# Electron-phonon interactions in insulating nanoparticles: Eu<sub>2</sub>O<sub>3</sub>

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The temperature and particle size dependencies of the linewidth of spectral holes burned in the  ${}^{7}F_{0} \rightarrow {}^{5}D_{0}$  transition of Eu<sup>3+</sup> ions in Eu<sub>2</sub>O<sub>3</sub> are calculated and compared with experiment. The power-low temperature behavior  $\sim T^{7}$ , well-known experimentally and theoretically for the bulk, is observed to be strongly weakened to  $\sim T^{3}$  for the nanoparticles. A calculation is performed that assumes a two-phonon Raman-scattering mechanism involving the discrete phonon modes of a homogeneous nanoparticle with stress-free boundary conditions. The experimental results are successfully described assuming that the phonon modes broaden with frequency as  $\sim \omega^{2}$ . A quantitative comparison of the calculations with experiment allows the determination of the linewidth of the phonon resonances of the nanoparticles. The calculations predict that the size dependence of the hole linewidth is  $\sim D^{-2.5}$ , in close agreement with experiment.

## I. INTRODUCTION

Nanoscale materials exhibit properties that are quite distinct from those of bulk materials because of their sizerestricted nature. In semiconducting nanoparticles the confinement of the electrons leads to an increase in the band-gap absorption energy and to the formation of discrete electronhole states. In addition, the size restriction leads to important vibrational effects such as the appearance of a "gap" in the acoustic-phonon spectrum and the formation of discrete vibrational states. Experimental studies of electron-phonon interactions in semiconducting nanocrystals indicate that the homogenous dephasing rate  $\Gamma_h$  is linear in temperature T, and depends inversely as the square of the particle size, d.<sup>1,2</sup> Theoretical calculations for semiconductor nanoparticles predict  $\Gamma_h \propto T$  in the high-temperature limit where kT is larger than the minimum confined-phonon-mode energy and  $\Gamma_h$  $\propto 1/d^2$  for the deformation potential or 1/d in the piezoelectric coupling model for the electron-phonon interaction.<sup>2</sup> For the calculations presented in this paper that describe experiments on insulating nanoparticles it must be noted that (1)the electronic states are highly localized, (2) the nanoparticles are nearly free and are not imbedded in a glass matrix, which adds additional possible mechanisms for the electronphonon interaction in the semiconductor case, (3) the temperature range of the experiments is in the low-temperature regime where kT is less than the minimum phonon energy, and (4) the mechanism is two-phonon Raman scattering. Thus, while the results presented here cannot be directly compared with those on semiconducting nanoparticles, they may still be of considerable relevance to that system.

We have previously described the observation of an unusual temperature dependence of the linewidth of spectral holes for  $Eu^{3+}$  in both porous sol-gel  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>,<sup>3</sup> a nanostructured material, and in  $Eu_2O_3$  and  $Y_2O_3$  nanoparticles.<sup>4</sup> In these two cases, the experiments were interpreted with a simplified description of the electron-phonon interaction assuming there, as we also do in the present work, that the dephasing is produced by two-phonon Raman scattering. In that calculation we considered a smoothed density of states for the confined phonon modes of the nanoparticle and a model for the electron-phonon interaction in which the interaction involves localized vibrations as in glasses. The results of this simplified model successfully described the observed size dependence,  $\Gamma_h \propto 1/d^2$ , but yielded a temperature dependence that depended much too strongly on temperature.

In this paper we present a calculation for the size and temperature dependence of the electron-phonon interaction, assuming the same two-phonon Raman-scattering mechanism, but we consider the specific confined modes of the nanoparticle, including their resonance widths, and utilize a more exact treatment of the electron-phonon interaction. The calculation provides a good description of these observations regarding the spectral hole linewidths. We first provide a review of the experimental results in  $Eu_2O_3$ . The calculation begins with a treatment of a spherical nanoparticle considering its specific low-frequency normal modes and the effect of the size restriction on both the vibrational eigenstates and on the electron-phonon interactions. We find that a best fit to the data requires the assumption that the nanoparticle phonon resonances broaden as the square of the phonon frequency. We then consider the effect of a reduction in symmetry of the nanoparticles.

