the calculated vacancy formation energy is much too high.

Consideration of Jansen exchange forces[31–33] and four-dipole interactions[26–30] lowers both the energy of formation of a vacancy and the activation energy for divacancy self-diffusion to give good agreement with experiment. The agreement between experiment and calculation suggests that diffusion in rare-gas solids may be primarily via divacancies at high temperatures.

It was shown that it is not implausible that the relatively scarce divacancies move sufficiently rapidly compared to single vacancies to be responsible for the observed self-diffusion in solid rare gases.

ACKNOWLEDGMENTS

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Quantum Dielectric Theory of Electronegativity in Covalent Systems. I. Electronic Dielectric Constant*

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Electronegativity difference is redefined as a scaling parameter, generalizing the concept of valence difference. A procedure for its evaluation is developed in terms of the dielectric constants of diatomic crystals. A simple alternative to the Clausius-Mossotti theory of the electronic dielectric constant is developed in terms of this concept. The effect of *d*-electron states and of hydrostatic pressure are discussed, and procedures for their approximate evaluation are developed. The treatment is extended to 68 crystals of the diamond, zinc-blende, wurtzite, and rock-salt types; values of the electronegativity parameter are tabulated for these crystals.

I. INTRODUCTION

THE concept of the relative electronegativity of the elements is an old one which arose in connection with oxidation-reduction potentials in the eighteenth century. Thomson appears to have been first to discuss a microscopic dielectric model.[1] With the advent of quantum mechanics, interest in dielectric models of electronegativity seems to have waned, apparently because of difficulties with extensive numerical solutions to Schrödinger's equation, which a theory of dielectric functions seemed to require.

Attempts have frequently been made to place the concept on firm ground either semiempirically or through one-electron quantum theory formulated in terms of atomic orbitals.[2] Pauling[3] defined electronegativity as "the power of an atom in a molecule to attract electrons to itself." But his, and all other, efforts to render this definition more precise have met with only partial success. It may be correct to say that many currently regard the concept as qualitatively useful but not refinable quantitatively.

Here we reexamine the concept of electronegativity in the light of modern theory of the dielectric properties of crystals. We use a phase-space model that is consistent with the results of many of those extensive numerical calculations that were unmanageable before the widespread availability of computers.

Previous discussions of electronegativity have centered primarily on the binding or cohesive energies of atoms or molecules. Thus, Mulliken[4] defined atomic electronegativity as the average of the ionization potential and the electron affinity, $X_{m,\alpha}=\frac{1}{2}(I_\alpha+E_\alpha)$, and defined the relative electronegativity difference of two atoms α and β as

$$X_{\alpha\beta}=X_\alpha-X_\beta. \tag{1.1}$$

The relation (1.1) is necessary if $X_{\alpha\beta}$ is to be transitive,

$$X_{\alpha\beta}+X_{\beta\gamma}=X_{\alpha\gamma}. \tag{1.2}$$

Pauling observed that the energy $D_{\alpha\beta}$ binding the atoms α and β in the system α-β is generally larger than the mean of the energies $D_{\alpha\alpha}$ and $D_{\beta\beta}$ binding the systems α-α and β-β. Thus he defined the "extraionic energy" Δ:

$$\Delta=D_{\alpha\beta}-\tfrac{1}{2}(D_{\alpha\alpha}+D_{\beta\beta}), \tag{1.3}$$

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[1] J. J. Thomson, Phil. Mag. **27**, 757 (1914), especially p. 769; also, G. N. Lewis, J. Am. Chem. Soc. **38**, 762 (1916).

[2] The standard review article remains H. O. Pritchard and H. A. Skinner, Chem. Rev. **55**, 745 (1955).

[3] L. Pauling, J. Am. Chem. Soc. **54**, 3570 (1932).

[4] R. S. Mulliken, J. Chem. Phys. **2**, 782 (1934).

and proposed a table of atomic electronegativities, $X_{p,\alpha}$, such as would yield the relationship

$$|X_\alpha - X_\beta| = 0.208\Delta^{1/2}, \tag{1.4}$$

where Δ is in kilocalories per mole.

Neither of the above definitions in terms of ground state energies is wholly satisfactory. With Mulliken's atomic binding definition, we known that the addition or removal of an electron to an open-shelled atom alters the energy of the remaining electrons appreciably. In large molecules or crystals this rearrangement energy is usually much less (Koopmans's theorem[5]). Pauling's definition in terms of molecular binding energies does not suffer from this defect. However, it is crude in two senses: (1) It defines electronegativities independently of the coordination number (valence environment) of the atom; and (2) it does not distinguish between contributions to the cohesive energy of *s-p* hybridized electrons and polarized *d* electrons. The latter may play a greater role in cohesive energies than in other physical properties and their effect is not in general transitive. Indeed, if α and γ contain *d* states of low excitation or binding energy but β does not, then one would not expect (1.2) to hold owing to the α-γ *d* resonance.

These comments are meant to illustrate but not exhaust all the difficulties inherent in defining an electronegativity scale. The author proposes to minimize them without recourse to accurate, quantum-mechanical, many-electron calculations by regarding electronegativity as a scaling parameter which generalizes the concept of valence difference.

Thus we being by considering some observable $\mathcal{O}_n$ and determine empirically its dependence on the valence difference $Z_\alpha - Z_\beta$ of atoms α and β when these belong to the *same* row of the periodic table and both are in definite states of hybridization [e.g., we might find $\mathcal{O}_n$ proportional to $(Z_\alpha - Z_\beta)^2$]. Knowing this functional dependence and its variation from one row to the next for $Z_\alpha = Z_\beta$, we attempt to predict the value of $\mathcal{O}_n(\alpha,\beta)$ in terms of $X_{\alpha\beta}$ when α and β have different valence *and* belong to different rows of the periodic table. To do this we adopt a quantum-mechanical model which approximates the real situation. Thus electronegativity represents a quantum-mechanical scaling parameter which enables one to treat simultaneous size and valence differences knowing only the effects of valence and size differences separately.

Initially we consider the static electronic dielectric constant of crystals of the diamond, zinc-blende, and wurtzite, and rocksalt type composed of elements from the first four rows of the periodic table. All such crystals have a full eight-electron *s-p* valence band. We do not treat any crystals containing transition elements. The author believes that the static electronic dielectric constant represents a useful weighted average of many polarization processes that may occur. In latter papers, the present scaling approach is applied to individual transition energies of definite symmetries as well as to cohesive energies of molecules and crystals.

