

## Infrared Lattice Absorption in Ionic and Homopolar Crystals\*

MELVIN LAX, *Physics Department, Syracuse University, Syracuse, New York and Naval Research Laboratory, Washington, D. C.*

AND

ELIAS BURSTEIN, *Crystal Branch, Naval Research Laboratory, Washington, D. C.*

(Received July 12, 1954)

The evidence, from the photoelastic properties of alkali halides and MgO, and from the deviations from the Cauchy relation among the elastic constants in these crystals, for the existence of an appreciable deformation of the charge distribution about the atoms during lattice vibration, is discussed. The deformation of the charge distribution is suggested as a possible alternative explanation to that of anharmonic forces for the auxiliary bands in the infrared absorption and reflection spectra of the alkali halides and MgO. It is suggested, on the other hand, that the infrared absorption spectra of pure homopolar crystals, such as diamond, silicon, and germanium in which a linear moment is absent, must involve the deformation of the charge distribution during vibration, since anharmonic forces alone cannot account for any infrared absorption in the absence of a linear moment.

The deformation of the charge distribution in a crystal during vibration is shown to lead to a second order electric moment

(quadratic in the displacements) as well as to a modification of the first order moment. A qualitative understanding of the contribution of the second order moment to infrared absorption is obtained with the help of a one-dimensional calculation.

An analysis is made of the infrared absorption in diamond, silicon, and germanium. Part of the absorption is judged to be intrinsic and to be reasonably explained by a second order electric moment arising from charge deformation. The remainder seems to vary with the specimen and is explained as an impurity-induced first order moment. The second order electric moment can also be used to explain the side bands in the absorption and reflection spectra of the alkali halides. However, it fails to explain the observed broadening of the main absorption line, indicating that anharmonic forces are probably the principal mechanism in the latter phenomenon.

### 1. INTRODUCTION

THE absorption of infrared light by an ionic cubic diatomic crystal would be expected, according to elementary theory, to yield a single band associated with the optical mode of essentially zero propagation constant. Observations of Czerny,<sup>1</sup> Barnes,<sup>1</sup> and others<sup>1</sup> on alkali halide crystals indicated, however, the presence of side bands on the short wavelength side of the main absorption or reflection band. Attempts at explaining these side bands by Born and Blackman,<sup>2</sup> Blackman,<sup>3</sup> and Barnes, Brattain, and Seitz,<sup>4</sup> were based on the presence of anharmonic terms (e.g., cubic) in the potential energy associated with lattice vibrations. Since these terms are difficult to calculate from fundamental considerations they were introduced phenomenologically. The location of the bands could reasonably be explained by regarding them as combination bands.

Recently, Born<sup>5</sup> in his work on pyroelectricity, and Burstein *et al.*<sup>6</sup> in explaining the infrared properties of MgO, have suggested that the side bands may be due

to second order terms in the electric moment rather than to third order terms in the potential energy. Furthermore, in homopolar materials like diamond, silicon, and germanium where the linear terms in the electric moment are absent, Burstein and Oberly<sup>7</sup> have suggested that the intrinsic lattice absorption must be explained on the basis of a second order electric moment, since anharmonicity alone provides no mechanism for absorption.

The purpose of the present paper is: (1) to review the experimental evidence for second order electric moment terms; (2) to define the concepts more precisely by formulating the transition probabilities on a quantum mechanical basis; and (3) to illustrate the qualitative nature of the results to be expected by performing a one-dimensional calculation.

### 2. EXPERIMENTAL BACKGROUND

#### Polar Crystals

The reflection spectra for a series of alkali halides and for MgO are given in Fig. 1. These spectra exhibit a main peak and a secondary side peak at a shorter wavelength. As can be seen from Table I, the relative width of the main peak decreases in the order LiF, MgO, NaF, NaCl, KCl. The relative heights of the secondary to the major peak also decrease in exactly the same order. A similar trend is found in these crystals for the deviation from the Cauchy relations  $(C_{44}/C_{12}) - 1$  and for the strain polarizability constant  $\lambda_0$  (see Table I).

The deviation from the Cauchy relations in a classical treatment implies a deviation from central forces. Löwdin,<sup>8</sup> in a quantum-mechanical treatment using free

\* This work has also been supported in part by the U. S. Air Force under a contract monitored by the Office of Scientific Research, Air Research and Development Command, and in part by the Office of Naval Research.

<sup>1</sup> M. Czerny, *Z. Physik* **65**, 600 (1930); R. B. Barnes and M. Czerny, *Z. Physik* **72**, 447 (1931); R. B. Barnes, *Z. Physik* **75**, 723 (1932); K. Korth, *Nachr. Akad. Wiss. Göttingen, Math.-phys. Kl.*, 576 (1932); C. H. Cartwright and M. Czerny, *Z. Physik* **85**, 269 (1933); **90**, 457 (1934); H. W. Hohls, *Ann. Physik* **29**, 433 (1937).

<sup>2</sup> M. Born and M. Blackman, *Z. Physik* **82**, 551 (1933).

<sup>3</sup> M. Blackman, *Z. Physik* **86**, 421 (1933); *Trans. Roy. Soc. (London)* **A236**, 102 (1936).

<sup>4</sup> Barnes, Brattain, and Seitz, *Phys. Rev.* **48**, 582 (1935).

<sup>5</sup> M. Born, *Revs. Modern Phys.* **17**, 245 (1945).

<sup>6</sup> Burstein, Oberly, and Plyler, *Proc. Indian Acad. Sci.* **28**, 388 (1948).

<sup>7</sup> E. Burstein and J. J. Oberly, *Phys. Rev.* **78**, 642 (1950).

<sup>8</sup> Per Olav Löwdin, *J. Chem. Phys.* **18**, 365 (1950).

spherical-ion wave functions, was able to show that some Cauchy relation deviations could be obtained from the non-orthogonality terms arising in his Heitler-London treatment. However the deviations he obtained did not follow the trend exhibited in Table I. It therefore seems necessary to take account of the deformation of the ionic wave functions to explain the experimental results. (Such a deformation and its changes during vibration will lead to terms in the electric moment of second order in the displacement, as well as to a modification of the "effective charge" in the first order terms.)

The strain polarizability  $\lambda_0$  represents the fractional change in molar polarizability with fractional change in density. The existence of a strain polarizability also suggests the existence of charge deformation, and its magnitude is also a measure of the extent of charge deformation with strain. As a consequence, both the Cauchy deviations and the strain polarizability represent a measure of the charge deformation that will occur during lattice vibrations.

The experimental evidence therefore indicates a correlation between the peak widths and side-band intensities with a measure of the size of the second order terms in the electric moment. As we shall show later in this paper, second order moments can give rise to combination bands and the latter may constitute the mechanism for the side-band absorption.

We can visualize the mechanism for absorption involving second order terms in the electric moment by considering the effect of compressional modes on a rocksalt lattice. A compressional mode produces a shift in the effective charges on the ions, but no moment. If in addition an optical vibration is present, a second order contribution to the electric moment will be made

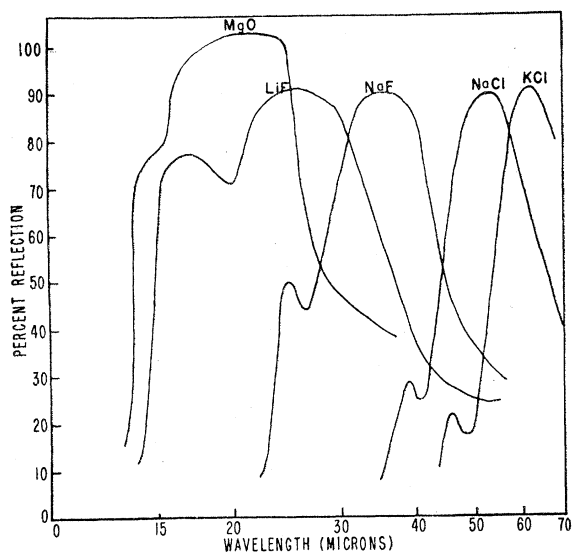


FIG. 1. Infrared reflection spectra of alkali halides and magnesium oxide.

TABLE I. Infrared reflection peaks.

Crystal	Major peak ( $\mu$ )	Fractional band width	Minor peak ( $\mu$ )	Height ratio	$\lambda_0$	$\frac{C_{44}}{C_{12}} - 1$
MgO	22 <sup>a</sup>	0.43	16	0.7	1.4 <sup>e</sup>	0.4 <sup>d</sup>
LiF	26 <sup>b</sup>	0.46	17	0.85	0.7 <sup>e</sup>	0.3 <sup>e</sup>
NaF	36 <sup>b</sup>	0.34	25	0.56	...	0.2 <sup>f</sup>
NaCl	53 <sup>b</sup>	0.28	39	0.32	0.6 <sup>e</sup>	0.1 <sup>e,d</sup>
KCl	63 <sup>b</sup>	0.18	46	0.25	0.6 <sup>e</sup>	0.0 <sup>e,d</sup>

<sup>a</sup> See reference 6.

<sup>b</sup> H. W. Hohls, Ann. Physik 29, 433 (1937).

<sup>c</sup> E. Burstein and P. L. Smith, Proc. Indian Acad. Sci. 28, 377 (1948).

<sup>d</sup> M. A. Durand, Phys. Rev. 50, 449 (1936).

<sup>e</sup> H. Huntington, Phys. Rev. 72, 321 (1947).

<sup>f</sup> Burstein, Smith, and Arenberg, Phys. Rev. 82, 314 (1951).

by the vibration of the charge increments. This contribution is proportional to the product of the amplitudes of both the acoustical and optical modes, and results in absorption at the sum and difference frequencies. Because of the high density of short-wavelength modes, a combination of short-wavelength acoustical and optical modes will lead to side bands.

### Homopolar Crystals

In this section we shall be concerned primarily with homopolar crystals of diamond structure (e.g., diamond, silicon, germanium, and gray tin). The diamond structure consists of two identical interpenetrating face-centered cubic lattices with one of these lattices displaced relative to the other one-quarter of the distance up the main body diagonal. Because of the crystal symmetry ( $O_h$ ), the displacement of one sublattice relative to another will not result in an electric moment. The fundamental optical vibration is therefore infrared-inactive, although it is Raman-active. Weak absorption bands have been observed, however, in diamond,<sup>9</sup> and more recently in silicon<sup>7,10</sup> and germanium.<sup>7,10,11</sup>

The lattice vibration absorption bands in diamond are shown in Fig. 2. Diamond crystals are found to fall into two types which exhibit different absorption spectra. Type I diamonds exhibit absorption in two regions: from 2 to 6 $\mu$  and from 8 to 13 $\mu$ . Type II diamonds, on the other hand, exhibit absorption only in the 2 to 6 $\mu$  region. The absorption in the 8 to 13 $\mu$  region for Type I diamonds varies from specimen to specimen and appears therefore to be an impurity or structure sensitive property. The 2 to 6 $\mu$  absorption does not vary from specimen to specimen nor from Type I to Type II diamonds<sup>12-14</sup> and therefore may be regarded as an intrinsic property of diamond.

The classification of diamond into two types is based

<sup>9</sup> Robertson, Fox, and Martin, Trans. Roy. Soc. (London) A232, 463 (1934).

