J. Phys. Chem. Solids Pergamon Press 1963. Vol. 24, pp. 135–139. Printed in Great Britain.

SOME OPTICAL PROPERTIES OF IODINE SINGLE CRYSTALS

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(*Received* 29 *June* 1962)

Abstract—The absorption edge of iodine single crystals shifts in the direction of longer wavelengths with increasing temperature: $-8{\cdot}3 \times 10^{-4}$ eV/degree between liquid air (L.A.T.) and room temperatures (R.T.). Specular reflectivity in the region of strong absorption shows a structure similar to the photoconductivity response curve. The refractive index is about 2 as calculated from the reflectivity in the infrared. Weak thermoluminescence glow peaks in the visible were obtained after irradiation with X-rays at L.A.T. The peaks at 105°K and 172°K have thermal activation energies of about 0·11 and 0·13 eV.

INTRODUCTION

IODINE single crystals were the subject of intense research in this department during the past few years.[1, 2] These crystals, although molecular, show interesting semiconducting properties and it was found that the phenomenological behaviour of iodine is not fundamentally different from that of other covalent or ionic crystals. The results of the photoconductivity measurements[1] stimulated this study of the optical properties of iodine, as the information found in the literature is very scant.[3] Optical work with iodine involves severe experimental difficulties because of the peculiar physical and chemical properties of iodine. The present work reports the results of absorption, specular reflectivity, and thermoluminescence measurements on iodine single crystals.

EXPERIMENTAL

Single crystals were grown from the vapor phase of resublimated iodine (A.C.S. specifications), and are obtained in the form of thin ($\approx 0{\cdot}1$ mm), lustrous plates from which larger samples of 5×10 mm dimensions are selected.

The absorption and thermoluminescence measurements were performed on crystals placed in a vacuum cryostat[4] where they could be cooled to L.A.T. and warmed up to higher temperatures. A Beckman DK spectrophotometer was used for absorption measurements and the thermoluminescence detection system was composed of an EMI 6256B photomultiplier, a Keithley 410 micro-microammeter, and a Brown recorder.

Reflectivity spectra were taken with a special attachment designed to fit the sample compartment of the Beckman DK spectrophotometer (Fig. 1). The "sample beam" from the monochromator is deflected by an evaporated aluminum

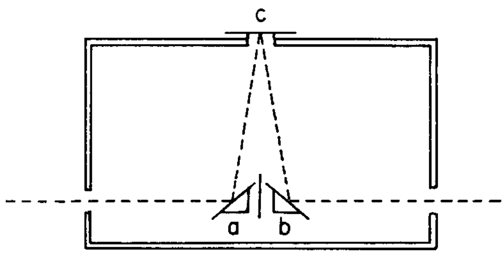

FIG. 1. Reflectance attachment diagram.

surface mirror *a* to nearly normal incidence on the crystal *c*. The reflected beam is brought back into the optical path by mirror *b*. A similar arrangement with a freshly evaporated aluminum mirror or other reference material at *c* in the "reference beam" of the spectrophotometer is not shown in

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Fig. 1. It was found more reliable, however, to compare two successive measurements of reflectance, one with the investigated crystal in the "sample beam" and the other after replacing the crystal by a reference material. The reported reflectivity spectra were calculated from such measurements. Freshly evaporated aluminum films and a polished and etched germanium crystal served as reference materials.[5, 6]

Thermoluminescence was measured in crystals after irradiation with X-rays or u.v. light at L.N.T. as described for other crystals[4,7].

RESULTS

Absorption

Iodine has a broad maximum of absorption in the ultra-violet but is transparent in the infrared.[3] The absorption of crystals was measured from the absorption edge (if we may call it so in a molecular crystal) up to $2{\cdot}5\,\mu$ between L.A.T. and room temperature. An allowance was made for the reflectance. Figure 2 represents the absorption spectra at various temperatures up to $1{\cdot}0\,\mu$, as the absorption is constant at longer wavelengths. The absorption edge is shifted with increasing temperature

