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Theory of spectral thermal shift and R-line thermal-shift calculations of MgO:Cr^{3+}

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The thermal shift of the crystal-field spectra of $3d$ or $4f$ ions includes contributions of different characters. In this paper we develop an approach to calculating all those contributions in detail. The thermal shift caused by thermal expansion is interpreted and calculated by use of the theory of pressure-induced spectral shift. Contributions of phonons of optical branches are given using a single frequency model. Taking into account contributions of all the $\Gamma\gamma$ in the electron-phonon interaction, two terms coming from phonons of acoustic branches are derived in detail, and theoretical formulas for the parameters in the most important term are given. By adequately taking into account all the contributions, we calculated the R-line thermal shift of MgO:Cr^{3+} by fitting the experimental data. The results show good agreement with thermal-shift experimental data and a series of other experimental data of MgO:Cr^{3+}. Values of the most important parameters are calculated theoretically with wave functions obtained from diagonalization of complete d^3 energy matrices. They are in good agreement with those from fitting the experimental data. We found that it is the mixing of wave functions caused by the Coulomb interaction and/or the spin-orbital interaction that makes $D(\Gamma_6)$ and $D(\Gamma_8)$ nonzero. Our investigation shows that among all the contributions to thermal shifts, the $t_2^3\,{}^2T_1$ term (resulting in redshift) is the most important one; the Raman term (resulting in blueshift) eliminates part of the $t_2^3\,{}^2T_1$ term; their algebraic sum gives the contribution of electron-phonon interaction of the acoustic branches; contributions of optical branches (resulting in redshift) increases rapidly with temperature, and exceeds that of the acoustic branches when $T \geq 175$ K; contribution by thermal expansion (resulting in blueshift) holds about 30% of total thermal shift in absolute value.

I. INTRODUCTION

The optical spectra of the rare-earth or transition-metal ions ($3d$ or $4f$ ions) in crystals shift with temperature. In practice, the shift closely relates to the stability and change of emission frequencies of lasers as well as to temperature-tunable lasers, and in theory it relates to the electron-phonon interaction (EPI). Therefore, these kinds of thermal shifts (TS) have attracted great interest. Much research has been undertaken both theoretically and experimentally.[1-7] Still, there are problems to be solved theoretically. A thorough investigation in more detail is needed. In this paper we are going to solve the following problems.

(i) In Refs. 1, and 4–7 the formulas given for TS calculations usually include two terms, i.e., the "Raman term" and "direct-process term," but generally, in quantitative calculations only the Raman term was taken into account.[1-4] We will study all possible contributions to TS by EPI in acoustic branches in more detail and derive formulas for numerical calculations.

(ii) Up to now, when calculating the contributions of phonon modes to TS people paid attention only to the acoustic branches—the optical branches were ignored. In this paper, the contribution of the optical branches will be given in detail.

(iii) Thermal shift comes not only from EPI, but also from thermal expansion of the crystal. However, no effort has been made to take this factor into account. We will give an approach to enable the calculation of its contribution.

(iv) After all those contributions to TS mentioned above are made clear, numerical calculations of R-line TS for MgO:Cr^{3+} will be given in detail by fitting the experimental data.

Finally, the expressions of the parameters in the most important term (the contributions from $t_2^3\,{}^2T_1$) will be derived microscopically and their values will be calculated and compared with those obtained by fitting the experimental data.

In Sec. II, the approaches of various contributions to TS and corresponding formulas will be given. Section III is devoted to the derivation of formulas for the acoustic branches where all possible contributions of the $\Gamma\gamma$ terms in EPI corresponding to the site group at $3d$ or $4f$ ions are taken into account. In Sec. IV, numerical TS calculations for the R line of MgO:Cr^{3+}, as well as formulas for parameters in the expression for contributions from

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$t_2^3\,{}^2T_1$, are presented. Conclusions and discussions are given in Sec. V.

II. THEORETICAL CALCULATIONS OF VARIOUS CONTRIBUTIONS TO TS

We are going to deal with the TS of the crystal-field spectra, i.e., purely electronic (zero-phonon) transition spectra, of $3d$ or $4f$ ions.

The TS of a spectral line is the algebraic sum of the TS of the two levels involved in the transition. The contributions to TS consist of two parts: that of thermal expansion and those of EPI.

A. Contribution of thermal expansion

Let us consider $3d$ or $4f$ ions in a crystal field. The energy of a crystal-field level related to TS may be considered a statistical average of microscopic quantity, i.e., a thermodynamic quantity.[5] If the temperature T and volume of crystal V are taken as independent variables, the energy of a crystal-field level can be expressed as

$$E = E(T,V) \ . \tag{1}$$

As a general thermodynamic relation, we have

$$(\partial E/\partial T)_p = (\partial E/\partial T)_V + \left[\frac{\partial E}{\partial V}\right]_T \left[\frac{\partial V}{\partial T}\right]_p , \tag{2}$$

where $(\partial E/\partial T)_p$ is the TS rate of a crystal-field level at normal pressure; $(\partial E/\partial T)_V$ is the shift rate of a level caused solely by temperature variation, i.e., contribution of the EPI; $(\partial V/\partial T)_p$ is thermal expansion rate at normal pressure; and $(\partial E/\partial V)_T$ is the shift rate of a level caused solely by volume (or interionic distance) variation. Obviously, $(\partial E/\partial V)_T(\partial V/\partial T)_p$ is the contribution of thermal expansion to TS.

According to our theory on pressure-induced spectral shift,[8] distances between ions reduce under hydrostatic pressure, their interactions change, and the radial electronic wave functions expand, which causes Dq (crystal-field parameter), B, C (Racah parameters), and ζ (spin-orbital coupling parameter), as well as levels, to vary.

According to experimental data, the pressure-induced shift rate of the R_1 line of ruby does not depend on temperature,[9] i.e., independent of EPI; in the temperature interval 2 5°C–200 °C and pressure interval 0–40 Kbar, the temperature and pressure coefficients of the shift of the ruby R_1 line were found to be independent of each other.[10]

From these experimental results and Eq. (2) it can be suggested that the level shifts caused by variations of interionic distances R (whether the variations are brought about by thermal expansion or by compression) are independent of EPI and temperature, and are determined only by the variations of R. As has been shown above, the variation of R and the corresponding expansion of radial electronic wave functions give rise to the shift of a level. This is the mechanism of the level shift caused by thermal expansion or compression. Therefore, the same variation of R from thermal expansion or compression should cause the same level shift, and TS caused by thermal expansion can be calculated by use of the thermal expansion coefficient and theory of the pressure-induced spectral shift.

