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Covalent Bonding Effect on Optical Phonons—Empirical Relation*

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It is shown empirically that the force constant $k=m\omega^2$ of transverse optical vibrations in dielectric solids depends strongly on the fraction of covalent bonding $C=1-i$ between neighboring atoms, where i is the fraction of ionic character in the bond. For solids in the heavy isoelectronic series (e.g., the mixed series of Si-Ge, the Ge series, the mixed series of Ge-α-Sn, and the α-Sn-series), where the internuclear distances are kept nearly constant within the same isoelectronic series, k depends solely on C and is approximately proportional to C^n with $1<n<2$. The covalent dependence of the force constant may be interpreted in terms of Pauling's theory of the chemical bond or parameters in the shell model of lattice vibration.

MANY theoretical and empirical relations have been established between the lattice vibrations and other properties of solids. Notably, Szigeti derived relations between the force constant k of transverse optical vibrations and (1) the Szigeti charge,[1] which is responsible for the splitting of the longitudinal and transverse optical phonon near the zone center, and (2) the compressibility[2] of the crystal. Brout deduced the Brout sum relation[3] between force constants and compressibility. Badger's rule[4] empirically correlates k to the interatomic distance d in a molecule. Plendl, Mitra, and Gielisse[5] have compiled empirical relations between characteristic lattice-vibration frequencies, cohesive energy, compressibility, and hardness of solids.

In this paper an empirical relation on a strong effect from a more fundamental origin is reported. It is a simple correlation between the force constant k of transverse optical vibrations and the amount of covalency C in the bonding between neighboring atoms in the solids. The force constant k increases with $C=1-i$, where i represents the amount of ionic character[6] in bonding. For heavy solids of an isoelectronic series, where d is nearly constant within each heavy series, k depends solely on C and is proportional to C^n with $1<n<2$. We define, conventionally, the force constant k (dyn/cm) as $m\omega^2$, where m is the reduced mass and ω is the transverse optical frequency.

As a general survey on the force constants of various simple dielectric solids we plot k versus the internuclear distance d at equilibrium in Fig. 1. For convenience of characterization, points belonging to the same isoelectronic series are connected with thin lines, each having approximately the same reduced mass. Force constants of solids made of elements from the same columns of the periodic table are connected by thick lines horizontally, each representing approximately the same amount of covalency in the bonding. Figure 1 shows that k increases with (1) decreasing d and (2) increasing amount of covalent bonding C, i.e., in the order of I-VII, II-VI, III-V, to IV-IV compounds. Figure 1 also shows that as solids become heavy, with reduced mass $m \gtrsim 3.6\times10^{-23}$ g, the internuclear distance d is nearly constant within each isoelectronic series. For these heavy solids k should depend solely on C within each isoelectronic series. The references used in Figs .1 and 2 are tabulated in Table I.

To show the effect of covalency on the force constant more explicitly, k versus C is plotted on linear scales in Fig. 2. The amount of covalency C in the bonding between nearest neighbors A and B is evaluated from their respective empirical values of electronegativity,[6] x_A and x_B, via Pauling's empirical relation[6]:

$$C=1-i=\exp[-(\tfrac{1}{2}x_A-\tfrac{1}{2}x_B)^2],$$

where i is the amount of ionic character[6] in the bonding. Figure 2 shows that k rises smoothly with C for most of solids within each isoelectronic series. As expected, solids in a lighter isoelectronic series (because of smaller internuclear distance) have larger k than the similar

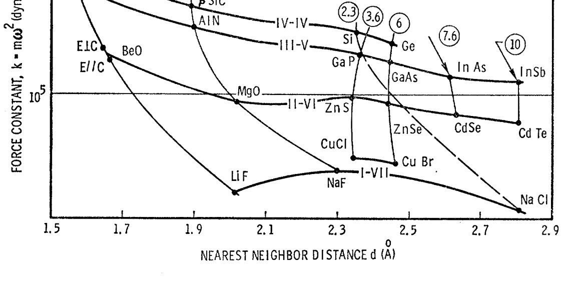

FIG. 1. Force constant of transverse optical phonon versus nearest-neighbor distance in solids. (Numbers in circles are reduced mass in units of 10^{-23} g for solids on the same thin curve. References in Figs. 1 and 2 are listed in Table I.)