#### **II. REVIEW OF EXPERIMENTS**

Nanoparticles of  $Eu_2O_3$  were studied in the size range of 5–12 nm. Three nanoparticle samples were produced by gasphase condensation with cw-CO<sub>2</sub> laser vaporization as described previously.<sup>5</sup> The average particle size was controlled by the N<sub>2</sub> gas pressure in the synthesis chamber and was characterized with transmission electron microscopy. The three particle-size distributions are shown in Fig. 1. The mean particles sizes of these three samples are E1 (11.6 nm), E2 (7.6 nm), and E3 (5.4 nm) each with a distribution spread of  $\pm 2$  nm.

Fluorescence and excitation spectroscopy on these nanoparticles along with x-ray diffraction have shown,<sup>6</sup> that the nanoparticles crystallize in the monoclinic phase of  $Eu_2O_3$ . This phase contains three crystallographically inequivalent  $Eu^{3+}$  sites, rather than the two sites present in the normal cubic phase. In the monoclinic phase, the three Eu sites are

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FIG. 1. Particle-size distributions for the three  $Eu_2O_3$  samples, determined by transmission electron microscopy.

resolved in excitation and emission. The excitation spectra for the  ${}^7F_0 \rightarrow {}^5D_0$  transition of two of the nanoparticle samples are shown in Fig. 2. Note that for the largest particle size three absorption lines are seen despite the fact that both the ground and excited states are nondegenerate. Thus, these can be identified as belonging to the three sites in the monoclinic structure. Identification with the specific sites has been tentatively made by Dexpert-Ghys *et al.*<sup>7</sup> Note that as the particle size is reduced, the lines broaden and the *B/C* sites become unresolved. The linewidth of the *A* site is always significantly broader than those of the *B* or *C* sites. In addition, there is a background absorption that includes the region between the *A* and the *B/C* sites and extends beyond these site absorptions as well.

Spectral hole burning was performed on the  ${}^{7}F_{0} \rightarrow {}^{5}D_{0}$  transition of all three sites of Eu<sup>3+</sup> located at 582.4 nm (*C* site), 582.2 nm (*B* site), and 578.5 nm (*A* site) in Eu<sub>2</sub>O<sub>3</sub>. Transient hole burning is observed on all three sites. The mechanism is assigned to population redistribution among the hyperfine levels of Eu as has been seen previously in bulk crystals,<sup>8</sup> disordered crystals,<sup>9</sup> and glasses<sup>10</sup> based on the observation of antihole and sidehole structure within



FIG. 2.  ${}^{7}F_{0}\rightarrow{}^{5}D_{0}$  Eu<sup>3+</sup> excitation spectra at T=1.5 K for samples *E*1 (5.4 nm) and *E*3 (11.6 nm) showing the three sites for each of these monoclinic samples.



FIG. 3. Examples of the hole spectra for the three samples and for the three sites at T = 1.5 K.

about  $\pm$  200 MHz of the main hole, which reflects the ground and excited state quadrupole spittings of the two Eu isotopes. Hole lifetimes at 1.5 K fall in the range between 0.1 to 10 s with the shorter lifetimes occurring in the smaller particles and also for the *A* site, which behaves quite differently from the *B* and *C* sites.

The hole burning is performed with a single-frequency (2-MHz bandwidth) tunable dye laser. The holes are detected in a repetitive burn/scan sequence in which the holes are burned for 30 ms followed by a 10-ms delay and a 20-ms scan. The burn and scan power densities are about 200 and 30 mW/cm<sup>2</sup>, respectively. The  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  fluorescence at 610 nm is monitored, through wavelength selective filters, as the laser is scanned through the hole. Spectra are obtained by averaging 300–3000 burn/scan sequences. Figure 3 presents some representative hole spectra at 1.5 K for the three samples. The holes have a typical depth of 20%.

### **III. RESULTS**

A summary of the temperature dependence of the hole linewidths is presented in the form of a log-log plot in Fig. 4. The instrumental contribution of about 4 MHz has not been subtracted from the data. The upper temperature limits on the measurement of the hole linewidths are determined by two factors, the hole lifetime and the magnitude of the hyperfine splittings. When the lifetime becomes shorter than about 100 ms, the holes are refilled before the scan of the spectrum and no hole remains. This occurs around 12 K for the B/C sites and 6 K for the A sites. In addition, when the holes broaden beyond the maximum hyperfine splittings in the the ground or excited states, about 200 MHz, transient hyperfine hole burning becomes impossible since the laser cannot selectively pump a particular hyperfine transition.

