Color Centers in Cesium Halide Single Crystals*

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(Received August 12, 1960)

Color centers have been investigated in the CsCl-type alkali halides. Cesium chloride, bromide, and iodide single crystals were grown from the melt and CsCl crystals also from solution. Coloration was produced by 130-kev x rays, 3.0-Mev electrons, and by electrolysis. In CsI coloration resulted from electrolysis only. The absorption of uncolored and colored crystals has been measured from 0.175 to 3.5 μ at 25°, 78°, and -190°C. After coloration all three crystals show one strong band in the visible (near infrared for CsI) and several weaker bands at shorter and longer wavelengths, which shift with temperature change. The spectral positions in μm for a number of the bands at -190°C are:

Crystals grown from the melt show deeper and more stable coloration than those grown from solution. The strongest band (λα) behaves similarly to the F band in the NaCl-type alkali halides. The half-width of the band (0.23 ev at -190°C) and its increase with temperature, the shifting of the band maximum toward longer wavelengths upon warming to room temperature (by ~0.08 ev), and the conversion by bleaching with light into other bands support the assignment of this band as the F band. The spectral position of the band maximum approximately follows the Mollwo relation (λ_max = const d^n, where d = interionic distance and n = 2.5).

Bleaching experiments suggest the assignment of the band λ10 as the M band and the bands between the F and M bands as R bands. The origin of the ultraviolet bands is still uncertain.

UP to now, color-center studies have been confined mainly to the face-centered cubic NaCl-type crystals. The present work is extended to the simple cubic CsCl-type alkali halides CsCl, CsBr, and CsI which had been studied only cursorily. In these crystals one would expect relatively small modifications of color centers compared with those in the NaCl-type.

Cesium chloride has been colored previously with electrons, radium rays, and x rays. Radium-irradiated crystals (grown from solution and from the melt) show absorption at 560 μm. Pohl reported the maximum at 600 μm and Jacobs at 603.9±0.7 μm.

The color centers in CsCl are very unstable. In daylight the color fades away in minutes. Bleaching proceeds about 10 times faster than in KCl and about 1000 times faster than in NaCl. Thermal bleaching of CsCl is also faster than in KCl and NaCl. The bleaching properties resemble those of RbCl.

*This work was sponsored by the Office of Naval Research; based on a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Physics at the Massachusetts Institute of Technology.
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GROWTH OF CRYSTALS

Using e.p. grade starting materials, CsBr and CsI crystals were grown from the melt in a Vycor crucible by the Bridgman method (i.e., unidirectional cooling of the melt). Cesium chloride was grown by a double-growth technique because of its transition at 469°C.

The face-centered cubic modification was first grown from the melt, and then the crystal was transformed into the simple cubic phase by repeating the procedure. Cesium chloride crystals were also grown from solution with urea additive. These crystals, however, contained 0.01% NH₄Cl impurity.

The melt-grown crystals of all three salts showed almost no absorption (Fig. 1) except for CsCl which showed a weak band (probably caused by some impurity) at 188 and a still weaker one at 243 μm. For crystals of several millimeter thickness the absorption

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Optical absorption was measured between 0.175 and 3.5 μm with a Beckman DK-1 extended-range spectrophotometer. Since color centers in cesium halides are not very stable at room temperature, the samples were usually irradiated and measured in a special cryostat at dry-ice and liquid-nitrogen temperatures. Hard x rays (130 kv, 9 ma) and 3.0-Mev electrons were used for the coloration.

Photochemical bleaching was carried out by illuminating the colored crystal with the spectrophotometer.

Fig. 1. Ultraviolet absorption of uncolored CsCl, CsBr, and CsI crystals grown from the melt.

Fig. 2. Absorption spectrum of a melt-grown CsCl crystal (4.8 mm thick) after irradiation with 3.0-Mev electrons (dose: 8x10⁹ rad) at -78°C. The dashed curves give the ultraviolet absorption of the uncolored crystal. (*) Impurity band.

