4] results of MgO : Co^{2+}. In Sec. III the vibronic interactions are incorporated for both the $^4T_{1g}$ and the $^4T_{2g}$ orbitals, and the different experimental results are shown to be accounted for satisfactorily, with physically justified values of $\hbar\omega_E$ and E_{JT}. In this analysis, orbital coupling is considered with the E_g mode of vibration only. The reasons why we neglect the coupling with the T_{2g} mode of vibration are also discussed in Sec. III. It should be noted that the order of magnitude of the splitting of the ground orbital triplet $^4T_{1g}$ due to spin-orbit interaction is same as the energy corresponding to the peak of the phonon distribution function[21] in pure and Ni^{2+}-doped MgO crystals, and, as the effective frequency of vibration of the cluster is expected to be close to this value, we have considered the vibronic and spin-orbit interactions in the ground orbital triplet $^4T_{1g}$ numerically, taking proper account of the second-order effects of the excited orbital $^4T_{2g}$ as well. It is found that the variables k, k' (which take into account the covalency effects in the ground and excited orbitals, respectively), $\hbar\omega_E$, and E_{JT} can be varied only within limited range of values in order that the experimentally known g value, spin-lattice coupling parameter F_{11}, and energy separation between the ground doublet Γ_6 and the quadruplet Γ_8 of the orbital $^4T_{1g}$ can be simultaneously explained. E_{JT} is found to be small but not negligible for $^4T_{1g}$. For the excited orbital $^4T_{2g}$ the spin-orbit splitting is small compared to the effective phonon energy and E_{JT}, so we can use Ham's theory directly, taking the spin-orbit interaction as a perturbation due to the excited vibronic states $|T_{2g}n_\theta n_\epsilon\rangle$ on the ground vibronic states $|T_{2g}00\rangle$. The second-order contribution to the spin-orbit splitting due to the presence of near-lying electronic orbital states is also taken into account. The results indicate that $\hbar\omega_E$ is nearly the same for the ground and excited triplet (~ 400 cm^{-1}), though E_{JT} differs very much for the two orbitals, being ~ 100 cm^{-1} for the ground and ~ 420 cm^{-1} for the excited triplet. It is interesting to note that the fitting with experimental values cannot be achieved if the pure covalency parameters k and k' are taken to be unity. Best fits are obtained when k and k' lie in the range 0.96–0.98.

The splittings and the shifts of the spin-orbit states of the excited orbital $^4T_{2g}$ of KMgF$_3$: Co^{2+} have recently been studied by Sturge and Guggenheim[3] as functions of applied stress and the Zeeman field. We have explained his results quite satisfactorily, using the same model of calculation as for the $^4T_{2g}$ orbital of MgO : Co^{2+} and have obtained k ~ 0.97, k' ~ 0.95, $\hbar\omega_E$ ~ 200 cm^{-1}, and E_{JT} ~ 175 cm^{-1}. The significance of the results of our analysis for both MgO : Co^{2+} and KMgF$_3$: Co^{2+} is discussed in Sec. IV.

In Appendix A, we have shown that the orbital ^2E_g, which lies in between the ground (T_{1g}) and excited (T_{2g}) orbitals and is very close[4] to T_{2g}, has very little effect in changing the spin-orbit splittings of either $^4T_{1g}$ or $^4T_{2g}$ in the second order. In Appendix B we have given the derivations and magnitudes of V_E and V_T, which are the coupling parameters of the electron orbital with the E_g and T_{2g} modes of vibration of the cluster, both for the T_{1g} and T_{2g} orbitals, on the basis of the point-charge model for the ligand ions.

II. LIMITATIONS OF STATIC CRYSTAL FIELD THEORY TO EXPLAIN AVAILABLE SPECTROSCOPIC DATA ON MgO : Co^{2+}

The Co^{2+} ion is of $3d^7$ configuration and has a lowest term ^4F (Fig. 1). In octahedral symmetry this term splits into the ground orbital triplet $^4T_{1g}$ and the excited orbitals $^4T_{2g}$, a triplet, and $^4A_{2g}$, a singlet. The ^4P term,[18] which is 12 500 cm^{-1} above the ground term ^4F, results in a $^4T_{1g}$ level in octahedral symmetry, and, consequently, there is mixing between the two $^4T_{1g}$ triplets. The ground orbital triplet is given by

$$\psi(T_{1g}) = \psi(T_{1g})_F \cos\theta + \psi(T_{1g})_P \sin\theta \quad , \tag{1}$$

where

$$\theta = \tan^{-1}\frac{-\{(15B+6Dq)-[(15B+6Dq)^2+64(Dq)^2]^{1/2}\}}{8Dq} .$$

The values of Dq and B are taken[18] to be 930 and 840 cm^{-1}, respectively. The result of this mixing[22] is to change the effective angular momentum $\vec{l}$ of the ground orbital triplet by a factor $a = (\cos^2\theta - \frac{2}{3}\sin^2\theta)$. A slight change[4,5] in the values of Dq and B alters this factor insignificantly. The ground orbital triplet T_{1g} splits into spin-orbit levels Γ_6, $\Gamma_{8,1}$, $\Gamma_{8,2}$, and Γ_7, with Γ_6 lying lowest. The g value[18] for this doublet is found to be 4.278. No direct measurement of the energy separations between these levels is available. Measurements of the spin-lattice relaxation time[23] do not show any Orbach-type mechanism to be active, so that the positions of the excited spin-orbit levels cannot be obtained from such measurements. The separation between the first excited level $\Gamma_{8,1}$ and the ground level Γ_6 has been estimated indirectly from the magnetic susceptibility of the system and is found[20] to be 306 cm^{-1}. The $\Gamma_{8,2}$ and Γ_7 levels are degenerate in the first order. They split due to second-order spin-orbit interactions.

The excited orbital triplet $^4T_{2g}$, which lies about

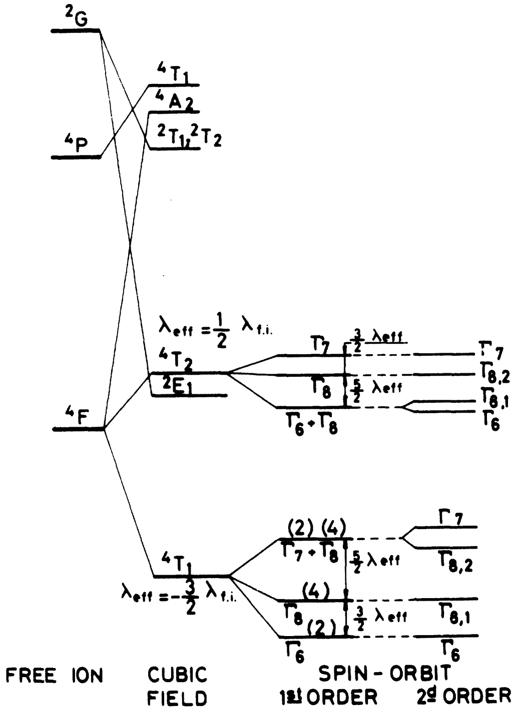

FIG. 1. Low-lying energy levels of Co^{2+} in MgO crystal in static crystal field model($\lambda_{f,i} = -180$ cm^{-1}).

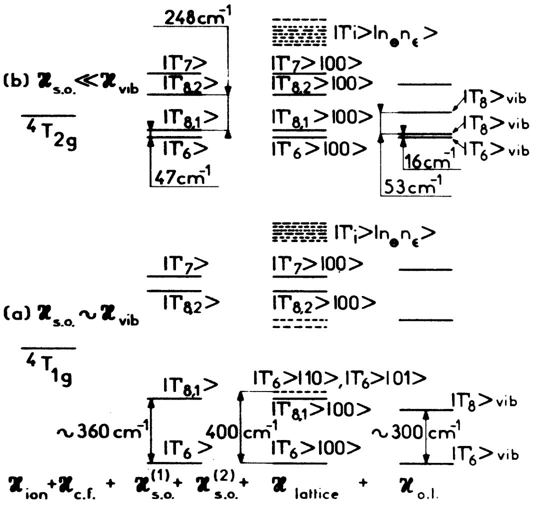

FIG. 2. Schematic diagram of the splitting of the orbitals $^4T_{1g}$ and $^4T_{2g}$ of Co^{2+} in MgO crystal in dynamic crystal field model. In case (a) a numerical analysis is necessary, whereas in case (b) a perturbation procedure is valid. The spin-orbit splittings 360, 47, and 248 cm^{-1} are the theoretical values obtained with no orbital quenching, corresponding to the semiexperimental value of 305 cm^{-1} and the experimental values of 16 and 53 cm^{-1}, respectively.