B. Contributions of EPI (the acoustic branches)

Let us consider an interaction system of the local electronic state of $3d$ or $4f$ ions and lattice vibration. Its Hamiltonian is

$$H = H_{\text{latt}} + H_{\text{ion}} + H_{\text{int}} \ . \tag{3}$$

Assuming isotropy of the elastic waves and simplifying the interaction Hamiltonian (i.e., EPI) H_{int} ($H_{\text{int}} = H' + H''$), Di Bartolo[6] gave the contribution of EPI (the acoustic branches) of i-level TS as

$$\begin{aligned}\delta E_i &= \delta E_i^{(1)} + \delta E_i^{(2)} \\ &= \alpha_i \left[\frac{T}{T_D}\right]^4 \int_0^{T_D/T} \frac{x^3}{e^x - 1}\,dx \\ &\quad + \sum_{j\neq i} \beta_{ij} \left[\frac{T}{T_{ij}}\right]^2 \\ &\quad \times \mathrm{P}\int_0^{T_D/T} \frac{x^3\,dx}{(e^x-1)[x^2-(T_{ij}/T)^2]} ,\end{aligned} \tag{4a}$$

where δE_i is in cm^{-1} and α_i in Eq. (4a) is

$$\begin{aligned}\alpha_i &= \frac{3}{4\pi^3 \rho v^5 C} \left[\frac{kT_D}{\hbar}\right]^4 \\ &\quad \times \left[\sum_{j\neq i} \frac{|\langle \psi_i^{\text{el}} | V_1 | \psi_j^{\text{el}} \rangle|^2}{E_i^{\text{el}} - E_j^{\text{el}}} + \langle \psi_i^{\text{el}} | V_2 | \psi_j^{\text{el}} \rangle \right] ,\end{aligned} \tag{4b}$$

where ρ is the crystal density, v is the average sound velocity, C is the velocity of light, k is Boltzmann constant, $\hbar = h/2\pi$, h is Planck's constant; T_D is the Debye temperature, and V_1 and V_2 are expansion coefficients in H_{int}. $\delta E_i^{(1)}$ is often called the Raman term, where the summation $\sum_{j\neq i}$ is taken only for those energy levels which satisfy $|E_i^{\text{el}} - E_j^{\text{el}}| \gg kT_D$. All the j levels which satisfy $|E_i^{\text{el}} - E_j^{\text{el}}| \lesssim kT_D$ give their contributions in the second term of Eq. (4a), $\delta E_i^{(2)}$ (called the direct-process term), where $T_{ij} = (E_i^{\text{el}} - E_j^{\text{el}})/k$, P indicates the principal value of the integral (when $T_{ij} < T_D$, there will be a singular point in the integrand), and

$$\beta_{ij} = -\frac{3(E_i^{\text{el}} - E_j^{\text{el}})^3}{4\pi^3 \rho v^5 \hbar^4 C} |\langle \psi_i^{\text{el}} | V_1 | \psi_j^{\text{el}} \rangle|^2 \ . \tag{4c}$$

Usually, α_i and β_{ij} are treated as adjustable parameters.

C. Contributions of EPI (the optical branches)

So far, nothing has been done to take into account the contributions to TS by phonon modes of optical branches in the references. Our work on TS of R_1 and R_2 levels of $\text{YAlO}_3{:}\text{Nd}^{3+}$ (Ref. 11), as well as our research in this paper, shows definitively that ignorance of the contribution of the optical branches is unreasonable. We derive its expression as follows.

Starting from H_{int} as

$$H_{\text{int}}=H'+H''=i\sum_{\mathbf{K},\lambda}V_{\mathbf{K}\lambda}\left[\frac{\hbar}{2M\omega_{\mathbf{K}\lambda}}\right]^{1/2}(b_{\mathbf{K}\lambda}-b^{\dagger}_{\mathbf{K}\lambda})-\sum_{\mathbf{K}\lambda;\mathbf{K}'\lambda'}V_{\mathbf{K}\lambda;\mathbf{K}'\lambda'}\frac{\hbar}{2M}\left[\frac{1}{\omega_{\mathbf{K}\lambda}\omega_{\mathbf{K}'\lambda'}}\right]^{1/2}\times(b_{\mathbf{K}\lambda}-b^{\dagger}_{\mathbf{K}\lambda})(b_{\mathbf{K}'\lambda'}-b^{\dagger}_{\mathbf{K}'\lambda'})\ ,\tag{5}$$

where $\mathbf{K}$ is a wave vector, λ is the label of the branch, $\omega_{\mathbf{K}\lambda}$ is the frequency, M is the total mass of the crystal, and $b_{\mathbf{K}\lambda}$ and $b^{\dagger}_{\mathbf{K}\lambda}$ are the phonon annihilation and creation operators, we obtain

$$\delta E_i^{(3)}=\frac{\hbar}{2M}\sum_{\mathbf{K}\lambda}\frac{n_{\mathbf{K}\lambda}}{\omega_{\mathbf{K}\lambda}}\left\{\sum_{j\neq i}|\langle\psi_i^{\text{el}}|V_{\mathbf{K}\lambda}|\psi_j^{\text{el}}\rangle|^2\times\left[\frac{1}{E_i^{\text{el}}-E_j^{\text{el}}-\hbar\omega_{\mathbf{K}\lambda}}+\frac{1}{E_i^{\text{el}}-E_j^{\text{el}}+\hbar\omega_{\mathbf{K}\lambda}}\right]+2\langle\psi_i^{\text{el}}|V_{\mathbf{K}\lambda;\mathbf{K}'\lambda'}|\psi_i^{\text{el}}\rangle\right\}\ ,\tag{6}$$

where the summation $\sum_{\mathbf{K}\lambda}$ is taken for all the optical branches. Since the spectrum of optical phonons is confined to a very narrow frequency region, the single-frequency model may be taken as a simplification, i.e., $n_{\mathbf{K}\lambda}=1/(e^{\hbar\omega_{\mathbf{K}\lambda}/kT}-1)$ is substituted by $1/(e^{\hbar\omega_{\text{eff}}/kT}-1)$ and is taken out of the summation sign. Then we have

$$\delta E_i^{(3)}=\gamma_i(e^{\hbar\omega_{\text{eff}}/kT}-1)^{-1}\ ,\tag{7a}$$

where

$$\gamma_i=\frac{\hbar}{2M}\sum_{\mathbf{K}\lambda}\frac{1}{\omega_{\mathbf{K}\lambda}}\left\{\sum_{j\neq i}|\langle\psi_i^{\text{el}}|V_{\mathbf{K}\lambda}|\psi_j^{\text{el}}\rangle|^2\times\left[\frac{1}{E_i^{\text{el}}-E_j^{\text{el}}-\hbar\omega_{\mathbf{K}\lambda}}+\frac{1}{E_i^{\text{el}}-E_j^{\text{el}}+\hbar\omega_{\mathbf{K}\lambda}}\right]+2\langle\psi_i^{\text{el}}|V_{\mathbf{K}\lambda;\mathbf{K}\lambda}|\psi_i^{\text{el}}\rangle\right\}\ .\tag{7b}$$

γ_i, independent of temperature, may be taken as an adjustable parameter. ω_{eff} may be taken from the peaks of the optical branches in the density of states of phonons.

III. REDERIVATION OF $\delta E_i^{(1)}$, $\delta E_i^{(2)}$, AND β_{ij}

Numerical calculations show that the second term in Eq. (4a) (i.e., the term from the j levels which satisfy $|E_i^{\text{el}}-E_j^{\text{el}}|\lesssim kT_D$) play a main role among various contributions to TS. It is necessary to study it in more detail. We will especially derive the expression for β_{ij} from microscopic theory and compare it numerically with that obtained by fitting the theory with the experimental data.

For this purpose, the isotropic approximation is inadequate, and the dynamic strains $\varepsilon(\Gamma\gamma)$ for all possible $\Gamma\gamma$ under the point group of the site of the impurity ion must be involved.

