

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

R. A. EPPLER AND H. G. DRICKAMER

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

(Received December 21, 1959)

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 Dekeyser⁵ 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

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

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).

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).

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

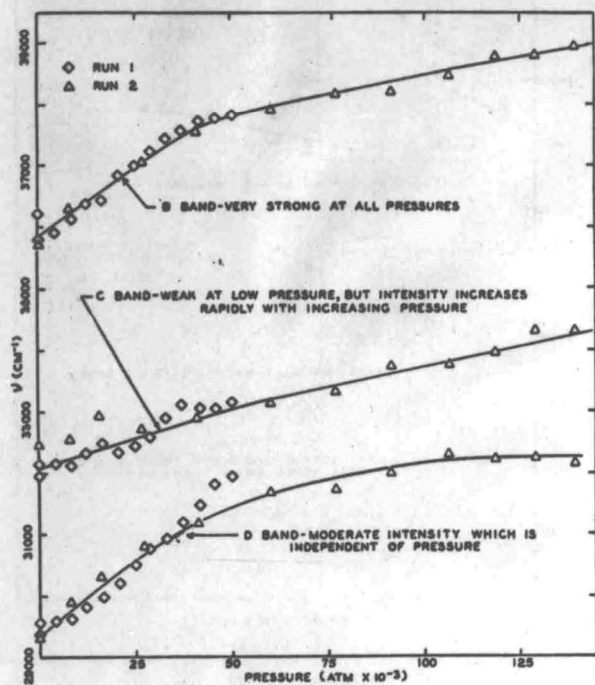


FIG. 1(a). The effect of pressure on the spectra of color centers in NaCl: 0.1% AgCl, Part 1.

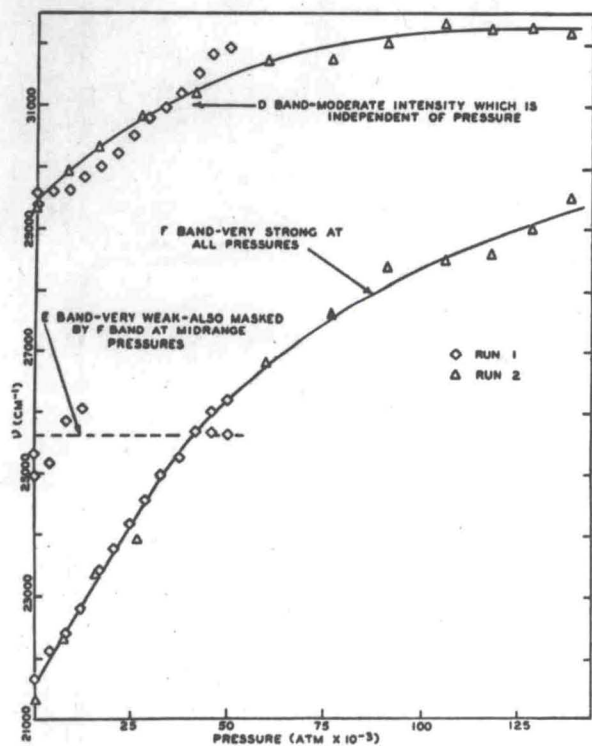


FIG. 1(b). The effect of pressure on the spectra of color centers in NaCl: 0.1% AgCl, Part 2.

