

Luminescence of Pure and Cu-Doped Alkali Halide Single Crystals*

R. OGGIONI AND G. SPINOLO†

Istituto di Fisica dell' Università Milano, Italy and Istituto Nazionale di Fisica Nucleare, Sezione di Milano, Italy

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In order to understand some x-ray excited emission bands in pure alkali halides, crystals were doped with the corresponding copper halides. It has been found that a band, which is also often present in "pure" or thermally treated alkali halides, is due to a Cu center. The excitation spectrum of the Cu impurity at room temperature has also been measured. It is shown that the radiative transitions connected with Cu centers involve electrons.

INTRODUCTION

THE luminescence of Cu impurities in single crystals of alkali halides has been investigated.

A second luminescence band connected with the Cu impurity has been observed, which, together with a previously reported band at about 400 m μ ,¹ shows a behavior very similar to the luminescence of Cu impurity in CdS and ZnS.²

The study on these centers was done by exciting them with x rays and ultraviolet radiation, and detecting the emission in a range of λ from 300 to 750 m μ and over a temperature range from 77 to 300°K; in the excitation spectra the exciting light runs from 240 to 380 m μ .

It was further observed that a luminescence due to oxygen³ sometimes masks the Cu band at lower energies. This happens both in thermoluminescence measurements⁴ and in luminescence stimulated by ionizing radiation.⁵

From the present measurements some information concerning the effect of thermal treatment on alkali halide crystals has been obtained. Measurements of emission spectra under F light excitation have indicated the type of carrier involved in the emission processes which occur during x irradiation or thermoluminescence glow peaks in which carriers, namely, electrons and holes, are released.

EXPERIMENTAL DETAILS

The pure crystals used were furnished by Harshaw Chemical Company, Dr. Karl Korth and Light and Company; the doped crystals were grown using Korth seeds and Merk reagents in our laboratory by Kyropoulos method in a temperature-regulated furnace. The quartz crucibles were kept in a furnace through which it was possible to flow a suitable gas. Single crystals were cooled in about three hours.

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† Present address: University of Illinois, Physics Department, Urbana, Illinois.

¹ A. Levaldi and G. Spinolo, *Nuovo Cimento* **26**, 1153 (1962).

² M. Bancia Grillot and E. Grillot, *Compt. Rend.* **254**, 1605 (1962).

³ J. Rolfe, F. R. Lipsett, and W. J. King, *Phys. Rev.* **123**, 447 (1961).

⁴ A. Halperin, A. A. Braner, and N. Kristianpoller, in *Proceedings of the International Conference on Color Centers and Crystal Luminescence*, Turin, 1960 (unpublished).

⁵ R. Fieschi and G. Spinolo, *Nuovo Cimento* **23**, 738 (1962).

The salts used for the doping (from 0.01 to 0.1 mole %) were from Merk or prepared from Merk reagents in the laboratory.¹

Absorption measurements were done with a Beckmann DU spectrophotometer equipped with a double vessel cryostat for liquid-nitrogen temperature measurements; the samples were clamped to a copper block at the bottom of the cryostat and ranged in thickness from 0.3 to 5.2 mm. Some of the luminescence measurements were carried out with an apparatus described elsewhere⁵ and improved with a 9558 B trialkali EMI photomultiplier having a wide spectral response and very low dark current.

Many measurements were performed with a newly built apparatus with a larger optical aperture ($f/4.4$): a single quartz prism monochromator, type D285 from Hilger and Watts was used and a cryostat designed by Dr. Cantù of Koristka Company.

A Machlett OEG 50T x-ray tube operated 40 kV, 40 mA, a hydrogen lamp, and a 500-W tungsten lamp were used as excitation sources.

The excitation spectra were measured by exciting with monochromatic light produced by the Hilger monochromator and analyzing the emitted light with various interference filters so as to know roughly the type of light emitted after excitation in a certain absorption band. We have obtained F -stimulated emission spectra by irradiating an x-ray colored Cu-doped crystal with F light.

All the emission spectra are corrected for the photomultiplier response and prism dispersion, and the excitation spectra are corrected for the emission of the hydrogen lamp and prism dispersion.