Following Kushida and Kikuchi,[12] we can write H' as

$$H'=\sum_{\Gamma\gamma}C(\Gamma\gamma)\varepsilon(\Gamma\gamma)\ ,\tag{8}$$

where Γ is the irreducible representation of the point group about the central metal ion and γ is the component of the representation. The $C(\Gamma\gamma)$'s are orbital operators of impurity d or f electrons and the $\varepsilon(\Gamma\gamma)$'s are phonon operators. These operators transform in the same way as the γ base of the Γ representation. So we have

$$\sum_j{}'\frac{|(H')_{ij}|^2}{E_i-E_j}=\sum_{j;\mathbf{K}\lambda}\left\{\frac{\sum_{\Gamma\gamma}|\langle\psi_i^{\text{el}}|C(\Gamma\gamma)|\psi_j^{\text{el}}\rangle|^2|\langle n_{\mathbf{K}\lambda}|\varepsilon(\Gamma\gamma)|n_{\mathbf{K}\lambda}+1\rangle|^2}{E_i^{\text{el}}-(E_j^{\text{el}}+\hbar\omega_{\mathbf{K}\lambda})}+\frac{\sum_{\Gamma\gamma}|\langle\psi_i^{\text{el}}|C(\Gamma\gamma)|\psi_j^{\text{el}}\rangle|^2|\langle n_{\mathbf{K}\lambda}|\varepsilon(\Gamma\gamma)|n_{\mathbf{K}\lambda}-1\rangle|^2}{E_i^{\text{el}}-(E_j^{\text{el}}-\hbar\omega_{\mathbf{K}\lambda})}\right\}\ ,\tag{9}$$

where the summation for λ covers only the acoustic branches [the optical branches have been included in Eq. (7)]. ε represents the dynamic strain due to the phonon field. We can get

$$\begin{aligned}|\langle n_{\mathbf{K}\lambda}|\varepsilon_{lm}|n_{\mathbf{K}\lambda}+1\rangle|^2&=\frac{\hbar}{8M\omega_{\mathbf{K}\lambda}}(n_{\mathbf{K}\lambda}+1)|e_{\mathbf{K}\lambda,l}K_m+e_{\mathbf{K}\lambda,m}K_l|^2\ ,\\|\langle n_{\mathbf{K}\lambda}|\varepsilon_{lm}|n_{\mathbf{K}\lambda}-1\rangle|^2&=\frac{\hbar}{8M\omega_{\mathbf{K}\lambda}}n_{\mathbf{K}\lambda}|e_{\mathbf{K}\lambda,l}K_m+e_{\mathbf{K}\lambda,m}K_l|^2\ ,\end{aligned}\tag{10}$$

where $|e_{\mathbf{K}\lambda,l}K_m+e_{\mathbf{K}\lambda,m}K_l|^2$ must be averaged over all directions of propagation and polarization. This average has been done by Van Vleck,[13] Blume *et al.*,[14] and Kushida and Kikuchi[12] for a cubic crystal. If the point group about the central metal ion is cubic (for example, it is O_h for MgO:Cr^{3+}, i.e., the six oxygen ions nearest to Cr^{3+} form a regular octahedron), the only even vibrations of such a cluster which need to be considered are the E and T_2 vibrations.[13,14] So we have[12]

$$|\langle n_{\mathbf{K}\lambda}|\varepsilon(\Gamma\gamma)|n_{\mathbf{K}\lambda}+1\rangle|^2=\left\{\begin{array}{ll}\left.\begin{array}{l}(\frac{16}{15})\pi K^2A\,(\text{longitudinal})\\ \\ (\frac{12}{15})\pi K^2A\,(\text{transverse})\end{array}\right\} & \text{for } \varepsilon(T_2\xi),\ \varepsilon(T_2\eta),\ \text{and } \varepsilon(T_2\zeta)\\ \left.\begin{array}{l}(\frac{128}{15})\pi K^2A\,(\text{longitudinal})\\ \\ (\frac{96}{15})\pi K^2A\,(\text{transverse})\ ,\end{array}\right\} & \text{for } \varepsilon(Eu) \text{ and } \varepsilon(Ev)\end{array}\right. \tag{11}$$

where $A=\hbar(n_{\mathbf{K}\lambda}+1)/(8M\omega_{\mathbf{K}\lambda})$. $|\langle n_{\mathbf{K}\lambda}|\varepsilon(\Gamma\gamma)|n_{\mathbf{K}\lambda}-1\rangle|^2$ has a similar result.

After inserting them into Eq. (9), summing over three acoustic branches, and disregarding the temperature-independent zero-field contribution, we have

$$\begin{aligned}\sum_j{}'\frac{|(H')_{ij}|^2}{E_i-E_j}=\frac{2\pi\hbar}{15M}\sum_{j\neq i}&\left\{\left[\sum_\gamma|\langle\psi_i^{\text{el}}|C(T_2\gamma)|\psi_j^{\text{el}}\rangle|^2+8\sum_\gamma|\langle\psi_i^{\text{el}}|C(E\gamma)|\psi_j^{\text{el}}\rangle|^2\right]\right.\\&\left.\times\sum_{\mathbf{K}}\frac{n_{\mathbf{K}l}K^2}{\omega_{\mathbf{K}l}}\left[\frac{1}{E_i^{\text{el}}-E_j^{\text{el}}-\hbar\omega_{\mathbf{K}l}}+\frac{1}{E_i^{\text{el}}-E_j^{\text{el}}+\hbar\omega_{\mathbf{K}l}}\right]\right\}\\+\frac{\pi\hbar}{5M}\sum_{j\neq i}&\left\{\left[\sum_\gamma|\langle\psi_i^{\text{el}}|C(T_2\gamma)|\psi_j^{\text{el}}\rangle|^2+8\sum_\gamma|\langle\psi_i^{\text{el}}|C(E\gamma)|\psi_j^{\text{el}}\rangle|^2\right]\right.\\&\left.\times\sum_{\mathbf{K}}\frac{n_{\mathbf{K}t}K^2}{\omega_{\mathbf{K}t}}\left[\frac{1}{E_i^{\text{el}}-E_j^{\text{el}}-\hbar\omega_{\mathbf{K}t}}+\frac{1}{E_i^{\text{el}}-E_j^{\text{el}}+\hbar\omega_{\mathbf{K}t}}\right]\right\}\ .\end{aligned} \tag{12}$$

Two cases can be distinguished.

(i) When $|E_i^{\text{el}}-E_j^{\text{el}}|\gg\hbar\omega_D$, we can get the contribution of all the j levels in the sum $\sum_j{}'|(H')_{ij}|^2/(E_i-E_j)$ which satisfy the condition (adopting the Debye model)

$$\begin{aligned}\delta E_i^{(1a)}\approx\frac{1}{15\pi^2C\rho}\left[\frac{1}{v_l^5}+\frac{3}{2v_t^5}\right]\sum_{j\neq i}&\frac{\left[\sum_\gamma|\langle\psi_i^{\text{el}}|C(T_2\gamma)|\psi_j^{\text{el}}\rangle|^2+8\sum_\gamma|\langle\psi_i^{\text{el}}|C(E\gamma)|\psi_j^{\text{el}}\rangle|^2\right]}{E_i^{\text{el}}-E_j^{\text{el}}}\\&\times\left[\frac{kT_D}{\hbar}\right]^4\left[\frac{T}{T_D}\right]^4\int_0^{T_D/T}\frac{x^3}{e^x-1}dx\ .\end{aligned} \tag{13}$$

Adding $\delta E_i^{(1a)}$ in contributions from the second term of Eq. (4b), we get the new expression for $\delta E_i^{(1)}$ (the Raman term).

(ii) When $|E_i^{\text{el}}-E_j^{\text{el}}|\lesssim\hbar\omega_D$, all the j levels in the sum $\sum_j{}'|(H')_{ij}|^2/(E_i-E_j)$ which satisfy this condition should be treated differently than those in the Raman term. We will see later that it is of great importance.

