

## Letters to the Editor

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### Spectra of Halogen Solutions and $V$ Bands in Alkali Halides

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**T**HE  $V$  bands observed in alkali halides present key problems in solid state physics.<sup>1</sup> We believe that an insight into the nature of some of these  $V$  bands may be obtained as a result of knowledge of the spectra of halogens in various solvents, the properties of solid polyhalides and halide ions, and the chemistry of the interaction of halogens with alkali halides, together with the observations reported in this paper. In particular, the main features of Mollwo's  $V$  bands relate to well-known spectrochemical phenomena not specifically related to the solid state. Some of the  $V$  bands produced at room temperature or higher in KI, KBr, and KCl correspond to the absorption bands produced by dissolving halogens in aqueous halide solutions. Further, the prominent absorption bands ( $H$  and  $V_1$ ) produced at low temperatures seem to follow the absorption of halogen diatomic molecules or halogens dissolved in inert solvents.

Figure 1 (curves 2 and 3) shows the spectra of KI and CsI in water solution to which a little iodine is added, making the colorless solution yellow-brown.

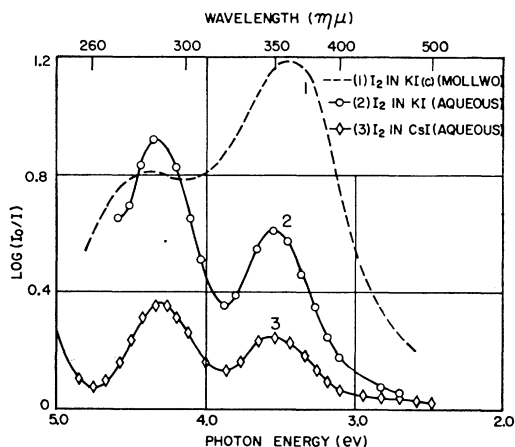


FIG. 1. Spectra of iodine dissolved in crystalline potassium iodide and in aqueous iodide solutions.

The peak wavelengths are strikingly similar to Mollwo's (curve 1). An analogous situation prevails for KBr+Br<sub>2</sub>+water or KBr+I<sub>2</sub> (or IBr)+water and Mollwo's KBr  $V$  bands, as well as for KCl+Cl<sub>2</sub>+water and x-irradiated KCl. These bands in solution are widely held to be due to the formation of polyhalide ions such as I<sub>3</sub><sup>-</sup>, Br<sub>3</sub><sup>-</sup>, IBr<sub>2</sub><sup>-</sup>, and Cl<sub>3</sub><sup>-</sup>, as a result of electron donor-acceptor interactions between halide ion and halogen molecule.<sup>2</sup> They are also formed in high yield when an alkali halide aqueous solution is irradiated with ionizing "rays" or electrolyzed. Among other ways in which we have produced similar spectra are: (1) adsorption of I<sub>2</sub> onto crystal surfaces, (2) x-irradiation of polycrystalline alkali halides (shown to liberate free halogen which is then adsorbed on the surfaces),<sup>3</sup> and (3) dissolution of colored crystals (making possible an analysis for halogen by well-known spectrochemical methods related to the nature of the  $V$  centers themselves).

We conclude that the  $V_2$  and  $V_3$  bands in KI and KBr, and the  $V_2$  band in KCl, arise from one center which may be described as a linear array of halogen molecule and halide ion in which the crystallinity of the alkali halide plays only a minor role. Such a configuration is achievable within the crystal lattice and without (e.g., along dislocation sub-boundaries, etc.). Alternative descriptions of the actual *transition* depend on whether the electronic excitation is localized or not. Any part of the interaction complex  $X_2-X^-$  can be considered optically active, rather than the complex as a whole.<sup>4,5</sup> This requires the transitions to be localized in either (1)  $X^-$  perturbed by  $X_2$  or in a local field similar to that given by  $X_2$  or (2)  $X_2$  perturbed by  $X^-$  or in a local field similar to that given by  $X^-$ , where  $X$  is any halogen atom.