While hole burning occurs on all three resonant transi-



FIG. 4. Observed temperature dependence of the spectral hole linewidth for the three samples and for the different sites. The solid lines are fits to the low-temperature behavior as described in the text.

tions, hole burning is also observed at all wavelengths between these resonances and even outside this wavelength range indicating the presence of a continuum of sites. The presence of sites that absorb at other wavelengths has already been noted above based on the excitation spectra shown in Fig. 2. The narrowest holes occur in the region of the B/Csite absorption. At other wavelengths the holewidths are much broader and are similar to those of the *A* site.

The smaller nanoparticles have larger linewidths at any given temperature than those of the larger particle samples. Note that they all have a linewidth which, at low temperatures, is nearly independent of temperature but which is much larger than the laser bandwidth limit (4 MHz). Above about 4 K the linewidths grow rapidly, approximately as  $T^{\alpha}$ where  $3 < \alpha < 3.5$  for the *B/C* sites, as described below. Generally speaking, the magnitude of the temperaturedependent increase of linewidth grows monotonically as the particle diameter decreases. It is the rapid rise in linewidth with temperature above 4 K that is of central interest in this paper. It is assumed that the very weak temperature dependence below 4 K results from a different mechanism than that of the rapid increase above 4 K. We therefore first fit the slow increase below 4 K with a constant low-temperature linewidth plus a small linear temperature-dependent contribution for each sample. These fits are shown by the solid curves in Fig. 4. In Fig. 5 a log-log plot of the temperature dependence of the linewidths for the B/C sites is shown. In Fig. 5, the contribution to the linewidth of the characteristic low-temperature behavior (solid curves shown in Fig. 4) have been subtracted from the experimental results. In order that the values of the experimental points used to compare with the calculations have adequate statistical significance, only those points whose linewidths (after the subtraction of the low-temperature behavior) exceed 20 MHz are shown. A best fit to the data is obtained for a power law in temperature with  $\alpha = 3.5$ , 3, and 3 for E1, E2, and E3, respectively.



FIG. 5. Comparison of the temperature and particle-size dependence of the calculated spectral hole linewidth to that of the experiment. The calculation is performed for each particle size assuming that the phonon modes broaden with frequency as  $\omega^q$  with q=0, 1, and 2.

These fits yield reduced  $\chi_R^2$  of 0.18, 1.54, and 0.61, respectively.

For the *A* site the hole linewidths are much larger than those of the *B/C* sites at all corresponding temperatures. As for the *B/C* sites, the temperature dependence follows a  $T^{\alpha}$ behavior with  $\alpha \approx 4$  and the linewidth increases monotonically as the inverse of the particle size. Because the temperature range for the *A* sites is so limited, the calculations that are described in the following will be compared only with the data from the *B/C* sites.

The sources of the low-temperature nonzero value of the linewidth and the linewidth contribution that is linear in temperature are not fully understood. Spectral diffusion, which occurs over a large range of time scales, can account for the nonzero limiting value at low temperature. Since the time delay between burning and measurement is of the order of milliseconds, significant spectral diffusion can occur, broadening the hole, prior to measurement. For example, such effects associated with glass rearrangements that occur with the energy release in downhill energy transfer have recently been reported in organic glasses.<sup>11</sup> The linear contribution is probably associated with residual disorder in the nanoparticles due to the presence of two-level systems. It is well known in glasses and disordered crystals that this adds a nearly linear temperature dependence to the homogeneous linewidth.<sup>8,12</sup>

## IV. CALCULATION OF THE ELECTRON-PHONON INTERACTIONS FOR NANOPARTICLES

A comparison of the temperature behavior of the spectral hole linewidths for the three samples reveals a strong dependence of the dynamics of the system on particle size. This occurs despite the nearly identical excitation and fluorescence spectra that indicate a well-ordered material with similar local site environments. While the particle-size-dependent dynamics might result from disorder near the surface that could lead to enhanced dynamics such as, for example, two-level systems, we believe that it can be understood in terms of the enhanced electron-phonon (e-p) interaction that occurs with a reduction in particle size. Such a calculation explains the unusual power-law behavior of the temperature dependence of the hole linewidths as is shown below. It also describes quantitatively the particle-size dependence of the hole linewidths.

