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VUV EXCITATION OF LUMINESCENCE IN PURE AND Tl^+ DOPED KI

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Excitation spectra of pure and Tl^+ doped KI have been measured at room temperature (RT) and liquid nitrogen temperature (LNT) between 13 and 30 eV. Energy transfer between the host lattice ions and the Tl^+ impurities, and intrinsic recombination of electron-hole pairs, have been studied at different temperatures and excitation energies. Energy transfer has been observed only at RT while at LNT the intrinsic recombination, V_k centers-electrons, is the dominant process.

The energy transfer between an excited atom or ion and a recombination center, where the radiative emission takes place, is one of the most interesting, and not completely solved, problems of solid state spectroscopy. Phosphors like $KI:Tl^+$ are well known systems where energy transfer occurs between the host lattice ions, excited by UV and X-ray radiation, and the Tl^+ impurities[1-3].

The main process is explained in the following way: the primary ionizing excitation produces an electron-hole pair. The hole is easily trapped at a Tl^+ ion, forming a Tl^{++}. The much more mobile electron wanders through the crystal until it is trapped into one of the excited states of Tl^{++} to form an excited Thallium ion $(Tl^+)^*$. The system behaves now exactly like a Tl^+ ion excited in one of the UV absorption bands (the A band at 4.40 eV and the C band at 5.30 eV at liquid nitrogen temperature (LNT) in $KI:Tl^+$)[4]. The radiative deexcitation gives rise to the well known Stokes-shifted emission, called A_X band, characteristic of the Tl^+ impurities, centered at about 3 eV in $KI:Tl^+$.

Although the general features of the process are well described by the above mechanism, it would be interesting to obtain more information on certain aspects of the excitation, such as its temperature and energy dependence. For example, an increase of the quantum efficiency of the Tl^+ emission at room temperature (RT) was measured at certain excitation energies, $E_n = nE_{gap}$ (with $n = 2,3,...$), in thin films and single crystals of $NaCl:Ag^+$, $KCl:Tl^+$ and $KBr:Tl^+$.[5,6] Older results show similar effects also in phosphors of K, Rb and Cs iodides, but the data were collected over a narrower excitation region[7]. Moreover some discrepancies exist among the results obtained by the different authors [8]. Another open question is the importance of the intrinsic processes. The energy migration towards a recombination center competes, at low temperature, with the direct recombination process characteristic of the pure crystal. In the latter the hole is self-trapped in the lattice, forming a V_k center, and the electron-hole recombination gives rise to the intrinsic luminescence (in KI at 3.34 eV and 4.15 eV)[9-11]. In order to obtain new results on these processes, we have examined the spectral dependence of both the emission and the excitation of the luminescence in pure and doped KI, at LNT and at RT.

The experiments were performed with the luminescence set-up built at the PULS facility at the Frascati National Laboratories: a detailed description of the VUV beam-line is reported elsewhere[12]. The VUV portion of the synchrotron radiation from the Adone storage ring is dispersed by a modified 1 m Hilger-Watts monochromator, providing a tunable excitation source in the range 3-30 eV. The VUV beam from the monochromator is refocussed on the samples mounted on the cold finger of a liquid nitrogen cryostat. The samples of KI and $KI:Tl^+$ with various amounts of doping were home grown. The luminescence is collected at 90° with respect to the exciting beam from the front surface of the sample and focussed on the analysing monochromator working between 6 eV and 2 eV. The signals are processed by a single-photon counter and recorded.

In order to compare the energy transfer process with the intrinsic process we have studied in identical conditions a pure KI crystal and various Tl^+-doped KI crystals. Fig. 1 shows the RT excitation spectrum (recorded between 14 eV and 30 eV approximately) of the light emitted at 2.95 eV by a crystal doped with 0.0003 mol % of Thallium. This excitation spectrum shows a main, broad peak around 18 eV and subsidiary structures. Above 19 eV the minima coincide with the positions of the strongest maxima of the K^+ 3p core absorption spectrum (for example, the Γ exciton at 21.2 eV and the X exciton at 21.2 eV)[13]. The emission excited at 22.5 eV, shown in Fig. 2 (full line), consists only of the Tl^+ A_X band. In the same conditions, no emission was measured above 2 eV in pure KI. Indeed, the intrinsic mechanism is forbidden by the thermal instability

