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Two-photon absorption spectroscopy of precipitated phases of Eu^{2+} in KCl single crystals

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Two-photon absorption (TPA) spectroscopy is used to study the aggregation kinetics of Eu^{2+} in KCl single crystals at two different annealing temperatures. The sharp $f \rightarrow f$ transitions allow an easy observation of different precipitated phases of Eu^{2+} as opposed to the one-photon absorption and fluorescence of the $4f^65d$ transition, where overlapping bands make the analysis of the aggregated phases difficult. Since it is possible to measure the precipitated phases simultaneously, this technique is better than previous techniques used to study the first aggregation products and that detect only the impurity-vacancy (I-V) dipole concentration. The order of the kinetics equation has been established for two types of clusters. We also report the TPA spectrum of the Suzuki phase.

I. INTRODUCTION

Alkali halide crystals doped with M^{2+} impurities present charge-compensating vacancies, which, at room temperature, are close to the impurities forming the so-called impurity-vacancy (I-V) dipole. The strong elastic and electric interactions among dipoles enable the formation of precipitated phases which has been the subject of several investigations during the last two decades. Dryden and co-workers[1,2] were the first to analyze the kinetics of dipole aggregation by means of the dielectric absorption technique. They came to the conclusion that the initial stage of the aggregation process was governed by a third-order kinetics law, meaning that the first aggregation product is a trimer formed directly from three I-V dipoles. This conclusion raised some criticism due to the low probability of three-body encounters compared to two-body encounters. A few years later, Unger and Perlman[3,4] have established, by analyzing the original data of Dryden as well as their own, that the aggregation process at the first stage starts with dimer formation. In order to do so, they included a dissociation term in the second-order kinetics equation. This back term appears to be quite important to the analyses of clustering and if neglected without a strong physical basis, misleading results could be obtained. Anyway, there was a controversy concerning the products in the aggregation process. Several authors[5-7] have reported they are dimers, while evidence has also been gathered to show that trimers are the predominant clusters formed.[8] Recently, in a comprehensive paper, Rubio and co-workers[9] performed electron-paramagnetic-resonance (EPR) measurements to study the evolution of dipole concentration as a function of the annealing time at several different temperatures and concentration. Their results indicate unambiguously that dimers are really the complexes which are formed during the very initial stage of the clustering process.

That the controversy has lasted so long is due to the fact that the techniques employed to study the aggregation process such as EPR and ionic thermocurrent (ITC) measure only the concentration of isolated I-V dipoles and not the aggregation products. On the other hand, one-photon absorption spectra show some change due to cluster formation but the strong overlapping of the broad bands make the analysis difficult. It was recently shown[10] that two-photon absorption (TPA) spectroscopy provides a unique way for studying the formation of precipitated phases of Eu^{2+}. Each of these phases shows a group of lines in different regions of the spectrum, making the analysis of the clustering process easier. Figure 1 shows part of the energy-level diagram for Eu^{2+} as a dopant in alkali halides relevant to this work. Although the $4f^7$ and the broad $4f^65d$ configurations overlap in these crystals, the parity selection rule for TPA supresses the strong electric-dipole-allowed $4f^7 \rightarrow 4f^65d$ transition and sharp $4f^7 \rightarrow 4f^7$ lines are easily observed. Two-photon excitation spectra are measured by monitoring the violet fluorescence from the $4f^65d$ configuration. No fluorescence is observed directly from the $4f^7$ excited states. Instead, the excitation is transferred to the

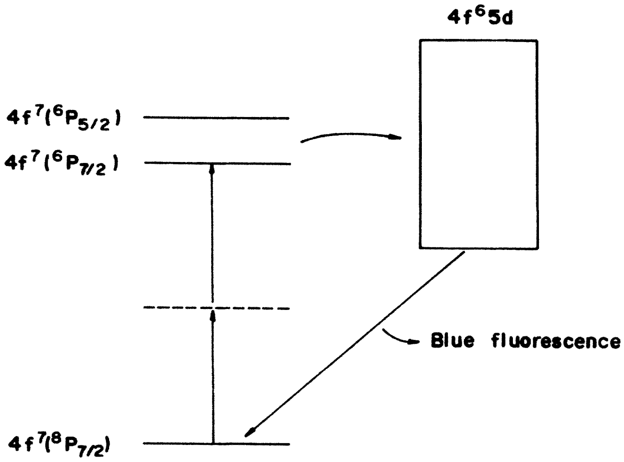

FIG. 1. Energy-level diagram for Eu^{2+} in the alkali halides showing the $^8S_{7/2} \rightarrow {}^8P_{7/2}$ two-photon transition and the decay through the overlapping $4f^65d$ configuration.

overlapping $4f^65d$ band via odd-parity lattice vibrations, followed by the fluorescence around 4100 Å. The fluorescence yield is essentially unity because of the large energy gap (24 000 cm^{-1}) separating the lowest excited state from the ground state. Consequently, the fluorescence intensity is proportional to the TPA.