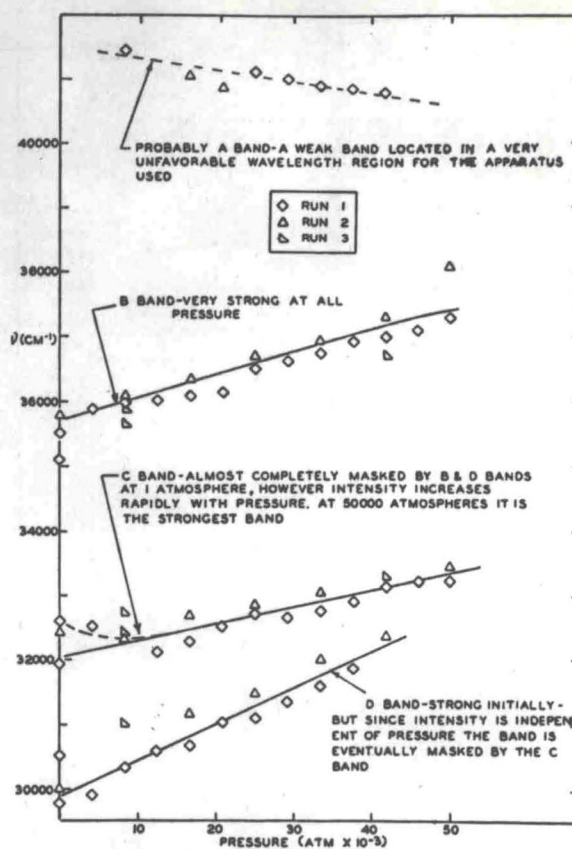


FIG. 2(a). The effect of pressure on the spectra of color centers in NaCl: 1.0% AgCl, Part 1.

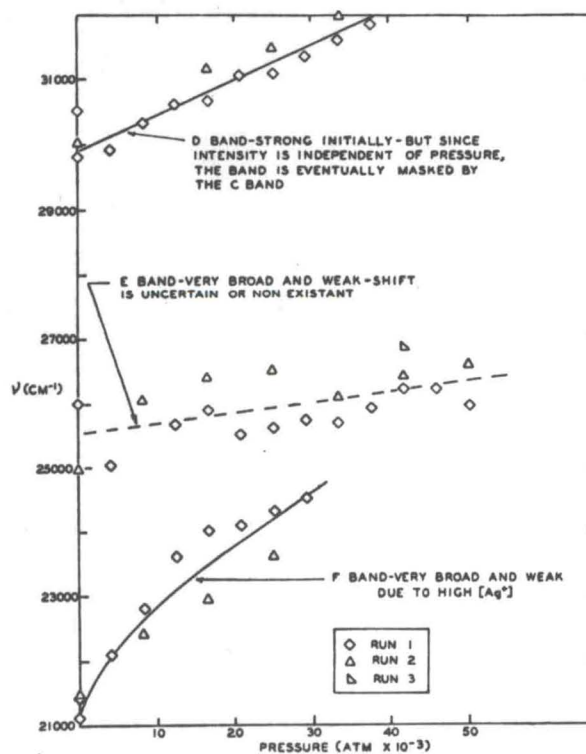


FIG. 2(b). The effect of pressure on the spectra of color centers in NaCl: 1.0% in AgCl, Part 2.

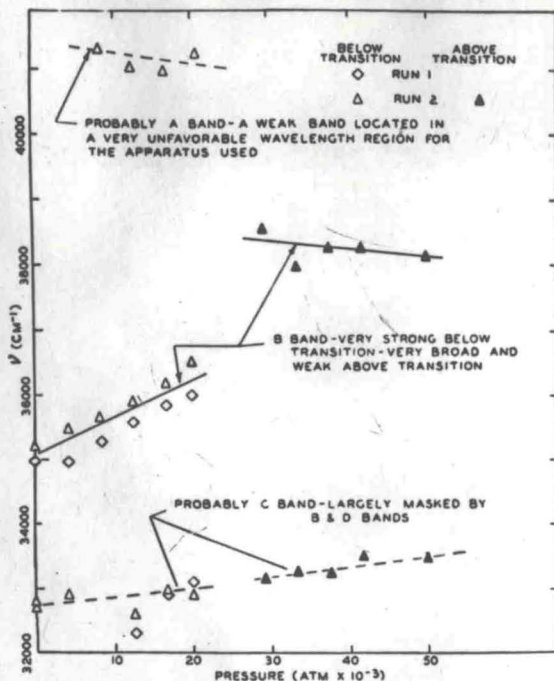


FIG. 3(a). The effect of pressure on the spectra of color centers in KCl: 1% AgCl, Part 1.

