

Electron-lattice coupling parameters and oscillator strengths of cerium-doped lutetium oxyorthosilicate

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Optical absorption of single-crystal, cerium-doped lutetium oxyorthosilicate has been carefully measured in the temperature interval 10–300 K. Prominent Gaussian absorption peaks occur at 3.432 ± 0.002 eV (peak a), 3.502 ± 0.002 eV (peak b), 4.236 ± 0.0002 eV (peak c), and 4.746 ± 0.0002 eV (peak d), in excellent agreement with previously reported excitation spectra. The second moments are well described by the usual linear model, yielding the Huang-Rhys parameter (S) and vibrational quantum energies for the individual peaks. All absorption bands are characterized by $S > 5$ indicating strong coupling between the Ce^{3+} ion and lattice. Temperature dependence of the band centroids exhibits contrasting behavior that is dominated by higher-order coupling terms in the linear harmonic oscillator model or by crystal-field effects. Oscillator strengths of the $4f \rightarrow 5d$ transitions are calculated from Smakula's formula and knowledge of the Ce^{3+} distribution between the two crystallographically inequivalent sites. Values for peaks b, c, and d range from approximately 0.003 to 0.004, and peak a spans magnitude approximately 0.012 to 0.018. From the known correlation between average Ce^{3+} -ion-ligand distance and oscillator strength, we tentatively conclude that peak a is correlated with the seven-oxygen-coordinated site, and peaks b, c, and d are associated with the six-oxygen-coordinated site. These results support the previously proposed two-activation-center model and identify the centers as the two crystallographically inequivalent substitutional sites.

I. INTRODUCTION

Optical properties and luminescence mechanisms of cerium-doped lutetium oxyorthosilicate ($\text{Lu}_2\text{SiO}_5:\text{Ce}$, hereafter referred to as LSO) are of considerable interest owing to its importance as a promising new scintillator.^{1–3} Characterized by excellent light yield, relatively high density (7.4 g/cm³), and fast decay time (~ 40 ns), LSO is one of a class of cerium-doped oxyorthosilicates that is currently being investigated for use in myriad scintillator applications.⁴ Results of various experimental studies, including thermally stimulated luminescence,^{4–6} optical absorption,^{7,8} emission, and excitation spectra,⁹ have established that electronic transitions of the Lu^{3+} -substituted Ce^{3+} ions are responsible for the strong absorption and emission of LSO. However, fundamental properties of the Ce-ion-lattice interaction are not currently understood. In the present work we carefully examine temperature-dependent optical-absorption data on highly polished, single-crystal specimens and extract vibrational quantum energy, electron-lattice coupling magnitude (Huang-Rhys parameter), and oscillator strengths of the prominent optical transitions. Analysis of the data provides insight into the identification of the sites associated with each absorption band.

The incorporation of Ce ions into the host lattice, Lu_2SiO_5 , purportedly occurs via substitution for Lu^{3+} , with Ce presumably having the 3+ oxidation state.⁹ The crystal symmetry is monoclinic with space group $C2/c$; Ce ions occupy two crystallographically inequivalent cation sites with coordination number 6 or 7. Suzuki *et al.*⁹ have measured the excitation spectra of LSO and concluded that the corresponding emission emanates from the two Ce sites

characterized by maxima at 393 and 427 nm (Ce1) and 460 nm (Ce2). Moreover, it was shown that Ce2 emission is weak and obscured by the more intense Ce1 emission for temperatures above 80 K. The double-peaked emission from Ce1 was attributed to electronic deexcitation from the lowest crystal-field level split level of the $5d$ manifold to the spin-orbit split $4f$ doublet. Excitation (absorption) peaks at 263, 296, and 356 nm were correlated with the emission of Ce1, whereas peaks at 326 and 376 nm were associated with Ce2 emission.

