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Resonance Electronic Raman Scattering in Erbium Phosphate Crystals

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Resonance enhancement factors of 10 to 100 have been observed for
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Resonance enhancement factors of 10 to 100 have been observed for
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Electronic Raman scattering effects in rare-earth crystals have been the subject of numerous studies since the initial work of Hougen and Singh in 1963.\textsuperscript{1,2} Most of the experiments, however, were performed using a nonresonant experimental configuration, with the exciting line well removed in frequency from any electronic transition of the subject rare-earth ion. With the exception of the work of Koningstein\textsuperscript{3} and of Wadsack and Chang,\textsuperscript{4} there are few reports of resonance electronic Raman scattering in trivalent rare-earth doped crystals. In the resonance Raman studies noted above, enhancement factors that were on the order of 5 at most were reported. In the present work, we have observed resonance enhancement factors of 10-100 for electronic Raman transitions within the ground \textsuperscript{4}I\textsubscript{15/2} multiplet of Er\textsuperscript{3+} in concentrated and dilute erbium phosphate crystals. The resonance excitation occurs between the crystal field levels of the \textsuperscript{4}F\textsubscript{7/2} multiplet and the \textsuperscript{4}I\textsubscript{15/2} ground levels. To our knowledge, this represents the first time that such large enhancement effects have been observed. It should be noted, however, that somewhat similar resonance effects have been observed for other nonlinear optical processes in rare-earth crystals, such as four-wave mixing phenomena.\textsuperscript{5}

The scattering amplitude for a Raman transition from a state \( n \) to a state \( k \) is given by:

\[
(a_{\rho\sigma})_{nk} = -\frac{1}{\hbar} \sum_{r} \left[ \frac{\langle k | D | r \rangle \langle r | D_{\rho} | n \rangle}{\nu_{rn} - \nu + i \Gamma_{r}} + \frac{\langle k | D_{\rho} | r \rangle \langle r | D_{\sigma} | n \rangle}{\nu_{rk} + \nu + i \Gamma_{r}} \right] \tag{1}
\]

where \( D_{\rho} \) is the electric dipole operator, \( \rho \) and \( \sigma \) are Cartesian coordinates, \( \hbar \nu_{rn} \) is the energy difference \( E_{r} - E_{n} \) (\( E_{r} \) is the energy of
the intermediate state r), \( v \) is the frequency of the incident radiation, and \( \Gamma_r \) is a damping factor that is inversely proportional to the lifetime of the intermediate state. For a \( 4f^N \) configuration, \( 4f^N + 4f^N \) transitions are forced electric-dipole in nature with very small oscillator strengths\(^6\) so the intermediate states that dominate Eq. (1) arise from configurations of opposite parity to \( 4f^N \), namely \( 4f^N-1n^d \) or \( 4f^N-1ng \). For \( \text{Er}^{3+} \) (\( N=11 \)), the \( 4f^{10} 5d \) configuration begins approximately 70,000 \( \text{cm}^{-1} \) above the ground state.\(^7\) The other opposite parity configurations lie at higher energies. Judd-Ofelt closure techniques can be used to perform the sum over intermediate states, and the results of such intensity calculations have been reported previously.\(^8,9\) The situation can be altered if the energy of the exciting radiation is very close to that of a \( 4f^N + 4f^N \) transition. The energy denominator is then very small and this tends to compensate for the weakness of the \( 4f^N + 4f^N \) matrix elements. Therefore, one may expect a noticeable change to occur in the electronic Raman intensity pattern with respect to the polarization of the incident and scattered photons.\(^10\) This situation occurs in the case of \( \text{Er}^{3+} \) as a result of a near coincidence in energy between the argon-ion laser excitation line at 488.0 nm and the transitions between the crystal field states of the ground \( ^4I_{15/2} \) multiplet and those of the excited \( ^4F_{7/2} \) multiplet.

The nonresonant electronic Raman spectrum of \( \text{ErPO}_4 \) and the experimental procedure employed in all of these studies, have been reported previously.\(^8\) In that work, the excitation sources were the 514.5 and 457.9 nm lines of an argon-ion laser, and the electronic Raman spectra produced by those two lines were identical. When the argon-ion
laser blue line at 488.0 nm (20,486.7 cm$^{-1}$ in vacuum) is incident on the crystal, drastic changes occur in the Raman spectra. Figure 1 shows part of the energy level scheme of Er$^{3+}$ in LuPO$_4$ and the positions of the relevant laser excitation lines. The widths of the multiplets result from crystal field splittings and range from 100 cm$^{-1}$ to 300 cm$^{-1}$. A detailed study of the optical absorption and crystal-field levels of 1% Er in LuPO$_4$ has been reported previously.$^{11}$

