Cooling luminescence in cesium iodide*

Robert A. Reitz and Bruce R. Thomas

Carleton College, Northfield, Minnesota 55057

(Received 21 July 1975)

In most studies of thermoluminescence in alkali halides following treatment with ionizing radiation, it is assumed that sweeping the temperature through a given interval completely empties all of the traps associated with that interval, so that there will be no further luminescence in that temperature range until the sample is again irradiated. We have discovered that warming a CsI crystal which has been x-rayed at liquid-nitrogen temperature does not completely erase the luminescence. Further luminescence during a subsequent cooling and again on rewarming through the same interval is readily observable, although much weaker than the original thermoluminescence. Bleaching with visible light at 300°K or warming to 380°K, which releases more thermoluminescence, is sufficient to wipe out the luminescence during subsequent temperature cycles. It appears that the cooling luminescence is a form of deformation luminescence, in which some still-filled traps are emptied by dislocations moving as a result of thermal contraction of the crystal.

I. INTRODUCTION

In the course of studying thermoluminescence (TL) of x-rayed CsI crystals we have discovered that the crystals also luminesce upon cooling. This same cooling luminescence (CL) is also present in CsBr and CsCl and to a much smaller extent in the other alkali halides we have investigated. It appears that the luminescence is a form of deformation luminescence associated with mechanical strains that occur during cooling. This paper will be concerned mainly with a description of the phenomena associated with the CL in CsI since we have not yet investigated other crystals thoroughly.

II. DESCRIPTION OF THE EFFECT

If a CsI crystal is warmed following x-raying at liquid-nitrogen temperature it exhibits thermoluminescence as shown in Fig. 1(a). (Our measurements differ in some details from previously reported work using α and β radiation to excite the CsI.[1]) The behavior is similar to that of the other alkali halides, viz., luminescence during the warming portion of the cycle that disappears at sufficiently high temperature and no luminescence during the cooling portion.

But if the warming is interrupted at an intermediate temperature and the crystal cooled, it luminesces as in region B of Fig. 1(b). We call this cooling luminescence. It has not been previously reported in the literature.

When the crystal is subsequently warmed following the CL it luminesces again [region C of Fig. 1(b)]. We believe that this is regular thermoluminescence due to the same processes as in region A which have been restimulated during the cooling, e.g., by photostimulation due to self-absorption of some of the CL, or by electrons released into the conduction band as part of the

CL process. The strongest peaks in region A are still perceptible in region C although their magnitudes are significantly reduced. Continu-
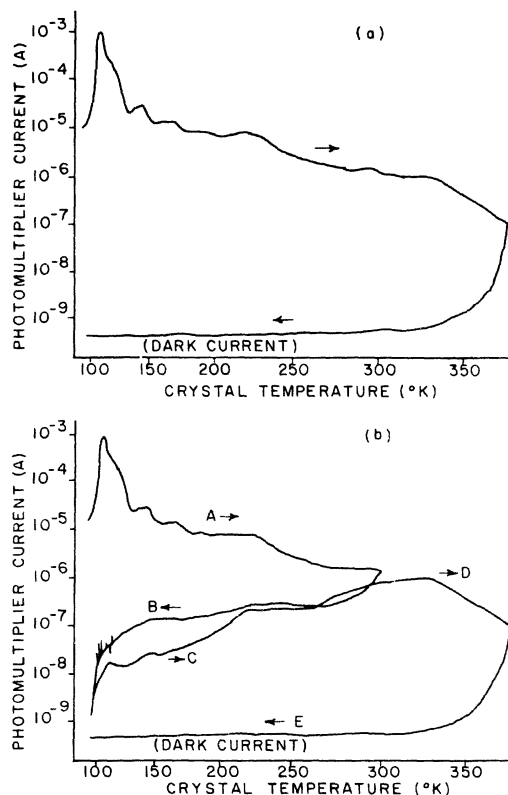

FIG. 1. Photomultiplier current due to luminescence of x-rayed CsI crystal during thermal cycling. The arrows show the time evolution of the curves. (a) Normal cycle. (b) Interrupted cycle. Regions A, D, and E are identical to corresponding portions of (a). Region B shows the cooling luminescence. Region C shows the restimulated thermoluminescence.

ing the warming (region D) produces further TL due to the original x raying. This finally disappears at about 380°K. A final cooling (region E) shows no detectable luminescence.