A simplified energy level structure of the Ce^{3+} ion ($4f^1$) consists of the excited-state $5d$ level, comprised of five lines with energy spacing approximately 0.35 eV, and the $4f$ doublet ground state with energy splitting approximately 0.25 eV.¹⁰ The positions of the excited-state energy levels with respect to the bottom of the conduction band ($E_g \approx 6.5$ eV) have not been unambiguously determined.⁷

II. EXPERIMENT

Single-crystal specimens of LSO were extracted from a boule grown by the usual Czochralski method.¹¹ Cerium concentration in the melt was 0.25 at. % relative to Lu^{3+} ; however, because the Ce ion is much larger than Lu (1.034 vs 0.848 Å) there is a much smaller concentration in the final sample. Using the reported crystal-to-melt distribution coefficient 0.22 (Ref. 1), we calculate the sample cerium content to be 0.055 at. %.

A sample of dimensions $1 \text{ cm}^2 \times 0.065 \text{ cm}$ thickness was optically polished to obtain parallel opposing faces with an rms surface roughness of 0.7 nm. Optical-absorption measurements were made with a Cary 5E spectrophotometer

modified to accommodate an optical cryostat for obtaining data in the temperature interval 10–300 K. Data were taken at 10 and 20 K, and at each 20-K interval thereafter up to 300 K. Sample temperature was measured with a carbon-glass resistor and controlled to within ± 2 K of each set point by a LakeShore Cryotronics Model 340 temperature controller. After reaching each set point, and prior to making the optical-absorption measurement, the sample was maintained at that value for 10 min to ensure that thermal equilibrium had been attained. Raw data were acquired as absorbance and plotted as decadic absorption coefficient α ($\alpha = 0.4343\kappa$, where κ is the absorption coefficient to base e) vs energy.¹²

III. RESULTS AND DISCUSSION

Shown in Fig. 1 are representative optical-absorption spectra of LSO taken at 10 (dotted line) and 300 K (solid line). Four peaks occurring near 3.4, 4.2, 4.7, and 5.7 eV are observed at all temperatures; for $T \geq 100$ K an additional maximum appears near 6.2 eV and for $T \leq 100$ K a small peak is resolved near 3.8 eV. The band edge at 300 K is approximately 6.5 eV, but shifts to slightly higher values as temperature decreases. Overall, the spectra are very similar to those previously reported by other researchers.^{1,5,8} However, careful analysis of the spectra reveal that the main peak near 3.4 eV is not a single peak but is comprised of two closely spaced peaks as shown in Fig. 2. The solid line is the 10-K spectrum and the dotted lines are Gaussian fits with a linear baseline. All spectral fitting was done with the commercial software package GRAMS/32® (Ref. 13) utilizing the Levenberg-Marquardt nonlinear least-squares routine. We have limited our analysis to the prominent spectral features consisting of two closely spaced peaks near 3.4 eV and the single peaks near 4.2 and 4.7 eV. The weak peak near 3.8 eV

was analyzed only at 10 K to determine its Gaussian-fitted peak position (3.821 ± 0.004 eV).

The best fit at 10 K to the main feature near 3.4 eV was obtained with two Gaussians exhibiting maxima at 3.432 ± 0.002 eV (peak a) and 3.502 ± 0.002 eV (peak b) with goodness of fit 0.998. Experimental spectral resolution was ± 0.5 nm for all wavelengths; quoted errors are statistical and derived from the fitting procedure. Attempts to fit the spectra with a Lorentzian function to account for possible spectral lifetime broadening yielded poor results, as did combinations of Gaussian and Lorentzian (Voigt) line shapes. The two remaining principal absorption bands exhibited similar behavior; at 10 K their Gaussian maxima were 4.236 ± 0.0002 eV (peak c) and 4.746 ± 0.0002 eV (peak d) with goodness of fit 0.999. We conclude therefore that Ce^{3+} -ion optical absorption in LSO is Gaussian and that the strongest absorption band is actually two overlapping bands, rather than one as usually reported. The current results are in excellent agreement with the excitation spectra reported by Suzuki *et al.*⁹ Comparing our present optical-absorption data to their excitation spectra, we conclude that absorption peaks with maxima at 3.432 and 3.821 eV are associated with Ce2, and peaks with maxima at 3.502, 4.236, and 4.746 eV are associated with absorption of Ce1.

Having established that LSO absorption is Gaussian and comprised of components from two cerium sites, we now analyze the temperature dependence of the Gaussian-fitted spectral moments to determine ion-lattice coupling parameters and oscillator strengths of the prominent absorption bands.

