Temperature dependence of two-photon absorption linewidths of Eu^{2+} in CaF_2

Luiz A. O. Nunes, L. Ioriatti, Jarbas C. Castro, and S. C. Zilio
Instituto de Fisica e Química de São Carlos, Universidade de São Paulo, Caixa Postal 369, 13560 São Carlos, São Paulo, Brazil
(Received 15 September 1987)

Two-photon absorption linewidths of $^8S_{7/2} \rightarrow {}^6P_{7/2}$ transitions in Eu^{2+}-doped CaF_2 are studied as a function of the temperature. Linewidths are shown to have a linear dependence on the occupation number of LO phonons (n_{LO}) of the CaF_2 lattice. This result is explained by means of the different polarizabilities of the ground and the excited states, which give rise to elastic phonon scattering. By using the polarizability of Eu^{2+} in EuF_2 we predict a slope for the linewidth $\Gamma(T)$ versus $n_{LO}(T)$ curve, which is in fairly good agreement with the experimental data. The linewidth at T close to zero is ascribed to inelastic phonon scattering which causes the $4f^7$-$4f^6 5d$ configuration mixing. The theory also predicts a line shift proportional to the occupation number.

I. INTRODUCTION

Two-photon transitions between levels of the $4f^7$ configuration of Eu^{2+} were recently reported for a few alkaline-earth fluorides[1-3] and alkali-metal halides.[4] Although the $4f^7$ and the broad $4f^6 5d$ configurations overlap in these crystals, the parity selection rule for two-photon absorption (TPA) supress the strong electric-dipole-allowed $4f^7 \rightarrow 4f^6 5d$ transition and sharp $4f^7 \rightarrow 4f^7$ lines are easily observed. Measurements of the frequencies and relative intensities of these lines allow the calculation of free-ion and crystal-field parameters for the host lattice[3] besides providing a unique way for studying the formation of precipitated phases of Eu^{2+}.[4] According to Fig. 1, which shows part of a typical energy-level diagram for Eu^{2+} as a dopant in these crystals, two-photon excitation spectra are measured by monitoring the violet fluorescence from the $4f^6 5d$ configuration. No fluorescence is observed directly from the $4f^7$ excited states. Instead, the excitation is transferred to the overlapping $4f^6 5d$ band via odd-parity lattice vibrations, followed by the fluorescence around 4100 Å. Since the transfer mechanism involves phonons, it is strongly dependent on the temperature and this dependence will be reflected in the lineshape.

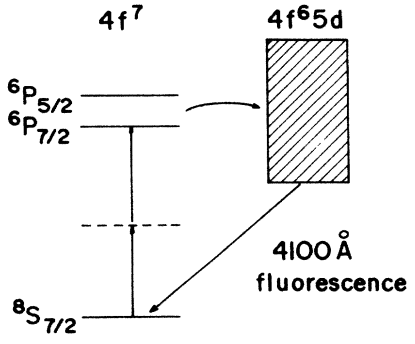

FIG. 1. Energy-level diagram for Eu^{2+} in CaF_2 showing the two-photon excitation of the $^6P_{7/2}$ level and the decay through the overlapping $4f^6 5d$ configuration.

In the present work, TPA spectroscopy is used to measure linewidths of $^8S_{7/2} \rightarrow {}^6P_{7/2}$ transitions in Eu^{2+}:CaF_2 as a function of temperature. This is, to the best of our knowledge, the first study of TPA linewidths of impurities in solids. The aim is to find out how lattice dynamics affects the $4f^7 \rightarrow 4f^6 5d$ transfer mechanism. This has been ignored in previous works and no temperature dependence of TPA linewidths is reported in the literature. The experimentally observed spectra are presented in Sec. III. Linewidths show a linear dependence on the occupation number of LO phonons at 463 cm^{-1} in CaF_2. This same sort of behavior has already been found in molecular mixed crystals[5] and was explained by means of both Redfield[6] and modified McCumber-Sturge[7] theories. In this work, however, we present a different approach, based on the different polarizabilities of the Eu^{2+} in ground and excited states, in order to explain the above results. In this case, assuming the polarizability of Eu^{2+} in CaF_2 to be close to the one in EuF_2 and with the knowledge of the phonon dispersion relation in CaF_2, we are able to find the slope of $\Gamma(T)$ versus $n_{LO}(T)$ curve without any adjustable parameter. Even with a few approximations the theoretical prediction agrees with the experimental result within 20%. The line shift as a function of the temperature is also predicted to be proportional to n_{LO} and is in agreement with the theories mentioned above. This approach based on the different polarizabilities is presented in Sec. III.