If the approximation of the Debye model is adopted as we did above, from Eq. (12) we get

$$\delta E_i^{(2)}=\sum_{j\neq i}\beta_{ij}\left[\frac{T}{T_{ij}}\right]^2\mathrm{P}\int_0^{T_D/T}\frac{x^3dx}{(e^x-1)[x^2-(T_{ij}/T)^2]}\ , \tag{14a}$$

where

$$\begin{aligned}\beta_{ij}&=-T_{ij}^3D_{ij}\ ,\\ D_{ij}&=\frac{k^3}{15\pi^2C\rho\hbar^4}\left[\frac{1}{v_l^5}+\frac{3}{2v_t^5}\right]\\&\quad\times\left[\sum_\gamma|\langle\psi_i^{\text{el}}|C(T_2\gamma)|\psi_j^{\text{el}}\rangle|^2\right.\\&\qquad\left.+8\sum_\gamma|\langle\psi_i^{\text{el}}|C(E\gamma)|\psi_j^{\text{el}}\rangle|^2\right]\ .\end{aligned} \tag{14b}$$

As for D_{ij}, we will calculate it in more detail with wave functions later in the example of MgO:Cr^{3+}.

IV. CALCULATIONS OF THE *R*-LINE TS OF MgO:Cr^{3+}

A. Calculations of energy spectrum and wave functions

The sites of most of the Cr^{3+} ions in MgO:Cr^{3+} possess O_h symmetry. Cr^{3+} has a $(3d)^3$ electronic configuration. According to Runciman and Schroeder,[15] making use of their matrices of spin-orbital coupling in the $\alpha S\Gamma\beta\Gamma_T\gamma_T$ scheme, and the electrostatic and cubic crystal-field matrix elements of Sugano, Tanabe, and Kamimura,[16] we have the complete matrices of the d^3 configuration (including a 21×21 submatrix and two 9×9 submatrices). The next step is to diagonalize the matrices by computer to fit the experimental data by a least-squares method.

In the calculation of the energy spectrum here, we have applied a pressure-induced shift of the experimental data[17] and four experimental data at normal pressure in order to obtain more accurate results. By a least-squares fitting of all the data we get crystal-field parameters for MgO:Cr^{3+} at normal pressure, $Dq=1619\ \text{cm}^{-1}$, $B=648\ \text{cm}^{-1}$, $C=3180\ \text{cm}^{-1}$, and $\zeta=212\ \text{cm}^{-1}$. The calculated

TABLE I. Energy spectrum of MgO:Cr^{3+} at normal pressure and part of the mixing coefficients of wave functions.

			Energy levels (cm^{-1})		
$\alpha^{2S+1}\Gamma\beta$		$\beta\Gamma_T$	calculated	observed	Mixing coefficients[a]
t_2^3	${}^4A_2$	Γ_8	0		
t_2^3	${}^2E$	Γ_8	14 302.1	14302[b]	$a_0=0.975\,68$
t_2^3	${}^2T_1$	Γ_8	14 861.8	58[c]	$b_0(\Gamma_8)=0.984\,60$
		Γ_6	14 919.1	(splitting of $t_2^3\,{}^2T_1$)	$b_0(\Gamma_6)=0.984\,32$
$t_2^2({}^3T_1)e$	${}^4T_2$	Γ_7	16 105.7		
	${}^4T_2$	Γ_8	16 160.9		
				16200[d]	
	${}^4T_2$	Γ_6	16 266.2		
	${}^4T_2'$	Γ_8	16 278.8		
t_2^3	${}^2T_2$	Γ_8	21 423.4		$a_l=0.0196\,37$, $b_m(\Gamma_8)=0.029\,164$
		Γ_7	21 512.8		
$t_2^2({}^3T_1)e$	${}^4T_1'$	Γ_8	22 670.6		
	${}^4T_1$	Γ_7	22 697.3		
				22700[c]	
	${}^4T_1$	Γ_8	22 706.7		
	${}^4T_1$	Γ_6	22 714.2		
$t_2^2({}^1E)e$	${}^2A_1$	Γ_6	28 333.7		
$t_2^2({}^3T_1)e$	${}^2T_2$	Γ_7	30 353.5		
		Γ_8	30 398.9		$a_l=-0.002\,100\,8$
$t_2^2({}^1T_2)e$	${}^2T_1$	Γ_6	30 647.4		
		Γ_8	30 818.7		$a_l=0.019\,723$
$t_2^2({}^1E)e$	${}^2E$	Γ_8	32 451.7		$a_l=0.089\,220$
$t_2^2({}^3T_1)e$	${}^2T_1$	Γ_8	35 214.5		$a_l=-0.001\,629\,2$, $b_m(\Gamma_8)=0.078\,243$
		Γ_6	35 233.0		$b_m(\Gamma_6)=0.070\,288$
$t_2e^2({}^3A_2)$	${}^4T_1$	Γ_7	35 601.0		
	${}^4T_1'$	Γ_8	35 613.6		
	${}^4T_1$	Γ_6	35 733.6		
	${}^4T_1$	Γ_8	35 770.8		
$t_2^2({}^1T_2)e$	${}^2T_2$	Γ_7	39 890.3		
		Γ_8	39 967.2		$a_l=0.004\,6461$, $b_m(\Gamma_8)=0.013\,690$
$t_2^2({}^1E)e$	${}^2A_2$	Γ_7	41 291.1		
$t_2e^2({}^3A_2)$	${}^2T_1$	Γ_6	46 516.3		
		Γ_8	46 618.2		
$t_2e^2({}^1E)$	${}^2T_2$	Γ_7	48 109.2		
		Γ_8	48 221.0		
$t_2^2({}^1A_1)e$	${}^2E$	Γ_8	49 645.9		
$t_2e^2({}^1E)$	${}^2T_1$	Γ_6	52 892.6		
		Γ_8	53 003.0		
$t_2e^2({}^1A_1)$	${}^2T_2$	Γ_8	67 460.8		
		Γ_7	67 631.4		
e^3	${}^2E$	Γ_8	69 774.3		

[a] Only part of the mixing coefficients concerned with $D(\Gamma_6)$ and $D(\Gamma_8)$ was tabulated.
[b] Reference 17.
[c] Reference 19.
[d] Reference 18.

energy spectrum at normal pressure and the pressure-induced shift are in good agreement with the experimental data (the pressure-induced shift calculations will be reported later). The results of the energy spectrum and part of the wave-function mixing coefficients are shown in Table I. For the sake of simplicity, we have omitted the subscript g denoting the even-parity character throughout the paper.

B. TS experimental data and calculations of the contribution of thermal expansion

Imbusch *et al.*[2] measured TS for the R line of MgO:Cr^{3+} relative to 4.2 K. Since TS from 0 to 4.2 K is insignificant, we can consider their results as being relative to 0 K. The results at 14 experimental points ΔE_{exp} were taken from Ref. 2 and are shown in Table II. The contributions to TS of the R line from thermal expansion ΔE_{te} are calculated as follows.

Ganesan[20] measured the linear expansion coefficient α of MgO from 140 to 284.5 K with an accuracy of better than 3%. For lower temperatures we failed to find any experimental data. So the following formula of Gao[21] is used:

$$\alpha=\frac{\alpha_v}{3}=\frac{\alpha_v^0}{3C_p^0}C_p\Bigg/\left[1-\frac{\alpha_v^0}{C_p^0}(\delta_S+\delta_T-B_S')\int_{T_0}^{T}C_p\,dT\right] \tag{15}$$

where α_v^0 and C_p^0 are the volume-expansion coefficient and heat capacity at temperature T_0,

$$B_S'=(\partial B_S/\partial p)_T\ ,$$

$$\delta_S=-(\alpha_v B_S)^{-1}(\partial B_S/\partial T)_p\ ,$$

$$\delta_T=-(\alpha_v B_T)^{-1}(\partial B_T/\partial T)_p\ ,$$

and B is the bulk modulus. Some numerical values from the measurements are given also as $\delta_S=3.1$, $\delta_T=4.7$, $B_S'=4.5$.[21]

By use of the experimental data of α from Ref. 20, C_p [from 9.759 to 269.793 K (Ref. 22) and above 273.15 K (Ref. 23)] and the values of α calculated for various temperatures are given in Table III, where the data of Ref. 20 are listed too. We see surprisingly good agreement within experimental error.