In this calculation of the e-p interaction for the nanoparticles we consider the dynamics to be dominated by the twophonon Raman process. This is justified by the fact that both the ground and metastable excited states of the optical transition studied are isolated from their nearest higher-lying electronic states by more than 170 cm<sup>-1</sup> and 1600 cm<sup>-1</sup> respectively, so that below 20 K the direct process whereby phonons directly couple these optically coupled states to nearby electronic states, can be neglected. Dynamics related to disorder associated with defects either on the surface or internal in the nanoparticle, which might give rise to twolevel systems, may also be non-negligible, but for the moment these will be ignored. In support of this, it is noted that a nearly linear temperature dependence of the linewidth, characteristic of the two-level system (TLS), is also not observed except for a very weak linear behavior below 4 K that perhaps can be assigned to the presence of TLS. The rather sharp experimental inhomogeneous linewidths suggest a low level of internal defects.

The two-phonon Raman process is calculated in a manner analogous to the procedure in bulk crystalline materials that leads, for the bulk material at low temperatures, to a  $T^7$ temperature dependence to the homogeneous linewidth.<sup>13</sup> There are two factors that make the results for nanoparticles very different. In the first place, the acoustic-phonon modes become discrete in energy with a low-frequency "gap." This simply follows from the solution of the vibrational modes of a homogeneous solid with boundary conditions.<sup>14</sup> This results in a very different temperature dependence for the dynamics than is the case for the infinite crystal. Secondly, the confinement of the vibrational excitations results in a particle-size-dependent amplitude of the motion of the atoms thereby producing a greatly enhanced interaction between the electronic states of the impurity ion and the vibrational modes of the nanoparticle as the particle size is reduced.

An important feature of the eigenstates of the vibrational modes is the spatial dependence of the amplitude of the individual atomic motions, which is a natural consequence of the fact that these modes are standing waves determined by the boundary conditions. This means that the interaction of a particular vibrational mode with a  $Eu^{3+}$  ion will be a function of the ion's location in the nanoparticle. However, this spatial dependence will be different for each vibrational mode and will tend to be averaged out at higher temperatures when a large number of the vibrational modes become activated. In addition, we assume that the  $Eu^{3+}$  ions are randomly distributed within the nanoparticles. This spatial dependence is ignored here.

In the discussion that follows, the calculation of the twophonon Raman scattering is first presented for the bulk, thereby illustrating the procedure and the origin of the wellknown  $T^7$  behavior. Next, the eigenvalues and eigenvectors of the normal modes of a spherical homogeneous particle are described, showing the discreteness of the phonon spectrum and the appearance of the low-frequency "gap." The calculation of the two-phonon Raman scattering is then obtained for the case of a spherical nanoparticle. The result leads to a prediction for both the temperature and size dependence of the homogenous linewidth. Finally, the consequences of removing some of the simplifying assumptions, such as the assumption of sphericity, are considered. As will be shown, a satisfactory description of the observed dependence of linewidth on temperature and particle size can be obtained with reasonable assumptions. It is also demonstrated that the strength of the e-p interaction required to describe the experimental nanoparticle results is consistent with the known strength of the two-phonon Raman e-p interaction in the bulk crystal case using reasonable parameters. This provides considerable confidence in the model. The quantitative extension of the homogeneous linewidths from the bulk to the nanoparticle also allows one to estimate the homogeneous widths of the nanoparticle vibrational resonances, yielding an estimate of their dephasing times and their dependence on phonon frequency.

The mechanism of two-phonon Raman scattering involves the scattering from either the ground or excited electronic state of the optical probe ion of a phonon of state k into a phonon state k'. This scattering involves a virtual state of the ion-phonon system and because no real states are involved, phonons of all frequencies can participate.

The Hamiltonian for the e-p interaction is written

$$H = H_0 + V_1 \varepsilon + V_2 \varepsilon^2, \tag{1}$$

where the strain is written in terms of the phonon creation and destruction operators,  $a_k^{\dagger}$  and  $a_k$ , respectively,

$$\varepsilon = \partial u / \partial x \big|_{x=0} = \sum_{k} (ik/V^{1/2}) (\hbar/2\rho\omega_k)^{1/2} (a_k^{\dagger} - a_k).$$
 (2)

For a continuum of phonon states, we use Fermi's Golden Rule that allows one to express the two-phonon Ramanscattering rate for electronic state *i* in terms of a coupling matrix element  $M_{kk}$  and the phonon density of states  $\rho(\omega_k)$ ,

$$W_{\text{Raman}} = (2 \pi/\hbar^2) \int \int |M_{kk'}|^2 \rho(\omega_k) \rho(\omega_{k'}) \,\delta(\omega_k - \omega_{k'}) d\omega_k d\omega_{k'}, \qquad (3)$$

where  $\omega_k$  is the phonon frequency and

$$M_{kk'} = (i\hbar/\rho V v_0^2) \omega_k^{1/2} \omega_{k'}^{1/2} n_k^{1/2} (n_{k'} + 1)^{1/2} \langle i | V' | i \rangle.$$
 (4)