To treat the electronic dielectric constant, we adopt a simple one-gap model for the electronic band structure. For diamond, zinc-blende, and wurtzite crystals, Phillips[6] has suggested that such a model may be used and the average gap separated into homopolar and heteropolar parts, E_h and C. The average homopolar energy gap E_h is taken to be a function of nearest-neighbor distance d only. Phillips[6] also suggested that the average heteropolar energy gap C is to be given by a simple expression, and that $C_{\alpha\beta}$ is a suitable measure of the electronegativity difference between elements α and β.

Figuratively speaking, E_h and C measure the average energy gaps due to covalent and ionic effects. The total average energy gap E_g is given by

$$E_g^2 = E_h^2 + C^2. \tag{1.5}$$

Phillips also suggested that one can define the fractions of ionic and covalent character, f_i and f_c, by

$$f_i = C^2/E_g^2, \quad f_c = E_h^2/E_g^2. \tag{1.6}$$

We review the basis of Phillips's model in Sec. II. Modifications of the model must be made to take into account the effect of *d*-core states for atoms from rows 3 and 4. These modifications are discussed in Sec. III. A critical analysis of the model for all tetrahedrally coordinated crystals is given in Sec. IV, where it is shown that Phillips's model (with *d*-core corrections included) establishes C to about 7% accuracy.

A characteristic feature of Phillips's theory is that the crystal structure factor nowhere appears explicitly. Therefore in Sec. V the discussion is extended to include crystals belonging to the NaCl structure. Although it has been customary to treat these by the Born closed-shell model, from a dielectric viewpoint this would be justifiable only if almost all the optical oscillator strength were exhausted by excitons. Actually, even in the alkali halides, excitons represent less than 10% of the total oscillator strength.[7] Thus although exciton effect are neglected in Phillips's model, it was thought that it should apply to NaCl-type crystals with only slightly less success than for conventional covalent crystals. This proves to be the case after allowance is made for the effects of ionicity on lattice constant.

All the formulas in this work are general and hold for arbitrary lattice constant, equilibrium or compressed. Indeed the model used here constitutes a universal theory for all crystals of the diamond, zinc-blende, wurtzite, and NaCl types, with each described by two parameters E_h and C. It predicts the derivative of the static electronic dielectric constant with hydrostatic

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[5] T. Koopmans, Physica **1**, 104 (1933).

[6] J. C. Phillips, Phys. Rev. Letters **20**, 550 (1968); *Covalent Bonding in Molecules and Solids* (University of Chicago Press, Chicago, to be published).

[7] H. R. Phillip and H. Ehrenreich, Phys. Rev. **131**, 2016 (1963).

pressure. Hitherto this derivative has usually been discussed in terms of the Clausius-Mossotti model, which is only able to account for the results, in even the most ionic crystals, at the expense of introducing a new parameter for each ion.

Within the limits of available experimental data, our model gives good results for the 68 crystals considered. The fraction of ionic character, f_i, of these crystals ranges from 0.00 to 0.96.

II. ONE-GAP MODEL: BOTH ATOMS BELONG TO SAME ROW

Several models have been proposed to describe the dielectric properties of insulators. One may formulate a general theory[8] of the dielectric response of a crystal to an external electric field of wave vector $\mathbf{q}$ (modulo a reciprocal lattice vector $\mathbf{G}$) and frequency ω in terms of a complex, nonlocal dielectric tensor $\boldsymbol{\varepsilon}_1(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}';\omega)+i\boldsymbol{\varepsilon}_2(\mathbf{q}+\mathbf{G},\mathbf{q}+\mathbf{G}';\omega)$. Within the random-phase approximation this theory reduces to the Hartree, or one-electron, model of energy levels and oscillator strengths.[9]

In practice even the latter theory requires elaborate computations, and it has been developed in detail only for a few semiconductors such as Si and Ge. At the opposite extreme one has the classical Clausius-Mossotti model with polarizable point ions. The dielectric constant of a strongly ionic crystal is calculated using local-field corrections and constant-ionic polarizabilities. These polarizabilities are treated as parameters to be fitted to experiment. Because no allowance is made for the effects of covalency, the theory is satisfactory only for alkali halides. For example, it has been found[10] that the value obtained for a given nonhalide ion is not at all constant from one compound to another and there does not seem to be any clear pattern to the variations. (The value of ionic polarizability for O^{--}, apparently a bad case because of covalent effects, varies from 0.5 to 3.2 Å^3).

We begin our analysis of the dielectric properties of covalent systems with Fig. 1, where it is seen that the reciprocal of the electric susceptibility of the diamond, zinc-blende, and wurtzite crystals made up of atoms from the same row of the periodic table is linear in the square of the valence difference ΔZ and that the constant of proportionality decreases with increasing row number γ. We may write this relationship in the form

$$[\epsilon_1(0)-1]^{-1}=\alpha_\gamma+\beta_\gamma(\Delta Z)^2. \qquad (2.1)$$

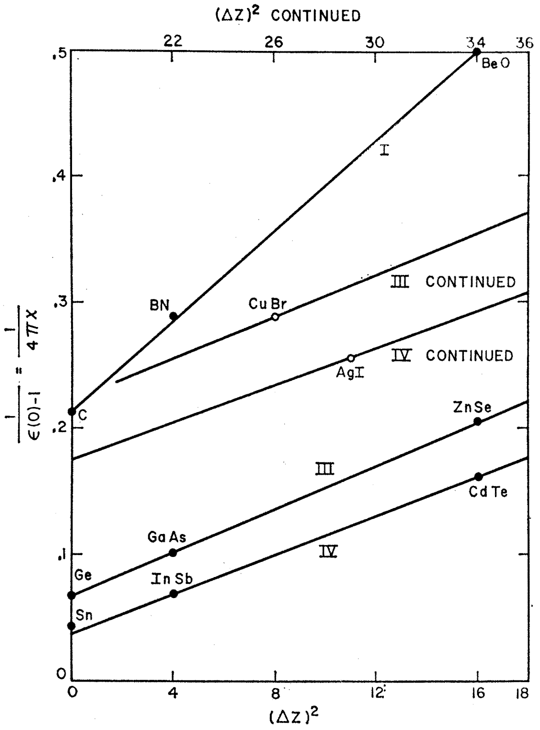

FIG. 1. Inverse of the electronic dielectric constant minus one, $1/(\epsilon_1(0)-1)$, versus the square of the valence difference, $(\Delta Z)^2$, for diamond and zinc-blende-type crystals for which both elements in the compound belong to the same row of the periodic table. Data are available for at least three such crystals for rows I, III, and IV. Rows III and IV have been continued by shifting the line obtained to the left. The points plotted for CuBr and AgI (the open circles) are the intercepts of the continuation of the lines for rows III and IV with the experimental values of $1/(\epsilon_1(0)-1)$. These points indicate "effective values" of $(\Delta Z)^2$ of about 26 and 29, respectively.