<sup>10</sup> R. C. Lord, Phys. Rev. 85, 140 (1952).

<sup>11</sup> H. B. Briggs, J. Opt. Soc. Am. A42, 686 (1952); R. J. Collins and H. Y. Fan, Phys. Rev. 86, 648 (1952).

<sup>12</sup> G. B. B. M. Sutherland and H. H. Willis, Trans. Faraday Soc. 41, 289 (1945).

<sup>13</sup> K. G. Ramanathan, Proc. Indian. Acad. Sci. A24, 130 (1946).

<sup>14</sup> D. E. Blackwell and G. B. B. M. Sutherland, J. chim. phys. 46, 9 (1949).

TABLE II. Some properties in which Type I and Type II diamonds differ.

	Type I	Type II
Infrared absorption <sup>a</sup>	2 to 6 $\mu$ and 8 to 13 $\mu$	Only 2 to 6 $\mu$
Ultraviolet absorption <sup>a</sup>	Below 3000A	Below 2250A
Photoconductivity <sup>a</sup>	Poor	Good
Radiation counting <sup>b</sup>	Poor	Good
Anomalous x-ray spots <sup>c</sup>	Present	Absent
Crystal texture <sup>d</sup>	Perfect	Mosaic

<sup>a</sup> Robertson, Fox, and Martin, Trans. Roy. Soc. (London) **A232**, 463 (1934).

<sup>b</sup> R. Hofstadter, Phys. Rev. **73**, 631 (1948); F. C. Champion, Proc. Phys. Soc. (London) **B65**, 465 (1952).

<sup>c</sup> K. Lonsdale, Proc. Roy. Soc. (London) **A179**, 315 (1942).

<sup>d</sup> K. Lonsdale, Phys. Rev. **73**, 1467 (1948).

on differences in physical properties<sup>9</sup> (see Table II). The properties that distinguish the two types of diamond are those which are commonly sensitive to impurities and structure defects in other materials. Properties such as lattice constant, refractive index, dielectric constant, Raman spectra, and specific heat which are not structure-sensitive exhibit essentially no differences between the two diamond types.

We believe that Type I diamonds have the same fundamental octahedral structure as Type II diamonds, but differ from the latter by the presence of impurities<sup>7,15</sup> or structure defects which are introduced during growth, and whose concentration determines the extent to which the properties of a given crystal differ from the perfect octahedral structure.

Recent data,<sup>16</sup> obtained at the Naval Research Laboratory, on the influence of impurities on the growth and properties of a wide variety of crystals indicate that certain types and concentrations of impurities reduce the mosaic structure of crystals and make possible the growth of large, clear crystals which could not otherwise be obtained. It is therefore probable that it is precisely the presence of appropriate impurities that enable near-perfect Type I diamonds to grow in nature.

The infrared absorption bands from 8 to 13 $\mu$  in Type I diamond occur in the region of the fundamental optical vibration frequencies of the diamond lattice in spite of the fact that absorption associated with the "optical modes" of vibration are explicitly forbidden by the selection rules associated with the octahedral symmetry of the diamond lattice. The presence of these bands can be readily accounted for by impurities since they destroy locally the center of symmetry of the diamond structure and thereby permit an electromagnetic coupling to the fundamental optical vibration frequencies.

The 2 to 6- $\mu$  bands do not vary from specimen to specimen and hence constitute intrinsic absorption.

<sup>15</sup> Blackwell and Sutherland (reference 14) have also suggested that impurities may play a role.

<sup>16</sup> Paul H. Egli and S. Zerfoss, Discussions Faraday Soc. No. 5, 61 (1949).

They cannot be explained on the basis of a first order (fundamental) lattice absorption, since the latter is forbidden for the perfect diamond lattice. Furthermore these bands occur at a higher frequency than the fundamental optical vibration at 1332 cm<sup>-1</sup>. We suggest that this 2 to 6- $\mu$  intrinsic absorption is lattice absorption associated with two-phonon processes arising from second-order terms in the electric moment produced by charge deformation.

The customary mechanism for explaining summation bands (in the alkali halides), namely anharmonic forces, is inadequate in diamond structures since anharmonic forces without charge deformation can produce no electric moment of any order and hence no absorption.

Second order electric moments are adequate to explain the existence of summation bands without benefit of anharmonic terms, although the latter may indeed be present and produce additional broadening and/or side bands.

It may be of interest to note that a charge deformation mechanism has also been invoked to explain the pressure dependent fundamental infrared absorption of homonuclear molecules.<sup>17</sup> Although anharmonic forces are present in such molecules, no vibrational absorption is to be expected unless an electric moment is induced, *viz.*, by collisions.

We can visualize the second-order terms in the electric moment in a manner similar to that described in the alkali halides: one vibrational mode induces charges on the atoms (which would otherwise not be present). A second mode simultaneously causes a vibration of the induced charges thus producing an electric moment and coupling to the radiation field. Since a long-wavelength acoustical or optical mode does not alter the effective charges of the atoms on the two equivalent Bravais lattices, we expect that such long-wavelength modes will be ineffective in producing second order moments. On the other hand, short-wavelength modes introduce asymmetric displacements within the two sublattices and therefore produce charge deformations. Thus we

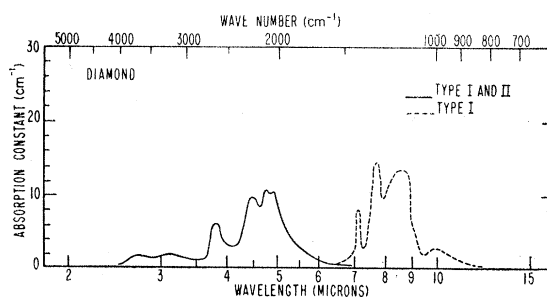


FIG. 2. Infrared absorption spectra of Type I and Type II diamond.

<sup>17</sup> Crawford, Walsh, and Locke, Phys. Rev. **75**, 1607 (1949); **76**, 580 (1949); J. Van Kranendonk and R. Byron Bird, Physica **17**, 953 (1951); **17**, 968 (1951).

may expect that the absorption will be produced primarily by a pair of short-wavelength phonons.

### 3. THE TRANSITION PROBABILITY

Let the initial and final states of the crystal be denoted by  $\psi_i(\mathbf{r}, \mathbf{x})$  and  $\psi_f(\mathbf{r}, \mathbf{x})$ , where  $\mathbf{r}$  is an abbreviation for the electronic coordinates  $\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_j, \dots$  and  $\mathbf{x}$  is an abbreviation for the nuclear positions  $\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_l, \dots$ . In the presence of an incident electromagnetic field described by the vector potential  $\mathbf{A}(\mathbf{r})$ , the perturbing potential,

$$V = -\sum (e_j/m_j c) \mathbf{A}(\mathbf{r}_j) \cdot \mathbf{p}_j - \sum (Z_l/M_l c) \mathbf{A}(\mathbf{x}_l) \cdot \mathbf{P}_l, \quad (3.1)$$

determines the rate at which transitions occur. Here  $e_j = -e$  is the charge on the  $j$ th electron and  $Z_l$  is the charge on the  $l$ th nucleus. Also  $M_l$  is the mass of the  $l$ th nucleus,  $\mathbf{p}_j = -i\hbar \nabla_{\mathbf{r}_j}$ ,  $\mathbf{P}_l = -i\hbar \nabla_{\mathbf{x}_l}$ .

For a system such as a crystal, whose size is large compared to the wavelength, the customary electric dipole approximation cannot be applied. Since we are dealing, however, with valence or core electrons, we are always concerned with *filled* bands. And such a determinant of band functions can always be rewritten as a determinant of localized orbitals. Finally, since we are concerned with the matrix elements of one-body operators, the determinant may be replaced by the corresponding Hartree product of localized orbitals. Thus we may regard each electron  $\mathbf{r}_j$  as attached to a given atom, of equilibrium position  $\mathbf{r}_j^0$  in the lattice. It is then permissible to make the "dipole" approximation:

$$\exp(i\mathbf{v} \cdot \mathbf{r}_j) \rightarrow \exp(i\mathbf{v} \cdot \mathbf{r}_j^0), \quad (3.2)$$

$$\sum \exp(i\mathbf{v} \cdot \mathbf{r}_j^0) [e_j \mathbf{p}_j / m_j + Z_j \mathbf{P}_j / M_j] \rightarrow 2\pi i \nu [\sum \exp(i\mathbf{v} \cdot \mathbf{r}_j^0) (e_j \mathbf{r}_j + Z_j \mathbf{x}_j)]. \quad (3.3)$$

The effect of phase retardation is therefore taken into account by adding the dipole moments of each atom with an appropriate phase factor. With this modification all of the formulas associated with electric dipole radiation and absorption may be applied. The transition from the initial Born-Oppenheimer state,

$$\psi_i(\mathbf{r}, \mathbf{x}) = \varphi_a(\mathbf{r}, \mathbf{x}) X_{am}(\mathbf{x}), \quad (3.4)$$

to the final state,

$$\psi_f(\mathbf{r}, \mathbf{x}) = \varphi_b(\mathbf{r}, \mathbf{x}) X_{bn}(\mathbf{x}), \quad (3.5)$$

is accordingly described by an absorption cross section:<sup>18</sup>

$$\sigma(\nu) = \left[ \frac{n}{\epsilon} \left( \frac{E_a}{E} \right)^2 \right] \frac{8\pi^3 \nu}{c} I_{ba}(\nu), \quad (3.6)$$

$$I_{ba}(\nu) = A \nu_m \sum_n \left| \int X_{bn}^*(\mathbf{x}) \mathbf{M}_{ba}(\mathbf{x}, \nu) X_{am}(\mathbf{x}) d\mathbf{x} \right|^2 \times \delta(E_{bn} - E_{am} - h\nu). \quad (3.7)$$

<sup>18</sup> See M. Lax, J. Chem. Phys. **20**, 1752 (1952), Eqs. (2.1), (2.3), ff for further discussion.