II. EXPERIMENTS AND RESULTS

The experimental apparatus and procedure have been fully described elsewhere[4,8] and only a few details will be given here. The homemade dye laser of the Littman type with an intracavity prism expander is pumped by the second harmonic of a Quanta Ray DCR-1 neodymium: yttrium-aluminum-garnet (Nd:YAG) laser and presents typical characteristics such as a peak power of 1 MW, a linewidth of 0.1 cm^{-1}, a pulse duration of 5 ns and a repetition rate of 10 Hz. The Eu^{2+}-doped CaF_2 was grown

by the Bridgman method under a controlled HF atmosphere and the doping with europium was achieved by the addition in the melt of 0.5 mol % of $EuCl_2$. A Janis 6DT Dewar and a homemade temperature controller were used to cool the samples to constant temperatures in the range of 10–240 K.

Figure 2 shows TPA spectra of the transition from the ground $^8S_{7/2}$ state to the $^6P_{7/2}$ states in CaF_2:Eu^{2+} for three representative temperatures. The vertical scale indicates TPA intensities of the same internally consistent scale, with the Γ_8^- line normalized to 1 at 77 K. The spectrum comprises three lines as predicted by group theory for a $J=\frac{7}{2}$ level in a crystal field with O_h symmetry. The main features of the spectra are the following: (1) At temperatures lower than 100 K the lines are very sharp and no sidebands are observed. This suggests that TPA in this case is essentially due to zero-phonon transitions. (2) As the temperature increases, all lines shift to lower frequencies, the linewidths increase, and the integrated absorptions remain approximately constant. (3) The background, which corresponds to $4f^7 \rightarrow 4f^6 5d$ transitions, increases with the temperature.

Figure 3 shows the linewidth [full width at half maximum (FWHM)] of the Γ_7^- transition as a function of the temperature. Since the other two lines have a similar behavior, they are not shown here. Below 100 K, linewidths are essentially unchanged. As shown in Fig. 4, the experimental data follows a curve $\Gamma(T)=\Gamma_0+\Gamma_1 n(\nu,T)$, where $n(\nu,T)=[\exp(-\hbar\nu/kT)-1]^{-1}$ is the mean occupation number of phonons with frequency ν at the temperature T and Γ_0 is the linewidth at 0 K. The best fit to the data of Fig. 4 is achieved for $\Gamma_0=1.1\ \text{cm}^{-1}$ and $\nu=1.4\times10^{13}$ Hz. This frequency corresponds to that of LO phonons in the CaF_2 lattice.[9]

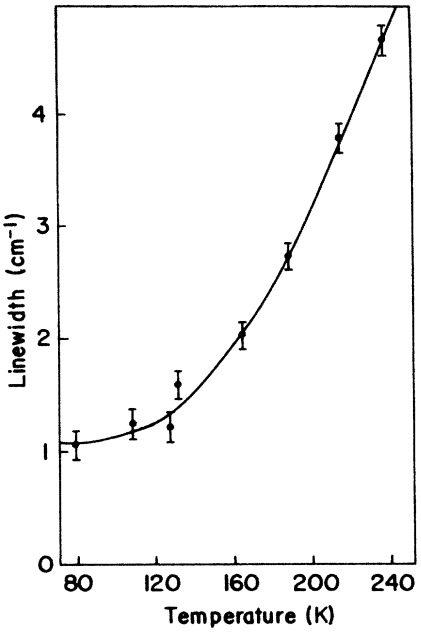

FIG. 3. Temperature dependence of the Γ_7^- linewidth in CaF_2:Eu^{2+}. The solid line is the $\Delta\nu(T)$ curve discussed in the text.

