

This raises serious questions as to the validity of the Boltzmann equation and the nearly-free-electron description of the electronic states. Several attempts have been made to bypass some of these problems by explicitly introducing relaxation effects in the electron-phonon interaction. Gunn,<sup>8</sup> for example, has replaced the usual Fermi "golden rule" by a Wigner-Breit type theory, which attributes a certain lifetime broadening to the electronic states. It is also possible to introduce these effects phenomenologically by adding a relaxation term to the usual density-matrix kinetic equation. It would be desirable to treat the electron states in the presence of impurities by methods similar to those employed in Green's-function theory of the multiple scattering problem,<sup>9</sup> but here again most of these results are invalid for  $kl_l \sim 1$ . We are presently studying this problem. Finally we wish to stress that all determinations of the deformation-potential constant in InSb are subject to the same criticism, since these problems have not been dealt with adequately. This might explain the rather large spread in the deformation potential values reported in the literature.<sup>10-13</sup>

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## ABSORPTION OF OXYGEN IN SILICON IN THE FAR INFRARED

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An absorption line of oxygen in silicon has been observed at  $29.3 \text{ cm}^{-1}$  at  $1.8^\circ\text{K}$ . Assignment to oxygen has been confirmed by observation of the oxygen isotope effect. Effects of uniaxial stress on the line have been measured. Additional lines observed at  $37.7$ ,  $43.5$ , and  $48.9 \text{ cm}^{-1}$  when the crystals are heated to  $35^\circ\text{K}$  are assigned to a bending vibrational mode of  $\text{Si}_2\text{O}$ .

Many investigations have been made in the past of the absorption of oxygen in silicon in the near infrared.<sup>1-4</sup> It has been proposed<sup>1</sup> that oxygen dissolves interstitially in silicon forming a complex which may be approximately described as  $\text{Si}_2\text{O}$ . The intense  $9\text{-}\mu$  absorption has been ascribed<sup>2,3</sup> to the antisymmetric stretching mode of the nonlinear  $\text{Si}_2\text{O}$  complex. There is also the possibility of motion of the oxygen in the plane perpendicular to the Si-Si axis; structure observed on the  $9\text{-}\mu$  band<sup>2,3</sup> suggests the presence of low-lying quantized states associated with such motion.

We have extended the investigation of oxygen in

silicon into the far infrared where we have observed absorption features associated with an in-plane  $A_1$  bending motion of the  $\text{Si}_2\text{O}$  complex. These new observations and their interpretation will enable a resolution of most of the outstanding problems<sup>2-4</sup> concerning the motion of oxygen in silicon.

The dominant far-infrared line due to the  $^{16}\text{O}$  isotope appears at  $29.3 \pm 0.1 \text{ cm}^{-1}$  at  $1.8^\circ\text{K}$ . The linewidth at  $1.8^\circ\text{K}$  is less than  $0.2 \text{ cm}^{-1}$ . We have confirmed that the line is due to oxygen by measuring the isotope shift in a crystal containing 75% of  $^{18}\text{O}$  and 25% of  $^{16}\text{O}$  [Fig. 1(a)]. The  $^{18}\text{O}$  line occurs at  $27.2 \text{ cm}^{-1}$ . Measurements of

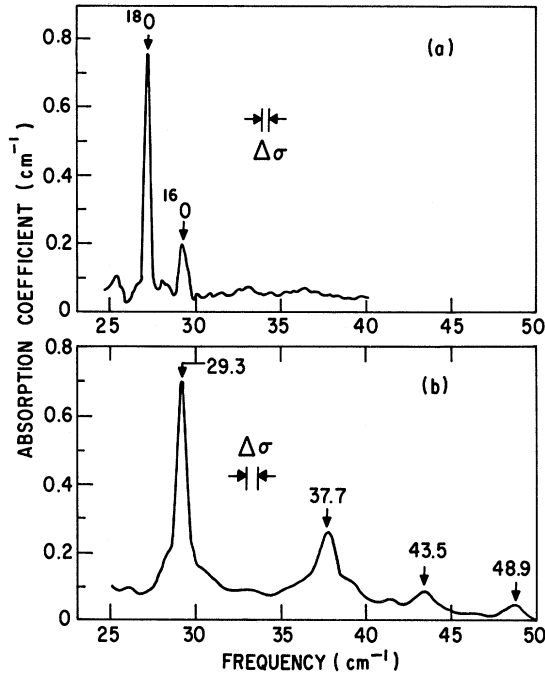


FIG. 1. (a) Absorption of oxygen in silicon at 1.8°K; this crystal contained <sup>18</sup>O (75%) and <sup>16</sup>O (25%).  $\Delta\sigma$  (instrumental) = 0.35 cm<sup>-1</sup>. (b) Absorption of <sup>16</sup>O in silicon at 35°K;  $\Delta\sigma = 0.7$  cm<sup>-1</sup>.

