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Study of Excited States of Ag^- Centres in Alkali Halides

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Two photon excitation of Ag^- centres in RbCl and KCl have been presented. From the dependence of luminescence on the polarization of the exciting beams, the symmetry of the final levels could be obtained. In both the crystals, an intense band was assigned to the ${}^1A_{1g} \rightarrow {}^1A_{1g}$ transition. At higher energies ${}^1A_{1g} \rightarrow {}^1E_g$ and ${}^1A_{1g} \rightarrow {}^1E_{2g}$ transitions could be identified, but their presence and intensity change in different crystals. On the high energy side of the investigated range, an intense luminescence signal arising from a two-step excitation process is observed.

Key Words: Two-photon, Exciting beams, Luminescence, Polarization.

INTRODUCTION

Impurity ions entering substitutionally into an ionic lattice consitute a model case for the study of interaction of their electronic orbitals with the host crystal field. To get a sufficiently complete knowledge of the electronic orbitals of these ions, one should be able to measure the energy position of all the excited states, but it is well known that transitions from an *s*-like ground state to another *s* or to a *d*-like orbital are forbidden in first-order dipole approximation. The position of the even-parity excited states can in turn be obtained through measurements of two-photon transitions. However, these second-order processes have a probability that is orders of magnitude smaller than that of the first-order processes, and their observation has been possible only in a few favourable cases[1–3].

The transition probabilities of second-order processes depend on the polarization of the excitation light even in cubic systems, in contrast to the behaviour of first-order processes. The symmetry assignment of the transition can therefore be derived from the observation of the appropriate polarization-dependent, characteristic of each transition[4, 5].

Two-photon-allowed transitions in a Tl^+-like centre have been previously studied[2, 3] in crsytals of RbBr doped with Ag^- ions. In this system, the first ${}^1A_{1g} \rightarrow {}^1A_{1g}$ transition was measured together with weaker signals tentatively assigned to ${}^1A_{1g} \rightarrow {}^1E_g$ transitions. A schematic diagram of the energy levels of Ag^- ion in a cubic environment is shown in Fig. 1. This diagram shows the ${}^1A_{1g} \rightarrow {}^3T_{1u}$, ${}^3T_{2u} + {}^3E_u$ and ${}^1T_{1u}$ (s → p) transitions observed in the one-photon experiment (called A, B and C bands) and the ${}^1A_{1g} \rightarrow {}^1A_{1g}$ (s → s) and ${}^1A_{1g} \rightarrow {}^1E_g$, ${}^1T_{2g}$ (s → d) measured in this work.

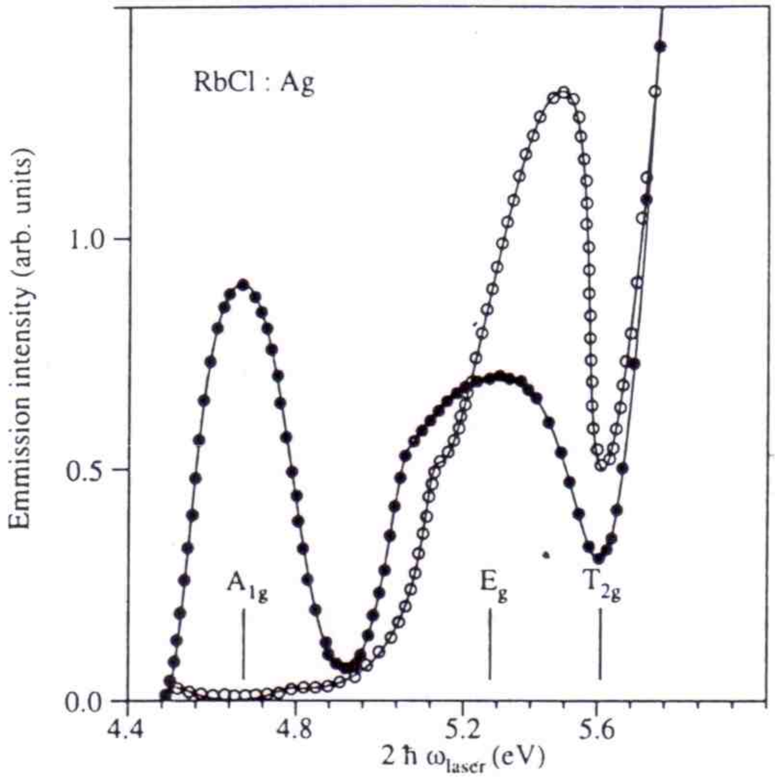

Fig. 1. Two-photon excitation spectra of RbCl : Ag^- for two different polarizations of exciting laser beam

After the absortpion, the system relaxes toward the relaxed excited state (RES) from which the emission takes place. At high temperature ($T > 50$ K) only the $^3T_{1u}$ RES is populated whichever is the excitation enegy and the A′ emission band alone is observed. At low temperature, upon excitation in the higher $^1T_{1u}$, $^1A_{1g}$, ^1E_g and $^1T_{2g}$ states, the only RES populated is the $^1T_{1u}$ state and therefore the only emission band is the C-band.

