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## One- and two-photon spectroscopy of monovalent copper ions in calcium fluoride

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**Abstract.** The spectroscopy of  $\text{Cu}^+$  ions embedded in an alkaline earth fluoride ( $\text{CaF}_2$ ) is reported for the first time. The absorption, emission and excitation spectra, as well as the lifetimes have been studied as a function of the temperature. It is shown that  $\text{Cu}^+$  ions occupy non-centro-symmetric sites. Furthermore, the analysis of the polarization dependence of two-photon absorption shows that, in fact,  $\text{Cu}^+$  ions appear to be located at sites of nearly cubic symmetry, in off-centre positions in the cube. The  $^1\text{E}$  and  $^1\text{T}_2$  singlet states are responsible for the main absorption in the near-UV range, and the emitting level is shown to be the  $^3\text{T}_2$  triplet state. This state is in fact split by the spin-orbit coupling into four components but two close sub-levels could be responsible for the strong temperature dependence of the lifetime in the low-temperature range.

### 1. Introduction

There has been a long history of research on  $\text{Cu}^+$  in solids, more especially in simple crystals such as alkali halides. Excellent reviews have been compiled by Fowler for the early works [1] and by McClure more recently [2, 3]. As pointed out by the latter, these systems are especially useful as models of impurity ions in crystals, and through a combination of one- and two-photon spectroscopies and theory a considerable degree of understanding of these systems can be reached.

The need for new tunable solid state laser materials was also at the origin of a number of investigations of  $\text{Cu}^+$  doped crystals [4, 5] and glasses [6–9]. Fluorides are usually good host lattices for laser materials. However,  $\text{CuF}$  does not exist at room temperature and the introduction of  $\text{Cu}^+$  ions in fluorides is difficult. Only few  $\text{Cu}^+$  doped fluorides are known, such as  $\text{NaF}:\text{Cu}^+$  [10],  $\text{RbMgF}_3:\text{Cu}^+$  [4] and  $\text{KF}:\text{Cu}^+$  [11].

The introduction of silver and copper into the alkaline earth fluorides was shown to be possible when oxygen is absent during crystal growth, and investigations of the Jahn–Teller effect in  $\text{Ag}^{2+}$  and  $\text{Cu}^{2+}$  centres were recently reported using ESR measurements [12–14]. However, no spectroscopic studies of  $\text{Cu}^+$  or  $\text{Ag}^+$  ions in such crystals with the fluorite structure have been published yet. In this paper, we report on the fluorescence properties of  $\text{CaF}_2:\text{Cu}^+$ , in which the luminescent centres were clearly identified as  $\text{Cu}^+$  impurity ions.

## 2. Experimental procedure

The single crystals were grown in carbon crucibles in a Bridgman type furnace. This laboratory-built equipment consists of a high-vacuum chamber connected to a diffusion pump and to gas inlets through liquid nitrogen traps. The crucible is heated by RF power with the aid of a movable coupling coil. The high-purity starting materials (quality Optran or Optipur from Merck) were preheated under high vacuum at 180 °C. Then, crystallization took place at 1420 °C in an atmosphere consisting of 5N9 Argon + 1% fluorine gas. Single crystals of approximately 2 cm<sup>3</sup> volume were grown. The nominal Cu concentration was 0.2 at.% and the actual concentration was not measured.

The absorption spectra were obtained in the range 200–400 nm (26000–38000 cm<sup>-1</sup>) on a Cary 2300 spectrophotometer with the sample housed in an SMC (Société des Matériels Cryogéniques) liquid helium cryostat.

Measurements of the fluorescence spectra used as optical excitation source Q-switched Nd<sup>3+</sup>:YAG pumped-dye laser (YAG 481 + TDL IV model from Quantel) associated with frequency-doubling systems. The fluorescence was analysed spectrally with a Hilger computer scannable 1 m monochromator and detected with a Hamamatsu R1477 PMT followed by an amplifier/discriminator and an Ortec photon counting system connected to a computer. Lifetime measurements were performed with a Stanford SR430 multichannel analyser with a minimum dwell-time per channel of 5 ns. The excitation spectra were obtained using the synchrotron light source of Super Aco of Lure at Orsay and a 3 m home-made vacuum-UV monochromator.

The experimental set-up used for the two-photon absorption study was similar to that previously described elsewhere [15].