Here V is the volume of the nanoparticle,  $v_0$  is the speed of sound,  $|i\rangle$  is either the ground or metastable-excited state connected to the ground state by the hole-burning transition and

$$n_k = (e^{\hbar \omega/kT} - 1)^{-1} =$$
 phonon occupation number. (5)

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TABLE I. Parameters for obtaining the eigenfrequencies of the nanoparticle normal vibrational modes of  $Eu_2O_3$ .

	α	β	γ
Spheroidal			
Transverse, $j = 1$	1.3 - 0.014(l)	0	0
Transverse, $j > 1$	1.3	3.14	-3.14
Longitudinal	2.53	6.12	0
Torsional			
j = 1	1.25 - 0.007(l)	0	0
<i>j</i> >1	1.3	3.14	-1.57

V' in Eq. (4) contains contributions from both strain terms in Eq. (1), the linear term to second order, summed over all intermediate states *t* and the quadratic term in first order. It is given by

$$\langle i|V'|i\rangle = \langle i|V_2|i\rangle + \sum_t \langle i|V_1|t\rangle \langle t|V_1|i\rangle / \Delta_t, \qquad (6)$$

where  $\Delta_t$  is the energy difference between the states  $\langle i |$  and  $\langle t |$ . For the bulk crystal  $\rho(\omega_k) = 3V\omega_k^2/2\pi^2 v_0^3$ , which leads to the result

$$W_{\text{Raman}}(\text{bulk}) = (9|\langle i|V'|i\rangle|^2 / 2\pi^3 \rho^2 v_0^{10}) \int_0^{\omega_D} \omega^6 n(n+1) d\omega.$$
(7)

For  $kT \ll \hbar \omega_D$  integration of Eq. (7) yields

$$W_{\text{Raman}}(\text{bulk}) = 9 \cdot 6! (k/\hbar)^7 |\langle i|V'|i\rangle|^2 (2\pi^3 \rho^2 v_0^{10})^{-1} T^7,$$
(8)

which produces the standard result that  $W_{\text{Raman}}(\text{bulk}) \alpha T^7$  at low temperatures. A comparison to the observed temperature dependence of the homogeneous linewidth in the bulk<sup>15</sup> determines that  $\langle i|V'|i\rangle = 0.375 \text{ eV}$ .

For the nanocrystal, the normal modes are standing waves. The frequencies were first obtained by Lamb<sup>11</sup> in 1882. The eigenvalues and eigenvectors were described in second quantized form by Takagahara<sup>2</sup> who obtained the modes of a homogeneous sphere under stress-free boundary conditions by introducing a scalar and vector potential. The modes are classified into two types, spheroidal and torsional. They are characterized by a set of three quantum numbers; *l*, *m* are the angular momentum indices, and *j* is the radial quantum number. The approximate eigenvalues described by Tamura,<sup>16</sup>

$$\omega_{il}^{\sigma} = (v_{\sigma}/R)(\alpha_{\sigma}l + \beta_{\sigma}j + \gamma_{\sigma}), \qquad (9)$$

are used in the following calculation, where *R* is the particle radius,  $\sigma$  labels the type of mode (i.e., spheroidal, torsional, longitudinal, etc.) and  $\alpha$ ,  $\beta$ , and  $\gamma$  are constants of order unity that are determined by a fit of the eigenvalues calculated from the calculations described by Takagahara<sup>2</sup> using materials constants appropriate to Eu<sub>2</sub>O<sub>3</sub> (density=7.42 ×10<sup>3</sup> kg m<sup>-3</sup> and sound velocity= $3.5 \times 10^3$  m s<sup>-1</sup>). For Eu<sub>2</sub>O<sub>3</sub> they take on the values given in Table I. However, for the lowest-frequency modes, the approximate formula given in Eq. (9) is not sufficiently accurate so the actual eigenfrequencies are utilized.