RESULTS

In Fig. 1 we see the emissions produced by x-ray irradiation at room temperature and liquid-nitrogen temperature of "pure" KI, KBr, and KCl. Some emissions, and particularly that of KI at liquid-nitrogen temperature, have been thoroughly studied by other authors^{5,6} but are not yet well understood. In pure and doped KBr and KCl we have seen emissions at about the same wavelength, with a similar temperature dependence but a much lower intensity. These are the 350-m μ emission

⁶ K. Teegarden and R. Weeks, *J. Phys. Chem. Solids* **10**, 211 (1959).

of KBr and the emission of KCl, which lies in the same wavelength range, but has a poorly defined maximum, Fig. 2(a). Similar observations have been reported by Bonanomi and Rossel⁷ on the alkali iodides. Up to now there is agreement in considering the low-temperature emission at 376 mμ in KI and the analogous emission in the other alkali iodides as due to the recombination of free electrons with trapped holes.⁵⁻⁷ Such a mechanism may also account for the occurrence of a similar phenomenon in KCl and KBr. In Fig. 2 we show emissions due to x-ray irradiation of KI, KBr, and KCl doped with the corresponding copper halide, at room temperature and liquid-nitrogen temperature. A comparison with the emissions shown in Fig. 1 shows that

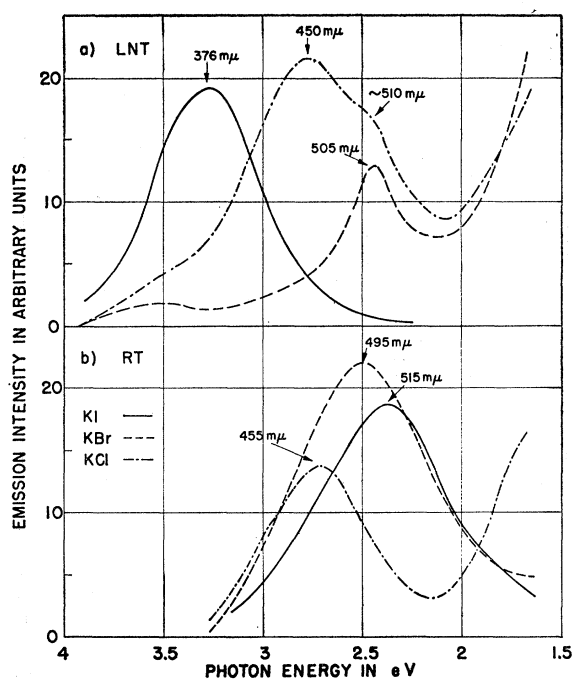


FIG. 1. Emission spectra of "pure" KI, KBr, and KCl at room temperature (RT) and liquid-nitrogen temperature (LNT) under x-ray irradiation. (The scale for KI at LNT should be multiplied by 20.)

the possibility exists, particularly for the room-temperature emissions, that the latter are a mixture of two bands: one due to an emitter connected with the Cu impurity, the other due to O₂⁻ which has various peaks at about 2.5 eV, as shown by Rolfe *et al.*³

In Fig. 2 the emission at liquid-nitrogen temperature of KI is not shown because the 376 mμ emission is so strong that it does not permit the analysis of other bands even if the band peak is at a very different wavelength.

In Figs. 1 and 2, and also in Fig. 6, we see the tail of a red luminescence. We hope soon to extend the sensitivity of our detection system up to 1.1 μ, in order to study this red luminescence.

⁷ J. Bonanomi and J. Rossel, *Helv. Phys. Acta* **25**, 725 (1952).

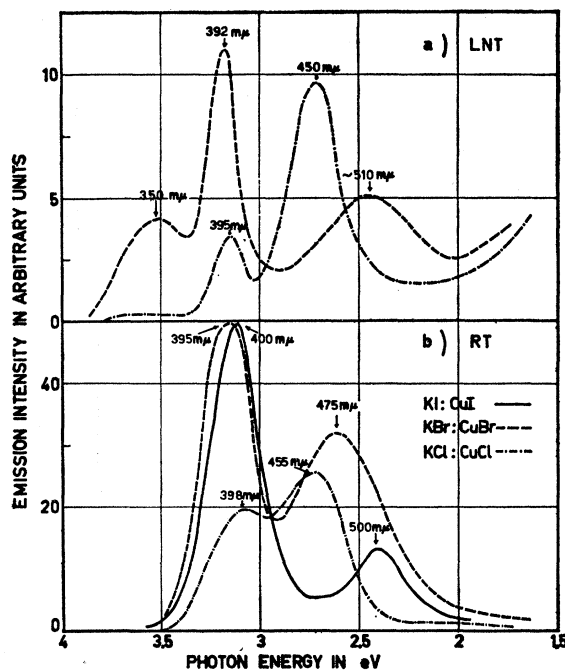


FIG. 2. Emission spectra of KI:CuI, KBr:CuBr, and KCl:CuCl at RT and LNT under x-ray irradiation.

