

SEP 20 1966

Reprinted from THE PHYSICAL REVIEW, Vol. 134, No. 6A, A1599-A1602, 15 June 1964  
 Printed in U. S. A.

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

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(Received 24 January 1964)

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 $\mu$  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 CsBr<sup>1-3</sup> 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 Schulman<sup>2</sup> 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 Schulman<sup>2</sup> 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 $\mu$  in the high-pressure form. Jacobs<sup>4</sup> 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.*<sup>5,6</sup> 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

\* This work was supported in part by the U. S. Atomic Energy Commission.

† Based on part of a thesis submitted to the University of Illinois in partial fulfillment of the requirements for the Ph.D. degree (1962). A preliminary report of this aspect of the work was given by D. Lazarus at the Conference on Crystal Lattice Defects, Kyoto, Japan, September 1962.

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

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

<sup>3</sup> D. W. Lynch, Phys. Rev. **127**, 1537 (1962).

<sup>4</sup> I. S. Jacobs, Phys. Rev. **93**, 993 (1954).

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

<sup>6</sup> 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.<sup>7</sup> 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 manin gauge except at temperatures where the helium solidified, when thermodynamic PVT data for solid helium were used to estimate<sup>7</sup> 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  $80 \text{ cm}^{-1}$ .

The crystallographic aspects of this type of structure transformation, which achieves a 15% reduction in volume,<sup>8</sup> have been discussed by Buerger<sup>9</sup> and applied to the phenomenon of opacity by Jacobs.<sup>4</sup> 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,<sup>8</sup> 6000 atm by Pierce,<sup>10</sup> 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, Jacobs<sup>11</sup> 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  $m\mu$ . In the present runs, the principal absorption grew slowly at about 510  $m\mu$ . Because of the very high background absorption, only the range of 420–620  $m\mu$  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  $m\mu$ , 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  $m\mu$ . 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

<sup>7</sup> D. B. Fitchen, *Rev. Sci. Instr.* **34**, 673 (1963).

<sup>8</sup> P. W. Bridgman, *Z. Krist.* **67**, 363 (1928).

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

<sup>10</sup> C. B. Pierce, *Phys. Rev.* **123**, 744 (1961).

<sup>11</sup> R. B. Jacobs, *Phys. Rev.* **54**, 468 (1938).