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edges for CsCl, CsBr, and CsI are around 175, 210, and 235 μm, respectively. The present values for CsBr and CsI are in agreement with the older data. ¹⁸ ¹⁹


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**ABSORPTION MEASUREMENTS AND COLORATION OF CRYSTALS**
RESULTS

Cesium Chloride

The absorption spectra of a CsCl crystal irradiated at $-78^\circ$C and recorded at $-78^\circ$, $-190^\circ$, and $25^\circ$C are displayed in Fig. 2. The spectrum recorded at $-190^\circ$C shows five new bands at 980, 579, 430, 370, and 270 $\mu$m, and a sixth is indicated at 227 $\mu$m. This last band is quite intense for crystals grown from solution (Fig. 3). The 270-$\mu$m band is much broader than the others. Its half-width of 1.0 ev upon irradiation at $-78^\circ$C, compared to 0.65 ev for irradiation at $-190^\circ$C, indicates the presence of more than one band in this region. When the colored crystal is warmed to room temperature, all bands decrease except that at 227 $\mu$m, and those at 270 and 980 $\mu$m practically disappear (Fig. 4). Very strong electron irradiation ($10^4$ rad) produces additional bands (Fig. 5). Table I lists the spectral position of color-centered band maxima and half-widths of the bands for CsCl.

![Absorption spectrum of a melt-grown CsCl crystal (4.8 mm thick) after irradiation with 3.0-Mev electrons (dose: 8 $\times$ 10$^4$ rad) recorded at $-190^\circ$C. (a) directly after the irradiation, (b) after warming to 25$^\circ$C and recooling to $-190^\circ$C. (*) Impurity band.

![Absorption spectrum at $-190^\circ$C of a CsCl crystal (3.15 mm thick) grown from the melt after irradiation with 3.0-Mev electrons (dose: 10$^4$ rad) at $-78^\circ$C. The dashed curve gives the absorption prior to irradiation.](image)

### Table I. Spectral position of color-center absorption band-maxima and their half-widths for CsCl.

<table>
<thead>
<tr>
<th>Temperature, $^\circ$C</th>
<th>Position of the maxima* ($\mu$m)</th>
<th>Half-widths of the bands$^b$ (ev)</th>
<th>Temperature, $^\circ$C</th>
<th>Half-widths of the bands$^b$ (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-190^\circ$</td>
<td>227</td>
<td>229</td>
<td>231</td>
<td>3.3</td>
</tr>
<tr>
<td>$-78^\circ$</td>
<td>227</td>
<td>229</td>
<td>231</td>
<td>3.3</td>
</tr>
<tr>
<td>$+25^\circ$</td>
<td>227</td>
<td>229</td>
<td>231</td>
<td>3.3</td>
</tr>
<tr>
<td>$-190^\circ$</td>
<td>579</td>
<td>579</td>
<td>590</td>
<td>603</td>
</tr>
<tr>
<td>$-78^\circ$</td>
<td>579</td>
<td>579</td>
<td>590</td>
<td>603</td>
</tr>
<tr>
<td>$+25^\circ$</td>
<td>579</td>
<td>579</td>
<td>590</td>
<td>603</td>
</tr>
<tr>
<td>$-190^\circ$</td>
<td>855</td>
<td>855</td>
<td>860</td>
<td>603</td>
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<tr>
<td>$-78^\circ$</td>
<td>855</td>
<td>855</td>
<td>860</td>
<td>603</td>
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<td>603</td>
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<td>$-190^\circ$</td>
<td>980</td>
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<td>1000</td>
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<td>980</td>
<td>980</td>
<td>990</td>
<td>1000</td>
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<tr>
<td>$+25^\circ$</td>
<td>980</td>
<td>980</td>
<td>990</td>
<td>1000</td>
</tr>
</tbody>
</table>

* Average uncertainty is between 1 and 5 $\mu$m depending on the intensity, position, and half-width of the band. There are also bands at 1325 and 1675 $\mu$m at $-190^\circ$C.

$^b$ Average uncertainty is 10 to 15%.