The quantum model that is adopted here is the isotropic two-band model of a covalent solid. (This model has recently been widely used and discussed.[11,12]) We assume that the unperturbed electronic system is a free-electron gas and apply a three-dimensional generalization of the results of one-dimensional perturbation theory. It has been shown[12] for the case of the wave-vector-dependent dielectric function of Si that this approximate and greatly simplified approach gives results in good agreement with rigorous band-structure calculations.

Recall that in one dimension a small potential with only one nonzero Fourier component V_G will mix only states which have wave numbers differing by G and will have small effects except when there is near degeneracy of the unperturbed energy of the states that are mixed. Near such a degeneracy one may solve the 2×2 secular equation for the coefficients of the unperturbed states, $\psi^0(k)$ and $\psi^0(k-G)$, which are mixed and find that the energies split into bands with a single energy gap $E_g=2|V_G|$ according to

$$E^{\pm}(k)=\tfrac{1}{2}\{E_k^0+E_{k-G}^0 \pm[(E_k^0-E_{k-G}^0)^2+4V_G^2]^{1/2}\}, \qquad (2.2)$$

where $E_k^0=\hbar^2k^2/2m$. If, by analogy with the diatomic crystal, the perturbing potential separates into parts

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[8] P. Nozieres and D. Pines, Phys. Rev. **109**, 762 (1958); Nuovo Cimento **9**, 470 (1958).

[9] H. Ehrenreich and M. H. Cohen, Phys. Rev. **115**, 786 (1959).

[10] J. R. Tessman, A. H. Kahn, and W. Schockley, Phys. Rev. **92**, 890 (1954).

[11] D. Penn, Phys. Rev. **128**, 2093 (1962).

[12] H. Nara, J. Phys. Soc. Japan **20**, 778 (1965).

centered about different points, i.e., if we have two atoms per one-dimensional unit cell, then it is convenient to place the coordinate origin midway between them and divide the Fourier transform, which is now complex, into symmetric and antisymmetric parts. That is, if

$$V(x)=V_1(|x_1-x|)+V_2(|x_2-x|)$$
$$=V_1(|x-\tau|)+V_2(|x+\tau|),\quad(2.3)$$

where $x_{1,2}$ is the position of atom 1, 2 (in the unit cell) and τ is half the interatomic distance and is also the coordinate of atom 1 with respect to the above choice of origin, then

$$V(x)=\sum_G(S_G^sV_G^s+iS_G^aV_G^a)e^{iGx},\quad(2.4)$$

where

$$V_G^s=\tfrac{1}{2}(V_{G1}+V_{G2}),\quad V_G^a=\tfrac{1}{2}(V_{G1}-V_{G2}),\quad(2.5\text{a})$$

$$S_G^s=\cos G\tau,\qquad S_G^a=\sin G\tau,\quad(2.5\text{b})$$

$V_{G\,1,2}=(2/l)\int V_{1,2}(x)e^{-iGx}dx$ is the Fourier transform of the potential $V_{1,2}$, and l is the length of the unit cell. With this complex Fourier potential component, $V_G=S_G^sV_G^s+iS_G^aV_G^a$, the solution of the 2×2 secular equation goes through as before. The quantity $V_GV_G^*$ replaces V_G^2 in (2.2) and the single energy gap is seprable into a symmetric, homopolar part and an antisymmetric, heteropolar part[13]:

$$E_{g,G}^2=E_{h,G}^2+C_G^2=(2S_G^sV_G^2)^2+(2S_G^aV_G^a)^2.\quad(2.6)$$

Of course, in a real three-dimensional solid the band structure remains, but there are many V_G's and significant mixing of states with wave vectors **G** in several directions may occur. The traditional approach is to work with the complicated, actual Brillouin-zone geometry. In the present model we concern ourselves only with the average gap between the valence and conduction bands and represent the average effect of all the V_G's by one complex parameter $\mathcal{E}_g=E_h+iC$ such that the effective valence-conduction band gap E_g is given by

$$E_g^2=\mathcal{E}_g\mathcal{E}_g^*=E_h^2+C^2.\quad(2.7)$$

Penn[9] has evaluated the wave-vector-dependent dielectric function $\epsilon(\mathbf{q})$ for this model. The static limit of his expression is

$$\epsilon(0)=1+[(\hbar\omega_p)^2/E_g^2](1-B+\tfrac{1}{3}B^2)$$
$$=1+(\hbar\omega_p)^2A/(E_h^2+C^2),\quad(2.8)$$

where $B=E_g/4E_f$, $A=1-B+\frac{1}{3}B^2$, E_f is the Fermi energy, and ω_p is the free-electron-plasma frequency $\omega_p=(4\pi e^2N/m)^{1/2}$ where we take $N=4$ electrons per atomic volume. Comparing (2.8) with the empirically observed relationship (2.1) we find

$$\alpha_\gamma\equiv\frac{1}{\epsilon_\gamma(0)-1}=\frac{E_g^2}{(\hbar\omega_p)^2A},\quad(2.9)$$

where $\epsilon_\gamma(0)$ is the static electronic dielectric constant of the diamond-type crystal of row γ. Since $C=0$ for the diamond-type crystals, the E_g of (2.8) is identically equal to E_h, i.e., $E_g\equiv E_h$ for diamond-type crystals. Thus we may solve (2.9) to find E_h in terms of the known quantities α_γ [or $\epsilon(0)$], ω_p, and E_f. We now observe that the nearest-neighbor distance r, or, equivalently, the lattice constant, of the crystals formed of pairs of atoms from the same row is almost constant. Thus ω_p and E_f are constant and Fig. 1 and (2.1) imply that E_h is constant for these crystals. We define $E_{h,\gamma}=E_h$, the quantity E_h being determined by (2.9) for each row γ. (Indeed, Cohen and Bergstresser[13] achieved very satisfactory results for band-structure calculations by assuming the symmetric part of the potential is constant for all pairs of atoms belonging to the same row.)

Returning to the comparison of (2.1) and (2.8), we also find

$$\beta_\gamma(\Delta Z)^2=\frac{C^2}{E_{h,\gamma}^2}\Bigg/\frac{(\hbar\omega_p)^2}{E_{h,\gamma}^2}A=\frac{C^2\alpha_\gamma}{E_{h,\gamma}^2},\quad(2.10)$$

so that

$$C=(\beta_\gamma/\alpha_\gamma)^{1/2}E_{h,\gamma}\Delta Z.\quad(2.11)$$

We see from (2.11) that C is a measure of the electronegativity or valence difference between the two atoms when they belong to the same row of the periodic table. Before we generalize the discussion to include atoms from different rows, we should discuss the variation of $E_{h,\gamma}$ with γ. As we shall see, this variation is strongly correlated with the appearance of d shells in the atomic cores.