Bands at about 400 mμ have been studied before.^{1,3,8} In the present investigation it was found that for the ~400-mμ x-ray stimulated emission, the efficiency of the radiative process decreases as the temperature is lowered; on the other hand with uv excitation, the

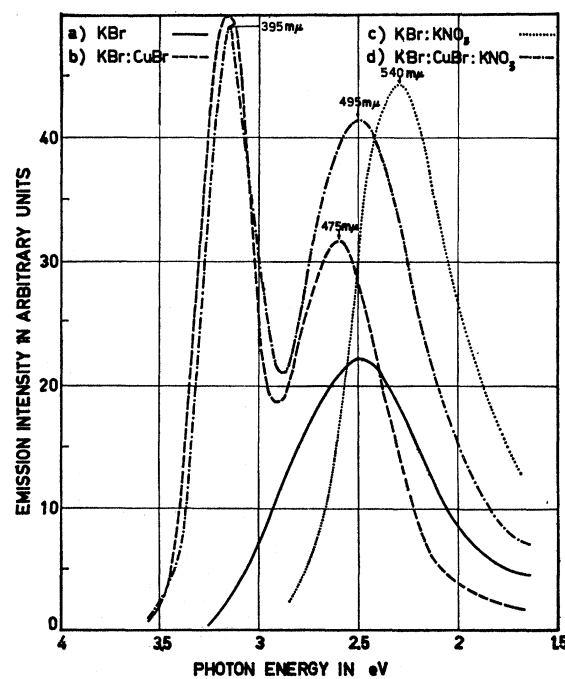


FIG. 3. Emission spectra of pure KBr, KBr:CuBr, KBr:CuBr:KNO₃, and KBr:KNO₃ at RT under x-ray irradiation.

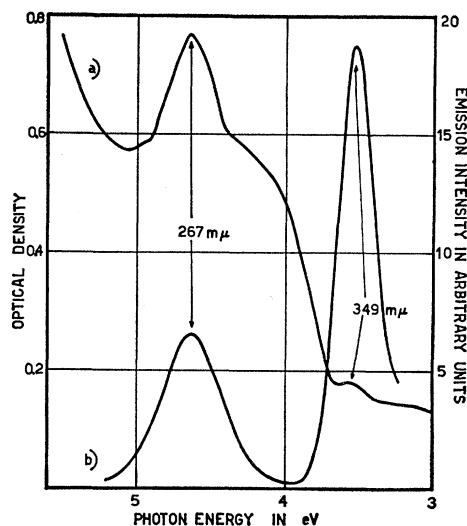


FIG. 4. KBr:CuBr—curve (a): absorption at RT (thickness of the specimen=5.28 mm); curve (b): excitation spectrum at RT (emission observed with an interference filter centered at 418 $m\mu$ and of half-width of 10 $m\mu$).

efficiency of radiative process goes up as the temperature decreases.¹ Under x-ray excitation the same thing happens to the emissions at 500, 475, and 455 $m\mu$ of KI, KBr, and KCl, respectively.

Since we cannot eliminate the band at 510 $m\mu$ in KBr and as the emission which peaks at 376 $m\mu$ at liquid-nitrogen temperature in KI overlaps the other bands, we can only observe the behavior of the 455- $m\mu$ emission at low temperatures for KCl.

In Fig. 3 the emission spectra of "pure" and doped crystals of KBr are given. The doping with³ KNO_3 and CuBr has the effect of introducing oxygen and Cu impurities, respectively. The fact that the position of the maximum of the band in pure KBr ranges from 480 to

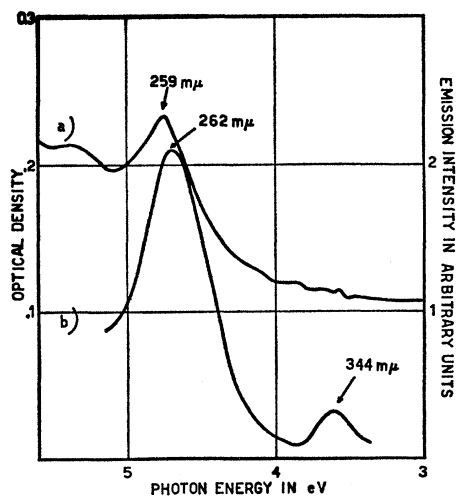


FIG. 5. KCl:CuCl—curve (a): absorption at LNT (thickness of the specimen=3.4 mm); curve (b): excitation spectrum at RT (emission observed with an interference filter centered at 402 $m\mu$ and of half-width of 25 $m\mu$).