Parentheses signify indication only.

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tungsten (or hydrogen) source (with a slit opening of about 1 mm).

Cesium iodide could be colored by electrolysis only. Up to 2500 volts were applied to the crystal (at $\sim$400$^\circ$C) and a half-megohm current-limiting resistor. A platinum electrode, a set of point electrodes, or an edge electrode was used as the cathode. The crystal was held against a carbon anode with a platinum-rhodium tension clip which also applied the voltage to the cathode. The crystals were quenched in a stream of dry nitrogen.

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**Fig. 3.** Absorption spectrum at $-78^\circ$C of a CsCl crystal (1.67 mm thick) grown from a water solution with 10% urea additive after irradiation with x-rays (130 kV, 9 ma) for 44 hours at $-78^\circ$C. The dashed curve represents the absorption prior to irradiation. (*) Impurity bands.
widths for CsCl. Crystals grown from the melt colored more deeply than those grown from solution (Fig. 6).

The most prominent band, at 603 mp, can be bleached by exposing the crystal to light in its spectral region. The band at 370 mp is also affected but not that at 231 mp. At −78°C the 990-mp band increases during the initial bleaching of the 590-mp band (at 603 mp at room temperature); it then decreases while other long-wavelength bands increase slowly but continuously.

Cesium Bromide

As in CsCl, CsBr crystals were colored with x rays and electrons, mostly at −78°C, and some by electrolysis.

The absorption spectrum of colored CsBr (Fig. 7) is similar to that for CsCl (Fig. 2). Again the broad ultraviolet band (at 315 mp) and the infrared band

<table>
<thead>
<tr>
<th>Position of the maxima a (mp)</th>
<th>Half-widths of the bands b (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C</td>
<td>Temperature, °C</td>
</tr>
<tr>
<td>−190° −78° +25°</td>
<td>−190° −78° +25°</td>
</tr>
<tr>
<td>λ1 241</td>
<td>H1 0.25</td>
</tr>
<tr>
<td>λ2 ~270°</td>
<td>H2 0.3</td>
</tr>
<tr>
<td>λ3 ~315°</td>
<td>H3 0.5</td>
</tr>
<tr>
<td>λ4 390 (400)d</td>
<td>H4 0.35</td>
</tr>
<tr>
<td>λ5 480 ~400</td>
<td>H5 0.20</td>
</tr>
<tr>
<td>λ6 645 ~662</td>
<td>H6 0.28</td>
</tr>
<tr>
<td>λ7 (780)</td>
<td>H7 0.32</td>
</tr>
<tr>
<td>λ8 840 (850)d</td>
<td>H8 0.32</td>
</tr>
<tr>
<td>λ9 (~930)d (~980)d</td>
<td>H9 (0.1)d</td>
</tr>
<tr>
<td>λ10 1055 ~1065 ~1070</td>
<td>H10 0.04 0.06</td>
</tr>
</tbody>
</table>

a Average uncertainty is between 1 and 5 mp depending on the intensity position, and half-width of the band.

b Average uncertainty is 10 to 15%.

In Table II the position and half-widths of the absorption bands for CsBr grown from a water solution are listed.

Fig. 6. Intensity of the most prominent band (at 590 mp) as a function of time upon irradiation with x rays at −78°C of a CsCl crystal: (a) grown from a water solution with urea additive (1.67 mm thick), and (b) grown from the melt (1.76 mm thick).

Fig. 7. Absorption spectrum of a CsBr crystal (1.82 mm thick) after irradiation at −78°C with 3.0-Mev electrons (dose: 5 X 10^6 rad). The dashed curves give the ultraviolet absorption of the uncolored crystal.
(1065 μm at −78°C) are unstable at room temperature. Coloration at −190°C results in a new ultraviolet band near 270 μm and in some changes in the infrared region. Crystals colored by electrolysis showed a spectrum similar to that of irradiated ones.

Table II lists the spectral positions and half-widths of color-center absorption bands in CsBr. Several bands not shown in Fig. 7 but indicated for some other samples are also included.

