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Determination of the local compressibilities for Cr^{3+} ions in some garnet crystals from high-pressure spectroscopy

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Abstract. By using the bond length dependence of the covalency reduction factor obtained from the pressure-induced spectral shifts of ruby ($\text{Al}_2\text{O}_3:\text{Cr}^{3+}$), the local compressibilities of $\text{Cr}^{3+}-\text{O}^{2-}$ bonds for Cr^{3+} in the octahedral a sites of $\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{La}_3\text{Lu}_2\text{Ga}_3\text{O}_{12}$ crystals have been determined from their high-pressure spectroscopies. The results are obviously different from the compressibilities of the host crystals. The reasons for the difference are discussed.

1. Introduction

The electronic properties due to a transition-metal impurity M placed in an insulator material can be understood to a great extent only on the basis of an MX_n group formed by the impurity and the n nearest neighbours or ligands [1]. So, the optical spectrum of a $3d^n$ impurity ion in an ionic lattice depends mainly on the nature and number of ligands as well as on the true value of the impurity–ligand distance R . For a given MX_n group in crystals, the useful information about the impurity–ligand distance R can be obtained by studying the optical spectrum. For example, the $\text{Mn}^{2+}-\text{F}^-$ distances and $\text{Mn}^{2+}-\text{Cl}^-$ distances for Mn^{2+} ions in several perovskite complexes ABF_3 and ABCl_3 were studied from the optical spectra of these crystals [2–4]. The results show that the impurity–ligand distances are different from the metal–ligand distances in the pure crystals. When the impurity–ligand distance is changed by applying hydrostatic pressure or by temperature variations, the shifts of the optical spectrum lines can be found and so one can estimate the local compressibility and thermal expansion coefficient for the $M-X$ bond by studying these shifts. Some workers [5, 6] determined the local thermal expansion coefficient α for the $\text{Mn}^{2+}-\text{F}^-$ bond in $\text{KZnF}_3:\text{Mn}^{2+}$ crystal from the temperature dependence of the optical spectra. The result is also unlike that in the pure crystal. However, for $3d^n$ impurity ions in some crystals, the local compressibilities have not been studied although the pressure dependence of the optical spectra of these crystals was reported. For example, the pressure-induced shifts of energy levels (or spectral lines) $dE(^4\text{T}_2)/dP$ and $dE(\bar{\text{R}})/dP$ (where $E(^4\text{T}_2)$ and $E(\bar{\text{R}})$ stand for the energy levels of the excited states $^4\text{T}_2$ and ^2E , respectively) for Cr^{3+} ions in the octahedral a sites of $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) and $\text{La}_3\text{Lu}_2\text{Ga}_3\text{O}_{12}$ (LLGG) garnet crystals were measured [7, 8], but studies on the local compressibilities of $\text{Cr}^{3+}-\text{O}^{2-}$ bonds in the two crystals have not been made. Considering that the Cr^{3+} -doped garnet crystals are important solid state laser materials

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and that useful information on the local compressibility is helpful to the understanding of the changes in width, position and lifetimes of electronic transitions and their vibrational side bands as function of applied pressure, studies of the local compressibilities are of significance. In this paper, we study the local compressibilities for Cr^{3+} ions in YAG and LLGG crystals from the pressure dependence of optical spectra.

2. Bond length dependence of the covalency reduction factor

The above studies are based on the bond length dependence of the covalency reduction factor obtained from the pressure dependence of the optical spectra of ruby. The reasons for the above consideration are as follows.

(i) The pressure dependence of the optical spectra of ruby ($\text{Al}_2\text{O}_3\text{Cr}^{3+}$) has been extremely well studied and its R_1 and R_2 luminescence lines are extensively used as a high-pressure standard in diamond-anvil cells.

(ii) The $(\text{CrO}_6)^{9-}$ group in ruby is similar to those in YAG: Cr^{3+} and LLGG: Cr^{3+} crystals.

