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LINE NARROWING CAPABILITIES OF Nd\textsuperscript{3+} PAIRS IN LiYF\textsubscript{4}

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Résumé - Les paires d'ions Nd\textsuperscript{3+} dans LiYF\textsubscript{4} sont utilisées pour mesurer la corrélation entre les distributions inhomogènes des deux transitions successives nécessaires à leurs doubles excitations. Les profils et les intensités des raies sont bien interprétés. Nous déduisons une faible largeur homogène qui est proche de celle qui peut être déduite du temps de vie des états excités.

Abstract - Pairs of Nd\textsuperscript{3+} ions in LiYF\textsubscript{4} are used to test the correlation between the inhomogeneous distributions of the two successive transitions needed for their double excitation. The experimental line shape and line intensities are well accounted for by a single model. We measure a small homogeneous linewidth which can be connected to the lifetime of the excited levels.

I - INTRODUCTION

Optical transitions in condensed matter or in gas are always homogeneously broadened, so that structures of physical importance are unobservable. The fluorescence line narrowing effect is very effective for the resonant fluorescence transition, for the other transitions in spite of some "accidental coincidences" /1/ their inhomogeneous distributions are not correlated to the resonant one and their widths remain partially inhomogeneous. For the same reason the A.L.N. technique is not suitable for the extraction of small homogeneous linewidth from inhomogeneously broadened transition. Rare earth ion pairs in ionic crystals are systems for which previous experiment /2/ have shown they are suitable for line narrowing effects. We want to show here that both theoretical arguments and new experimental results obtained with a new technique allow the extraction of small homogeneous width from inhomogeneously broadened transitions.

II - THEORY

As a first step we consider trivalent rare earth ions (R.E.) substituted to some trivalent anions in a perfect ionic crystal. The spectroscopic properties of pairs has been given previously /2/. At first sight a pair made up with two ions a and b can be doubly excited by the excitation of the ion a followed by the excitation of the ion b and conversely. However, due to the proximity of the two ions, the coulombic interaction perturbs the energy levels of each ion, this perturbation being different if the neighbour ion is excited or not. Consequently the two successive transitions (at $\nu_1$ and $\nu_2$) must occur at different frequencies ($\nu_2 \neq \nu_1$) even if the energy levels of a and b are the same. This frequency difference, $\varepsilon = \nu_2 - \nu_1$, will be an important experimental parameter.

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In a real crystal the transitions are inhomogeneously broadened. The physical origins of this broadening are numerous: microscopic internal strains, random electric field and field gradients induced by charged defects, etc. In ref. 3 we have developed some qualitative arguments to show that the imperfections could have less effects on the quantities $\varepsilon$ than on the ion transition frequencies. In other words, the inhomogeneous distribution of the two successive transitions needed for a double excitation of a pair can be strongly correlated, if some conditions are met.

Now we can examine the spectroscopic consequences of this correlation. Since only one c.w. monochromatic laser was used for the experiments reported in Section III, we shall consider only the case of successive absorption of two photons of equal frequencies. For a given pair we assume that each of the two successive transitions can be described by an homogeneous line of Lorentzian shape, $L_{\Delta v_1}(\nu - \nu_1)$ and $L_{\Delta v_2}(\nu - \nu_2)$ of width $\Delta v_1$ and $\Delta v_2$. The population of the singly and doubly excited states of a given class of pairs characterized by the set $(\nu_1, \nu_2, \Delta v_1, \Delta v_2)$ are proportional to $L_{\Delta v_1}(\nu - \nu_1)$ and $L_{\Delta v_2}(\nu - \nu_2)$ respectively, where $\nu$ is the laser frequency. For the above class of pairs, $\nu_1$ and $\nu_2$ are random variables. Let $D_{\sigma_1}(\nu_1 - \Omega_1)$ be a distribution function of $\nu_1$, centered at $\Omega_1$ of width $\sigma_1$. It is possible to take into account the correlation between $\nu_1$ and $\nu_2$ if we suppose that for each value of $\nu_1$ we have the same distribution of $\nu_2$ centered at $\nu_1 + \varepsilon$. In order to simplify the following calculation we represent this distribution by a Lorentzian $L_c(\nu_2 - (\nu_1 + \varepsilon))$. The width $c$ of this distribution is a characteristic parameter of the correlation. It is then easy to calculate the singly and doubly excited state population

$$J_1(\nu) = \int d\nu_1 L_{\Delta v_1}(\nu - \nu_1) D_{\sigma_1}(\nu_1 - \Omega_1)$$
$$J_2(\nu) = \int d\nu_1 L_{\Delta v_1}(\nu - \nu_1) L_c + D_{\sigma_2}(\nu - (\nu_1 + \varepsilon)) D_{\sigma_1}(\nu_1 - \Omega_1)$$

From which it is easy to compute the areas ($A_1$ and $A_2$) and barycenters ($M_1$ and $M_2$) of the lines. For the single excitation line $A_1$ and $M_1$ don't depend on the homogeneous widths of the transitions. On the contrary, for the doubly excited line ($L_2$) we have

$$A_2 = \frac{\Delta v_1 + \Delta v_2 + c}{2\pi} \frac{1}{\varepsilon^2 + (\Delta v_2 + \Delta v_2 + c)^2}$$
$$M_2 = \frac{\Delta v_1 \cdot \varepsilon}{\Delta v_1 + \Delta v_2 + c} + \Omega_1$$

which is a new result: the area and barycenter of the $L_2$ line depend on the homogeneous widths of the two transitions and on the correlation between the inhomogeneous distribution, but don't on the inhomogeneous distribution of each transition.