III. DISCUSSION

The narrow linewidths ($\sim 1\ \text{cm}^{-1}$) of two-photon $^8S_{7/2} \rightarrow {}^6P_{7/2}$ transitions, and the absence of phonon sidebands associated to them, clearly suggest that the interaction of the europium ion with its neighbors is essentially

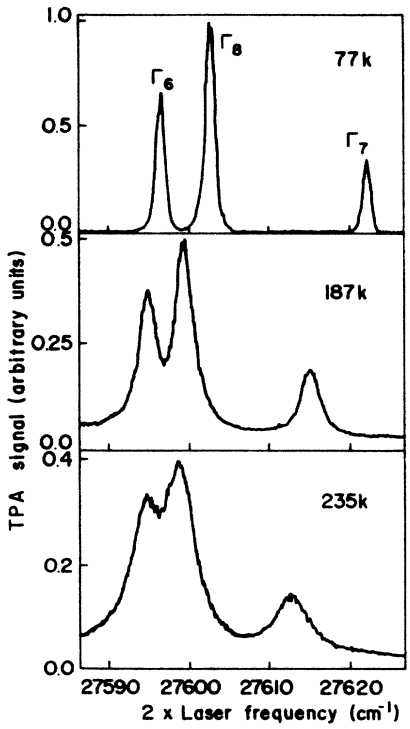

FIG. 2. Experimental TPA spectra of the $^8S_{7/2} \rightarrow {}^6P_{7/2}$ transition in CaF_2:Eu^{2+} at three representative temperatures.

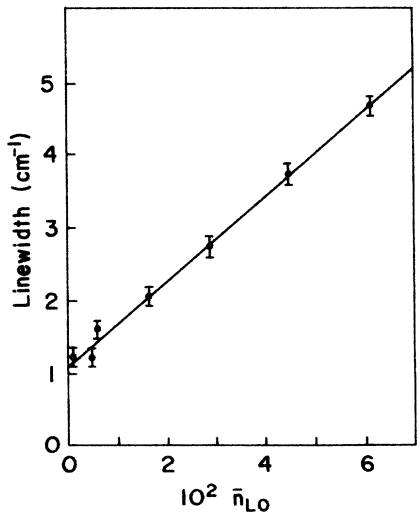

FIG. 4. Experimental linewidths plotted as a function of the occupation number of LO phonons in CaF_2. The solid line is drawn for $\Delta\nu=1.1\ \text{cm}^{-1}$, $\gamma=57\ \text{cm}^{-1}$, and $\nu_{LO}=1.4\times10^{13}$ Hz.

the same for both ground and excited states and that these two-photon transitions represent zero-phonon lines. This is due to the fact that $4f^7$ electrons are shielded by $5s$ and $5p$ shells and therefore their coupling to the lattice is very weak in the sense that the initial and the final states differ very little in their sensitivity to change in the environment. Consequently, the Huang-Rhys parameter S is close to zero for upward $f \rightarrow f$ transitions.[10] Moreover, the insensitivity of the linewidth, for temperatures below 150 K, can be taken as an experimental evidence that effects due to changes of the force constant between the impurity and the neighboring atoms, when the impurity undergoes an electronic transition, is not relevant for the present case. If there was any such change this effect would be observed due to the coupling of the impurity to even-parity acoustic phonons which are certainly present for $T < 150$ K. On the other hand, the centers of gravity of the $4f^7$ and $4f^6 5d$ configurations are relatively close for divalent ions allowing their coupling via odd-parity lattice vibrations. This effect is expected to be particularly important for the Eu^{2+} ion where the $4f^6 5d$ configuration is broadened by the crystal field and overlaps with the $^6P_{7/2}$ levels. Taking into consideration that the configuration $4f^6 5d$ is closer to the $^6P_{7/2}$ multiplet than to the $^8S_{7/2}$ ground state (see Fig. 1), the atomic polarizabilities of these two states are different and in this way it is plausible to expect that the dependence of the linewidth on the temperature has its origin on these different polarizabilities. As a first approximation, important effects associated with different polarizabilities have their origin in the coupling between different induced dipole moments and the local electric field. Both induced dipole and local field are produced by some vibrational configuration.