In the present paper, the properties of the Ag^- ion in RbCl and KCl were measured and over a much broader wavelength interval. A compartive analysis among the different crystals as well as the broader energy range investigated allowed us to identify the $^1A_{1g} \rightarrow {}^1A_{1g}$ ($s \rightarrow s$) transition in all the three host lattices and some of the $^1A_{1g} \rightarrow {}^1E_g$, $^1T_{2g}$ ($s \rightarrow d$) transitions split by the crystal field.

EXPERIMENTAL

Two photon excitation is a much more sensitive tool than two-photon absorption when dealing with diluted systems. Measurements have been performed at two temperatures, 12 and 80 K. The choice between these two temperatures was dictated by the better measurement conditions, one obtained monitoring the shorter-wavelength luminescence. In this way, it is possible to tune the exciting photons to higher energies up to the limit set by the resonance with the triple $^3T_{1u}$ state, where the two-stip process becomes the dominating effect. Results obtained in the linear spectroscopy of Ag^- in several alkali halides[6, 7] have shown that lowering the temperature causes the A′ decay channel to become more efficiently excited on the high-energy side of the C absorption band compared to the C′ channel, leading to substantially different excitation spectra.

The measurements presented in this work have all been obtained with single-beam excitation, hence the polarization vectors of the exciting photons are always parallel. The polarization analysis of the two-photon transition was obtained by monitoring the emission as a function of the angle between the impinging electric vector and the sample direction. Indeed, we found that some of the structures obtained previously with circularly polarized light in RbBr[3] were due to linearly polarized components present in the otherwise circularly polarized beam at wavelengths shorter and longer than the wavelength at which the compensator was adjusted.

The conversion from Ag^+ to Ag^- centres is obtained *via* an additive coloration of the crystals in potassium vapour. The excess of vacancies introduced by the coloration is removed from the sample by a subsequent electrolyic discoloration[8]. The two-photon excitation spectra were recorded in the energy interval between 4 and 6 eV, corresponding to a laser tuning between 2 and 3 eV.

In some of the spectral regions investigated, at energies higher than that of the A_{1g} band, an up-conversion linearly propotional to the intensity of the pumping beam was dtected. The linear contribution was always subtracted in order to obtain a pure quadratic effect.

RESULTS AND DISCUSSION

The two-photon excitation spectra of Ag^- in RbCl for linear polarization ($\in \parallel [100]$) and for circular polarization are reported in Fig. 1. Four strong absorptions are clearly visible. At the energy $2\hbar\,\omega_{\text{laser}} = 4.68$ eV, a very pronounced band is visible only with linear polarization and disappears with circular polarization. This behaviour is characteristic[3] of ${}^1A_{1g} \rightarrow {}^1A_{1g}$ transition, as summarized in Table-1. Two other bands are measured at 5.31 and 5.56 eV. They are assigned to the ${}^1A_{1g} \rightarrow {}^1E_g$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transitions derived from the crystal-field split, atomic d level.

The intensity of these bands is of the same order of magnitude as that of the ${}^1A_{1g} \rightarrow {}^1A_{1g}$ band as it should be for a two-photon-allowed transition. The symmetry assignment is based on the polarization dependence of the two bands shown in Fig. 2. The polarization dependnce of a ${}^1A_{1g} \rightarrow {}^1E_g$ transition as well as that of a ${}^1A_{1g} \rightarrow {}^1T_{2g}$ transition is clearly visible. However, the symmetry of the states cannot be that of a pure E_g or T_{2g} state because some discrepancies exist between the expected relative intensities and the measured ones. For example, the intensity of the E_g band as a function of θ should change from the maximum (at $\theta = 0°$) to the minimum (at $\theta = 45°$) with a modulation depth of 75%. The observed modulation is instead of the order of 25% from which we derive a 53% E_g character for the transition, with a 20% T_{2g} admixture. Consistently, the difference between linear and circular signals in the E_g band is smaller than predicted.