6800 cm^{-1} above[3] the ground orbital $^4T_{1g}$, also splits into spin-orbit levels Γ_6, $\Gamma_{8,1}$, $\Gamma_{8,2}$, and Γ_7. The levels Γ_6 and $\Gamma_{8,1}$ are degenerate in the first-order spin-orbit interaction, but they split in the second order, with Γ_6 lying lowest. These spin-orbit levels of the excited orbital $^4T_{2g}$ have been identified from near-infrared fluorescence and absorption spectra of Co^{2+} in MgO.[4,5] Ralph and Townsend's[4] results are better resolved, and we get $E(\Gamma_{8,1}) - E(\Gamma_6) = 16$ cm^{-1} and $E(\Gamma_{8,2}) - E(\Gamma_6) = 53$ cm^{-1}. Corresponding values given by Pappalardo, Wood, and Lineares[5] are 16.8 and 56.6 cm^{-1}. The g value is not available for any of these levels.

The energies of the spin-orbit levels can be calculated due to the following effective spin-orbit Hamiltonian considered up to the second order[24]:

$$\mathcal{H}_{so} = \lambda_{eff}\, \vec{l} \cdot \vec{S} + \frac{15}{4\Delta E}\lambda^2[(\vec{l} \cdot \vec{S})^2 - 2(l_x^2 S_x^2 + l_y^2 S_y^2 + l_z^2 S_z^2)] \quad , \tag{2}$$

where

$$\begin{aligned} \lambda_{eff} &= -\tfrac{3}{2} a k \lambda_{\text{free ion}} \quad \text{for } {}^4T_{1g} \\ &= \tfrac{1}{2} k' \lambda_{\text{free ion}} \quad \text{for } {}^4T_{2g} \quad , \\ \lambda^2 &= a k k' \lambda^2_{\text{free ion}} \quad , \end{aligned} \tag{3}$$

and

$$\begin{aligned} \Delta E &= +|\Delta E| \quad \text{for } {}^4T_{1g} \\ &= -|\Delta E| \quad \text{for } {}^4T_{2g} \quad . \end{aligned} \tag{4}$$

k and k' take account of the reductions due to covalency in the orbital angular momentum of T_{1g} and T_{2g}, respectively. $\lambda_{\text{free ion}}$ for the Co^{2+} ion is -180 cm^{-1}. ΔE is the separation between the orbitals T_{1g} and T_{2g}. The expression of the energies of the different spin-orbit levels is given in Table I.

It should be noted that the second-order part in $\mathcal{H}_{so}$ in Eq. (2) is derived taking only $^4T_{1g}$ and $^4T_{2g}$ orbitals into consideration. The effect of other orbitals—even that due to ^2E_g, which lies very near $^4T_{2g}$—is neglected, because the contributions are small, as discussed in Appendix A.

We can similarly write the effective Zeeman interaction up to the second order,[24]

$$\begin{aligned} \mathcal{H}_{\text{Zeeman}} = \mu_B \vec{H}(\gamma\vec{l} + 2\vec{S}) + \frac{15}{4}\frac{\beta\gamma'\lambda_{\text{free ion}}}{\Delta E}(\vec{H} \cdot \vec{l})(\vec{l} \cdot \vec{S}) \\ + (\vec{l} \cdot \vec{S})(\vec{H} \cdot \vec{l}) - 4(l_x^2 S_x H_x + l_y^2 S_y H_y + l_z^2 S_z H_z) \quad , \end{aligned} \tag{5}$$

where

$$\begin{aligned} \gamma &= -\tfrac{3}{2} a k \quad \text{for } {}^4T_{1g} \\ &= \tfrac{1}{2} k' \quad \text{for } {}^4T_{2g} \end{aligned} \tag{6}$$

and

$$\gamma' = a k k' \quad .$$

The g value for the lowest spin-orbit doublet Γ_6 is then given by

$$\begin{aligned} g &= -\frac{2}{3}\gamma + \frac{10}{3} - \frac{15}{2}\frac{\gamma'\lambda_{\text{free ion}}}{\Delta E} \quad \text{for } {}^4T_{1g} \\ &= -\frac{2}{3}\gamma - 2 - \frac{15}{2}\frac{\gamma'\lambda_{\text{free ion}}}{\Delta E} \quad \text{for } {}^4T_{2g} \quad . \end{aligned} \tag{7}$$

ΔE is positive when we consider T_{1g} and negative

TABLE I. Spin-orbit states of the orbitals $^4T_{2g}$ and $^4T_{1g}$ from the static crystal field theory.

Spin-orbit states		Energy
Γ_6	Γ_7	$-\frac{5}{2}\lambda_{eff} - \frac{45}{16}(\lambda^2/\Delta E)$
$^4T_{1g}: \Gamma_7$	$^4T_{2g}: \Gamma_6$	$\frac{3}{2}\lambda_{eff} - \frac{45}{16}(\lambda^2/\Delta E)$
Γ_8	Γ_8	$\frac{1}{2}(\frac{1}{2}\lambda_{eff} - \frac{405}{16}(\lambda^2/\Delta E) \pm \{[\frac{5}{2}\lambda_{eff} - \frac{117}{16}(\lambda^2/\Delta E)]^2 + 81(\lambda^2/\Delta E)^2\}^{1/2})$

TABLE II. Spin-orbit energy level separations for T_{1g} and T_{2g} from static crystal field calculations. The free-ionic values with $B=840$ cm^{-1} and $Dq=930$ cm^{-1} are quoted within brackets.

g for Γ_6 doublet of the orbital T_{1g}	Covalency factor for $^4T_{1g}$ (k)	Covalency factor for $^4T_{2g}$ (k')	$E(\Gamma_{8,1})-E(\Gamma_6)$ for $^4T_{1g}$ (cm^{-1}) (Ref. 20) semiexpt.	$E(\Gamma_{8,1})-E(\Gamma_6)$ for $^4T_{1g}$ (cm^{-1}) calc.	$E(\Gamma_{8,1})-E(\Gamma_6)$ for $^4T_{2g}$ (cm^{-1}) (Ref. 4) expt.	$E(\Gamma_{8,1})-E(\Gamma_6)$ for $^4T_{2g}$ (cm^{-1}) calc.	$E(\Gamma_{8,2})-E(\Gamma_6)$ for $^4T_{2g}$ (cm^{-1}) (Ref. 4) expt.	$E(\Gamma_{8,2})-E(\Gamma_6)$ for $^4T_{2g}$ (cm^{-1}) calc.
	1.00	0.06		378.0		2.5		14.7
	0.98	0.19		367.0		7.8		46.2
	0.96	0.33		357.0		13.0		78.9
	0.94	0.47	306.0	347.0	16.0	18.3	53.0	112.8
4.278			(357.0)^a		(47.0)^a		(248.0)^a	
(4.420)^a	0.92	0.61		336.0		23.6		148.0
	0.90	0.77		325.7		28.6		184.7
	0.89	0.93		320.5		31.2		203.6

[a] Free-ionic values.

when we consider T_{2g}. The g value is a fairly precisely known experimental parameter, so that we can use the above expressions to get an idea of the relative magnitudes of k and k'. From the nature of the d-electron configuration in the T_{1g} and T_{2g} orbitals, namely, $(t_{2g}^5\, e_g^2)$ and $(t_{2g}^4\, e_g^3)$, respectively, the covalency effects are expected to be stronger in the excited orbital. We therefore take $k' < k$ as a condition to be satisfied. Then, with the same set of values of k and k' for which we get the calculated value of g for the doublet Γ_6 of the orbital $^4T_{1g}$ equal to its experimental value 4.278, we calculate the energy separations between the spin-orbit levels, which are tabulated in Table II. The failure of the static crystal field theory is evident from the discrepancies between the calculated and experimental values. One can explain approximately the ground orbital splitting assuming sufficient quenching of the orbital angular momentum of the excited level, but even then the T_{2g} level splitting is very far from the experimental values.