## 3. One-photon spectra

Figure 1 illustrates the absorption and emission spectra measured at low temperature. The absorption spectrum in the near-UV range (26000–38000 cm<sup>-1</sup>) exhibits two main distinct peaks near 33170 and 30450 cm<sup>-1</sup>, and a third weaker one in the lower energy side around 28000 cm<sup>-1</sup>. The shape of the peaks is gaussian and a very good fit to the absorption spectrum is obtained with three gaussians. The half-band widths  $\sigma_a$  are nearly identical for the three peaks, around 2000 cm<sup>-1</sup> at low temperature. Such broad bands account for a strong electron-phonon coupling. No zero-phonon lines were detected, even at very low temperature. The broadening of the bands with temperature is well described, in the framework of the configurational coordinate model, by the well-known relation:

$$\sigma_a(T) = \sigma_a(0) [\coth(\hbar\omega_g/2kT)]^{1/2} \quad (1)$$

where  $\hbar\omega_g$  represents the average phonon energy of the breathing mode for the ground state. For the strongest absorption peak, the best fit is obtained with  $\sigma_a(0) = 2016$  cm<sup>-1</sup> and  $\hbar\omega_g = 262$  cm<sup>-1</sup>. The intensity of the absorption bands  $I(T)$  (the integrated area) does not exhibit any temperature dependence between 4.2 K and 300 K.

The peak energy similarities between the present absorption bands and those reported for alkali halides and other fluorides strongly suggest that these three bands

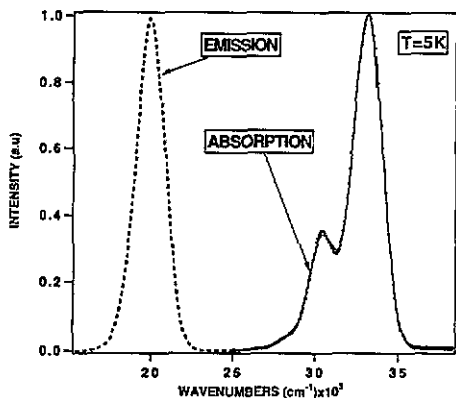


Figure 1. Absorption and emission spectra of  $\text{CaF}_2:0.2\% \text{CuF}_2$ . The full curve represents the best fit to absorption data using three gaussians. The emission band was obtained under 290 nm ( $\approx 34\,500 \text{ cm}^{-1}$ ) laser excitation.

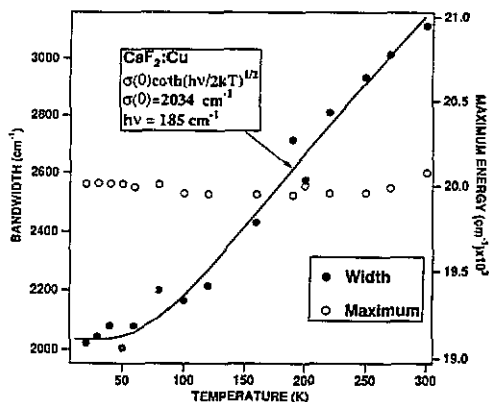


Figure 2. Temperature dependence of the maximum and of the width of the emission band of  $\text{CaF}_2:0.2\% \text{CuF}_2$ . The parameters deduced from a fit of relation (1) to experimental data are indicated in the insert.

are due to the  $3d^{10} \rightarrow 3d^9 4s$  transitions of  $\text{Cu}^+$  ions. Since  $d \rightarrow s$  transitions are parity forbidden, their transitions probabilities can be induced by vibrations and in the case of centrosymmetric complexes, a temperature dependence of  $I(T)$  is expected [16, 17]. The transitions follow a temperature dependence of the form

$$I(T) = I(0) \coth(\hbar\omega/2kT) \quad (2)$$

In the present case, the fact that  $I(T)$  is nearly temperature independent indicates a lack of centre of inversion due either to a charge compensation in the surrounding of the impurity ion or  $\text{Cu}^+$  being in an off-centre position in the cube as it is the case in some alkali halides.