In the present work, the transition from the ground state ($^8S_{7/2}$) to the first excited state ($^6P_{7/2}$) is used to monitor aggregration processes of Eu^{2+} in KCl. Although $4f$ electrons are shielded by $5s$ and $5p$ electrons, and consequently their sensitivity to change in the environment is small, the crystalline field is quite different for each type of cluster and as a result, each one of the phases has its own signature in the TPA spectrum. This signature is used to study the cluster formation for samples annealed at 50 and 250 °C. In both cases absorption bands due to dimers and isolated *I-V* dipoles are observed. Besides them, a trimer phase shows up in the former case while a 5-mer phase is detected in the latter. In order to establish the order of the clustering process a simple theory is presented in Sec. III. The evolution of the areas under the absorption bands as a function of the time for a specific annealing temperature gives the order of the kinetic equation for each process. The Suzuki phase in well-aged crystals is also reported.

II. EXPERIMENT AND RESULTS

The experimental apparatus and procedure have been fully described elsewhere[10,11] and only a few details will be given here. The laser source is a home-made dye laser of the Littman type, modified to include an intracavity prism beam expander. The dye laser is pumped by the second harmonic of a Quanta Ray DCR-1 Nd:YAG (YAG denotes yttrium-aluminum-garnet) laser and its typical characteristics are pulse duration, 5 ns; repetition rate, 10 Hz; peak power, 1 Mw; and linewidth, 0.1 cm^{-1}.

The europium-doped KCl samples were grown in our institution by the Czochralski method under a controlled dry argon atmosphere. The doping with europium was achieved by the addition in the melt of $EuCl_2$. The impurity concentration was determined from the one-photon absorption spectrum of the freshly quenched samples, employing a Cary model 17 spectrophotometer. The concentration value is 310 ppm and holds for all data presented here. The TPA measurements were carried out at liquid-nitrogen temperature in a Janis 6DT dewar.

As-grown crystals without any previous thermal treatment show two groups of lines with centers of gravity, around 27 540 and 27 600 cm^{-1}. The latter is due, as seen in Fig. 2, to isolated *I-V* dipoles and dimers[10] and will be discussed in the next paragraph. The absorption bands around 27 540 cm^{-1} disappear when the samples are annealed above 90° C and are ascribed to the so-called Suzuki phase of the divalent europium in the KCl host with the stoichiometry $6KCl{\cdot}EuCl_2$. This phase was first reported by Suzuki,[12] who has performed an extensive study by x-ray diffraction of the nature of the precipitates in the alkali halides. Later on, Rubio *et al.*[13,14] have associated the changes of the optical absorption and luminescence spectra to this phase. Their results show that the thermal resolution takes places in a narrow range of temperatures (90–150 °C) in agreement with our results. In Table I we summarize the peak positions of the bands ascribed to the Suzuki phase together with bands associated to other phases discussed next.

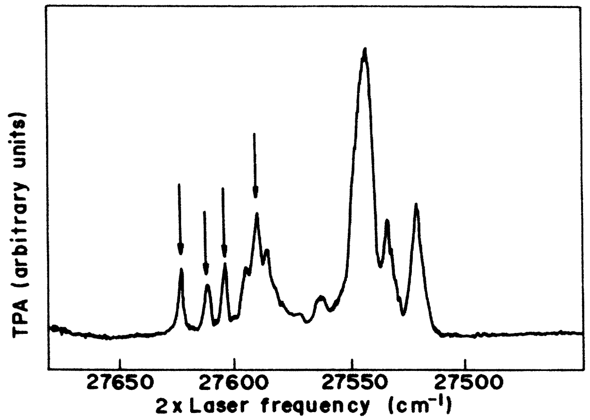

FIG. 2. Experimental TPA spectrum of well-aged samples of KCl doped with 310 ppm of Eu^{2+} showing the Suzuki-phase signature around 27 540 cm^{-1}. The temperature of the sample is 77 K. The arrows indicate peaks corresponding to the isolated *I-V* dipole.