For simplicity, in the studies we use the cubic approximation for $(\text{CrO}_6)^{9-}$ groups in these crystals. The Hamiltonian of the 3d electrons of Cr^{3+} in cubic symmetry can be written as [9, 10]

$$H = H_0 + H_{\text{cubic}} + H_{\text{Coul}} \quad (1)$$

where H_0 is that of the Cr^{3+} ion and results in the usual (degenerate) 3d-electron orbitals. H_{cubic} is the cubic (O_h) crystal field. It splits the one-electron 3d orbitals into two, e and t_2 , separated by $\Delta (= 10Dq)$, the cubic crystal-field parameter. H_{Coul} represents the Coulomb interaction between the three 3d electrons of the Cr^{3+} ion and is treated as a perturbation of the single-electron orbitals. This causes splittings of the e and t_2 orbitals of the order of the Racah parameters B and C . Thus, from the crystal-field theory [9, 10], the energy level $E(\bar{R})$ can be obtained by diagonalizing the 4×4 2E energy matrix representing Coulomb interaction and, from the point-charge model, the energy level $E({}^4T_2)$ can be written as

$$E({}^4T_2) = 10Dq \propto R^{-5}. \quad (2)$$

The experimental data for NiO [11] and the results based on molecular orbital calculations for $3d^n$ ions in many crystals [12, 13] show that $Dq \propto R^{-5}$ is approximately valid. Thus, from equation (2), we have

$$dE({}^4T_2)/dP \approx -5E_n({}^4T_2)[d(\ln R)/dP] \quad (3)$$

where the subscript n denotes the value at normal pressure (and hereafter), and $d(\ln R)/dP = (1/R)(dR/dP)$ is the compressibility of the impurity–ligand bond. For ruby, from the high-pressure spectroscopy, $dE({}^4T_2)/dP \approx 84(3) \text{ cm}^{-1} \text{ GPa}^{-1}$ with the zero-phonon line $E_n({}^4T_2) \approx 16730(50) \text{ cm}^{-1}$ [14] and $dE(\bar{R})/dP \approx -7.6 \text{ cm}^{-1} \text{ GPa}^{-1}$ with $E_n(\bar{R}) \approx 14417 \text{ cm}^{-1}$ [15] were obtained. Using the pressure dependence of absorption spectra for Cr^{3+} and other $3d^n$ ions in Al_2O_3 , Drickamer and coworkers [16, 17] concluded that the local compressibility is almost the same as the bulk compressibility, perhaps due to the stiffness of the corundum lattice. Indeed, if we apply the compressibility $d(\ln R)/dP \approx \frac{1}{3}d(\ln V)/dP \approx -1.05 \times 10^{-3} \text{ GPa}^{-1}$ of Al_2O_3 [18] and the $E_n({}^4T_2)$ of the zero-phonon line of ruby to equation (3), we obtain

$$dE({}^4T_2)/dP \approx 87.8 \text{ cm}^{-1} \text{ GPa}^{-1}. \quad (4)$$

The result is consistent with the above-observed value. So, the value of $d(\ln R)/dP$ is suitable and can be used for the study of $dE(\bar{R})/dP$.

As has been said before, the position of the R line is deduced by diagonalizing the 4×4 2E matrix. So, the pressure-induced shift of the R line is related to the changes in the Racah parameters B and C and the cubic field parameter Dq under pressure. At normal pressure, the parameters B_n and C_n in crystals can be written as [19, 20]

$$B_n = f_n B_0 \quad C_n = f_n C_0 \quad (5)$$

where f_n is the covalency reduction factor at normal pressure. B_0 and C_0 are the values in the free ion. For the Cr^{3+} ion, from the empirical d orbital [20], we have $B_0 = 920.48 \text{ cm}^{-1}$ and $C_0 = 3330.71 \text{ cm}^{-1}$. Thus, for $\text{Al}_2\text{O}_3 : \text{Cr}^{3+}$, from the values of $E_n({}^4T_2)$ and $E_n(\bar{R})$, we obtain $f_n \approx 0.8677$.

As pointed out in theoretical work [19–21], the factor f is a function of impurity–ligand distance R and the ratio B/C can be assumed to be unchanged with pressure. Thus, for the Racah parameters at pressure P , we have

$$\begin{aligned} B_p &= B_0 f_n \{1 + [d(\ln f)/dP]P\} = B_0 f_n \{1 + [d(\ln f)/d(\ln R)][d(\ln R)/dP]P\} \\ C_p &= C_0 f_n \{1 + [d(\ln f)/dP]P\} = C_0 f_n \{1 + [d(\ln f)/d(\ln R)][d(\ln R)/dP]P\}. \end{aligned} \quad (6)$$

By using the above $d(\ln R)/dP$ in equation (6) and then diagonalizing the 4×4 2E energy matrix, we find that, for fitting the observed value $dE(\bar{R})/dP \approx -7.6 \text{ cm}^{-1} \text{ GPa}^{-1}$, the bond length dependence of the covalency reduction factor is

$$d(\ln f)/d(\ln R) \approx 0.7353. \quad (7)$$

Obviously, the value of $d(\ln f)/d(\ln R)$ for the $(\text{CrO}_6)^{9-}$ group in ruby is also approximately applicable to the $(\text{CrO}_6)^{9-}$ groups in other similar crystals because it does not depend upon the value f_n at normal pressure.

