

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

Temperature	Pressure (atm)	$\lambda_m$ (m $\mu$ )	$H$ (eV)
Helium	6400	509	$0.22 \pm 0.01$
Nitrogen	5230	517	$0.25 \pm 0.01$
Room	7370	514	$0.35 \pm 0.03$

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  $\lambda_m$  and  $d$  at low temperature for CsCl and CsBr,<sup>2</sup> and the value of  $d$  for the high-pressure form of RbCl from Bridgman's density measurements,<sup>8</sup> the new  $F$  center should appear at 514 m $\mu$ , in good agreement with experiment.

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

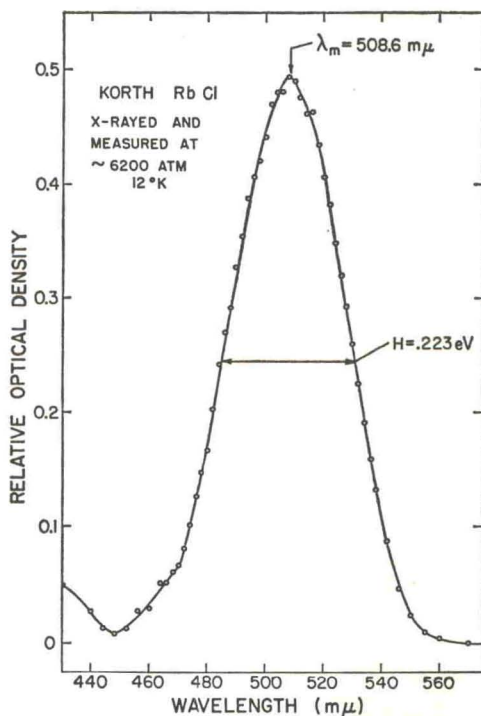


FIG. 1. Shape of the  $F$  band formed in the high-pressure CsCl phase of RbCl. The curve shows the difference in optical density measured before and after x irradiation for 220 min at this temperature and pressure for a sample 0.27 mm thick.

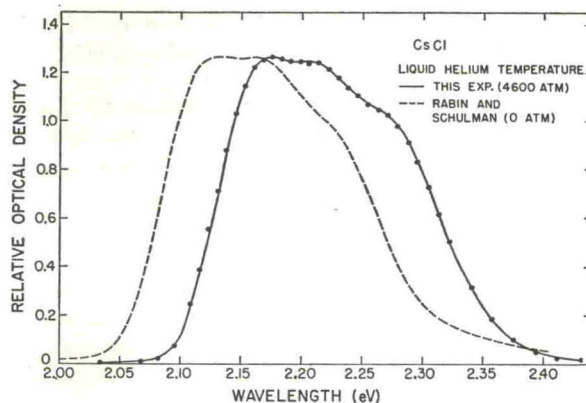


FIG. 2. Pressure shift of the  $F$  band in CsCl. The solid curve is for centers formed at this temperature and pressure after x irradiation for 15 min with a sample 0.84 mm thick. The comparison curve is taken from Ref. 2.

and CsBr at liquid-helium temperature is not caused by a crystal-field effect indigenous to the CsCl-type lattice. Hughes and Rabin<sup>12</sup> 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 Suffczynski<sup>13</sup> 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, Knox<sup>14</sup> has proposed that a spin-orbit type splitting of the conduction band might be responsible. Calculations<sup>15,16</sup> 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 Schulman<sup>2</sup> 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

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

<sup>13</sup> M. Suffczynski, *J. Chem. Phys.* **38**, 1558 (1963).

<sup>14</sup> R. S. Knox, *Phys. Rev.* **133**, A498 (1964).

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

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



Jacobs' room-temperature shift<sup>4</sup> 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. Jacobs<sup>4</sup> also measured an apparent increase in half-width in CsCl at room temperature of about 5% in 4000 atm.

Maisch and Drickamer<sup>5</sup> 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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