In Sec. III we see how these discrepancies are removed when we incorporate the vibronic interactions for both the $^4T_{1g}$ and $^4T_{2g}$ orbitals (Fig. 2).

III. EFFECTS OF VIBRONIC INTERACTIONS

In the approximation of the molecular-cluster model we can write the total vibronic Hamiltonian for an orbital triplet in an octahedral symmetry as

$$\mathcal{H}_{\text{vib}} = E_0\mathcal{I} + [(1/2\mu)(P_\theta^2+P_\epsilon^2)\mathcal{I} + \tfrac{1}{2}\mu\omega_E^2(Q_\theta^2+Q_\epsilon^2)\mathcal{I} + V_E(Q_\theta\mathcal{E}_\theta+Q_\epsilon\mathcal{E}_\epsilon)]$$

$$+ [(1/2\mu)(P_\xi^2+P_\eta^2+P_\zeta^2)\mathcal{I} + \tfrac{1}{2}\mu\omega_T^2(Q_\xi^2+Q_\eta^2+Q_\zeta^2)\mathcal{I} + V_T(Q_\xi\mathcal{T}_\xi+Q_\eta\mathcal{T}_\eta+Q_\zeta\mathcal{T}_\zeta)] \quad . \quad (8)$$

Q_θ and Q_ϵ are the symmetry-adapted displacements corresponding to the E_g mode of vibration of the cluster having frequency ω_E. P_θ and P_ϵ are the corresponding momentum conjugates. Similarly, ξ, η, ζ represent the three components of the T_{2g} mode of vibration having frequency ω_T, which is the only other mode of vibration of the cluster interacting with the orbital triplet. μ is the effective mass, which in this case is the mass of the ligand oxygen atom. V_E and V_T are the coupling parameters of the electron orbital with the E_g and T_{2g} modes of vibration, respectively. E_0 is the electronic energy of the orbital triplet. $\mathcal{I}$, $\mathcal{E}_\theta$, $\mathcal{E}_\epsilon$, $\mathcal{T}_\xi$, $\mathcal{T}_\eta$, and $\mathcal{T}_\zeta$ are the matrices defined by Ham[1] in the electronic manifold of states.

For the ground orbital T_{1g} of MgO:Co^{2+}, direct measurement of the spin-lattice coupling constants of the effective dynamical spin Hamiltonian has been made,[19] from which we can estimate the orbit lattice coupling parameters for T_{1g}. For the ground spin-orbit doublet Γ_6 of the orbital triplet T_{1g}, we can write the effective dynamical Hamiltonian as

$$\mathcal{H}_{\text{dyn}} = \mu_B \sum_{i,j} H_i\, \delta g_{ij} S_j \quad ,$$

where $\delta g_i = F_{ij}\, e_j$. F_{ij}, which is a fourth-rank tensor, gives the magnetoelastic constants and e_j is the strain tensor. $\mathcal{H}_{\text{dyn}}$ arises due to the second-order effect of $\mathcal{H}_{\text{strain}}$ and $\mathcal{H}_{\text{Zeeman}}$, i.e.,

$$\langle\Gamma_6^i|\mathcal{H}_{\text{dyn}}|\Gamma_6^j\rangle = -\sum_{n,1}\frac{1}{E_n-E_6}\,(\langle\Gamma_6^i|\mathcal{H}_{\text{strain}}|\Gamma_n^1\rangle$$

$$\times\langle\Gamma_n^1|\mathcal{H}_{\text{Zeeman}}|\Gamma_6^j\rangle+\langle\Gamma_6^i|\mathcal{H}_{\text{Zeeman}}|\Gamma_n^1\rangle \times\langle\Gamma_n^1|\mathcal{H}_{\text{strain}}|\Gamma_6^j\rangle)\ , \tag{9}$$

where

$$\mathcal{H}_{\text{strain}}=V_E R(\mathcal{E}_\theta e_\theta+\mathcal{E}_\epsilon e_\epsilon)+V_T R(\mathcal{T}_\xi e_{yz}+\mathcal{T}_\eta e_{zx}+\mathcal{T}_\zeta e_{xy})\ , \tag{10}$$

$$\mathcal{H}_{\text{Zeeman}}=\mu_B\vec{\text{H}}(\gamma\vec{\text{l}}+2\vec{\text{S}}),\quad \gamma=-\tfrac{3}{2}ak\ .$$

e_θ and e_ϵ are the symmetry-adapted strain components corresponding to E_g-type distortion, given by

$$e_\theta=(1/\sqrt{3})\ (2e_{zz}-e_{xx}-e_{yy}),\quad e_\epsilon=e_{xx}-e_{yy}\ . \tag{11}$$

e_{yz}, e_{zx}, and e_{xy} are strain components corresponding to T_{2g}-type distortion. R is the distance of the nearest O^{2-} ion from the Co^{2+} ion. We thus get

$$V_E=\frac{3\sqrt{3}}{4}\,\frac{E(\Gamma_8)-E(\Gamma_6)}{(\gamma-2)R}F_{11}\ ,\qquad V_T=\frac{3}{2}\,\frac{E(\Gamma_8)-E(\Gamma_6)}{(\gamma-2)R}F_{44}\ . \tag{12}$$

Using the experimental values of F_{11} and F_{44}, we obtain $|V_E|/|V_T|\sim 6$, showing that the electron orbital T_{1g} is coupled to the E_g mode more strongly. This is supported by calculating V_E and V_T on an effective-point-charge model for the ligand charges, which gives $V_E/V_T\sim 8$ (Appendix B).

For the excited orbital T_{2g}, however, we do not have any direct estimation of V_E and V_T and the estimation of $V_E/V_T\sim 1.2$, made on the basis of an effective-point-charge model for the ligands, seems too small to be correct. On physical arguments, one should expect V_E to be relatively much bigger than V_T in the case of the orbital T_{2g} $(t_{2g}^4e_g^3)$ compared to that in the case of the orbital T_{1g} $(t_{2g}^5e_g^2)$, because of the predominance of the e_g-type electron in the excited triplet. That the point-charge calculations do not tally with the physical reasoning is probably evidence of the limitations of the point-charge model and of the uncertainty in the radial integrals $\langle r^2\rangle$ and $\langle r^4\rangle$ for the excited orbital states. Recent stress experiments[3] on the excited orbital T_{2g} in $KMgF_3:Co^{2+}$ also confirm that the E_g mode is far more strongly coupled to the electron orbital than the T_{2g} mode. In our subsequent calculations for both T_{1g} and T_{2g}, we shall consider uniquely the E_g-mode coupling.

A. Ground orbital triplet $^4T_{1g}$

It is useful to have an approximate idea of the magnitude of E_{JT} from Eqs. (12). Taking the experimental value[19] of F_{11}, $R=3.97$ a.u., $k=1$, and the separation between the Γ_8 and Γ_6 levels to be 305 cm^{-1}, we get $|V_E|\sim 7800\times10^{-8}$ erg cm^{-1}. Since $E_{JT}=V_E^2/2\mu\omega_E^2$, we get $E_{JT}\sim 110$ cm^{-1} for $\omega_E\sim 400$ cm^{-1}, which corresponds to the peak in the phonon distribution curve in MgO and $MgO:Ni^{2+}$ crystals. We therefore conclude that the JT stabilization energy is small for $^4T_{1g}$, but it is not negligible and the vibronic interactions should be considered in the calculations of spin-orbit states and the g value.