3. Determination of local compressibility

Now let us study the local compressibility of the $\text{Cr}^{3+}\text{--O}^{2-}$ band for the $\text{YAG}:\text{Cr}^{3+}$ crystal by using the value of $d(\ln f)/d(\ln R)$. From the high-pressure spectroscopy of $\text{YAG}:\text{Cr}^{3+}$, Wamsley and Bray [7] obtained $dE({}^4T_2)/dP \approx 90 \text{ cm}^{-1} \text{ GPa}^{-1}$ with $E_n({}^4T_2) \approx 16400 \text{ cm}^{-1}$. Thus, according to equation (3), we obtain, for $\text{YAG}:\text{Cr}^{3+}$,

$$d(\ln R)/dP \approx -1.1 \times 10^{-3} \text{ GPa}^{-1}. \quad (8)$$

The result is different from that (approximately $-1.85 \times 10^{-3} \text{ GPa}^{-1}$ [22]) in the host YAG crystal but is close to the value for $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$. It appears that, for Cr^{3+} ions in similar $(\text{AlO}_6)^{9-}$ groups in crystals, the local compressibilities of $\text{Cr}^{3+}\text{--O}^{2-}$ bonds are close to each other. To check further the result of local compressibility, we study the pressure-induced \bar{R} line shift. For the $\text{YAG}:\text{Cr}^{3+}$ crystal, there is a small separation between the \bar{R} (i.e. R_1 and R_2) lines due to the trigonal distortion. In the cubic approximation, we have $E_n(\bar{R}) \approx \frac{1}{2}[E_n(R_1) + E_n(R_2)] \approx 14524 \text{ cm}^{-1}$ [7]. So, from the values of $E_n(\bar{R})$ and $E_n({}^4T_2)$, we obtain $f_n \approx 0.8751$. By substituting the values of f_n , B_0 , C_0 , $d(\ln f)/d(\ln R)$ and $d(\ln R)/dP$ into equation (6), we can calculate B_p and C_p . Thus, diagonalizing the 4×4 2E matrix, we obtain

$$dE(\bar{R})/dP \approx -7.9 \text{ cm}^{-1} \text{ GPa}^{-1}. \quad (9)$$

The result is close to the observed value (table 1). However, if the compressibility of the YAG crystal is used, the calculated \bar{R} line shift (and also the shift of $E({}^4T_2)$) with pressure

Table 1. Pressure-induced shifts of optical spectra for Cr³⁺ ions in YAG and LLGG crystals.

	dE(⁴ T ₂)/dP (cm ⁻¹ GPa ⁻¹)			dE(\bar{R})/dP (cm ⁻¹ GPa ⁻¹)			
	Calculation ^a	Calculation ^b	Experiment	Calculation ^a	Calculation ^b	Experiment	
YAG:Cr ³⁺	90	152	90	[7] -7.9	-25.4	-8.2	[7] ^c
LLGG:Cr ³⁺	100	167	100±5	[8] -10.6	-20.7	-8±3	[8]

^a Calculation using the local compressibility.

^b Calculation using the compressibility of host crystal.

^c Obtained from the formula $dE(\bar{R})/dP \approx \frac{1}{2}[dE(R_1)/dP + dE(R_2)/dP]$.

are obviously unlike the observed values (see table 1). So, the study of the pressure-induced \bar{R} line shift supports the local compressibility.

A similar method can also be applied to the LLGG:Cr³⁺ crystal. Thus, from the observed value $dE(^4T_2)/dP \approx 100 \text{ cm}^{-1} \text{ GPa}^{-1}$ with $E_n(^4T_2) \approx 13350 \text{ cm}^{-1}$ [8], we obtain the local compressibility

$$d(\ln R)/dP \approx -1.5 \times 10^{-3} \text{ GPa}^{-1}. \quad (10)$$

From the local value and $E_n(\bar{R}) \approx 14350 \text{ cm}^{-1}$ [8], we obtain

$$dE(\bar{R})/dP \approx -10.6 \text{ cm}^{-1} \text{ GPa}^{-1}. \quad (11)$$

The result is consistent with the observed value (see table 1), suggesting that the local compressibility in LLGG:Cr³⁺ is reasonable.