III. EFFECT OF *d* STATES IN ATOMIC CORES

The form of Eq. (2.8) is common in the elementary discussion of the optical properties of semiconductors. A standard result of such studies[14] is

$$\epsilon_1(\omega)=1+\omega_p^2\sum_j{}'\frac{f_j}{\omega_j^2-\omega^2},\quad(3.1\text{a})$$

where

$$\epsilon_1(0)=1+\sum_j{}'f_j\frac{\omega_p^2}{\omega_j^2},\quad(3.1\text{b})$$

where $\omega_j=(s_j-s_0)/\hbar$, s_0 is the energy of the ground state (here the average valence state), s_j is the energy of the jth *excited or core* state, f_j is the oscillator strength of the transition, and $\sum'$ means that the sum is taken only over the higher, unoccupied states. In Penn's model one neglects the effect of the core electrons and

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[13] M. L. Cohen and T. K. Bergstresser [Phys. Rev. **141**, 789 (1966)] discuss this in their analysis of the electronic structure of 14 diamond and zinc-blende semiconductors.

[14] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, London, 1964), Sec. 8.2.

takes N to be the density of valence electrons, i.e., four per atomic volume or eight per unit cell, when computing ω_p. This is equivalent to assuming that the well-known f-sum rule will give

$$\sum_j{}'' f_j = 4, \tag{3.2a}$$

where $\sum''$ means the sum is taken over the *conduction-band states* and one does not go to such high energies that core states are excited. This approximation works well for diamond and Si where the core states are well separated from the valence band (by some 80 eV in Si). However, it leads to difficulties when core d states are present.[15] The trouble is[16,17] that the f sum rule is proved for a sum over *all* other states, i.e., including those below s_0 as well as above, and the core states do contribute terms. These terms are negative because the energy difference is negative. There is a corresponding increase in the sum of the f's connecting the valence and conduction states. Thus when the atomic core contains d states one may have

$$\sum_j{}'' f_j > 4, \tag{3.2b}$$

or, equivalently, the effective plasma frequency is greater than that found by taking N to be four electrons per atomic volume.

For a rigorous treatment one must consider the total electron density and the total f sum. A general result[18] of the f-sum rule is

$$\int_0^\infty \omega\epsilon_2(\omega)d\omega = \tfrac{1}{2}\pi\Omega_p^2, \tag{3.3}$$

where Ω_p is the plasma frequency as calculated from the total electron density.[19] At least in principle, this allows one to define empirically an effective number of free valence electrons per atom, n_{eff} in the notation of Ref. 17, for use in connection with the simple theory discussed earlier, on which our model is based. We define $n_{\text{eff}}(\omega_0)$ by

$$\frac{2\pi^2 N_a e^2}{m} n_{\text{eff}}(\omega_0) = \int_0^{\omega_0} \omega\epsilon_2(\omega)d\omega, \tag{3.4}$$

where N_a is the atomic density. The quantity $n_{\text{eff}}(\omega_0)$ is a measure of the fraction of available oscillator strength which has been exhausted by electronic transitions of energy up to $\hbar\omega_0$. If there is a frequency ω_1 which is high enough that when used in (3.4) the valence to conduction-band oscillator strength is exhausted but low enough that the core excitations have not yet begun to affect ϵ_2, then we may define $N_{\text{eff}} = n_{\text{eff}}(\omega_1)$. For the reader's convenience we reproduce in Fig. 2 values of $n_{\text{eff}}(\omega_0)$ for several semiconductors.[17] We see that for Si, $n_{\text{eff}}(\omega_0)$ saturates at a value of 4, as expected, around 20 eV. When $\hbar\omega_0$ reaches the core excitations energy, there should be a knee in the n_{eff} curve. This is seen at about 18 eV in the InSb curve, when the excitation of d-core states begins. [Note that $n_{\text{eff}}(\omega_0)$ is well above 4 at this point.] One might extrapolate the $n_{\text{eff}}(\omega_0)$ curve beyond the knee to obtain an estimate of the value for the N_{eff} that would be found were it not for these excitations, i.e., the value of the f sum connecting the valence and conduction states.

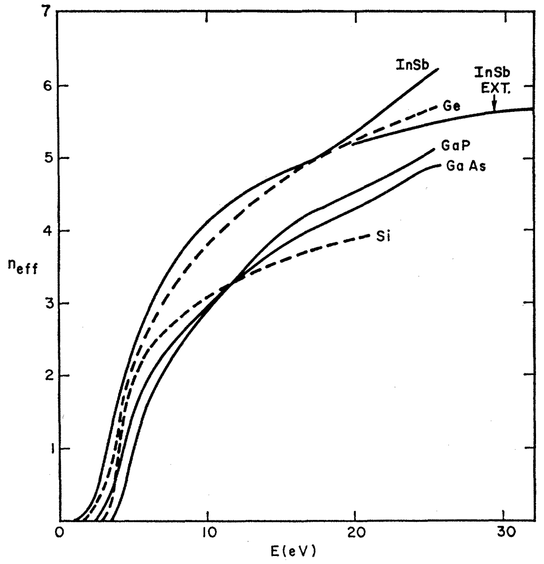

FIG. 2. Experimental $n_{\text{eff}}(\omega)$ versus energy $\hbar\omega$ for several semiconductors. Except for the extrapolation to the right-hand limit of the curve for InSb below the knee around 18 eV, this figure has been borrowed from Ref. 17, where it is labeled Fig. 5.

Recall that the Kramers-Kronig relation for $\epsilon_1(0)$ is

$$\epsilon_1(0) = 1 + \frac{2}{\pi}\int_0^\infty \frac{\epsilon_2(\omega)}{\omega} d\omega. \tag{3.5}$$

Because the integrand in (3.5) is ϵ_2/ω instead of $\omega\epsilon_2$ as in the equation for $n_{\text{eff}}(\omega_0)$ [Eq. (3.4)], the core excitations which cause the increase in $n_{\text{eff}}(\omega_0)$ above the knee do not contribute substantially to the value of $\epsilon_1(0)$. Thus the dominant effect of the d states on $\epsilon_1(0)$ is described by the increase over 4 of N_{eff}, as defined above.

In practice determination of N_{eff} by extrapolation above the knee is difficult because it requires the measurement of the absolute value of the reflectance. Furthermore, at high energies the surface condition of the crystal is critical; the presence of an oxide layer will introduce a large error because of the strong absorption of oxide compounds in the range 10–20 eV. Despite these

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[15] These are about 30 eV below the valence band in Ge and Sn, 20 eV in Ga and In, and 10 eV in Zn and Cd.