The vibronic spin-orbit states are calculated by considering the effect of the following Hamiltonian on the orbital level:

$$\mathcal{H}=\mathcal{H}_{so}+\mathcal{H}_{\text{lattice}}+\mathcal{H}_{ol}\ , \tag{13}$$

where the Hamiltonians are defined by Eqs. (2) and (8), respectively. We have already discussed in Sec. I why we cannot use the perturbation approach in this case, because the spin-orbit splitting of $^4T_{1g}$ is of the same order of magnitude as the vibrational energy of the molecular cluster in $MgO:Co^{2+}$, though E_{JT} is not large. We therefore diagonalize the total Hamiltonian in Eq. (13), using symmetrized combinations of vibrational spin-orbit states $|\Gamma_\alpha^i\rangle|n_\theta n_\epsilon\rangle$ as basis functions, and obtain linear combinations of such functions giving the symmetrized vibronic eigenstates of the system. The purpose of starting with symmetrized combinations of $|\Gamma_\alpha^i\rangle|n_\theta n_\epsilon\rangle$ as basis functions is to reduce the dimensions of the energy determinants that are to be solved. The maximum values of the vibrational quantum numbers n_θ and n_ϵ are limited from the consideration of the convergence of the eigenvalues. In this particular case $n=n_\theta+n_\epsilon=3$ is found to be adequate.

Construction of symmetrized vibrational spin-orbit basis functions

The pure spin-orbit states arising from the orbital $^4T_{1g}$ belong to Γ_6, Γ_7, and Γ_8 representations and, since we are considering only the E_g mode of vibration, the vibrational states $|n_\theta n_\epsilon\rangle$ would always belong to the Γ_1, Γ_2, and Γ_3 representations of the O_h group. The ground vibrational state $|00\rangle$ is a Γ_1 state and any excited state $|n_\theta n_\epsilon\rangle$ can be constructed from this one by operating on it with $\hat{Q}_\theta$ and $\hat{Q}_\epsilon$, n_θ and n_ϵ times, respectively, where

$$\hat{Q}_\theta|n_\theta\rangle=\left(\frac{\hbar}{2\mu\omega_E}\right)^{1/2}[(n_\theta+1)^{1/2}|n_\theta+1\rangle+(n_\theta)^{1/2}|n_\theta-1\rangle]\ ,$$
$$\hat{Q}_\epsilon|n_\epsilon\rangle=\left(\frac{\hbar}{2\mu\omega_E}\right)^{1/2}[(n_\epsilon+1)^{1/2}|n_\epsilon+1\rangle+(n_\epsilon)^{1/2}|n_\epsilon-1\rangle]\ . \tag{14}$$

We therefore have to find the symmetrized combinations of the product $\hat{Q}_\theta^n\hat{Q}_\epsilon^n$ following the method of the projection operator:

$$\hat{Q}^n(\Gamma_{\alpha,r}^i)=\frac{h_\alpha}{g}\sum_R\Gamma_\alpha^{i,j\,*}(R)\,\hat{Q}_\theta^n\hat{Q}_\epsilon^n \tag{15}$$

TABLE III. Symmetrized displacement operators and the corresponding symmetrized vibrational states for MgO : Co^{2+} cluster for vibrational quantum number up to 3.

$n=n_\theta+n_\epsilon$	Representation	Symmetrized operator $\hat{Q}^n$ $(\Gamma^i_{\alpha,r})$	Symmetrized vibrational function
0	Γ_{1g}		$\vert 00\rangle$
1	Γ^1_{3g}	$\hat{Q}_\theta$	$\vert 10\rangle$
	Γ^2_{3g}	$\hat{Q}_\epsilon$	$\vert 01\rangle$
2	Γ_{1g}	$\frac{1}{\sqrt{2}}\hat{Q}^2_\theta+\frac{1}{\sqrt{2}}\hat{Q}^2_\epsilon$	$\frac{1}{\sqrt{2}}\vert 20\rangle+\frac{1}{\sqrt{2}}\vert 02\rangle$
	Γ^1_{3g}	$-\frac{1}{\sqrt{2}}\hat{Q}^2_\theta+\frac{1}{\sqrt{2}}\hat{Q}^2_\epsilon$	$-\frac{1}{\sqrt{2}}\vert 20\rangle+\frac{1}{\sqrt{2}}\vert 02\rangle$
	Γ^2_{3g}	$\sqrt{2}\hat{Q}_\theta\hat{Q}_\epsilon$	$\vert 11\rangle$
3	Γ_{1g}	$-\frac{1}{2}\hat{Q}^3_\theta+\frac{3}{2}\hat{Q}_\theta\hat{Q}^2_\epsilon$	$-\frac{1}{2}\vert 30\rangle+\frac{1}{2}\sqrt{3}\,\vert 12\rangle$
	Γ_{2g}	$\frac{3}{2}\hat{Q}^2_\theta\hat{Q}_\epsilon-\frac{1}{2}\hat{Q}^3_\epsilon$	$\frac{1}{2}\sqrt{3}\vert 21\rangle-\frac{1}{2}\vert 03\rangle$
	Γ^1_{3g}	$\frac{1}{2}\hat{Q}^3_\theta+\frac{1}{2}\hat{Q}_\theta\hat{Q}^2_\epsilon$	$\frac{1}{2}\sqrt{3}\vert 30\rangle+\frac{1}{2}\vert 12\rangle$
	Γ^2_{3g}	$\frac{1}{2}\hat{Q}^2_\theta\hat{Q}_\epsilon+\frac{1}{2}\hat{Q}^3_\epsilon$	$\frac{1}{2}\vert 21\rangle+\frac{1}{2}\sqrt{3}\vert 03\rangle$

Thus we get the symmetry-adapted displacement operators of the molecular cluster belonging to the ith component of the αth representation, r being the index of repetition of this representation. h_α is the dimension of the representation, g is the order, and R is the element of the point group. Operating on the ground state $\vert 00\rangle$ by $\hat{Q}^n(\Gamma^i_{\alpha,r})$, we get the symmetrized vibrational states corresponding to different quantum numbers n_θ and n_ϵ. These symmetrized operators and the corresponding symmetrized vibrational states are given in Table III for n up to 3. The symmetrized vibrational spin-orbit basis functions are then constructed by taking the direct products of the so states of representations Γ_6, Γ_7, $\Gamma_{8,1}$, and $\Gamma_{8,2}$ with these symmetrized vibrational functions which belong to the representations Γ_1, Γ_2, and Γ_3. The representations of the final basis functions and the number of times they occur for different values of $n_\theta+n_\epsilon$ are given in Table IV. The total matrix of the Hamiltonian in Eq. (13) thus breaks up into three irreducible matrices: two ten-dimensional ones for Γ_6- and Γ_7-type basis functions and one 20-dimensional for Γ_8-type basis functions. Typical nonzero matrix elements of the Hamiltonian in Eq. (13) are worked out from the following:

$$\langle\Gamma_\beta n'_\theta n'_\epsilon \vert \mathcal{H}_{\mathrm{so}}+\mathcal{H}_{\mathrm{lattice}} \vert \Gamma_\alpha n_\theta n_\epsilon\rangle=[\langle\Gamma_\alpha \vert \mathcal{H}_{\mathrm{so}} \vert \Gamma_\beta\rangle + (n_\theta+n_\epsilon)\,\hbar\omega_E]\,\delta_{\Gamma_\alpha,\Gamma_\beta}\,\delta_{n_\theta,n'_\theta}\,\delta_{n_\epsilon,n'_\epsilon} \qquad (16)$$

and

$$\langle\Gamma_\beta n'_\theta n'_\epsilon \vert \mathcal{H}_{\mathrm{ol}} \vert \Gamma_\alpha n_\theta n_\epsilon\rangle=(\hbar\omega_E E_{\mathrm{JT}})^{1/2}\,\{[(n_\theta+1)^{1/2}\,\delta_{n'_\theta,n_\theta+1}+(n_\theta)^{1/2}\,\delta_{n'_\theta,n_\theta-1}]\,\langle\Gamma_\beta \vert \mathcal{E}_\theta \vert \Gamma_\alpha\rangle + [(n_\epsilon+1)^{1/2}\,\delta_{n'_\epsilon,n_\epsilon+1}+(n_\epsilon)^{1/2}\,\delta_{n'_\epsilon,n_\epsilon-1}]\,\langle\Gamma_\beta \vert \mathcal{E}_\epsilon \vert \Gamma_\alpha\rangle\} \quad . \qquad (17)$$

It should be noted that Γ_α and Γ_β refer to the electronic spin-orbit states and $\mathcal{H}_{\mathrm{so}}$ includes both the first- and second-order so interactions as defined by Eq. (2). On diagonalizing numerically the matrices of the Hamiltonian $\mathcal{H}$ in Eq. (13), we obtain finally the vibronic eigenvectors and corresponding eigenvalues. The ground vibronic state is of Γ_6 type and is 98% $\vert \Gamma_6 00\rangle$, and the first excited state is Γ_8 type and is 90% $\vert \Gamma_8 00\rangle$, admixing more with the other Γ_8-type vibrational spin-orbit functions. The g value within the ground doublet Γ_6 is also calculated numerically, taking the first- and second-order Zeeman interactions defined in Eq. (5).

