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The de-excitation mechanism of Cu^+ in KBr

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Abstract. The fluorescence of the Cu^+ impurity centre in KBr was investigated in the range 19–300 K: in particular, lifetime and quantum yield data were recorded in the same sets of measurements. The de-excitation mechanism is interpreted in terms of the Pedrini model: two excited states in thermal equilibrium are involved in the emission process, one of which is metastable and lies close below the emitting level.

In several host matrices Cu^+ (as well as other ions) does not occupy the position of the ion it substitutes, going towards an ‘off-centre’ position. The forecast of off-centre displacement was obtained by one of the present authors [1–3], but essentially it concerned the ground-state configuration of monovalent impurity ions (Li^+ , F^- , Cl^- , Na^+ , Ag^+ , Cu^+) in alkali halide crystals as well as of Mn^{2+} impurity ions in some oxides.

Nevertheless, it must be noted that, in principle, the position in the lattice of Cu^+ in the relaxed excited state (RES) could be different from that in the ground state. The possibility of this occurrence was a matter for research in the past; lifetime measurement as a function of the sample temperature (T) seemed to be one of the best methods to detect it.

Piccirilli and Spinolo [4] carried out such measurements in the alkali halides not containing Li and F: it was assumed [4] that ‘the involved $3d^94s^1 \rightarrow 3d^{10}$ forbidden transition is made possible by odd lattice vibrations that dynamically mix the initial and final wave-functions with different parity wave-functions’. These authors subsequently apologized [5] for an instrumental error in their lifetime measurements at low T . Consequently, Spinolo *et al* repeated the experiment [6] by using a better technique, but restricting the investigation to NaCl, NaBr, KBr and RbBr. They noticed [6] that in some cases the lifetime, $\tau(T)$, as a function of T can be expressed as a coth function; furthermore, they stressed that this dependence is similar to that of the oscillator strength when Cu^+ is in an on-centre configuration. In conclusion they suggested [6] the possibility of a change from an on-centre (at low T) to an off-centre configuration (at high T).

A completely different interpretation of the Cu^+ de-excitation mechanism in alkali halides was introduced, in 1978, by Pedrini [7]. He suggested that the temperature dependence of the Cu^+ lifetime in LiCl can be fairly well explained by the presence of a metastable level lying close below the emitting level: it is worth stressing that, subsequently in several papers, he verified the validity of his model, by changing some host materials as well as the impurity ion (Ag^+). Contrary to the Spinolo suggestions, Pedrini assumed

(i) that there are two excited states for which the thermal equilibrium (after excitation) is reached in a short space of time and

(ii) that the lowest excited state is metastable and takes a prominent part in lengthening the luminescence decay time at low T , the part assigned to the lattice vibrations being considered as minor.

In conclusion, we were compelled to repeat the lifetime measurements in order to verify the validity of the models proposed above. Basically, here, we would like to present our lifetime and quantum yield data, which were recorded in the same sets of measurements concerning a KBr host: indeed, to our knowledge this material was not tested by Pedrini and, from what has already been said, both the Spinolo experiments and suggestions need checking.

Our measurements were carried out using a Perkin-Elmer LS-50 luminescence spectrometer whose wavelength range of operation is 220–850 nm; both the emission and the excitation spectra were corrected by taking into account the variation of the source intensity (a xenon discharge lamp with 8 μ s pulse width) and the photomultiplier sensitivity as a function of wavelength. The samples were mounted in a Galileo K1C-SC cryocooler (with vacuum apparatus supplied by Bis-Italia), ranging from 19 K to 300 K. The excitation light was passed through an Oriel UV interferential 260 nm filter when we detected the emission spectra, while an Oriel band-pass colour glass 300 nm filter was adopted when we detected the excitation spectra. Both filters were used in lifetime measurements.

KBr:Cu⁺ samples were kindly supplied by Spinolo: they were doped directly in the melting.