III - EXPERIMENTAL RESULTS

The Nd$^{3+}$:LiYF$_4$ energy levels of interest are shown in figure 1. We focus our attention on the $^{4}I_{g/2}(0) \rightarrow ^{4}G_{e/2}(0)$ transition in absorption. Due to a fast multiphonon relaxation the population of $^{4}F_{3/2}(0)$ is quickly established. Its well known near infrared fluorescence will serve as a probe of the $^{4}G_{e/2}(0)$ population. For the Nd$^{3+}$:Nd$^{3+}$ pairs, a cooperative relaxation can occur, it gives rise to an up conversion fluorescence which results from the double excitation of the pairs. It has some components in the U.V. and will serve as a probe of the doubly excited state population. We have focussed our attention on a well resolved pair line (manned satellite $B_2$ in Ref. 3).
Fig. 1 - Energy levels of Nd$^{3+}$:LiYF$_4$.

Fig. 2 - U.V. and I.R. excitation spectra of the satellite line B$_2$ obtained with the single mode c.w. dye laser. In the right part of the figure, the dotted line represents the fitting of the lineshape at 40 K, as explained in Section IV.

As it is clearly shown in figure 2, at low temperature the narrow U.V. and I.R. excitation lines have nearly the same shapes and linewidths, but there is a small frequency difference between their maximum which is $\Delta \nu = (0.28 \pm 0.02)$ GHz. In the range of intermediate temperatures, where the linewidths and lineshapes are not much affected, this frequency difference is easily measured and remains constant. In the range of high temperatures one can see, that the U.V. and I.R. excitation spectra have not the same lineshapes and linewidths. The I.R. line can be fitted by a Lorentzian function while the U.V. lineshape is, in first approximation, the square of the I.R. line. The frequency difference between their maximum is more difficult to observe. However the barycenter of each line can be easily computed after subtraction of the main line wings and we deduce the same value as before for the $\Delta \nu$ quantity.

Finally we may note a strong variation of the U.V. excitation line area shown in figure 3.

Fig. 3 - Temperature dependence of U.V. and I.R. excitation line area.
The evolution of the excitation spectra of the up conversion is complex, but is explainable in the frame of our theoretical model.

- At low temperatures, the main features of the U.V. and I.R. excitation spectra, i.e. their identical lineshapes and a frequency difference between their maximum ($\Delta \nu = 0.3 \text{ GHz}$), are well accounted for by expression (II) if the inhomogeneous distribution is dominating over both the homogeneous contribution, $\nu$ and $c$. This is the first indication of a correlation between the inhomogeneous distribution of the two successive transitions.

- For high temperatures on the contrary the homogeneous broadening becomes the dominant term. The I.R. and U.V. lines, respectively $J_1(v)$ and $J_2(v)$ in the theoretical section, have not the same shape but they are well accounted for by expression II if $\Delta \nu_1 = \Delta \nu_2 + c$ and $\nu << \Delta \nu_1$. These conditions combined with the theoretical expression of $\Delta \nu$ imply $\Delta \nu = \nu/2$ and consequently $\nu = 0.56 \text{ GHz}$.

The fact that the $\Delta \nu$ value remains constant in the whole temperature leads us to conclude that the condition $\Delta \nu_1 = \Delta \nu_2 + c$ is always valid even for the smallest homogeneous widths $\Delta \nu_1(0)$ and $\Delta \nu_2(0)$ obtained at 4 K. This means that we are in the strong correlation case: $c < \Delta \nu_1(0)$.

The U.V. line area dependence on the temperature $A_2(T)$ shown in figure 3 can be accounted for by the theoretical area dependence on the homogeneous widths (expression III) because they have qualitatively the same shape. This indicates that the homogeneous linewidths dependence on the temperature: $\Delta \nu_1(T) + \Delta \nu_2(T)$ is a monotonic function which increases as the temperature. It is possible to deduce the temperature dependence of $\Delta \nu_1 + \Delta \nu_2 + c$ by the computation of $\Delta \nu_1(T) + \Delta \nu_2(T) + c = \frac{g}{2} |A_2(T)|$ for each experimental value of the area measured at a given temperature. The results are reported in figure 4. We may note a strong variation of $\Delta \nu_1 + \Delta \nu_2 + c$ except for the very low temperature domain where $\Delta \nu_1 + \Delta \nu_2 + c$ takes the constant value $\Delta \nu_1(0) + \Delta \nu_2(0) + c = 8 \pm 2 \text{ MHz}$. This last result combined with the $\Delta \nu_1 = \Delta \nu_2 + c$ conditions leads us to conclude that $\Delta \nu_1(0) = 4 \pm 1 \text{ MHz}$.

Fig. 4 - Temperature dependence of $\Delta \nu_1 + \Delta \nu_2 + c$ deduced from data of fig. 3.
At this stage it would be interesting to compare these linewidth values to those which could be obtained in a more classical manner. At very low temperatures the main contribution to the homogeneous linewidths of the two transitions is certainly the fast multiphonon relaxation from the \(^4\Sigma_{5/2}\) (0) state. The linewidth \(\Delta \nu = 1/\pi \tau\) deduce from our lifetime estimation is \(10 \pm 7\) MHz. In spite of its low accuracy, this result is consistent with \(\Delta \nu_1 (0) = 4\) MHz.

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