[16] F. Seitz, *The Modern Theory of Solids* (McGraw-Hill Book Co. New York, 1940), p. 644.

[17] H. R. Phillip and H. Ehrenreich, Phys. Rev. **129**, 1550 (1963).

[18] P. Nozieres and D. Pines, Phys. Rev. **113**, 1254 (1959).

[19] The lower limit of the integral in (3.3) must be taken to be larger than the reststrahlung frequency to avoid the effects of lattice vibrations.

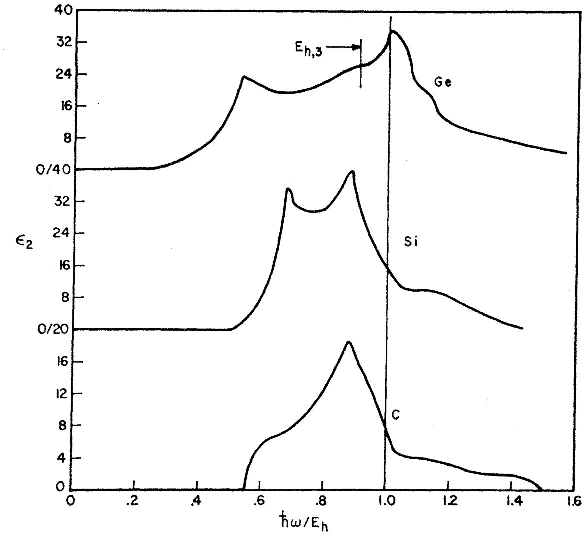

FIG. 3. Imaginary part of dielectric function $\epsilon_2(\omega)$ versus energy in units of the effective homopolar potential E_h as defined by Eq. (3.6). In this method the value of E_h for Ge is found by extrapolating the value of the Penn-model energy gap for diamond and Si as a function of nearest-neighbor distance. The value of $E_{h,3}$, the Penn-model energy gap, for Ge is also indicated.

objections, we conclude from Fig. 2 (by comparing Ge with GaAs) that N_{eff} is not the same for all crystals made up of pairs of elements belonging to the same row of the periodic table; i.e., N_{eff} is not independent of ΔZ.

Now consider another aspect of the effect of the *d* core states on the excitation spectrum. Take Ge as an example. Between the $3s^2 3p^6$ core electrons and the $4s^2 4p^2$ valence electrons there is a region of large $3d$ charge density. In this region the central potential seen by the valence electrons is quite large—of the order of the free-atom *d*-electron binding energy, i.e., 50–100 eV. This potential is much larger than one would find outside the $2s^2 2p^6$ core in Si. As a result, the binding energy of a $4s$ electron in Ge^{+3} exceeds that of a $4p$ electron by 28.3%, while in Si the difference is only 24.4%. This difference of 3.9% is 1.8 eV.

To compare spectra proceed as follows: Write for diamond and Si

$$E_h \propto r^{-s}, \tag{3.6}$$

where r is the nearest-neighbor distance. From the observed values $\epsilon_1(0) = 5.7$ and 12.0 for diamond and Si, respectively, one obtains the indicial value $s = 2.48$.[20] We then use (3.6) to extrapolate[6] to obtain an estimate of the value of E_h for Ge in the absence of *d*-state effects. We use these values of E_h to plot $\epsilon_2(\omega)$ versus the dimensionless variable $\hbar\omega/E_h$ for the three crystals (Fig. 3).

On this scale the spectra of diamond and Si are rather similar; they begin about 0.5, rise until about 0.7, and then have a large peak about 0.9. The largest peak in Ge is found at E_h and appears more spread out; the low-energy region contains a second peak and has shifted down to about 0.5. Detailed band calculations[21] have shown that the low-energy region is associated with bonding $p \rightarrow$ antibonding s transitions in all three crystals. The shift of this region between Si and Ge is about 1.1 eV. (The low-energy peak in Ge is due to Λ_3-Λ_1 transitions which have shifted by about 1.7 eV between Si and Ge according to alloy studies.[21])

The value of $\epsilon_1(0)$ for Ge in the absence of *d*-state effects, which we estimate by our approximations, is about 13 as compared with the observed values of 12.0 for Si and 16.0 for Ge. (Note that the lattice constant of Ge is only 4% larger than that of Si.) Using the Kramers-Kronig transform [Eq. (3.5)], one can verify that the shift of the low-energy region accounts semi-quantitatively for the increase in $\epsilon_1(0)$. The s-bonding$\rightarrow$ p-antibonding transition energies, which are much larger, are increased by the *d* states. They contribute to the increase in n_{eff} [see Eq. (3.4)]. They probably also account for the spreading of the large peak in Ge relative to Si and for its shift to somewhat higher energy.

Thus the effect of the *d*-state core, which is well localized in real space, is to increase $\epsilon_1(0)$ and n_{eff} above the values predicted by (2.8) and (3.6). One can correct for this in several ways. One might insist on taking N equal to four valence electrons per atom and reduce E_h to fit $E_{h,\gamma}$. We prefer to renormalize N (i.e., use an N_{eff}) and retain E_h as extrapolated, because it seems to yield more consistent results when we deal with atoms from different rows, to lead to better electronegativity scaling factors C, and to lead to better comparisons between spectra. (Note the position of $E_{h,3}$ in Fig. 3.) Moreover, the *d*-states do not seem to affect certain phenomena arising outside the core.[20] Thus we define a parameter D by

$$D = \tfrac{1}{4} N_{\text{eff}}. \tag{3.7}$$

We continue to compute and quote the plasma frequency assuming four free electrons per atomic volume and use (3.6). In cases where the *d*-state effects are relevant, such as $\epsilon_1(0)$, we multiply ω_p by $D^{1/2}$. Thus (2.8) becomes

$$\epsilon_1(0) = 1 + (\hbar\omega_p)^2 DA/(E_h^2 + C^2). \tag{2.8'}$$

We do not try to infer N_{eff} and thus D from curves such as are found in Fig. 2, because of the experimental difficulties mentioned above. We take D equal to 1.0 for diamond and Si and find [Eq. (2.8′)] $D = 1.25$ and 1.46 for Ge and α-tin by using the extrapolated values, E_h, the observed values of $\epsilon_1(0)$, and the fact that $C = 0$ due to symmetry.

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[20] K. M. Guggenheimer [Proc. Phys. Soc. (London) **58**, 456 (1946)] has found that the force constants k for bond stretching vibrations of 100 diatomic molecules depends only on the valence numbers and $r^{-2.46}$ within a mean error of 1.64%, and irrespective of the presence of *d* states.

[21] J. C. Phillips, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1966), Vol. **18**; also, E. Schmidt, Phys. Status Solidi **27**, 57 (1968).