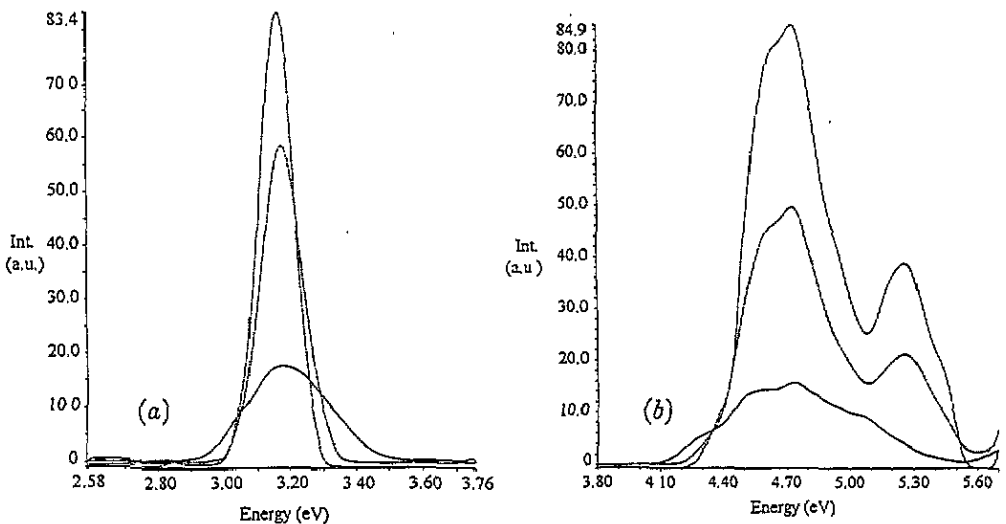


Figure 1. Emission (a) and excitation (b) spectra at various temperatures: from the top, 20.10 K, 74.24 K, 300.4 K.

We studied the transition $3d^9 4s^1 \rightarrow 3d^{10}$, where the excitation peak is at 4.68 eV and the emission peak is at 3.17 eV. The position of the peaks is practically independent of temperature.

Some examples of emission and excitation spectra at various temperatures are given in figure 1, whereas in figure 2 the lifetime reciprocal values are presented as a function of $1/T$. The results we obtained for the lifetime τ are listed in table I. In figure 3 we also present the quantum yield data for the emission process as a function of T : in fact these data (expressed as integrated intensity) can be correlated with the lifetime values as shown

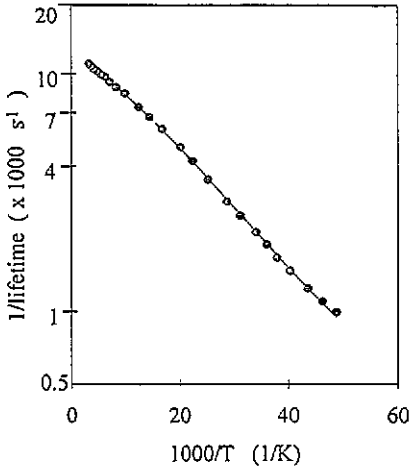


Figure 2. Experimental lifetime reciprocal values and best fit as a function of $1/T$.

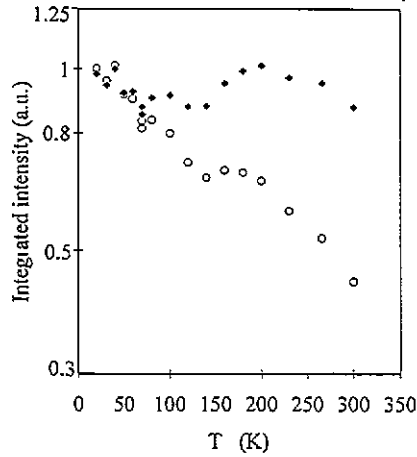


Figure 3. Uncorrected (\circ) and corrected (\blacklozenge) emission quantum yield values as a function of T

below.

