

***U* Centers in CsBr†**

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The formation and optical properties of *U* centers (H^- ions at vacant halogen sites) in CsBr is reported. The infrared absorption spectrum due to the localized vibrational mode of this center has been studied between 80 and 300°K. At 80°K, the local-mode resonance occurs at 363 cm^{-1} . The first electronic transition of the center (*U* band) has been studied between 6 and 360°K. At 6°K the *U*-band position is measured at 5.11 eV, and its limiting half-width is 0.26 eV. The effective phonon frequency contributing to the width has a value of 95 cm^{-1} .

WE report here for the first time the formation and optical properties of *U* centers in an alkali halide of the CsCl structure. The infrared absorption due to *U*-center local mode and the ultraviolet absorption due to its first electronic transition have been observed for CsBr which crystallizes in the CsCl structure.

The *U* center consists of a H^- ion occupying the vacant halogen-ion site and shows the characteristic electronic absorption band (*U* band) in the ultraviolet region. Martienssen¹ has reported the *U* band in several alkali halides of the NaCl structure. Impurity centers are also known to affect the lattice vibration spectrum of a crystal. In addition to modifying the frequency distribution of the host lattice, certain new features known as the local modes are introduced in certain cases. In a diatomic crystal when the substituent is lighter than both the host lattice atoms, as is the case with the *U* centers, one expects resonance absorption due to the local-mode vibration situated above the optic band of the host lattice.² The infrared absorption due to *U*-center local modes for a number of alkali halides of the NaCl structure has been reported by Schaeffer.³

In the present investigation, the *U* centers were produced by heating additively colored (with K) CsBr in an atmosphere of H_2 gas at about 500°C until all the *F* centers were converted into *U* centers. Initial attempts to produce additively colored CsBr using single crystals from Semi-Elements, Incorporated, were unsuccessful. Single crystals from Harshaw Chemical Company with much higher purity, were more amenable to additive coloration and to subsequent hydrogenation. By this method we obtained typical concentrations of 10^{17} – 10^{18} *U* centers per cm^3 . Compared to NaCl-type crystals the centers were relatively unstable at room temperature, but showed little decrease in concentration over a long period of time (six months) when stored in liquid N_2 .

The infrared local-mode absorption was studied by a Perkin-Elmer Model 301 spectrophotometer. The spectra at 300 and 80°K are shown in Fig. 1. At 80°K the local-mode frequency occurs at 363 cm^{-1} (half-width 10 cm^{-1}). An Ivey plot of the peak position with lattice constant for all alkali halides with available data is

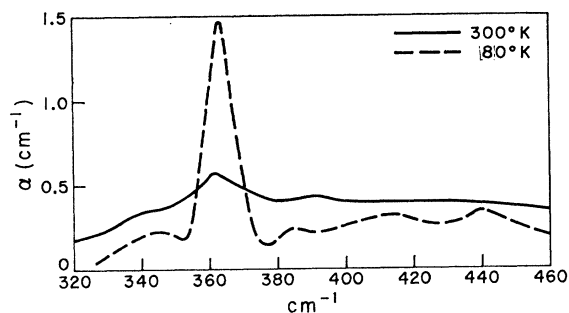


FIG. 1. Local-mode absorption spectrum due to *U* centers in CsBr.

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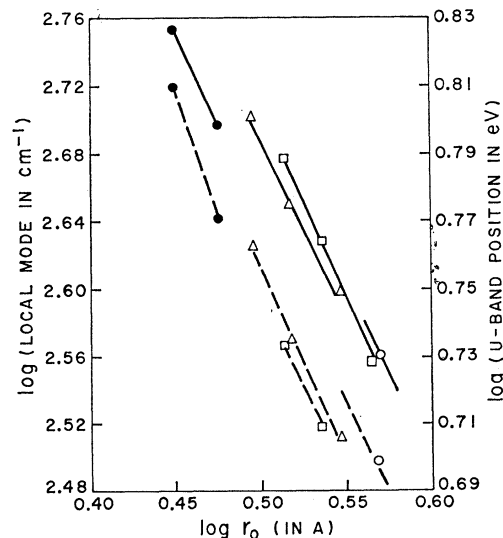


FIG. 2. Ivey plots of *U*-center local mode (solid line) and *U*-center electronic band (dashed line) in alkali halides as functions of nearest-neighbor distance. Na halides—●, K halides—△, Rb halides—□, and Cs halides—○.

shown in Fig. 2. Side bands due to interaction of local-mode phonons with perturbed lattice phonons in the case of NaCl-type crystals have been reported previously.⁴ There are indications of a few side bands in the case of the CsBr U local mode (Fig. 1). The first side band observed on both high- and low-energy sides is probably due to summation and difference processes involving a TA(X) mode with an average value of 20 cm^{-1} . The slight difference in the separation of the sum and difference band from the main resonance may be due to anharmonicity in the crystal potential.

The first electronic transition of the U center in CsBr was studied at temperatures ranging from 6 to 360°K. Figure 3 shows the U band at 80°K after correction for the absorption edge of the host lattice. The Ivey plot of the U -band position for the various alkali halides is shown in Fig. 2. The variation of the peak position and

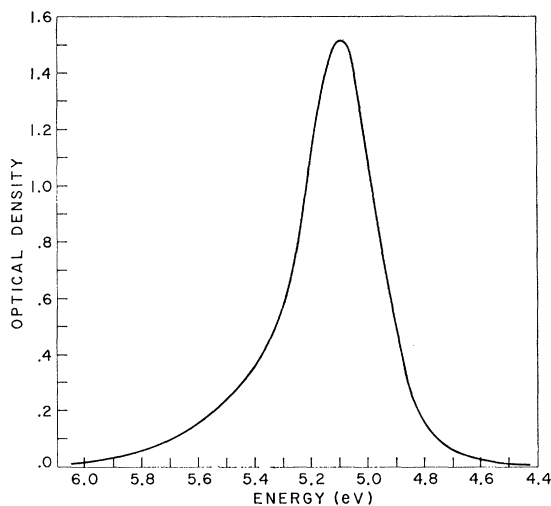


FIG. 3. U band in CsBr at 80°K.

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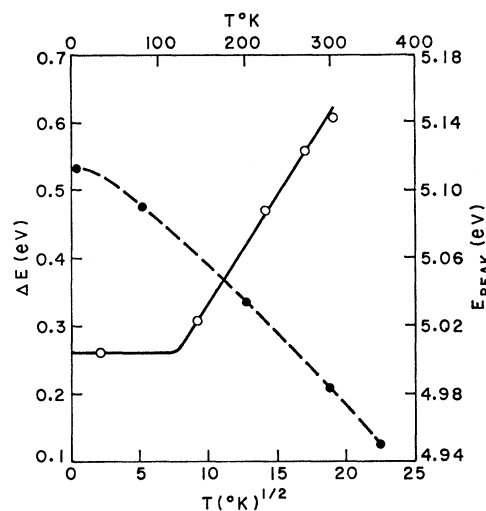


FIG. 4. Half-width (solid line) versus $T^{1/2}$, and peak position (dashed line) versus T for the U band in CsBr.

half-width with temperature is shown in Fig. 4. A Williams-Hebb⁵ plot of the half-width with temperature yields an effective phonon frequency of 95 cm^{-1} . This value lies between the transverse and longitudinal optic branches of CsBr. A similar situation is known to exist in the case of F centers in alkali halides.⁶

Work on the band-shape calculation by the method of moments, and similar studies on the U center in CsCl and CsI are in progress and will be reported elsewhere.

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