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solids in the heavier series. Solids in the same light series, i.e., diamond series, SiC series and Si series, also appear to show stronger covalency dependence of k because of the additional effect due to closer internuclear distance in more covalent solids. For all other heavy series, k depends solely on C in each isoelectronic series because of the near constancy of d as shown previously in Fig. 1. These series are represented by four solid curves in the lower part of Fig. 2. They show the genuine effect of covalency on the force constant. The relation is as follows:

$$k \propto C^n \quad \text{or} \quad k = k_0 C^n \quad \text{with} \quad 1 < n < 2 \qquad (1)$$

for each (heavy) isoelectronic series, where k_0 is the optical force constant of the solids with 100% covalent bonding in that particular series.

TABLE I. References used in Figs. 1 and 2.

Crystal	Source of reference
Diamond	E. Anastassakis *et al.*, Phys. Rev. Letters **17**, 1051 (1966).
Cubic BN	P. J. Gielisse *et al.*, Phys. Rev. **155**, 1039 (1967).
BeO	E. Loh Phys. Rev., **166**, 673 (1968).
LiF	J. R. Jasperse *et al.*, Phys. Rev. **146**, 526 (1966).
β-SiC	W. G. Spitzer *et al.*, Phys. Rev. **113**, 133 (1959).
AlN	A. T. Collins *et al.*, Phys. Rev. **158**, 833 (1967).
MgO	J. R. Jasperse *et al.*, Phys. Rev. **146**, 526 (1966).
NaF	S. S. Mitra *et al.*, Phys. Rev. Letters **18**, 455 (1967).
Si	J. H. Parker, Jr. *et al.*, Phys. Rev. **155**, 712 (1967).
NaCl	C. M. Randall *et al.*, Solid State Commun. **2**, 273 (1964).
GaP	H. W. Verleur and A. S. Barker Jr., Phys. Rev. **149**, 715 (1966).
ZnS	S. S. Mitra *et al.*, Phys. Rev. Letters **18**, 455 (1967).
CuCl	J. N. Plendl *et al.*, Appl. Opt. **5**, 397 (1966).
Ge	J. H. Parker, Jr. *et al.*, Phys. Rev. **155**, 712 (1967).
GaAs	H. W. Verleur and A. S. Barker Jr., Phys. Rev. **149**, 715 (1966).
ZnSe	R. E. Halstead *et al.*, J. Phys. Chem. Solids **22**, 109 (1961).
CuBr	J. N. Plendl *et al.*, Appl. Opt. **5**, 397 (1966).
InAs	M. Hass and B. W. Henvis, J. Phys. Chem. Solids **23**, 1099 (1962).
CdSe	R. Geick, J. Appl. Phys. **37**, 1994 (1966).
InSb	M. Hass and B. W. Henvis, J. Phys. Chem. Solids **23**, 1099 (1962).
CdTe	R. E. Halstead *et al.*, J. Phys. Chem. Solids **22**, 109 (1961).

The covalency dependence of optical force constants, Eq. (1), can also be expressed in terms of the additional ionic resonance energy Δ, due to additional ionic character, in the bond. With the relation from the theory of the chemical bond,[6]

$$\Delta(\text{eV}) = (x_A - x_B)^2,$$

Eq. (1) can be rewritten in terms of Δ as

$$k \propto C^n \propto \exp[-\Delta/(4/n)],$$

or

$$k = k_0 \exp[-\Delta/(4/n)] \quad \text{with} \quad 1 < n < 2. \qquad (2)$$

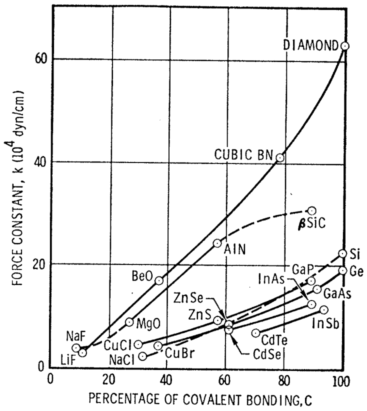

FIG. 2. Force constant of transverse optical phonons versus percentage of covalent bonding in solids. (References in the figure are listed in Table I.)

Equation (2) states that the optical force constant of a solid is reduced from that with complete covalent bonding, k_0, by a factor $\exp[-\Delta/(4/n)]$ due to the additional ionic character i in the bond with additional ionic resonance energy Δ (eV). Graphically, Eq. (2) shows that as the energy curve, E (in eV) versus the internuclear distance r of an ionic solid, becomes flattened owing to large Δ (eV) above that of a covalent solid, the force constant $k = d^2E/dr^2$ is expected to decrease.