A. Electron-lattice coupling parameters

Configuration-coordinate models are frequently used to describe optical processes in solids and have been thoroughly discussed in the literature.¹⁴ A principal result is that the ground-state energy level of the impurity ion can, to first

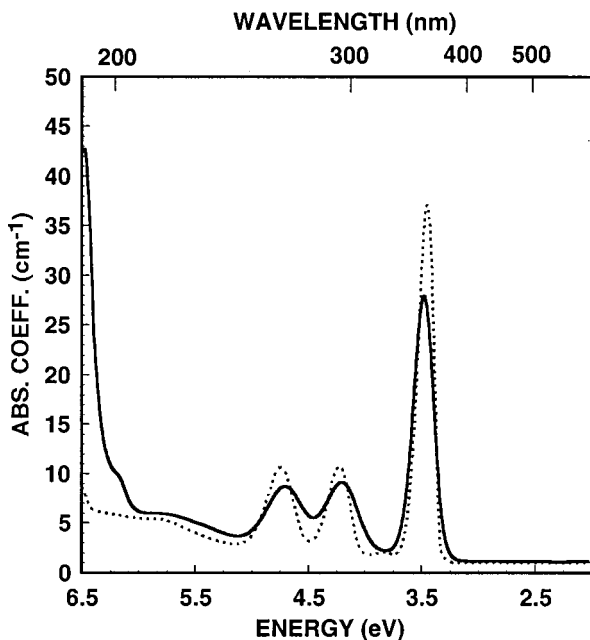


FIG. 1. Optical absorption of LSO taken at 300 K (solid line) and 10 K (dotted line). The ordinate refers to the decadic absorption coefficient α of the 0.65-mm-thick single-crystal specimen.

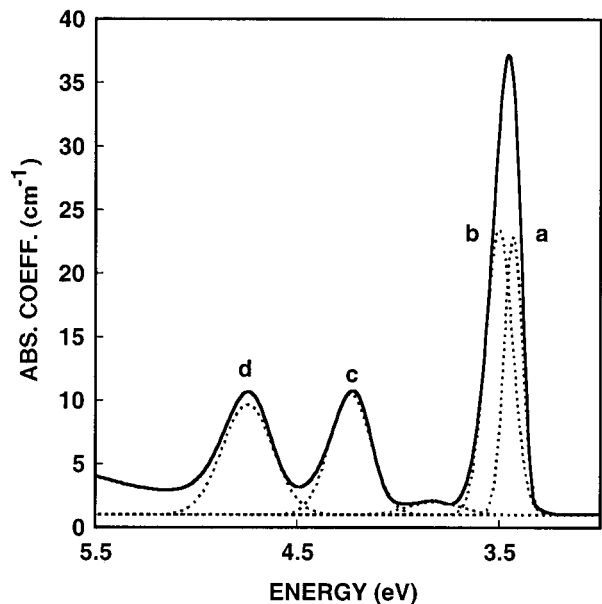


FIG. 2. 10-K absorption spectrum (solid line) of LSO with Gaussian fits (dotted lines) to the four prominent peaks.

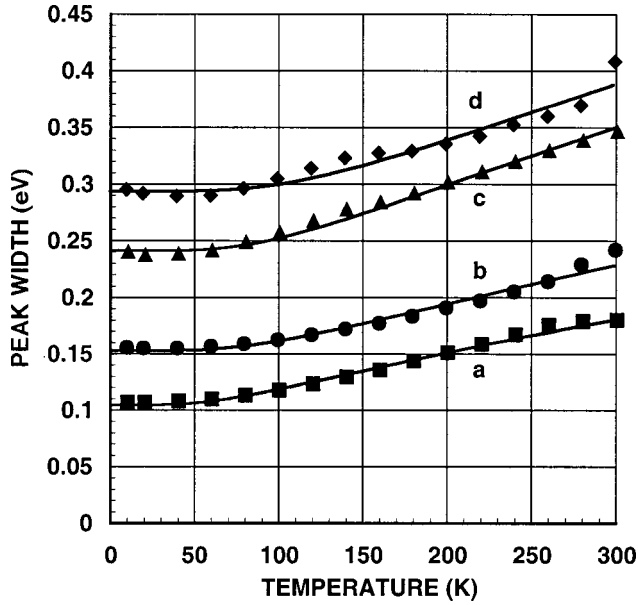


FIG. 3. Temperature dependence of second moments (symbols) of major peaks in LSO with fits (lines) to the standard linear model. a, b, c, and d refer to the peaks shown in Fig. 2.