The growth rate of the most prominent band (662 μm at −78°C) resembles that in solution-grown CsCl (Fig. 6, Curve a) but is somewhat slower. Upon photochemical bleaching of the 646-μm band at −190°C, a broad band developed toward longer wavelengths, with the superposition of a narrower band at 840 μm. Bleaching at −78°C yielded more bands (Fig. 8). As a result of bleaching, the 662-μm band tends to broaden. As in CsCl the band shows some asymmetry even before bleaching.

The band near the absorption edge (245 μm at 25°C), similarly to the analogous band in CsCl, did not bleach upon illumination with the spectrophotometer hydrogen lamp.

**Table III.** The spectral position of color-center absorption-band maxima and their half-width for CsI.

<table>
<thead>
<tr>
<th>Position of the maxima* (μm)</th>
<th>Half-width of the bandsa (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature, °C</td>
<td>Temperature, °C</td>
</tr>
<tr>
<td>−190°</td>
<td>−78°</td>
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<tr>
<td>λ₁</td>
<td>270</td>
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<tr>
<td>λ₂</td>
<td>330</td>
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<tr>
<td>λ₃</td>
<td>425</td>
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<tr>
<td>λ₄</td>
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<td>λ₆</td>
<td>690</td>
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<tr>
<td>λ₇</td>
<td>1050</td>
</tr>
<tr>
<td>λ₈</td>
<td>1185</td>
</tr>
</tbody>
</table>

* Average uncertainty is between 1 and 5 μm depending on the intensity, position, and half-width of the band. There is also an indication for bands at 1010 and 1480 μm (at −190°C).

Cesium Iodide

Although color centers were produced in CsCl and CsBr by irradiation with x rays within a few minutes, such irradiation did not produce measurable coloration in CsI, even after several hours, nor did coloration result from electron doses of 10⁶ rad and more. Cesium iodide crystals could be colored by electrolysis only.

The absorption spectra of a colored CsI crystal (Fig. 9) are similar to those of CsCl and CsBr. Table III shows the positions and half-widths of color-center
bands in CsI. It lists some bands not shown in the sample of Fig. 9. In particular, the 1080-μm band was much broader than others in its vicinity.

Illuminating the crystal with light in the spectral region of the strongest band (~770 μm) caused a decrease in its intensity and an increase of absorption at longer wavelengths. At room temperature the increased absorption is mostly in the 1220-μm band, while at lower temperatures a variety of bands can be produced.

The results of bleaching at −78°C are illustrated in Fig. 10. After the first four minutes of illumination, the intensity of the 768-μm band diminished by about 20%. Additional illumination for 34 minutes decreased the band intensity by only 18% more, while the absorption at longer wavelengths increased substantially. In addition to enhancement of the 1010-μm and 1185-μm bands, the spectrum recorded at −190°C shows new bands at 1255, 1335, 1450, and 1800 μm; while the band at 535μm remained essentially unaffected, that at 425 μm almo..disappeared. As a result of the bleaching (for 38 minutes), the half-width of the 768-μm band at −78°C increased from 0.31 to 0.37 ev and at −190°C from 0.23 to 0.36 ev. The shape of the top of the band (at −190°C) furthermore indicates a slight splitting in the band. The crystal was restored to its unbleached state by storage at room temperature in darkness for half a day.

**DISCUSSION**

It is quite certain that the coloration in cesium halides is due to electrons and holes trapped in lattice vacancies that are partly present in uncolored crystals and partly created by irradiation. The appearance of several absorption bands suggests the existence of a variety of traps. The absorption spectra of the three crystals show certain similarities in position, shape, and intensity of bands (see Figs. 2, 7, and 9). The strongest band in all three crystals appears in or near the visible spectral range. Its half-width is 0.32 to 0.37 ev at room temperature, and 0.20 to 0.23 ev at −190°C. In NaCl-type crystals the analogous band, the F band, has a half-width of 0.31 to 0.47 ev at room temperature, and 0.22 to 0.34 ev at −190°C.30 As temperature decreases to −190°C, the maximum shifts by about 0.08 ev toward higher energies (or shorter wavelengths), compared to about 0.06 ev in other alkali halides.30 Another similarity appears upon bleaching with light which is absorbed in the band. During bleaching, the band decreases while another one between 0.95 and 1.25 μ increases.

