

account for energy losses due to the absorption by the mica window, air space, and aluminum foil. Possible unaccountable errors in this experiment may be due to (1) background variations, since the spectrometer was located in the pile building, (2) magnetic variations near the photo-multiplier tube and (3) generator hash in the magnet current at times.

Work is being continued to further investigate the pulse height-energy variation in the low energy range and in the energy range above 650 kev.

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\*\* On leave from Vanderbilt University, Nashville, Tennessee, 1949-1950.

<sup>1</sup> H. Kallmann, *Natur und Technik* (July, 1947).

<sup>2</sup> M. Deusch, M.I.T. Technical Report No. 3 (December, 1947).

<sup>3</sup> W. H. Jordan and P. R. Bell, *Rev. Sci. Inst.* **18**, 703 (1947).

<sup>4</sup> L. E. Glendenin, *Nucleonics* **2**, 12 (1948).

### Energy Bands and Mobilities in Monatomic Semiconductors

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FOR a cubic crystal subject to a homogeneous strain,  $\epsilon_{ij}$ , the linear shift in energy band with strain may be expressed in the form

$$E = E_0 + \sum \beta_{ij} \epsilon_{ij} = E_0 + E_1 \Delta, \quad (1)$$

where  $\Delta = \epsilon_{11} + \epsilon_{22} + \epsilon_{33}$  is the dilation since all terms containing  $\epsilon_{ij}$  with  $i \neq j$  must vanish by symmetry. The shifts in the energy levels corresponding to the top of the filled band,  $E_f$ , and the bottom of the conduction band,  $E_c$ , produced by a periodic dilation of a lattice wave are shown schematically in Fig. 1(a). As illus-

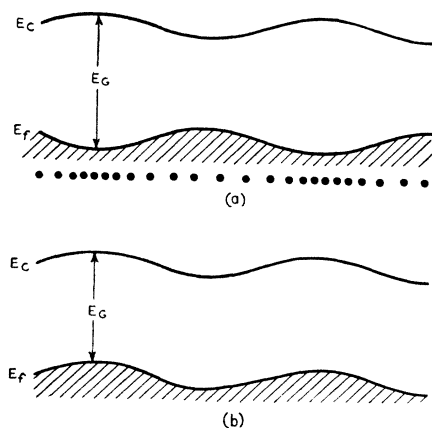


FIG. 1. (a) Shift of energy bands with varying dilation. (b) Shift of energy bands with varying electrostatic potential.

trated, the bands may shift in opposite directions. In crystals with the diamond structure, such as Ge and Si, the energy gap,  $E_G$ , decreases with a positive dilation; in others, such as Te, the shift is in the opposite direction. The difference between the shifts in  $E_c$  and  $E_f$  is equal to the shift in  $E_G$ :

$$E_{1G} = E_{1c} - E_{1f}. \quad (2)$$

On the other hand, a varying electrostatic potential makes the bands move up and down together, as in Fig. 1(b).

The theories of Peckar<sup>1</sup> and of James<sup>2</sup> may be extended to show that the effective mass concept may be applied to gradual shifts in energy bands produced by distortions as well as by a varying electrostatic potential.<sup>3</sup> In both cases, the position of the energy band may be used as an effective potential for the electron provided that the variation is sufficiently gradual. This is the case for shifts caused by lattice vibrations of long wave-length which interact with electrons of thermal velocities in semiconductors.