We now consider what value D will take when ΔZ, and thus C, is not zero. In our calculations we found empirically a general formula for D [Eq. (3.11)] which yields values for C that the author believes are accurate on the basis of evidence to be presented. Because N_{eff} is experimentally observable, this formula may also be tested directly. A plausibility argument is now offered in favor of the author's empirical formula.

As was discussed above, D increases above 1 (N_{eff} increases above 4) because of the contribution of negative terms in the f sum due to oscillator strength between the d core around the ions and the valence band throughout the crystal. Therefore, let us assume that the effect of the d-core at atom α will be proportional to the product of the average valence charge density around α, which we denote by φ_α, and some parameter Ψ_α, which is characteristic of the d-core at α. We also assume that, because the effect is a cooperative one between the two types of atoms present, the total effect will be multiplicative rather than additive. Thus we assume that for elements α and β

$$D(\alpha,\beta)=\varphi_\alpha\Psi_\alpha\varphi_\beta\Psi_\beta. \tag{3.8}$$

Ψ_α should be roughly proportional to the probability that an s electron be found within the d-core and this should be roughly proportional to $1/Z$ because of the decrease in the radius of the core. If we make use of the relation of Ψ_α to the increase in s-state over p-state binding energy we can substantiate this conjecture. Let us define Ψ_α' to be the percent difference of s-state to p-state binding energy for the hydrogenic ion of element α. Consider the percent difference in the values of Ψ_α' for the elements of the same valence of rows 2 and 3 of the periodic table[22] which we denote Ψ_Z'. This is shown in Table I.

Assuming that the Ψ_Z''s are roughly proportional to the Ψ_α''s for row 3, we conclude that indeed $\Psi_\alpha'\propto 1/Z$.

If there were no charge transfer the valence density would be proportional to Z, i.e., $\varphi_\alpha\propto Z_\alpha$, and we would find

$$D\propto(Z_\alpha)(1/Z_\alpha)(Z_\beta)(1/Z_\beta)=\text{const}.$$

TABLE I. Effect of the presence of a d core on the s to p energy-level splittings of free hydrogenic ions. Ψ_α' is the difference in energy between the lowest p level and the ground-state s level for the hydrogenic ion of element α expressed as a percentage of the binding energy. Ψ_Z' is the difference in Ψ_α' between the third-row and the second-row elements with valence Z. The last row shows the product of Ψ_Z' and Z, which is approximately constant. Thus Ψ_α' is roughly proportional to $1/Z$ as proposed.

	Mg	Al	Si	P	S	Cl
ψ_α'	41.67%	30.55%	24.35%	20.34%	17.52%	15.39%
	Zn	Ga	Ge	As	Se	Br
ψ_α'	50.29%	35.70%	28.29%	23.81%	20.64%	···
ψ_Z'	8.62%	5.15%	3.94%	3.47%	3.12%	···
$Z\psi_\alpha'$	17.24%	15.45%	15.76%	17.39%	18.72%	···

TABLE II. Parameters used in calculations presented. Δ and δ are the parameters used with Eq. (3.11) to calculate D, the effect of the d-core levels on the effective plasma frequency. r is the covalent radius introduced in Sec. IV, which is equal to half the nearest-neighbor distance in the diamond-type crystal of the group-IV element in the row listed.

row	Δ	δ	r_α/a_0
I	1.0	1.0	1.45929
II	1.0	1.0	2.22178
III	1.12	1.0025	2.31460
IV	1.21	1.005	2.65576

The actual charge transfer should be proportional to ΔZ. Suppose $Z_\beta>Z_\alpha$. Then, to within a constant of proportionality,

$$\varphi_\alpha=Z_\alpha-\eta\Delta Z\,,\quad \varphi_\beta=Z_\beta+\eta\Delta Z\,, \tag{3.9}$$

where η is a parameter characteristic of the rows to which α and β belong. Thus

$$\begin{aligned}D&\propto(Z_\alpha-\eta\Delta Z)(1/Z_\alpha)(Z_\beta+\eta\Delta Z)/Z_\beta\\&=1-\eta\Delta Z^2/Z_\alpha Z_\beta-\eta^2\Delta Z^2/Z_\alpha Z_\beta\\&=1-\tfrac{1}{16}(\eta+\eta^2)\Delta Z^2\\&\qquad+[(\eta+\eta^2)/16\times 64)]\Delta Z^4+\cdots.\end{aligned} \tag{3.10}$$

Therefore, the lowest-order change in D is a decrease proportional to $(\Delta Z)^2$. Physically this comes about because more electrons are localized near the ion of higher valence, where, because the d-core states are more tightly bound, there is less valence–d-core hybridization. The general prescription for D we have used is

$$D(\alpha,\beta)=\Delta_\alpha\Delta_\beta-(\delta_\alpha\delta_\beta-1)(Z_\alpha-Z_\beta)^2\,, \tag{3.11}$$

where Δ and δ are parameters for the rows of the periodic table to which α and β belong. [Thus (3.11) holds also in the case where α and β do not belong to the same row, which is discussed in Sec. IV.] Because there are no d core electrons, $\Delta=\delta=1$ for rows 1 and 2. For rows 3 and 4, Δ is given by $D_{\text{Ge}}^{1/2}$ and $D_{\text{Sn}}^{1/2}$. We have chosen the δ's for rows 3 and 4 to given a good fit to the experimental data. (See Sec. IV.) Table II contains a summary of all parameters used. Table III presents our results as calculated from (2.8′) using our calculation of C which we now present.

IV. GENERAL ZINC-BLENDE AND WURTZITE CRYSTALS; ATOMS FROM DIFFERENT ROWS

As we noted in Sec. II from Fig. 1, the average antisymmetric potential, the C in (2.7), is proportional to $|Z_\alpha-Z_\beta|$ when the atoms α and β belong to the same same row of the periodic table. Because C has the dimensions of energy, one might guess that

$$C_{\alpha\beta}\propto(Z_\alpha/r_\alpha-Z_\beta/r_\beta). \tag{4.1}$$

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[22] C. E. Moore, in *Atomic Energy Levels*, Natl. Bur. Std. (U.S.) Circ. No. 467 (U. S. Government Printing Office, Washington, D. C., 1949).