According to the above picture, optical phonons play a very important role in the absorption line-broadening mechanism since the opposite motion of neighbor ions produces intense polarization fields. In other words, the observed linewidths are expected, as a first approximation, to be dependent on the local-field fluctuations and therefore to exhibit a linear dependence on the optical-phonon density. As presented in Fig. 4, the experimental points are proportional to the occupation number of long-wavelength LO phonons ($\omega_{LO} \sim 463$ cm^{-1}) of the CaF_2 lattice. When the linewidths are compared to curves describing the occupation number of TO ($\omega_{TO} \sim 260$ cm^{-1}) modes, marked discrepancies are observed. Although group theory predicts the contribution of these phonons to the configurations mixing, and consequently to the line-broadening mechanism, the experimental evidence is that only LO phonons play an important role to the mechanism. We do not understand this point and further investigation is still needed to clarify it.

After this preliminary consideration, we will propose a model where the different atomic polarizabilities give rise to different contributions to the impurity-lattice interaction energy for a given vibrational configuration. This new contribution may be written as

$$H' = -\tfrac{1}{2}\alpha \mathbf{E}^{*2} , \qquad (1)$$

where α stands for the change in the atomic polarizabilities between the states $^8S_{7/2}$ and $^6P_{7/2}$, and E^* is the local Lorentz field at the Eu^{2+} site. For long-wavelength LO modes, the Lorentz field is given by[11]

$$\mathbf{E}^* = -\frac{8\pi}{3}\left[\frac{\hbar}{2\gamma v N \omega_0}\right]^{1/2} \sum_{\mathbf{q}} \frac{\mathbf{q}}{|\mathbf{q}|}(a_{\mathbf{q}}^{\dagger} + a_{\mathbf{q}}) , \qquad (2)$$

where N is the number of unit cells, $v = 40.758$ Å^3 is the volume of one of these cells, and $\gamma^{-1} = \omega_0^2(1/\epsilon_\infty - 1/\epsilon_0)/4\pi$ is the Fröhlich coupling parameter with $\epsilon_\infty = 2.05$ and $\epsilon_0 = 6.53$.[12]

Within the framework of the Franck-Condon approximation, where the two-photon transition operator is supposed to be independent on the vibrational coordinates, zero-phonon transitions are represented as in the central portion of Fig. 5, where $|\beta\rangle = |\{n_q\}\rangle$ denotes a stationary vibrational configuration with the europium ion in the ground state. As stated earlier, the interaction energy between the ion in the $^6P_{7/2}$ state and the lattice differs from that where the ion is in the ground state by the term given in Eq. (1). Since the vibrational configuration $|\beta\rangle$ is not an eigenstate of the Hamiltonian H', it becomes unstable and therefore can be scattered to another configuration $|\beta'\rangle$ with the same energy. On the other hand, inelastic scattering processes starting from $|\beta\rangle$ must be followed by a change in the electronic configuration of the Eu^{2+} ion and in this case there is an atomic excitation transfer to the vibronic $4f^6 5d$ band with the emission of several types of phonons. Since this band goes from well below (~ 3000 cm^{-1}) to well above (~ 1000 cm^{-1}) the $^6P_{7/2}$ multiplet, these inelastic processes are expected to be nearly independent of the initial vibrational configuration $|\beta\rangle$ and consequently independent of the temperature. In this way, the temperature dependence of two-photon transitions observed in the experiment is due to the finite lifetime of the vibrational states, via elastic scattering of LO phonons. According