In case of isotropy or approximate isotropy, we can take $\kappa=R/R_{293}=(V/V_{293})^{1/3}$, where R and V are the interionic distance and crystal volume at T, respectively, and R_{293} and V_{293} are quantities at $T=293$ K.

By use of the α values in Table III, the values of κ at various temperatures are calculated. As we argued in Sec. II, TS caused by thermal expansion with a certain variation of interionic distance $\kappa(T)$ is equal to the pressure-induced shift with the same variation of interionic distance. The latter can be calculated as follows.

The P-κ dependence can be calculated from the Murnaghan equation

$$P=\frac{B_0}{B_0'}(\kappa^{-3B_0'}-1)\ , \tag{16}$$

TABLE II. Thermal shift of the R line of MgO:Cr^{3+} and various contributions to it (in cm^{-1}).

T (K)	76.8	97.4	106.5	116.9	125.6	139.6	154.9	175.1	184.3	195.2	204.4	231.6	244.0	265.5
$\Delta E_{\text{exp}}{}^{a}$ (cm^{-1})	−0.37	−0.84	−1.18	−1.64	−2.13	−2.84	−4.40	−5.81	−6.78	−7.83	−8.95	−12.12	−13.93	−16.65
ΔE_{te}	0.090	0.23	0.32	0.45	0.58	0.84	1.17	1.69	1.96	2.30	2.60	3.58	4.06	4.95
$\Delta E_{e\text{-}p}{}^{a}$	−0.46	−1.07	−1.50	−2.09	−2.71	−3.68	−5.57	−7.50	−8.74	−10.13	−11.55	−15.70	−17.99	−21.60
$\Delta E_{e\text{-}p}^{\text{calc}}$	−0.44	−1.09	−1.51	−2.10	−2.69	−3.81	−5.29	−7.58	−8.75	−10.22	−11.54	−15.77	−17.84	−21.64
$\Delta E^{(1)}$	3.401	6.810	8.634	10.92	12.97	16.50	20.62	26.41	29.14	32.46	35.30	43.94	47.98	55.11
$\Delta E^{(2)}$	−3.793	−7.665	−9.747	−12.35	−14.70	−18.75	−23.49	−30.14	−33.29	−37.10	−40.38	−50.34	−54.99	−63.21
$\Delta E^{(3)}$	−0.044	−0.234	−0.400	−0.665	−0.956	−1.56	−2.42	−3.85	−4.60	−5.58	−6.46	−9.37	−10.83	−13.54
$\Delta E^{(1)}+\Delta E^{(2)}$	−0.392	−0.855	−1.11	−1.43	−1.73	−2.25	−2.87	−3.73	−4.15	−4.64	−5.08	−6.40	−7.01	−8.10

[a] ΔE_{exp} is taken from Fig. 4 (enlarged) of Ref. 2. It seems that the accuracy of the measurement for ΔE_{exp} in Ref. 2 is within about 0.1 cm^{-1}, but two figures after the decimal point are taken for convenience in the calculations. The same has been done for $\Delta E_{e\text{-}p}$.

where B_0 and B'_0 are the isothermal bulk modulus and its pressure derivative at zero pressure. From ultrasonic measurements,[24] $B_0=1622$ Kbar and $B'_0=4.54$. Calculated P-κ dependence agrees well with experiment.[25] Chopelas and Boehler[17] measured the redshifts of the R line of MgO:Cr^{3+} and MgO:V^{2+} under hydrostatic pressure at room temperature. They found the shifts to be linear with the slope $\eta=d\lambda/dp=0.437$ Å/Kbar for MgO:Cr^{3+} up to 30 Kbar. We may calculate the P-κ data with Eq. (16) and then get the corresponding shift of the R line by

$$\Delta E_p \approx \frac{-\eta P}{\lambda_0(\lambda_0+\eta P)} \times 10^8 \ (\mathrm{cm}^{-1}) , \tag{17}$$

where $\lambda_0=6992$ Å,[17] P is in Kbars, and ΔE_p is equal to TS of the R line caused by thermal expansion with the same κ value, relative to room temperature (293 K). After converting it into TS relative to 0 K, we finally get a contribution to TS of the R line by thermal expansion ΔE_{te} as shown in Table II. The positive values of ΔE_{te} mean blueshifts.

C. Calculations of the contribution of EPI

As for the TS of the R line as we mentioned above, the contribution caused by EPI is

$$\Delta E_{e\text{-}p} = \Delta E_{\mathrm{exp}} - \Delta E_{\mathrm{te}} . \tag{18}$$

$\Delta E_{e\text{-}p}$ is shown in Table II.

TABLE III. The linear expansion coefficient of MgO (in 10^{-6} K^{-1}).

T (K)	α_{calc}	α_{exp}[a]
10.0	0.001 313	
30.0	0.038 47	
50.0	0.2338	
76.8	1.031	
97.4	2.042	
106.5	2.552	
116.9	3.153	
125.6	3.667	
139.6	4.486	
140.0	4.510	4.60
154.9	5.342	
159.1	5.566	5.55
175.1	6.383	
179.1	6.577	6.63
184.3	6.821	
195.2	7.303	
195.8	7.329	7.47
204.4	7.685	
211.3	7.961	8.13
225.8	8.496	8.67
231.6	8.699	
239.6	8.961	9.06
244.0	9.102	
252.2	9.351	9.35
260.1	9.582	9.57
265.6	9.735	

[a] Reference 20.

It was mentioned that the contribution to TS of the i level by EPI (including acoustic and optical branches) is

$$\delta E_i = \delta E_i^{(1)} + \delta E_i^{(2)} + \delta E_i^{(3)} . \tag{19}$$

Let the i level be $t_2^3\,{}^2E\Gamma_8$ (it is the excited-state level of the R-line transition), then δE_i represents its TS. But $\Delta E_{e\text{-}p}$, as a contribution by EPI to TS of the R line, is the algebraic sum of TS of the excited state $t_2^3\,{}^2E\Gamma_8$ and that of the ground state $t_2^3\,{}^4A_2\Gamma_8$. Since $t_2^3\,{}^4A_2\Gamma_8$ is far away from other levels (≥ 14302 cm^{-1}), its EPI with those levels may be ignored. From Eqs. (4b) and (7b) we see that the diagonal elements $\langle \psi_g^{\mathrm{el}} | V_2 | \psi_g^{\mathrm{el}} \rangle$ and $\langle \psi_g^{\mathrm{el}} | V_{\mathbf{K}\lambda;\mathbf{K}\lambda} | \psi_g^{\mathrm{el}} \rangle$ (g denotes ground state) might give contributions, but they can be absorbed simply into coefficients α_i of $\delta E_i^{(1)}$ and γ_i of $\delta E_i^{(3)}$ and only make α_i and γ_i change into α'_i and γ'_i. Hence, with α'_i and γ'_i, Eq. (19) is still effective for the calculation of $\Delta E_{e\text{-}p}$.

For the sake of clarity, we rewrite the expression of TS of the R line by EPI as

$$\Delta E_{e\text{-}p}^{\mathrm{calc}} = \Delta E^{(1)} + \Delta E^{(2)} + \Delta E^{(3)} , \tag{20}$$

where $\Delta E^{(2)} = \delta E^{(2)}$ and there are α' and γ' in $\Delta E^{(1)}$ and $\Delta E^{(3)}$. The subscript i is omitted here and hereafter.