Under excitation in these absorption peaks, the crystal exhibits a strong green fluorescence. The single, broad emission band, peaking around  $20\,000 \text{ cm}^{-1}$ , has a regular gaussian shape. Its maximum is nearly temperature independent and its broadening is very well described by relation (1) (figure 2). The best fit is obtained with  $\sigma_e(0) = 2034 \text{ cm}^{-1}$  and  $\hbar\omega_e = 185 \text{ cm}^{-1}$ . The phonon energy in the excited state is found to be weaker than in the ground state. In other words, the potential curve of the excited state has a less curvature near the minimum than the curve of the ground state. This phenomenon, usually expected, reflects a more diffuse charge distribution of the excited state.

The excitation spectra, recorded using a radiation synchrotron in the region  $25\,000\text{--}100\,000 \text{ cm}^{-1}$ , are displayed in figure 3. The bands in the near UV are identical to the absorption bands. Another group of three bands, well separated from the former, was observed in the vacuum-UV range above  $45\,500 \text{ cm}^{-1}$ . By comparison with other  $\text{Cu}^+$  doped systems [10, 18, 19], the two bands peaking near  $50\,000$  and  $60\,000 \text{ cm}^{-1}$  are assigned to  $3d^{10} \rightarrow 3d^9 4p$  transitions in  $\text{Cu}^+$ .

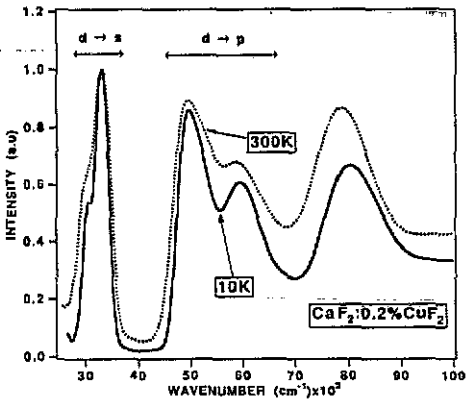


Figure 3. Normalized excitation spectra obtained by using the synchrotron radiation.

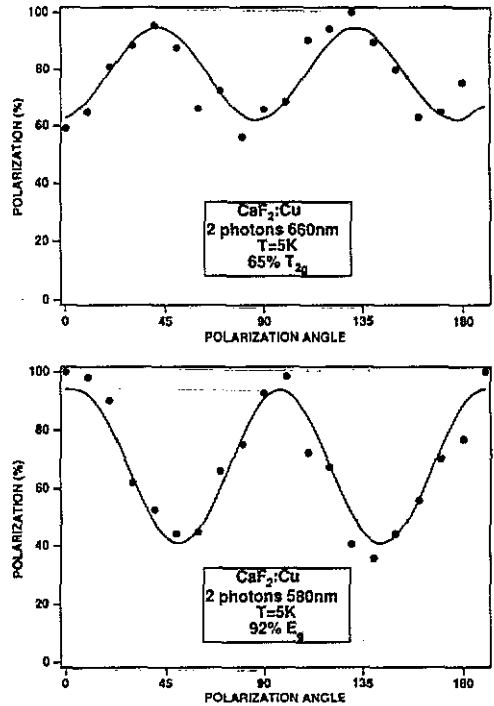


Figure 4. Polarization dependence of two-photon signal of  $\text{CaF}_2:0.2\% \text{CuF}_2$ . The full curves are the best fits of relations indicated in the text to experimental data. Propagation vector [001]; polarization angle measured from [100] in degrees.

#### 4. Polarization dependence of two-photon absorption

In the case of a cubic crystal, the symmetry of the excited states cannot be investigated by using one-photon absorption measurements. However, by polarization dependence of two-photon absorption, one can straightforwardly determine the symmetry of absorbing levels of the impurity ion [15, 20]. The polarization dependence of the rate of two-photon absorption has been calculated for cubic crystals by Bader and Gold [21]. For the  $O_h$  symmetry site and two identical photons propagating along the [001] axis the angular dependence functions for the  $A_{1g} \rightarrow {}^1E_g$  and  ${}^1A_{1g} \rightarrow {}^1T_{2g}$  transitions of  $\text{Cu}^+$  in a  $\text{Ca}^{2+}$  site of  $\text{CaF}_2$  are:

$$\begin{aligned} A_{1g} \rightarrow E_g & : 1 - \left(\frac{3}{4}\right) \sin^2 2\theta \\ A_{1g} \rightarrow T_{2g} & : \sin^2 2\theta \end{aligned}$$

where  $\theta$  is the angle between the [100] axis and the polarization vector.

