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Ruidan Wang† and Xiao-Yi Huang‡

† Department of Physics, Hunan Normal University, Changsha, Hunan 410006, People's Republic of China
‡ Department of Physics, Chenzhou Teachers' College, Chenzhou, Hunan 423000, People's Republic of China

Abstract. The electron–phonon interaction causes a spectral thermal shift (TS) in crystals with impurities. In this paper we develop an approach to calculate the different contributions to the TS of MgO:V^{2+} in detail; these include Raman scattering, the direct process and the optical branch. It is found that the direct process plays a predominant role in the TS. Moreover, the TS caused by thermal expansion is interpreted and calculated using the theory of the pressure-induced spectral shift. Taking account of the contributions, we calculated the R-line TS of MgO:V^{2+} by fitting the experimental data. Our results show good agreement with the TS experimental data and other experimental data for MgO:V^{2+}.

1. Introduction

The optical spectra of 3d or 4f ions in crystals are shifted with temperature. In practice, this shift is closely related to the stability of and change in the emission frequencies of lasers as well as temperature-tunable lasers, and theoretically it is related to the electron–phonon interaction (EPI). So these kinds of thermal shift (TS) have attracted great research interest [1–7]. However, there are some problems to be solved and a thorough investigation in more detail is needed. In this paper we solve the following problems.

(i) In [1, 4–7], the formulae for TS calculations usually include two terms, i.e. the 'Raman term' and the 'direct-process term', but generally only the Raman term was considered in quantitative calculations [1–4]. We shall study all possible contributions to the TS by the EPI and thermal expansion of the crystal.

(ii) We think that the direct process plays the predominant role in the R-line TS of MgO:V^{2+}. Therefore, it is important to calculate this term accurately. Thus, the assumption that the crystal is isotropic or nearly isotropic must be abandoned. Considering the wavefunction mixing, we shall derive microscopically expressions for the parameters in the most important term (the direct process) and calculate their values.

(iii) When all these contributions to the TS are clarified, numerical calculations of the R-line TS for MgO:V^{2+} will be given in detail by fitting the experimental data.

The R-line of MgO:V^{2+} is assigned to the transition $t_2^3\,{}^2E\,\Gamma_8 \rightarrow t_2^3\,{}^4A_2\,\Gamma_8$. MgO:V^{2+} is a crystal of face-centred cubic structure. In MgO:V^{2+}, the vanadium ions enter substitutionally for magnesium ions; the measured spectral lines are contributions from V^{2+} ions in a site of perfect octahedral symmetry (i.e. O$_h$ symmetry) [8].

2. Various contributions to the thermal shift

We now 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 TSs of the two levels involved in the transition. The contributions to the TS consist of two parts: the contribution of thermal expansion and that of the EPI.

2.1. Contribution of thermal expansion

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

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

According to the general thermodynamic relation, we have

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

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 the thermal expansion rate at normal pressure and $(\partial E/\partial V)_T$ is the shift rate of a level caused solely by the volume (or interionic distance) variation. Obviously, $(\partial E/\partial V)_T(\partial V/\partial T)_p$ is the contribution of thermal expansion to the TS.

According to the theory for the pressure-induced spectral shift [8], the distances between ions are reduced under hydrostatic pressure, their interactions change and the radial electronic wavefunctions expand which causes a variation in Dq (crystal-field parameter), B, C (Racah parameters) and ζ (spin–orbital coupling parameter), as well as the energy level.

According to the experimental data, the pressure-induced shift rate of the R_1 line of ruby does not depend on the temperature [9], i.e. it is independent of the EPI. In the temperature interval 25–200 °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 equation (2) it can be suggested that the level shifts caused by the variation in interionic distances R (whether or not the variations are brought about by thermal expansion or by compression) are independent of the EPI and temperature and are determined only by the variations in R. As has been shown above, the variation in R and the corresponding expansion of the radial electronic wavefunctions give rise to the shift in a level. This is the mechanism of the level shift caused by thermal expansion or compression.

Therefore, the same variation in R from thermal expansion or compression should cause the same level shift, and the TS caused by thermal expansion can be calculated by use of the thermal expansion coefficient and theory of the pressure-induced spectral shift.

2.2. Contributions of the electron–phonon interaction

The crystalline field at the impurity ion is a function of the local strain ϵ. When ϵ is a dynamic strain due to the lattice vibrations, the interaction between the impurity and local crystalline field causes TSs in the energy levels of the ions. The ion–vibration interaction Hamiltonian can be written as follows:

$$H_{\text{int}} = H' + H'' = V_1\epsilon + V_2\epsilon^2 \tag{3}$$

where V_1 and V_2 are expansion coefficients in H_{int}.