(Gordy[23] noted that an expression of this form would yield Pauling's electronegativity table.) Previously,[2,23] the single-bond covalent radii of the atoms α and β have been used for the r_α's in (4.1). We have defined a new covalent radius which may be more appropriate to solids. Let $d_{\alpha,\gamma}$ be the nearest-neighbor distance in the diamond-type crystal of the group-IV element of the same row, γ, as element α. In crystals with an average of four valence electrons per atom this length $d_{\alpha,\gamma}$ is taken to be a prototypical covalent bonding length for row γ and, as a first approximation (to be refined in a moment), we assume $2r_\alpha = d_{\alpha,\gamma}$. This assumption implies that the nearest-neighbor distance, or, equivalently, the lattice constant, is the same for all crystals in which the two elements involved belong to the same row. We have already noted that this is a good approximation. (In BeO the lattice constant is 7% larger than in diamond; in all other cases the variation is less than 2%.) The assumption would also imply that the nearest-neighbor distance in a crystal containing atoms from different rows would be the mean of the nearest-neighbor distances of the group-IV elements of the rows involved and thus, for a given pair of rows, this distance would also be constant. Reference to the lattice constants in Table III will show that while there is somewhat more variation when atoms are from different rows, both predictions are basically correct. It should be noted that the crystals showing a variation larger than 4% (CuF, BeS, BAs, BeSe, BeTe, and MgTe) are all rather unstable, so much so that the author has been able to find experimental values of $\epsilon_1(0)$ only for BeSe and MgTe, and these are tentative values. Thus crystals that vary greatly from the above prediction do not enter the present discussion. Indeed

TABLE III. Crystal data and calculated parameters. The experimental dielectric constants are listed according to method of observation, either by refraction (refract.) or by reststrahlen (rest.) measurements. The value we believe is most reliable is in italics. The column labeled "Var." gives the variation of the lattice constant from the predicted value.

Crystal	Row Nos.	Type	Lattice[a] const. (a_0)	Expt $\epsilon(0)$ (refract.)	Expt $\epsilon(0)$ (rest.)	b	C (eV)	E_h (eV)	N_{eff}	Var. (%)
C	1-1	diamond	6.740	5.7^{n}			0.0	13.6	4.0	
BN	1-1	zinc-blende	6.831		4.5^{j}	1.55	7.8	13.1	4.0	+1.4
BeO	1-1	wurtzite	7.195	3.0^{b}		1.55	14.1	11.5	4.0	+6.8
LiF	1-1	NaCl	7.592	1.9^{b}	1.9^{d}	1.90	23.0	7.0	4.0	+12.6
Si	2-2	diamond	10.263	*12.0*^{n}	11.7^{c}		0.0	4.8	4.0	
AlP	2-2	zinc-blende	10.301	8.5^{r}		1.50^{r}	3.1^{r}	4.7	4.0	+0.4
MgS	2-2	NaCl	9.833	5.1^{b}		1.50	7.1	3.7	4.0	−4.2
NaCl	2-2	NaCl	10.639	2.3^{b}	2.3^{d}	2.00	11.8	3.1	4.0	+3.7
Ge	3-3	diamond	10.691	*16.0*^{n}	15.9^{c}		0.0	4.3	5.0	
GaAs	3-3	zinc blende	10.684		11.3^{c}, *10.9*^{d,f}	1.50	2.9	4.3	4.9	−0.1
ZnSe	3-3	zinc blende	10.710	*5.9*^{g}	6.0^{c}, 5.8^{d}, 5.4^{e}	1.45	5.6	4.3	4.7	+0.2
CaSe	3-3	NaCl	11.168	5.1^{b}		2.30	8.1	2.7	4.3	+4.5
CuBr	3-3	wurtzite	10.865	*4.4*^{b}, 4.0^{q}		1.50	6.9	4.1	4.5	+1.6
KBr	3-3	NaCl	12.472	2.4^{b}	*2.3*^{d}	2.30	9.3	2.1	4.1	+16.7
Sn	4-4	diamond	12.267	24^{l}			0.0	3.1	5.9	
InSb	4-4	zinc blende	12.242		$15.7^{d,f}$	1.50	2.1	3.1	5.7	−0.2
CdTe	4-4	zinc blende	12.246	*7.2*^{g}	7.2^{c}, 7.1^{e}, 7.6^{m}	1.55	4.4	3.1	5.2	−0.2
SrTe	4-4	NaCl	12.227	5.8^{b}		2.35	6.7	2.2	4.4	−0.3
AgI	4-4	zinc blende	12.232	4.9^{b}		1.60	5.7	3.1	4.9	−0.3
RbI	4-4	NaCl	13.875	*2.7*^{b}	2.6^{d}	2.25	7.1	1.6	4.3	+13.1
SiC	1-2	zinc blende	8.217		6.7^{d}	1.40	3.9	8.3	4.0	−1.2
BP	1-2	zinc blende	8.576	$\sim 9^{n}$	8.6^{r}	1.30^{r}	0.7^{r}	7.4	4.0	+3.1
BeS	1-2	zinc blende	9.165	7.1^{r}		1.30^{r}	4.0^{r}	6.3	4.0	+10.2
LiCl	1-2	NaCl	9.693	2.7^{b}	2.7^{d}	2.30	11.6	3.8	4.0	+16.6
AlN	1-2	wurtzite	8.257		4.8^{o}	1.20	7.3	8.2	4.0	−0.7
MgO	1-2	NaCl	7.958	3.0^{b}		1.45	14.5	6.3	4.0	−4.3
NaF	1-2	NaCl	8.731	1.7^{b}	1.7^{d}	1.90	20.9	5.0	4.0	+5.0
GaN	1-3	wurtzite	8.483	5.0^{r}		1.30^{r}	7.6^{r}	7.6	4.4	−0.1
ZnO	1-3	wurtzite	8.628	*4.0*^{b}	3.6^{c}	1.10	9.3	7.3	4.3	+1.7
CaO	1-3	NaCl	9.091	3.3^{b}		1.90	14.6	4.5	4.0	+7.1
CuF	1-3	zinc blende	8.041	2.5^{r}		1.30^{r}	15.8^{r}	8.7	4.2	−5.3
KF	1-3	NaCl	10.104	*1.8*^{b}	1.5^{d}	1.95	16.1	3.5	4.0	+19.0
BAs	1-3	zinc blende	9.027	10.4^{r}		1.30^{r}	0.3^{r}	6.6	4.4	+6.4
BeSe	1-3	zinc blende	9.581	$\sim 7.3^{p}$	8.5^{r}	1.30^{r}	3.4^{r}	5.7	4.3	+12.9
LiBr	1-3	NaCl	10.396	3.2^{b}	3.2^{d}	2.30	9.5	3.2	4.1	+22.5
InN	1-4	wurtzite	9.399	5.5^{r}		1.30^{r}	6.8^{r}	5.9	4.8	+0.3
CdO	1-4	NaCl	8.873	6.2^{b}		0.9	7.6	4.8	4.5	−2.4
SrO	1-4	NaCl	9.751	*3.2*^{b}, 3.3^{q}		1.90	13.4	3.8	4.0	+7.2
AgF	1-4	NaCl	9.298	2.9^{r}		1.30^{r}	12.2^{r}	4.3	4.3	+2.3
RbF	1-4	NaCl	10.658	1.9^{b}	1.9^{d}	1.85	13.9	3.0	4.1	+17.2
BeTe	1-4	zinc blende	10.469	11.6^{r}		1.30^{r}	2.1^{r}	4.5	4.5	+15.1
LiI	1-4	NaCl	11.338	3.8^{b}		2.55	7.4	2.6	4.1	+24.7

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[23] W. Gordy, Phys. Rev. **69**, 604 (1946), especially Appendix (ii) or Ref. 2.