Firstly we found that the τ values we measured are substantially independent of Cu^+ concentration. Thus, for the sake of brevity, here we give the data concerning just one kind of sample.

Each emission decay is clearly interpolated by a single exponential function at all temperatures. The lifetime values we obtained are of the same order of magnitude as those reported in the literature [4, 6]. Their temperature behaviour is in agreement with the model adopted in our analysis, which forecasts the following law for $\tau(T)$:

$$\frac{1}{\tau} = \frac{A_m + A_2 \exp(-\Delta/kT)}{1 + \exp(-\Delta/kT)} \quad (1)$$

where, according to Pedrini [7], we assume that the emission is composed of a double level (the lowest being metastable). The terms A_m and A_2 are the rate of emission from the metastable level and from the normal one, respectively, whereas Δ is the energy difference between the two levels. Therefore, the observed lifetime is a thermal average of the lifetimes of the two levels.

We display the interpolation of our data by (1) in figure 2 where the dots are experimental data and the line is the best fit. The values of the terms we found are

$$A_m = 259 \text{ s}^{-1} \quad A_2 = 24\,762 \text{ s}^{-1} \quad \Delta = 6.27 \text{ meV.}$$

We determined the values (I_{exp}) of the quantum yield by integrating the emission intensity. Furthermore we corrected them (I_{corr}), because the optical density varies with the temperature, according to the relationship proposed in [8]:

$$I_{corr} = I_{exp}/[\mu(T)/\mu(0)] \quad (2)$$

where μ is the optical density of the analysed transition.

In the temperature range we considered, the competitive contribution due to the ionization transition can be disregarded for the decay mechanism [9]. Consequently the emission quantum yield must be unitary. Our quantum yield experimental results,

Table 1. A survey of the lifetime data as a function of T and their reciprocals together with the fitting values obtained by using the relationship (1).

Temperature (K)	Lifetime τ (μs)	$1000/T$ (K^{-1})	$1/\tau$ (10^3 s^{-1})	Fitting values (10^3 s^{-1})
20.51	1006	48.76	0.994	0.946
21.64	909	46.21	1.100	1.081
22.94	799	43.59	1.252	1.246
24.80	674	40.32	1.484	1.498
26.33	595	37.98	1.681	1.715
27.70	526	36.10	1.901	1.913
29.33	465	34.09	2.151	2.153
32.10	396	31.15	2.525	2.563
34.75	345	28.78	2.899	2.949
39.61	278	25.25	3.597	3.629
44.63	232	22.41	4.310	4.275
49.47	203	20.21	4.926	4.839
59.62	170	16.77	5.882	5.845
69.48	151	14.39	6.623	6.626
79.98	138	12.50	7.267	7.295
100.3	120	9.970	8.333	8.255
120.2	113	8.319	8.850	8.913
140.1	107	7.138	9.346	9.400
160.0	102	6.250	9.804	9.773
180.0	99.7	5.556	10.03	10.07
209.7	96.2	4.769	10.39	10.41
239.6	94.4	4.174	10.59	10.66
269.6	91.6	3.709	10.92	10.87
300.4	90.1	3.329	11.10	11.03

uncorrected and corrected, are presented in figure 3: as expected the corrected values are nearly equal to unity.

In conclusion, our results strongly support the validity of the Pedrini model when applied to the fluorescent emission Cu^+ in KBr. In particular we want to stress that

(i) the Spinolo *et al* data for $\text{KBr}:\text{Cu}^+$ [6] are of the same order of magnitude as those obtained by us, but the differences are remarkable at low T ;

(ii) Spinolo *et al* [6] used two different interpolating functions at low and high T (with a different physical meaning in the two T ranges), whereas we adopted a single model in the whole T range;

(iii) every attempt to fit our $\tau(T)$ data with the interpolating functions of Spinolo *et al* [6] was unsuccessful.

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