approximation, be described as a classical quantum-mechanical harmonic oscillator with quantum energy spacing $\hbar\omega$. This ‘‘linear model’’ assumes identical vibrational frequencies of the ground and excited states. An important prediction of this model is that the width (second moment) of the absorption band, taken as the full width at half maximum (FWHM) and measured as a function of temperature, obeys the relation

$$W(T) = W(0) \left[\coth \left(\frac{\hbar\omega}{2kT} \right) \right]^{1/2}. \quad (1)$$

For a Gaussian line shape this is written

$$W(T) = \hbar\omega \left[8S \ln 2 \coth \left(\frac{\hbar\omega}{2kT} \right) \right]^{1/2}, \quad (2)$$

where S is a dimensionless measure of the electron-lattice coupling magnitude and referred to as the Huang-Rhys factor.¹⁵

The filled symbols in Fig. 3 are the temperature-dependent second moments extracted from the Gaussian-fitted data of the four prominent absorption peaks illustrated in Fig. 2. Errors are smaller than the plot symbols and the designations a–d refer to the individual peaks in order of increasing maximum absorption energy. The solid lines represent best fits of the data to Eq. (2) from which the electron-lattice coupling parameters ω and S are extracted; the results are listed in Table I. S values for peaks a and b (6.1 and 6.8, respectively) are considerably smaller than those of peaks c and d (14.7 and 13.7, respectively), indicating their excited-state energy levels are less diffuse than those associated with the latter peaks.¹⁶ Similar studies of F^+ centers in MgO, CaO, and SrO report S values ranging from 13 to 39 (Ref. 17). Systems characterized by $S > 5$ are in the strong-coupling regime whereby the zero-vibrational transition is

TABLE I. Electron-lattice coupling parameters.

Peak	$W(0)$ (eV)	ω (10^{13} s^{-1})	ω_{exc} (10^{13} s^{-1})	$E_2 - E_1$ (eV)	S
a	0.105	2.74	4.83	3.422	6.1
b	0.156	3.85	6.77	3.489	6.8
c	0.242	4.06			14.7
d	0.297	5.17			13.7

very weak and usually not detected in the spectrum.¹⁸ Large S values also imply a large Stokes shift, which for LSO is ~ 0.50 eV.

Temperature variations in the first moments (centroids) of the four absorption peaks are shown by the filled symbols in Fig. 4 (error bars are smaller than the plot symbols). Although the upturn of peaks a and b with increasing temperature is in striking contrast to the downturn of peaks c and d, similar effects have been seen in transition-metal ions.¹⁹ The frequency of the optical-absorption transition depends on the strength $\Delta = 10Dq$ of the crystalline electric field, which, in turn, depends on the spatial separation R of the absorbing ions and the surrounding ligands. Of course R varies with temperature through the thermal expansion coefficient.