It is known from the energy spectrum of MgO:Cr^{3+} that $\Delta E^{(2)}$ includes two terms: contributions of $t_2^3\,{}^2T_1\Gamma_8$ and $t_2^3\,{}^2T_1\Gamma_6$. As for the other levels in the energy spectrum, since they all satisfy $|E_i^{\mathrm{el}} - E_j^{\mathrm{el}}| \gg kT_D$, they may be included in $\Delta E^{(1)}$ (contributions of acoustic branches).

For convenience, the expression of $\Delta E_{e\text{-}p}^{\mathrm{calc}}$ may be rewritten as

$$\Delta E_{e\text{-}p}^{\mathrm{calc}}(T) = \alpha R(T) + D(\Gamma_6) S(T) + \gamma O(T) , \tag{21}$$

where

$$\begin{aligned} R(T) &= \left[\frac{T}{T_D} \right]^4 \int_0^{T_D/T} \frac{x^3}{e^x-1} dx , \\ S(T) &= T_{31}^3 \left[\frac{T}{T_{31}} \right]^2 \int_0^{T_D/T} \frac{x^3}{(e^x-1)[x^2-(T_{31}/T)^2]} dx \\ &\quad + \mu T_{21}^3 \left[\frac{T}{T_{21}} \right]^2 \\ &\quad \times \int_0^{T_D/T} \frac{x^3}{(e^x-1)[x^2-(T_{21}/T)^2]} dx \\ &\qquad\qquad \left[\mu = \frac{D(\Gamma_8)}{D(\Gamma_6)} \right] , \\ O(T) &= \frac{1}{e^{T_0/T}-1} , \quad \left[T_0 = \frac{\hbar\omega_{\mathrm{eff}}}{k} \right] . \end{aligned} \tag{22}$$

The value of T_0 in Eq. (22) may be determined as follows: Ref. 26 gives the phonon density of states for MgO (inelastic neutron-scattering and lattice-dynamics calculations) and the vibrational sideband of the optical spectrum of the ${}^2E_g \rightarrow {}^4A_{2g}$ transition of MgO:Cr^{3+}. The peaks of the sideband spectra match the peaks in the phonon density of states. Taking into account Fig. 1 and

Table 1 in Ref. 26, we take the average of the phonon energies of the strong peaks in the optical branches, 422.5 cm^{-1}, as $\hbar\omega_{\mathrm{eff}}$; hence, we have $T_0=\hbar\omega_{\mathrm{eff}}/k=608$ K. Then, we calculate $\Delta E_{e\text{-}p}^{\mathrm{calc}}$ by least-squares fitting the experimental data with the adjustable parameters α, γ, $D(\Gamma_6)$, T_D, and μ. Finally, we get $T_D=380$ K ($\hbar\omega_D=264$ cm^{-1}), $\mu=1.85$ (corresponding to $q_{\mathrm{eff}}=-1.08|e|$), $\alpha=420$ cm^{-1}, $\gamma=-120$ cm^{-1}, and $D(\Gamma_6)=7.01\times10^{-6}$ $\mathrm{cm}^{-1}\,\mathrm{K}^{-3}$. Corresponding $\Delta E_{e\text{-}p}^{\mathrm{calc}}$ and its three constituent terms are shown in Table II.

D. Theoretical calculations for $D(\Gamma_6)$

It is shown in Table II that $\Delta E^{(2)}$ gives the main contribution to $\Delta E_{e\text{-}p}$. In order to check our theory and to have a better understanding of the microscopic mechanism of TS, it is necessary to calculate theoretically two parameters, $D(\Gamma_6)$ and $D(\Gamma_8)$ (or μ), in the expression of $\Delta E^{(2)}$.

Here the i level is $t_2^3\,{}^2E\Gamma_8$ and $\Delta E^{(2)}$ includes contributions of $j_1\equiv t_2^3\,{}^3T_1\Gamma_6$ [for $D(\Gamma_6)$] and $j_2\equiv t_2^3\,{}^2T_1\Gamma_8$ [for $D(\Gamma_8)$]. From Eq. (14b) we have

$$D(\Gamma_6)=\frac{k^3}{15\pi^2 C\rho\hbar^4}\left[\frac{1}{v_l^5}+\frac{3}{2v_t^5}\right]I(\Gamma_6)\,,$$

$$\begin{aligned}I(\Gamma_6)=&\sum_{\gamma,\gamma'}|\langle\psi_{i,\gamma_i}^{\mathrm{el}}|C(T_2\gamma)|\psi_{j1,\gamma'}^{\mathrm{el}}\rangle|^2\\&+8\sum_{\gamma,\gamma'}|\langle\psi_{i,\gamma_i}^{\mathrm{el}}|C(E\gamma)|\psi_{j1,\gamma'}^{\mathrm{el}}\rangle|^2\,,\end{aligned}\tag{23}$$

$$D(\Gamma_8)=\frac{k^3}{15\pi^2 C\rho\hbar^4}\left[\frac{1}{v_l^5}+\frac{3}{2v_t^5}\right]I(\Gamma_8)\,,$$

$$\begin{aligned}I(\Gamma_8)=&\sum_{\gamma,\gamma'}|\langle\psi_{i,\gamma_i}^{\mathrm{el}}|C(T_2\gamma)|\psi_{j_2,\gamma'}^{\mathrm{el}}\rangle|^2\\&+8\sum_{\gamma,\gamma'}|\langle\psi_{i,\gamma_i}^{\mathrm{el}}|C(E\gamma)|\psi_{j_2,\gamma'}^{\mathrm{el}}\rangle|^2\,,\end{aligned}\tag{24}$$

where

$$\langle\psi_{i,\gamma_i}^{\mathrm{el}}|=a_0\langle t_2^3\,{}^2E\Gamma_8\gamma_i|+\sum_l a_l\langle\alpha_l S_l\bar{\Gamma}_l\Gamma_8\gamma_i|\,,$$

$$\begin{aligned}|\psi_{j_1,\gamma'}^{\mathrm{el}}\rangle=&\,b_0(\Gamma_6)|t_2^3\,{}^2T_1\Gamma_6\gamma'\rangle\\&+\sum_m b_m(\Gamma_6)|\alpha_m S_m\bar{\Gamma}_m\Gamma_6\gamma'\rangle\,,\end{aligned}\tag{25}$$

$$\begin{aligned}|\psi_{j_2,\gamma'}^{\mathrm{el}}\rangle=&\,b_0(\Gamma_8)|t_2^3\,{}^2T_1\Gamma_8\gamma'\rangle\\&+\sum_m b_m(\Gamma_8)|\alpha_m S_m\bar{\Gamma}_m\Gamma_8\gamma'\rangle\,.\end{aligned}$$

The mixing coefficients involved in Eq. (25) were gained in diagonalization of the complete energy matrices of MgO:Cr^{3+}. All the necessary mixing coefficients in the calculation are given in Table I. The wave-function mixing occurring here comes from a Coulomb interaction and/or a spin-orbital interaction.

We found through the calculations that both Eqs. (23) and (24) were irrelevant to components γ_i. This indicates the fact that both $t_2^3\,{}^2T_1\Gamma_6$ and $t_2^3\,{}^2E\Gamma_8$, by interaction H' with $t_2^3\,{}^2E\Gamma_8$, make it shifted rather than split.