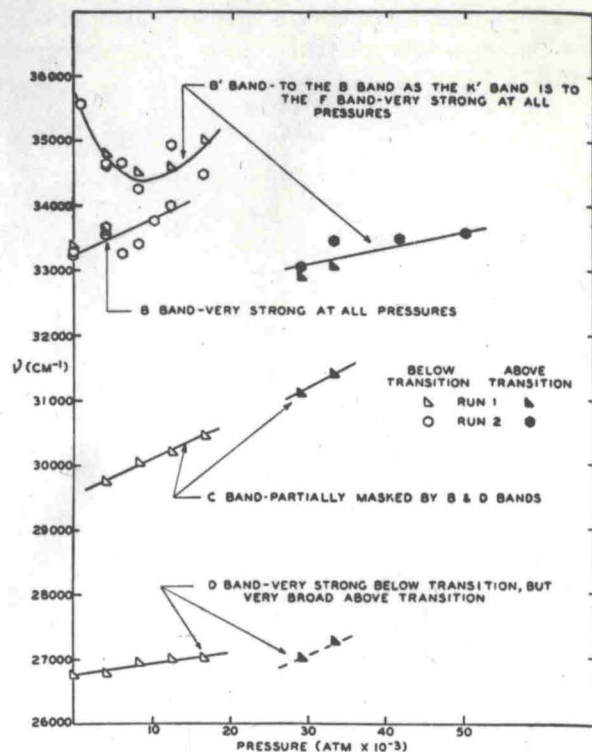


FIG. 4(a). The effect of pressure on the spectra of color centers in KBr: 0.1% AgBr, Part 1.

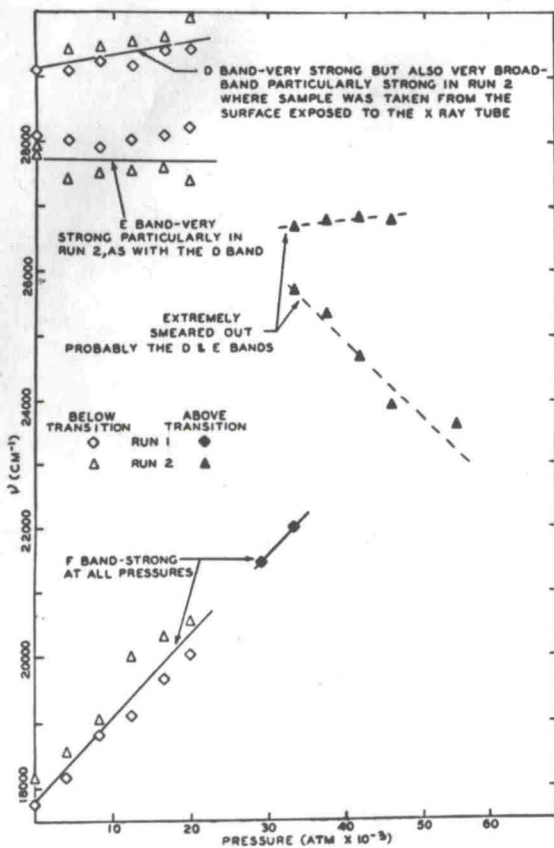


FIG. 3(b). The effect of pressure on the spectra of color centers in KCl: 1% AgCl, Part 2.

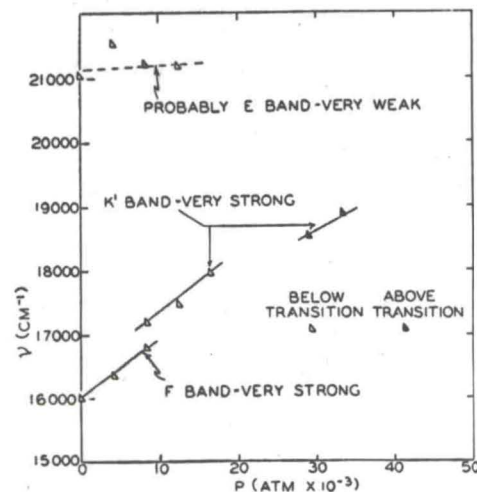


FIG. 4(b). The effect of pressure on the spectra of color centers in KBr: 0.1% AgBr, Part 2.