It is thus possible to calculate scattering by lattice waves by taking as the interaction potential,  $U(\mathbf{r})$ , the shift in energy band resulting from dilation,  $E_1 \Delta(\mathbf{r})$ :

$$U(\mathbf{r}) = E_1 \Delta(\mathbf{r}). \quad (3)$$

The matrix element involved in scattering,

$$M_{kk'} = \int \psi_{k'}^* U(\mathbf{r}) \psi_k d\tau = \int \exp[i(\mathbf{k} - \mathbf{k}') \cdot \mathbf{r}] E_1 \Delta(\mathbf{r}) d\tau \quad (4)$$

vanishes unless  $\mathbf{k}' = \mathbf{k} \pm \mathbf{q}$ , in which case

$$|M_{kk'}|^2 = E_1^2 |\mathbf{q} \cdot \mathbf{A}_q|^2, \quad (5)$$

where  $\mathbf{A}_q$  is the complex amplitude of the lattice wave of wave vector  $\mathbf{q}$ . The interaction constant  $C$  used by Sommerfeld and Bethe and by Seitz<sup>4</sup> is equal to  $(3/2)E_1$ ; that used by Wilson is equal to  $E_1$ .

The expression for mobility,  $\mu$ , derived in the usual way, may be expressed in the form:

$$\mu = 2(2\pi)^{1/2} e \hbar^4 \rho c_i^2 / 3m_e^{5/2} (k_0 T)^{3/2} E_1^2 \\ = (3.2 \times 10^{-5}) \rho c_i^2 / T^{3/2} E_1^2 \text{ cm}^2/\text{volt sec.} \quad (6)$$

In deriving the numerical factor we have set the effective mass ratio equal to unity and expressed  $E_1$  in ev. The product of the density,  $\rho$ , and the square of longitudinal wave velocity,  $c_i^2$ , can be expressed in terms of the elastic constants.

Equation (6) may be used to derive  $|E_{1c}|$  and  $|E_{1f}|$  from mobilities of conduction electrons and holes, respectively. The calculations for diamond, Si, Ge, and Te, together with relevant data, are given in Table I. The anisotropy of Te has been neglected.

TABLE I. Derivation of shift of energy bands with dilation from mobility data and comparison with shift of energy gap with dilation.

	Diamond	Silicon	Germanium	Tellurium
$\rho c_i^2 \times 10^{-12}$ (c.g.s.)	10.8 <sup>a</sup>	2.0 <sup>c</sup>	1.55 <sup>b</sup>	0.5 <sup>e</sup>
$\mu_n$ (electrons) (cm <sup>2</sup> /volt sec., 295°K)	900 <sup>d</sup>	300 <sup>e</sup>	3500 <sup>f</sup>	530 <sup>g</sup>
$\mu_p$ (holes) (cm <sup>2</sup> /volt sec., 295°K)	>200 <sup>h</sup>	100 <sup>e</sup>	1700 <sup>f</sup>	530 <sup>g</sup>
$\mu_n T^{3/2}$	45 × 10 <sup>5</sup>	15 × 10 <sup>5</sup>	180 × 10 <sup>5</sup>	27 × 10 <sup>5</sup>
$\mu_p T^{3/2}$	>10 × 10 <sup>5</sup>	5 × 10 <sup>5</sup>	86 × 10 <sup>5</sup>	27 × 10 <sup>5</sup>
$ E_{1c} $ (ev)	8.8	6.5	1.7	2.4
$ E_{1f} $ (ev)	<30	11.3	2.4	2.4
$ E_{1c}  +  E_{1f} $	<39	17.8	4.1	4.8
$ E_{1G} $ (ev)	?	~30 <sup>i</sup>	~5 <sup>i</sup>	5.0 <sup>i</sup>

<sup>a</sup> Longitudinal velocity in [110] direction calculated from elastic constants. See R. F. S. Hearmon, *Rev. Mod. Phys.* **18**, 409 (1946).

<sup>b</sup> Calculated from elastic constants measured by McSkimin, Mason, and Bond on single crystal sample prepared by K. M. Olson.

<sup>c</sup> Estimated from compressibility.

<sup>d</sup> C. C. Klick and R. J. Maurer, *Phys. Rev.* **76**, 179 (1949).

<sup>e</sup> Reference 5.

<sup>f</sup> Unpublished data of J. R. Haynes.

<sup>g</sup> Vivian A. Johnson, *Phys. Rev.* **74**, 1255 (1948).