The "phased" transition electric moment  $\mathbf{M}_{ba}(\mathbf{x}, \nu)$  is defined by:

$$\mathbf{M}_{ba}(\mathbf{x}, \nu) = \sum_j \exp(i\mathbf{v} \cdot \mathbf{r}_j^0) \times \int \varphi_b^*(\mathbf{r}, \mathbf{x}) (e_j \mathbf{r}_j + Z_j \mathbf{x}_j) \varphi_a(\mathbf{r}, \mathbf{x}) d\mathbf{r}. \quad (3.8)$$

For electronic transitions ( $b \neq a$ ), the term in  $\mathbf{x}_j$  vanishes because of orthogonality. We shall be concerned primarily with pure vibrational transitions:  $b = a$ . In this case, the nuclear charge  $Z_j$  is of importance. It will, however, be largely cancelled by the moments associated with the core electrons that move "rigidly" with the nucleus, namely those electrons  $j$  for which the wave function,  $\varphi_a(\mathbf{r}, \mathbf{x}) = \varphi(\mathbf{r}_1, \mathbf{r}_2, \dots; \mathbf{x}_1, \mathbf{x}_2, \dots)$ , is a function only of  $\boldsymbol{\rho}_j = \mathbf{r}_j - \mathbf{x}_j$ . By introducing the change of variable,

$$\varphi_a(\mathbf{r}, \mathbf{x}) = \varphi_a(\boldsymbol{\rho} + \mathbf{x}, \mathbf{x}) = \chi(\boldsymbol{\rho}, \mathbf{x}), \quad (3.9)$$

the electric moment can be written

$$\mathbf{M}_{aa}(\mathbf{x}, \nu) = \sum_j \exp(i\mathbf{v} \cdot \mathbf{r}_j^0) \times \left[ Z_j^{\text{ion}} \mathbf{x}_j + \int \chi^*(\boldsymbol{\rho}, \mathbf{x}) (e_j \boldsymbol{\rho}_j) \chi(\boldsymbol{\rho}, \mathbf{x}) d\boldsymbol{\rho} \right], \quad (3.10)$$

where  $Z_j^{\text{ion}}$  is the net charge of the nucleus plus all electrons at the site  $j$ , i.e. it is the ionic charge in an ionic crystal, or zero in a nonionic crystal. The moment  $\mathbf{M}_{aa}(0, \nu)$  is usually zero, and if not, is a static moment of no consequence for optical transitions. We are concerned, therefore, only with the part of  $\mathbf{M}(\mathbf{x}, \nu)$  that depends on the nuclear positions  $\mathbf{x}$ . For all of the core electrons, however,  $\chi$  depends only on  $\boldsymbol{\rho}_j$ , so these yield no contribution to the  $\mathbf{x}$  dependence. We shall call deformable those electrons whose wave function depend on  $\mathbf{x}$  as well as  $\boldsymbol{\rho}$ . It is then permissible to regard  $\chi(\boldsymbol{\rho}, \mathbf{x})$  as the many-body wave function of all the *deformable* electrons.

If we expand  $\chi(\boldsymbol{\rho}, \mathbf{x})$  in powers of  $\mathbf{x} = (\mathbf{x}_1, \mathbf{x}_2, \dots)$  and set

$$\int \chi^*(\boldsymbol{\rho}, \mathbf{x}) e_j \boldsymbol{\rho}_j \chi(\boldsymbol{\rho}, \mathbf{x}) d\boldsymbol{\rho} = \sum_l \mathbf{B}_l^j \cdot \mathbf{x}_l + \sum_{l,m} \mathbf{x}_l \cdot \mathbf{C}_{lm}^j \cdot \mathbf{x}_m + \dots, \quad (3.11)$$

the electric moment (3.10) can be written

$$\mathbf{M}(\mathbf{x}, \nu) = \sum \exp(i\mathbf{v} \cdot \mathbf{r}_j^0) [\mathbf{B}_l \cdot \mathbf{x}_l + \mathbf{x}_l \cdot \mathbf{C}_{lm} \cdot \mathbf{x}_m], \quad (3.12)$$

where

$$\mathbf{B}_l = \sum_j \exp[i\mathbf{v} \cdot (\mathbf{r}_j^0 - \mathbf{r}_l^0)] \mathbf{B}_l^j + Z_l^{\text{ion}}, \quad (3.13)$$

$$\mathbf{C}_{lm} = \sum_j \exp[i\mathbf{v} \cdot (\mathbf{r}_j^0 - \mathbf{r}_l^0)] \mathbf{C}_{lm}^j.$$

We may interpret  $\mathbf{B}_l$  as the effective charge on atom  $l$ , with the lattice in its equilibrium position, and  $\mathbf{C}_{lm} \cdot \mathbf{x}_m$

as the charge induced at  $l$  due to displacement  $\mathbf{x}_m$  of atom  $m$  from its equilibrium position.

Note that in three dimensions,  $\mathbf{x}_l$  and  $\mathbf{M}$  are vectors, so that  $\mathbf{B}_l$  is a dyad, and  $\mathbf{C}_{lm}$  is a triad.

#### 4. GENERAL INVARIANCE REQUIREMENTS

In this section, we shall be concerned with deriving those relations obeyed by the expansion coefficients  $\mathbf{B}_l$  and  $\mathbf{C}_{lm}$  of the electric moment that follow from general invariance requirements. For this purpose it will usually be convenient to work with the static moment  $\mathbf{M}(\mathbf{x}) = \mathbf{M}(\mathbf{x}, 0)$  whose transformation properties are known to be those of an ordinary vector.

The requirement that a crystal be invariant against lattice displacements may be expressed in the statements that  $\mathbf{B}_l$  is a function only of  $(j-l)$  and  $\mathbf{C}_{lm}$  is a function only of the relative indices  $(j-l)$  and  $(l-m)$ . It follows from (3.13) then, that  $\mathbf{B}_l$  is independent of  $l$  and  $\mathbf{C}_{lm}$  is a function only of  $l-m$ . Of course, if there are several atoms per unit cell, the type of atom denoted by  $\alpha$  or  $\beta$ , our statement would take the more complicated form

$$\mathbf{B}_l^\alpha = \mathbf{B}^\alpha, \quad (4.1)$$

$$\mathbf{C}_{lm}^{\alpha\beta} = \mathbf{C}^{\alpha\beta}(m-l). \quad (4.2)$$

The expansions (3.13) for  $\mathbf{B}_l$  and  $\mathbf{C}_{lm}$  converge extremely rapidly since we may expect the displacement of a nucleus introduces moments only on nearby atoms. Furthermore, since the infrared wavelengths are large compared to the lattice spacing, it is permissible to set  $\mathbf{v} \simeq 0$  in (3.13) so that  $\mathbf{B}_l^\alpha$  and  $\mathbf{C}_{lm}^{\alpha\beta}$  are closely approximated by their static ( $\mathbf{v}=0$ ) values.

The static moment can now be written in the form

$$\mathbf{M}(\mathbf{x}) = \sum_{l,\alpha} \mathbf{B}^\alpha \cdot \mathbf{x}_l^\alpha + \sum_{l,\alpha} \mathbf{x}_l^\alpha \cdot \mathbf{C}_{lm}^{\alpha\beta} \cdot \mathbf{x}_m^\beta, \quad (4.3)$$

where  $\mathbf{x}_l^\alpha$  is the displacement of the atom of type  $\alpha$  in cell  $l$  and

$$\mathbf{C}_{lm}^{\alpha\beta} = \mathbf{C}_{ml}^{\beta\alpha}, \quad (4.4)$$

since any coefficient of a quadratic form can be symmetrized.

If the complete crystal is electrically neutral, the electric moment is independent of the origin used to calculate it, i.e., it is invariant against an arbitrary displacement:

$$\mathbf{M}(\mathbf{x} + \mathbf{d}) = \mathbf{M}(\mathbf{x}). \quad (4.5)$$

This leads to the requirements

$$\sum_{\alpha} \mathbf{B}^\alpha = 0, \quad \sum_{m,\beta} \mathbf{C}_{lm}^{\alpha\beta} = 0, \quad \sum_{l,\alpha} \mathbf{C}_{lm}^{\alpha\beta} = 0, \quad (4.6)$$

the first of which states that any adjustment of the equilibrium effective charges must be such as to preserve the neutrality of the unit cell. The second requirement is equivalent to the third because of (4.4).

#### 5. THE ABSORPTION CONSTANT

The linear absorption constant,  $k(\mathbf{v})$ , may be obtained from the cross section for absorption of the crystal (3.6) by dividing by the volume of the crystal:

$$k(\mathbf{v}) = (N\Omega)^{-1} \sigma(\mathbf{v}) = \left[ \frac{n}{\epsilon} \left( \frac{E_e}{E} \right)^2 \right] \frac{8\pi^3 \nu}{c} \frac{I(\mathbf{v})}{N\Omega}, \quad (5.1)$$

where  $N$  is the total number of cells and  $\Omega$  is the volume of each. Using (3.7) and omitting unnecessary indices (since  $b=a$ ), one gets

$$I(\mathbf{v}) = A v_i \sum_f \left| \int X_f^*(\mathbf{x}) \mathbf{M}(\mathbf{x}, \mathbf{v}) X_i(\mathbf{x}) d\mathbf{x} \right|^2 \times \delta(E_f - E_i - h\nu), \quad (5.2)$$

where the electric moment from (3.12) and (4.1) takes the form

$$\mathbf{M}(\mathbf{x}, \mathbf{v}) = \sum_{l,\alpha} \exp(i\mathbf{v} \cdot \mathbf{r}_l^0) \mathbf{B}^\alpha \cdot \mathbf{x}_l^\alpha + \sum_{l,\alpha,m,\beta} \exp(i\mathbf{v} \cdot \mathbf{r}_l^0) \mathbf{x}_l^\alpha \cdot \mathbf{C}_{lm}^{\alpha\beta} \cdot \mathbf{x}_m^\beta. \quad (5.3)$$

The vibrational wave functions  $X_m(x)$  are products of harmonic oscillator wave functions, one for each normal coordinate. The normal coordinates may be obtained by solving the equations of motion associated with the Hamiltonian:

$$H = \frac{1}{2} \sum (p_l^\alpha)^2 / M_\alpha + \frac{1}{2} \sum \mathbf{x}_l^\alpha \cdot \mathbf{K}_{lm}^{\alpha\beta} \cdot \mathbf{x}_m^\beta, \quad (5.4)$$

where  $\mathbf{K}_{lm}^{\alpha\beta}$  obeys the same general invariance requirements (4.2, 4.4, and 4.6) as  $\mathbf{C}_{lm}^{\alpha\beta}$ . A typical solution of these equations may be written in the form

$$\mathbf{x}_l^\alpha = \mathbf{b}^\alpha \exp(i\mathbf{k} \cdot \mathbf{r}_l^0) \exp(-i\omega t), \quad (5.5)$$

where  $\mathbf{b}^\alpha(\mathbf{k})$  and  $\omega(\mathbf{k})$  are obtained by solving the set of simultaneous equations:

$$\sum_{\beta} \mathbf{R}^{\alpha\beta}(\mathbf{k}) \mathbf{b}^\beta = M_\alpha \omega^2 \mathbf{b}^\alpha, \quad (5.6)$$

where

$$\mathbf{R}^{\alpha\beta}(\mathbf{k}) = \sum_m \mathbf{K}_{lm}^{\alpha\beta} \exp[i\mathbf{k} \cdot (\mathbf{r}_m^0 - \mathbf{r}_l^0)]. \quad (5.7)$$

The number of solutions of (5.6) is equal to three times the number of atoms per cell, in three dimensions. These solutions are labelled by the index  $t$  (e.g., longitudinal acoustic) and can be made to obey the orthogonality requirement:

$$\sum_{\alpha} \mathbf{b}_l^{\nu\alpha}(\mathbf{k})^* \cdot M_\alpha \mathbf{b}_l^{\nu\alpha}(\mathbf{k}) = \delta_{\nu\lambda}. \quad (5.8)$$

Because  $\mathbf{R}^{\alpha\beta}(-\mathbf{k}) = \mathbf{R}^{\alpha\beta}(\mathbf{k})^*$ , we can require that

$$\mathbf{b}_l^{\nu\alpha}(-\mathbf{k}) = \mathbf{b}_l^{\nu\alpha}(\mathbf{k})^*. \quad (5.9)$$