RESULTS

a. A Center

The data on this band are scanty and of very poor quality, due to the band's location far into the ultraviolet. The shift with increasing pressure appears to be slightly to lower energy. This is consistent with the generally held conclusion that this is a hole phenomenon, (that is, a phenomenon associated with the ab-

FIG. 5. Typical spectra vs wave number: NaCl—0.1% AgCl.

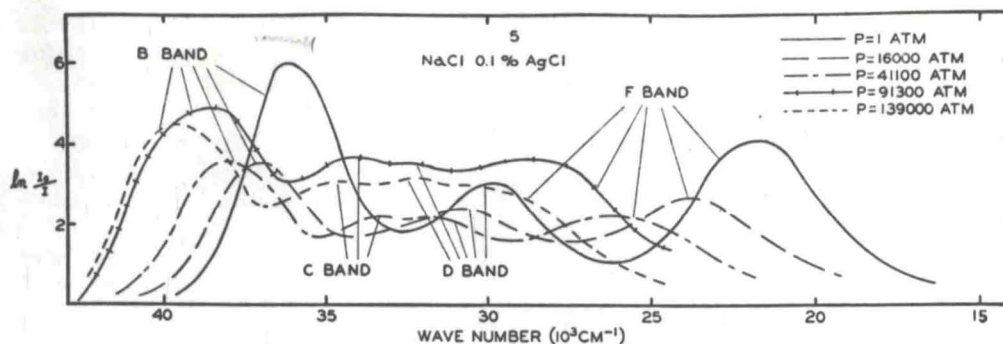


FIG. 6. Typical spectra vs wave number: NaCl—1.0% AgCl.

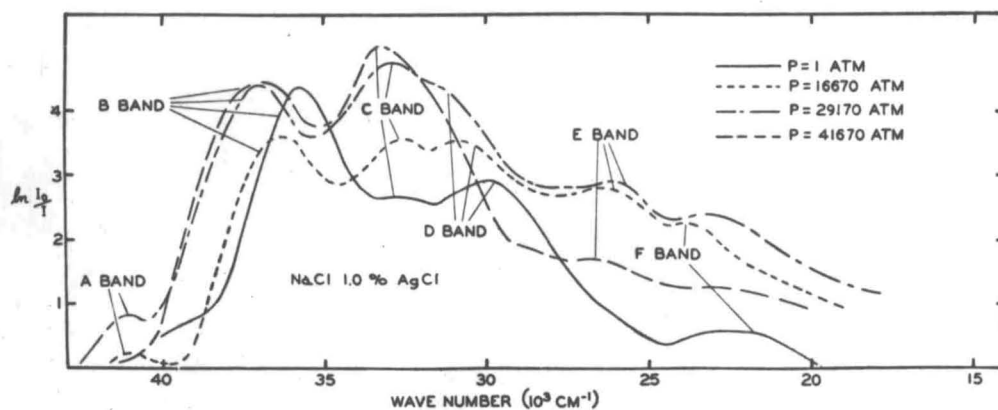
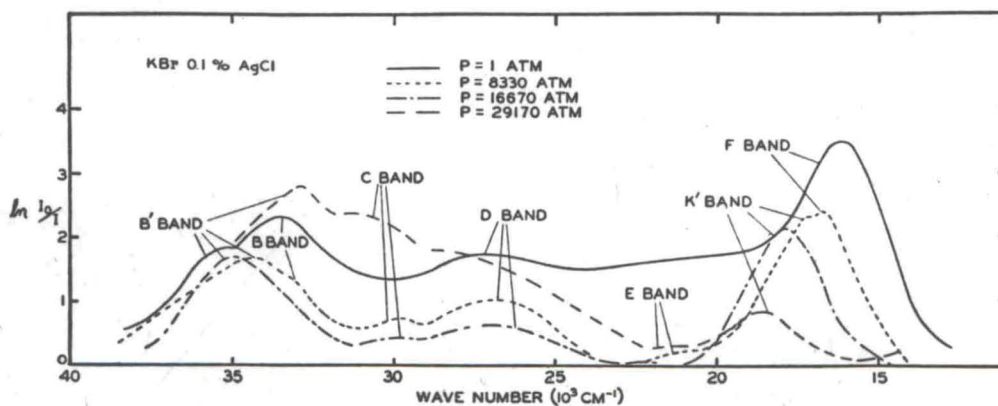