<sup>h</sup> K. G. McKay (private communication).

<sup>i</sup> See text.

If  $E_{1c}$  and  $E_{1f}$  have opposite signs, as in Fig. 1(a), we should have

$$|E_{1G}| = |E_{1c}| + |E_{1f}|. \quad (7)$$

Various independent estimates of  $|E_{1G}|$ , given in the last row of the table, are in reasonable agreement with (7). These estimates were obtained as follows:

**Silicon.** The variation of  $E_G$  with temperature, derived from intrinsic concentration,<sup>5</sup> combined with the thermal expansion coefficient.

**Germanium.** (a) As for Si, (b) change of intrinsic conductivity with pressure,<sup>6</sup> (c) change of resistance of  $n-p$  junction with pressure.<sup>7</sup>

*Tellurium.* From analysis of Bridgman's data on variation of intrinsic conductivity with pressure.<sup>8</sup> The high mobility of electrons and holes in germanium is thus correlated with a small shift in energy gap with dilation.

<sup>1</sup> S. Peckar, J. Phys. USSR, 10, 431 (1946).

<sup>2</sup> Hubert M. James, Phys. Rev. 76, 1602 (1949).

<sup>3</sup> A proof, together with a direct calculation of the pertinent matrix element without making use of the effective mass concept, will be given in a forthcoming paper by the authors.

<sup>4</sup> See A. Sommerfeld and H. Bethe, *Handbuch der Physik*, Vol. XXIV, 1; A. H. Wilson, *The Theory of Metals* (Cambridge University Press, London, 1936); Frederick Seitz, Phys. Rev. 73, 549 (1948).

<sup>5</sup> G. L. Pearson and J. Bardeen, Phys. Rev. 75, 865 (1949).

<sup>6</sup> P. H. Miller and Julius Taylor, Phys. Rev. 76, 179 (1949) and personal communication from Professor Miller.

<sup>7</sup> Unpublished measurements of G. L. Pearson.

<sup>8</sup> John Bardeen, Phys. Rev. 75, 1777 (1949).

## Color Centers in Calcium Fluoride and Barium Fluoride Crystals

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THE color centers produced photochemically (x-rays, ultra-violet light) or additively (metal vapor, electrons) have been investigated by Pohl<sup>1</sup> and his school mainly in monovalent ionic crystals, such as, alkali halides. The first results on color centers produced by x-rays in calcium fluoride (CaF<sub>2</sub>) and barium fluoride crystals (BaF<sub>2</sub>) are presented in this note.

Natural and synthetic crystals of calcium fluoride and synthetic crystals of barium fluoride were used. The thickness of the crystals was between 0.5 and 1.0 cm. Hard x-rays (200 kv, 10 ma) were used to produce a uniform coloration throughout the entire crystals. The exposure time varied from 0.5 to 5.0 hours. Immediately after exposure to x-rays, the transmission of the colored crystals was measured with a Beckman spectrophotometer in the spectral region from 2200A to 10,000A. No change in coloration occurred during measurements.

The absorption spectrum of color centers in calcium fluoride

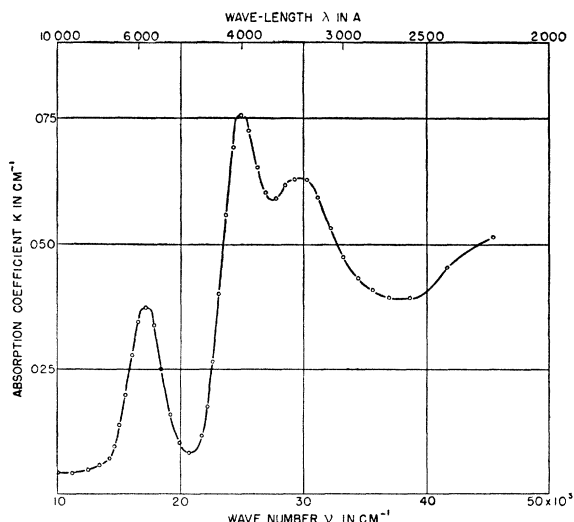


FIG. 1. Absorption spectrum of color centers in calcium fluoride (CaF<sub>2</sub>) crystal [ $k = (1/d) \log_{10}(I_0/I)$ ; 200 kv, 10 ma, exposure 5 hours].