The electric moment (5.3) can be expressed in terms of normal coordinates  $q_{\mathbf{k},t}$  by the transformation:

$$\mathbf{x}_l^\alpha = N^{-\frac{1}{2}} \sum_{\mathbf{k},t} q_{\mathbf{k},t} \mathbf{b}_l^{\nu\alpha}(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r}_l^0). \quad (5.10)$$

The linear part of the moment becomes

$$\mathbf{M}_1 = N^{\frac{1}{2}} \sum_{\alpha, t} \mathbf{B}^\alpha \cdot \mathbf{b}_t^\alpha(-\mathbf{v}) q_{-\mathbf{v}, t}, \quad (5.11)$$

and the second order moment becomes

$$\mathbf{M}_2 = \sum_{t', t, k} q_{k+\mathbf{v}, t'}^* q_{k, t} \mathbf{H}_{t' t}^k, \quad (5.12)$$

where

$$\mathbf{H}_{t' t}^k = \sum_{\alpha, \beta} \mathbf{b}_t^\alpha(\mathbf{k}+\mathbf{v})^* \cdot \mathbf{S}^{\alpha\beta}(\mathbf{k}) \cdot \mathbf{b}_t^\beta(\mathbf{k}), \quad (5.13)$$

and

$$\mathbf{S}^{\alpha\beta}(\mathbf{k}) = \sum_m \mathbf{C}_{lm}^{\alpha\beta} \exp[i\mathbf{k} \cdot (\mathbf{r}_m^0 - \mathbf{r}_l^0)]. \quad (5.14)$$

Reality requirements on  $\mathbf{x}_t^\alpha$  imply that

$$q_{-\mathbf{k}, t} = q_{\mathbf{k}, t}^*. \quad (5.15)$$

The operator  $q_{k, t}$  can be expressed in terms of conventional "creation" and "destruction" operators,  $a_{\mathbf{k}, t}^\dagger$  and  $a_{\mathbf{k}, t}$ , by the (canonical) transformation:

$$q_{k, t} = [\hbar/2\omega_t(\mathbf{k})]^{\frac{1}{2}} (a_{\mathbf{k}, t} + a_{-\mathbf{k}, t}^\dagger), \quad (5.16)$$

where the operators  $a_{\mathbf{k}, t}$  obey the commutation rules,

$$(a_{\mathbf{k}, t}, a_{\mathbf{k}', t'}^\dagger) = \delta_{\mathbf{k}\mathbf{k}'} \delta_{tt'}, \quad (5.17)$$

with all other commutators vanishing.

The linear part of  $\mathbf{M}$  leads to a vibrational transition in which one phonon is created or destroyed. On absorption, we need only consider the creation part of  $q_{-\mathbf{v}, t}$  or  $[\hbar/2\omega_t(\mathbf{v})]^{\frac{1}{2}} a_{\mathbf{v}, t}^\dagger$  so that (5.2) yields

$$I(\mathbf{v}) = N \sum_t |\sum_\alpha \mathbf{B}^\alpha \cdot \mathbf{b}_t^\alpha(-\mathbf{v})|^2 [\hbar/2\omega_t(\mathbf{v})] \times [\bar{n}(\omega_t(\mathbf{v})) + 1] \delta(h\nu - \hbar\omega_t(\mathbf{v})). \quad (5.18)$$

Thus the absorption is a line spectrum. Since the optical wavelength is large compared to the lattice constant,  $\mathbf{v}$  is small on the vibrational scale and the absorption peak occurs essentially at  $h\nu \simeq \hbar\omega_t(0)$ . It is sufficiently accurate, therefore, to set the photon propagation constant  $\mathbf{v} \simeq 0$  everywhere in (5.18).

We note that for any of the (three) acoustic modes,  $\mathbf{b}_t^\alpha(0)$  is independent of  $\alpha$ . The absorption is then proportional to  $\sum \mathbf{B}^\alpha$  which vanishes according to (4.6). Thus the requirement of displacement invariance shows that the acoustical modes make no contribution to the first order electric moment absorption—a well-known result.

In general,  $\sum_\alpha \mathbf{B}^\alpha \cdot \mathbf{b}_t^\alpha(0)$  represents the electric moment induced in one cell by the displacements  $\mathbf{b}_t^\alpha(0)$  associated with a normal mode of type  $t$ . The long-wavelength optical modes are thus completely intra-cell vibrations. The symmetry of these intra-cell vibrations can then be examined as one would the vibrations of a molecule to determine which normal modes are "optically active."

The quadratic part of the electric moment  $\mathbf{M}_2$  of (5.12) leads to two-phonon transitions. Because of (5.16) and (5.17), matrix elements are available to

create two phonons, to create one and destroy one, or to destroy two phonons. The last process is inconsistent with conservation of energy. The first process will lead to a "summation band" and the second process to a "difference band."

Upon inserting (5.13) and (5.16) into (5.2), the summation band yields the result

$$I(\mathbf{v}) = \text{Av} \sum_{k, t', t} |\mathbf{H}_{t' t}^k|^2 \frac{\hbar}{2\omega_{t'}(\mathbf{k}+\mathbf{v})} \frac{\hbar}{2\omega_t(-\mathbf{k})} \times [\bar{n}(\omega_{t'}(\mathbf{k}+\mathbf{v})) + 1] [\bar{n}(\omega_t(-\mathbf{k})) + 1] \times \delta(h\nu - \hbar\omega_t(-\mathbf{k}) - \hbar\omega_{t'}(\mathbf{k}+\mathbf{v})). \quad (5.19)$$

The process "Av" over the initial states replaces the initial occupation number  $n$  by its thermal equilibrium value:

$$\bar{n}(\omega) = [\exp(\hbar\omega/kT) - 1]^{-1}. \quad (5.20)$$

Since  $\mathbf{v} \ll \mathbf{k}$ , we can set  $\mathbf{v} \simeq 0$  in (5.19). Roughly speaking, the photon has zero momentum, so that the two phonons are created with equal and opposite propagation constants,  $\mathbf{k}$  and  $-\mathbf{k}$ . A further simplification in (5.19) can be made for nonpiezoelectric crystals by noting that

$$\omega_t(-\mathbf{k}) = \omega_t(\mathbf{k}). \quad (5.21)$$

At temperatures well below the Debye temperature,  $kT \ll \hbar\omega$  and  $\bar{n} \ll 1$ , so that only the spontaneous part (in the Einstein sense) contributes to the emission of phonons, the induced part being small since no phonons are present before the absorption of light. In this limiting case, the absorption is practically independent of temperature. If  $kT \sim \hbar\omega$ , the absorption increases with increasing temperature.

The difference band has two contributions of the form

$$I(\mathbf{v}) = \sum_{k, t', t} |\mathbf{H}_{t' t}^k|^2 \frac{\hbar}{2\omega_{t'}(\mathbf{k}+\mathbf{v})} \frac{\hbar}{2\omega_t(\mathbf{k})} \times [\bar{n}(\omega_{t'}(\mathbf{k}+\mathbf{v})) + 1] \bar{n}(\omega_t(\mathbf{k})) \times \delta(h\nu - \hbar\omega_{t'}(\mathbf{k}+\mathbf{v}) + \hbar\omega_t(\mathbf{k})), \quad (5.22)$$

$$I(\mathbf{v}) = \sum_{k, t', t} |\mathbf{H}_{t' t}^k|^2 \frac{\hbar}{2\omega_{t'}(-\mathbf{k}-\mathbf{v})} \frac{\hbar}{2\omega_t(-\mathbf{k})} \times \bar{n}(\omega_{t'}(-\mathbf{k}-\mathbf{v})) [\bar{n}(\omega_t(-\mathbf{k})) + 1] \times \delta(h\nu + \hbar\omega_{t'}(-\mathbf{k}-\mathbf{v}) - \hbar\omega_t(\mathbf{k})). \quad (5.23)$$

If one sets  $\mathbf{v} \simeq 0$  and uses (5.21), these two contributions are equal. At temperatures well below the Debye temperature,  $\bar{n} \ll 1$  for the optical modes. Thus the contribution in which an optical phonon is absorbed will be small. It is possible, however, to get an appreciable contribution from the creation of an optical (or acoustic) phonon, and the destruction of a low energy acoustic phonon. In this case  $\bar{n}$  can be given its classical value

$kT/\hbar\omega$ , and the absorption associated with the difference band will be approximately proportional to the temperature.

The extent to which a given pair of modes  $l'$  and  $l$  will interact to give absorption is determined by the coefficient  $\mathbf{H}_{l'l}^{\mathbf{k}}$ . This coefficient may be readily interpreted using (5.13) and (5.14). If the electric moment for an arbitrary displacement  $\mathbf{x}$  is written in the suppressed index form

$$\mathbf{M} = \mathbf{x}\mathbf{C}\mathbf{x}, \quad (5.24)$$

the coefficient  $\mathbf{H}_{l'l}^{\mathbf{k}}$  is given by

$$\mathbf{H}_{l'l}^{\mathbf{k}} = \mathbf{x}_{l'}(\mathbf{k}) \cdot \mathbf{C} \cdot \mathbf{x}_l(\mathbf{k}), \quad (5.25)$$

where  $\mathbf{x}_l(\mathbf{k})$  represents the displacements associated with the normal mode  $\mathbf{b}_l^{\alpha}(\mathbf{k}) \exp(i\mathbf{k} \cdot \mathbf{r})$ . We can interpret  $\mathbf{Q} = \mathbf{C} \cdot \mathbf{x}_l$  as the charge induced by the normal mode  $x_l$ , and  $\mathbf{H} = \mathbf{x}_{l'} \cdot \mathbf{Q}$  as the moment produced by allowing the induced charge  $Q$  to vibrate in the mode  $x_{l'}(\mathbf{k})$ . A comparison between the symmetry properties of  $\mathbf{C}_{lm}^{\alpha\beta}$  compared to the vibrational matrix  $\mathbf{K}_{lm}^{\alpha\beta}$  will lead to selection rules for  $\mathbf{H}_{l'l}^{\mathbf{k}}$ .

## 6. ONE-DIMENSIONAL MODEL FOR DIAMOND-TYPE LATTICES

The coefficients  $\mathbf{C}_{lm}^{\alpha\beta}$  in the electric moment expansion are not all independent when any crystal symmetry is present. The symmetry requirements available to all crystals have already been considered in Sec. 4. A given crystal will in addition be characterized by a group of symmetry operators  $S$  that transform the crystal into itself. Under such a symmetry operation, the displacement  $\mathbf{x}$  gets replaced by  $S\mathbf{x}$  and the electric moment, as a function of the displacements  $\mathbf{x}$ , becomes

$$S\mathbf{M}(\mathbf{x}) = \mathbf{M}(S\mathbf{x}). \quad (6.1)$$

On the other hand, the electric moment must transform as an ordinary vector under rotations, reflections, etc., so that we also have

$$S\mathbf{M}(\mathbf{x}) = \mathbf{M}'(\mathbf{x}), \quad (6.2)$$

where  $\mathbf{M}'$  is related to  $\mathbf{M}$  by a rotation or reflection. The requirement that (6.1) and (6.2) be consistent with one another leads to a set of conditions on the coefficients  $\mathbf{C}_{lm}^{\alpha\beta}$ . This consistency requirement can be applied for each element of the group, but some of the conditions obtained will be redundant. It is sufficient to use the generating elements of the group.

