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F-Band Shape in the CsCl Structure Under Pressure*†

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Color centers have been formed by x irradiation of RbCl above the polymorphic transition pressure, and the shape of the new *F* band at 509 m μ in this CsCl-type structure has been examined under a pressure of 6200 atm at liquid-helium temperature. The band shows no evidence of the multiplet structure observed in the cesium halides, thus indicating that the lattice structure is not responsible for this effect. The *F* band in CsCl has also been formed and studied under pressure at helium temperature, and the triplet components show the usual relative intensity and the characteristic *F*-band shift. No evidence of *K'* bands was observed for these hydrostatic pressures.

INTRODUCTION

RECENT studies of color centers in CsCl and CsBr¹⁻³ revealed structure on the principal absorption band, in contrast to the usual *F* band in alkali halides with the NaCl-type lattice. This structure, which Rabin and Schulman² decomposed into three components at liquid-helium temperature, appears to be identical for centers formed by x irradiation or additive coloring, is unaffected by bleaching or heat treatment, and is not sensitive to sample purity. It therefore seems reasonable to associate these multiplets with a single electron-excess center, presumably an *F* center composed of an electron bound to a negative-ion vacancy. Rabin and Schulman² first proposed that if these components are all due to one center, then they must represent a splitting of the excited *F* state by a

crystal-field effect peculiar to the CsCl-type lattice, or a splitting caused by the cesium ion itself.

The present work was undertaken to determine the influence of crystal structure by studying the *F* band formed in the pressure-induced simple cubic phase of a normally face-centered cubic alkali halide. RbCl transforms from the NaCl lattice structure to the CsCl lattice structure at about 5000-6000 atm. On the basis of a Mollwo relation between peak position and lattice constant for other CsCl-type crystals, one expects the *F* center to appear at about 520 m μ in the high-pressure form. Jacobs⁴ looked for this peak in RbCl crystals x rayed or additively colored at atmospheric pressure prior to the structure transformation, but was unable to detect any new center. Drickamer *et al.*^{5,6} found a new band, which they called the *K'* band, which replaced the *F* band in simple cubic phases at very high pressures and room temperature.

With the apparatus described below, it is possible to transform the crystal first and then form the CsCl-type centers by x raying under pressure at room or low temperatures. In particular it is possible to form

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¹ P. Avakian and A. Smakula, Phys. Rev. **120**, 2007 (1960).

² H. Rabin and J. H. Schulman, Phys. Rev. Letters **4**, 280 (1960); Phys. Rev. **125**, 1584 (1962).

³ D. W. Lynch, Phys. Rev. **127**, 1537 (1962).

⁴ I. S. Jacobs, Phys. Rev. **93**, 993 (1954).

⁵ W. G. Maisch and H. G. Drickamer, Phys. Chem. Solids **5**, 328 (1958).

⁶ R. A. Eppler and H. G. Drickamer, J. Chem. Phys. **32**, 1418 (1960).

and study the new F center at helium temperature to investigate whether it has the triplet structure observed in the cesium halides.

In addition, the F band was formed in CsCl under pressure at helium temperature to verify that the triplet components grow in the same ratio and exhibit the characteristic F -band pressure shift.

EXPERIMENTAL PROCEDURES

The four-window pressure cell and cryostat used in this experiment have been described in detail elsewhere.⁷ Color centers were produced at high pressure and low temperature by irradiating the sample with 50-kV x rays through a beryllium window in the pressure cell. Optical absorption spectra were measured at right angles through sapphire windows, using a Beckman DU spectrophotometer. The sample was suitably masked to measure only a region of nearly uniform coloration, and the radiation-induced coloration was determined by subtracting the pre-irradiation spectrum from those measured at later times. Helium gas was used to apply hydrostatic pressure in the range 0–8000 atm, the pressure being determined with a manganin gauge except at temperatures where the helium solidified, when thermodynamic PVT data for solid helium were used to estimate⁷ the pressure in the cell.

RESULTS AND DISCUSSION

a. RbCl

Two runs were made using samples 0.43 and 0.27 mm thick cleaved from a piece of "pure" Korth RbCl. Pressure was applied at room temperature at a rate of about 300 atm per min, and the transition pressure was detected by monitoring the optical transmission of the sample. At about 7300 atm, the transmission dropped abruptly to 0.17% in the first case and 1% in the second case. These values correspond to an optical density of roughly 80 cm^{-1} .

The crystallographic aspects of this type of structure transformation, which achieves a 15% reduction in volume,⁸ have been discussed by Buerger⁹ and applied to the phenomenon of opacity by Jacobs.⁴ The transformation proceeds from a large number of nucleation centers giving rise to many mismatched grains. Light is scattered at the boundaries of these microscopic regions causing the observed opacity.