In order to perform the integration of Eq. (3) for the case of nanoparticles, it is necessary to explicitly utilize the density of states for the vibrational modes of the nanoparticle. Since the modes are discrete and may be well separated from one another in frequency, the integral is broken up into a sum of integrals, each term accounting for one of the resonant vibrational frequencies. Each resonance is treated as having a degeneracy of 2l+1. For the lower-frequency phonon modes, which are of main concern at low temperatures, scattering takes place among the degenerate phonon states within each resonance. Thus k and k' in Eq. (3) are identified with modes *jlm* and *jlm'*, where *m* and *m'* span the 2l+1degenerate states. At higher frequencies, modes of different *jl* may overlap so that scattering among different *jl* modes can occur. The density of states of each resonance is treated as a normalized Lorentzian,  $g_{il}(\omega)$  of width  $\Delta \omega_{il}$  weighted by the degeneracy. This results in a density of states,

$$\rho(\omega) = \sum_{jl} (2l+1)g_{jl}(\omega)$$
  
=  $\sum_{jl} (2l+1)\Delta \omega_{jl}(2\pi)^{-1}[(\omega-\omega_{jl})^2 + (\Delta \omega_{jl}/2)^2]^{-1}.$  (10)

The contribution of each term in the sum of Eq. (3) is obtained by integrating over the range  $\pm 10\Delta \omega_{il}$ .

The result of integrating Eq. (3) using the phonon spectrum of the nanoparticle depends strongly on the magnitude of the phonon resonance width,  $\Delta \omega_{jl}$ , and how this width depends on frequency. While one might expect that the resonances broaden with frequency, the nature of the phonon dynamics in nanoparticles is not presently known. We have therefore performed the integration assuming various frequency dependencies of the form  $\Delta \omega_{jl} = \Delta \omega_{q0} \omega_{jl}^{q}$  where q = 0, 1, 2 and where  $\Delta \omega_{q0}$  is a parameter chosen to yield the correct magnitude of the observed temperature dependence of the hole linewidth.

The calculated densities of states for particles of diameter 5.4 and 11.6 nm for the case of q = 2 are shown in Fig. 6. For ease of visualization, the value of  $\Delta \omega_{20}$  is taken as 1000 times the value required to fit the experimental temperature dependence of the hole width. Thus, in actuality, the resonances are narrower than shown by a factor of 1000. Note that at higher frequencies, the energy density of resonances increases and the resonances broaden to form a continuum whose density of states increases  $\approx \omega^2$  (as in the bulk). The lower-energy modes for the 5.4-nm particles are labeled: ST<sub>i</sub>, *l* for spherical transverse and  $T_{j}$ , *l* for torsional, where *j* and *l* are the radial and angular-momentum quantum numbers, respectively. Since the resonance energies scale as 1/R, for the smaller particles the corresponding resonance energies and widths for a given value of *j*, *l* become larger, inversely as the particle size. Note the larger "gap" and reduced density of states for the smaller particles.

The temperature dependencies of the calculated hole linewidths, for the average size of the three particle-size distributions, are shown in Fig. 5 (curves) as a function of the exponent q that describes the frequency dependence of the phonon resonance width.



FIG. 6. Calculated phonon density of states for 5.4- and 11.6-nm particles assuming the phonon resonances broaden  $\propto \omega^2$  (i.e., q = 2). The modes for the 5.4-nm particles are labeled:  $ST_{j,1}$  for spherical transverse and  $T_{j,1}$  for torsional, where j,1 are the radial and angular-momentum quantum numbers, respectively.

The results of the calculations for the 11.6-nm particles are shown by the dashed curves for q = 2, 1, and 0. They can be compared with the experimental hole widths (open triangles), obtained by subtracting from the observed hole widths the low-temperature contributions indicated by the solid curve in Fig. 4. It is seen that the case of q=2 best describes the data for the 11.6-nm particles. Similarly, the solid curves present the calculated results for the 7.6-nm particles. Comparison to the experimental results for this size particle suggests that the q=2 results also best describe the temperature dependence. Finally, the dotted lines present the results for the 5.4-nm particles with a comparison to experiment (open circles). For the smaller nanoparticles at low temperatures, the calculated temperature dependence of the homogeneous linewidth goes from a power-law behavior to one that is exponential when  $kT < \hbar \omega_{\min}$ , where  $\omega_{\min}$  is the frequency of the lowest-energy phonon mode. Here the agreement is not very good, although at the higher temperatures, the experimental data is converging to the calculations. We suspect that for these smallest particles, disorder and the role of the surface make a contribution to the dephasing, likely from two-level systems associated with the disorder. This idea is supported by the excitation and emission spectra of the 5.4-nm particles that yield much larger inhomogeneous linewidths for all three sites than similar spectra of larger-sized particles. Because dephasing due to TLS increases only linearly with temperature, in the highertemperature region the role of the nanoparticle vibrational modes acting through two-phonon Raman processes ( $\propto T^3$ ) become dominant.