One point should be kept in mind: not only does  $S\mathbf{x}_l^{\alpha}$  perform some rotation or reflection of the components of the vector  $\mathbf{x}_l^{\alpha}$ , it also produces the same rotation or reflection of the equilibrium position  $(\alpha, l)$  from which  $\mathbf{x}_l^{\alpha}$  is the displacement, i.e., it converts  $\mathbf{x}_l^{\alpha}$  to  $\mathbf{x}_m^{\beta}$  where  $(\beta, m)$  is the new position of equilibrium point  $(\alpha, l)$ .

To illustrate the concepts involved, and to obtain some qualitative conclusions, we shall apply the above

procedure to a one-dimensional model of the diamond structure.

The diamond structure can be represented by a one-dimensional chain with two identical atoms per unit cell equidistant from the center of each cell (see Fig. 3).

The center of each cell is a center of symmetry. The cell is labelled by the index  $l$ , and the left and right hand atoms of any cell are labelled  $\alpha = -1$  and  $\alpha = +1$  respectively.

This model exhibits the inversion symmetry of the three-dimensional diamond lattice but not the latter's tetrahedral symmetry. The symmetry requirements on the electric moment matrix  $\mathbf{C}_{lm}^{\alpha\beta}$  derived from this one-dimensional model remain valid in three dimensions. The presence of tetrahedral symmetry simply leads to additional requirements.

We shall consider displacements only along the chain, and we shall regard the electric moment  $M$  as a vector that changes sign under inversion, i.e.,

$$M' = IM = -M, \quad (6.3)$$

under the transformation

$$Ix_l^{\alpha} = -x_{-l}^{-\alpha}. \quad (6.4)$$

Application of (6.3) and (4.6a) demonstrates that the linear part of  $M$  vanishes. For the quadratic part,

$$M = \sum x_l^{\alpha} C_{lm}^{\alpha\beta} x_m^{\beta}, \quad (6.5)$$

and

$$\begin{aligned} IM &= \sum (-x_{-l}^{-\alpha}) C_{lm}^{\alpha\beta} (-x_{-m}^{-\beta}) \\ &= \sum x_l^{\alpha} C_{-l, -m}^{-\alpha, -\beta} x_m^{\beta}. \end{aligned} \quad (6.6)$$

From (4.2),

$$C_{-l, -m}^{-\alpha, -\beta} = C_{m, l}^{-\alpha, -\beta}. \quad (6.7)$$

The requirement (6.3) then leads to the condition,

$$C_{m, l}^{-\alpha, -\beta} = -C_{lm}^{\alpha\beta}. \quad (6.8)$$

If we set  $\alpha = -1$ ,  $\beta = 1$  in (6.8) and use (4.4), we learn that

$$C_{m, l}^{1, -1} = -C_{m, l}^{1, -1} = 0, \quad (6.9)$$

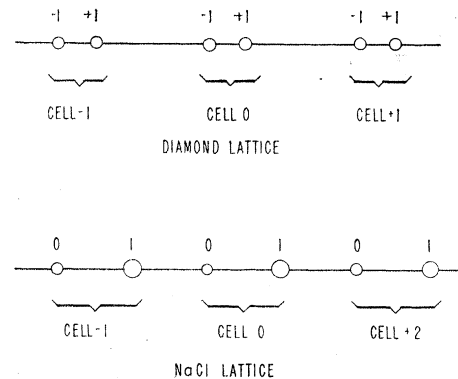


FIG. 3. One-dimensional diamond and sodium chloride lattices.

for all  $m, l$ . If we set  $\alpha=1, \beta=1$  in (6.8) and use symmetry (4.2), we find that

$$C_{m, l^{-1}, -1} = -C_{l, m^{11}} = -C_{ml^{11}}. \quad (6.10)$$

If one uses the notation  $C_{lm^{11}} = C^{11}(m-l)$ , the only independent coefficients that remain are  $C^{11}(m)$  for  $m=0, 1, 2, 3, \dots$ . [Note that  $C^{11}(m)$  is even in  $m$ .]

Displacement invariance (4.6b) then leads to one additional constraint:

$$\sum_{-\infty}^{+\infty} C^{11}(m) = C^{11}(0) + 2C^{11}(1) + 2C^{11}(2) + \dots = 0. \quad (6.11)$$

The number of coefficients  $C_{lm^{\alpha\beta}}$  has therefore been drastically reduced by symmetry requirements. A further reduction can be made by requiring that interactions extend no further than second nearest neighbors. In this case  $C^{11}(m) = 0$  for  $m > 1$  and

$$C^{11}(0) = -2C^{11}(1), \quad (6.12)$$

so that only *one independent coefficient remains!*

These results (6.9) to (6.12) may be summarized by writing the general matrix in the form

$$C_{lm^{\alpha\beta}} = \alpha\delta_{\alpha\beta} [\delta_{l+1, m} + \delta_{l-1, m} - 2\delta_{l, m}] C^{11}(1). \quad (6.13)$$

Thus  $C_{lm^{\alpha\beta}}$  is completely known except for a normalizing constant.

To calculate the infrared absorption we need the quantities

$$S^{\alpha\beta}(k) = -2(1 - \cos kd) C^{11}(1) \alpha\delta_{\alpha\beta} = S(k) \alpha\delta_{\alpha\beta}, \quad (6.14)$$

$$H_{\nu, l^k} = S(k) [b_{\nu, l^k} * b_{l^k} - b_{\nu, l^{-1}} * b_{l^{-1}}], \quad (6.15)$$

calculated from (5.14) and (5.13) with  $d$  as the lattice constant.

To obtain selection rules on  $H_{\nu, l^k}$ , we need information concerning the normal modes  $b_{l^k}$ . The requirement that the potential energy remain invariant under inversion leads to the conditions:

$$|b_{l^{-\beta}}(k)| = |b_{l^{\beta}}(k)| = (2M)^{-\frac{1}{2}}, \quad (6.16)$$

where the mass dependence of the result follows from the orthonormality condition (5.8). Combining (6.16) with (6.15) we obtain the selection rule that

$$H_{ll^k} = 0. \quad (6.17)$$

In other words, there are no two-phonon contributions to infrared absorption with both phonons coming from the same branch. In the one-dimensional case this implies that one phonon is optical and the other phonon acoustical. In three dimensions there will in addition be the possibility of infrared absorption by optical phonons from two distinct optical branches, or acoustical phonons from two distinct acoustic branches.

If use is made of the orthogonality of the optical ( $o$ ) and acoustical ( $a$ ) modes, it follows from (6.15) that

$$|H_{oa^k}| = |H_{ao^k}| = M^{-1} |S(k)| \\ = 2(1 - \cos kd) C^{11}(1) / M. \quad (6.18)$$

The absorption spectrum (5.19) may be simplified by converting the sum over  $k$  to an integral:

$$\sum \rightarrow (N/\pi) \int_0^\pi d\phi, \quad (6.19)$$

where  $\phi = kd$ , and introducing the change of variable  $x = (1 - \cos\phi)$ :

$$I(\nu) = \frac{N\hbar}{4\pi\omega_o^3(0)} \sum_{\nu' l} \int_0^2 \frac{dx}{[x(2-x)]^{\frac{1}{2}}} |H_{\nu' l^k}|^2 \\ \times \frac{(\bar{n}_l + 1)(\bar{n}_{\nu'} + 1)}{f_l(x) f_{\nu'}(x)} \delta(\epsilon - f(x)), \quad (6.20)$$

$$= \frac{N\hbar}{4\pi\omega_o^3(0)} \sum_{\nu' l} \frac{|H_{\nu' l^k}|^2}{[x(2-x)]^{\frac{1}{2}}} \frac{(\bar{n}_l + 1)(\bar{n}_{\nu'} + 1)}{f_l(x) f_{\nu'}(x)} \frac{dx}{df} \Big|_{\epsilon=f(x)}, \quad (6.21)$$

where

$$\epsilon = \hbar\nu / \hbar\omega_o(0) \quad (6.22)$$

is a measure of the photon energy in units of the long-wave optical energy  $\hbar\omega_o(0)$ ,

$$f_l(x) = \omega_l(k) / \omega_o(0), \quad (6.23)$$

$$f(x) = f_l(x) + f_{\nu'}(x). \quad (6.24)$$

To illustrate this result more specifically, we shall assume that the stiffness constant between two atoms in the same cell is  $K$ , and that between a pair of adjacent atoms in neighboring cells is  $K' = \alpha K$ . Then the two vibrational branches are given by

$$\left. \begin{aligned} M\omega_o^2(k) \\ M\omega_a^2(k) \end{aligned} \right\} = (K + K') \\ \pm [(K + K')^2 - 2KK'(1 - \cos kd)]^{\frac{1}{2}}. \quad (6.25)$$

Then

$$\omega_o(0) = [2K(1 + \alpha)/M]^{\frac{1}{2}}, \quad (6.26)$$

$$f_o(x) = 2^{-\frac{1}{2}} \{1 + [1 - (2\alpha x / (1 + \alpha))^2]^{\frac{1}{2}}\}^{\frac{1}{2}}, \quad (6.27)$$

$$f_a(x) = 2^{-\frac{1}{2}} \{1 - [1 - (2\alpha x / (1 + \alpha))^2]^{\frac{1}{2}}\}^{\frac{1}{2}}, \quad (6.28)$$

$$x = (1 + \alpha)^2 (\epsilon^2 - 1) / (2\alpha). \quad (6.29)$$

In terms of the dimensionless photon energy  $\epsilon$ , the spectrum  $I(\nu)$  can now be rewritten in the form:

$$I(\nu) = \frac{2N\hbar}{\pi\omega_o^3(0)} |H_{oa}|^2 \frac{\epsilon[\bar{n}(\omega_o) + 1][\bar{n}(\omega_a) + 1]}{(\epsilon^2 - 1)[(\epsilon^2 - \epsilon_l^2)(\epsilon_m^2 - \epsilon^2)]^{\frac{1}{2}}}, \quad (6.30)$$



where

$$|H_{0a}|^2 = |C^{11}(1)|^2(1+\alpha)^4(\epsilon^2-1)^4/(M\alpha)^2, \quad (6.31)$$

$$\epsilon_l = (1-\sqrt{\alpha})/(1+\alpha)^{\frac{1}{2}}, \quad (6.32)$$

$$\epsilon_m = (1+\sqrt{\alpha})/(1+\alpha)^{\frac{1}{2}}, \quad (6.33)$$

$$\bar{n}(\omega) = [\exp(\hbar\omega/kT) - 1]^{-1}, \quad (6.34)$$

$$\left. \begin{array}{l} \omega_o \\ \omega_a \end{array} \right\} = \omega_o(0) [1 \pm \epsilon(2 - \epsilon^2)^{\frac{1}{2}}] 2^{-\frac{1}{2}}. \quad (6.35)$$

An examination of the spectrum (6.30) indicates that it covers the range  $1 \leq \epsilon \leq \epsilon_m$ . The point  $\epsilon_l$  is outside this range. The factor  $(\epsilon^2-1)^3$  emphasizes the high end of the spectrum over the low end. In addition, the factor  $(\epsilon_m - \epsilon)^{-\frac{1}{2}}$  exhibits an integrable singularity at the top of the spectrum. This singularity arises because  $\partial\omega/\partial k$  vanishes for the highest propagation constant. The nature of this singularity is similar to the one which usually arises in the calculation of the density of states (per unit frequency interval). In two dimensions a  $\log|\epsilon_m - \epsilon|$  singularity would be expected, and in three dimensions a  $(\epsilon_m - \epsilon)^{\frac{1}{2}}$  singularity would be expected.<sup>19</sup> The singularity need not always occur at the maximum of the spectrum. In general, its location depends on the vanishing of  $\nabla_k \hbar\nu(\mathbf{k})$ . In most cases, however, the maximum energy  $\epsilon_m$  will also be a relative maximum, so that a singularity will frequently occur at the top of the spectrum.