505 $m\mu$ at room temperature, depending on the origin of the crystals, appears to rule out the possibility of a single center luminescence, particularly as concentration effects should be unimportant. For this reason, we believe that the band at 495 in "pure" KBr was in effect a mixture of a band due to oxygen and one due to an emitter connected with the Cu. The emission at 395 in Cu-doped KBr which is typical of^{1,3} Cu^+ is not observed in the undoped sample. The reason for this seems to be that the Cu^+ has a great tendency to precipitate and produce optically inactive clusters.³ It would appear, therefore, that by the time the "pure" aged crystals were examined such a process had occurred.

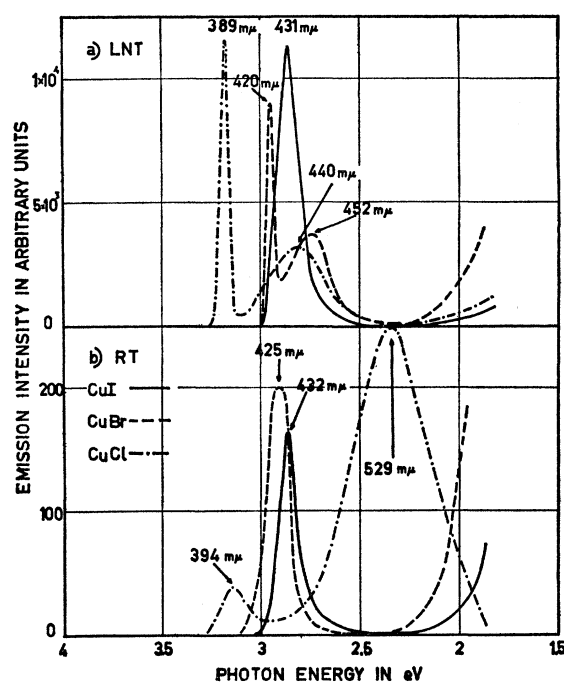


FIG. 6. Emission spectra of CuI, CuBr, and CuCl at LNT (a) and RT (b). For CuI the scale should be multiplied by 10 at RT and by 3 at LNT.

In Figs. 4 and 5 the absorption and excitation spectra of KBr:CuBr and KCl:CuCl are shown; for KBr:CuBr, in particular, the correspondence between two absorption and two excitation bands is evident. In Fig. 5 the shift between absorption and excitation maxima of the band at higher energy is due to the fact that curve (a) was taken at liquid-nitrogen temperature to allow better resolution of the bands.

Further, KBr:CuBr was excited between 5 and 3.2 eV and the luminescence was examined between 400 and 500 $m\mu$ with eight interference filters: we have established that substantially the excitation band at 267 $m\mu$ excites only 395 $m\mu$ emission and the excitation band at 349 $m\mu$ excites, in the range 400 to 500 $m\mu$, two bands that correspond to the two emission bands at 395 and

⁸ H. Leutz and H. Muuss, Z. Physik 155, 531 (1959).

(475 ± 10) $m\mu$. Excitation with F light at room temperature (interference filter with a maximum at 641 $m\mu$ and half-width 14 $m\mu$ together with the tungsten lamp) gave for a crystal of KBr:CuBr, colored for 30 min with x rays (40 kV, 40 mA), an emission curve very similar to that of KBr:CuBr [Fig. 2(b)] with well defined maxima at 395 and 475 $m\mu$.

In Fig. 6 the x-ray-excited emission spectra at room temperature and liquid-nitrogen temperature of CuI, CuBr, and CuCl used in the doping of alkali halides are given.

DISCUSSION

Little information about x-ray-induced luminescence in pure alkali halides is available in the literature, particularly with reference to the nature of the emitters and radiative processes. Various emissions have been assigned as being due to recombinations of free and trapped carriers near lattice defects.