The calculations predict a much weaker power-law behavior for the hole linewidth with temperature than for the bulk, which is  $T^7$ . Rather, for the nanoparticles, the behavior is  $T^{\alpha}$  with  $\alpha = 5.5$ -q; i.e., 5.5, 4.5, and 3.5 for q = 0, 1, and 2, respectively. Comparison with the experiments suggests that  $\alpha$  lies between 3 and 4 implying that q falls between 1 and 2. As a result, it is concluded that the nanoparticle vibrational modes broaden either linearly or quadratically with frequency (at least for the lower-frequency modes). The reason



FIG. 7. Comparison of calculated and experimental spectral hole linewidths as a function of particle size for  $T \cong 10$  K.

for the decrease of the temperature exponent  $\alpha$  as q increases is the dependence of Eq. (3) on the square of the phonon density of states. The larger the value of q, the more rapidly the phonon resonances broaden. While the total number of phonon modes remains constant, the magnitude of the spectral density for each mode decreases inversely as its width. As a result, since the integrand of Eq. (3) contains the density of states squared, when the integration is performed, the higher-frequency modes, which are increasingly populated as the temperature increases, make a reduced contribution to the integral; the effect being more pronounced the more rapidly the modes broaden (i.e., as q increases). Thus, the larger the value of q, the smaller the value of  $\alpha$ .

The calculations also correctly describe the size dependence of the hole widths, for all the examined values of q. This is shown in Fig. 7, where the experimental linewidths at 9 K for the three particle sizes is compared with the calculated linewidths for the corresponding sizes at nearly the same temperature. The calculations indicate that  $\Gamma_{\text{hole}} \sim D^{-2.5}$ . This is similar to the result that has been determined for semiconducting quantum dots, where it was found (albeit at higher temperatures where the optic-phonon modes dominate) that the homogeneous linewidth varies as  $\sim D^{-2}$ .<sup>1,2</sup>

One must also examine the consequence of relaxing some of the simplifying assumptions about the nanoparticles since the particles are not perfectly round but are faceted and often oblong in overall shape. The removal of spherical symmetry breaks up the 2l+1 degeneracy of each mode of quantum number *jl*. If the splitting is greater than the phonon resonance width, the higher-frequency modes, which have the larger degeneracy, will not contribute as effectively to the integral of Eq. (3). Although each term in the sum corresponding to a given value of 1 will yield 2l+1 terms under



FIG. 8. Comparison of temperature dependence of spectral hole width for a spherical and distorted nanoparticle (11.6 nm) with each other and with experiment for the case q = 2.

the reduced symmetry, the contribution of each of these terms will drop by a factor  $(2l+1)^{-2}$  since this prefactor will no longer multiply each of the normalized Lorentzians in the density of states that appear twice in the integrand of Eq. (3). As a result, the magnitude of the hole width is decreased and the temperature dependence is weakened. To provide a best fit to the experiments, the phonon resonance widths used in the calculation must be reduced relative to their values for spherical particles to bring the magnitude of the calculated results into agreement with experiment. A comparison of the calculations for the spherical and nonspherical particles for q=2 with each other and with the experimental hole linewidths is shown in Fig. 8 after an appropriate decrease in the phonon widths  $\Delta \omega_{il}$  for the nonspherical case. It is seen that  $\alpha$  is approximately reduced by about 0.5, from about 3.5 to 3.0. In general, it is found that  $\alpha = 5 - q$  (nonspherical) instead of 5.5-q (spherical).

