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Effect of Pressure on Color Centers in Ag⁺-Doped Alkali Halides*

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The effect of pressure on various color centers in silver-doped alkali halides has been studied. The crystals include NaCl (two concentrations), KCl, and KBr. The resulting shifts are used to confirm the assignments of some peaks, and, in certain cases, to decide among conflicting interpretations.

INTRODUCTION

IF alkali-halide crystals containing small amounts (from 0.05 to 2%) of silver halide impurities are subjected to x-rays, five bands appear in addition to the *F* band. This was discovered independently by Kats¹ and by the group at the Naval Research Laboratory,²⁻⁴ who named these bands *A* through *E*. Etzel and Schulman⁴ made an extensive investigation of the properties of these bands. More recently, Maenhout-van der Vorst and Dekeyser⁵ and Ishiguro^{6,7} have made further studies on these bands. Although it is true that the nature of these centers is not yet certain, models have been proposed for them which will be described in the next section.

THEORY

a. *A* Center

The *A* center is almost certainly a hole phenomenon. Etzel and Schulman⁴ propose that the center is a substitutional silver ion which has been trapped by a hole, while Maenhout-van der Vorst and Dekeyser⁵ propose that it is a substitutional silver ion adjoining a *V* center (hole trapped in a positive ion vacancy).

b. *B* Center

It is generally agreed^{4-6,8} that this center is a substitutional silver ion adjoining an *F* center (electron trapped at a negative ion vacancy).

c. *C* Center

The fact that the strength of the *C* band is strongly dependent on concentration has led both Etzel and Schulman⁴ and Maenhout-van der Vorst and Dekeyser⁵

to postulate that there are two silver ions in the center. The latter adds to this two *F* centers, while the former only one.

d. *D* Center

The greatest amount of controversy concerns this band; Kats¹ attributed this band to the *B* center. Etzel and Schulman's⁴ bleaching experiments led them to the conclusion that no unbound electrons were involved in the center, and they proposed a center consisting of a substitutional silver atom adjoining a *V* center. Maenhout-van der Vorst and Dekeyser,⁵ however, found the band in additively colored crystals where only electron centers are to be found. They attribute the band to a substitutional silver ion adjoining an *M* center (electron trapped at a negative ion vacancy plus a vacancy pair).

e. *E* Center

Maenhout-van der Vorst and Dekeyser⁵ attributed this band to an interstitial silver ion adjoining an *F* center. Ishiguro,^{6,7} however, has found that while bleaching in the *F* center at room temperature enhances the *B* band, bleaching at liquid nitrogen temperature enhances the *E* band. Moreover, the *E* center is thermally unstable at only slightly above room temperature.⁸ From all this Ishiguro concludes that the *E* center is an electron trapped in the field of a substitutional silver ion, or, in other words, a *B* center which has lost its associated vacancy.

EXPERIMENTAL

The crystals used in this study were single crystals of NaCl (0.1% and 1.0% AgCl), KCl (1.0% AgCl), and KBr (0.1% AgBr). (All concentrations are in the melt.) The doped crystals were obtained from J. H. Schulman of the Naval Research Laboratory. They were cleaved to 0.5 × 0.5 × 2-mm and irradiated 1 in. from an x-ray tube with tungsten target and beryllium windows for 1 to 20 hr. All irradiation and handling was done in the dark or in a very dim red light.

The high-pressure equipment and techniques used have been previously described.^{9,10}

The effect of pressure on these bands has been studied in sodium chloride with two impurity-concentration

⁹ R. A. Fitch, T. E. Slykhouse, and H. G. Drickamer, *J. Opt. Soc. Am.* **47**, 1015 (1957).

¹⁰ R. A. Eppler and H. G. Drickamer, *J. Chem. Phys.* (submitted for publication).

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¹ M. L. Kats, *Doklady Akad. Nauk. U.S.S.R.* **85**, 539 (1952); *Zhur. Eksp. Teoret. Fiz.* **23**, 720 (1952).

² E. Burstein, J. J. Oberly, B. W. Hennis, and M. White, *Phys. Rev.* **86**, 255 (1952).

³ H. W. Etzel, J. H. Schulman, R. J. Gintler, and E. W. Claffy, *Phys. Rev.* **85**, 1063 (1952).

⁴ H. W. Etzel and J. H. Schulman, *J. Chem. Phys.* **22**, 1549 (1954).

⁵ W. Maenhout-van der Vorst and W. Dekeyser, *Physica* **23**, 903 (1957).

⁶ M. Ishiguro, T. Okuno, and Veda, *Mem. Inst. Sci. Ind. Research, Osaka Univ.* **13**, 69 (1956).

⁷ M. Ishiguro, T. Okuno, and Kojima, *Mem. Inst. Sci. Ind. Research, Osaka Univ.* **15**, 1 (1958).

⁸ H. N. Hersh, *J. Chem. Phys.* **30**, 790 (1959).

levels, in potassium chloride and in potassium bromide [see Figs. 1(a) through 4(b)]. Figure 5-7 show typical spectra.