The variables in these numerical calculations are E_{JT}, $\hbar\omega_E$, k (the covalency parameter of the ground orbital T_{1g}), and k' (the covalency parameter of the excited orbital T_{2g}). It is necessary to note here that when we are calculating the second-order spin-orbit effect on the ground T_{1g} the factor k' represents effectively the total orbital quenching of T_{2g} due to both covalency and vibronic effects.

$k > k'$ is therefore a justified condition to be satisfied in these calculations. There is another factor which is helpful in these calculations. It is the semiexperimental proportionality scale between $\hbar\omega_E$ and E_{JT}, which we can work out from Eq. (12), using Tucker's[19] experimental value of F_{11}. For $E(\Gamma_8) - E(\Gamma_8)$, we have used 305 cm^{-1}, the value obtained from magnetic-susceptibility data by Cossee,[20] and thus we have an approximate idea of the relative magnitude of $\hbar\omega_E$ and E_{JT}. The final results are discussed later.

TABLE IV. Representations of the symmetrized vibrational spin-orbit basis functions for different values of $n_\theta + n_\epsilon$.

$n_\theta + n_\epsilon$	Number of the different representations of the symmetrized basis functions
0	Γ_6, Γ_7, $2\Gamma_8$
1	$2\Gamma_6$, $2\Gamma_7$, $4\Gamma_8$
2	$3\Gamma_6$, $3\Gamma_7$, $6\Gamma_8$
3	$4\Gamma_6$, $4\Gamma_7$, $8\Gamma_8$

B. Excited orbital triplet $^4T_{2g}$

The vibronic interaction is much more important for the orbital $^4T_{2g}$, as is shown by the optical-absorption and fluorescence spectra[4] of MgO : Co^{2+}. According to Ralph and Townsend,[4] E_{JT} for $^4T_{2g}$ is approximately 1.3 times larger than $\hbar\omega_E$. Also from the analysis of the spectra, they indicate the presence of three localized phonon frequencies, viz., 170, 230, and 400 cm^{-1}. As the E_g-mode coupling with the electron orbital is expected to involve optical phonons only, which we discuss in Sec. IV, one can suppose E_{JT} to be of the order of 500 cm^{-1} from these experiments. The effective spin-orbit splitting of $^4T_{1g}$ is, on the other hand, of the order of 90 cm^{-1}. Hence in the case of this excited orbital we apply Ham's original theory[1] directly, by taking the spin-orbit interaction acting as perturbation on the ground vibronic states $|T^i_{2g}00\rangle$. The spin-orbit interaction $\mathcal{H}_{so}$, taken up to the second order, can then be written as

$$\mathcal{H}_{so} = \lambda_{eff} \exp(-3E_{JT}/2\hbar\omega_E)\; \vec{l}_g \cdot \vec{S} + [\lambda_1(l_{gx}^2 S_x^2 + l_{gy}^2 S_y^2 + l_{gz}^2 S_z^2) + \lambda_2(l_{gx} l_{gy} S_x S_y + l_{gy} l_{gx} S_y S_x + l_{gx} l_{gz} S_x S_z + l_{gz} l_{gx} S_z S_x + l_{gy} l_{gz} S_y S_z + l_{gz} l_{gy} S_z S_y)] \quad . \tag{18}$$

$\vec{l}_g = 1$ is the effective orbital angular momentum of the vibronic triplet $|T^i_{2g}00\rangle$. The first-order term involves the effect within this triplet and the second-order terms take into account any effect on $|T^i_{2g}00\rangle$ due to the excited vibronic levels $|T^i_{2g} n_\theta n_\epsilon\rangle$ and due to the ground electronic triplet $^4T_{1g}$. Thus we have

$$\lambda_1 = -\frac{\lambda_{eff}^2}{\hbar\omega_E} \exp\left(\frac{-3E_{JT}}{\hbar\omega_E}\right) G\left(\frac{3E_{JT}}{\hbar\omega_E}\right) + \frac{15}{4}\,\frac{\lambda^2}{|\Delta E|} \quad ,$$

$$\lambda_2 = -\frac{\lambda_{eff}^2}{\hbar\omega_E} \exp\left(\frac{-3E_{JT}}{\hbar\omega_E}\right) G\left(\frac{3E_{JT}}{2\hbar\omega_E}\right) - \frac{15}{4}\,\frac{\lambda^2}{|\Delta E|} \exp\left(\frac{-3E_{JT}}{2\hbar\omega_E}\right) \quad . \tag{19}$$

The first terms in λ_1 and λ_2 are due[1] to the excited vibronic states $|T_{2g} n_\theta n_\epsilon\rangle$ and the second terms denote the effect of the ground $^4T_{1g}$ on the vibronic states $|T^i_{2g}00\rangle$. These last terms in λ_1 and λ_2 are written directly from Eq. (2). The only difference is the replacement of the effective angular momentum $\vec{l}$ by $\vec{l}_g$; i.e., the vibronic quenching is being taken into account for the orbital T_{2g}. λ_1 is associated with E_g-type operator and hence this part of λ_1 remains unchanged from the corresponding factor in Eq. (2). But λ_2 is associated with T_{2g}-type angular momentum operator, so that the additional quenching factor $\exp(-3E_{JT}/2\hbar\omega_E)$ is incorporated in the corresponding term in λ_2.

As ΔE is very large compared to $\hbar\omega_E$ and E_{JT} is small for the ground orbital $^4T_{1g}$, we have neglected the vibronic character of this orbital in the calculation of the second-order term in $\mathcal{H}_{so}$ [Eq. (18)]. Thus we arrive at the following vibronic spin-orbit energy levels:

$$E(\Gamma_6) = \tfrac{3}{2}\lambda_g + \tfrac{3}{2}\lambda_1 + \tfrac{3}{4}\lambda_2 \quad ,$$

$$E(\Gamma_8) = \tfrac{1}{2}\left\{\tfrac{1}{2}\lambda_g + 5\lambda_1 - \tfrac{7}{4}\lambda_2 \pm \left[\left(\tfrac{5}{2}\lambda_g + 2\lambda_1 - \tfrac{5}{4}\lambda_2\right)^2 + \lambda_1\lambda_2 + \lambda_g\left(-2\lambda_1 + \tfrac{9}{2}\lambda_2\right)\right]^{1/2}\right\} \quad , \tag{20}$$

$$E(\Gamma_7) = -\tfrac{5}{2}\lambda_g + \tfrac{7}{2}\lambda_1 + \tfrac{11}{4}\lambda_2 \quad ,$$

where we have written λ_g for $\lambda_{eff}\exp(-3E_{JT}/2\hbar\omega_E)$. For the low-lying doublet Γ_6, we can evaluate the g value, using the following Zeeman Hamiltonian:

$$\mathcal{H}_z = \mu_B \vec{H}\left[\gamma \exp\left(\frac{-3E_{JT}}{2\hbar\omega_E}\right)\vec{l}_g + 2\vec{S}\right] + \{g_1\mu_B(l_{gx}^2 H_x S_x + l_{gy}^2 H_y S_y + l_{gz}^2 H_z S_z) + g_2\mu_B[(l_{gx}l_{gy} + l_{gy}l_{gx})(S_x H_y + S_y H_x)$$

$$+(l_{gx}l_{gz}+l_{gz}l_{gx})(S_xH_z+S_zH_x)+(l_{gy}l_{gz}+l_{gz}l_{gy})(S_yH_z+S_zH_y)]\} \quad , \tag{21}$$

where

$$\begin{aligned} g_1 &= -\frac{2\gamma^2\lambda_{\text{free ion}}}{\hbar\omega_E} \exp\left(\frac{-3E_{JT}}{\hbar\omega_E}\right) G\left(\frac{3E_{JT}}{\hbar\omega_E}\right) \\ &\quad + \frac{15\gamma'\lambda_{\text{free ion}}}{2\,|\Delta E\,|} \;, \\ g_2 &= -\frac{\gamma^2\lambda_{\text{free ion}}}{\hbar\omega_E} \exp\left(\frac{-3E_{JT}}{\hbar\omega_E}\right) G\left(\frac{3E_{JT}}{2\hbar\omega_E}\right) \\ &\quad - \frac{15}{4}\frac{\gamma'\lambda_{\text{free ion}}}{|\Delta E\,|} \exp\left(\frac{-3E_{JT}}{\hbar\omega_E}\right) \;. \end{aligned} \tag{22}$$