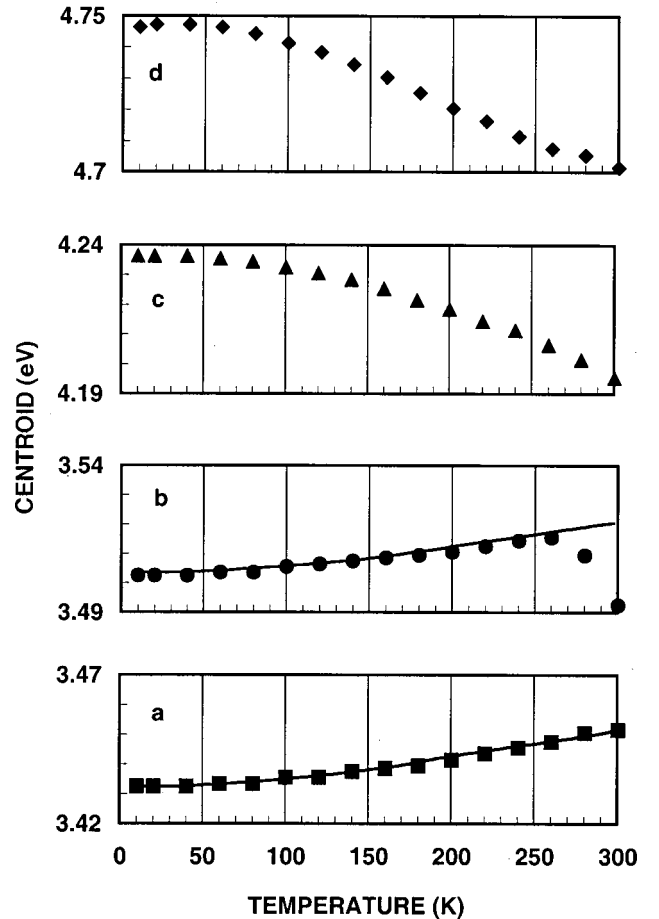


FIG. 4. Temperature dependence of first moments (symbols) for peaks a–d. The solid lines for peaks a and b are fits to the modified linear model, which includes higher-order, impurity-ion coupling terms.

Whether the transitions shift to the red or blue with increasing temperature depends on the slope $dE/d\Delta$ of the E vs Δ curve (Tanabe-Sugano diagram), with a negative slope shifting the transition toward the blue portion of the spectrum. Although details of the crystalline field and corresponding Tanabe-Sugano diagrams for Ce^{3+} ions in LSO are presently unavailable, it is plausible that the results shown in Fig. 4 are at least partially attributable to crystal-field effects.

Higher-order coupling terms are also known to contribute a temperature-dependent shift to the first moment of an optical-absorption band.¹⁷ Rather than assume the average vibrational frequencies of the ground and excited states to be identical, one can include the effects of higher-order coupling terms by introducing a different frequency ω_{exc} for the excited state. The centroid position is then given by

$$M_1(T) = E_2 - E_1 + \frac{1}{4} \hbar \omega \left[\frac{\omega_{\text{exc}}^2}{\omega^2} - 1 \right] \coth \left(\frac{\hbar \omega}{2kT} \right), \quad (3)$$

where $E_2 - E_1$ is the energy difference between the ground and excited states at the zero position of the configurational coordinate. Peaks a and b exhibit an increase in centroid with increasing temperature and fit Eq. (3) very well, as shown by the solid lines in Fig. 4. The excited-state frequencies and energy differences derived from the fit are listed in Table I.

B. Absorption band oscillator strengths

The integrated absorption of an optical transition is related to the concentration of absorbing centers N , index of refraction n , and oscillator strength f by the well-known Smakula formula²⁰

$$Nf = 8.21 \times 10^{15} \text{ cm}^{-3} \frac{n}{(n^2 + 2)^2} \int \alpha(E) d(E), \quad (4)$$

where α is the decadic absorption coefficient in cm^{-1} and E is energy in eV. For Gaussian absorption bands the integral is

$$\frac{1}{2} \sqrt{\frac{\pi}{\ln 2}} \alpha_{\text{max}} W \quad (5)$$

with maximum absorption α and full width at half maximum W . Equation (4) can be expressed as

$$Nf = 8.7 \times 10^{16} \text{ cm}^{-3} \frac{n}{(n^2 + 2)^2} \alpha_{\text{max}} W. \quad (6)$$

To compute the oscillator strengths of the four major absorption peaks in LSO we first calculate the Ce^{3+} concentrations associated with Ce1 and Ce2 sites. The formula weight of LSO is 458.017 g and density is 7.42 g/cm^3 , which yields a formula volume of $1.025 \times 10^{-22} \text{ cm}^3$ (containing two rare-earth sites). The actual Ce^{3+} concentration in the sample is a product of the melt concentration (0.25%) and segregation coefficient¹ (0.22), viz., 0.055%; however, cerium is not evenly distributed between the two crystallographically inequivalent sites. Naud *et al.*²¹ measured the integrated emission from sites Ce1 and Ce2 for an LSO sample containing melt concentration 0.25% and found the ratio to be 4.11. They concluded that this ratio should be a measure of the respective site concentrations, i.e., $[\text{Ce1}]/[\text{Ce2}] = 4.11$. Thus

in the present work we assign the Ce distribution as 80% to site Ce1 and 20% to site Ce2. Using our calculated formula volume we obtain concentrations for $[\text{Ce1}] = 4.290 \times 10^{18} \text{ cm}^{-3}$ and $[\text{Ce2}] = 1.073 \times 10^{18} \text{ cm}^{-3}$.