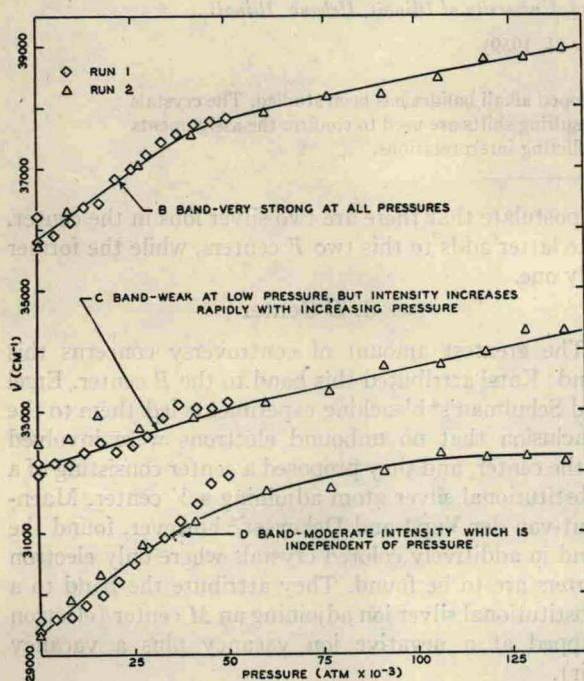


FIG. 1(a). The effect of pressure on the spectra of color centers in $\text{NaCl}: 0.1\% \text{AgCl}$, Part 1.

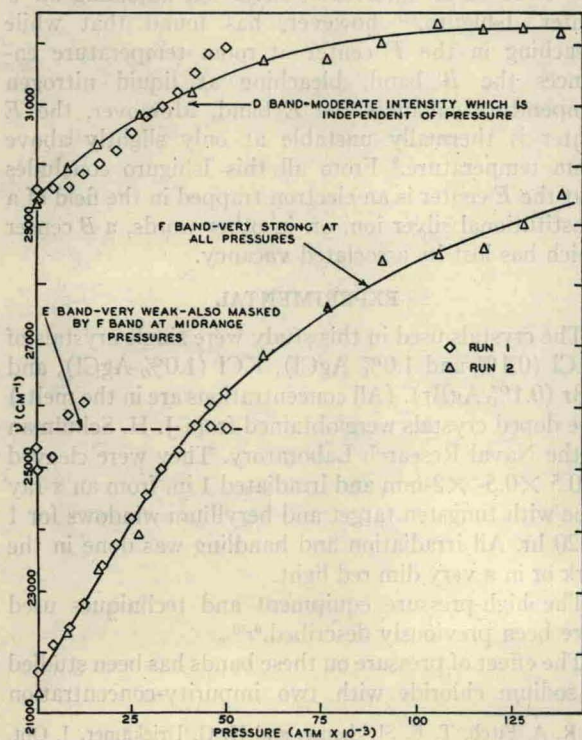


FIG. 1(b). The effect of pressure on the spectra of color centers in $\text{NaCl}: 0.1\% \text{AgCl}$, Part 2.

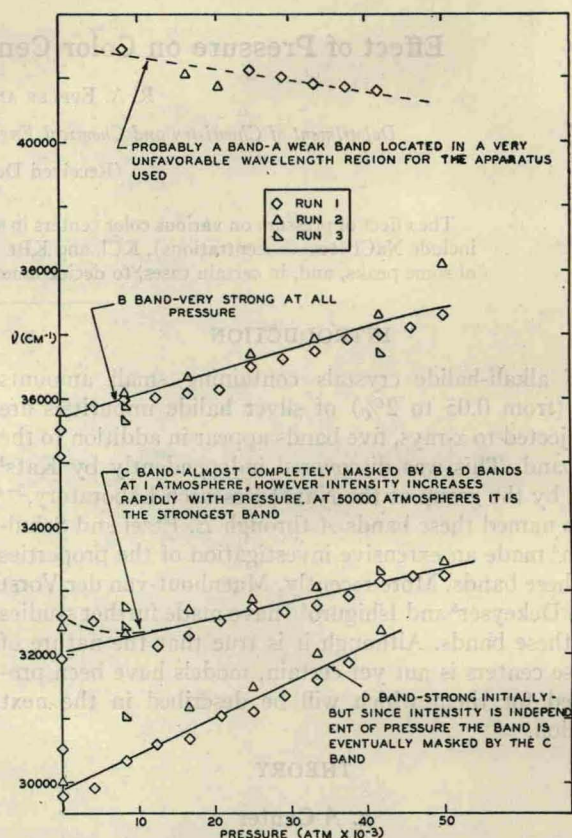


FIG. 2(a). The effect of pressure on the spectra of color centers in $\text{NaCl}: 1.0\% \text{AgCl}$, Part 1.

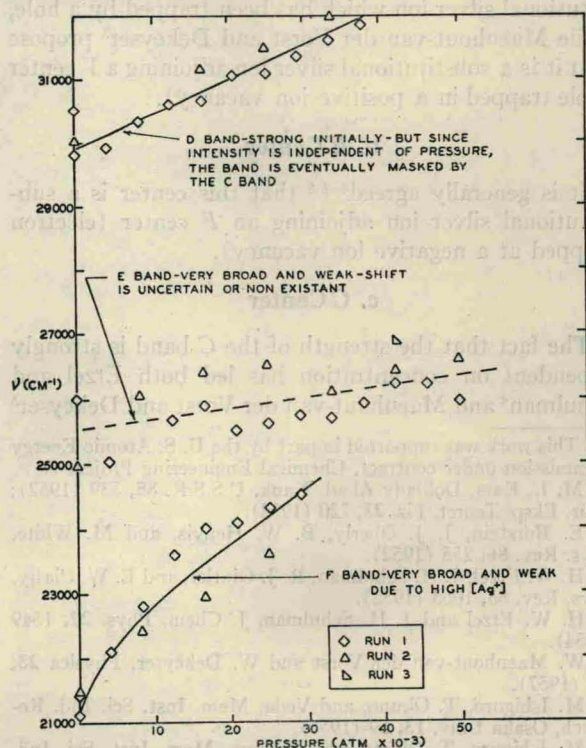


FIG. 2(b). The effect of pressure on the spectra of color centers in $\text{NaCl}: 1.0\%$ in AgCl , Part 2.