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Line shift of two-photon transitions of Eu^{2+} in CaF_2 as a function of temperature

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Line shifts of two-photon ${}^8S_{7/2}\rightarrow{}^6P_{7/2}$ transitions in Eu^{2+}-doped CaF_2 are studied as a function of temperature. They show a linear dependence on the occupation number of LO phonons (n_{LO}) of the CaF_2 lattice. The proportionality constant agrees better than 10% with the theoretical value found previously. The role played by LO and TO phonons in the line shift and broadening mechanisms is discussed.

We recently reported the results of two-photon absorption (TPA) spectroscopy of the $\delta S_{7/2}\rightarrow{}^6P_{7/2}$ transition in Eu^{2+}-doped CaF_2 as a function of temperature.[1] The experimentally observed linewidths show a linear dependence on the occupation number of LO phonons (n_{LO}) at 463 cm^{-1} in the CaF_2 lattice. Although there are theories[2-3] to explain this sort of behavior, which is also found in molecular mixed crystals,[4] we presented a different approach, based on the different polarizabilities of the Eu^{2+} in ground and excited states, as an alternative way of explaining the results. This theory is very interesting in the sense that it is able to predict the slope of the linewidth $\Gamma(T)$ versus the $n_{\mathrm{LO}}(T)$ curve without the need of any adjustable parameter. Even with a few approximations, theory and experiment agree within 20%. As a by-product of this approach, the line shift is also predicted to be proportional to n_{LO}, in agreement with the theories mentioned above. However, using the same approximations employed to evaluate $\Gamma(T)$ we were able to find the proportionality constant in contrast with these previous treatments. According to Ref. 1, the line shift $\delta\sigma$ may be written as

$$\delta\sigma = -\left[\frac{8\pi}{9}\right]\left[\frac{\alpha}{v}\right]\omega_0\left[\frac{1}{\epsilon_\infty}-\frac{1}{\epsilon_0}\right]\left[n_{\mathrm{LO}}+\frac{1}{2}\right]$$
$$= -54\left[n_{\mathrm{LO}}+\frac{1}{2}\right]\ \mathrm{cm}^{-1} \qquad (1)$$

where $v = 40.758$ Å^3 is the volume of the CaF_2 unit cell, ω_0 is the frequency of LO phonons in this lattice, α stands for the change in atomic polarizabilities between the states ${}^8S_{7/2}$ and ${}^6P_{7/2}$, and $\epsilon_\infty = 2.05$ and $\epsilon_0 = 6.53$ are given in Ref. 5. In order to estimate the value of α, we multiplied the polarizability of Eu^{2+} in EuF_2 ($\alpha_0 = 1.7\times10^{-24}$ cm^3) by a factor of 3 corresponding to the decrease in the atomic separation.

in the present work, TPA spectroscopy is used to study the line-shift behavior of ${}^8S_{7/2}\rightarrow{}^6P_{7/2}$ transitions in Eu^{2+}:CaF_2 as a function of temperature. The results reported here are complementary to those of Ref. 1. The experimental apparatus and procedure have been fully described elsewhere[6,7] and no details will be given here. We are not concerned with the precise determination of transition frequencies but only with their relative positions as a function of the temperature. In order to achieve reliable results, the following conditions are required: (1) the dye laser must be mechanically stable in such a way that for a given temperature, consecutive runs must reproduce identical spectra, with lines at the same positions and (2) every run has to start at the same frequency and span the same range. These requirements are satisfied by our experimental setup.

The experimental TPA spectrum of the ${}^8S_{7/2}\rightarrow{}^6P_{7/2}$ transition in Eu^{2+}:CaF_2 comprises three lines as predicted by group theory for a $J=\frac{7}{2}$ level in a crystal field with O_h symmetry. As the temperature increases, all lines shift to lower frequencies in agreement with the negative signal of Eq. (1). On the other hand, the linewidths increase while the integrated absorptions remain approximately constant. Another feature of the spectra is that the background, which corresponds to $4f^7\rightarrow4f^6\,5d$ transitions, also increases with the temperature.

According to group theory, the central line (Γ_8^-) has a degeneracy 4 while the other two (Γ_6^- and Γ_7^-) have a degeneracy 2. Taking this fact into account we were able to evaluate the shift of the ${}^6P_{7/2}$ multiplet center of gravity as a function of the temperature. The result shown in Fig. 1 clearly confirms the linear dependence of $\delta\sigma(T)$ on $n_{\mathrm{LO}}(T)$. Moreover, the experimental slope found from this figure is 50 cm^{-1}, which differs from the experimental one by less than 10%.