The ratio of the maximum energy to the minimum energy, or to the long wave optical energy is simply  $\epsilon_m$ . An examination of (6.27) shows that  $\epsilon_m \leq \sqrt{2}$  and the latter value is assumed when  $\alpha = (K'/K) = 1$ . The particular value  $\sqrt{2}$  depends on our assumption of nearest neighbor forces and cannot be expected to hold too accurately in three dimensions. Furthermore, in a three-dimensional polyatomic lattice, many pairs of vibrational branches will interact. Each pair will give a spectrum of finite width, with one or more peaks. The complete spectrum will be a superposition of these many contributions.

### 7. ONE-DIMENSIONAL MODEL FOR NaCl TYPE LATTICES

The NaCl type lattice can be represented by a one-dimensional chain of equidistant atoms alternating Na, Cl, Na, Cl, etc. (see Fig. 3). Let us choose one Na atom as origin. That Na atom and its Cl neighbor to the right will be the members of a cell 0. The displacement of an arbitrary atom can be denoted by  $x_j^\alpha$ , where  $\alpha=0$  for Na and  $\alpha=1$  for Cl, and the integer 1 indicates the cell index.

For NaCl, the linear term in the electric moment makes the dominant contribution. With the help of (4.6), however, the effective charge on the sodium ion and that on the chlorine ion are related by  $B^0 = -B^1$

so that the ions have equal and opposite charges even in the presence of deformation. Thus the usual theory of absorption due to the linear terms results, with the ionic charge replaced by an "effective charge." Such an "effective charge" has already been introduced heuristically to explain the experimental results.<sup>20</sup> The formula for the absorption has, indeed, already been given: (5.18). It is simply necessary to insert the fact that for the long-wavelength optical mode, the amplitudes of the Na and Cl are out of phase and inversely proportional to the respective masses:<sup>21</sup>

$$b_o^0/b_o^1 \simeq -(M_1/M_0). \quad (7.1)$$

Together with the normalization condition (5.8), (7.1) and (5.18) determine the first order absorption.

The second order electric moment may be investigated by introducing an inversion through the Na atom at the origin:

$$Ix_j^\alpha = -x_{-j-\alpha}. \quad (7.2)$$

The condition  $IM = -M$  leads to the general requirement:

$$C^{\alpha\beta}(l-m+\alpha-\beta) = -C^{\alpha\beta}(m-l), \quad (7.3)$$

or

$$C^{\alpha\alpha}(m) = 0, \quad (7.4)$$

and

$$C^{01}(-m) = -C^{01}(m-1). \quad (7.5)$$

Thus the only independent coefficients are  $C^{01}(0)$ ,  $C^{01}(1)$ ,  $C^{01}(2)$ , etc. Displacement invariance (4.6b) leads to

$$\sum_{m=-\infty}^{+\infty} C^{01}(m) = 0. \quad (7.6)$$

However, (7.6) is automatically obeyed because of (7.5).

The final limitation on the number of independent constants can be made by limiting the interactions to second nearest neighbors. But  $C^{01}(1)$  is a third neighbor-interaction. Thus  $C^{01}(0)$  is the sole remaining independent coefficient:

$$C^{10}(0) = C^{01}(0), \quad C^{01}(-1) = -C^{01}(0). \quad (7.7)$$

Using (5.13) and (5.14) we obtain

$$S^{01}(k) = C^{01}(0)[1 - \exp(-i\phi)]; \quad S^{10}(k) = S^{01}(k),^* \quad (7.8)$$

$$H_{oo}^k = 2C^{01}(0)[(1 - \cos\phi) \operatorname{Re} b_o^0(k)^* b_o^1(k) + i \sin\phi \operatorname{Im} b_o^0(k)^* b_o^1(k)], \quad (7.9)$$

$$H_{aa}^k = 2C^{01}(0)[(1 - \cos\phi) \operatorname{Re} b_a^0(k)^* b_a^1(k) + i \sin\phi \operatorname{Im} b_a^0(k)^* b_a^1(k)], \quad (7.10)$$

$$H_{oa}^k = C^{01}(0)(1 - \cos\phi)[b_o^0(k)^* b_a^1(k) + b_o^1(k)^* b_o^0(k)] + iC^{01}(0) \sin\phi[b_o^0(k)^* b_a^1(k) - b_o^1(k)^* b_o^0(k)]. \quad (7.11)$$

<sup>20</sup> B. Szigeti, Trans. Faraday Soc. 45, 155 (1949); also, Rept. Brit. Elect. Allied Industr. Research Assoc. (Ref. L/T 203).

<sup>21</sup> L. Brillouin, *Wave Propagation in Periodic Structures* (McGraw-Hill Book Company, Inc., New York, 1946).

<sup>19</sup> L. van Hove, Phys. Rev. 89, 1189 (1953).

To illustrate these results more specifically we shall assume nearest neighbor interactions only with stiffness  $K$ . The frequencies and relative amplitudes are then given by<sup>21</sup>

$$M_0 M_1 \omega^2 = (M_0 + M_1) \pm (M_0^2 + M_1^2 + 2M_0 M_1 \cos \phi)^{\frac{1}{2}}, \quad (7.12)$$

$$b^0/b^1 = 2 \cos(\frac{1}{2}\phi) / [1 - \alpha \mp (1 + \alpha^2 + 2\alpha \cos \phi)^{\frac{1}{2}}], \quad (7.13)$$

$$\alpha = M_0/M_1, \quad (7.14)$$

where the upper and lower signs refer to the optical and acoustical cases respectively.

It follows from (7.13) that the amplitudes  $b^0$  and  $b^1$  are always in phase and hence can be chosen real. Thus the second terms in (7.9) and (7.10) may be dropped.

We see from (7.9)–(7.11) that all of the coefficients  $H$  vanish for  $\phi=0$ . Thus long-wavelength modes of any type are ineffective in producing an electric moment or dipole absorption.

The only other value of  $\phi$  that can lead to a singularity or peak in the absorption is  $\phi=\pi$  (the shortest wavelength). However, an examination of (7.13) near  $\phi=\pi$  shows that for the acoustic mode the light particle obeys  $b_a^0=0$  whereas for the optical mode the heavy particle obeys  $b_o^1=0$ . Thus  $b_a^0 b_a^1 = b_o^0 b_o^1 = 0$  and  $H_{aa^\pi} = H_{oo^\pi} = 0$ . Thus the double optical transition and the double acoustical transition will show no strong peak.

The mixed transition  $H_{oa}$  however takes the value

$$H_{oa^\phi} = \frac{C^{01}(0)}{M_1 \sqrt{\alpha}} \left[ \frac{(1 - \cos \phi)(1 - \alpha)}{(1 + \alpha^2 + 2\alpha \cos \phi)^{\frac{1}{2}}} - 2i \sin \phi \right], \quad (7.15)$$

which does not vanish at  $\phi=\pi$ . In addition,

$$d[\omega_o(\phi) + \omega_a(\phi)]/d\phi = 0$$

at  $\phi=\pi$ , so that as in the diamond case a singularity of the form  $(\epsilon_m - \epsilon)^{-\frac{1}{2}}$  will be observed in the spectrum. With the vibration spectrum (7.12), the absorption is still given by the diamond result (6.30) providing we replace  $|H_{oa}|^2$  by the value appropriate to NaCl:

$$|H_{oa}|^2 = \frac{|C^{01}(0)|^2}{4M_1^2 \alpha^3} \left[ \frac{(1 - \alpha^2)^2 (\epsilon^2 - 1)^4}{(2 - \epsilon^2) \epsilon^2} + 4(1 + \alpha)^2 (\epsilon^2 - 1)^2 (\epsilon^2 - \epsilon_l^2) (\epsilon_m^2 - \epsilon^2) \right]. \quad (7.16)$$

To summarize then, the only important transition for the NaCl case is the mixed optical acoustical transition, and its spectrum is qualitatively similar to the corresponding spectrum for the diamond case. We note that Eqs. (6.27)–(6.29) for diamond are directly applicable to the NaCl model with the new definition of  $\alpha$ . So too are Eqs. (6.32)–(6.35).

If we interpret the observed side band in NaCl as due to the acoustical optical transition at  $\phi=\pi$ , the

peak should be located at

$$\epsilon = \epsilon_m = [1 + \sqrt{\alpha}] / (1 + \alpha)^{\frac{1}{2}}, \quad (7.17)$$

measured in units of the main absorption frequency. The function  $\epsilon_m(\alpha)$  has an absolute and a relative maximum of  $\sqrt{2}$  at  $\alpha=1$  and is not sensitive to  $\alpha$  over a wide range. Since the observed ratio of side band/main band frequency is close to  $\sqrt{2}$  for all of the alkali halides the above suggested interpretation is plausible.

## 8. IMPURITY INDUCED LATTICE ABSORPTION

We have already considered in some detail the linear and quadratic terms in the electric moment for perfect lattices. If impurities are present, certain of the invariance requirements used to simplify or eliminate terms in the electric moment expansion are no longer valid. In this section we shall indicate qualitatively the major changes brought about by abandoning these invariance requirements.