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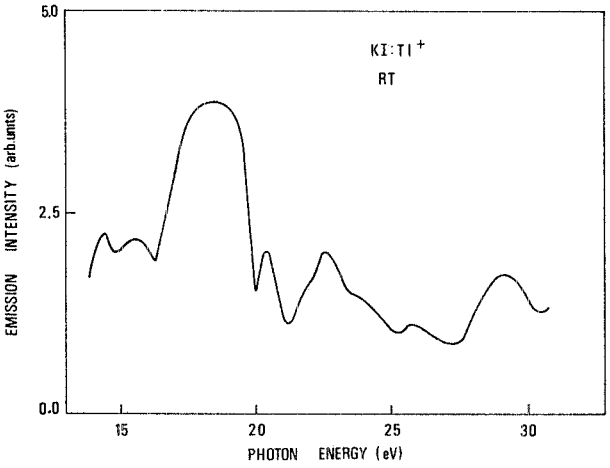

Figure 1: Room temperature excitation spectrum in the vacuum ultraviolet of the 2.95 eV emission of $KI:Tl^+$.

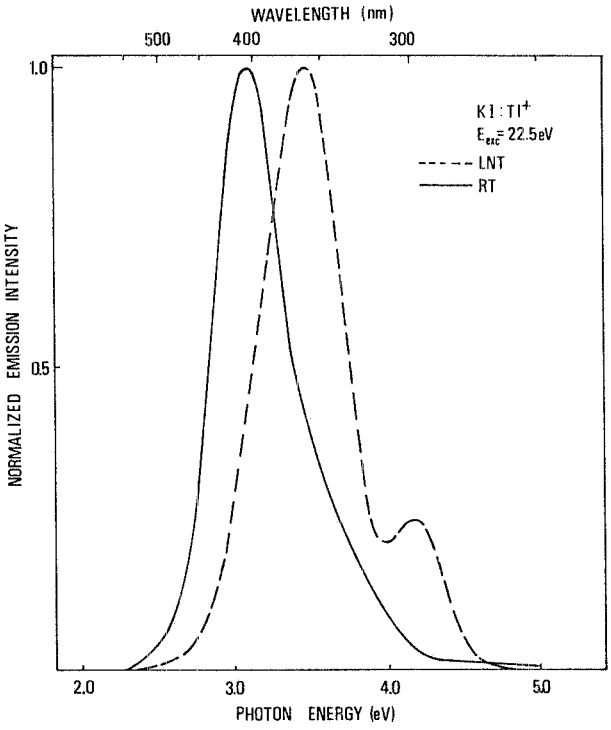

Figure 2: Emission spectra of $KI:Tl^+$ excited at 22.5 eV measured at 77 K and 300 K. The spectra have been normalized to the maximum intensity value.

of the V_K centers at temperatures above 105 K [10]. A very weak luminescence in pure KI appears around 2 eV and it is probably the same as that identified by Fieschi et al. [14] as due to O_2^- contamination of the sample surface. The energy of the main excitation peak in $KI:Tl^+$ at 18 eV roughly corresponds to $3E_{gap}$ and it could reflect the photon multiplication process described by various authors[5-7]. Experimental difficulties have prevented us from measuring the excitation spectrum in the region around $2E_{gap}$ in order to confirm this hypothesis.

The behaviour of KI and $KI:Tl^+$ crystals at low temperature is completely different from that observed at RT. At LNT both pure and doped crystals do show the same excitation spectra (see Fig. 3) and the same emission bands. These bands, shown in Fig. 2 (dashed line), coincide with the

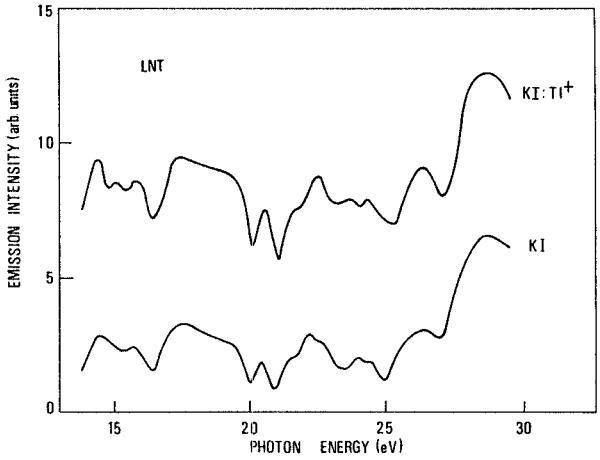

Figure 3: Liquid nitrogen temperature excitation spectra in the vacuum ultraviolet of the $KI:Tl^+$ (upper curve) and pure KI (lower curve) emissions at 3.44 eV. The pure KI excitation spectrum overlaps the $KI:Tl^+$ one and has been shifted downwards for clarity.