crystals is reproduced in Fig. 1. The three absorption bands fall at 5800A, 4000A, and 3350A. A strong increase of absorption

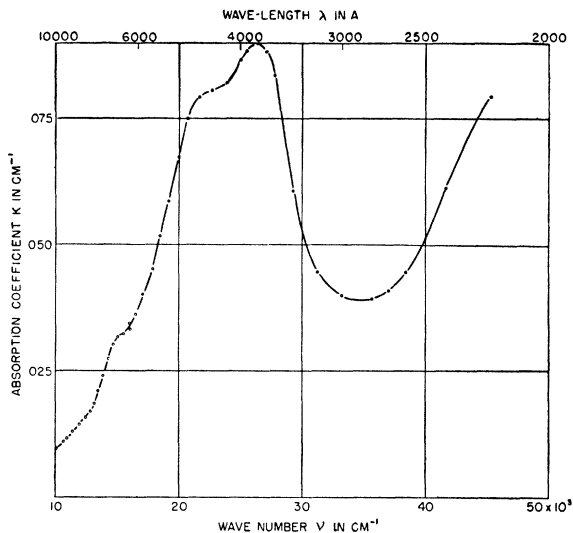


FIG. 2. Absorption spectrum of color centers in barium fluoride (BaF<sub>2</sub>) crystal [ $k = (1/d) \log_{10}(I_0/I)$ ; 200 kv, 10 ma, exposure 0.5 hour].

toward shorter wave-length indicates a fourth band with a maximum below 2200A.

In Fig. 2 is given the absorption spectrum of color centers in barium fluoride crystal. As for calcium fluoride, three absorption bands are seen at 6700A, 4800A, and 3800A. A fourth band below 2200A is also apparent. As compared with calcium fluoride the bands are shifted to longer wave-lengths and they overlap to a greater extent.

The formation of absorption bands with increase of exposure time is shown in Fig. 3. All three bands show saturation with

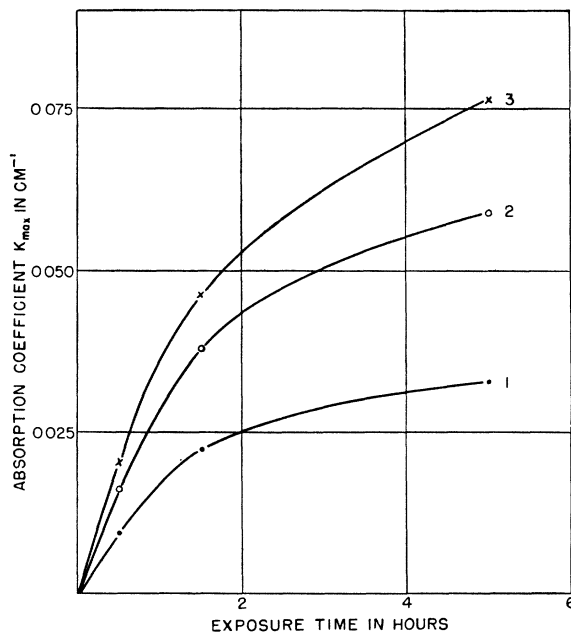


FIG. 3. Change of the absorption band intensity of calcium fluoride with increase of exposure time to x-rays (200 kv, 10 ma). 1. Absorption band at 5800A. 2. Absorption band at 3350A. 3. Absorption band at 4000A.

increase in exposure similar to the saturation of the coloration of alkali halides.<sup>2</sup>

In additively colored natural calcium fluoride crystals Mollwo<sup>3</sup>