If an impurity is introduced into the lattice that modifies the electronic structure in its neighborhood, the predominate effect will be the introduction of a polar character, i.e., linear terms in the electric moment, in the immediate vicinity of the impurity. To see this point we note that the crystal is no longer perfectly periodic, or invariant against lattice displacements so that (4.1) is no longer valid. The effective charge  $B_l^\alpha$  does depend on  $l$ . In addition it depends on the position  $(\beta, m)$  at which the impurity is introduced. Thus an additional term in the electric moment will be introduced of the form

$$\mathbf{M} = \sum \mathbf{B}_l^\alpha \begin{pmatrix} \beta \\ m \end{pmatrix} \cdot \mathbf{x}_l^\alpha \exp(i\mathbf{v} \cdot \mathbf{r}_l^0). \quad (8.1)$$

The effective charges  $\mathbf{B}_l^\alpha \begin{pmatrix} \beta \\ m \end{pmatrix}$  will depend on  $l-m$  and will decrease rapidly as  $l-m$  increases, since the presence of an impurity will disturb the electronic structure only locally. If (8.1) is re-expressed by using (5.10) in terms of the normal coordinates,  $q_k$ :

$$\mathbf{M} = N^{-\frac{1}{2}} \sum_l \sum_\alpha b_l^\alpha(\mathbf{k}) \cdot \mathbf{D}^{\alpha\beta}(\mathbf{k} + \mathbf{v}) q_l(\mathbf{k}) \times \exp[i(\mathbf{k} + \mathbf{v}) \cdot \mathbf{r}_m^0], \quad (8.2)$$

where

$$\mathbf{D}^{\alpha\beta}(\mathbf{k} + \mathbf{v}) = \sum_l \mathbf{B}_l^\alpha \begin{pmatrix} \beta \\ m \end{pmatrix} \exp[i(\mathbf{k} + \mathbf{v}) \cdot (\mathbf{r}_l^0 - \mathbf{r}_m^0)]. \quad (8.3)$$

The coefficient  $\mathbf{D}^{\alpha\beta}(\mathbf{k})$ , that measures the extent to which mode  $\mathbf{k}$  will contribute to the electric moment, is the Fourier transform of  $\mathbf{B}_l^\alpha \begin{pmatrix} \beta \\ m \end{pmatrix}$ . If  $\mathbf{B}_l^\alpha \begin{pmatrix} \beta \\ m \end{pmatrix}$  is appreciable to a certain range of values of  $l-m$ ,  $\mathbf{D}^{\alpha\beta}(\mathbf{k})$  will be appreciable for all  $\mathbf{k}$  whose wavelengths are comparable to, or longer than, the range associated with  $l-m$ . Since these wavelengths for an optical branch usually have only a small range of frequencies, we may expect in the absence of damping effects a

fairly sharp absorption maximum close to the fundamental optical vibration frequency.

If the presence of the impurity does not modify the vibration properties of the lattice in the immediate neighborhood of the impurity, an absorption peak should occur at each of the maxima in the density of optical modes (per unit energy). In such a case the absorption bands would provide a rough mapping of this density of modes.

If on the other hand, the impurity distorts the lattice in its vicinity, the vibrational spectrum will be modified near the impurity and a quasi-molecular viewpoint toward the absorption can be adopted. In such cases the observed frequencies will be shifted from those determined by the density of modes of the normal lattice.

If  $\mathbf{B}_l^\alpha \binom{\beta}{m}$  had an extremely long range, i.e., if it were essentially independent of  $l$ , then we would rediscover in  $D^{\alpha\beta}(\mathbf{k}+\mathbf{v})$  the usual selection rule  $\delta(\mathbf{k}+\mathbf{v}, 0)$  appropriate to a perfect crystal.

In addition to the impurity induced linear term (8.1), corresponding additional terms will appear in the second order electric moment. Since the concentration of impurities is not large, these second order terms may be difficult to observe in presence of the absorption associated with the intrinsic second order terms.

#### 9. COMPARISON BETWEEN THEORY AND EXPERIMENT

The body of this paper has been concerned primarily with charge deformation effects, the resulting second order electric moments and the infrared absorption associated with the latter. The infrared absorption is also influenced by the presence of cubic terms in the potential energy. In this section, we shall review the experimental evidence briefly in the light of the present theory and of Born and Blackman's<sup>2,3</sup> so as to assess the relative importance of charge deformation and anharmonic effects in various situations.

##### A. The Side Bands in the Alkali Halides

According to the treatment of Born and Blackman,<sup>2</sup> Blackman,<sup>3</sup> and Seitz,<sup>4</sup> the radiation couples to the linear part of the electric moment, which would produce a single band, but the anharmonicity introduces combination frequencies in the vibration and hence also in the absorption. Blackman, who studied the alkali halides in detail, predicted the location of the side bands by treating them as summation bands. In the deformation theory the second order terms in the electric moment also give rise to summation bands. Thus both theories predict the same location of the major side band.

In Sec. 2 we discussed the ratio of the height of the reflection side band to that of the corresponding main reflection peak. This height decreased in the order LiF, MgO, NaF, NaCl, and KCl. This order correlated with

changes in Cauchy relation deviations and with the strain polarizability both of which may be related to the charge deformation. Thus the side-band intensities support a charge deformation hypothesis. We do not mean to imply by these remarks that cubic terms in the potential have no important influence on the absorption or reflection spectrum, but that second order electric moments must, on the experimental evidence, be considered.

##### B. Fundamental Absorption in the Alkali Halides

The integrated strength of the fundamental absorption line depends on the effective charge  $B^\alpha$  on the ions. This effective charge may differ from  $e$  because of the presence of some "homopolar bonding" in the formation of the crystal. In addition, we have shown that there will be a dynamic contribution to  $B^\alpha$  associated with charge deformation, i.e., the displacement of the center of charge of the electrons on an ion may differ from the displacement of the corresponding nucleus. The presence of cubic terms as such will not yield any dynamic modification of the effective charge on the ions. No attempt has as yet been made to estimate the effective charge from the infrared absorption intensity. Szigeti<sup>20</sup> has, however, been able to estimate the effective charge on the ions using the static dielectric constant, the refractive index and the fundamental lattice absorption frequency. He obtains an effective charge of the order of  $0.9e$  for the alkali halides indicating that homopolar and dynamic contributions together are of the order of 10 percent.

##### C. Broadening of Bands in the Alkali Halides

Second order electric moments can produce absorption near the main band by combining an optical phonon with a low-energy acoustical phonon. (This process is not too probable in the one-dimensional calculation.) Such a two-phonon process occurs independently of the main absorption, however, and will not change the latter from an infinitely sharp line. It merely superimposes a continuous background to the main line.

Anharmonicity has been shown by Blackman to provide a logical explanation of the broadening of the main absorption line into a band. Since the experimental results exhibit a broad band, we can conclude that anharmonic terms are appreciable in the alkali halides.

The second order electric moment yields side bands that are already a continuum. The breadths so obtained are relatively insensitive to temperature (well below the Debye temperature). Similar conclusions apply to the side bands produced by anharmonic terms.

Since we have concluded that anharmonic broadening is important for the main band, we can use the relative width of the main band as a measure of the importance of the cubic terms. There is a systematic correlation, through the alkali halides, between the main band

width and the side-band intensity (see Table I). A mechanism based on anharmonicity as an explanation of the side bands is therefore also consistent with the trends in the data.

#### D. Diamond: Intrinsic Absorption

Anharmonic forces are undoubtedly present in the diamond structure, but without the help of second order electric moment terms they can yield no absorption. The second order moment due to charge deformation is therefore necessary to account for the absorption. Since absorption resulting from a second order moment is already a continuum consisting of sum and difference bands, anharmonicity is not necessary to explain broadening. The effect of anharmonicity is to produce additional broadening and to produce higher order side bands.

The prominent peaks in the intrinsic absorption of diamond (see Fig. 2) at  $3.98, 4.20, 4.59, 4.85,$  and  $4.98\mu$  ( $2510, 2380, 2180, 2060, 2010\text{ cm}^{-1}$ ) are within a factor of 2 of the fundamental vibration at  $1332\text{ cm}^{-1}$  and may reasonably be designated as summation bands associated with two-phonon processes of the sort discussed in this paper. An accurate prediction of the locations of these peaks requires a detailed analysis of the vibration spectrum of the sort carried out by Smith.<sup>22</sup> In addition, a determination of the electric moment coefficients  $C_{lm}^{\alpha\beta}$  and the intensity factors  $|H_{\nu} t^k|^2$  must be made to determine which lines will appear in strength and which will be forbidden. Simeral<sup>23</sup> has made a detailed analysis of the locations of the summation bands based on the peaks in the vibration spectrum as determined by Helen Smith. F. Herman and J. Calloway (private communication) have made a corresponding analysis for germanium, extending Helen Smith's vibrational calculations by adding interactions to third neighbors. Such analyses lead in general to a great number of possible lines because there are six vibrational branches which may combine in pairs at many different propagation constants. Simeral eliminates lines by assuming that the selection rules for

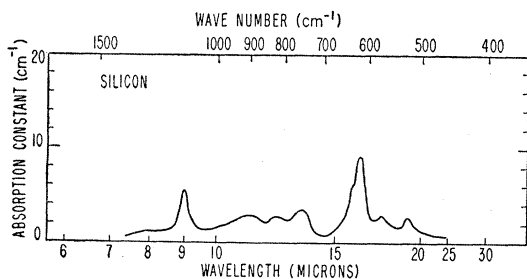


FIG. 4. Infrared absorption spectrum of high-purity silicon due to lattice vibration.

<sup>22</sup> Helen M. J. Smith, *Trans. Roy. Soc. (London)* **A241**, 105 (1948).

<sup>23</sup> W. G. Simeral, thesis, University of Michigan (unpublished); also presented as a technical report of the Engineering Research Institute of Michigan.

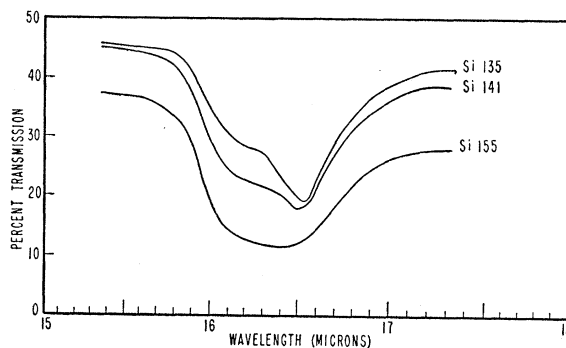


FIG. 5. Variations in the 16-micron lattice vibration band in silicon.

infrared absorption are complementary to the second order Raman selection rules which were obtained by Helen Smith. The major contribution of the present paper, in this connection, is to indicate the basis on which correct selection rules may be obtained. An extension of the present analysis to the three-dimensional diamond structure is now being made by Hirshberg.<sup>24</sup> The selection rules that she has obtained thus far indicate that Simeral's complementarity assumption is not valid.

The weak intrinsic absorption lines at  $3660$  and  $3120\text{ cm}^{-1}$  are in a region to be explained by three-phonon processes. Such three-phonon processes could occur through third order terms in the electric moment, or the absorption could be produced by second order electric moment terms in conjunction with anharmonicity effects.

#### E. Diamond: Impurity Absorption

According to our discussion in Sec. 8, linear terms in the electric moment can contribute to lattice absorption in the diamond structure if "impurities" are present. The strongest band in the absorption spectrum of Type I diamond at  $1280\text{ cm}^{-1}$  can indeed be interpreted as an impurity-induced coupling of the radiation to the fundamental optical vibrations of the diamond lattice. The fact that this band has about 4 percent lower frequency than the Raman frequency ( $1332\text{ cm}^{-1}$ ) is in agreement with Smith's result<sup>22</sup> (see her Fig. 6) that maximum density of the optical modes occurs at 5 or 6 percent below the Raman frequency. From the observed sharpness of this fundamental line we can conclude that anharmonic forces are considerably less important in diamond than in the alkali halides.

The bands in the region from  $1000$  to  $1330\text{ cm}^{-1}$  may perhaps be regarded as a rough mapping of the density of the optical vibrational modes in the diamond spectrum for low impurity densities. Distortion occurs because of the presence of the weighting coefficient  $D^{\alpha\beta}(\mathbf{k})$  of (8.3) that favors long-wavelength modes.

<sup>24</sup> J. F. Hirshberg, thesis in progress, Syracuse University (unpublished).

But the correspondence between the absorption and the density of modes in Fig. 6 of Helen Smith's paper is not too unreasonable considering the distortions involved.