The polarization dependence of the two-photon signal is shown in figure 4 for two excitations at 600 nm ( $15\,150 \text{ cm}^{-1}$ ) and at 580 nm ( $17\,240 \text{ cm}^{-1}$ ) in the two major

absorption bands of the  $3d \rightarrow 4s$  transitions. The results clearly show a dominant  $T_2$  character for the lowest excited state and a strong E character for the highest one. The fraction of E or  $T_2$  character was determined by the same procedure as used previously [15]. In contrast to all the cases previously investigated where the  $\text{Cu}^+$  impurity ions occupied octahedral sites in alkali halides and where the E states were found below the  $T_2$  states as expected, the situation is reversed in the present case, because of eightfold cubic coordination of  $\text{Cu}^+$  in  $\text{CaF}_2$  which inverts the order of the e and t orbitals.

## 5. Discussion

Replacing  $\text{Ca}^{2+}$  by  $\text{Cu}^+$  leads to the problem of charge compensation. The fluorite lattice is very adaptable and provides the necessary charge compensation in a variety of ways, often leading to a number of different microscopic sites in a single crystal. In the case at hand, however, from the spectroscopic investigation, we have not found evidence of multisites and we therefore consider that only one kind of site is present.

Two-photon excitation spectroscopy showed that the lowest excited state has a dominant  $T_2$  character, indicating that the  $\text{Cu}^+$  ions appear to be located at sites of nearly cubic symmetry. A charge compensation occurring in the close surrounding of the impurity ions is therefore unlikely. The symmetry would be strongly lowered: for instance, a  $\text{F}^-$  vacancy at one of the height corners of the cube would reduce the symmetry from  $O_h$  to  $C_{3v}$ . For the same reasons, the green fluorescence cannot be due to possible  $(\text{Cu}^+)_2$  pair centres which could easily form in  $\text{CaF}_2$ . Owing to the large Stokes shift, this possibility could be considered. However, a similar Stokes shift has been observed in  $\text{Cu}^+$  doped  $\text{RbMgF}_3$  [4] where the luminescent centres were assigned to isolated  $\text{Cu}^+$  ions.

A charge compensation far from the impurity must be considered therefore. Such a situation often arises in trivalent rare-earth doped alkaline earth fluorides [22]. Furthermore, we know from the temperature dependence of the absorption intensity that the impurity centre is not centrosymmetric so we must consider that  $\text{Cu}^+$  is located in an off-centre position in the cube.

We have seen that the three absorption bands observed in the near-UV range can be attributed to the  $3d^{10} \rightarrow 3d^9 4s$  transitions of  $\text{Cu}^+$  ions. The two main ones peaking near  $33\,170$  and  $30\,450 \text{ cm}^{-1}$  are therefore assigned to  $^1A_1 \rightarrow ^1E$  and  $^1A_1 \rightarrow ^1T_2$  spin-allowed transitions, respectively. The weaker one appearing around  $28\,000 \text{ cm}^{-1}$  is probably due to the  $^1A_1 \rightarrow ^3T_2$  spin-forbidden transition,  $^3T_2$  being the emitted level. Its energy can be evaluated from the study of the optical line shapes in the framework of the linear vibronic coupling. The second moment of the emission band is related to the full width at half-maximum by [23]

$$\sigma_e(0) \simeq [8 \ln 2 M_2(0)]^{1/2} \quad \text{at } T = 0 \text{ K} \quad (3)$$

where the second moment  $M_2(0) = S(\hbar\omega_e)^2$ . The Huang-Rhys factor,  $S$ , is then deduced from the experimental data  $\sigma_e(0) = 2034 \text{ cm}^{-1}$  and  $\hbar\omega_e = 185 \text{ cm}^{-1}$  and found to be  $21.7 \simeq 22$ . The Stokes shift, given by  $2S\hbar\omega_e$ , is  $8030 \text{ cm}^{-1}$  and finally the calculated energy of the emitting state is  $28\,030 \text{ cm}^{-1}$  which is close to the energy of the weak band ( $28\,180 \text{ cm}^{-1}$ ) observed at 10 K on the lower energy side of the absorption spectrum.