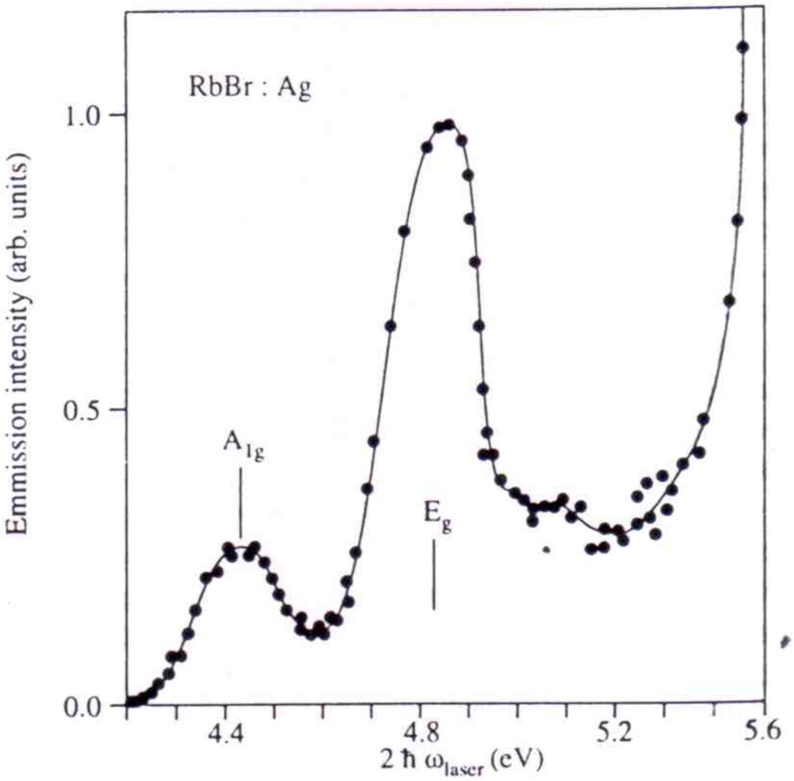

Fig. 2. Two-photon excitation spectrum of RbBr : Ag^-

The T_{2g} band should vanish in the linear polarization measurements of Fig. 1 and reach its maximum value in the circularly polarized experiment. Also in this case, the predicted modulation is larger than the observed one, yielding 60% T_{2g} character for this band, with a 20% E_g admixture. In both cases, we included a component constant with respect to θ, that is, of A_{1g} symmetry, mixed to the E_g and T_{2g} states.

The huge signal observed on the high-energy side of Fig. 2 and also present in all systems investigated, stems from a two-step transition whose intermediate state is the $^3T_{1u}$ state. The first step of the process is therefore a one photon-allowed $^1A_{1g} \rightarrow {}^3T_{1u}$ transition. From this state, the second photon carries the excited electron to the conduction band. The peak of the two-step transition is expected at the peak of the A band at an energy of 2.98 eV[6]. We could not observe this peak since it falls beyond the investigated energy range. The intensity of the quadratic signal around 5.7 eV convinced us that we are observing a two-step process whose probability is much larger than that of a two-photon absorption exploiting a virtual intermediate state.

RbBr : Ag^- and KCl : Ag^-

The results of RbBr shown in Fig. 2 are limited to 4.6 eV, the A_{1g} band region and the contribution of the E_g bands peaks at 4.82 eV. The signal in this region shows the expected modulation behaviour, but with a smaller modulation depth (about 40%). In the region between the E_g band and the onset of the two-step process at 5.5 eV, no signal was observed that could be assigned to a transition toward a T_{2g} level.

In KCl, the position of the energy levels allows for the observation of a clearly resolved $^1A_{1g} \rightarrow {}^1A_{1g}$ transition (Fig. 3), but the onset of the two-step process at 5.3 eV prevents the observation of either the E_g or the T_{2g} transitions.