For the LLGG crystal, to our best knowledge, no compressibility has been reported. Smdenskii *et al* [23] found an approximately linear relation between the elastic constants c_{ij} and the lattice constant a_0 for garnet crystals from many observed data. According to the relation and the lattice constant a_0 ($\approx 12.95 \text{ \AA}$ [24]) of the LLGG crystal, we obtain for LLGG

$$d(\ln R)/dP \approx \frac{1}{3} d(\ln V)/dP \approx -2.5 \times 10^{-3} \text{ GPa}^{-1}. \quad (12)$$

Obviously, the local compressibility for LLGG:Cr³⁺ is, as also is that for YAG:Cr³⁺ smaller than that in the bulk. Notably, if the compressibility of the host LLGG crystal is used, the calculated values of $dE(^4T_2)/dP$ and $dE(\bar{R})/dP$ are also significantly different from the observed values (see table 1).

4. Discussion

From the above studies, one can find that the local compressibilities for Cr³⁺ ions in YAG and LLGG crystals are smaller than those in the host crystals. Usually, there are two cases in which the local compressibility differs from that in the bulk, i.e.

(i) the charge and/or radius of impurity ion are unlike those of the replaced host ion, and

(ii) the crystal under study has complex composition and structure.

In the case of size-misfitting substitution, in general, when the impurity ion is larger than the host ion that it replaces, it may be expected that there will be a substantial enhancement in the bonding strength and hence a decrease in the compressibility between the impurity ion and the ligands compared with that between the host ion and ligands in the pure lattice because the coupling of the impurity to the lattice is tighter. In contrast, if the impurity ion

is smaller, the local compressibility should increase. However, although the size of Cr³⁺ ($r_{Cr^{3+}} \approx 0.63 \text{ \AA}$ [25]) is between those of the replaced Al³⁺ ($r_{Al^{3+}} \approx 0.51 \text{ \AA}$ [25]) and Lu³⁺ ($r_{Lu^{3+}} \approx 0.85 \text{ \AA}$ [25]), both the local compressibilities of (CrO₆)⁹⁻ groups in YAG:Cr³⁺ and LLGG:Cr³⁺ crystals are smaller than those in the distinctive host crystal. So, the size-misfitting substitution may not be the main cause of the difference between the local and host compressibilities. Another factor, i.e. the inhomogeneous internal deformation of the unit cell as a function of pressure, should be taken into account here.

In fact, when the composition and structure of crystals are complex, studies of the crystal structure by the x-ray method as a function of pressure show that most compounds do not compress uniformly even if the impurity ion is absent [26–28]. That is to say, different bonds and groups (or polyhedra) in the same crystal change by different amounts with increasing pressure because the interactive forces in different bonds and groups are not the same. This means that the bonding or local compressibilities for the distinctive groups are quite different, while the usual compressibility represents only the average value for the whole crystal. The structure of garnet is quite complicated. There are three types of cation site, with different coordination of oxygen ions in the crystals, i.e. within a unit cell one can find 24 oxygen tetrahedra, 16 oxygen octahedra and 24 oxygen dodecahedra. These polyhedra (or groups) have different bond lengths and hence different bonding strengths and bond compressibilities. Notably, because the large oxygen dodecahedra compress more than the oxygen octahedra, the octahedra can be less compressible than the unit cell as a whole. The point has been confirmed for the garnets Ca₃Al₂Si₃O₁₂ and Mg₃Al₂Si₃O₁₂ from their x-ray data under high pressures [27]. From these data, e.g. the bulk modulus of octahedra and that of crystal as a whole, we find that the local compressibilities of octahedra in both crystals are about 0.61 ± 0.15 of those of whole crystals. Interestingly, from the above studies, we have, for YAG:Cr³⁺,

$$[d(\ln R)/dP]_l : [d(\ln R)/dP]_h \approx 0.59 \quad (13)$$

and, for LLGG:Cr³⁺,

$$[d(\ln R)/dP]_l : [d(\ln R)/dP]_h \approx 0.60 \quad (14)$$

where the subscripts *l* and *h* stand for the local value and the bulk value, respectively. Obviously, the two results are consistent with those in the above Ca₃Al₂Si₃O₁₂ and Mg₃Al₂Si₃O₁₂ garnets, suggesting that the smaller compressibilities of (CrO₆)⁹⁻ groups in YAG:Cr³⁺ and LLGG:Cr³⁺ crystals than those of host crystals are due mainly to the inhomogeneous internal deformation in these crystals under pressure. It appears that one can obtain some useful information about the local compressibility for the M–X bond in crystals by analysing their pressure-induced shifts of optical spectrum.

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