In order to study the formation of precipitated phases of Eu^{2+} in the potassium chloride host the as-grown crystal was always heated for one hour at 600 °C and then quenched to room temperature by letting it cool down in the alumina boat in which it was heated. In this case the TPA spectrum presents absorption bands ascribed to both isolated *I-V* dipoles and dimers[10] as listed in Table I and shown in Fig. 3(a). The isolated *I-V* dipole spectrum comprises four sharp lines as predicted by group theory for $J=\frac{7}{2}$ level in a C_{2v} local symmetry, assuming that the degeneracy of the ground state is not raised by the crystal field. All four lines have the same representation E'' of the C_{2v} group therefore no polarization effect is observed in their relative intensities. The weaker dimer lines do not show up when the sample is fast-quenched by dropping it onto a copper block, since this procedure guarantees the almost complete absence of clusters. However, the present work is concerned with higher-order aggregates and the absence of dimers is not relevant to the purpose of analysis, therefore we choose to quench the samples in the alumina boat. The quenched sample was then annealed at either 50 or 250° C in a home-made furnace and from time to time it was quenched to room temperature and inserted into the dewar in order to collect the TPA spectrum. Figure 3 shows the evolution of the TPA spectrum as a function of the annealing time for samples kept at 50 °C. The measurements were carried out for 12 aging times but only four of them are shown. For aging times above 250 h, an almost complete conversion to a new phase occur. The spectrum in this case presents a group of lines between 27 500 and 27 550 cm^{-1}, the same region where the absorption bands of the Suzuki phase occur. However, it should be pointed out that the number and positions of the lines are different in these two cases, as is

TABLE I. TPA lines for Eu^{2+} in KCl depending on the thermal treatment given to the crystal, as well as their assignment in terms of the cluster order n.

Thermal treatment	Peak position (cm^{-1})	n
Quenched from 600 °C	27 622	1
	27 611	
	27 603	
	27 588	
Slow quenched from 600 °C	27 595	2
	27 586	
	27 581	
Annealed at 50 °C	27 541	3
	27 534	
	27 526	
	27 522	
	27 513	
	27 511	
Annealed at 250 °C	27 677	5
	27 664	
Well aged at room temperature	27 559	Suzuki phase
	27 544	
	27 534	
	27 521	

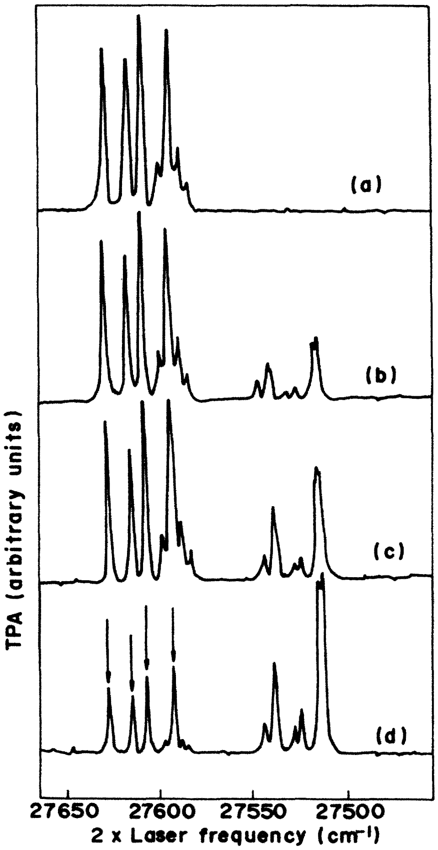

FIG. 3. Evolution of the TPA spectrum for Eu^{2+} in KCl as function of the aging time for quenched samples kept at 50 °C. The figure shows only four representative times: (a) $t=0$ h, (b) $t=150$ h, (c) $t=183$ h, and (d) $t=263$ h. The isolated I-V dipole bands are indicated by arrows.

the general shape of the spectrum. This suggests that the precipitated phase formed when the samples are kept at 50 °C is not the same as the Suzuki phase. In the present case, the aggregate phase is destroyed if the sample is heated above 150 °C.

Figure 4 shows the evolution of the TPA spectrum for samples annealed at 250 °C for three out of the 13 aging times used to carry out the measurements. A new phase shows its signature as a relatively broad absorption at approximately 27 670 cm^{-1}. It should be noted that this phase does not evolve from the one formed at 50 °C, rather it evolves from I-V dipoles and dimers. This phase was reported[14] to appear when the samples were annealed at 200 °C and was ascribed to metastable {111} and {310} $EuCl_2$-like plate zones. The phase is destroyed if the sample is heated above 350 °C.