From our measured Gaussian absorption bands and the known index of refraction¹ ($n = 1.82$), we calculate the oscillator strengths of the four major bands as a function of temperature. The results, shown in Fig. 5, indicate a weak temperature dependence for peaks b, c, and d but a relatively strong dependence for peak a. Recall that peak a is associated with site Ce2, whereas the three remaining peaks are associated with site Ce1. The oscillator strengths of peaks b, c, and d are approximately twice as large as those reported for the strongest bands in cerium-doped LaF_3 at 300 K, and the strength of peak a absorption is nearly ten times larger.²² A comparison of $4f \rightarrow 5d$ calculated and observed oscillator strengths for Ce^{3+} in various host lattices has been compiled by Williams *et al.*²³

A currently unresolved question is whether the absorption and emission of site Ce2 is due to Ce ions residing in a substitutional site (with different oxygen coordination as compared to site Ce1) or in an interstitial position.²¹ Although our present data do not allow unambiguous resolution of this key issue, they provide evidence in favor of the substitutional site. Mainly, we note that the oscillator strength of peak a is 3–6 times greater than any of the other peaks and that it is associated with site Ce2. Williams *et al.*²³ note that variations in f are most obviously correlated with the average Ce^{3+} -ion-ligand distance, and, in general, a smaller separation corresponds to a smaller f value relative to the expected free-ion value. To see how this correlation arises we express f in quantum-mechanical terms:

$$f_{nm} = \frac{8 \pi^2 m \nu_{nm} |\langle n | \mathbf{M} | m \rangle|^2}{3 e^2 h}, \quad (7)$$

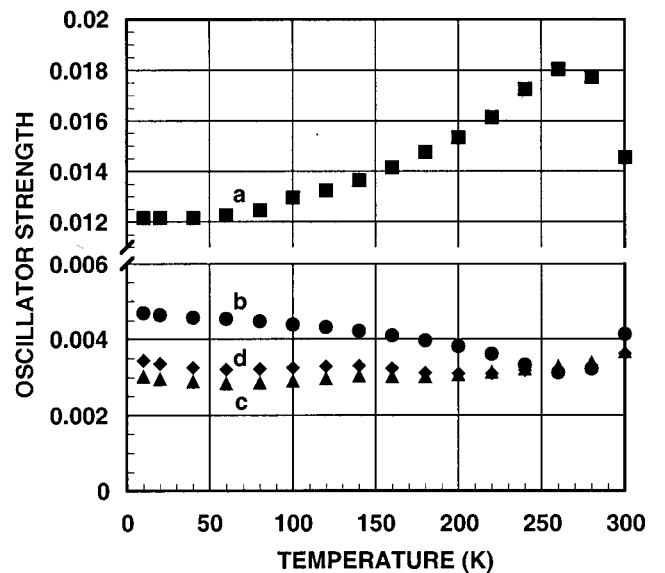


FIG. 5. Temperature dependence of the oscillator strengths for peaks a–d. The results suggest that peak a belongs to the seven-oxygen-coordinated site and the remaining peaks are associated with the six-oxygen-coordinated site.

where ν_{nm} is the transition frequency between the states n and m , and $|\langle n|\mathbf{M}|m\rangle|^2$ is the squared dipole matrix element connecting the two states. \mathbf{M} is the electric dipole moment; in terms of charge density $\rho(\mathbf{r})$ and electron charge e we write

$$\mathbf{M} = e \int \rho(\mathbf{r}) \mathbf{r} d\tau. \quad (8)$$

It is generally accepted that introduction of a rare-earth ion into a lattice causes the rare-earth orbitals to expand radially as a result of overlap with ligand orbitals, the expansion being much greater for the $5d$ orbitals relative to the shielded $4f$ orbitals. This differential expansion should lead to a greatly reduced dipole matrix element, $\langle 4f|\mathbf{r}|5d\rangle$, especially given that the respective wave functions have opposite signs for some values of separation \mathbf{r} .²⁴