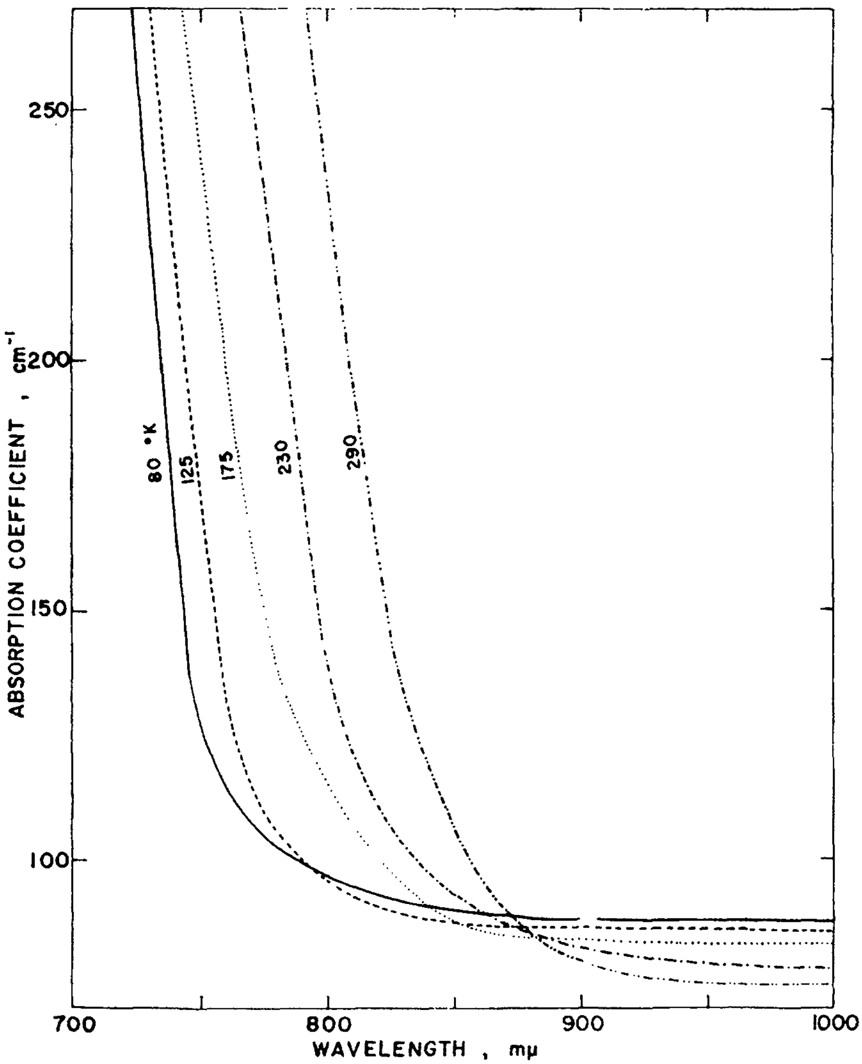

Fig. 2. Absorption of iodine single crystals near the absorption edge at various temperatures.

to longer wavelengths. This shift is illustrated by Fig. 3 for an arbitrarily chosen absorption (170 cm^{-1}). The shift parameter as derived from the straight part of Fig. 3 is $-8{\cdot}3\times10^{-4}$ eV/deg.

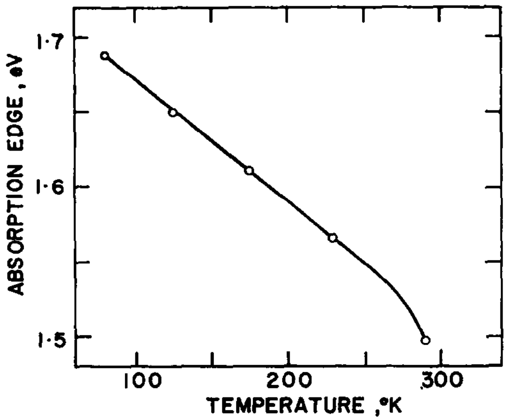

FIG. 3. Shift of the absorption edge with temperature.

Reflectivity

The spectrum of reflectivity was measured at R.T. only and the results are given in Fig. 4. After a steep rise between 220 and 300 mμ there are two maxima in the region of strong absorption at 320 and 460 mμ and a lower maximum near the absorption edge at 900 mμ. Between 1·0 μ and 2·6 μ the reflectivity was constant at 11 per cent. No correction was made for the reflection from the back surface of the crystal as this is not expected to influence the result appreciably and in addition the back surface was generally not parallel to the front one.

In the transmitting region we can obtain the refractive index from reflectance data by using the expression $n = (1+R^{1/2})/(1-R^{1/2}) \approx 2$.

The relative spectral photosensitivity as obtained by MANY *et al.*(1) was replotted in Fig. 4 for purposes of comparison.

Thermoluminescence

The thermoluminescence glow curve, as given in Fig. 5a, was obtained after irradiation of the crystal at L.A.T. with X-rays (35 kVp, 14 mA, Cu-target) for 20 min in the dark. The heating rate was kept constant at 10°/min. The glow was detected with a blue sensitive photomultiplier and was found to be extremely weak; no thermoluminescence was detectable with a red-sensitive photomultiplier. The spectral composition of the glow can be estimated by the use of Wratten Light Filters. The glow measured through Filter No. 4 (λ > 460 mμ) is given by curve *b* and that through Filter No. 23A (λ > 570 mμ) by curve *c*. Filter No. 0 (λ > 300 mμ) transmits most of the glow.