The growth of the band intensity in CsCl (Fig. 6) and CsBr as function of time during irradiation with x rays is similar to that of the F band in the face-centered cubic alkali halides. The concentrations of color centers for this band, computed from Smakula’s equation,31 is of the same order as those achieved in other alkali halides.

The half-width and its change with temperature, the shifting of the band maximum with temperature, and its partial conversion into a new band upon bleaching support the assignment of this band in cesium halides (in or near the visible spectral range) as the F band (i.e., absorption due to an electron trapped at a negative ion vacancy).

The spectral position of the F band in NaCl-type alkali halides is related to the interionic distance by the Mollwo relation \( r_{\text{max}}^2 = \text{constant} \).32 The exponent, according to lvey,32 is 1.84 rather than 2.0. From the slope of the logarithmic plot of the F-band intensity at −190°C versus the lattice constant \( a \) in cesium halides (Fig. 11) one obtains a value 2.5 for the exponent.

According to Mollwo,34 the ratio of the F-band excitation energy to \( 3/8(\epsilon/k_{B}R) \) is close to unity for the face-centered cubic alkali halides. In the above expression, \( \epsilon \) is the electronic charge, \( k_{B} \) the high-frequency dielectric constant, and \( R \) the cation radius. The expression gives the excitation energy for a \( 1s-2p \) transition of an electron associated with a hydrogen-type impurity imbedded in a dielectric medium, when \( R \) is allowed to stand for the Bohr radius. The ratio ranges from 1.0 to 1.24 for the NaCl-type alkali halides. Levy reports 1.64 for CsCl. The present data yield ratios of 1.67, 1.57, and 1.48 for CsCl, CsBr, and CsI, respectively. Therefore, Levy’s ratio is about 1.1 for the face-centered 1.6 for the simple cubic alkali halides.

The partial conversion of the F band into a new band by bleaching (with light in the F band) suggests that the new band between 0.95 and 1.25 μ corresponds to the M band (i.e., absorption due to an electron trapped at a negative ion vacancy adjacent to a cation-anion vacancy pair). The assignment of the M band is also

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22 E. Mollwo, Z. Physik 85, 56 (1933).
23 A. Smakula, Z. Physik 59, 603 (1930).
supported by the fact that this band is already present in moderately colored CsCl and CsBr after irradiation with x rays or electrons, even prior to exposure to "F light." The logarithmic plot of the spectral position of the M-band maximum with respect to the lattice constant approximates a straight line. The average exponent for the Mollwo-Ivey relation for $-190^\circ$, $-78^\circ$, and $25^\circ$C is 1.8. According to Ivey, the exponent for the M band in face-centered cubic alkali halides is 1.56.

In analogy with face-centered cubic alkali halides, the bands between the F and M bands in cesium halides might be called R bands. According to Seitz, $R_1$ and $R_2$ centers are, respectively, one and two electrons at an anion-vacancy pair. Upon exposing the colored crystal at $-78^\circ$C to light absorbed in the F band, the M band at first increases most rapidly. As bleaching continues, however, it starts to decrease in intensity while the growth of bands between the F and M bands and toward longer wavelengths from the M band continues, as in NaCl-type crystals. The band beyond the M band might be correlated to the N band.

A correlation of absorption bands at shorter wavelengths from the F band is more difficult. The broad bands observed in CsCl around 270 mp and in CsBr near 315 mp might possibly be due to V centers (i.e., one or more trapped holes). They appear only upon irradiation of the crystals at low temperatures ($-78^\circ$, and $-190^\circ$C), disappear at room temperature, and are about twice as broad as the F band. Some electrolytically colored samples, however, also show bands in this region.