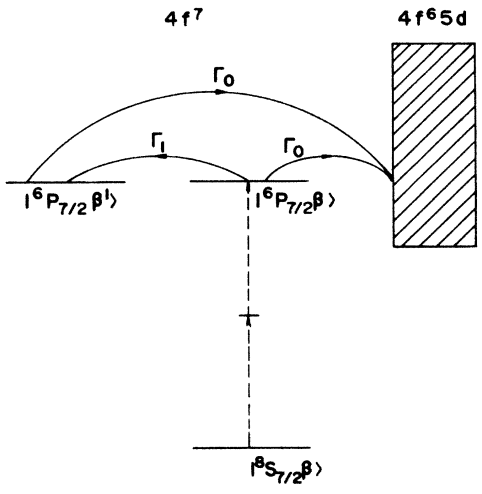

FIG. 5. Line-broadening mechanism proposed for Eu^{2+}:CaF_2. Γ_1 is the rate of the inelastic scattering while $\Gamma_0 \ll \Gamma_1$ takes into account inelastic processes.

to perturbation theory, the transition rate can be written as

$$\Gamma=\Gamma_0+\frac{2\pi}{\hbar^2}\left\langle\sum_{\beta'}|\langle\beta'|H'|\beta\rangle|^2\delta(\omega_{\beta'}-\omega_\beta)\right\rangle_{\rm th}, \quad (3)$$

where $\langle\cdots\rangle_{\rm th}$ stands for the thermal average on the initial $|\beta\rangle$ states and Γ_0 is the temperature-independent transition rate corresponding to the inelastic excitation transfer to the $4f^6 5d$ band. For the temperature range used in the experiment the observed line shapes were essentially Lorentzians, in accordance with the homogeneous broadening predicted by Eq. (3). No experimental evidence was found for inhomogeneous broadening. The broadening mechanism is represented in Fig. 5, where Γ_1 stands for the elastic scattering.

The theoretical evaluation of the sloped $\Gamma(t)\times n(T)$ is carried out by combining Eqs. (1)–(3), which yields

$$\Gamma=\Gamma_0+\frac{2\pi}{\hbar^2}\left[\left[\frac{8\pi}{3}\right]^2\frac{\hbar\alpha}{2\gamma v\omega_0}\right]^2 \times\frac{1}{N^2}\sum_{\mathbf{q}',\mathbf{q}}\left[\frac{|\mathbf{q}\cdot\mathbf{q}'|}{|\mathbf{q}|\,|\mathbf{q}'|}\right]\delta^2(\omega_{\mathbf{q}}-\omega_{\mathbf{q}'})(1+n_{\mathbf{q}})n_{\mathbf{q}} . \quad (4)$$

Assuming a parabolic dispersion relation $[D(\omega)\alpha(\omega_0-\omega)^{1/2}]$ for ω_q, which according to Elcombe and Pryor[13] spans a range $\Delta\omega\sim 100$ cm^{-1}, and neglecting this dispersion in the occupation number, Eq. (4) may be written as

$$\Gamma=\Gamma_0+\frac{2\pi}{\hbar^2}\left[\left[\frac{8\pi}{3}\right]^2\frac{\hbar\alpha}{2\gamma v\omega_0}\right]^2\frac{1}{3}\frac{9}{8\Delta\omega}n_{\rm LO}(T) , \quad (5)$$

where the factor $\frac{1}{3}$ comes from the average over all possible scattering directions and the term $n_{\rm LO}^2(T)$ is neglected when compared to $n_{\rm LO}(T)\sim 10^{-2}$. The change in the polarizability of Eu^{2+} in CaF_2 may be estimated by multiplying its polarizability in EuF_2 (Ref. 14) ($\alpha_0=1.7\times10^{-24}$ cm^3) by a factor of 3 corresponding to the decrease in the atomic separation. In this way we have

$$\Gamma=\Gamma_0+\tfrac{16}{27}\pi^3\left[\frac{1}{\epsilon_0}-\frac{1}{\epsilon_\infty}\right]^2\frac{(\hbar\omega_0)^2}{\hbar\Delta\omega}\left[\frac{\alpha}{v}\right]^2 =\Gamma_0+70n_{\rm LO}(T) . \quad (6)$$

