



FIG. 2. The infrared absorption spectrum of  $\text{SrTiO}_3$ .

pure specimen of powdered strontium titanate ( $\text{SrTiO}_3$ ) was observed between  $2\mu$  and  $15\mu$  (Fig. 2). It is identical with that of barium titanate obtained under similar conditions over that region of the spectrum. Noland<sup>1</sup> has recently reported the spectrum of a single crystal of strontium titanate between  $1\mu$  and  $10.5\mu$ , at which wavelength the extinction coefficient is greater than  $100 \text{ cm}^{-1}$  and is still increasing. He finds two weak bands near  $5.5\mu$  and  $7.5\mu$ . These could easily have been missed by us since our effective thickness was much less than the thickness he used. We might add that the spectrum of a single crystal of barium titanate just run in this laboratory by M. Haas shows a weak band at  $8\mu$  and a "cutoff" near  $11.2\mu$ . The spectrum of ilmenite ( $\text{FeTiO}_3$ ) has been recorded by Hunt and others.<sup>2</sup> With the exception of a weak band at  $1000 \text{ cm}^{-1}$ , it is also very similar to that of barium titanate.

Apart from impurity bands, there appears to be no difference between the spectrum of barium titanate in the hexagonal and in the tetragonal form over the range  $2\mu$  to  $15\mu$ . No change was observed in the spectrum of barium titanate (ceramic) when heated to  $150^\circ\text{C}$ .

The foregoing observations may be considered in the light of recent theories about the ferroelectric character of barium titanate.

Jaynes<sup>3</sup> has predicted from an electronic theory that there should be an infrared absorption at  $1000 \text{ cm}^{-1}$ . There is definitely no *strong* absorption band in the neighborhood of  $1000 \text{ cm}^{-1}$ . Although a few specimens have shown a very weak absorption near  $1000 \text{ cm}^{-1}$ , this is most probably due to  $\text{BaO}$  impurity.

Megaw<sup>4</sup> has proposed that the change from the cubic form (above the Curie point of  $120^\circ\text{C}$ ) to the tetragonal form corresponds to a change in the character of the bonds round the Ti and O atoms. If this were so, one might expect a change in the spectrum on heating to  $150^\circ\text{C}$  and also differences between the spectra of the tetragonal and hexagonal forms of  $\text{BaTiO}_3$  since the latter is not ferroelectric. This change should be very marked in the strong band near  $600 \text{ cm}^{-1}$  since this band [which is common to all titanates and is found also in rutile ( $\text{TiO}_2$ )] is undoubtedly connected with a vibration of the  $\text{TiO}_4$  tetrahedra. No such change was ob-

served. It is possible, of course, that changes may have occurred at lower frequencies beyond our range of detection.

\* This work was sponsored by the Signal Corps. Engineering Laboratory.

<sup>1</sup> J. A. Noland, Phys. Rev. **94**, 724 (1954).

<sup>2</sup> Hunt, Wisherd, and Bonham, Anal. Chem. **22**, 1478 (1950).

<sup>3</sup> E. T. Jaynes, *Ferroelectricity* (Princeton University Press, Princeton, 1953), p. 69.

<sup>4</sup> H. D. Megaw, Acta Cryst. **5**, 739 (1952).

## Hyperfine Splitting of Donor States in Silicon

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(Received September 3, 1954)

ELECTRON spin resonances exhibiting hyperfine structure have recently been observed in *n*-type Si by Fletcher *et al.*<sup>1</sup> The number of hyperfine lines of these resonances corresponds exactly to the nuclear spin of the added Group V atoms, showing conclusively that the resonances are due to electrons localized near such atoms. It has therefore been assumed<sup>1</sup> that the resonances arise from the well-known donor states with ionization energies of about 0.04 to 0.05 eV. We have made a theoretical estimate of the hyperfine splitting of phosphorus donor states to be expected on this assumption and find agreement with experiment within a factor of  $\sim 2.5$ . (We estimate the uncertainty of our theoretical result as about a factor of 5.)