Di Bartolo [6] gave the contribution of the EPI of the i-level TS as

$$\delta E_i = (H'')_{ii} + \sum_j{}' \frac{|(H')_{ij}|^2}{E_i - E_j} = \sum_j{}' \frac{\langle i|H'|j\rangle\langle j|H'|i\rangle}{E_i - E_j} + \langle i|H''|i\rangle \tag{4}$$

where $|i\rangle$ represents a state of the system (ion+vibrations). Taking account of all the relevant processes and calculating them in detail, we may express the TS of the energy levels of MgO:V²⁺ as made up of the following three parts [6]. First,

$$\delta E_i^{(1)} = \alpha_i \left(\frac{T}{T_D}\right)^4 \int_0^{T_D/T} \frac{x^3}{\exp x - 1}\, dx \tag{5}$$

where $x = \hbar\omega_k/kT$. T_D is the Debye temperature and α_i is an independent coefficient of temperature. This is called the Raman term. Secondly,

$$\delta E_i^{(2)} = \sum_{j\neq i} \beta_{ij} \left(\frac{T}{T_{ij}}\right)^2 P\left(\int_0^{T_D/T} \frac{x^3\, dx}{(\exp x - 1)[x^2 - (T_{ij}/T)^2]}\right) \tag{6}$$

where $T_{ij} = (E_i - E_j)/k$, P indicates the principal value of the integral (when $T_{ij} < T_D$, there will be a singular point in the integrand) and

$$\beta_{ij} = -\frac{3(E_i - E_j)^3}{4\pi^3 \rho v^5 \hbar^4 c} |\langle\psi_i|V_1|\psi_j\rangle|^2 \tag{7}$$

where ρ is the crystal density, v is the average sound velocity and c is the velocity of light. The term in equation (6) is called the direct-process term. Thirdly

$$\delta E_i^{(3)} = \gamma_i \frac{1}{\exp(\hbar\omega_{\text{eff}}/kT) - 1} = \gamma_i \frac{1}{\exp(T_0/T) - 1} \tag{8}$$

where ω_{eff} is the optical branch frequency and γ_i is an independent coefficient of temperature. This is called the optical branch term.

The formula for the TS from the EPI can be written as

$$\delta E_i = \delta E_i^{(1)} + \delta E_i^{(2)} + \delta E_i^{(3)}. \tag{9}$$

Numerical calculations show that the term in equation (6) (i.e. the term from the j levels which satisfy $|E_i - E_j| \lesssim kT_D$) plays the main role of the various contributions to TS. It is necessary to study that for the R line of MgO:V²⁺ in more detail. In particular we shall derive the expression for β_{ij} from microscopic theory.

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

Following Kushida and Kikuchi [11], we can write H' as

$$H' = \sum_{\Gamma\gamma} C(\Gamma\gamma)\epsilon(\Gamma\gamma) \tag{10}$$

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

If the point group about the central metal ion is cubic, the only even vibrations of such a cluster which need to be considered are the E and T_2 vibrations. So we have

$$\beta_{ij} = -T_{ij}^3 D_{ij}$$

$$D_{ij} = \frac{k^3}{15\pi^2 c\rho\hbar^4} \left(\frac{1}{v_l^5} + \frac{3}{2v_t^5}\right) \left(\sum_\gamma |\psi_i| C(T_2\gamma)|\psi_j\rangle|^2 + 8\sum_\gamma |\langle\psi_i| C(E\gamma)|\psi_j\rangle|^2\right). \tag{11}$$

As for D_{ij}, we shall calculate it in detail with wavefunctions later.

3. Calculations of the R-line thermal shift of MgO:V^{2+}

3.1. Calculations of the contribution of thermal expansion to the thermal shift

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

The p–κ dependence can be calculated from the Murnaghan equation

$$p = \frac{B_0}{B_0'}(\kappa^{-3B_0'} - 1) \tag{12}$$

where B_0 and B_0' are the isothermal bulk modulus and its pressure derivative at zero pressure, respectively. From ultrasonic measurements [12], $B_0 = 1622$ kbar and $B_0' = 4.54$. Chopelas and Boehler [13] measured the red shifts of the R line of MgO:V^{2+} under hydrostatic pressure at room temperature. They found the shifts to be linear with slope $\eta = \mathrm{d}\lambda/\mathrm{d}p = 0.585$ Å kbar^{-1} for MgO:V^{2+}. We may obtain the corresponding shift of the R line from

$$\Delta E_p \approx \frac{-\eta p}{\lambda_0(\lambda_0 + \eta p)} \times 10^8 \text{ cm}^{-1} \tag{13}$$

where $\lambda_0 = 6992$ Å [13], p is in kilobars and ΔE_p is equal to the TS of the R line caused by thermal expansion with the same κ-value, relative to room temperature (293 K). We finally obtain the contribution ΔE_{te} to the TS of the R line by thermal expansion as shown in table 1.

