Rayne[8] who finds no evidence of breakdown in fields of less than about 1.5 kG.

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PHOSPHORESCENCE IN ALKALI HALIDES CONTAINING LATTICE DEFECTS*

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In studying Tl-activated KI and KBr[1] and undoped KI, KBr, and KCl,[2] we have observed effects, commonly attributed to internal metastable states of Tl,[3] in specimens containing essentially no Tl at all. The results reported here lead us to believe that the traps which play a major role in energy storage and infrared stimulability in impurity-activated alkali-halide phosphors are characteristic of the undoped host crystal.

After x-ray excitation at 5 or 78°K the Tl-doped crystals store energy in the form of filled electron traps associated with the impurity, and of self-trapped holes such as I_2^- molecule-ions[1,4] associated with the pure host crystal (KI), and possibly other centers not observed by spin-resonance or optical-absorption techniques. This energy can later be released as light by either optical or thermal means. Characteristic glow peaks[5] occur at temperatures at which these centers disappear. Similar glow peaks, processes, and metastable states have been discovered in undoped crystals which have been plastically deformed at pressures of about 10^8 kg/m^2.

Figure 1 shows the glow curves of strained and of well-annealed KCl and of KCl:Tl. The major glow peak at about 228°K in the undoped-but-strained crystals is associated with the disappearance of Cl_2^- and unidentified electron centers; this same phenomenon occurs in KCl:Tl at a slightly lower temperature.[4] The approximate glow-peak temperature of plastically deformed KBr and of KBr:Tl is 185°K, and of plastically deformed KI and of KI:Tl, 110°K.

Figure 2 shows the major optical absorption, due to Br_2^-, in undoped KBr which has been plastically deformed and also in well-annealed KBr:Tl. Also shown is the optical-absorption band of Cl_2^- observed in undoped KCl which has been deformed and in KCl:Tl.[4] In both cases it may be seen that the same curves are obtained for deformed and doped crystals. In strained KCl and KBr these trapped hole and certain electron centers[6] seem to be produced in pairs. These effects do not occur to any significant extent in pure crystals containing few lattice defects.

It has been shown that the maximum rate of dis-

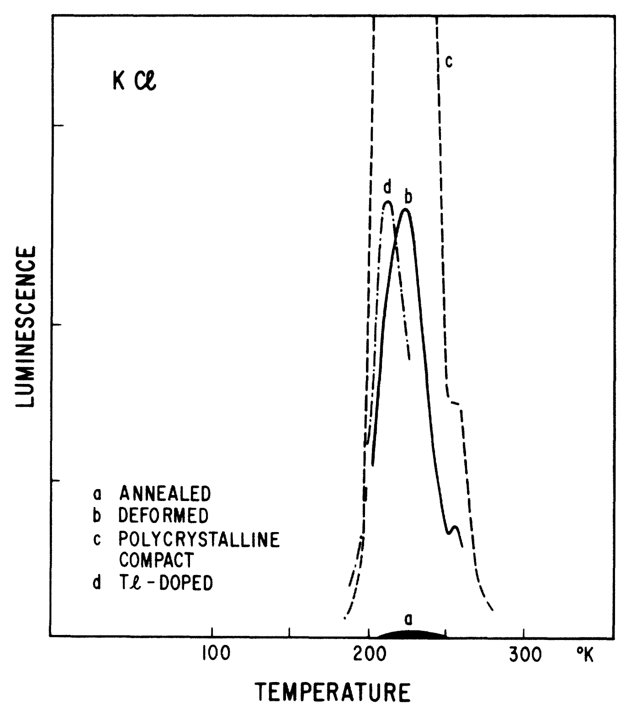

FIG. 1. Thermal glow curve of nominally pure KCl in different mechanical states and of KCl:Tl.

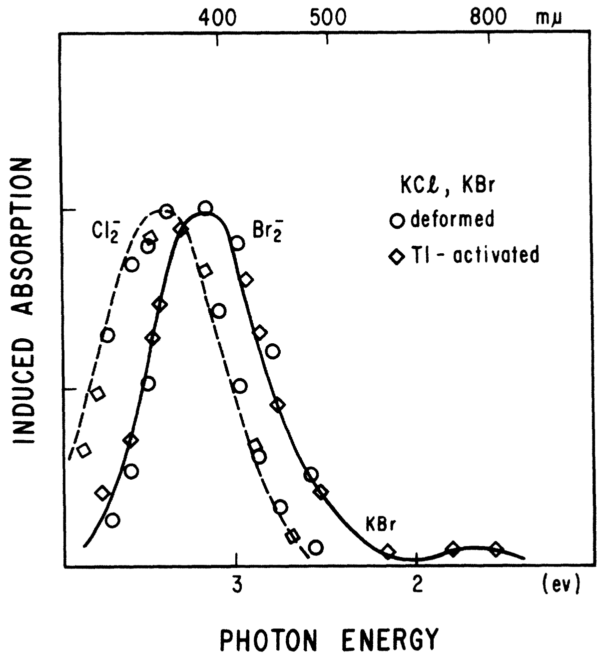

FIG. 2. Optical absorption of trapped holes in undoped KCl and KBr which have been plastically deformed and in thallium-doped crystals not subjected to plastic deformation.

appearance of halogen molecule-ions (V_K centers) coincides with the first glow peak in Tl-activated[1] and other doped alkali halides[4]; this also occurs in undoped (but strained) crystals. This indicates that the excited state is not directly associated with a specific impurity (since these crystals have no appreciable Tl content) but is connected in some manner with the host crystal. This concept was first proposed in connection with the phosphorescence properties of KI:Tl.[1] The following additional facts pertaining to deformed crystals further support this view: (1) As may be seen from Fig. 1, well-annealed undoped crystals give rise to insignificantly small (and usually variable) glow peaks as compared to plastically deformed crystals; (2) as compared with well-annealed undoped crystals the nature of the hole centers is changed qualitatively, and in the same way, by both lattice defects and impurities (V_K and not V_1 centers); (3) the rate of formation of V_K centers is enhanced in undoped (but strained) crystals in the same way as in doped crystals.[7] Since the glow peak is associated with the thermal release of V_K (hole) centers and other electron centers responsible for characteristic optical and magnetic absorption, this rate-controlling process appears to be indifferent to the details of the internal electronic structure of any impurity such as Tl except insofar as the excess energy may be radiatively released (e.g., when a hole encounters an electron trapped at or near an impurity).

Further information has been obtained by examining the infrared stimulability of these salts. Irradiation of a crystal in the metastable state using 1- to 2-μ radiation gives rise to stimulated emission in the visible in Tl-activated crystals. If lattice defects are responsible for storing energy, it might be expected that an undoped crystal (which is not IR-stimulable) could be rendered IR-stimulable merely by mechanically generating lattice defects in it. This was done for undoped KI, KBr, KCl, and NaCl with positive results: IR-stimulability comparable in some cases to that of the most active Tl-containing phosphors was observed.

Tl-activated alkali halides are classical luminescent systems.[3,8] At the time of inception of the Seitz theory[8] the dominant experimental observation was the similarity of the Tl absorption bands in different alkali-halide hosts. The dominant theme in the present results is the similarity between impurity-activated phosphors and the present "imperfection-activated" crystals. From the foregoing it seems that internal metastable states of the impurity are not important and that structural defects of the host crystal play a role in phosphorescence which must be taken into account in any valid theory.

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