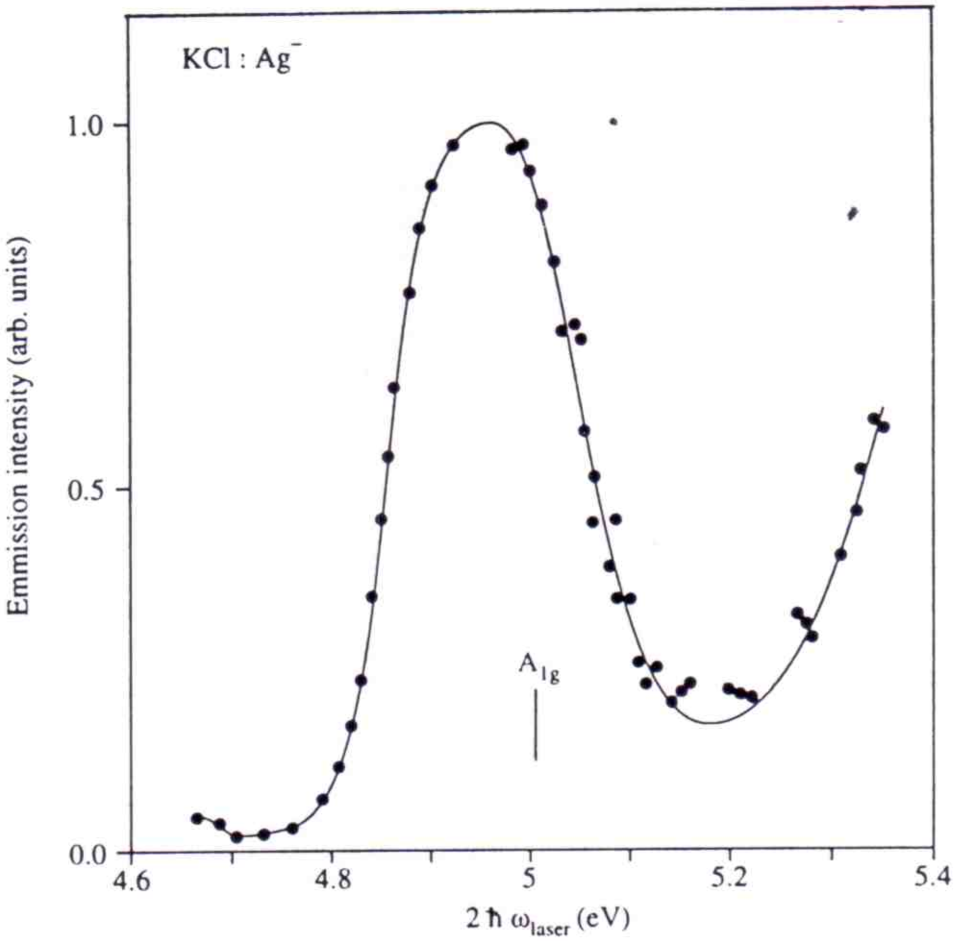

Fig. 3. Two-photon excitation spectrum of KCl : Ag^-

The peak of the A absorption band in KCl is at 3.11 eV[9], again too high in energy for us to measure *via* the two-step process, whereas in RbBr, it lies at 2.9 eV and indeed the two-step signal shows an excitation spectrum that closely follows the shape and position of the A band as measured in one-photon experiments. This fact suggests the idea that the second step carries the electron to a nonlocalized state high in the conduction band of the host crystal. In the case of RbBr, the peak intensity of the two-step signal is about two orders of magnitude stronger than the A_{1g} peak.

Conclusion

The origin of this up conversion, linearly depending on the pumping power, remains somewhat of a puzzle. In fact, the energy of the emitted photons is higher than that of the exciting photon, ruling out any effect either due to scattered light reaching the photomultiplier or to one-photon-excited luminescence. The up conversion one is observing could be explained by supposing that the F-centre coloration and bleaching of the crystals leave some unknown electron traps. Electrons belonging to these traps, excited to the conduction band by a linear process, are subsequently trapped by neutral Ag atoms and the resulting emission band is the usual C′ band. The traps should, therefore, decrease in number with time, but the measured rate of the emitted photons is so low that exhaustion of the traps can occur only in times much longer than those of an excitation spectrum recording. In the case of RbBr : Ag^- this picture is supported by the strong variation of the up-conversion intensity in going from one sample to another with a differnt coloration and bleaching history.

Another hypothesis for the linear contribution is the following: after the relaxation that takes place upon two-photon excitation or after low-temperature exposure of the sample to UV light in the C- and A-band regions, a number of Ag^- centres are to be found in the lower-lying $^3A_{1u}$ triplet state. This relaxed excited state cannot decay radiatively nor lose the electron to the higher triplet components as long as the sample is kept at low temperature. In agreement with this picture, preliminary measurement of one-photon-excited luminescence in KBr : Ag^- revealed at room temperature the presence in the A′ liminescence of a very slow component, which disappears at liquid-nitrogen temperature. Moreover, excited state absorption in RbBR : Ag^- was studied by Schmitt[10], who showed that from the excited triplet state it is possible to reach higher states, whose exact nature is yet to be clarified.