the oxygen spectrum of this crystal in the near infrared indicate that the concentration of <sup>18</sup>O is  $2 \times 10^{17}$ /cc. When the crystal doped with natural oxygen is maintained at 35°K new lines appear at 37.7, 43.5, and 48.9 cm<sup>-1</sup>, as a result of thermal occupation of excited states [Figs. 1(b) and 2]. The <sup>18</sup>O line corresponding to the 37.7 line has been observed (Table I), but the <sup>18</sup>O equivalents of the 43.5 and 48.9 lines are too weak for observation. At 77°K all these lines are broadened beyond detection.

More detailed information concerning the structure of the oxygen complex was obtained by investigating the effect of uniaxial stress  $\vec{P}$  on the 29.3-cm<sup>-1</sup> line. Stress splittings of this line, one order of magnitude greater than the line-width, were readily obtained. All nearest-neighbor Si-Si directions are along  $\langle 111 \rangle$  and our ob-

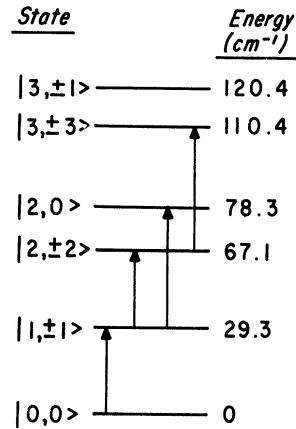


FIG. 2. Observed transitions of <sup>16</sup>O in silicon. The position of the  $|3, \pm 1\rangle$  level has been estimated using Eq. (3) (text).

served stress effects are due to the raising of the orientational degeneracy of a  $\langle 111 \rangle$ -oriented complex. With  $\vec{P} \parallel [100]$  the line shifts to lower energy but does not split; a pressure of 24 kg/mm<sup>2</sup> in this direction moves the line 1.0 cm<sup>-1</sup>. With  $\vec{P} \parallel [110]$  the line splits into two doubly degenerate components and with  $\vec{P} \parallel [111]$  the line splits into a singly degenerate and a triply degenerate component.

It is possible to determine whether the line is due to a  $\pi$  (parallel to the defect axis) or a  $\sigma$  (perpendicular to the defect axis) oscillator by measuring the relative intensities of the stress-split components, even with unpolarized light. With  $\vec{P} \parallel [111]$ , for example, and with the wave vector of the incident light perpendicular to  $\vec{P}$ , the absorption of the singly and triply degenerate components will be in the ratio 3:13 for a  $\sigma$  oscillator and 3:5 for a  $\pi$  oscillator.<sup>5</sup> Our measured ratio of 3:12 indicates a  $\sigma$  oscillator. This result may be confirmed by measuring, for example, the absorption of the triply degenerate component with polarized light. For this component the ratio of intensities of absorption for light polarized parallel and perpendicular to  $\vec{P}$  should be<sup>5</sup> 1:4 for a  $\pi$  oscillator and 8:5 for a  $\sigma$  oscillator. Our experiments give a ratio of about 8:4, confirming the

Table I: Observed and calculated transitions (cm<sup>-1</sup>) of oxygen in silicon.

T (°K)	Transition	<sup>16</sup> O		<sup>18</sup> O		<sup>16</sup> O- <sup>18</sup> O	
		Obs.	Calc.	Obs.	Calc.	Obs.	Calc.
1.8	$ 0,0\rangle \rightarrow  1,\pm 1\rangle$	29.3 ± 0.1	29.0	27.2 ± 0.1	26.3	2.1 ± 0.2	2.7
35	$ 1,\pm 1\rangle \rightarrow  2,\pm 2\rangle$	37.7 ± 0.3	39.0	35.3 ± 0.1	35.9	2.4 ± 0.6	3.1
35	$ 1,\pm 1\rangle \rightarrow  2,0\rangle$	48.9 ± 0.3	49.0	...	...	...	...
35	$ 2,\pm 2\rangle \rightarrow  3,\pm 3\rangle$	43.5 ± 0.3	44.0	...	...	...	...

assignment to a  $\sigma$  oscillator.