III. DISCUSSION

The TPA spectra of samples annealed at 50 and 250 °C show two precipitated phases besides the absorption bands due to dimers and isolated I-V dipoles. For both cases we write the equation describing the conservation of the europium ion concentration as

$$X_1+2X_2+nX_n=N \ , \qquad (1)$$

where X_1, X_2, and X_n are, respectively, the concentrations of monomers, dimers, and n-mers, and N is the concentration of Eu^{2+} in the KCl host lattice. Defining $X=X_1+2X_2$ and taking the derivative of (1) with respect to the time we have

$$\frac{dX}{dt}=-n\frac{dX_n}{dt} \ . \qquad (2)$$

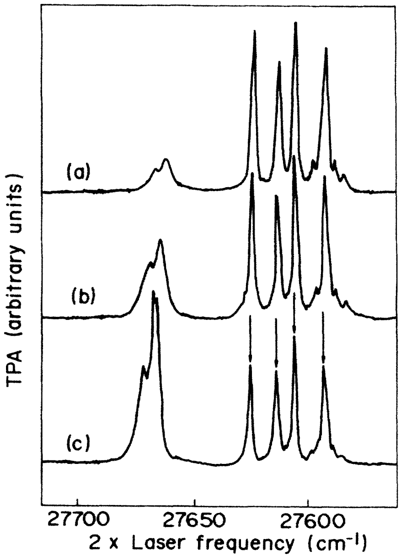

FIG. 4. Evolution of the TPA spectrum for Eu^{2+} in KCl samples kept at 200 °C for three representative aging times: (a) $t=300$ h, (b) $t=360$ h, and (c) $t=470$ h. The arrows show isolated dipoles lines.

A clustering process in which dipoles and dimers combine to form an n-mer may be expressed by a kinetic equation of the form

$$\frac{dX}{dt} = -aX^n + bX_n \ , \tag{3}$$

where the second term in the right-hand side takes into account the cluster dissociation. However, the measurements indicate that dX/dt goes to zero only when X goes to zero, i.e., there is no plateau in the aging curve. This means that the dissociation term is negligibly small and from now on we consider $b=0$. Indeed, the possibility of complete conversion of dimers and dipoles to these two kinds of aggregates for sufficiently long aging times was previously shown.[10] The combination of (1)–(3) gives a kinetic equation describing the formation of the precipitated phases:

$$\frac{dX_n}{dt} = \frac{a}{n}(N - nX_n)^n \ . \tag{4}$$

Considering $X_n(t=0)=0$, the integration of Eq. (4) gives

$$\frac{nX_n(t)}{N} = 1 - [1 + a(n-1)N^{n-1}t]^{1/(1-n)} \ . \tag{5}$$

In order to find the values of n and a, the time evolution of the areas under the cluster absorption bands is needed since the integrated absorption is proportional to nX_n. However, the experimental procedure does not allow us to find an absolute value for the TPA cross section since this value depends on several parameters such as the focalization of the laser beam on the sample. The spectrum at each aging time is obtained after moving the sample from the oven to the Dewar and in this way cannot guarantee the same focalization condition. Therefore we decide to use the integrated absorption bands of dipoles and dimers as a normalizing factor. Let us call the area under the dipoles and dimers lines I, and the area under the cluster bands I_n. In this way, I and I_n are, respectively, proportional to X and nX_n. As the next step we will assume that the oscillator strengths in I and I_n are essentially the same, therefore $I+I_n$ is proportional to N, the concentration of Eu^{2+} in the KCl lattice. The left-hand side of Eq. (5) is $I_n/(I+I_n)$, i.e., the area of the cluster bands divided by the integrated absorption of all lines in the TPA spectrum. The experimental points corresponding to this ratio are plotted as a function of time in Fig. 5 for the annealing temperatures used in this work. The figure also shows the best fit to these points using the right-hand side of Eq. (5). The Eu^{2+} concentration N was determined by means of one-photon absorption spectroscopy, therefore the fitting gives us the values of a and n. In order to carry out this fitting, it is important to start with some realistic value for the parameter a. This value may be estimated from first principles if we assume that the energy necessary for the cluster formation is close to the energy of the thermal dissolution, i.e., $E \sim KT'$ where $T' \approx 150$ and 350 °C for samples annealed at 50 and 250 °C, respectively. In this way we can estimate the value of a according to the equation

$$a = \tau^{-1} e^{-E/kT} \tag{6}$$

with $\tau = \tau_0 e^{-H/kT}$ and $\tau_0 = 3.7 \times 10^{-14}$ s and $H = 0.68$ eV for Eu^{2+} in KCl.[15] This gives us $a=174$ and 2.2×10^6 s^{-1} as the estimated values for samples kept, respectively, at 50 and 250 °C, which are close to the values obtained through the fitting procedure ($a=498$ and 2×10^6 s^{-1}).