III. EXPERIMENTAL DETAILS

The phenomenon has been observed in a number of nominally pure CsI crystals from different suppliers.[2] Samples were approximately $1 \times 10 \times 10$ mm and were clamped to a copper plate which was part of a temperature control head of a cryostat. Various greases and adhesives were used to provide thermal contact between crystal and copper.[3] Generally, the effect was enhanced by preheating the sample in air to 500°C for 10 min followed by rapid cooling to room temperature.

The samples were placed in an evacuable cryostat, equipped with an aluminum foil entrance window for the x rays, and a quartz exit window for the luminescence. X-ray exposures were provided by a molybdenum target operated at 50 kV, 20 mA for 1 min. Luminescence was measured with an EMI 9558 QA photomultiplier operated at 1500 V. The rate of heating and cooling was 1–2°K/sec.

IV. DISCUSSION

The cooling luminescence may be a direct result of mechanical effects associated with thermal contraction of the crystal. There are a number of indications that it is strongly dependent upon mechanical influences. The CL is only readily observable at temperatures where the bonding agent is solidified, e. g., below 230°K for Dow-Corning silicone grease, below 270°K for Apiezon-N, at all temperatures for the epoxies (as in Fig. 1). In the low-temperature portion of the cooling process [see region B of Figure 1(b)] pulses of light are occasionally emitted that may be due to sudden mechanical relaxations in the crystal. Further pulses can be induced by tapping lightly on the cryostat as the crystal cools or after it has reached liquid-nitrogen temperature. There is often a significant drop in the intensity of the continuous glow following both the regular pulses and the induced ones.

It appears that the cooling luminescence depends on the presence of a defect that becomes thermally unstable above room temperature, possibly the same one that produces the thermoluminescence in the region from 300 to 380°K. The CL decreases monotonically with increasing turnaround temperature and disappears completely if the crystal is heated to 380°K before cooling. Further x raying at liquid-nitrogen temperature restores both the TL and the CL. Both effects show some growth with repeated x raying. The CL can also be reduced by bleaching with visible

light at the turn-around temperature prior to cooling. The effectiveness of the bleaching light seems to peak at the known position of the F band in CsI, about 7200 Å.[4,5] (We were not able to detect any absorption in our crystals by direct measurement, which is consistent with previously reported work.[4,5]) It is possible to make several cycles similar to B and C of Fig. 1(b) following a single x raying by gradually raising the turnaround temperature to allow some strong TL before each cooling. The CL increases with increasing TL, but saturates rather quickly. In turn, the restimulated TL in region C seems to scale with the immediately preceding CL. Our measurements indicate that the total light output (integral of photomultiplier current with respect to time) associated with cooling through any temperature interval is independent of the rate of cooling. If the cooling is halted and the temperature held constant, the luminescence disappears abruptly and reappears when the cooling is reinitiated. Furthermore, if the cooling is interrupted and the crystal heated slightly, but not enough to produce TL, and then cooled there is no CL until the temperature passes below the previous minimum, at which point it turns back on abruptly.

The phenomena described in the two preceding paragraphs closely parallel the luminescence produced by KCl and KCl:Cu crystals subjected to elastic deformation as reported by Senchukov and Shmurak.[6] They colored crystals with x or γ radiation and deformed them by direct mechanical means. They observed a luminescence with a spectrum characteristic of the known combination centers (Cu^+) and accompanied by a decrease in F-center concentration as determined by optical absorption measurements. They conclude that the "deformation luminescence" is a result of mobile dislocations interacting with F centers to release electrons which subsequently recombine with holes at luminescence centers. Their mechanism also explains the "memory effect,"[7] whereby a once-deformed crystal does not luminesce again until the deformation exceeds the previous amount, since the dislocations move back and forth along the same paths and therefore do not encounter any new F centers until the deformation exceeds the previous maximum. We feel that the behavior of our crystals when the cooling is interrupted as described in the preceding paragraph is explained by this same mechanism.