This reasoning lends strong support to the suggestion that peak a belongs to one type of Ce center and peaks b, c, and d belong to another. As shown in Fig. 5, f values of the latter peaks are similar in magnitude but 3–6 times smaller than those of peak a, implying a larger Ce³⁺-ion-ligand distance for the peak-a Ce site. Although the lattice parameters for LSO are presently unknown, we expect the average Ce³⁺-ion-ligand distance to be larger for the seven-oxygen-coordinated substitutional site than the six-oxygen site. As noted by Merenga,²⁵ yttrium oxyorthosilicate has the same structure as LSO, the only difference being the size of the metal ions (0.89 and 0.85 Å for Y³⁺ and Lu³⁺, respectively). The average ion-ligand distances for the seven- and six-oxygen-coordinated sites in this system are 2.32 and 2.22 Å, respectively. Collectively, these results suggest that absorption peak a is correlated with the seven-oxygen-coordinated site, which has been previously referred to as site Ce2, and peaks b, c, and d are associated with the six-oxygen-coordinated site, previously labeled site Ce1. Tabulated values of f and Ce³⁺-ion-ligand separation for several hosts suggest that variations in f by factors of 3–6 for correspondingly small changes in the ion-ligand distance are consistent with available data.²³

Last, we consider the possibility that Ce³⁺ ions occupy an interstitial site in the LSO lattice and produce measurable absorption (and emission). The expected small Ce³⁺-ion-ligand separation for an interstitial site would likely produce a center with very low oscillator strength and render detection of an optical transition very difficult at best. Moreover, it is counterintuitive to expect the dopant Ce³⁺ ions to preferentially occupy the smaller interstitial sites over the larger substitutional ones, at least until the latter are almost filled. However, this statement warrants caution because our present results suggest preferential occupancy of the smaller six-coordinated substitutional sites over the

larger seven-coordinated ones. Nevertheless, based on our present results we tentatively conclude that absorption peak a is correlated with the seven-oxygen-coordinated Ce site (Ce2), and peaks b, c, and d are associated with the six-oxygen-coordinated Ce site (Ce1). These results strongly support the two-activation-center model proposed by Suzuki *et al.*,⁹ and tentatively identify the two centers as substitutional sites rather than one substitutional and one interstitial.

IV. SUMMARY

We have carefully measured the optical absorption of single-crystal LSO in the temperature interval 10–300 K and found prominent Gaussian absorption bands at 3.432 ± 0.002 eV (peak a), 3.502 ± 0.002 eV (peak b), 4.236 ± 0.0002 eV (peak c), and 4.746 ± 0.0002 eV (peak d), which are in excellent agreement with the excitation spectra of Suzuki *et al.*⁹ The temperature dependence of the second moments are well described by the usual linear model, from which the Huang-Rhys parameter (S) and vibrational quantum energies are extracted. All four peaks are characterized by $S > 5$, indicating strong coupling between the impurity ion and lattice vibrations, as well as a large Stokes shift. Temperature dependence of the absorption band centroids exhibit contrasting behavior; peaks a and b show an upturn with increasing temperature, whereas peaks c and d exhibit a downturn. The former behavior is reasonably well explained by introducing higher-order coupling terms into the linear model and allowing excited-state vibrational frequencies that are different from the ground-state frequencies. Crystal-field effects are most likely responsible for the behavior of peaks c and d.

Oscillator strengths of the major peaks were calculated from Smakula's formula and knowledge of the cerium distribution among the two crystallographically inequivalent sites. Peaks b, c, and d exhibit weak temperature dependence with typical values ranging from approximately 0.003 to 0.004, whereas peak a is characterized by a stronger temperature dependence and larger magnitude, approximately 0.012–0.018. Based on the work of Williams *et al.*,²³ which shows a correlation between the average Ce³⁺-ion-ligand distance and oscillator strength, we tentatively conclude that absorption peak a is correlated with the seven-oxygen-coordinated site, and peaks b, c, and d are associated with the six-oxygen site. Furthermore, these results support the previously proposed two-activation-center model of Suzuki *et al.*⁹ and identify the centers as the two crystallographically inequivalent substitutional sites.

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