It is the mixing of wave functions in Eqs. (25) that makes $D(\Gamma_6)$ and $D(\Gamma_8)$ different from zero. After a detailed calculation we finally obtained,

$$\begin{aligned}I(\Gamma_6)=&\tfrac{1}{3}[0.004\,483P^2+0.000\,062\,27Y^2\\&+0.009\,990Z^2+0.001\,577YZ]\,,\end{aligned}\tag{26}$$

$$\begin{aligned}I(\Gamma_8)=&\tfrac{1}{3}[0.004\,487P^2+0.003\,279Y^2\\&-0.001\,074YZ+0.017\,73Z^2]\,,\end{aligned}\tag{27}$$

and

$$\mu=\frac{D(\Gamma_8)}{D(\Gamma_6)}=\frac{I(\Gamma_8)}{I(\Gamma_6)}\,.\tag{28}$$

In order to obtain the values of $I(\Gamma_6)$ and $I(\Gamma_8)$, we must evaluate those of P, Y, and Z ($P\equiv\langle t_2\|C(E)\|t_2\rangle$, $Y\equiv\langle t_2\|C(T_2)\|t_2\rangle$, and $Z\equiv\langle t_2\|C(T_2)\|e\rangle$). On the basis of the point-charge model, Refs. 12 and 27 gave formulas for P, Y, and Z,

$$\begin{aligned}P&=-2.949\frac{\langle r^2\rangle}{R^3}-1.827\frac{\langle r^4\rangle}{R^5}\,,\\Y&=8.349\frac{\langle r^2\rangle}{R^3}-9.527\frac{\langle r^4\rangle}{R^5}\,,\\Z&=-6.817\frac{\langle r^2\rangle}{R^3}-5.834\frac{\langle r^4\rangle}{R^5}\,,\end{aligned}\tag{29}$$

where R is the distance between Cr^{3+} and O^{2-} in atomic units. Skinner[28] measured the lattice parameter of periclase $a_0=4.2117\pm0.0002$ Å at 298.16 K. So, $R=a_0/2=2.1059$ Å$=3.9796$ a.u.

It is well known that the point-charge model has its shortcomings. In an application of Eq. (29), adequate corrections must be taken. In fact, there are interactions between the electronic wave functions of central metal cation and ligand ions—overlap, covalence, etc. In comparison with those of free ions, wave functions of ions in crystal expand radially. We will still apply Eq. (29). However, $\langle r^2\rangle$ and $\langle r^4\rangle$ will not be the expected values of electronic wave functions of free Cr^{3+} ions, $\langle r^2\rangle_0$ and $\langle r^4\rangle_0$, but those of Cr^{3+} in crystal. The values of two parameters (Dq and μ) determined by the experimental data will be used to evaluate $\langle r^2\rangle$ and $\langle r^4\rangle$.

First, we make use of formula

$$Dq=\frac{eq_{\mathrm{eff}}}{6R^5}\langle r^4\rangle\,,\tag{30}$$

where $Dq=1619$ cm^{-1} has been determined from the calculation of the energy spectrum in the preceding section and q_{eff} is the effective charge of the ligand ion O^{2-}. Since we have had $\mu=1.85$ through least-squares fitting, we can find q_{eff} in the following way.

The relation

$$\frac{\langle r^2\rangle}{\langle r^2\rangle_0}=\left[\frac{\langle r^4\rangle}{\langle r^4\rangle_0}\right]^{1/2}\tag{31}$$

holds approximately.[29] According to Ref. 30, for free

Cr^{3+} ions $\langle r^2\rangle_0=1.434$ a.u. and $\langle r^4\rangle_0=4.277$ a.u. From Eqs. (26)–(31) and $\mu=1.85$, we get $q_{\mathrm{eff}}=-1.08|e|$. Then we finally obtained $\langle r^2\rangle=4.44$ a.u., $\langle r^4\rangle=40.9$ a.u.

Using Eqs. (26) and (29) and the values of $\langle r^4\rangle$ and $\langle r^2\rangle$, we get the theoretical value 3.36×10^{-24} erg^2 for $I(\Gamma_6)$. With this value of $I(\Gamma_6)$ and Eq. (23), the theoretical value of $D(\Gamma_6)$ can be obtained.

By use of the values of the elastic stiffness constants of MgO at room temperature,[31]

$$C_{11}=28.6\times10^{11}\ \mathrm{dyn/cm^2}\ ,$$

$$C_{44}=14.8\times10^{11}\ \mathrm{dyn/cm^2}\ ,$$

the density of periclase measured with the x-ray technique,[32] $\rho=3.5837\pm0.0013$ g/cm^3 (25 °C), and the calculated velocities of sound, $v_l=\sqrt{C_{11}/\rho}=8.93\times10^5$ cm/s and $v_t=\sqrt{C_{44}/\rho}=6.43\times10^5$ cm/s, we get from Eq. (23) $D(\Gamma_6)=6.9\times10^{-6}\ \mathrm{cm^{-1}\,K^{-3}}$ which agrees quite well with that obtained by fitting the experimental data $(7.0\times10^{-6}\ \mathrm{cm^{-1}\,K^{-3}})$.

V. DISCUSSION AND CONCLUSIONS

$\Delta E^{(2)}$, related to $D(\Gamma_6)$ and $D(\Gamma_8)$, gives a main contribution to TS. Since $D(\Gamma_6)$ and $D(\Gamma_8)$ depend solely on the interaction of $t_2^3\,{}^2T_1\Gamma_6$ and $t_2^3\,{}^2T_1\Gamma_8$ with $t_2^3\,{}^2E\Gamma_8$, and are irrelevant to other levels, they can be calculated more accurately. Therefore, the good agreement of the theoretical value of $D(\Gamma_6)$ with that from fitting the experimental data is a good support to our theory as well as calculations based on it.

When T_0 in the optical branches is determined by their peaks in the phonon spectrum taken from the references, by least-squares fitting we get $\hbar\omega_D=264\ \mathrm{cm^{-1}}$ and $q_{\mathrm{eff}}=-1.08|e|$. This value of $\hbar\omega_D$ agrees well with the peak of the acoustic branch ($\sim270\ \mathrm{cm^{-1}}$).[2,26] Noticing that the Debye model is applicable only to the acoustic branch, T_D defined in the Debye model is available for the acoustic branch, also. The q_{eff} obtained is reasonable, in comparison with that usually adopted in the references $(q_{\mathrm{eff}}/|e|\approx-1)$.[33]

Table II shows that our calculations of TS are in good agreement with the experimental data of TS. In our calculations, a series of other experimental data (including thermal expansion coefficients, heat capacities, equations of state, pressure-induced spectral shifts, absorption spectrum at normal pressure, density of states of phonons, elastic stiffness constants, and density of crystal and lattice constants) were applied, too. This indicates that our theoretical calculations agree with many experimental data.

Table II shows $\Delta E_{\mathrm{te}}/|\Delta E\ \mathrm{exp}|=29.7\%$ (at 265.5 K) or 27.4% (at 97.4 K), indicating that the contribution from thermal expansion is important among various contributions to TS. Similar results are obtained in our work on TS for the *R* lines of MgO:V^{2+} and ruby. Therefore, it is incorrect that previous researchers ignored the contribution of thermal expansion to TS for *R* lines of these crystals.

