

Effect of Pressure on the Spectra of Color Centers*

EPPL RA60 0118

R. A. EPPLER AND H. G. DRICKAMER

Department of Chemistry and Chemical Engineering, University of Illinois, Urbana, Illinois

(Received October 20, 1959)

The effect of pressure on the spectra of certain color centers produced in the alkali halides by x irradiation has been measured to pressures as high as 166 000 atm.

For the *F* center a shift to higher energies with increasing pressure is observed. The slope of the shift versus density is at least twice the value that would be predicted from Ivey's relation at low pressure, and decreases with increasing pressure. This indicates that the compressibility in the neighborhood of the *F* center is greater than in the bulk crystal, particularly at low pressure.

For the *M* center in LiCl a shift to higher energy with increasing pressure is observed, about one-fifth as great as the shift observed for the *F* center.

INTRODUCTION

THE effect of pressure on the spectra of certain color centers in alkali halide lattices produced by ionizing radiation has been studied to as high as 166 000 atm.

There have been three previous investigations of the effect of pressure on color centers in alkali halides. Burstein *et al.*¹ measured the shift of the *F*-band peak frequency to 2000 atm in three alkali halides. Jacobs² measured the effect of pressure on the peak frequency of the *F* band to as high as 8000 atm in seven alkali halides. Maisch and Drickamer³ studied the effect of pressure on the spectra of the *F* band in six alkali halides and the *M* band in one other alkali halide to 50 000 atm.

They found that, in general, a shift to higher energy occurred for all bands with pressure as long as no phase transition occurred. Maisch and Drickamer³ also found that in some alkali halides, there appears at higher pressures a new band on the high energy side of the *F* band which they called the *K*¹ band.

EXPERIMENTAL PROCEDURE

The types of crystals and color centers studied, the techniques used to introduce the centers, and the pressure ranges involved are summarized in Table I.

The crystals to be x irradiated were cleaved to about $2\frac{1}{2} \times 5 \times \frac{1}{2}$ mm and exposed at a distance of one inch for times ranging from one to twenty-five hours to an x-ray tube with a tungsten target and beryllium windows operated at 40 kv and 15 ma. The crystals were stored in the dark until used. They were loaded into the bomb in a very dim red light. This procedure was found by Maisch and Drickamer³ to give results identical to those obtained with additively colored crystals.

The crystals to be bleached were exposed from 5-10 min at a distance of 2-3 in. to the radiation from a

Hanovia type 16 200 mercury lamp, then used immediately.

The high-pressure optical system and techniques have been described previously.⁴

RESULTS AND DISCUSSION

A. *F* Center in the fcc Structure

The primary result of x irradiation of a pure alkali halide crystal is the introduction of a band in the visible called the *F* center. The commonly accepted model of the defect, due to deBoer,⁵ is that of an electron trapped at a negative ion vacancy. The shift of this peak with pressure is shown in Figs. 1 to 6 for six alkali halide crystals which have the fcc (NaCl) structure, at least at atmospheric pressure. The maximum scatter in the data is ± 300 cm⁻¹. Figures 7 to 10 show typical spectra for KCl, KBr, and KI.⁶

It was first suggested by Burstein and Oberly⁷ that the *F* center could, to the zeroth order, be treated as a particle trapped in a box. One of the important conclusions of this model is that $E \propto (1/l)^2$ where *l* is the box diameter. Thus

$$\nu_m = E/h \propto (1/A_0^2) \alpha \rho^{\frac{1}{3}}$$

where *A*₀ is the lattice parameter and ϵ is the density.

Mollwo,⁸ using data at one atmosphere and 25°C for several alkali halides having the fcc structure, showed that $\nu_m A_0^2$ is essentially constant. Later Ivey⁹ correlated the data and found that

$$E_m A_0^{1.84} = 1.76 \times 10^{-19} \nu \text{ m}^2.$$

The density of certain alkali halides has been measured as a function of pressure to 100 000 kg/cm² by

⁴ R. A. Fitch, T. E. Slykhouse, and H. G. Drickamer, J. Opt. Soc. Am. 47, 1015 (1957).

⁵ J. H. deBoer, Rec. trav. chim. 56, 301 (1937).

⁶ It may be noted that the half-widths do not agree particularly well with other published values.

⁷ E. Burstein and J. J. Oberly, Natl. Bur. Standards Circ. No. 5109, 285 (1952).

⁸ E. Mollwo, Nachr. Ges. Wiss. Göttingen, Math. phys. Kl. 97 (1931).

⁹ H. F. Ivey, Phys. Rev. 72, 341 (1947).

* This work was supported in part by U. S. Atomic Energy Commission contract, Chemical Engineering Project 5.

¹ E. Burstein, J. J. Oberly, and J. W. Davisson, Phys. Rev. 85, 729 (1952).

² I. S. Jacobs, Phys. Rev. 93, 993 (1954).

³ W. G. Maisch and H. G. Drickamer, J. Phys. Chem. Solids 5, 328 (1958).