Local Compressibility of Cr³⁺-centered Octahedron of Spinel Crystal

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The local (or polyhedron) compressibility of the Cr³⁺-centered octahedron in spinel crystal is studied from the pressure-induced R-line shift. The result suggests that the local compressibility is about 0.6 of the compressibility of the host spinel crystal. This local compressibility is also consistent with that obtained from the pressure-induced shift of the ⁴T₂ band and can be regarded as reasonable.

Key words: Optical Spectra; Local Compressibility; Crystal-field Theory; Cr³⁺; Spinel.

1. Introduction

The crystal of Cr³⁺-doped spinel (MgAl₂O₄) has attracted great interest because it shows a broad-band luminescence at room temperature and so can possibly be applied as a medium for a tunable laser [1–2]. Many spectral studies of MgAl₂O₄:Cr³⁺ were made [1–5]. Among them, the effect of high pressure on the position of the R-line (²E → ⁴A₂ transition) was recently reported [5]. It was found that the pressure-induced R-line shift dE(²E)/dP is –0.84 (4) cm^{–1}/kbar [5]. For Cr³⁺ in octahedral clusters of crystals, when the energy separation Δ between the ²E and ⁴T₂ states is small (i.e., Δ = |E(⁴T₂) – E(²E)| < 1000 cm^{–1}), the ²E and ⁴T₂ states can strongly couple through spin-orbit coupling, and the lowest excited state will be a mixture of both levels [6]. Thus, the pressure-induced R-line shift is complex and cannot be calculated from the conventional energy matrix related to the ²E energy level [6, 7]. However, if the separation Δ is large, the R-line emission closely approximates the emission from a pure ²E level (not perturbed by spin-orbit coupling). From the classical crystal-field theory, the pure ²E level can be calculated by diagonalizing the 4 × 4 ²E energy matrix [7]. The results show that the pressure-induced R-line shift is mainly due to a decrease in the Racah parameters B and C (the contribution to dE(²E)/dP from the increase of the cubic field parameter Dq with

pressure is much smaller than that from the changes of B and C). For MgAl₂O₄:Cr³⁺, the separation amounts to Δ ≈ 4000 cm^{–1} [3–5], so its dE(²E)/dP is attributed mainly to the decrease of the parameters B and C under pressure. As is known, at normal pressure, the Racah parameters B_n and C_n in crystals can be written as [8]

$$\begin{aligned} B_n &\approx f_n B_0, \\ C_n &\approx f_n C_0, \end{aligned} \quad (1)$$

where B₀ (≈ 920.48 cm^{–1} [8]) and C₀ (≈ 3330.71 cm^{–1} [8]) are the corresponding values in a free ion. f_n is the covalency reduction factor at normal pressure. Under a pressure P, the Racah parameters B_P and C_P can be expressed as [9]

$$\begin{aligned} B_P &= B_0 f_n \left[1 + \left(\frac{d \ln f}{dP} \right) \cdot P \right] \\ &= B_0 f_n \left[1 + \left(\frac{d \ln f}{d \ln R} \right) \left(\frac{d \ln R}{dP} \right) \cdot P \right], \\ C_P &= C_0 f_n \left[1 + \left(\frac{d \ln f}{dP} \right) \cdot P \right] \\ &= C_0 f_n \left[1 + \left(\frac{d \ln f}{d \ln R} \right) \left(\frac{d \ln R}{dP} \right) \cdot P \right], \end{aligned} \quad (2)$$

where d ln R/dP ≈ (1/R) dR/dP is the linear compressibility of the metal-ligand bond. Thus, the pressure-induced red shift of the R-line is mainly due to the decrease in the covalency reduction factor and hence in the metal-ligand distance under pressure. Based on this, and using the compressibility d ln R/dP (≈ 1.69 × 10^{–4}/kbar [10]) of the host MgAl₂O₄ crystal, Jovanic [5] explained the pressure-induced shift dE(²E)/dP for MgAl₂O₄:Cr³⁺. In his theoretical explanations, some adjustable parameters were used. From these we can find that

$$d \ln f / d \ln R \approx 0.46. \quad (3)$$

The value is quite different from that (≈ 0.7353 [9]) obtained from the pressure-induced red shift of the R-line in ruby (Al₂O₃:Cr³⁺). It is astonishing that this large difference in d ln f/d ln R occurs for the similar (CrO₆)^{9–} groups in both crystals with large separation Δ, because the d ln f/d ln R is nearly independent of

f_n [9]. A possible suggestion to overcome this difficulty is that the value of $d\ln f/d\ln R$ for $(\text{CrO}_6)^{9-}$ groups in ruby is also approximately applicable to similar $(\text{CrO}_6)^{9-}$ groups in $\text{MgAl}_2\text{O}_4:\text{Cr}^{3+}$ (and also other crystals), but the local compressibility $d\ln R/dP$ of the $(\text{CrO}_6)^{9-}$ groups in $\text{MgAl}_2\text{O}_4:\text{Cr}^{3+}$ is unlike that of the host MgAl_2O_4 crystal. The reasons are as follows:

1. The differences between the local compressibility and that in the bulk can be found in the two cases [9], i.e., (a) the size and/or charge of the impurity is unlike that of the replaced host ion, and (b) the crystal under study has a complex composition and structure. Case (a) is due to strain introduced in the structure by the impurity [9, 11, 12], and case (b) is caused by the inhomogeneous internal deformation of the unit cell as a function of pressure in the pure crystal [9, 13–15]. The high-pressure X-ray method showed that different bonds and groups (or polyhedra) in the same crystals (having complex composition and structure) change by different amounts with increasing pressure because the interactive forces in different bonds and groups are not the same [13–15]. This means that the bonding or local compressibilities for the different groups are quite different, while the usual compressibility represents only the average value for the whole crystal.
2. By using the value $d\ln f/d\ln R$ obtained in ruby, we studied the local compressibilities for Cr^{3+} -centered oxygen octahedra in $\text{Y}_3\text{Al}_5\text{O}_{12}$ and $\text{La}_3\text{Lu}_2\text{Ga}_3\text{O}_{12}$ garnets from the pressure-induced R-line shifts [9]. The results show that the local compressibilities of the $(\text{CrO}_6)^{9-}$ groups are about 0.6 of those of the host crystals. This point is consistent with the results in similar garnets $\text{Ca}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ and $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$, where the local compressibilities of the oxygen octahedra are about 0.61 ± 0.15 of these of the whole crystals from their X-ray data under high pressure [14]. In addition, from the value of $d\ln f/d\ln R$ in ruby and by using two different local compressibilities (which are unlike that in the bulk) obtained from high-pressure X-ray measurements, we [16] explained reasonably the pressure-induced R-line shifts for Cr^{3+} ions in two Al^{3+} sites of chrysoberyl ($\text{BeAl}_2\text{O}_4:\text{Cr}^{3+}$). So, the above value of $d\ln f/d\ln R$ (≈ 0.7353) is reasonable and applicable.

2. Calculation and Discussion

Now we apply the suggestion to study the local compressibility of $\text{MgAl}_2\text{O}_4:\text{Cr}^{3+}$ from its pressure-induced R-line shift. According to the optical spectra of $\text{MgAl}_2\text{O}_4:\text{Cr}^{3+}$ [4, 5, 17], we obtain $f_n \approx 0.96$. Thus, the values of B_p and C_p can be obtained from (2). Substituting B_p , C_p and $Dq(P)$ ($\approx Dq + (dDq/dP) \cdot P$, where $Dq \approx 18690 \text{ cm}^{-1}$ [17] is the cubic field parameter at normal pressure and $dDq/dP \approx 10.3$ (6) $\text{cm}^{-1}/\text{kbar}$ is obtained from high-pressure experiment [17]) into the 4×4 ^2E energy matrix and then diagonalizing it, we find that, to reach a good fit between the calculated and experimental $dE(^2\text{E})/dP$ (≈ -0.84 (4) $\text{cm}^{-1}/\text{kbar}$ [5]), the local compressibility in $\text{MgAl}_2\text{O}_4:\text{Cr}^{3+}$ should be

$$d\ln R/dP \approx 1.17(6) \times 10^{-4}/\text{kbar} \quad (4)$$

The result is about 0.6 of the above compressibility in the whole MgAl_2O_4 crystal. However, it shows excellent agreement with the local compressibility $d\ln R/dP$ ($\approx 1.07(16) \times 10^{-4}/\text{kbar}$ [17]) obtained from the pressure-induced blue shift of the $^4\text{T}_2$ level of $\text{MgAl}_2\text{O}_4:\text{Cr}^{3+}$. The latter is based on the relationship

$$E(^4\text{T}_2) \approx 10Dq \propto R^{-5}, \quad (5)$$

and so

$$dE(^4\text{T}_2)/dP \approx -5E(^4\text{T}_2) d\ln R/dP. \quad (6)$$

The validity of (5) has been proven from the experimental studies of high-pressure spectra of NiO [18] and the results based on molecular orbital calculations for the $3d^n$ ion in many crystals [19, 20] and quantum mechanical calculations of polarized optical spectra of fayalite [17, 21]. So, the local compressibilities of $(\text{CrO}_6)^{9-}$ groups in $\text{MgAl}_2\text{O}_4:\text{Cr}^{3+}$ obtained from both the pressure-induced blue shift of $^4\text{T}_2$ level in [17] and the pressure-induced red shift of the ^2E level in this paper (they are very close to each other) can be regarded as reasonable. It appears that, like the pressure-induced blue shift of the $^4\text{T}_2$ level (which was often used), the pressure-induced red shift of ^2E level can be applied in the studies of local compressibility. This is noteworthy, since the band of the ^2E level is much sharper than that of the $^4\text{T}_2$ level, the local

compressibility, using $dE(^2E)/dP$, may be subject to a smaller error than that using $dE(^4T_2)/dP$.

Considering that the spinel has a complex composition and structure, we think that, similar to the cases of garnets [14], Cr^{3+} -doped garnets and chrysobery [15] crystals, the inhomogeneous internal deformation of the unit cell as a function of pressure may be

the main cause that the local compressibility of the $(CrO_6)^{9-}$ group in $MgAl_2O_4$ is smaller than the compressibility of the whole $MgAl_2O_4$ crystal. Thus, useful information about the local compressibility of the oxygen octahedron in the spinel $MgAl_2O_4$ can also be obtained from the above studies.

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