From the present measurements it appears that the number of x-ray-induced emissions due to defects of pure crystals is restricted. From observation of x-ray-induced emission spectra of "pure" alkali halides, we see some poorly resolved bands that can be enhanced by thermal treatment, or by suitable dopings; in thermoluminescence the same emission bands appear in various glow peaks and are also greatly influenced by thermal treatments.

The present results seem to suggest that in the case of thermal treatment the effect is often merely an introduction of oxygen, copper and possibly other activators or a dispersion of clusters of activators already present in the crystal. A discussion of these effects, mainly in connections with the emissions at ~ 400 $m\mu$, is given in Ref. 1.

Our interest was mainly centered on a band that we now think is to be attributed to a Cu center not yet clearly identified; this band is at 455 $m\mu$ in KCl, 475 $m\mu$ in KBr, and 500 $m\mu$ in KI.

The role of Cu is essential for the presence of this emission band as is shown from Figs. 2, 3, and also from the spectral analysis of the light emitted during the excitation measurements. The energy absorbed at 349 $m\mu$, Fig. 4 is re-emitted at 395 $m\mu$ due to Cu^+ and at 475 $m\mu$ (in KBr). However, we do not think that a second transition of the Cu^+ is involved because with different dopings the ratio of intensities of the 395 to 475 $m\mu$ emission band in KBr is not constant; further, on x-ray irradiation at room temperature, the emission intensities of these bands decrease with different rates.

No definite conclusion can be reached at this time concerning the identity of the Cu center responsible for the 475 $m\mu$ emission in KBr and the analogous emissions in KI and KCl; however, some possibilities can be suggested. It may be a Cu^+ near a lattice defect or an impurity ion. The importance of oxygen or halides in the occurrence of Cu green centers in ZnS and CdS is well known.²

Returning to the significance of the excitation measurements, we feel that the emission at 475 $m\mu$ as a result of the energy absorbed at 349 $m\mu$ by a transition of Cu^+ (the absorbed energy can also be emitted at 395 $m\mu$) occurs as a direct re-emission by a modified Cu^+ center, say a Cu^+ plus an ion vacancy. Alternatively, a process in which energy transfer occurs from the Cu^+ to a neighbor impurity ion, where the radiative transition then occurs, is possible. A similar mechanism has been proposed for the Cu centers in ZnS and CdS.²

However, it seems that further work is required to clarify this point.

We think that our results throw some light on measurements of other workers. In particular, we believe that the bands at 2.63 eV in⁸ KBr and⁹ 2.67 eV are identical and cannot be attributed to lattice imperfections in the same way as F and V centers, but rather occur because of impurities.

The luminescence stimulated by irradiation in the F band shows that the emissions at 395 and 475 $m\mu$ in KBr are due to free electrons which, after being trapped near certain impurities, make a transition typical of the impurity, and this (as regards 395 $m\mu$ emission) is in contrast with previous conclusions.¹⁰

Further, the excitation band of these photostimulated emissions coincides with the F band, as shown by Camagni and Chiarotti.¹¹ The latter workers did not observe the spectral distribution of the emitted light.

Good agreement also exists with the experimental data of Spicer,¹² who studied the $h\nu_F$ photostimulated emission in NaCl, specifically in connection with the ~ 3.5 -eV emission which was shown in an earlier paper¹ to have the same origin as the 395 $m\mu$ of KBr. A paper of Timusk and Martienssen has appeared recently¹³ and another on the α -band luminescence is to be published soon. These papers report recombination emissions and α -band emissions in KCl and KBr which are, within experimental error, at the same wavelength as the emissions reported in this paper. This seems like a remarkable coincidence, and further work should be directed toward understanding these separate phenomena, if they are really different.

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⁹ G. Bonissoni, P. Camagni and G. Chiarotti, in Proceedings of the International Conference on Color Centers and Crystal Luminescence, Turin, 1960 (unpublished).

¹⁰ A. Halperin, A. A. Braner, M. Schlesinger, and N. Kristianpoller, in Proceedings of the 1962 International Conference on Semiconductor Physics, Prague, 1960 (Academic Press Inc., New York, 1961), p. 16.

¹¹ P. Camagni and G. Chiarotti, Internationales symposium über farbzentren in alkalihalogeniden, Stuttgart, 1962 (unpublished).

¹² W. E. Spicer, Phys. Rev. **106**, 727 (1957).

¹³ T. Timusk and W. Martienssen, Phys. Rev. **128**, 1657 (1962).