The lines at 457.9 and 514.5 nm are at least 300 cm$^{-1}$ away from the closest Er$^{3+}$ 4f$^{11}$ excited levels, which precludes any significant role that these levels might play as intermediate states. For these two excitation frequencies, the dominant contributions to the electronic Raman amplitude are from the excited configurations 4f$^{10}$nd and 4f$^{10}$ng.$^9$ The line at 488.0 nm, however, is coincident with the $^4F_{7/2}$ multiplet which now contributes significantly to the electronic Raman intensities. Another favorable factor is that the oscillator strengths of the transitions between the ground multiplet and the $^4F_{7/2}$ excited multiplet are relatively large (on the order of $5 \times 10^{-6}$ as determined by laser absorption measurements,$^{12}$ which classifies them as being among the strongest transitions of the Er$^{3+}$ ion$^6$).

Resonant and nonresonant Raman spectra were obtained for both pure ErPO$_4$ and 1% Er$^{3+}$ in LuPO$_4$. The nonresonant electronic Raman intensities for ErPO$_4$ were on the order of a few hundred counts per second for the existing experimental conditions. Using the identical experimental arrangement and similar laser input powers of about 50mW, resonant Raman signals as high as 10,000 counts per second were observed. Polarized spectra are shown in Figs. 2 and 3 for nonresonant...
excitation at 514.5 nm and for resonant excitation at 488.0 nm. It should be noted that while the electronic Raman intensities have been strongly enhanced, the phonon intensities remain at about the same level. This effect is quite apparent for the \( E_g \) phonons at 134 cm\(^{-1} \) and 188 cm\(^{-1} \). The fact that the phonons are not affected by the electronic resonance indicates that the coupling between the electronic states of \( \text{Er}^{3+} \) and the lattice vibrations is very weak.

Resonance Raman spectra were also obtained for 1% \( \text{Er}^{3+} \) in \( \text{LuPO}_4 \). In this case, the signal level is much lower than that observed for pure \( \text{ErPO}_4 \); and, with nonresonant excitation at 514.5 nm, most of the electronic peaks cannot be observed. Table 1 lists the values determined for the crystal field levels of \( ^4I_{15/2} \) by the resonance and nonresonance Raman scattering experiments for both \( \text{ErPO}_4 \) and 1% \( \text{Er}^{3+} \) in \( \text{LuPO}_4 \). Also listed in Table 1 are the calculated values from the crystal field fit, and the values determined from 77 K optical absorption measurements.

Several arguments can be made to demonstrate that the observed signal is, in fact, a Raman signal and not fluorescence. First, the 488.0 nm exciting laser line is not exactly in coincidence with one of the four crystal field levels of the \( ^4F_{7/2} \) multiplet (see Fig. 4). The four levels are labeled by the irreducible representations \( \Gamma_6 \) and \( \Gamma_7 \) of the point group \( D_{2d} \) which describes the \( \text{Er}^{3+} \) site symmetry. One would then expect to see differences of a few cm\(^{-1} \) between Raman and fluorescent peaks. For \( \text{ErPO}_4 \), the transitions from the ground state to the excited levels \( e_1, e_2, e_3, \) and \( e_4 \) are observed with both resonant and nonresonant excitation and no frequency shifts are found within an
accuracy of 1 cm\(^{-1}\). Second, the fluorescence from the \(^4F_{7/2}\) levels in ErPO\(_4\), excited by the higher-lying argon-ion laser line at 476.5 nm is quenched by energy transfer among the Er\(^{3+}\) ions and nonradiative decay to lower multiplets. In contrast, the resonant Raman peaks persist up to \(T=100\) K. They gradually decrease in intensity as the crystal field levels broaden significantly with temperature and begin to absorb both the incident laser radiation and the scattered Raman radiation. This latter absorption occurs when the higher-lying crystal field levels of the \(^4I_{15/2}\) multiplet become populated.

