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Two-photon spectroscopy in KCl:Eu^{2+}

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Two-photon excitations of the $f \rightarrow f$ transitions in Eu^{2+}-doped KCl have been studied. The splitting of the ${}^8S_{7/2} \rightarrow {}^6P_{7/2}$ transition confirms that the symmetry of the Eu^{2+} ion is lower than cubic because of the presence of a charge-compensating cation vacancy. ${}^6D$ and ${}^6I$ multiplets have also been measured and their centers of gravity are compared with those observed in CaF_2:Eu^{2+}.

Two-photon spectroscopy of rare-earth-metal-ion impurities in crystals has assumed in recent years a growing importance as a necessary complement of one-photon investigations. This technique has been extensively applied to the study of Eu^{2+} in CaF_2 and SrF_2, and of Gd^{3+} in LaF_3.[1-5] The observation of the narow bands due to two-photon allowed, one-photon forbidden transitions between levels of the $4f^n$ multiplet enables one to evaluate the symmetry and the intensity of the crystal field acting on the rare-earth ion. Moreover, from the intensity and from the polarization dependence of the nonlinear absorption, one can obtain information on the relative strength of second- and higher-order terms in the transition probability.[6,7]

In the alkaline-earth-metal fluorides, the Eu^{2+} ion enters the lattice substitutionally at the metal site which possesses O_h symmetry. In order to obtain information on the behavior of Eu^{2+} in other systems, we have measured two-photon absorption of Eu^{2+} in KCl.

Divalent impurities in monovalent crystals require, for electrical neutrality, the presence of a charge-compensating lattice vacancy. In alkali halides with NaCl structure the substitutional rare-earth metal is thus accompanied by a cation vacancy in one of the next-nearest-neighbor sites along one of the $\langle 110 \rangle$ directions. The symmetry of the impurity environment is therefore reduced from O_h to C_{2v} and for this reason we expect, whenever possible, a further splitting of the absorption lines.

After beginning this work, we became aware that the same system was also studied by another group who uses one of the two-photon allowed Eu^{2+} transitions to monitor the kinetics of aggregation of the Eu^{2+}-vacancy dipoles.[8] Their results on this transition are qualitatively similar to ours.

We chose to measure the two-photon excitation (TPE) spectrum of the luminescence emitted after relaxation, at energies lower than the absorption band. TPE allows higher sensitivity than two-photon absorption. The excitation was performed by means of the simulataneous absorption of two photons of a flash-lamp-pumped dye laser (peak power ~5 kW, pulse width ~1 μs, repetition rate 16 Hz) operating with Rhodamine 6G, Kiton Red, LD700 and focused by a lens of 10 cm focal length on the sample surface cleaved along the (100) plane.

The sample was mounted on the cold finger of a liquid-nitrogen cryostat. The luminescence was collected at 90° from excitation. Dispersion by a prism and approprite filtering allowed an almost complete rejection of laser radiation. The photomultiplier signal was digitized and processed by a single-photon counter and normalized to the square of the laser intensity. Laser wavelength was carefully checked for every excitation line using a 0.5-m calibrated monochromator. An absolute precision of ± 3 cm^{-1} was obtained, while the spacing between the sharpest lines of the same multiplet was accurate to ± 1 cm^{-1}.

A schematic diagram of the electronic levels belonging to the $4f^7$ and to the $4f^6 5d$ configurations is shown in Fig. 1 with the one-photon and two-photon absorption spectra. As in the case of the alkaline-earth fluorides, in KCl the excited states of the Eu^{2+} ion of the two configurations are overlapping. However, the one-photon spectrum (on the left-hand side of Fig. 1) shows only the parity-allowed transitions from the ground state to the $4f^6 5d$ levels. The transitions are broadened by the electron-lattice interaction and are split into two bands interpreted as due to the cubic-symmetry splitting of the d-like state into the Γ_3^+ and Γ_5^+ components.[1] The one-photon spectrum of Eu^{2+} in KCl has the same spectral shape measured for CaF_2:Eu^{2+} (Ref. 9) indicating that the diffuse orbit of the d-electron is not very sensitive to the symmetry lowering discussed above.