An important aspect concerning the line shift and broadening mechanism is the experimental evidence that only LO phonons contribute to the $4f^7$-$4f^6\,5d$ configurations mixing. This fact needs some theoretical consideration in order to be clarified. Since these configurations are close in energy, the wave function $|\psi_f\rangle$ of the $4f^7$ configuration is adiabatically modified due to the lattice distortion around the Eu^{2+} ion:

$$|\psi\rangle = \frac{1}{(1+|a|^2)^{1/2}}(|\psi_f\rangle + a\,|\psi_d\rangle) \qquad (2)$$

where $|\psi_d\rangle$ is a representative state of the $4f^6 5d$ configuration and a is a parameter associated with the distortion. In this case, the energy of the ion in the pres-

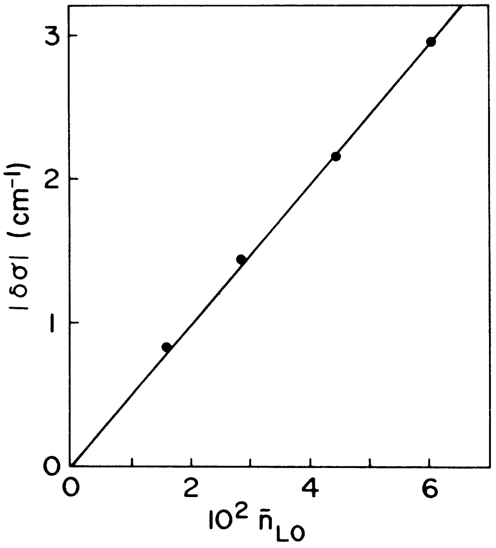

FIG. 1. Experimental line shift plotted as a function of the occupation number of LO phonons in CaF_2. The solid line is drawn for $\nu_{\rm LO}=1.4\times10^{13}$ Hz and $\gamma=50\ {\rm cm}^{-1}$.

ence of such distortion is given by

$$U_i=\frac{|a|^2\varepsilon_{df}}{1+|a|^2} \tag{3}$$

where $\varepsilon_{df}=\varepsilon_d-\varepsilon_f$ is the energy difference between the unperturbed f and d states. Assuming that the coupling between the Eu^{2+} ion and the lattice is described by the electric dipole moment $\boldsymbol{\mu}$ induced in the impurity due to the distortion, the total energy of the ion-lattice system may be written as

$$H'(a)=\frac{|a|^2\varepsilon_{df}}{1+(a)^2}+\sum_\alpha\frac{\boldsymbol{\mu}\cdot\boldsymbol{\rho}_\alpha-3(\hat{\mathbf{n}}_\alpha\cdot\boldsymbol{\mu})(\hat{\mathbf{n}}\cdot\boldsymbol{\rho}_\alpha)}{d_\alpha^3} \tag{4}$$

where

$$\boldsymbol{\mu}=\frac{a^*\langle\psi_d|\mathbf{D}|\psi_f\rangle+a\langle\psi_f|\mathbf{D}|\psi_d\rangle}{1+|a|^2} \tag{5}$$

and $\mathbf{D}$ is the electric dipole operator of the Eu^{2+} $4f^7$ electrons.

The second term in the right-hand side of Eq. (4) stands for the electrostatic interaction between the Eu^{2+} ion and the lattice polarization, described by dipoles $\boldsymbol{\rho}_\alpha$, with $\hat{\mathbf{n}}_\alpha$ being a unit vector specifying the positions of the lattice atoms with respect to the Eu^{2+} site and d_α the distance from these atoms to the Eu^{2+} impurity. This term is associated with the CaF_2 lattice dynamics and it is very difficult to evaluate. This difficulty may be overcome if we consider, as an approximation, only those modes whose wavelengths are longer than the lattice parameter. In this case, atoms close to the impurity are uniformly polarized and do not generate any field at the impurity site.[8] Therefore we have to take into account only the contribution arising from regions far from the impurity, where the lattice may be considered as a continuum characterized by a macroscopic polarization $\mathbf{P}(\mathbf{X})$. Formally this can be accomplished by replacing the sum by an integration on the volume V' outside a sphere centered on the Eu^{2+} and with radius larger than the lattice parameter. Therefore, the second term in Eq. (4) may be written as

$$W=-\int_{V'}\mathbf{E}_0(\mathbf{X},\boldsymbol{\mu})\cdot\mathbf{P}(\mathbf{X})dv \tag{6}$$

where $\mathbf{E}_0(\mathbf{X},\boldsymbol{\mu})$ is the electric field due to the impurity and $\mathbf{P}(\mathbf{X})$ consists of two components, one transverse $\mathbf{P}_t(\mathbf{X})$ and another longitudinal $\mathbf{P}_l(\mathbf{X})$, corresponding respectively to TO and LO modes of the CaF_2 lattice. Since the field $\mathbf{E}_0(\mathbf{X},\boldsymbol{\mu})$ due to the impurity is longitudinal ($\nabla\times\mathbf{E}_0=0$), the dot product with $\mathbf{P}_t(\mathbf{X})$ vanishes ($\nabla\times\mathbf{P}_t=0$), and the polarization present in Eq. (6) is associated only with LO phonons. This explains why TO phonons do not take part in the line shift and broadening mechanism.

As a concluding remark, we have experimentally shown that the line shift behaves in the same way as the linewidth; both depend linearly on $n_{\rm LO}$. The theory that we have presented in Ref. 1 gives the slopes of both curves with good accuracy. An interesting feature of the spectrum that we intend to study next is the increase of the background with the temperature. In this case, both $4f^7$ and $4f^65d$ configurations are accessible by two photons and these two absorption channels may interfere, leading to an asymmetry of the line. This is the so-called Fano resonance.[9] For Eu^{2+}, the $4f^7$ and $4f^65d$ configurations are mixed via odd-parity lattice vibrations and the line symmetry must be dependent on the temperature. In order to study this effect we are carrying out experiments on Eu^{2+}-doped KI:K Cl mixed crystals.

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