## 6. Mechanisms of fluorescence

The lifetime of the luminescence shows a remarkable temperature dependence as illustrated in figure 5. The fluorescence decays are exponential. The rapid decrease of the lifetime without any loss of luminescence intensity is characteristic of the thermalization of two close emitting levels with different oscillation strengths, the lowest one being more metastable than the other [24]. At very low temperature, the decay time is very long (1.5 ms) and constant between 1.5 and 8 K. It is characteristic of the lowest excited state which only emits. At higher temperature ( $T > 25$  K) the time constant slowly decreases and is more typical of the emission of the upper state.

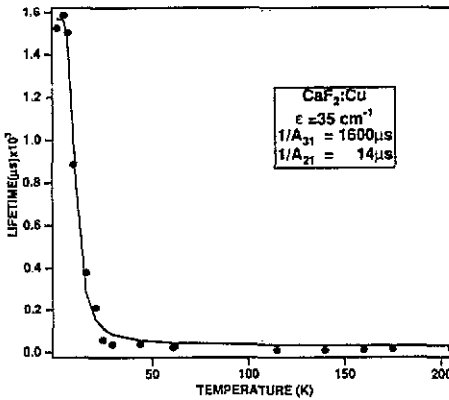


Figure 5. Temperature dependence of the fluorescence decay times of  $\text{CaF}_2:0.2\% \text{CuF}_2$ . The parameters deduced from a fit of relation (4) to experimental data (full curve) are indicated in the insert.

This particular temperature dependence of the lifetime is a general feature of the  $\text{Cu}^+$  emission in any host. In alkali halides, when  $\text{Cu}^+$  is on-centre in a octahedral site, it was shown [24] that the two emitting levels are the two components  $T_1$  and  $T_2$  of  ${}^3E_g$  which have different fractions of singlet character due to the spin-orbit interaction.  ${}^3E_g, T_1$  lies lower and is a pure triplet state while the upper state  ${}^3E_g, T_2$  gets some singlet character from the mixing with the  ${}^1T_{2g}$  state. This mechanism was confirmed by studying the effect of a magnetic field on the lifetime at low temperature [25]. In the case of  $\text{Cu}^+$  doped  $\text{RbMgF}_3$ ,  $\text{Cu}^+$  occupies lower symmetry sites  $D_{3h}$  and  $C_{3v}$  and the  ${}^3E$  levels are still the emitting levels. In the present case of eightfold cubic coordination of  $\text{Cu}^+$ , the  ${}^3T_2$  states are probably the emitting levels. Considering the description of the electronic structure of the  $\text{Cu}^+$  impurity centre in sodium chloride [26], it is clear that a three-level model can still be used to explain the fluorescence mechanisms in  $\text{CaF}_2:\text{Cu}^+$ . The two emitting states could be  ${}^3T_2, E$  and  ${}^3T_2, T_1$ , the latter being pure triplet because not mixed with singlet states by spin-orbit coupling. Then the excited-state dynamics can be described by the equation [27]:

$$\tau^{-1} = [A_{31} + A_{21} \exp(-\epsilon/kT)] / [1 + \exp(-\epsilon/kT)] \quad (4)$$

where  $\epsilon$  represents the energy mismatch between the levels 2 and 3 and  $A_{31}$  and  $A_{21}$  the radiative transition probabilities from the lower and the upper excited states to the ground state 1.

A very good fit to experimental data is obtained (figure 5) and the best fit values are:

$$\epsilon = 35 \text{ cm}^{-1} \quad 1/A_{31} = 1.6 \times 10^{-3} \text{ s} \quad 1/A_{21} = 1.4 \times 10^{-5} \text{ s}.$$

## 7. Summary

This study shows that  $\text{Cu}^+$  ions embedded in  $\text{CaF}_2$  are located at sites of nearly cubic symmetry in off-centre positions in the cube. The symmetry of the absorbing states in the near-UV range was clearly identified as E for the upper state and as  $T_2$  for the lower one, in agreement with the eightfold cubic coordination of  $\text{Cu}^+$  in  $\text{CaF}_2$ . The emitting state is probably  $^3T_2$  and the temperature dependence of the fluorescence lifetime can be explained by the thermalization of two energy sub-levels separated only slightly in energy but with different oscillator strengths.

Further experiment are now in progress in order to study the fluorescence dynamics thoroughly and a molecular orbital calculation on this system is also considered.

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