On the right-hand side of Fig. 1 we have sketched the

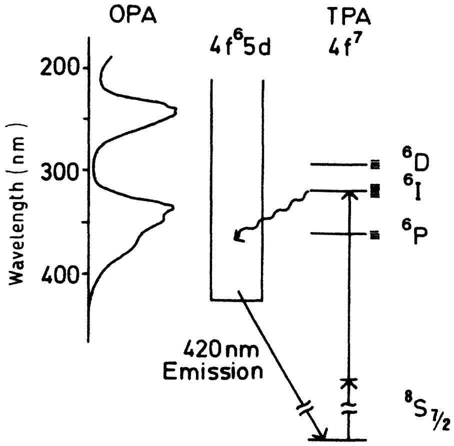

FIG. 1. Schematic diagram of the lower energy levels of Eu^{2+} in KCl. The levels reached by the two-photon absorption (TPA), the relaxation, and the recombination luminescence are shown. The one-photon absorption spectrum (OPA) is drawn for comparison on the left-hand side.

TABLE I. Center of gravity (in cm^{-1}) of the ^6P, ^6I, ^6D multiplets in CaF_2:Eu^{2+} and in KCl:Eu^{2+}.

	CaF_2:Eu^{2+} Reference 5	KCl:Eu^{2+} Reference 8	KCl:Eu^{2+} Present work
$^6P_{7/2}$	27 569	27 605	27 559
$^6P_{5/2}$	27 972	. . .	. . .
$^6I_{7/2}$	30 840	. . .	30 852
$^6I_{9/2}$	30 135	. . .	31 161
$^6I_{17/2,11/2}$	31 503	. . .	31 394
$^6I_{13/2,15/2}$		. . .	31 584
$^6D_{9/2}$	33 930	. . .	33 960
$^6D_{1/2}$	34 503	. . .	. . .
$^6D_{7/2,3/2,5/2}$	34 773	. . .	34 771

levels of the $4f^7$ multiplet reached by two-photon absorption, the interconfigurational relaxation, and the luminescent emission to the ground state observed at ~420 nm. Comparison of our results with the lines measured both in the free Eu^{2+} ion[10] and in CaF_2:Eu^{2+} (Ref. 5) suggests the assignment of the groups of lines appearing at 360, 320, and 295 nm to the $^8S \rightarrow {}^6P$, ^6I, and ^6D transitions, respectively. The transitions to the $4f^65d$ states are now suppressed by the selection rules and reduced to a small, unstructured background.

Table I summarizes the values of the center of gravity of the multiplets observed by two-photon spectroscopy in CaF_2:Eu^{2+} and in KCl:Eu^{2+}.

The transitions toward the ^6P, ^6I, and ^6D multiplets are split by the crystal field into several components. The best resolution was obtained in the transition $^8S_{7/2} \rightarrow {}^6P_{7/2}$, as shown in Fig. 2. We observe a splitting of the line into four Kramers doublets, as predicted by group theory for the C_{2v} symmetry. The C_{2v} symmetry removes the degeneracy allowed by the O_h symmetry, where one observes a splitting of the $^6P_{7/2}$ level into only three components.[5] This splitting indicates that the compact distribution of the f electrons strongly feels the local symmetry of the defect.