intrinsic emission. No energy transfer towards a recombination center has been observed in the Tl^+ doped samples. Therefore the energy transfer takes place in these crystals only if the intrinsic emission is quenched by the temperature. At LNT the probability of the hole to be self-trapped is much greater than that of being trapped by the Tl^+ ion. Even in the most heavily doped samples investigated (up to 0.003 mol %) no luminescence in the Tl^+ A_X band was detected at LNT.

Also in Fig. 3 the positions of the minima of the excitation curves reflect those of the core excitons. This can be due to the increase of the reflectivity[13] or of the total photoemission yield[15] at these energies and also to the shorter penetration depth of the exciting radiation. The electron-hole pairs created near the surface in a thin crystal layer may find ways of non-radiative recombination. The detailed structures appearing in Fig. 1 and Fig. 3 yield a kind of an "inverted" absorption spectrum. The excitation spectra of Fig. 3 do not show the broad, pronounced peak around 18 eV. At present we cannot explain the behaviour of KI that does not agree with the results of the careful measurements performed in pure Na and Rb halides by Beaumont et al.[16]

The energy transfer in $KI:Tl^+$ crystals depends not only upon the temperature but also upon the wavelength of irradiation[17]. Emission spectra excited at LNT in the fundamental exciton region at 6.36 eV, 5.79 eV and 5.70 eV are plotted in Fig. 4. On decreasing the energy of

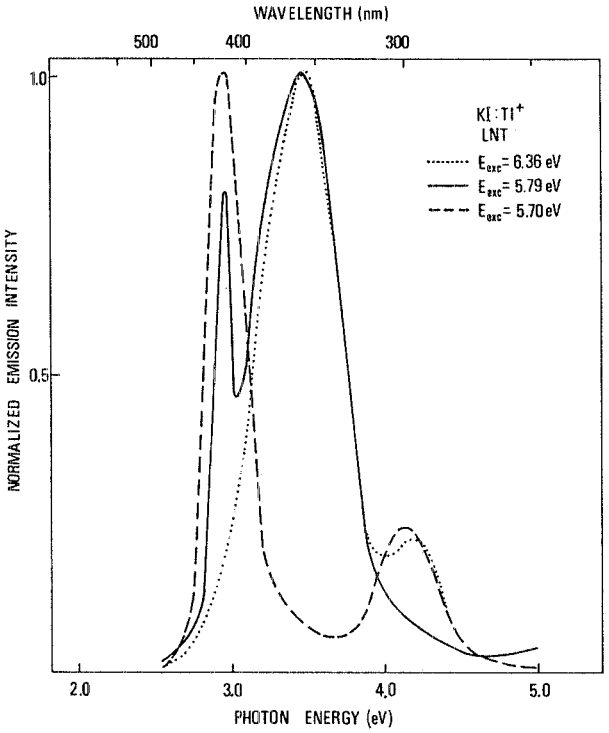

Figure 4: Liquid nitrogen temperature emission spectra of KI:Tl^+ excited at several energies in the fundamental exciton region. The spectra have been normalized to the maximum intensity value.

excitation, the intrinsic emission (3.5 eV) decreases and the Tl^+ emission at 3.0 eV (plus its companion at 4.1 eV) increases. Especially in heavily doped samples the pumping at 5.70 eV yields practically only Tl^+ emission with the quenching of the intrinsic recombination. We suspect that this energy corresponds to the tail of the so called D band (peaking at 5.52 eV) attributed to an exciton perturbed by a Tl^+ impurity. The energy transfer in this case would be strongly favoured by the close proximity of the excitation and recombination sites.

Similar experiments on pure and doped Potassium halides are in progress in our laboratory, in order to obtain further information on the energy transfer and on the photon multiplication processes.

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