We have mentioned that the EPI contributions to TS, $\Delta E_{e\text{-}p}$, are composed of those of acoustic as well as optical branches. As for the contribution of the acoustic branches, it includes the Raman term $(\Delta E^{(1)})$ and that from $t_2^3\,{}^2T_1$ (i.e., $\Delta E^{(2)}$). It is shown in Table II, that $\Delta E^{(2)}$ gives a main contribution [it can be considered as a "resonance" coming from the factor $(E_i^{\mathrm{el}}-E_j^{\mathrm{el}}-\hbar\omega_{Kl})$ at denominators in Eqs. (12)] and has the same sign as total TS (redshift), $\Delta E^{(1)}$ is second in magnitude but with opposite sign (blueshift), and $\Delta E^{(3)}$ is the least (redshift). However, if we compare the whole contribution of the acoustic branches $(\Delta E^{(1)}+\Delta E^{(2)})$ with that of the optical branches $(\Delta E^{(3)})$, the importance of the latter is quite clear: $\Delta E^{(3)}/\Delta E_{e\text{-}p}^{\mathrm{calc}}=10\%$ (at 76.8 K) or 50.8% (at 175.1 K) or 62.6% (at 265.6 K), i.e., the contribution of the optical branches becomes more and more important when the temperature is increased [it is clear from the $O(T)$ expression in Eq. (22)] and exceeds that of the acoustic branches at 175.1 K.

Usually, only the Raman term was taken to fit the experiments of TS in Refs. 1–4 so far, and its calculated contribution was the redshift, i.e., $\alpha_i<0$. But in our derivation, it is clear that the Raman term was merely one of four parts of contributions to TS.

After detailed numerical calculations we obtained the following.

(i) The Raman term is the blueshift, opposite in sign to the experimental TS result ΔE_{exp}.

(ii) The contribution of $t_2^3\,{}^2T_1$ $(\Delta E^{(2)})$ is the redshift, it is partly eliminated by the Raman term $(\Delta E^{(1)})$. The algebraic sum $(\Delta E^{(1)}+\Delta E^{(2)})$ is the whole contribution of the acoustic branches.

(iii) The contribution of the optical branches is the redshift $(\Delta E^{(3)})$, and $(\Delta E^{(1)}+\Delta E^{(2)})+\Delta E^{(3)}$ gives $\Delta E_{e\text{-}p}^{\mathrm{calc}}$.

(iv) The contribution of the thermal expansion ΔE_{te} is the blueshift, and the algebraic sum of $\Delta E_{e\text{-}p}^{\mathrm{calc}}$ and ΔE_{te} gives the total TS.

According to our derivation, the Raman term is the algebraic sum of the contribution caused by the interaction of the *i* level with those *j* levels which satisfy $|E_i^{\mathrm{el}}-E_j^{\mathrm{el}}|\gg\hbar\omega_D$ through H' and $[(H'')_{ii}-(H'')_{gg}]$ for the acoustic branches [$(H'')_{gg}$ is the contribution of the ground state $t_2^3\,{}^4A_2\Gamma_8$].

The Raman term is the blueshift, i.e., $\alpha>0$. Noticing the expression

$$\sum_{j\neq i}\frac{\left[\sum_{\gamma}|\langle\psi_i^{\mathrm{el}}|C(T_2\gamma)|\psi_j^{\mathrm{el}}\rangle|^2+8\sum_{\gamma}|\langle\psi_i^{\mathrm{el}}|C(E\gamma)|\psi_j^{\mathrm{el}}\rangle|^2\right]}{E_i^{\mathrm{el}}-E_j^{\mathrm{el}}}<0$$

(where *i* refers to $t_2^3\,{}^2E\Gamma_8$), it is clear from Eqs. (4b) and (13) that $\alpha_i>0$ occurs only when

$$(\langle\psi_i^{\mathrm{el}}|V_2|\psi_i^{\mathrm{el}}\rangle-\langle\psi_g^{\mathrm{el}}|V_2|\psi_g^{\mathrm{el}}\rangle)>0$$

and when it is the dominant part of α. Further study on this point is worthwhile.

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[1] D. E. McCumber and M. D. Sturge, J. Appl. Phys. **34**, 1682 (1963).

[2] G. F. Imbusch *et al.*, Phys. Rev. **133**, A1029 (1964).

[3] B. Di Bartolo and R. Peccei, Phys. Rev. **137**, A1770 (1965).

[4] T. Kushida, Phys. Rev. **185**, 500 (1969).

[5] B. Di Bartolo and R. C. Powell, *Phonons and Resonances in Solids* (Wiley, New York, 1976), pp. 454–456.

[6] B. DiBartolo, *Optical Interactions in Solids* (Wiley, New York, 1968), pp. 341–343, 372–377.

[7] A. A. Kaminskii, *Laser Crystals* (Springer-Verlag, Berlin, 1981), pp. 92–97.

[8] Ma Dong-ping *et al.*, J. Phys. C **21**, 3585 (1988).

[9] R. A. Noack and W. P. Holzapfel, in *High Pressure Science and Technology, Sixth AIRAPT Conference,* edited by K. D. Timmerhaus and M. S. Barber (Plenum, New York, 1979), Vol. I, p. 748.

[10] S. L. Wander and P. E. Schoen, J. Appl. Phys. **52**, 3772 (1981).

[11] Xu Yi-sun *et al.*, Acta Phys. Sin. **35**, 213 (1986); Chin. Phys. **6**, 601 (1986).

[12] T. Kushida and M. Kikuchi, J. Phys. Jpn. **23**, 1333 (1967).

[13] J. H. Van Vleck, Phys. Rev. **57**, 426 (1940).

[14] M. Blume, R. Orbach, A. Kiel, and S. Geschwind, Phys. Rev. **139**, A314 (1965).

[15] W. A. Runciman and K. A. Schroeder, Proc. R. Soc. London Ser. A **265**, 489 (1962).

[16] S. Sugano, Y. Tanabe, and H. Kamimura, *Multiplets of Transition-Metal Ions in Crystals* (Academic, New York, 1970).

[17] A. Chopelas and R. Boehler, Mat. Res. Soc. Symp. Proc. **22**, 275 (1984).

[18] S. Minomura and H. G. Drickamer, J. Chem. Phys. **35**, 903 (1961).

[19] W. M. Fairbank and G. K. Klauminzer, Phys. Rev. B **7**, 500 (1973).

[20] S. Ganesan, Philos. Mag. **7**, 197 (1962).

[21] Gao Zhan-peng, Acta Phys. Sin. **30**, 679 (1981).

[22] T. H. K. Barron, W. T. Berg, and J. A. Morrison, Proc. R. Soc. London Ser. A **250**, A70 (1959).

[23] A. C. Victor and T. B. Douglas, J. Res. Natl. Bur. Stand. Sec. A **67**, 325 (1963).

[24] O. L. Anderson, J. Phys. Chem. Solids **27**, 547 (1966).

[25] Ma Dong-ping, Zheng Xi-te, Zhang Zheng-gang, and Xu Yi-sun, Phys. Lett. A **121**, 97 (1987).

[26] A. Chopelas and M. Nicol, J. Geophys. Res. **87**, 8591 (1982).

[27] J. Kanamori, Prog. Theor. Phys. **17**, 197 (1956).

[28] B. J. Skinner, Am. Mineral. **42**, 39 (1957).

[29] M. D. Sturge, Phys. Rev. **130**, 639 (1963).

[30] K. W. H. Stevens and C. A. Bates, in *Magnetic Oxides Part 1,* edited by D. J. Craik (Wiley, New York, 1975), p. 146.

[31] H. B. Huntington, in *Solid State Physics: Advances in Research and Applications,* edited by F. Seity and D. Turnbull (Academic, New York, 1956), Vol. 7, p. 213; S. Bhagavantam, Proc. Indian Acad. Sci. A **41**, 72 (1955).

[32] *Handbook of Chemistry & Physics,* 66th ed., edited by R. C. Weast, M. J. Astle, and W. H. Beyer (CRC, Boca Raton, FL, 1985), p. 209.

[33] A. S. Marfunin, *Physics of Minerals and Inorganic Materials* (Springer-Verlag, Berlin, 1979), pp. 147–149, 279, 280.