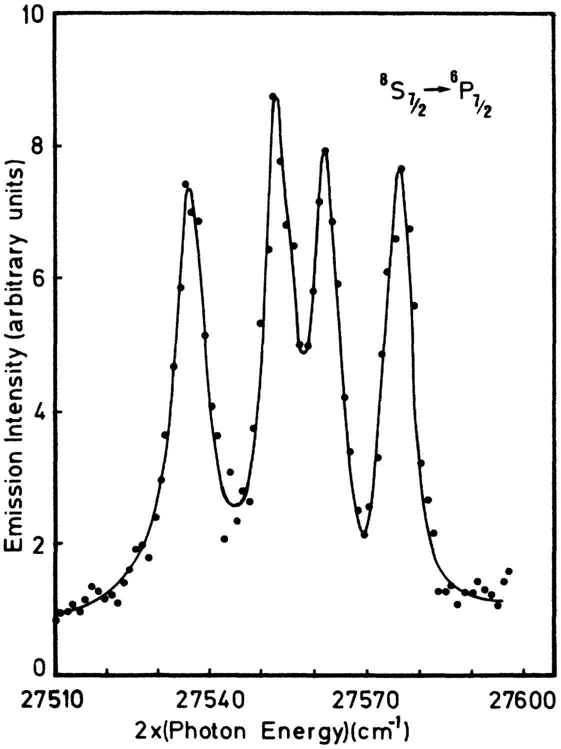

FIG. 2. Two-photon excitation spectrum due to the $^8S_{7/2} \rightarrow {}^6P_{7/2}$ transition in KCl:Eu^{2+} at 77 K.

The position of the lines of the $^8S_{7/2} \rightarrow {}^6P_{7/2}$ transition, split into a triplet (in CaF_2) or into a quartet (in KCl), is reported in Table II.

The measured intervals between the split lines are approximately 10% larger than those measured by Nunes, Matinaga, and Castro,[8] but the center of gravity is shifted ~50 cm^{-1}. The reason for this discrepancy is at present unknown. We have not been able to measure the lines corresponding to the transitions $^87_{7/2} \rightarrow {}^6P_{5/2}, {}^6P_{3/2}$: They are both very weak and at the edge of the range accessible to our present apparatus.

We have not measured, for all the two-photon transition lines, the dependence of the absorption on the polarization of the laser beam. The difficulties of normalizing the signals with respect to the laser power introduce an uncertainty of about 15% in the absolute values of the polarization data. Within this error, we did not observe changes in the absorption intensity of the $^8S_{7/2} \rightarrow {}^6P_{7/2}$ lines using a linear polarization varying in the incidence plane between the directions [001] and [010].

On the contrary, measurements with circularly polarized light indicate a decrease of the same absorption by almost an order of magnitude with respect to the above results obtained with linearly polarized light. The behavior is completely analogous to that observed in Eu^{2+}-doped CaF_2 and Gd^{3+}-doped LaF_3. The large intensity of the $^6P_{7/2}$ lines in the linear polarization has been interpreted in these cases as a demonstration of the importance in the transition matrix elements, of the third-order terms involving the spin-orbit interaction.[4,5]

The lines due to the transitions to the ^6I levels are reported in Fig. 3. The exact number of lines of the ^6I multiplet is obscured by unresolved splittings of some components. In analogy to the measurements on Eu^{2+} in CaF_2 and SrF_2, the results for KCl:Eu^{2+} show higher absorption in the high-energy lines, assigned to transitions toward the $^6I_{17/2,11/2}$ and the $^6I_{13/2,15/2}$ states.

One of the transitions due to the ^6D multiplet, split into two bands, is shown in Fig. 4. The band shape and the spectral position led us to assign this band to the $^8S_{7/2} \rightarrow {}^6D_{9/2}$ transition. Measurements performed with

TABLE II. Stark component energies (in cm^{-1}) for the $^6P_{7/2}$ multiplet in CaF_2:Eu^{2+} and KCl:Eu^{2+}.

	CaF_2:Eu^{2+} Reference 5	KCl:Eu^{2+} Reference 8	KCl:Eu^{2+} Present work
$^8S_{7/2} \rightarrow {}^6P_{7/2}$	27 558 27 564 27 588	27 587.9 27 603.2 27 611.2 27 622.4	27 538 27 555 27 564 27 578