For the doublet Γ_6, we get

$$g = -\tfrac{2}{3}\gamma \exp\left(\frac{-3E_{JT}}{2\hbar\omega_E}\right) - 2 - 2g_2 \quad . \tag{23}$$

Here again we have four variables: $\hbar\omega_E$, E_{JT}, k, and k'. When we were considering the vibronic effects of $^4T_{1g}$, the parameter k represented the pure covalency effects for this orbital and, by parameter k', we took account of the total reduction of the orbital angular momentum of the excited level $^4T_{2g}$; i.e., k' included both the covalency and vibronic effects. Now, when we are studying the vibronic effects of the orbital $^4T_{2g}$, the reverse is the case. k' now signifies the pure covalency parameter for $^4T_{2g}$ and k should in principle incorporate the quenching due to covalency as well as vibronic effects. But we can assume that k should not vary too much in the two cases, because the quenching due to vibronic reduction is small for $^4T_{1g}$, though the difference in k' may be relatively more important. We now discuss the results for both the ground and excited orbitals.

C. Results

Using Eq. (12) and the experimental value of F_{11} we get $(\hbar\omega_E)^2 E_{JT} = 0.867/(k+1.42)^2 \times 10^8$ cm^{-3} for the orbital $^4T_{1g}$, taking $E(\Gamma_8) - E(\Gamma_6)$ to be 300 cm^{-1}. In our calculations, for any particular value of ω_E we vary E_{JT} within a range of 10% of the value given by this relationship. For each value of E_{JT} we vary the covalency parameter k of the orbital $^4T_{1g}$ from 1 to 0.90. For each set of ω_E, E_{JT}, and k, the reduction parameter k' of the excited level $^4T_{2g}$ is then fixed by fitting the calculated value of g within the vibronic doublet Γ_6 with the experimental value of 4.278. For these sets of ω_E, E_{JT}, k, and k' the energies of the low-lying vibronic levels are verified and only those sets which give a near fit with the semiexperimental value of 305 cm^{-1} are given in Table V. Thus, depending on the available experimental results on the ground orbital triplet of MgO : Co^{2+}, we infer that $\hbar\omega_E$ is in the range of 400 cm^{-1}, E_{JT} is of the order of 90–100 cm^{-1}, and the pure covalency effect for $^4T_{1g}$ is as low as 2–4%. The reasons why we consider $\hbar\omega_E \sim 400$ cm^{-1} to be more feasible compared to $\hbar\omega_E \sim 450$ cm^{-1} will be clear as we look into the results for the excited triplet $^4T_{2g}$.

The phonon-assisted transitions in the fluorescence and absorption spectra of the excited orbital $^4T_{2g}$ could be accounted for[4] by two phonon

TABLE V. Set of values of $\hbar\omega_E$, E_{JT}, k, and k' which give simultaneous best fit of the numerically calculated values of g of the lowest doublet Γ_6 and the separation between the lowest Γ_6 and Γ_8 levels of the orbit $^4T_{1g}$ with 4.278 and 306 cm^{-1}, respectively.

Energy of E_g mode of vibrations $\hbar\omega_E$ cm^{-1}	Jahn-Teller stabilization energy E_{JT} cm^{-1}	Pure covalency parameter for the orbital $^4T_{1g}:k$	Reduction in the orbital angular momentum of $^4T_{2g}$ (cov. +other effects : k')	g value of the lowest doublet Γ_6	Energy of the lowest vibronic level $E(\Gamma_6)$ cm^{-1}	Energy of the next vibronic level $E(\Gamma_8)$ cm^{-1}	$E(\Gamma_8) - E(\Gamma_6)$ (cm^{-1})
350	120	1.00	0.29	4.278 ± 001	−674.5	−398.6	275.9
		0.92	0.87		−632.5	−375.8	256.7
	130	1.00	0.26		−671.1	−390.6	280.5
		0.92	0.85		−628.9	−367.7	261.2
400	90	0.98	0.35		−653.1	−341.0	312.1
		0.96	0.49		−642.3	−337.3	305.0
	100	0.98	0.36		−656.6	−349.3	307.3
		0.96	0.50		−645.9	−345.5	300.4
450	70	0.94	0.60		−626.1	−311.9	314.2
		0.92	0.75		−615.2	−310.2	305.0
	80	0.94	0.62		−630.0	−320.2	309.8
		0.92	0.77		−619.2	−318.4	300.8

TABLE VI. Set of values of $\hbar\omega_E$, E_{JT}, k, and k' which give the best fit of the theoretical values of $E(\Gamma_{8,1}) - E(\Gamma_6)$ and $E(\Gamma_{8,2}) - E(\Gamma_6)$ of the orbital ${}^4T_{2g}$ with the experimental values of 16 and 53 cm^{-1}, respectively.

Energy of E_g mode of vibration $\hbar\omega_E$ cm^{-1}	Jahn-Teller stabilization energy E_{JT} cm^{-1}	Pure covalency parameter for the orbital ${}^4T_{2g}$ (k')	Recuctions in the orbital angular momentum of ${}^4T_{1g}$ (k)	$E(\Gamma_{8,1}) - E(\Gamma_6)$ (cm^{-1})	$E(\Gamma_{8,2}) - E(\Gamma_6)$ (cm^{-1})
400	400	0.90	0.98	16.4	53.7
			0.96	15.9	53.5
	410	0.92	0.98	16.5	53.0
			0.96	16.0	52.8
			0.94	15.5	52.6
	420	0.96	0.98	16.7	53.4
			0.96	16.2	53.2
			0.94	15.7	53.0
		0.98	0.98	16.7	52.7
			0.96	16.3	52.4
			0.94	15.8	52.3

modes of energy 170 and 230 cm^{-1} or three modes of energy 170, 230, and 400 cm^{-1}. We find that with $\hbar\omega_E = 170$ or 230 cm^{-1}, the calculated values of the energy separations $E(\Gamma_{8,1}) - E(\Gamma_6)$ and $E(\Gamma_{8,2}) - E(\Gamma_6)$ of the triplet ${}^4T_{2g}$ are quite far from the corresponding experimental values for any reasonable set of covalency parameters k and k'. But for $\hbar\omega_E = 400$ cm^{-1}, the agreement between the calculated and experimental results is surprisingly good for reasonable values of E_{JT}, k, and k', as is evident from Table VI, where the best-fit results are quoted. In the absence of any other experimental parameter, such as g value or $E(\Gamma_7) - E(\Gamma_6)$, this is as much as we can deduce. It may be noted that the calculated g value of the doublet Γ_6 comes out to be of the order of 2.116. On comparing the results for the orbitals ${}^4T_{1g}$ and ${}^4T_{2g}$ we find that $\hbar\omega_E$ is nearly the same, whereas E_{JT} varies by a factor of 4.5. Also, pure covalency parameters are not significantly different from the free-ionic value of unity. In Sec. IV we discuss the implications of these results, and we also discuss the case of $KMgF_3 : Co^{2+}$ in the background of our results.