The effect of uniaxial stress on the orientational degeneracy of complexes in crystals has already been formulated<sup>5</sup> in terms of a piezospectroscopic tensor  $A_{ij}$ . For a  $\langle 111 \rangle$ -oriented complex, this tensor has only two independent components,  $A_1$  and  $A_2$ . From our measurements on the  $29.3\text{-cm}^{-1}$  line in the  $[110]$ ,  $[111]$ , and  $[100]$  directions we find that, within experimental error,  $A_1$  and  $A_2$  have the same value:

$$A_1 = A_2 = (-3.8 \pm 0.3) \times 10^{-10} \text{ cm}^{-1}/(\text{dyn}/\text{cm}^2). \quad (1)$$

The piezospectroscopic tensor when referred to the trigonal axes (e.g.,  $[111]$ ,  $[1\bar{1}0]$ , and  $[11\bar{2}]$ ) of the defect has the diagonal form<sup>6</sup>:

$$\begin{pmatrix} A_1 + 2A_2 & 0 & 0 \\ 0 & A_1 - A_2 & 0 \\ 0 & 0 & A_1 - A_2 \end{pmatrix} = \begin{pmatrix} -11.4 & 0 & 0 \\ 0 & 0.0 & 0 \\ 0 & 0 & 0.0 \end{pmatrix}, \quad (2)$$

where the units are the same as in (1). It is apparent from inspection of (2) that the line is shifted measurably only by stress components parallel to the defect axis. A general discussion of the piezospectroscopic tensors of absorption bands of oxygen in silicon in both the near and far infrared will be given elsewhere.<sup>6</sup>

We assume that our observed lines are due to motion of oxygen in the plane perpendicular to the Si-Si axis of  $\text{Si}_2\text{O}$ . This two-dimensional motion might be rotational, vibrational, or librational in type, depending on the size of the potential hill on the Si-Si axis<sup>7</sup> and the potential hills around the axis. The spacing of the energy levels of a free two-dimensional rotor increases<sup>8</sup> as  $J_z^2$  and the first two allowed transitions have energies in the ratio of 3:1. Our observed lines have roughly equal energies and we therefore conclude that the motion is primarily vibrational or librational rather than rotational in character. The energy-level structure of librational motion has already been considered<sup>8</sup> and it is not compatible with the present results. We therefore assume axial symmetry around the Si-Si axis and we can explain our results reasonably well using

the two-dimensional perturbed harmonic-oscillator potential

$$V = \frac{1}{2}M\omega_0^2 r^2 + A \exp(-r^2/q\gamma^2), \quad (3)$$

where  $M$  is the oxygen mass,  $\gamma = (\hbar/M\omega_0)^{1/2}$ , and  $\omega$ ,  $A$ , and  $q$  are constants to be determined by comparison with experiment. The transition frequencies calculated for  $^{16}\text{O}$  with

$$q = 1, \quad \omega_0/2\pi c = 49 \text{ cm}^{-1}, \quad A = 80 \text{ cm}^{-1}$$

are compared with experiment in Table I. The eigenstates are labeled  $|v, l\rangle$  (Table I and Fig. 2), where  $v$  is the vibrational quantum number and  $l$  determines the angular part of the wave function.<sup>7</sup> It is apparent (Fig. 2) that the  $v=2$  level which is threefold degenerate in a purely harmonic potential is split into a singlet and a doublet, and the  $v=3$  level, which is fourfold degenerate in a purely harmonic potential, is split into two doublets.

Our simple model accounts for the general features of the spectrum. In view of the simplicity of the model, which ignores coupling to the lattice, calculations of energy have been made only to first order; second-order effects are of the order of a few  $\text{cm}^{-1}$ . The calculated isotope shift is somewhat larger than observed (Table I) but this discrepancy could be removed by assuming a small ( $\sim 10\%$ ) increase in the effective mass of the oscillator.

The  $|0, 0\rangle \rightarrow |1, \pm 1\rangle$  transition is allowed for  $\sigma$ -polarized radiation in agreement with observation. Admixtures of  $|0, 0\rangle$  into  $|2, 0\rangle$  by the term in  $A$  in (1) changes the calculated relative intensities of the  $|1, \pm 1\rangle \rightarrow |2, \pm 2\rangle$  and  $|1, \pm 1\rangle \rightarrow |2, 0\rangle$  transitions from 2:1 to  $\sim 4$ :1 in agreement with observation [Fig. 1(b)]. Of the three allowed  $v=2 \rightarrow 3$  transitions, we have observed only the  $|2, \pm 2\rangle \rightarrow |3, \pm 3\rangle$  transition, which has the greatest calculated intensity. The position of the  $|3, \pm 1\rangle$  level in Fig. 2 has been calculated using (3).