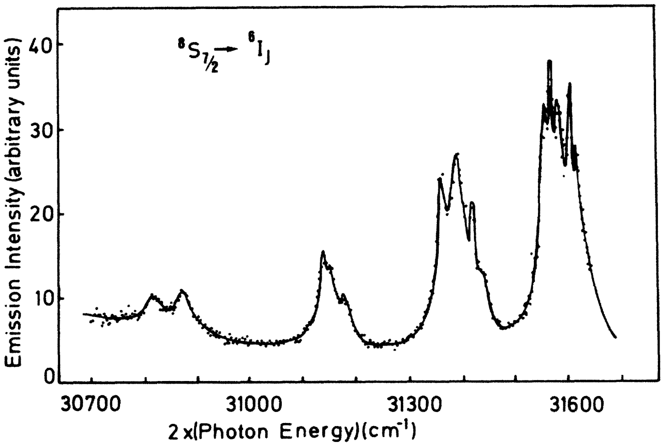

FIG. 3. Two-photon excitation spectrum due to the ${}^8S_{7/2} \rightarrow {}^6I_J$ transition in KCl:Eu^{2+} at 77 K.

linearly and circularly polarized light give results similar to those reported in Ref. 5. A second transition due to the ${}^8S_{7/2} \rightarrow {}^6D_{7/2}$ has been observed around 34 771 cm^{-1}.

The intensities of both the ${}^6D_{9/2}$ and the ${}^6D_{7/2}$ lines are approximately equal and this contradicts the conjecture of Nunes *et al.*[8] on the overwhelming importance of the third-order contributions to the two-photon intensities of some of the Eu^{2+} lines in KCl. The prediction that these terms increase more than an order of magntidue the intensity of the ${}^6P_{7/2}$ and ${}^6D_{7/2}$ lines above that of all the other lines, has not been verified in CaF$_2$ and SrF$_2$ (Ref. 5) and now not in KCl. The corrections of the third-order terms, suggested by Downer, Montalvo, and Crosswhite,[5] are probably valid also in this case.

Considering the position of all the observed lines reported in Table I, no uniform shift of the center of gravity of the lines is observed between CaF$_2$:Eu^{2+} and KCl:Eu^{2+}. This is somewhat surprising because the shift between the Eu^{2+} lines in CaF$_2$ and SrF$_2$, where the crystal structure remains the same, is about 100 cm^{-1}.[5] In the present case, the lines of the Eu^{2+} ion in a host crystal of different symmetry and different chemical composition are found to lie within ± 30 cm^{-1} from those of CaF$_2$.

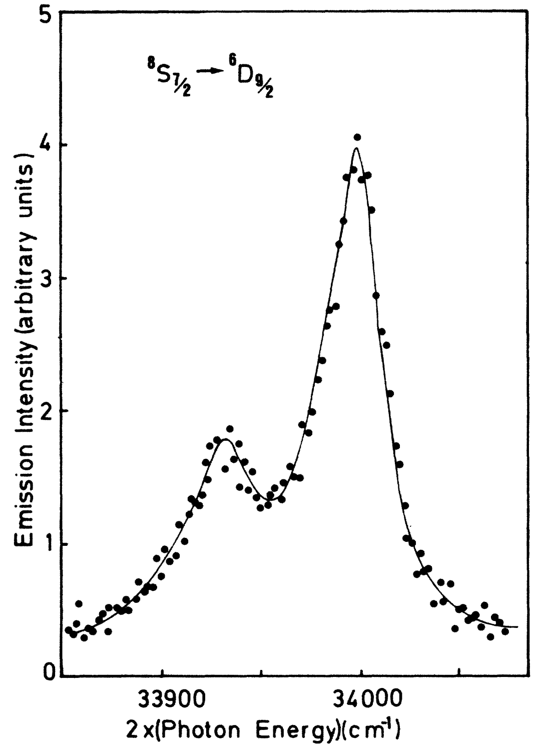

FIG. 4. Two-photon excitation spectrum due to the ${}^8S_{7/2} \rightarrow {}^6D_{9/2}$ transition in KCl:Eu^{2+} at 77 K.

We are presently extending these experiments by changing the local environment of the Eu^{2+} ion and its host lattice (using different alkali halides) in order to detect any regularities in the lines shifts and splittings, and thus to test the relative strength of the electron-lattice interactions.

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