Following is a brief summary of our calculations; a detailed report will be published shortly. The conduction band of Si has 6 minima on the (1,0,0) and equivalent axes.<sup>2</sup> The effective masses at one of these minima are  $0.19m$  (twice) and  $0.99m$ .<sup>3</sup> Let  $\psi(\mathbf{k}^{(i)}, \mathbf{r})$  be the Bloch function corresponding to the energy minimum at  $\mathbf{k}^{(i)}$ , so normalized that

$$\int_{\text{cell}} |\psi(\mathbf{k}^{(i)}, \mathbf{r})|^2 d\tau = \text{volume of unit cell}, \quad (1)$$

and phased so as to be real at  $\mathbf{r}=0$ . It may then be shown that in the so-called effective mass approximation, the normalized ground-state wave function of the donor electron has the following form:

$$\psi(\mathbf{r}) = \frac{1}{(6)^{\frac{1}{2}}} \sum_{i=1}^6 F^{(i)}(\mathbf{r}) \psi(\mathbf{k}^{(i)}, \mathbf{r}). \quad (2)$$

The  $F^{(i)}(\mathbf{r})$  satisfy effective mass equations with the above masses and the potential  $-e^2/\kappa r$  ( $\kappa$ =dielectric constant). They are taken as real and are normalized to unity over all space. The hyperfine splitting is then determined by the value of

$$|\psi(0)|^2 = 6 |F^{(1)}(0)|^2 |\psi(\mathbf{k}^{(1)}, 0)|^2. \quad (3)$$

To obtain agreement with experiment one requires

$$|\psi(0)|^2_{\text{exptl}} = 0.44 \times 10^{24} \text{ cm}^{-3}. \quad (4)$$

From an approximate solution of the effective mass equation we find  $|F^{(1)}(0)|^2 = (0.000037 \pm 10\%) \times 10^{24} \text{ cm}^{-3}$ , while an estimate of  $|\psi(\mathbf{k}^{(i)}, 0)|^2$ , if we use the tight-binding approximation, gives 370 within a factor of about 2. When substituted into (3), these values give

$$(|\psi(0)|^2)_{\text{eff. mass}} \approx 0.082 \times 10^{24} \text{ cm}^{-3}. \quad (5)$$

When the ionization energy is calculated by the effective mass formalism one finds 0.028 eV, in rather serious disagreement with the observed 0.044 eV.<sup>4</sup> We have made rough allowance for the breakdown of the effective mass theory near the impurity atom. The resulting wave function, when the experimental binding energy is used, is rather larger in the last cell, and results in an increase of (5) by a factor of about 13. The final value is

$$(|\psi(0)|^2)_{\text{theor}} \approx 1.1 \times 10^{24} \text{ cm}^{-3}. \quad (6)$$

The fact that (6) agrees with the experimental value [Eq. (4)], well within the uncertainty of the calculation, lends support to the picture that the observed resonances are associated with the usual donor states.

This work was carried out while we were guests of the Bell Telephone Laboratories, and we would like to thank the staff for their cooperation and friendliness.

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<sup>1</sup> R. C. Fletcher *et al.*, Phys. Rev. **94**, 1392 (1954); **95**, 844 (1954).

<sup>2</sup> C. Smith, Phys. Rev. **94**, 42 (1954); B. Lax and co-workers (private communication).

<sup>3</sup> B. Lax and co-workers (private communication).

<sup>4</sup> F. J. Morin *et al.*, Phys. Rev. **96**, 833 (1954).

## Elastoresistance in *p*-Type Ge and Si\*

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(Received September 10, 1954)

SMITH has reported<sup>1</sup> a large elastoresistance effect in Ge and Si of both *n*- and *p*-type. In *n*-type material there is an accumulation of evidence to support the explanation that the large elastoresistance is brought about by a strain-induced transfer of electrons between nonequivalent anisotropic energy minima in the conduction band.<sup>2</sup> However, no such electron transfer mechanism seems capable of explaining the large elastoresistance of *p*-type material, since the spin-orbit coupling model<sup>3</sup> now seems firmly established, and this model predicts that the two nearly degenerate surfaces in the valence band have cubic symmetry individually.