Table I shows the similarity of the  $H$  and  $V_1$  bands in potassium halides with the molecular absorption bands of the corresponding halogens. Grossweiner and Matheson<sup>6</sup> have obtained evidence for  $X_2^-$  in water, and Känzig<sup>7</sup> has obtained evidence for this molecular-ion in crystals irradiated at low temperatures. Känzig's work suggests that indeed the  $V_1$  center is molecular-like, and that our comparisons may not be capable of ascertaining the *electronic* nature of the molecule. The

TABLE I. Comparison of  $V$  bands and halogen bands.<sup>a</sup>

Salt	$V_1$	$H_1$	$X_2^b$	$V_2$	$V_3$	$X_2+X^-$	(H <sub>2</sub> O) <sup>c,d</sup>
KCl	356	345	335 <sup>e</sup>	233	218		230
KCl <sub>0.5</sub> Br <sub>0.5</sub> <sup>f</sup>	390		385 <sup>e</sup>	265		(390)	265
KBr	410	380	400 <sup>e</sup>	266	232	(410)	270 230
KI <sup>e</sup>	(a)570 (b)470	540 <sup>e</sup> 450 <sup>e</sup>	520 <sup>e</sup> (H <sub>2</sub> O)460	355	290		355 290

<sup>a</sup> Absorption peaks in mμ. Numerical values taken mostly from W. H. Duerig and J. J. Markham, Phys. Rev. **88**, 1043 (1952).

<sup>b</sup>  $X_2^-$  = halogen bands measured in CCl<sub>4</sub>, except as noted.

<sup>c</sup> H. N. Hersh (unpublished).

<sup>d</sup> Gilbert, Goldstein, and Lowry, J. Chem. Soc. **1931**, 1092.

<sup>e</sup> A. E. Gillam and R. A. Morton, Proc. Roy. Soc. (London) **A124**, 604 (1929).

<sup>f</sup> G. Miessner and H. Pick, Z. Physik **134**, 604 (1953).

<sup>g</sup> F. H. Getman, J. Am. Chem. Soc. **50**, 2883 (1928).

spectra of the irradiated crystals suggest the formation of some kind of molecule which can "react" under the influence of higher temperature or optical excitation to form complexes with halide ions and therefore  $V_{2,3}$  centers.

The analysis at the present state glosses over certain differences (e.g., between x-rayed and additively colored crystals) in order to point out similarities; it is hoped to extend these results so that they may form an adequate basis for explaining the more intimate details of  $V$  centers.

<sup>1</sup> F. Seitz, *Revs. Modern Phys.* **26**, 7 (1954).

<sup>2</sup> Sneed, Maynard, and Brasted, *Comprehensive Inorganic Chemistry, The Halogens* (D. Van Nostrand Company, Inc., New York, 1954), Vol. III.

<sup>3</sup> H. N. Hersh, *Bull. Am. Phys. Soc. Ser. II*, **1**, 213 (1956).

<sup>4</sup> R. S. Mulliken, *J. Phys. Chem.* **56**, 801 (1952).

<sup>5</sup> L. I. Katzin, *J. Chem. Phys.* **23**, 2055 (1955).

<sup>6</sup> L. I. Grossweiner and M. S. Matheson, *J. Chem. Phys.* **23**, 2443 (1955).

<sup>7</sup> W. Känzig, *Phys. Rev.* **99**, 1890 (1955).

### Elastoresistance Constants of $p$ -Type InSb at 77°K\*

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A PRELIMINARY experiment has been carried out to measure the elastoresistance constants of single-crystal specimens of  $p$ -type InSb at 77°K. The experimental arrangement used is similar to that employed by Smith,<sup>1</sup> whose notation and terminology are used below in reporting the data.

A zone-refined single-crystal ingot of InSb was obtained from the Chicago Midway Laboratory through the courtesy of its semiconductor group. A Hall measurement at 77°K gave a hole concentration of  $3 \times 10^{15}$  cm<sup>-3</sup>. Samples were cut from the oriented ingot in the form of rectangular rods of approximate dimensions 30 mm  $\times$  2 mm  $\times$  2 mm. The nominal resistivity of the samples at 77°K is 0.5 ohm-cm.