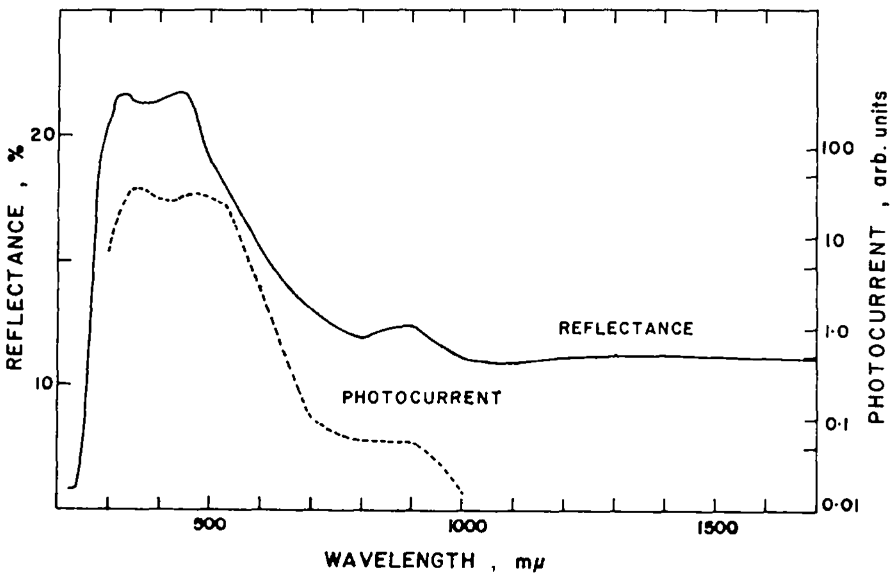

FIG. 4. Specular reflectivity spectrum (solid curve) and relative spectral photosensitivity (dashed curve) in iodine at room temperature.

Comparing the three curves we conclude that the thermoluminescence is composed of one or two spectral bands centered at about 500 mμ.

The rise in the glow curve near R.T. continued up to 320°K when the measurement was discontinued because of the sublimation of the crystal. A very weak thermoluminescence peak was also detected at about 110°K after the irradiation of the crystal with ultra-violet light from a high-pressure mercury vapor lamp.

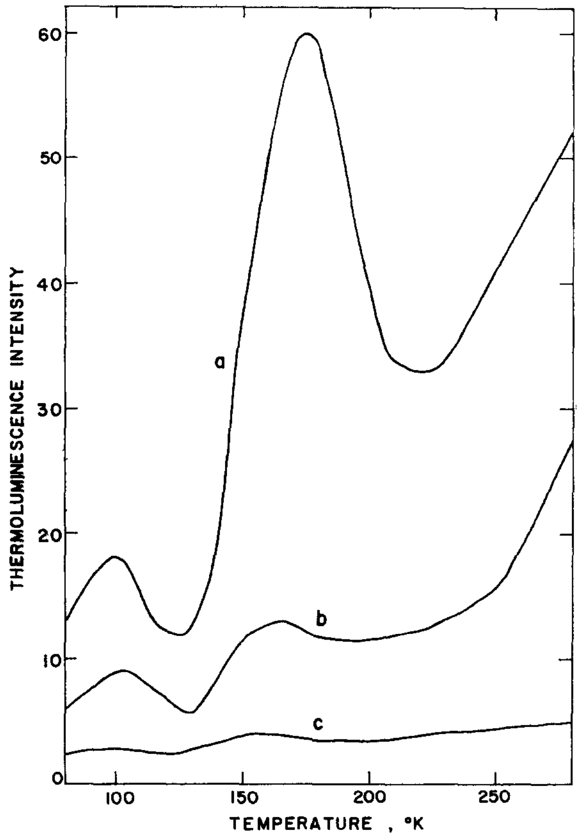

FIG. 5. Thermoluminescence glow curve of an iodine single crystal excited by 20 min of X-irradiation (Cu target, 35 kVp, 14 mA) at liquid air temperature,
a—without filter,
b—transmitted by a Wratten Light Filter No. 4 ($\lambda > 460$ mμ),
c—transmitted by a Wratten Filter No. 23A ($\lambda > 570$ mμ).

No color centers were observed by absorption measurements between the absorption edge and 2·6 μ after X-irradiation at L.A.T.

The thermal activation energies for the two major glow peaks at 105°K and 172°K were evaluated[8] to be about 0·11 and 0·13 eV.

DISCUSSION OF RESULTS

The equipment used in the absorption measurements was insufficient for the study of the detailed structure of the region of high absorption. Both the reflectivity and photoresponse curves (Fig. 4) indicate that structure should be expected.

The shift of the absorption edge as given in Fig. 3 is similar to curves obtained for other semiconducting materials. The shift of $-8{\cdot}0\times 10^{-4}$ eV/deg differs from the result quoted by Moss[3] -15×10^{-4} eV/deg. The latter result was obtained from different measurements by various investigators, so that the results presented here are expected to be more reliable.

The curves of reflectivity and spectral photoresponse in Fig. 4 are strikingly similar. It seems worthwhile to investigate the interrelation of these curves and to check whether the small apparent shift in the position of the two corresponding maxima is due to experimental error or has a physical meaning. The small increase in reflectivity at 850 mμ and the similar behavior of the photocurrent cannot be related only to the penetration of the light beam near the absorption edge into the bulk of the crystal and to the reflectance from its back surface.

In the studies of photoconductivity[1, 2] hole traps were found lying 0·4–0·5 eV above the valence band edge. The shallow traps responsible for the glow peaks in Fig. 5 have an even smaller thermal activation energy and probably differ from those investigated in photoconductivity.

Acknowledgements—The authors wish to thank Professor A. Many and Dr. M. Simhony for stimulating advice and helpful discussions. We are also indebted to Dr. Y. Brada for the use of the reflectance attachment.

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