The slope 70 cm^{-1} that we have found theoretically is in fairly good agreement with the experimental value (57 cm^{-1}) and turns out to be important evidence for the interpretation of the broadening mechanism due to elastic LO-phonon scattering. The theory described above may also be used to calculate the line shift $\delta\sigma$ as a function of the temperature. In order to do so, perturbation theory is used again and $\delta\sigma$ is given by

$$\delta\sigma=\langle\beta|H'|\beta\rangle/\hbar . \quad (7)$$

The same approximations used to find $\Gamma(T)$ are employed to evaluate the matrix element in Eq. (7) and as a result we get

$$\delta\sigma=-\left[\frac{8\pi}{9}\right]\left[\frac{\alpha}{v}\right]\omega_0\left[\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right](\bar{n}_{\rm LO}+\tfrac{1}{2}) =54(\bar{n}_{\rm LO}+\tfrac{1}{2}) . \quad (8)$$

The dependence of the $^6P_{7/2}$ multiplet center-of-gravity position as a function of the temperature given by Eq. (8) is the same as in Refs. 6 and 7. We may roughly compare the slope 54 cm^{-1} with our experimental data assuming that the center of gravity of the $^6P_{7/2}$ multiplet lies on the Γ_8^- line, which is doubly degenerate. Going from 77 K ($n_{\rm LO}\sim 0$) to 235 K ($n_{\rm LO}\sim 6.02\times10^{-2}$) this line shifts 3.9 cm^{-1}, which corresponds to a slope of 65 cm^{-1}, also in good agreement with the theoretical prediction.

IV. CONCLUSION

The linewidth of the $^8S_{7/2}\rightarrow{}^6P_{7/2}$ transition in Eu^{2+}-doped CaF_2 has been measured as a function of the temperature. The results show a linear dependence on the occupation number of LO phonons. We do not understand why TO phonons do not contribute to the broadening mechanism. The linear dependence is explained by means of the difference between the polarizabilities of ground and excited states, which give rise to a Hamiltonian describing the interaction between the impurity and the lattice. One advantage of such an approach is that it does not require any adjustable parameter in order to fit the experimental data. When compared to previous theories yielding the same temperature dependence, this Hamiltonian is also quadratic in the ion coordinates; therefore in this sense the theories are similar.

[1] U. Fritzler and G. Schaak, J. Phys. C **9**, L23 (1976).
[2] U. Fritzler, Z. Phys. B **27**, 289 (1977).
[3] M. C. Dower, C. D. Cordero-Montalvo, and H. Crosswhite, Phys. Rev. B **28**, 4931 (1983).
[4] L. A. O. Nunes, F. M. Matinaga, and J. C. Castro, Phys. Rev. B **32**, 8356 (1985).
[5] W. H. Hesselink and D. A. Wiersma, Chem. Phys. Lett. **50**, 51 (1977).
[6] P. de Bree and D. A. Wiersma, J. Chem. Phys. **70**, 790 (1979).
[7] G. J. Small, Chem. Phys. Lett. **57**, 501 (1978).
[8] L. A. O. Nunes, F. M. Matinaga, and J. C. Castro, Rev. Sci. Instrum. **55**, 1880 (1984).
[9] *Phonon Dispersion Relations in Insulators,* No. 10 of *Springer Series in Solids-States Sciences,* edited by H. Bilz and W. Kress (Springer-Verlag, Berlin, 1979), p. 124.
[10] *Laser Spectroscopy of Solids,* Vol. 49 of *Topics in Applied Physics,* edited by W. M. Yen and P. M. Selzer (Springer-Verlag, Berlin, 1981).
[11] $E^*=-(8\pi/3)P$ for LO phonons. See, for instance, J. M. Ziman in *Electrons and Phonons* (Oxford University Press, London, 1972).
[12] W. Hayes, *Crystals with the Fluorite Structure* (Oxford Uni-

versity Press, London, 1974), pp. 6, 48, and 49.

[13]*Crystals with the Fluorite Structure,* Ref. 12, pp. 52 and 53.

[14]$\alpha_0=(3v/4\pi)[(\epsilon_\infty-1)/(\epsilon_\infty+2)]-2\alpha_{F^-}$. The value of ϵ_∞ was taken from Ref. 12 with $\alpha_{F^-}=1.04\times10^{-24}$ cm^3 being the atomic polarizability of the fluorine ion (Pauling's value). The volume of the EuF_2 unit cell is $v=49.9$ Å^3.