Positive values of ΔE_{te} indicate a blue shift.

Table 1. Thermal shift caused by thermal expansion of the R line of MgO:V²⁺.

T (K)	κ	ΔE_{te} (cm^{-1})
74.7	0.998 799	0.068
91.3	0.998 821	0.153
110.4	0.998 864	0.318
134.0	0.998 947	0.633
160.6	0.999 078	1.13
187.4	0.999 247	1.78
200.0	0.999 338	2.12
232.8	0.999 605	3.13
263.2	0.999 884	4.19
288.2	0.999 913	4.96
300.0	1.000 257	5.59
333.5	1.000 621	6.95

3.2. Theoretical calculations for $D(\Gamma\gamma)$

For MgO:V²⁺, the i level is $t_2^3\,^2E\,\Gamma_8$ and $\delta E^{(2)}$ includes the contribution of the j_1 the level which is $t_2^3\,^2T_1\,\Gamma_6$ (for $D(\Gamma_6)$) and the j_2 level which is $t_2^3\,^2T_1\,\Gamma_8$ (for $D(\Gamma_8)$). From equation (11) we have

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

$$I(\Gamma_6) = \sum_{\gamma,\gamma'}|\langle\psi_{i,\gamma_i}|C(T_2\gamma)|\psi_{j_1,\gamma'}\rangle|^2 + 8\sum_{\gamma,\gamma'}|\langle\psi_{i,\gamma_i}|C(E\gamma)|\psi_{j_1,\gamma'}\rangle|^2$$

$$\tag{14}$$

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

$$I(\Gamma_8) = \sum_{\gamma,\gamma'}|\langle\psi_{i,\gamma_i}|C(T_2\gamma)|\psi_{j_2,\gamma'}\rangle|^2 + 8\sum_{\gamma,\gamma'}|\langle\psi_{i,\gamma_i}|C(E\gamma)|\psi_{j_2,\gamma'}\rangle|^2$$

$$\tag{15}$$

where

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

$$|\psi_{j_1,\gamma'}\rangle = b_0(\Gamma_6)|t_2^3\,^2T_1\,\Gamma_6\,\gamma'\rangle + \sum_m b_m(\Gamma_6)|\alpha_m S_m\bar{\Gamma}_m\Gamma_6\gamma'\rangle$$

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

a_0 and b_0 are the wavefunction coefficients, and a_l and b_j are the mixing coefficients. All the coefficients can be obtained by diagonalization of the d³ complete energy matrices by fitting to the energy levels of MgO:V²⁺ determined experimentally.

We finally obtained

$$I(\Gamma_6) = \tfrac{1}{3}(0.001\,855\,9P^2 + 0.000\,025\,776Y^2 + 0.010\,822\,5Z^2 + 0.001\,056\,34YZ) \tag{16}$$

$$I(\Gamma_8) = \tfrac{1}{3}(0.001\,857\,7P^2 + 0.001\,343\,66Y^2 - 0.019\,901\,5Z^2 - 0.000\,843\,68YZ). \tag{17}$$

Table 2. The thermal shift of the R line of MgO:V^{2+} and various contributions from the EPI.

T (K)	ΔE_{e-p} (cm^{-1})	ΔE_{e-p}^{cal} (cm^{-1})	$\Delta E^{(1)}$ (cm^{-1})	$\Delta E^{(2)}$ (cm^{-1})	$\Delta E^{(3)}$ (cm^{-1})
74.7	−0.27	−0.25	6.11	−6.35	−0.005
91.3	−0.66	−0.65	11.19	−11.81	−0.031
110.4	−1.37	−1.38	18.69	−19.96	−0.123
134.0	−2.69	−2.71	29.84	−32.15	−0.396
160.6	−4.64	−4.72	44.16	−47.90	−0.982
187.4	−7.12	−7.26	59.90	−65.26	−1.899
200.0	−8.90	−8.61	67.64	−73.81	−2.442
232.8	−12.70	−12.55	88.51	−96.90	−4.158
263.2	−16.53	−16.65	108.60	−119.10	−6.094
288.2	−19.99	−20.29	125.40	−137.80	−7.895
300.0	−22.19	−22.07	133.50	−146.70	−8.802
333.5	−27.45	−27.36	156.60	−172.40	−11.550

