Effect of Pressure on the Spectra of Color Centers*

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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. Jacobs[2] 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 Drickamer[3] 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 Drickamer[3] 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 Drickamer[3] 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 Oberly[7] 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

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

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 Ivey[9] correlated the data and found that

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

The density of certain alkali halides has been measured as a function of pressure to 100 000 kg/cm^2 by

[1] E. Burstein, J. J. Oberly, and J. W. Davisson, Phys. Rev. **85**, 729 (1952).
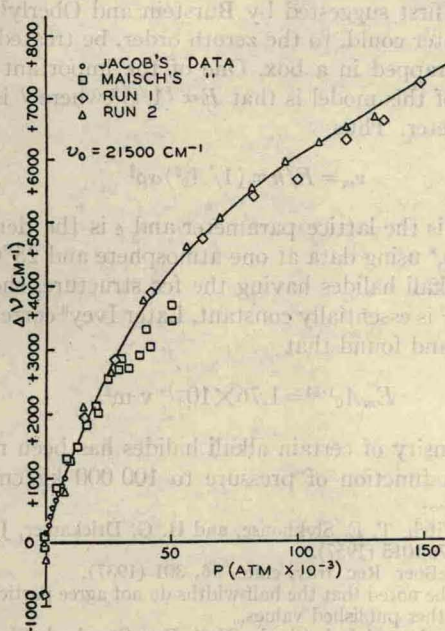[2] I. S. Jacobs, Phys. Rev. **93**, 993 (1954).
[3] W. G. Maisch and H. G. Drickamer, J. Phys. Chem. Solids **5**, 328 (1958).
[4] R. A. Fitch, T. E. Slykhouse, and H. G. Drickamer, J. Opt. Soc. Am. **47**, 1015 (1957).
[5] J. H. deBoer, Rec. trav. chim. **56**, 301 (1937).
[6] It may be noted that 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).

TABLE I. Preparation of color centers in alkali halides.

Study of	Starting material	Source	Preparation	Maximum pressure (atm)
F center in NaCl	Single crystal NaCl	Harshaw Chemical Company	x irradiation	166 000
F center in NaBr	Single crystal NaBr	Single Crystal Corporation	x irradiation	150 500
F center in KCl	Single crystal KCl	Harshaw Chemical Company	x irradiation	137 500
F center in KBr	Single crystal KBr	Harshaw Chemical Company	x irradiation	152 000
F center in KI	Single crystal KI	Harshaw Chemical Company	x irradiation	104 000
F center in LiCl	Single crystal LiCl	Semi-Elements Inc.	x irradiation	106 000
M center in LiCl	Single crystal LiCl	Semi-Elements, Inc.	x irradiation; bleaching	50 000

Bridgman.[10] Figures 10 to 14 are plots of $\log(\nu/\nu_0)_m$ vs $\log(\rho/\rho_0)$. If the compressibility in the neighborhood of the F center were the same as the bulk compressibility one should obtain a slope of $\frac{2}{3}$ (or 06.13 assuming the Ivey relation). Actually the slope is at least twice this at low pressures, but decreases rapidly with pressure in the low pressure region. At higher pressures the slope is constant at a value somewhat above $\frac{2}{3}$. The situation in KBr and KI is complicated by the presence of the K' and other bands. The results are generally quite consistent with the vacancy mechanism since the absence of the nuclear repulsive force should lead to a greater local compressibility than is exhibited by the bulk crystal.

The data also permit the evaluation of Jacob's function $f_T = \partial \ln R/\partial \ln A$) where R is the lattice constant in the neighborhood of the F center, if one accepts
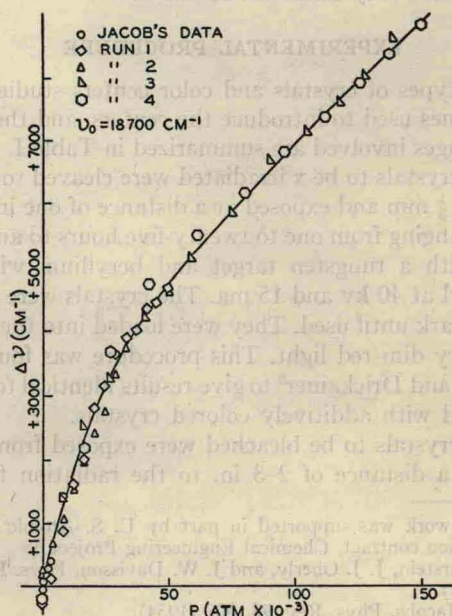
the validity of the Ivey relation as applied to the F center. By using this assumption, $\partial \ln R/\partial P$ can be calculated from the experimental data (Figs. 10–14) and converted to $\partial \ln R/\partial A$ using Bridgman's data. The values of f_T shown are based on the data in the region 0–20 000 atm. Table II compares the experimental values with Jacob's calculations.

The agreement is reasonably good considering the simplicity of the model.

The effect of pressure on the density of LiCl has not been measured directly. It can be estimated from the effect of pressure on the F center ν_m and the atmospheric lattice constant, assuming ν_m has a density dependence similar to the other chlorides. Results are listed in Table III.

B. Growth of the K' Band

Maisch and Drickamer[3] found that in KBr, KI, CsCl, CsBr a new band appeared on the high energy

FIG. 1. Effect of pressure on the spectra of the F band in NaCl.

[10] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 1 (1945).

FIG. 2. Effect of pressure on the spectra of the F band in NaBr.