The transition in RbCl has been observed at 5700 atm by Bridgman,⁸ 6000 atm by Pierce,¹⁰ and 6500 atm by Jacobs, who also used the opacity as an indicator. The higher transition pressure seen in this case could be due to three causes. In another study of

the polymorphic transformation in RbI with helium gas as a pressure fluid, Jacobs¹¹ found that the initial transformation for a virgin crystal occurred at about 10% higher pressures with the purely hydrostatic helium pressure medium than for liquid media. Apparently, the slight shear stresses due to viscosity of the liquid help to initiate the local shear involved in the transformation. A second reason might be hysteresis during the relatively rapid pressure rise, since Pierce found that the initial transformation required nearly 45 min to go to completion. However, no change in transmission was seen until the sudden abrupt and complete change. Finally, the crystals of less than "atomic-weight purity" usually have a higher transition pressure, but Pierce observed the transition at a lower pressure in Korth RbCl which had been doped with additional divalent impurity. Therefore, the first explanation seems the most probable here.

After the crystal had been transformed, it was cooled to helium temperature and x rayed under pressure. A preliminary run on the coloration of Korth RbCl at helium temperature below the transformation pressure had shown that the normal F band grows very slowly at about $590 \text{ m}\mu$. In the present runs, the principal absorption grew slowly at about $510 \text{ m}\mu$. Because of the very high background absorption, only the range of $420\text{--}620 \text{ m}\mu$ could be measured with any certainty, and readings outside this range fluctuated erratically. No systematic growth of any other major center was detected.

The shape of the new center was measured carefully twice in each run, and no indication of structure appeared, as shown in Fig. 1.

In the first run, a small peak was seen at $600 \text{ m}\mu$, presumably due to NaCl-type F centers formed in portions of the crystal which had not completely transformed. When pressure was released slowly at nitrogen temperature, very marked hysteresis was observed and the new centers were unaffected to about 3500 atm, at which point they disappeared and the NaCl-type F center appeared with almost identical magnitude at $600 \text{ m}\mu$. In the second run, the crystal was allowed to warm to room temperature under pressure and was then x rayed again. Instead of growth, the irradiation appeared to remove most of the residual centers which remained after warming. Similar hysteresis occurred when releasing pressure at room temperature. The optical density only began to decrease at about 4500 atm. At atmospheric pressure, the transmission had returned to about 20% of its initial value. The samples appeared milky and were highly strained but still intact.

The parameters of the new center as measured at various pressures and temperatures are listed in Table I.

While the designation of this new band as the F band is still tentative, the following evidence supports

⁷ D. B. Fitchen, *Rev. Sci. Instr.* **34**, 673 (1963).

⁸ P. W. Bridgman, *Z. Krist.* **67**, 363 (1928).

⁹ M. J. Buerger, in *Phase Transformations in Solids* (John Wiley & Sons, Inc., New York, 1951).

¹⁰ C. B. Pierce, *Phys. Rev.* **123**, 744 (1961).

¹¹ R. B. Jacobs, *Phys. Rev.* **54**, 468 (1938).

TABLE I. Parameters of the principal absorption band in transformed RbCl.

Temperature	Pressure (atm)	λ_m (m μ)	H (eV)
Helium	6400	509	0.22 ± 0.01
Nitrogen	5230	517	0.25 ± 0.01
Room	7370	514	0.35 ± 0.03

it. The band appears to be the principal absorption center formed and has a shape and half-width similar to the F center in the low-pressure form. The peak of this new center shifts with temperature and pressure in the same manner as the F center, and its half-width increases with temperature in the same way. In the first run, it was possible to convert these centers directly to the normal F centers by returning to the low-pressure structure at nitrogen temperature. Finally, the new band appears at just the position predicted by a Mollwo-like relation for the CsCl structure, $\lambda_m = K(d)^n$, where d is the interionic distance. Using values of λ_m and d at low temperature for CsCl and CsBr,² and the value of d for the high-pressure form of RbCl from Bridgman's density measurements,⁸ the new F center should appear at 514 m μ , in good agreement with experiment.

The lack of structure on this new F band in RbCl indicates that the triplet structure observed for CsCl

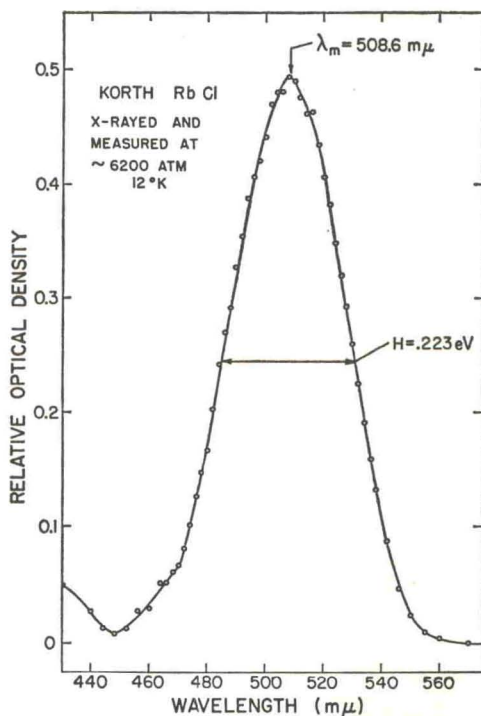


FIG. 1. Shape of the F band formed in the high-pressure CsCl phase of RbCl. The curve shows the difference in optical density measured before and after x irradiation for 220 min at this temperature and pressure for a sample 0.27 mm thick.