Formulae for P, Y and Z were given in [11, 14]:

$$P = -2.949\frac{\langle r^2 \rangle}{R^3} - 1.827\frac{\langle r^4 \rangle}{R^5}$$

$$Y = 8.349\frac{\langle r^2 \rangle}{R^3} - 9.527\frac{\langle r^4 \rangle}{R^5} \tag{18}$$

$$Z = -6.817\frac{\langle r^2 \rangle}{R^3} - 5.843\frac{\langle r^4 \rangle}{R^5}$$

where R is the distance between V^{2+} and O^{2-}; $\langle r^2 \rangle$ and $\langle r^4 \rangle$ can be determined from the electron radial wavefunciton of MgO:V^{2+}.

The values of $D(\Gamma_6)$ and $D(\Gamma_8)$ are

$$D(\Gamma_6) = 0.930 \times 10^{-5} \text{ cm}^{-1} \text{ K}^{-3}$$

$$D(\Gamma_8) = 0.517 \times 10^{-5} \text{ cm}^{-1} \text{ K}^{-3}$$

which agree quite well with those obtained by fitting the experimental data ($D(\Gamma_6) = 1.10 \times 10^{-5}$ cm^{-1} K^{-3}; $D(\Gamma_8) = 0.612 \times 10^{-5}$ cm^{-1} K^{-3}).

3.3. Calculations of the contribution from the electron–phonon interaction

For the TS of the R line as mentioned above, the contribution caused by the EPI is

$$\Delta E_{e-p} = \Delta E_{exp} - \Delta E_{te} \tag{19}$$

where ΔE_{exp} is the experimental value for the TS [2, 3].

In equation (9), the i level is $t_2^3\,^2E\,\Gamma_8$. Let us now rewrite the expression for the TS of the R line caused by the EPI as

$$\Delta E_{e-p}^{cal} = \Delta E^{(1)} + \Delta E^{(2)} + \Delta E^{(3)}. \tag{20}$$

The subscript i is omitted here and subsequently.

We calculate ΔE_{e-p}^{cal} by least-squares fitting the experimental data from equation (19). Finally, we obtain the values of the parameters: $T_D = 385$ K; $T_0 = 730$ K, $\alpha = 857$ cm^{-1}; $\gamma = -92$ cm^{-1}. The corresponding ΔE_{e-p}^{cal} and its three constituent terms are shown in table 2.

4. Discussion and conclusions

Table 2 shows that our calculations of the TS are in good agreement with the experimental data on the 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, density of crystal and lattice constants) were applied, too. This indicates that our theoretical calculations agree with many experimental data.

Equation (9) includes the contribution of the acoustic branches (the Raman term and the direct-process term) and optical branches. Moreover, the TS caused by thermal expansion is also considered. We have analysed the proportions of every term in the TS. The results above indicate that all the terms make obvious contributions. Nevertheless, table 2 shows that the direct-process term plays a predominant role. We think that the one-phonon resonant efficiency causes this. Therefore, it is rather important to calculate the direct-process $D(\Gamma\gamma)$ exactly.

After numerical calculations we obtained the following conclusions.

(i) The Raman term $\Delta E^{(1)}$ is a blue shift.

(ii) When $|E_i - E_j| \lesssim \hbar\omega_D$, the direct-process term $\Delta E^{(2)}$ must be calculated alone. We cannot include it in the Raman term. For MgO:V^{2+} the i level is $t_2^3\,^2E\,\Gamma_8$, the j_1 level is $t_2^3\,^2T_1\,\Gamma_6$ and the j_2 level is $t_2^3\,^2T_1\,\Gamma_8$. The direct process results in a red shift and plays the main role of the various contributions to the TS.

(iii) The contribution $\Delta E^{(3)}$ of the optical branches is a red shift. It increases rapidly with increasing temperature.

(iv) The contribution ΔE_{te} of the thermal expansion is a blue shift, and the algebraic sum of $\Delta E^{(1)}$, $\Delta E^{(2)}$, $\Delta E^{(3)}$ and ΔE_{te} gives the total TS.

(v) The total TS is a red shift.

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