V. FURTHER EVIDENCE

A convincing demonstration that the effect is in the crystal and not just an instrumental aberration is provided by a direct visual observation of the phenomenon. We have accomplished this in

a darkened room by holding a crystal in a pair of forceps, dipping it in liquid nitrogen, then exposing it to about 10 sec of x rays or light from an iron spark (rich in uv) before it can warm appreciably. As the crystal warms to room temperature a succession of thermoluminescent peaks are readily visible to the dark-adapted eye. This luminescence disappears if the warming is interrupted by holding the crystal in the vapor above the liquid nitrogen. When an edge of the crystal is slowly dipped again into the liquid nitrogen, a pronounced cooling glow is observed to move across the crystal slab. Numerous successive cycles produce visible warming and cooling glow without further irradiation. The initial thermoluminescent peaks are blue-violet in color. The color of the higher temperature warming glow and the cooling glow appears to shift toward the green, but the eye is not capable of reliable color differentiation at these low light levels. Measurements with interference filters and the photomultiplier tube indicate the cooling luminescence is largest between 5000 and 6000 Å, but extends over a wide range.

The cooling luminescence may be significant influence in two investigations. Paracchini,[8] in studying electroluminescence of CsI, observes an "initial flash" upon the first application of the electric field each time the crystal is cooled from room temperature to liquid-nitrogen temperature. As described previously, we can induce such a flash in a cooled crystal by a mild mechanical shock. Panova and Shiran[9] study the "prolonged

afterglow" present in x-rayed CsI: Na crystals which are quickly cooled from the region of strong thermoluminescence. They attribute the glow to color centers relaxing via tunneling transitions, but it seems likely that part of the glow is due to cooling luminescence.

The mechanism we propose to explain the cooling luminescence, viz., deformation luminescence driven by the contraction of the crystal during cooling, is not specific to CsI. In an attempt to correlate the TL and CL with accompanying changes in optical absorption, we have also made a number of measurements with CsBr which, in contrast to CsI, is readily colorable with x rays. Essentially, identical effects as those described above are observed in CsBr. CL is observed as long as there are F centers present in the crystal. However, the mere presence of F centers is not enough. For example, even if a crystal of CsBr is irradiated sufficiently at room temperature to produce a pronounced F-band absorption, no CL is observed on cooling to liquid nitrogen temperatures. Evidently there are no trapped holes at luminescence centers with which the released electrons can recombine.

ACKNOWLEDGMENTS

*Research supported in part by a Cottrell College Science Grant from Research Corp.

[1]A. A. Persinen, I. A. Vasil'ev, V. A. Shibaev, M. I. Mochenov, and B. T. Plachenov, Izv. Akad. Nauk SSSR Ser. Fiz. 33, 1050 (1969) [Bull. Acad. Sci. USSR Phys. Ser. 33, 971 (1969)].

[2]Harshaw Chemical Co., Semi-Elements, Inc., Univ. of Utah Crystal Growth Lab.

[3]Dow-Corning silicone grease, Apiezon-N, Techkits T-44, Devcon 5-minute Epoxy, Scotch Epoxy Adhesive.

[4]R. K. Dawson and D. Pooley, Phys. Status Solidi 35, 95 (1969).

[5]P. Avakian and A. Smakula, Phys. Rev. 120, 2007 (1960).

[6]F. D. Senchukov and S. Z. Shmurak, Fiz. Tverd. Tela 12, 9 (1970) [Sov. Phys.-Solid State 12, 6 (1970)].

[7]F. D. Senchukov and S. Z. Shmurak, Fiz. Tverd. Tela 14, 1551 (1972) [Sov. Phys.-Solid State 14, 1336 (1972)].

[8]C. Paracchini, Phys. Rev. B 7, 1603 (1973).

[9]A. V. Panova and N. V. Shiran, Opt. Spectrosk. 32, 212 (1972) [Opt. Spectrosc. 32, 108 (1972)].