Assuming the correctness of the model presented above, which is successful at describing the experimental temperature and particle-size dependencies of the hole linewidths, it is possible to use the resulting parameters that best describe the experiments to obtain information on the dynamics of the vibrational modes of the nanoparticle. The phonon resonance widths,  $\Delta \omega_{il}$  yield the values of  $T_2 (T_2^{jl} = 2/\Delta \omega_{il})$  for the phonon modes. The resulting frequency dependence of  $T_2$ for spherical (q=0,1,2) particles, based on the fits to experiment shown in Fig. 5, are shown in Fig. 9. T<sub>2</sub> contains contributions from both energy relaxation and pure dephasing. Pure dephasing can occur by scattering of the phonons among the 2l+1 degenerate phonon states. This results in dephasing of both the Eu<sup>3+</sup> electronic states and of the phonons. In addition, defects at the surface of the nanoparticle may provide additional sources of dephasing of the



FIG. 9. Phonon energy dependence of the phonon resonance width obtained by fitting the calculations for the case of a spherical nanoparticle to the experimental results of the spectral hole width as a function of temperature and particle size.

nanoparticle vibrational eigenstates. Energy relaxation among the modes of the nanoparticle are strongly hindered, especially at low temperature, due to the discreteness and low density of states of the vibrational modes. This greatly limits the number of processes that can conserve energy in the relaxation. However, since the particles are not truly isolated, as is evident from TEM pictures, relaxation processes involving the interaction among nanoparticles may provide other pathways.

### **V. CONCLUSIONS**

A calculation of the *e*-*p* interaction due to the two-phonon Raman process for nanoparticles as a function of particle size is shown to successfully describe the temperature and particle-size dependencies of the spectral hole linewidth of the  $Eu^{3+}$  ion in  $Eu_2O_3$ . The effects of the discrete nature of the nanoparticle phonon states and the increased amplitude of the atomic motions combine to enhance the magnitude of the *e-p* interaction and to alter the temperature dependence of the of the linewidth from  $T^7$  to approximately  $T^3$  and to generate a particle-size dependence of  $R^{-2.5}$ . The calculations lead to a determination of the phonon mode dephasing times that increase approximately as  $\omega^2$ , yielding for the spherical nanoparticles, a value at  $\omega = 25 \text{ cm}^{-1}$  of  $T_2$ =40ns. Removal of the assumption of spherical particle symmetry reduces the exponent in the power-law behavior of the temperature dependence of the hole linewidth by 0.5.

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- <sup>1</sup>D. M. Mittleman, R. W. Schoelein, J. J. Shiang, V. L. Colvin, A. P. Alivisatos, and C. V. Shank, Phys. Rev. B **49**, 14 435 (1994).
- <sup>2</sup>T. Takagahara, J. Lumin. **70**, 129 (1996).
- <sup>3</sup>S. P. Feofilov, A. A. Kaplyanskii, R. I. Zakharchenya, Y. Sun, K. W. Jang, and R. S. Meltzer, Phys. Rev. B 54, R3690 (1996).
- <sup>4</sup>K. S. Hong, R. S. Meltzer, B. Bihari, D. K. Williams, and B. M. Tissue, J. Lumin. **76**/**77**, 234 (1998).
- <sup>5</sup>H. Eilers and B. M. Tissue, Mater. Lett. **24**, 261 (1995).
- <sup>6</sup>H. Eilers and B. M. Tissue, Chem. Phys. Lett. 251, 74 (1996).
- <sup>7</sup>J. Dexpert-Ghys, M. Faucher, and P. Caro, Phys. Rev. B 23, 607 (1981).
- <sup>8</sup>R. M. Macfarlane and R. M. Shelby, in *Spectroscopy of Solids Containing Rare Earth Ions*, edited by A. A. Kaplyanskii and R.

M. Macfarlane (North-Holland, Amsterdam, 1987).

- <sup>9</sup>K. W. Jang and R. S. Meltzer, Phys. Rev. B 52, 6431 (1995).
- <sup>10</sup>Th. Schmidt, R. M. Macfarlane, and S. Volker, Phys. Rev. B 50, 15 707 (1994).
- <sup>11</sup>F. T. H. den Hartog, C. van Papendrecht, R. J. Silbey, and S. Volker, J. Chem. Phys. **110**, 1010 (1999).
- <sup>12</sup>K. W. Jang, K. S. Hong, T. T. Basiev, and R. S. Meltzer, J. Lumin. **66/67**, 8 (1996).
- <sup>13</sup>R. Orbach, Proc. R. Soc. London, Ser. A 264, 458 (1961).
- <sup>14</sup>H. Lamb, Proc. London Math. Soc. 13, 189 (1882).
- <sup>15</sup>W. R. Babbitt, A. Lezama, and T. W. Mossberg, Phys. Rev. B **39**, 1987 (1989).
- <sup>16</sup>A. Tamura, Phys. Rev. B **52**, 2668 (1995).