Since the relative intensities of the 1010, 1190, and 1280  $\text{cm}^{-1}$  peaks change somewhat from specimen to specimen, it is also possible that these peaks are associated with different impurities.<sup>25</sup>

The peak at 1390  $\text{cm}^{-1}$  is so much sharper than the other impurity bands and so much lower in integrated strength that it may be due to an impurity whose mechanical coupling to the lattice is weak. Other very sharp impurity peaks have been observed by Blackwell and Sutherland,<sup>14</sup> even in the intrinsic region. These impurities are apparently not simple substitutional impurities.

### F. Silicon and Germanium

The conclusions given above apply to all diamond structures, *viz.*, to silicon, germanium, and gray tin. Infrared absorption measurements on a wide variety of single crystal and polycrystalline specimens of silicon and germanium have been reported.<sup>7, 10-12</sup> There have been no data as yet reported for gray tin.

The lattice absorption spectrum in silicon is given in Figs. 4 and 5. Variations<sup>26</sup> have been observed from specimen to specimen in the structure of the 625- $\text{cm}^{-1}$  and 1110- $\text{cm}^{-1}$  bands in silicon, thus indicating that these bands may be due to impurities or imperfections.

In the absence of data for the fundamental Raman frequency the classification of the observed bands into fundamental and combination bands is somewhat ambiguous. An estimate of the fundamental optical frequency from the elastic constants by using Smith's<sup>22</sup> procedure yields 850  $\text{cm}^{-1}$ . For comparison, the Debye temperature in the same units is 460  $\text{cm}^{-1}$ . The impurity induced band at 625  $\text{cm}^{-1}$  probably provides the most reliable estimate of the Raman frequency. This would

TABLE III. Elastic constants.

Crystal	Debye temperature $\theta^\circ\text{K}$	Elastic constants <sup>a</sup>			Calculated Raman line <sup>b</sup>	
		$C_{11}$	$C_{12}$	$C_{44}$	$\lambda^{-1}(c)$ $\text{cm}^{-1}$	$\lambda^{-1}(\theta)$ $\text{cm}^{-1}$
Diamond	1950 <sup>c</sup>	9.5 <sup>d</sup>	4.3 <sup>d</sup>	3.9 <sup>d</sup>	1370 <sup>e</sup>	1360
Silicon	658 <sup>f</sup>	1.657 <sup>f</sup>	0.639 <sup>f</sup>	0.796 <sup>f</sup>	850	460
Germanium	362 <sup>g</sup>	1.288 <sup>g</sup>	0.483 <sup>g</sup>	0.671 <sup>g</sup>	390	250

<sup>a</sup> All stiffnesses measured in units of  $10^{12}$  dynes/cm<sup>2</sup>.

<sup>b</sup> First column  $\lambda^{-1}(c)$  is Raman line calculated from elastic constants by Helen Smith's method. Second column  $\lambda^{-1}(\theta)$  is Debye temperature converted to units of reciprocal centimeters.

<sup>c</sup> K. S. Pitzer, *J. Chem. Phys.* **6**, 68 (1938).

<sup>d</sup> S. Bhagavantam and J. Bhimasenachar, *Proc. Roy. Soc. (London)* **A187**, 381 (1946). The value of  $C_{44}$  is questionable according to Helen Smith.

<sup>e</sup> Experimental Raman line is at 1332  $\text{cm}^{-1}$ .

<sup>f</sup> N. Pearlman and P. H. Keesom, *Phys. Rev.* **88**, 398 (1952); H. J. McSkimin, *J. Appl. Phys.* **24**, 988 (1953).

<sup>g</sup> P. H. Keesom and N. Pearlman, *Phys. Rev.* **91**, 1347 (1953).

<sup>25</sup> Chesley has carried out a spectrographic analysis of a wide variety of diamonds and found the presence of an appreciable number of impurities. F. G. Chesley, *Am. Mineralogist* **27**, 20 (1942).

<sup>26</sup> We are indebted to Mrs. Bertha W. Hervis for the data given in Fig. 5.

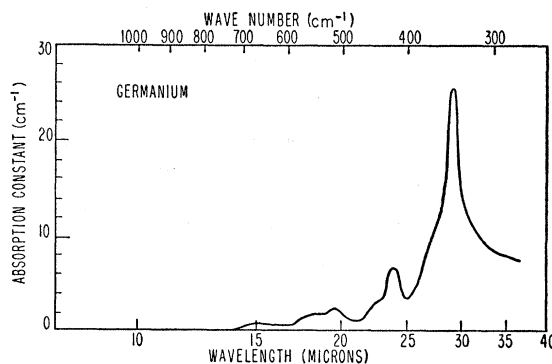


FIG. 6. Infrared absorption spectrum of relatively high-purity germanium due to lattice vibration.

indicate that the bands at 770, 830, and 910  $\text{cm}^{-1}$  are intrinsic summation bands. The band at 1110  $\text{cm}^{-1}$  which varies from specimen to specimen is possibly due to the presence of oxygen impurities.

The lattice absorption spectrum in germanium is shown in Fig. 6. Except for the occasional presence of a band at 830  $\text{cm}^{-1}$  (not shown in the figure) due to presence of impurities (analogous to the 1110  $\text{cm}^{-1}$  in silicon), the bands from 345  $\text{cm}^{-1}$  to 640  $\text{cm}^{-1}$  do not appear to vary significantly from specimen to specimen even with the addition of appreciable amounts of silicon as an impurity.

The Raman frequency for germanium has not yet been measured directly. An estimate from the elastic constants (see Table III) using Smith's<sup>22</sup> procedure is 390  $\text{cm}^{-1}$ . The Debye frequency for comparison is 250  $\text{cm}^{-1}$ . It would appear then, that the strong absorption at 345  $\text{cm}^{-1}$  is close to the Raman frequency, and may actually correspond to the fundamental optical vibration frequency of the germanium lattice. Since the 345- $\text{cm}^{-1}$  band has been observed in the purest specimens of germanium, and does not vary significantly with addition of 1 percent silicon, the present evidence is against interpreting this band as an impurity band.

There is always the possibility that the Raman frequency, when measured, will occur at a lower frequency than the above estimate, and the 345- $\text{cm}^{-1}$  band might then be an ordinary summation band.

Another possible explanation<sup>23</sup> for this band is the high isotope content for germanium: Simeral<sup>23</sup> has suggested that this high isotope concentration breaks down the selection rule against a linear moment. However, in the Born-Oppenheimer approximation the electronic structure for a given configuration is unchanged by an isotopic substitution, so that the electric moment and its selection rules will be unaltered. The magnitude and character of the vibrations in the neighborhood of the isotope will, however, be altered by the change in mass. Thus a pair of modes which at large distances from the isotope impurity would not absorb, may have an appreciable absorption near the impurity. This can lead,

for example, to a combination band absorption with frequency near the fundamental optical absorption.

#### ACKNOWLEDGMENT

The authors wish to acknowledge the helpful suggestions and active interest and encouragement given to our work by Mr. Paul H. Egli.

*Note added after completion of manuscript.*—R. J.

Collins and H. Y. Fan<sup>27</sup> have recently reported measurements on the infrared lattice absorption of germanium, silicon, and diamond as a function of temperature. They conclude that the observed absorption in silicon and germanium and of Type II diamond is made possible by the thermal vibrations of the atoms. However, they do not suggest any mechanism for the absorption.

<sup>27</sup> R. J. Collins and H. Y. Fan, *Phys. Rev.* **93**, 674 (1954).

## Soft X-Ray Absorption of Evaporated Thin Films of Tellurium\*

ROBERT W. WOODRUFF† AND M. PARKER GIVENS  
*Institute of Optics, University of Rochester, Rochester, New York*  
(Received July 28, 1954)

The linear absorption coefficient of tellurium has been measured in the wavelength region 100Å to 400Å. A double peak was observed at about 300Å; it is due to transitions from the  $N_{IV}$  and  $N_V$  levels to the conduction band. A large peak at shorter wavelengths was also observed.

### I. INTRODUCTION

THE energy levels of materials in the solid state are broadened into bands by the interaction of the overlapping atomic wave functions. The bands may be considered to be composed of a very large number of levels so close together that they may be described by a continuous function  $N(E)$ , where  $N(E)dE$  is the number of energy levels between  $E$  and  $E+dE$ .

The absorption of light associated with an electronic transition from some lower energy level to the levels in the range  $E$  to  $E+dE$  is proportional to the function  $N(E)$ , and also to the transition probability,  $f(E)$ . Since  $f(E)$  depends on the exact wave functions, its value is not known and, hence, measurement of the absorption can give only a qualitative picture of  $N(E)$ . Also to be considered is the fact that raising an electron out of an inner level alters the charge of one ion so that the observed energy level structure is that of a slightly perturbed lattice.

The lower or x-ray levels are broadened due to radiation damping and Auger transitions. These two effects have been studied by Prins.<sup>1</sup> He showed that on a linear energy scale the soft x-ray levels, which are about 100 volts below the valence band, are narrower than the deeper-lying levels such as the  $K$  and  $L$  levels. In studying the structure of the conduction band it is advantageous, therefore, to use the soft x-ray levels rather than the deeper-lying levels.

The experimental resolving power required to reveal a conduction band structure 0.1 volt wide is only about

1000 when using soft x-rays, but will be more than a hundred times that much when using transitions from the  $K$  levels. The soft x-ray region therefore offers experimental as well as theoretical advantage over the conventional x-ray region.

### II. EXPERIMENT

The vacuum spectrograph used in this research was modeled after one used by Skinner and Johnston<sup>2</sup> and has been described by Siegmund<sup>3</sup> with certain modifications discussed by Carter.<sup>4</sup> In brief, the instrument is a grazing incidence mount of a two meter aluminum grating with 30 000 lines/inch. The source, the grating and the photographic plate holder are on the Rowland circle. The angle of incidence is 85°.

A vacuum of  $5 \times 10^{-5}$  mm Hg is maintained by means of two oil diffusion pumps, one on the main chamber and the other on the source chamber. The source is a spark between copper or silver electrodes from a 0.15- $\mu$ f condenser charged to about 30 000 volts. This was effectively controlled by an air gap in series with the internal spark. The plate holder, situated behind an occulting diaphragm, was designed to be movable from outside through an "O" ring seal. Five exposures could be made on Eastman Kodak Spectroscopic Plates, type SWR Extra-thin, size 2 in.  $\times$  10 in.

The wavelengths were determined from tables of the copper spark spectrum prepared by Kruger and

<sup>2</sup> H. W. B. Skinner and J. E. Johnston, *Proc. Roy. Soc. (London)* **A161**, 420 (1937).

<sup>3</sup> W. P. Siegmund, thesis, The University of Rochester Library, 1951 (unpublished); for a brief account of this work see *Phys. Rev.* **85**, 313-314 (1952).

<sup>4</sup> D. E. Carter, thesis, The University of Rochester Library, 1954 (unpublished).

\* This research was supported by the U. S. Office of Naval Research.

† Now with the Research Division, Photo Products Department, E. I. du Pont de Nemours and Company, Inc., Parlin, New Jersey.

<sup>1</sup> J. A. Prins, *Physica* **2**, 231 (1935).