At present one can say very little about the remaining absorption bands. Several bands in the three salts can be correlated approximately by a Mollwo-Ivey type empirical relation. As one moves from the F band toward shorter wavelengths, the first two bands (in the region of 430 and 370 mp in CsCl, 485 and 390 mp in CsBr, and 540 and 430 mp in CsI) conform to an average exponent of 2.0 and 1.4, respectively. The narrow intense band near the ultraviolet absorption edge (around 229 mp in CsCl, 243 mp in CsBr, and 273 mp in CsI) has an average exponent of 1.7. The appearance of these bands in both irradiated and additively colored samples implies that they are caused by trapped electrons. (With the introduction of excess metal into the crystal, only excess electrons are introduced.)

The broadening of the F band during bleaching with light in the F band and the indication for the production of a band just to the long- and short-wavelength sides of the F band may correspond to the A and B bands reported by Petroff.

A slight asymmetry appears to be present in the F band. Duerig and Markham's measurements suggest

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Microwave Modulation of Light in Paramagnetic Crystals

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(Received August 3, 1960)

The considerations of Dehmelt and several other workers about the modulation of light by radio-frequency signals in atomic vapors are extended to paramagnetic solids. It is shown that these materials, driven near a microwave resonance at low temperatures may be used both to create and to detect modulation of light at microwave frequencies. Experimental design criteria are discussed at the hand of two numerical examples, modulated circular dichroism in ruby and modulated Faraday rotation in a broad class of ionic rare earth compounds. Some possible applications of microwave modulated light are reviewed.

I. INTRODUCTION

The modulation of light has a long history. As early as 1881 Righi obtained fluctuations in an interference pattern by a periodic mechanical rotation of one in a pair of crossed Nicols. Rupp produced unresolved side bands on light by operating a Kerr cell near $10^8$ cps and detected their passage through a vapor cell absorbing only the central component. More recently Dehmelt proposed that a precessing magnetization of atoms in alkali vapors should give a modulation of the absorption coefficient for circular polarized light propagating in the plane of the precessing component. Such a time-dependent magnetization may be created by polarization of the alkali atoms (e.g., by optical pumping) and driving the resonance between two Zeeman levels with a radio-frequency magnetic field.

The successful outcome of such an experiment at 550 kc/sec on Na vapor has been reported by Bell and Bloom. Bloom has announced a similar experiment on a higher frequency transition in K vapor. Series has reported related experiments on modulation in Hg vapor where the precessing magnetization is induced in the excited state.

It is well known that large precessing components of magnetization can be produced by exciting the spin resonance in paramagnetic crystals at low temperatures. It is the purpose of this paper to investigate what happens to a circularly polarized light beam which passes through a crystal in which a precessing magnetization is established by an exciting microwave field.

Several optical experiments and their interplay with the spin resonances in ruby have recently been reported. The analogy with corresponding experiments in alkali vapors has been pointed out. In paramagnetic crystals the polarization is established by thermal relaxation processes and need not be established by optical pumping. The characteristics of an experiment in ruby analogous to the Bell and Bloom experiment in Na vapor will be analyzed in Secs. II and III.

Kastler has pointed out that the Faraday rotation in paramagnetic crystals could be decreased by saturation of the microwave resonance(s) in the ground-state multiplet. Opechowski has given a detailed theory of the effect, which can be described simply by saying that microwave saturation changes the effective magnetic temperature. Daniels and Wesemeyer have demonstrated the disappearance of optical Faraday rotation in

ACKNOWLEDGMENTS

The authors appreciate the help of J. Kalnajs and Dr. A. Linz, Jr., with some aspects of the work. The authors are also indebted to Dr. K. A. Wright of the High Voltage Research Laboratory for irradiation of numerous crystals with high-energy electrons.

* The research reported in this paper was made possible through support extended Cruft Laboratory, Harvard University, jointly by the Navy Department (Office of Naval Research), the Signal Corps of the U. S. Army, and the U. S. Air Force.

1 A. Righi, J. phys. 2, 437 (1905).