IV. DISCUSSION

First, regarding the effective frequency of the E_g mode of vibration of the molecular cluster, the preceding analysis gives a value ~400 cm^{-1} for both the ground and excited orbitals. In the E_g-type motion of the XY_6 complex, the ligand ions move in opposite directions, the central ion remaining undisplaced, and this corresponds to the optical vibrations at the Brillouin zone boundary ($\vec{k} = \pi/a$) in a MgO crystal.[25] The inelastic-neutron-scattering experiments on MgO crystal done by Peckham[21] show that the LO phonons at the zone edge have frequencies near about 410 cm^{-1}, and consequently the distribution function for the phonons shows a sharp peak at this frequency. There ought to be some modifications in the lattice motions due to the substitution of Co^{2+}. But the results of the sidebands of the fluorescence and absorption spectra for $MgO : Co^{2+}$ indicate the presence of phonons at about 400 cm^{-1}. Similar results were obtained[21] for $MgO : Ni^{2+}$. So the value of $\hbar\omega_E$ for E_g type of vibration we obtain is consistent with these results. Also, the difference in the contribution to the force constant of the E_g-type vibration from the two orbitals ${}^4T_{1g}$ and ${}^4T_{2g}$ is expected to be small, so that nearly the same value of $\hbar\omega_E$ is obtained for both the ground and excited triplets.

Second, as regards the magnitude of E_{JT}, we get $(E_{JT})_{T_{2g}}/(E_{JT})_{T_{1g}} \sim 4.5$ from our analysis. As $\hbar\omega_E$ is nearly the same for the two orbitals, we get $(V_E)_{T_{2g}} \sim 2.2\,(V_E)_{T_{1g}}$. No experiment under stress has been done on the excited orbital, so that we have no direct knowledge of $(V_E)_{T_{2g}}$, as we have of $(V_E)_{T_{1g}}$. But from the calculations on the point-charge model (Appendix B) we have

$$\frac{(V_E)_{T_{2g}}}{(V_E)_{T_{1g}}} = \frac{875\langle r^4\rangle}{216R^2\langle r^2\rangle - 375\langle r^4\rangle} \;.$$

Using the free-ionic values of $\langle r^2\rangle$ and $\langle r^4\rangle$ for Co^{2+} and $R = 3.97$ a.u. for $MgO : Co^{2+}$, we get $(V_E)_{T_{2g}} \sim 1.1(V_E)_{T_{1g}}$. This is less than we obtain from our calculations. If we remember that a small expansion of the $3d$ function in a crystalline medium would cause the ratio $\langle r^2\rangle : \langle r^4\rangle$ to be smaller than the free-ionic value, the ratio $(V_E)_{T_{2g}}/(V_E)_{T_{1g}}$ should be larger, and a very small change can easily account for this difference.

Third, the pure covalency effects of the ground and excited orbitals seem to be very close to the free-ionic value of unity. Earlier, when the covalency parameters were deduced without taking account of the vibronic interactions,[26] the quenching of the orbital angular momentum or spin-orbit interaction was ascribed to covalency effects. We find that the covalency effects are rather small. It should be noted that our estimates k and k' may change slightly if we take account of the orbital ^2E_g in the second-order term of the vibronic calculations for $^4T_{2g}$ level. We show in Appendix A that the contribution from the ^2E_g level is expected to be small. Nevertheless, its inclusion would have reduced k slightly.

Case of $KMgF_3$: Co^{2+}

Recently Sturge and Guggenheim[3] have done optical experiments under stress on $KMgF_3$: Co^{2+} and have given the vibronic spin-orbit energy levels and the g values within the manifold of the excited orbital $^4T_{2g}$. It is worthwhile to apply Ham's model of calculations in the way we have done for the $^4T_{2g}$ level of MgO: Co^{2+} to this case. We thus find that, with k, k' varying in the range 0.94–0.96, good fit with experimental results is obtained with $\hbar\omega_E \sim 180$ cm^{-1} and $E_{JT} \sim 200$ cm^{-1}. Infrared experiments[27] indicate that there are three branches at LO phonons in $KCoF_3$ at $\vec{k}=0$, of energy corresponding to 165, 290, and 495 cm^{-1}, respectively. Since the dispersion of optical phonons is small, these energies would change by small amounts only, at the zone boundary ($\vec{k}=\pi/a$). We do not know the phonon distribution functions for $KMgF_3$ or $KCoF_3$ from inelastic-neutron-scattering experiments and hence we cannot justify the value $\hbar\omega_E \sim 180$ cm^{-1} more definitely, other than saying that is is a reasonable value. We should note here that our values of $\hbar\omega_E$ and E_{JT} come out to be different from those given by Sturge and Guggenheim, though the model of calculation is essentially the same. The main point of difference is in the parameters [Eqs. (19)] of the second-order spin-orbit Hamiltonian. It should be noted that our λ_1 and λ_2 are, respectively, $k+\rho$ and k in Sturge and Guggenheim's notation. In the limit of no vibronic interaction, λ_1 and λ_2, which in our case include the effect of spin-quartet terms only, are of opposite signs. In Appendix A we have shown that the orbital ^2E_g cannot have a very significant effect on $^4T_{2g}$. The question is whether the orbital $^2T_{1g}$ can have such an effect on the spin-orbit splitting of $^4T_{2g}$ as to change λ_1 and λ_2 drastically.

Secondly, we have included a vibronic correction factor in these parameters in the presence of vibronic interaction, which explains the factor $\exp(-3E_{JT}/2\hbar\omega_E)$ in the second term in λ_2. Supposing that the values of k and ρ given in Ref. 3 are justified in the static limit as due to the effects of all excited orbitals of spin multiplicity 2 which we have neglected, should they not change appreciably when vibronic effects in $^4T_{2g}$, as well as in these other orbitals, are taken into account?

We shall now discuss the possible sources of error in our calculations. First, in calculating the vibronic interactions within the ground orbital $^4T_{1g}$ we have diagonalized $\mathcal{H}_{so}+\mathcal{H}_{01}$, taking vibrational quanta $n=n_\theta+n_\epsilon$ up to 3. Working with symmetrized vibrational spin-orbit states, the three matrices that need to be solved are of dimensions 10, 10, and 20, respectively. This is equivalent to the solution of a 120×120 matrix, with unsymmetrized functions as bases. Testing for convergence, we find that, for $n=2$, the ground-level energy $E(\Gamma_6)$ and also the g value within this doublet change insignificantly, though for the first excited level Γ_8 the change in energy is 2.5%. The convergence can be improved by taking $n=4$, but this we have not done, in view of the fact that the position of this level is not known precisely. Second, in considering the vibronic effects of the excited orbital $^4T_{2g}$, we have taken into account the second-order effect on $|T_{2g}^i 00\rangle$ due to the higher vibronic levels $|T_{2g}^i n_\theta n_\epsilon\rangle$ and the ground electronic orbital $|T_{1g}^i\rangle$ operating through spin-orbit coupling.

The orbital ^2E_g, which is quite close to $^4T_{2g}$, is not taken into account, but the error due to this should be small, as discussed in Appendix A. The terms $^2T_{1g}$, $^2T_{2g}$, etc., which lie about 8000 cm^{-1} above $^4T_{2g}$, should have some second-order effect on the spin-orbit splitting of $^4T_{2g}$. But the magnitude of orbital quenching due to vibronic effects is expected to be important for these excited orbitals and, since these are not known, we have neglected all such terms in our calculations. The results of our analysis indicate that, for the case of MgO: Co^{2+}, this simplified model of the second-order spin-orbit Hamiltonian is good.

It should be noted that for both the ground and excited orbitals of MgO: Co^{2+} four independent parameters are involved, viz., $\hbar\omega_E$, E_{JT}, k, and k', whereas only three experimental observables are known in each case. For the fundamental, these are the g value, F_{11}, and the position of the first spin-orbit level, and for the excited orbital level these are the positions of the first two spin-orbit levels and $\hbar\omega_E$ (from the phonon sidebands). Further experiments such as infrared and optical absorption under stress and in the presence of the Zeeman field are expected to resolve the small uncertainties in the basic parameters of this model. In general, the analysis confirms that the molecular-cluster model works well for MgO: Co^{2+}.