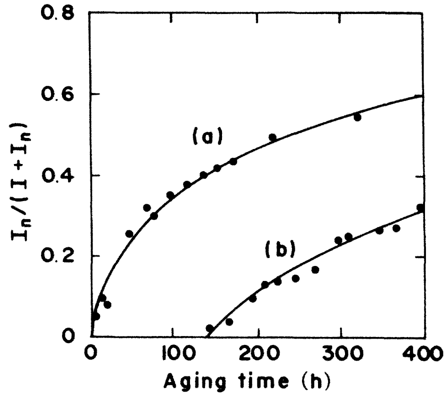

FIG. 5. Evolution of the cluster absorption band area relative to the integrated absorption of the TPA spectrum for samples kept at (a) 50 °C and (b) 250 °C. The solid lines are the best fitting to Eq. (5) with (a) $n=3,3$ and $a=498$ s^{-1} and (b) $n=4,9$ and $a=2\times 10^6$ s^{-1}.

For samples kept at 50 °C our results indicate the formation of trimers evolving from isolated I-V dipoles and dimers. Comparison of the spectrum of Fig. 2 with those of Fig. 3 led us to conclude that although the symmetry is quite different for Suzuki and trimer phases, the crystal field at the Eu^{2+} site has comparable strength in both cases, yielding groups of lines in the same region of the TPA spectrum. One-photon absorption and emission spectroscopy do not have enough resolution to distinguish between these two phases and as a consequence, the aggregation process for samples annealed at 50 °C has already been ascribed[13] to the Suzuki phase in contrast with the present results.

We have tentatively ascribed to a 5-mer the aggregation product of samples annealed at 250 °C. This attribution must, however, be taken with some reservation for the time being due to the following reason. The luminescence spectra of Eu^{2+} in KCl for samples aged at 200 °C show four bands which have been assigned[14] to I-V dipoles and dimers (419 nm), $EuCl_2$-like plate zones parallel to {111} and {310} planes of the matrix lattice (439 and 478 nm, respectively), and the stable dihalide phase $EuCl_2$ (410 nm). Although we have taken the care of scanning a wide range of wave numbers, we could not observe the TPA excitation bands which give rise to the luminescence around 439 and 478 nm. Since we are normalizing the area of the cluster band to the total concentration of europium cations, Eq. (5) is not true if there is any absorption band missing. Indeed, the analysis of the time evolution of the luminescence spectrum indicates that the phase emitting at 410 nm evolves from an intermediate phase which is not observed in the TPA spectrum. This explains why the group of lines around 27 670 cm^{-1} takes about 150 h to show up. There is one possible reason to explain why we did not see the TPA lines corresponding to the intermediate phase: they coincide with the isolated I-V dipole lines. In terms of the configurational coordinate model, for this to happen we should have, for the intermediate phase, parabolas in the same positions as in the isolated Eu^{2+} case (same Q_0), but with different curvatures (flatter). The luminescence spectrum in this case shows a broader line displaced to longer wavelengths in agreement with Ref. 14, but the TPA spectrum shows the same absorption for both cases since the lines are zero-phonon emissions. Physically, this corresponds to the case where the environment around the Eu^{2+} does not change for the intermediate phase (same crystal field) but we have other types of phonons contributing to the position and width of the luminescence line. If this situation is really happening, the TPA lines of the intermediate phase coincide with the lines of the isolated I-V dipoles and Eq. (5) is exactly true. Further investigation is still needed to clarify this point.

IV. CONCLUSION

The TPA spectrum for samples aged in a given temperature shows nonoverlapping groups of lines corresponding to different precipitated phases of Eu^{2+}. The number, strengths, and positions of the lines can be used in order to evaluate the local crystal field in the europium site as previously done in the CaF_2 host lattice.[16] Since the absorption bands for different stages of aggregation are well apart in the TPA spectrum, it immediately follows that this technique makes the analysis of the clustering process easier when compared to the one-photon absorption and luminescence techniques where the broad bands overlap. We have identified the Suzuki phase and two other new phases tentatively ascribed to a 3-mer and 5-mer. The latter is still under investigation due to the nonobservation of any intermediate phase in the TPA spectrum. This technique can also be used to study the first aggregation products for fast-quenched samples aged at room temperature. In this case the TPA spectrum gives both the monomer (X_1) and dimer (X_2) concentration as a function of the aging time when the deconvolution of the respective spectra is carried out. The values of X_1 and X_2 obtained experimentally are then plugged into the kinetic equation and its order is automatically determined. The present work does not emphasize this point since it is well established by now that the first aggregation product is dimer.

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