FIG. 7. Typical spectra vs wave number: KBr—0.1% AgCl.



sence of a normally present electron) although the data give no basis to define the model further.

b. B Center

The data on this band are of excellent quality and provide strong confirmatory evidence to the proposal that this center is a substitutional silver ion adjoining an *F* center. The shift with pressure is to higher energy, in magnitude roughly one-half that of the *F* band. A rough Ivey-like relation has been prepared for the *B* center (see Fig. 8). A comparison of the slope of the pressure shifts with the slope of the Ivey-like relation reveals the same approximate 2 to 1 relationship that was observed for the *F* center.¹⁰ However, the strongest evidence for this model of the center is the emergence

of a *B'* band on the high-energy side of the *B* band, and at the expense thereof, in potassium bromide. This occurrence is analogous to the emergence of the *K'* band in the same crystal.¹¹

c. C Center

A somewhat unusual phenomenon occurred with this center. In the rest of this color-center work (in Ag⁺-doped crystals), the intensities of the bands are relatively independent of pressure. In the case of the *C* center, however, the intensity of the band increases rapidly with increase of the pressure; often more than an order of magnitude in 50 000 atm. The shift in fre-

¹¹ W. G. Maisch and H. G. Drickamer, J. Phys. Chem. Solids 5, 328 (1958).

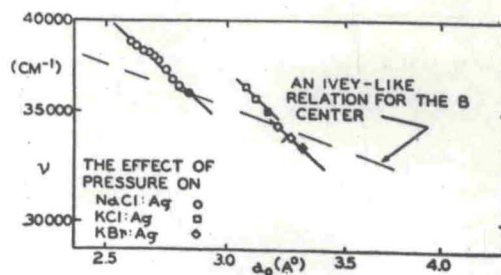


FIG. 8. An Ivey-like relation for the *B* center, and the compressibility near a *B* center.

quency of the spectra is to higher energy, although somewhat less so than the *B* band. This work is not inconsistent with the consensus of opinion that this band involves the interaction of two silver ions and the electron or electrons adjoining them. The model of Maenhout-van der Vorst and Dekeyser⁵ involving the joining of two *B* centers to form the *C* center is perhaps favored.

d. *D* Center

A great deal of controversy centers around this defect. Several authors have proposed models for the band, but no consensus of opinion exists.

When pressure is applied, the band shifts to higher energy initially, but levels off around 100 000 atm. The shift is in magnitude similar to the *B* center.

The strong shift to higher energy seems inconsistent with a hole picture for the center, as proposed by Etzel and Schulman.⁴

On the other hand, at first glance the other model proposed,⁵ that of a silver ion adjoining an *M* center also appears to be inconsistent, because the *M* band in pure LiCl has a much smaller pressure shift than the *F* band,¹⁰ while the *D* and *B* bands have comparable shifts. However, if one considers the Knox model of the *M* center¹² the smaller Ag^+ ion in the center of the cavity could offer less resistance to compression at low pressures, at least.

e. *E* Center

The data on this band are confined almost exclusively to potassium chloride, where the band is quite strong. Little or no pressure dependence of ν_m is detected. This is consistent with Ishiguro's model^{6,7} of an electron trapped in the field of a substitutional silver ion.

ACKNOWLEDGMENTS

The authors would like to thank Dr. J. H. Schulman of the Naval Research Laboratory for furnishing the doped crystals. R. A. Eppler would like to express his appreciation for fellowship support from the Shell Oil Company and the Dow Chemical Company.

¹² R. S. Knox, Phys. Rev. Letters 2, 87 (1959).