Let us now summarize the results obtained with the two-photon-excitation measurements. Table-1 contains the present results on even-parity excited states of the Ag^- ion in RbCl, RbBr and KCl. As already known for a large number of point defects in ionic crystals, the interaction of a defect with the surrounding ions is characterized by the size of the potential well formed by the nearest-neighbour ions. In this way, the difference between energy levels or the position of the absorption bands depends on the host lattice as described by the Mollwo-Ivey law[11]:

TABLE-1

KCl		RbCl		RbBr		Transition symmetry	Free-ion transition
E_p	HW	E_p	HW	E_p	HW		
4.37	0.147	4.17	0.16	4.07	0.15	$^1A_{1g} \rightarrow {}^1T_{1u}$	$^1S_0\ (5s^2) \rightarrow {}^1P_1\ (5s5p)$
4.98	0.23	4.68	0.21	4.43	0.22	$^1A_{1g} \rightarrow {}^1A_{1g}$	$^1S_0(5s^2) \rightarrow {}^1S_0\ (5s6s)$
		5.31	0.39	4.82	0.18	$^1A_{1g} \rightarrow {}^1E_g$	
							$^1S_0\ (5s^2) \rightarrow {}^1D_1\ (5s5d)$
		5.56	0.19			$^1A_{1g} \rightarrow {}^1T_{2g}$	

$$E_{peak} = cd^{-n}$$

where c is a proportionality constant and d is the nearest-neighbour distance. For an electron in a square-well potential, n = 2. Using n as a fitting parameter, it is found that the A_{1g} and E_g band values of N = 1.35 and 1.53, respectively, to be compared to the value n = 0.82 obtained for the one-photon-allowed A and C bands. A plot of the Mollwo-Ivey law of the Ag^- bands is presented in Fig. 4.

As mentioned before, the A_{1g} excited state is easily detected in the three investigated systems. The polarization dependence of this transition reveals that the state involved is, to the limit of our sensitivity, purely A_{1g} in character. The

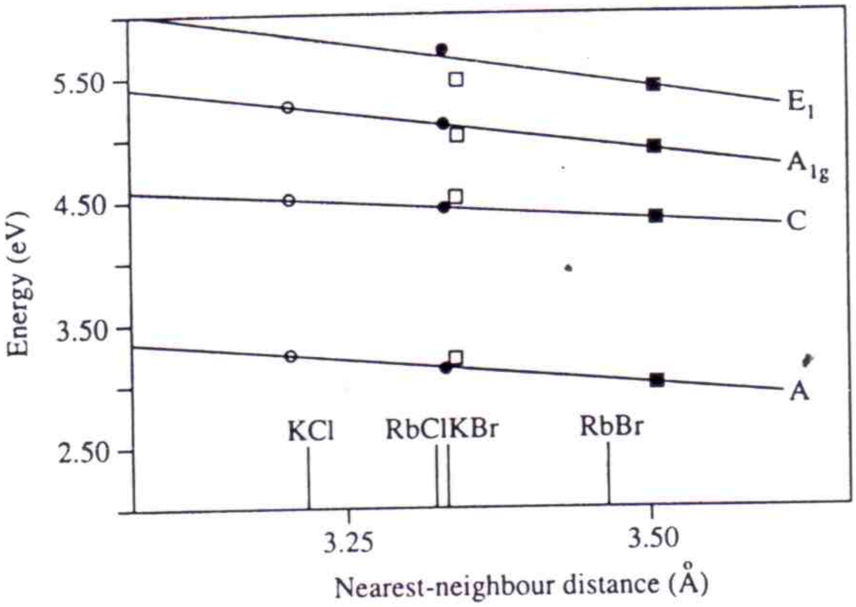

Fig. 4. Logarithmic plots of the Mollow-Ivey relation

situation is rather different for the next states belonging to the excited 5s5d multiplet. The worst case is that of KCl where no E_g or T_{2g} components could be detected. From the shape of the two-step tail and assuming that the intensity of the d bands is comparable to that of the A_{1g} transition, a lower limit for the distance in energy between the excited A_{1g} state and the E_g component of about 3000 cm^{-1} can be set. This energy separation appears greatly reduced in RbCl, where both the E_g and T_{2g} bands could be measured, and amounts to 2020 cm^{-1}.

From the position of the new even-parity levels that we found in this work, a more complete picture of $(ns)^2$ impurities in alkali halides is emerging, providing the basis for the extension of the existing theoretical models to include higher-energy s and d states coupled to vibration and close to the continuum of the host crystal conduction band.

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