The piezoresistance constants  $\Pi_{11}$ ,  $\Pi_{12}$ , and  $\Pi_{44}$  were determined by observing the effect of hydrostatic pressure and tensile stress on the "longitudinal" resistivity of two sets of four samples whose long dimensions were either along the [110] or [111] direction. The order of magnitude of the tensile stress was  $10^7$  dynes/cm<sup>2</sup>; that of the pressure, 150 atmospheres. The elastoresistance constants, relating the resistivity change to the strain, are obtained from  $\Pi_{11}$ ,  $\Pi_{12}$ ,  $\Pi_{44}$ , and the elastic constants.<sup>2,3</sup> Table I gives the piezo- and elastoresistance constants at 77°K.

In the notation of Dresselhaus,<sup>4</sup> for the case of a "simple many-valley" semiconductor,<sup>5</sup> we may draw the following conclusions about the position of the energy extrema from these results:

TABLE I. Piezo- and elastoresistance constants of InSb at 77°K.

$\Pi_{11}$ (cm <sup>2</sup> /dyne)	$(98 \pm 7) \times 10^{-12}$	$m_{11}$	$32 \pm 5$
$\Pi_{12}$ (cm <sup>2</sup> /dyne)	$(-49 \pm 6) \times 10^{-12}$	$m_{12}$	$-16 \pm 2$
$\Pi_{44}$ (cm <sup>2</sup> /dyne)	$(435 \pm 12) \times 10^{-12}$	$m_{44}$	$137 \pm 4$

(1) The point  $\Gamma$ ,  $K = \langle 000 \rangle$ , with doubly degenerate, spherical energy surfaces ( $\Gamma_6$  or  $\Gamma_7$ ), is ruled out since the elastoresistance is large.

(2) Points on the  $\Lambda$  or  $\langle 111 \rangle$  axes are ruled out since  $m_{11} \neq m_{12}$ .

(3) The points  $W$ ,  $K = (2\pi/a)\langle 10\frac{1}{2} \rangle$ , and points on the  $\langle 100 \rangle$  axes are ruled out since  $m_{44}$  is large.

The energy band calculations of Dresselhaus<sup>4</sup> suggest the points  $\Gamma$ ,  $\Lambda$ ,  $W$ , and a general point in the Brillouin zone as likely points for the occurrence of the extrema. In view of the above conclusions, nondegenerate energy surfaces at a general point in the zone, or fourfold-degenerate surfaces at  $\Gamma$  ( $\Gamma_8$ ), remain as possibilities for the  $p$ -type InSb investigated.

Additional experiments measuring the piezoresistance constants of several samples of both  $n$  and  $p$  types of InSb of different resistivities are now in progress. A preliminary measurement of the temperature dependence of these constants has been completed; more refined measurements will be reported in detail in the near future.

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<sup>1</sup> C. S. Smith, *Phys. Rev.* **94**, 42 (1954).

<sup>2</sup> L. H. De Vaux and F. A. Pizzarello, *Phys. Rev.* **102**, 85 (1956).

<sup>3</sup> R. F. Potter, *Bull. Am. Phys. Soc. Ser. II*, **1**, 53 (1956).

<sup>4</sup> G. Dresselhaus, *Phys. Rev.* **100**, 580 (1955).

<sup>5</sup> C. Herring, *Bell System Tech. J.* **34**, 237 (1955).

### Moving Striations

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MOVING striations have usually been investigated by one only of the following methods: (1) observations, such as Zaitsev's,<sup>1</sup> of appearance; (2) use of Langmuir probes, with a cathode-ray oscilloscope<sup>2,3</sup>; (3) optical studies, initially by rotating mirrors, more recently by photomultiplier tubes.<sup>4,5</sup>

In an investigation in progress here, measurement of all these types is being made simultaneously, in a tube of 2-cm radius with three fine probes fixed at the axis and a fourth capable of transverse motion. Anode and cathode are also movable.

Striations are observed by a photomultiplier moving along the discharge tube. A dual beam oscilloscope displays simultaneously two instantaneous quantities, e.g., light intensity, probe current. Striation speeds are