We find for a compressive stress of  $18.5 \text{ kg}/\text{mm}^2$  along  $[111]$  that the  $|0, 0\rangle \rightarrow |1, \pm 1\rangle$  transition of the  $\text{Si}_2\text{O}$  oriented along  $[111]$  shifts to lower energy by  $2.0 \text{ cm}^{-1}$ . A compressive stress should increase  $A$  and, if we assume no change in  $\omega$ , a reduction of  $2.0 \text{ cm}^{-1}$  in the transition energy would be accounted for by a  $10\%$  increase in  $A$ . However, the observed energy reduction may be due partly to an increase in  $A$  and partly to a reduction in  $\omega$ .

Work is at present in progress on the far-infrared spectrum of electron-irradiated silicon containing  $A$  centers.<sup>9</sup> The measurements reported

here have implications for the interpretation of the near infrared spectrum of oxygen in silicon and these implications will be discussed elsewhere.<sup>6</sup>

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## PARAMETRIC CONVERSION OF X RAYS

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We consider frequency conversion of x rays via the nonlinear interaction of short-wavelength radiation with crystalline solids. Phase-matched parametric down-conversion of Mo K $\alpha$  in diamond is computed to be observable with presently accessible sources.

The incoherent process of double Compton scattering, first discussed by Heitler and Nordheim,<sup>1</sup> in which a proton when interacting with a relativistic (and hence nonlinear) electron decays into two photons of lesser energy, is well known. We discuss here an analogous coherent phenomenon, the spontaneous parametric decay of x rays. This process is related to double Compton scattering in the same way that ordinary Bragg diffraction relates to ordinary Compton scattering, and is just one of a wide range of coherent nonlinear phenomena which, extensively studied in the optical region,<sup>2</sup> must exist also in the x-ray region of the spectrum. We emphasize here the parametric conversion of x rays because we find this new effect to be observable with available x-ray sources.

Many of the properties of spontaneous parametric conversion may be understood on the basis that this process arises as a result of the beating of the quantum fluctuations of the vacuum field with the input field. We accordingly begin our discussion by considering in the short-wavelength limit the parametric mixing of two waves in a nonlinear crystal. A semiclassical, nonrelativistic formalism is employed and we present here a discussion of only the situation in which all frequencies lie well above the K absorption edge of

the medium; resonance effects and their associated phase shifts are not included.

Consider summation of two waves at frequencies  $\omega_1$  and  $\omega_2$  in a nonlinear crystal to produce a third wave at  $\omega_3$ . In each atom of the crystal there is induced a small nonlinear polarization,  $\mathcal{P}(\omega_3)$ , which we write as

$$\mathcal{P}(\omega_3) = \beta(\omega_3 = \omega_1 + \omega_2)E(\omega_1)E(\omega_2) \quad (1)$$

with  $E(\omega_i)$  the field amplitude at  $\omega_i$ . The amplitude of the radiated field at  $\omega_3$  at some remote distance  $R$  is

$$E(\omega_3) = \frac{\omega_3^2}{Rc^2} E(\omega_1)E(\omega_2) \sum_a \beta(\vec{r}_a) e^{-i\vec{k} \cdot \vec{r}_a}, \quad (2)$$

where

$$\vec{k} \equiv \vec{k}_3 - (\vec{k}_1 + \vec{k}_2). \quad (3)$$

$\vec{r}_a$  is the position vector of atom  $a$ ,  $\vec{k}_i$  is the wave vector of the field at  $\omega_i$ , and the sum is over all atoms in the illuminated region of the crystal. Expanding  $\beta$  as a Fourier series in terms of the set of reciprocal lattice vectors of the crystal  $\vec{Q}(hkl)$ , we have

$$\sum_a \beta(\vec{r}_a) e^{-i\vec{k} \cdot \vec{r}_a} = \sum_{hkl} \sum_{\text{cells}} G(hkl) e^{i[\vec{Q}(hkl) - \vec{k}] \cdot \vec{r}_{\text{cell}}}, \quad (4)$$