The covalent dependence of optical force constants can also be described in terms of parameters in the shell model[7–10] of lattice vibrations. In the shell model, each ion consists of a core of tightly bound inner electrons and a shell of outer "valence" electrons. Each shell is conceived as attached to its core and to its neighboring shells by ideal, massless springs. The optical force constants of the solid depend on the force constants (1) between neighboring shells S_0, (2) between the shell and core of the anion k_-, and (3) between the shell and core of the cation k_+. For covalent solids, there is no particular weak force constant between shells and cores; k therefore approaches the force constant between shell and core of the covalent ion[8] itself, i.e.,

$$k \approx k_+ \approx k_-,$$

and k is large, ~10^5 to 10^6 dyn/cm.

In ionic crystals, the force constants between neighboring shells S_0 and between the loosely bound shell and core of anion k_- are much smaller than k_+ of the tight cation; k will approach the weakest force

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constant, i.e.,

$$k \approx k_- \ll k_+ \quad \text{or} \quad k \approx S_0 \ll k_+,$$

and k is small, $\sim 10^4$ dyn/cm.

In conclusion, the optical force constants of dielectric solids depend strongly on the amount of covalent bonding between neighboring atoms. This covalent dependence may be described in terms of Pauling's theory of the chemical bond or parameters in the shell model of lattice vibration.

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Direct Measurement of the Oxygen Vacancies Produced in Calcium Tungstate by Fast Reactor Neutrons*

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The present paper is intended to point out the usefulness of electron spin resonance for the direct measurement of defect concentration. Fast-neutron irradiation results in a variety of paramagnetic centers in calcium-tungstate single crystals. From the g tensors, the hyperfine interaction, and the result of a uniaxial-stress experiment, one of the centers has been identified as due to paramagnetic tungsten associated with a displaced nearest-neighbor oxygen. The concentration of oxygen displacements is measured by comparison with a copper-sulfate standard and is calculated using the Kinchin-Pease theory. The measured and calculated values are in good agreement.

I. INTRODUCTION

One of the fundamental problems in the study of radiation effects is the determination of the concentration of the defects. Even though many physical properties are changed by radiation, very few techniques provide an opportunity for direct measurement of the defect concentration. Besides the problem of identification of defects, the basic difficulty is that the dependence of changes in various properties due to the introduction of defects is not understood well enough theoretically to provide reliable methods for an absolute determination of defect concentrations.

One method, used successfully by Antal, Weiss, and Dienes,[1] employs the transmission of long-wavelength neutrons (beyond the Bragg cutoff of the crystal) through irradiated solids. This technique, however, is limited to materials of low neutron-capture cross section. The minimum detectable concentration of defects is governed by the available neutron intensity, the capture cross section, and the bound-atom coherent scattering cross section of the atoms of the solid. To date, only concentrations of the order of 0.1% or greater have been detected. This requires a very high integrated fast-neutron flux, of the order of 10^{19} to 10^{20} nV.

The second method of direct measurement of defect concentration was introduced by Levy.[2] Using unstrained single crystals of sodium chloride, Levy observed that all the negative-ion vacancies were converted to stable F centers following a γ-ray dose of about 10^7 R. If crystals were subsequently exposed for a time to reactor irradiation, he found that upon resumption of the γ irradiation, the F-center concentration increased in proportion to the integrated fast-neutron flux. The measured defect concentration due to fast neutrons was in agreement with radiation-damage theory. The determination of defect concentration requires additional information about the oscillator strength of the F centers.

When paramagnetic defects are produced, electron spin resonance can be a powerful technique. This is because in ESR technique, electrons are used as electric and magnetic microscopic probes. The defect concentration can be measured without difficulty, and the lowest detectable defect concentration is comparable with that of Levy's method. The integrated fast-neutron flux required is only 10^{14} to 10^{15} nV. At this low dose of irradiation, the simple model of independent (noninteracting) defects should be more reliable than at higher doses.

In a previous publication,[3] we reported three kinds of paramagnetic centers in fast-neutron irradiated calcium tungstate. One of the centers, namely, the γ center, has been tentatively identified as due to paramagnetic tungsten associated with a nearest oxygen vacancy. In this paper, we will concentrate on this γ center alone. The arguments leading to this identification are presented. The number of defects is measured

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