Several other lines appear as the temperature is increased above \(T=4.2\) K. A Raman transition at 20 cm\(^{-1}\) that originates in the 33 cm\(^{-1}\) state and ends in the 53 cm\(^{-1}\) state increases in intensity with temperature as the first excited crystal field state \(e_1\) becomes thermally populated. This peak is weakly observable with nonresonant excitation and is strongly enhanced by resonant excitation. As the temperature is raised, the Raman transition from the ground state to level \(e_1\) initially drops in intensity more rapidly than the transition to level \(e_2\). This is due to the fact that the thermal population of level \(e_1\) is significantly higher than that of \(e_2\) at low temperatures. This permits the radiation with a 30 cm\(^{-1}\) Raman shift to be more strongly absorbed. The 20 cm\(^{-1}\) line also appears on the anti-Stokes side, along with a 33 cm\(^{-1}\) line that corresponds to the transition from the \(e_1\) level to the ground state. Again, both are stronger than in the nonresonance case. The presence of the anti-Stokes peaks confirms that their corresponding Stokes peaks are Raman transitions.
An intriguing feature of the spectra for 1% \( \text{Er}^{3+} \) in \( \text{LuPO}_4 \) is that the relative intensities for the various resonant electronic Raman lines have changed relative to those observed for pure \( \text{ErPO}_4 \). These relative intensities are very sensitive to the positions of the associated crystal field levels and these levels shift significantly in diluting pure \( \text{ErPO}_4 \) to 1% \( \text{Er}^{3+} \) in \( \text{LuPO}_4 \) (see Fig. 4). We may separate the expression for the Raman amplitude into a resonant part and a nonresonant part:

\[
(a_{\rho \sigma}^\ell)_{nk} = -\frac{1}{\hbar} \sum_{\mathbf{F}_{7/2}} \frac{\langle j | D_{\rho} | r \rangle \langle r | D_{\sigma} | n \rangle}{E_{\text{r}n} - \hbar \nu + i\Gamma_r} + \text{non-resonant term (2)}
\]

For the resonant contribution, only the first term on the right-hand side of Eq. (1) was retained. This term contains the sum over the four crystal field levels of the \( \mathbf{F}_{7/2} \) multiplet whereas the nonresonant term involves a sum over the excited \( 4f^{10} \text{nd} \) and \( 4f^{10} \text{ng} \) configurations. Thus quantum-mechanical interference effects between the various intermediate states can be observed. The shift in energy levels that occurs between \( \text{ErPO}_4 \) and 1% \( \text{Er}^{3+} \) in \( \text{LuPO}_4 \) significantly changes the relative amplitude that each of the \( \mathbf{F}_{7/2} \) crystal field states contributes to the overall intensity.

Erbium phosphate systems are promising candidates for studies of resonance enhancements of other nonlinear optical processes. Since the electronic Raman intensities are greatly enhanced by the intermediate \( \mathbf{F}_{7/2} \) resonance, two-photon absorption or four-wave mixing should also be significantly enhanced by the same intermediate resonance. The
quantum-mechanical expressions for the amplitudes of these last two processes involve terms similar to those that appear in the electronic Raman amplitude (see Eq. 2).

Acknowledgements

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References:


Table 1. Crystal field energy levels of the $^4I_{15/2}$ ground multiplet of $\text{Er}^{3+}$, for both $\text{ErPO}_4$ and 1% Er in LuPO$_4$, from optical absorption measurements, resonance Raman measurements, and crystal field fits.$^a$

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<tr>
<th>Level</th>
<th>Symmetry</th>
<th>Optical Crystal Field Fit for 1% Er</th>
<th>Resonance Optical Absorption Measurements in LuPO$_4$</th>
<th>Raman Resonance Optical Non-resonance Raman Measurements</th>
<th>Raman Measurements</th>
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$^a$energy levels in cm$^{-1}$.

$^b$from reference 8.

$^c$not observed.
Figure Captions

Figure 1. Energy level structure of the $4f^{11}$ electronic levels of Er$^{3+}$ in LuPO$_4$ in the 20,000 cm$^{-1}$ region. The laser lines used in the Raman experiments are indicated. The wavelengths are in air and the wavenumbers in vacuum. The width of the excited multiplets represents the total crystal field splitting of that multiplet.

Figure 2. Polarized ErPO$_4$ Raman spectra at $T = 4.2$ K, with both resonant and non-resonant excitation, in $Y(XZ)X$ and $Y(ZY)Y$ polarizations.

Figure 3. Polarized ErPO$_4$ Raman spectra at $T = 4.2$ K, with both resonant and non-resonant excitation, in $Y(XY)X$ and $Y(ZZ)X$ polarization.

Figure 4. Crystal field energy levels of the $^4F_{7/2}$ multiplet of Er$^{3+}$ (in cm$^{-1}$). The symmetry of the levels is indicated, as is the position of the 488.0 nm line of the argon-ion laser (all wavenumbers in vacuum).
Figure 1
Excitation at 19,429.7 cm\(^{-1}\) (non-resonant)

Full Scale 1,000 cps

Excitation at 20,486.7 cm\(^{-1}\) (resonant)

Full Scale 10,000 cps
Excitation at $19,429.7 \text{ cm}^{-1}$ (non-resonant)

Full Scale 1,000 cps

Excitation at $20,486.7 \text{ cm}^{-1}$ (resonant)

Full Scale 10,000 cps

Full Scale 1,000 cps

Figure 3
Figure 4
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