We believe that the large elastoresistance of *p*-type specimens originates in a strain-induced mixing of the nearly degenerate bands and a consequent strong warping of the energy surfaces. We have carried through a formal theory of this process using the methods of Fuchs and Peng,<sup>4</sup> McClure,<sup>5</sup> and Shockley,<sup>6</sup> and assuming the spin-orbit coupling model. Our result is that to first order in the strain the energy states in the strained lattice are given by

$$E(\mathbf{p}) = (A + 2B)p^2/3 \pm R + \mathbf{p} \cdot \boldsymbol{\epsilon} \cdot \mathbf{p}/m - \mathbf{p} \cdot \boldsymbol{\epsilon} \cdot \nabla_{\mathbf{p}} E(\mathbf{p}) + (E_{11} + 2E_{12})\epsilon/3 \pm \Delta R, \quad (1)$$

with

$$R \equiv (A - B)^2 p^4/9 + [C^2 - (A - B)^2][p_x^2 p_y^2 + p_y^2 p_z^2 + p_z^2 p_x^2]/3, \quad (2)$$

$$\Delta R = (1/R)\{CE_{44}[p_x p_y \epsilon_{xy} + p_y p_z \epsilon_{yz} + p_z p_x \epsilon_{zx}]/3 + (A - B)(E_{11} - E_{12})[(3p_x^2 - p^2)(3\epsilon_{xx} - \epsilon) + (3p_y^2 - p^2)(3\epsilon_{yy} - \epsilon) + (3p_z^2 - p^2)(3\epsilon_{zz} - \epsilon)]/27\}. \quad (3)$$

The + and - signs refer to the energy surfaces for the carriers of small and large mass, respectively. In the above equations  $\boldsymbol{\epsilon}$  denotes the tensor of strain,  $\epsilon$  its trace. The constants  $E_{11}$ ,  $E_{12}$ , and  $E_{44}$  are three unknown matrix elements which enter the theory. Their designations are chosen to emphasize that they transform like the components of a fourth rank tensor under cubic symmetry operations. The  $E_{ij}$  are expected to have the order of magnitude of electron volts, so the terms in (1) proportional to the  $E_{ij}$  are by far the largest for the states responsible for semiconduction properties.

A theory of the elastoresistance based on the above expressions for the energy levels shows that in the notation of reference 1, the volume elastoresistance coefficient  $(M_{11} + 2M_{12})/3$  is small compared to  $M_{44}$ , in agreement with experiment. Of the other two principal coefficients,  $M_{44}$  is proportional to  $CE_{44}/kT$  and  $(M_{11} + M_{12}/2)$  is proportional to  $(A - B)(E_{11} - E_{12})/2kT$  as might be expected. Experimentally,  $(M_{11} - M_{12})/2$  is small compared to  $M_{44}$ . This we must interpret as implying that  $(E_{11} - E_{12})/2$  is small compared to  $E_{44}$ , since the parameters  $(A - B)$  and  $C$  as determined from the cyclotron resonance experiment have the same order of magnitude.

Our formal theory does not suggest why  $E_{44}$  is relatively so large. However, we believe the physical reason is not difficult to conjecture. Essentially  $E_{44}$  is a matrix element of the strain-induced incremental electron potential for a shear which changes the angles between the cubic axes while  $(E_{11} - E_{12})/2$  is a matrix element of the potential for a strain which does not change the angle. To first order in  $\boldsymbol{\epsilon}$  only the former type of strain can cause a change in the nearest neighbor distances, and we suspect that that is the underlying physical reason why  $E_{44}$  is relatively so large.

We think it encouraging that the spin-orbit coupling model is capable of giving a satisfactory account of the large elastoresistance in *p*-type material without the