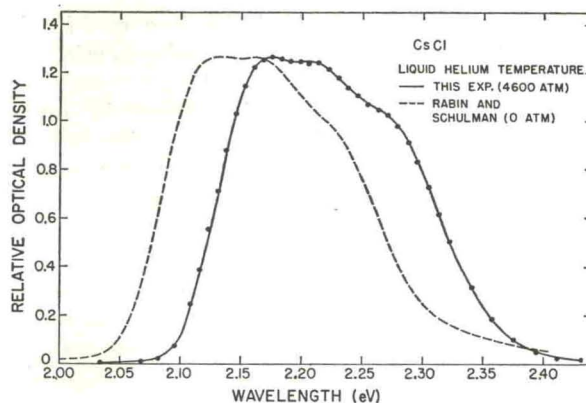


FIG. 2. Pressure shift of the F band in CsCl. The solid curve is for centers formed at this temperature and pressure after x irradiation for 15 min with a sample 0.84 mm thick. The comparison curve is taken from Ref. 2.

and CsBr at liquid-helium temperature is not caused by a crystal-field effect indigenous to the CsCl-type lattice. Hughes and Rabin¹² have confirmed this result by their observation of clearly resolved peaks in the principal absorption band of CsF, the only cesium halide having the NaCl-type lattice. Thus the cause of the splitting seems to be the cesium ion itself.

Speculation has centered on relativistic effects which would be appreciable only for the cesium halides. A calculation by Suffczynski¹³ of the spin-orbit splitting for a localized excited state in a cesium halide gave a result orders of magnitude smaller than the observed effect. Recently, Knox¹⁴ has proposed that a spin-orbit type splitting of the conduction band might be responsible. Calculations^{15,16} of the other relativistic effects on band structure for heavy ions suggest that these might also contribute for cesium.

b. CsCl

A subsidiary experiment was performed to test whether the three components of the principal absorption band observed in CsCl at helium temperature would exhibit the characteristic pressure shift of the F band.

A freshly cut and polished platelet of Semi-Elements CsCl was x rayed and measured at approximately 4600 atm and 11°K. Figure 2 shows one of the measured spectra with a zero-pressure spectrum of Rabin and Schulman² normalized to the same peak height for comparison. The component structure is clearly visible and appears essentially unchanged after a pressure shift of $\Delta E/E \approx 0.021$. (This shift is within 4% of

¹² F. Hughes and H. Rabin, *Phys. Chem. Solids* **24**, 586 (1963).

¹³ M. Suffczynski, *J. Chem. Phys.* **38**, 1558 (1963).

¹⁴ R. S. Knox, *Phys. Rev.* **133**, A498 (1964).

¹⁵ L. E. Johnson, J. B. Conklin, and G. W. Pratt, Jr., *Phys. Rev. Letters* **11**, 538 (1963).

¹⁶ F. Herman, C. D. Kuglin, K. E. Cuff, and R. L. Kortum, *Phys. Rev. Letters* **11**, 541 (1963).

Jacobs' room-temperature shift⁴ when corrected for the change in compressibility with thermal expansion.) If the two curves are superimposed, the low-energy side is almost identical, while the high-energy side differs slightly. The effect of this change is to increase the apparent total width at half-maximum under pressure by 3.5% to 0.017 eV. Jacobs⁴ also measured an apparent increase in half-width in CsCl at room temperature of about 5% in 4000 atm.

Maisch and Drickamer⁵ studied the effect of pressure to 50 000 atm on CsCl and found a new band, the K' band, with peak energy about 0.1 eV higher than the F band which grows at the expense of the F band with increasing pressure and is reversible upon decrease in pressure. It is thus possible that the high-energy component of the triplet is related to this K' band and is increasing in relative importance with pressure. However, no such K' band was seen in this range of hydrostatic pressures either for RbCl above or below its transition pressure, or for KBr, in which they observed a prominent K' band at considerably higher pressures. Either the K' band is not observable in the present range of pressures, or its appearance in Drickamer's experiments is due to shear and pressure inhomogeneities in his apparatus which are not present in our gas system.

SUMMARY

Using a novel technique a new absorption band has been formed by x irradiation of RbCl above its polymorphic transition pressure. The position, width, and temperature and pressure dependence of this band support its designation as the new F band in this CsCl-type phase. The band could be converted to the normal F band by reversing the transition at low temperatures. The shape of this new band has been examined under pressure at liquid-helium temperature, and shows no evidence of the multiplet structure observed in the cesium halides, thus indicating that the lattice structure is not responsible for this effect.

The pressure measurements on CsCl prove that for still another way of forming and observing the principal band, the triplet components all appear to be due to the F center.

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