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APPENDIX A: EFFECT OF ^2E_g TERM CLOSE TO $^4T_{2g}$ ON SPIN-ORBIT SPLITTINGS IN $^4T_{2g}$ AND $^4T_{1g}$ TERMS

From Ralph and Townsend[4] we find that the ^2E_g term lies 103 cm^{-1} below the $^4T_{2g}$ term. One can use arguments similar to those used by Pappalardo *et al.*[5] to show that the effect of ^2E_g on $^4T_{2g}$ is negligibly small. For MgO: Co^{2+}, we have used $B = 840$ cm^{-1}, $C = 3700$ cm^{-1}, and $|Dq| = 930$ cm^{-1}, and we get the lowest ^2E_g term as

$$|{}^2E_g\rangle = -0.0182\,|t_{2g}^3({}^2E)e_g^4\rangle - 0.1295\,|t_{2g}^4({}^1A_1)e_g^3\rangle + 0.0305\,|t_{2g}^4({}^1E)e_g^3\rangle + 0.9910\,|t_{2g}^6 e_g\rangle \quad .$$

The spin-orbit Hamiltonian does not connect $|{}^2E_g(t_{2g}^6 e_g)\rangle$ and $|{}^4T_{2g}(t_{2g}^4 e_g^3)\rangle$ and, since the state $|{}^2E_g\rangle$ is of the 99% $(t_{2g}^6 e_g)$ type, we should expect the total effect of ^2E_g on the so splittings in $^4T_{2g}$ to be negligibly small. As regards the ground orbital $^4T_{1g}$, it is composed of $(t_{2g}^4 e_g^3)$ and $(t_{2g}^5 e_g^2)$ configurations, and neither of them is connected to $|{}^2E_g(t_{2g}^6 e_g)\rangle$ by spin-orbit interaction.[28] The vibronic interaction would further reduce the effect of these excited orbital states on the ground orbital.

APPENDIX B: CALCULATION OF COUPLING PARAMETERS V_E AND V_T ON EFFECTIVE POINT-CHARGE MODEL FOR LIGAND IONS

For a d electron one can write the orbit-lattice interaction as

$$\mathcal{H}_{01} = A_{2,3}\, r^2 \sum_i Y_2(\Gamma_3^i)\, Q(\Gamma_3^i) + A_{4,3}\, r^4 \sum_i Y_4(\Gamma_3^i)\, Q(\Gamma_3^i) + A_{2,5}\, r^2 \sum_i Y_2(\Gamma_5^i)\, Q(\Gamma_5^i) + A_{4,5}\, r^4 \sum_i Y_4(\Gamma_5^i)\, Q(\Gamma_5^i) \;, \tag{B1}$$

where, under the approximation of an effective-point-charge ($|Ze|$) model of the ligands, we have

$$A_{2,3} = 6\left(\frac{3\pi}{5}\right)^{1/2}\frac{Ze^2}{R^4}, \quad A_{4,3} = 5\,\frac{(5\pi)^{1/2}}{3}\,\frac{Ze^2}{R^6} \;, \qquad A_{2,5} = -4\left(\frac{3\pi}{5}\right)^{1/2}\frac{Ze^2}{R^4}, \quad A_{4,5} = 2\,\frac{(5\pi)^{1/2}}{3}\,\frac{Ze^2}{R^6} \;. \tag{B2}$$

R is the ligand-ion distance. In terms of the total angular momentum $\vec{L}$,

$$\mathcal{H}_{01} = \left(\frac{15}{8\pi}\right)^{1/2} \alpha A_{2,3}\langle r^2\rangle \sum_i L_2(\Gamma_3^i)\, Q(\Gamma_3^i) + \frac{3}{4}\left(\frac{35}{2\pi}\right)^{1/2} \beta A_{4,3}\langle r^4\rangle \sum_i L_4(\Gamma_3^i)\, Q(\Gamma_3^i) + \left(\frac{15}{8\pi}\right)^{1/2} \alpha A_{2,5}\langle r^2\rangle \sum_i L_2(\Gamma_5^i)\, Q(\Gamma_5^i) + \frac{3}{4}\left(\frac{35}{4\pi}\right)^{1/2} \beta A_{4,5}\langle r^4\rangle \sum_i L_4(\Gamma_5^i)\, Q(\Gamma_5^i) \;, \tag{B3}$$

where

$$\begin{aligned}
L_2(\Gamma_3^1) &= \frac{1}{(6)^{1/2}}\left[3L_z^2 - L(L+1)\right] \;, \\
L_2(\Gamma_3^2) &= \frac{1}{2\sqrt{2}}\,(L_+^2 + L_-^2) \;, \\
L_4(\Gamma_3^1) &= \frac{1}{8(42)^{1/2}}\left[2(35L_z^4 + 25L_z^2 - 30L_z^2 L(L+1) + 3L^4 - 6L^2 - 7(L_+^4 + L_-^4)\right] \;, \\
L_4(\Gamma_3^2) &= -\frac{1}{4(14)^{1/2}}\left[(L_+^2 + L_-^2)(7L_z^2 - L(L+1) - 5) + (7L_z^2 - L(L+1) - 5)(L_+^2 + L_-^2)\right] \;, \\
L_2(\Gamma_5^1) &= \frac{1}{2\sqrt{2}\,i}\left[(L_+ - L_-)L_z + L_z(L_+ - L_-)\right] \;, \\
L_2(\Gamma_5^2) &= \frac{1}{2\sqrt{2}}\left[(L_+ + L_-)L_z + L_z(L_+ - L_-)\right] \;, \\
L_2(\Gamma_5^3) &= \frac{1}{2\sqrt{2}\,i}\,(L_+^2 - L_-^2) \;, \\
L_4(\Gamma_5^1) &= -\frac{i}{4(14)^{1/2}}\{(L(L+1) + 5 - 7L_x^2)\left[(L_+ - L_-)L_z + L_z(L_+ - L_-)\right] + \left[(L_+ - L_-)L_z + L_z(L_+ - L_-)\right] \times (L(L+1) + 5 - 7L_x^2)\} \;, \\
L_4(\Gamma_5^2) &= \frac{1}{4(14)^{1/2}}\{(L(L+1) + 5 - 7L_y^2)\left[(L_+ + L_-)L_z + L_z \times (L_+ + L_-)\right] + \left[(L_+ + L_-)L_z + L_z(L_+ + L_-)\right] \times (L(L+1) + 5 - 7L_y^2)\} \;, \\
L_4(\Gamma_5^3) &= -\frac{i}{4(14)^{1/2}}\left[(L(L+1) + 5 - 7L_z^2)(L_+^2 - L_-^2) + (L_+^2 - L_-^2)(L(L+1) + 5 - 7L_z^2)\right] \;.
\end{aligned} \tag{B4}$$

Taking the matrix elements of this Hamiltonian between the orbital triplet T_{1g}, we get

$$V_E = -\frac{\sqrt{3}}{7}\left(\frac{12}{5}\frac{Ze^2}{R^4}\langle r^2\rangle - \frac{25}{6}\frac{Ze^2}{R^6}\langle r^4\rangle\right) \;, \qquad V_T = -\frac{1}{7}\left(\frac{3}{5}\frac{Ze^2}{R^4}\langle r^2\rangle - 5\frac{Ze^2}{R^6}\langle r^4\rangle\right) \;. \tag{B5}$$

Similarly for the excited orbital $^4T_{2g}$, we get

$$V_E = -\frac{25\sqrt{3}}{18}\frac{Ze^2}{R^6}\langle r^4\rangle ,$$

$$V_T = -\frac{1}{7}\left(3\frac{Ze^2}{R^4}\langle r^2\rangle - \frac{5}{3}\frac{Ze^2}{R^6}\langle r^4\rangle\right) . \qquad \text{(B6)}$$

With $\langle r^2\rangle = 1.251$ a.u. and $\langle r^4\rangle = 3.655$ a.u. for Co^{2+} ions and $R = 3.97$ a.u. in MgO: Co^{2+}, we obtain $V_E/V_T \sim -8.6$ and 1.2 for the orbitals ${}^4T_{1g}$ and ${}^4T_{2g}$, respectively.

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[22] In Ref. 15, the factor $8Dq$ is missing in the denominator in Eq. (2). Also, for α one should read $\cos^2\theta - \frac{2}{3}\sin^2\theta$ in place of $\cos^2\theta + \frac{2}{3}\sin^2\theta$. Both are typographical errors. Also in Eqs. (7) and (9) of this reference $\mathcal{H}_{vib}$ should be read $\mathcal{H}_{ol}$ so that $\mathcal{H}_{vib} = \mathcal{H}_{lattice} + \mathcal{H}_{ol}$, to keep the nomenclature consistent.

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