TABLE III. (*continued*).

Crystal	Row Nos.	Type	Lattice^{a} const. (a_0)	Expt $\epsilon(0)$ (refract.)	Expt $\epsilon(0)$ (rest.)	b	C (eV)	E_h (eV)	N_{eff}	Var. (%)
AlAs	2-3	zinc blende	10.620	$\sim 10.2^{p}$	10.3^{r}	1.50^{r}	2.7^{r}	4.4	4.4	+ 1.4
MgSe	2-3	NaCl	10.301	5.9^{b}		1.60	5.4	3.3	4.3	− 1.7
NaBr	2-3	NaCl	11.288	2.6^{b}	2.6^{d}	2.00	9.8	2.6	4.1	+ 7.8
GaP	2-3	zinc blende	10.300	*9.1*^{k}	9.1^{c}, $8.5^{d,f}$	1.45	3.3	4.7	4.4	− 1.7
ZnS	2-3	zinc blende	10.222	*5.2*^{h}	5.1^{c}, 5.7^{e}	1.40	6.2	4.8	4.3	− 2.4
CuCl	2-3	zinc blende	10.215	*3.7*^{b}, 3.6^{q}	4.8^{d}	1.50	8.3	4.8	4.2	− 2.5
CaS	2-3	NaCl	10.753	4.5^{b}		2.30	9.1	3.0	4.0	+ 2.7
KCl	2-3	NaCl	11.892	*2.2*^{b}	2.1^{d}	2.25	10.4	2.3	4.0	+13.5
InP	2-4	zinc blende	11.090		$9.6^{d,f}$	1.40	3.4	3.9	4.8	− 1.1
CdS	2-4	wurtzite	11.047	*5.2*^{i}	5.1^{c}, 5.4^{e}	1.40	5.9	4.0	4.5	− 1.5
SrS	2-4	NaCl	11.376	4.4^{b}		2.15	8.5	2.6	4.0	+ 1.4
AgCl	2-4	NaCl	10.482	*4.2*^{b}, 4.0^{q}		1.35	7.8	3.2	4.3	− 6.6
RbCl	2-4	NaCl	12.436	2.2^{b}	2.2^{d}	2.15	9.7	2.1	4.1	+10.8
AlSb	2-4	zinc blende	11.593		$10.2^{d,f}$	3.05	3.1	3.5	4.8	+ 3.3
MgTe	2-4	wurtzite	12.050	$\sim 7^{p}$	8.3^{r}	1.50^{r}	3.6^{r}	3.2	4.5	+ 7.4
NaI	2-4	NaCl	12.232	3.1^{b}, 2.9^{q}	*3.0*^{d}	2.10	7.8	2.2	4.1	+ 9.0
GaSb	3-4	zinc blende	11.561		13.7^{c}, *14.4*^{d,f}	1.75	2.1	3.5	5.3	+ 1.0
ZnTe	3-4	zinc blende	11.510	*7.3*^{g}	7.3^{c}, 7.8^{d}, 6.7^{e}	1.60	4.5	3.6	4.9	+ 0.5
CaTe	3-4	NaCl	11.990	6.3^{b}		2.65	6.7	2.3	4.5	+ 4.7
CuI	3-4	zinc blende	11.419	5.5^{b}		1.55	5.5	3.7	4.7	− 0.3
KI	3-4	NaCl	13.352	2.7^{b}	2.7^{d}	2.35	7.4	1.7	4.1	+16.6
InAs	3-4	zinc blende	11.406		$12.3^{d,f}$	1.30	2.7	3.7	5.3	− 0.4
CdSe	3-4	wurtzite	11.489		6.1^{c}, *5.8*^{e}	1.50	5.5	3.6	4.9	+ 0.3
SrSe	3-4	NaCl	11.773	4.9^{b}		2.25	8.0	2.4	4.3	+ 2.8
AgBr	3-4	NaCl	10.912	*5.0*^{b}, 4.6^{q}		1.35	6.9	2.9	4.7	− 4.7
RbBr	3-4	NaCl	12.952	*2.4*^{b}	2.3^{d}	2.20	8.9	1.9	4.3	+13.1

[a] See Ref. 25, Vol. I. Note: For wurtzite structures an effective cubic lattice constant a_{eff} is given. In terms of the normal wurtzite parameters a and c, $a_{\mathrm{eff}}^3=\sqrt{3}a^2c$.
[b] *Handbook of Chemistry and Physics*, edited by R. C. Weast (The Chemical Rubber Co., Cleveland, 1965), 46th ed.
[c] J. W. Allen (private coommunication).
[d] E. Burstein, H. M. Brodsky, and G. Lucousky, Int. J. Quant. Chem. **1s**, 759 (1967).
[e] A. Manabe, A. Mitsuishi, and H. Yoshinaga, Japan. J. Appl. Phys. **6**, 593 (1967).
[f] M. Hass and B. W. Henvis, J. Phys. Chem. Solids **23**, 1099 (1962).
[g] D. T. F. Marple, J. Appl. Phys. **35**, 539 (1964).
[h] S. J. Czyzak, W. M. Baker, R. C. Crane, and J. B. Howe, J. Opt. Soc. Am. **47**, 240 (1957).
[i] T. M. Bieniewsky and S. J. Czyzak, J. Opt. Soc. Am. **53**, 496 (1963).
[j] P. J. Gielisse, S. S. Mitra, J. N. Plendl, R. D. Griffis, L. C. Mansur, R. Marshall, and E. A. Pasco, Phys. Rev. **155**, 1039 (1967).
[k] A. S. Barker, Phys. Rev. **165**, 917 (1968).
[l] R. E. Lindquist and A. W. Ewald, Phys. Rev. **135**, A191 (1964).
[m] K. J. Planker and E. Kauer, Z. Angew. Phys. **12**, 425 (1960).
[n] N. A. Goryunova, *Chemistry of Diamond-Like Semiconductors* (Chapman and Hall, London, 1965).
[o] A. T. Collins, E. C. Lightowlers, and P. J. Dean, Phys. Rev. **158**, 833 (1967).
[p] S. K. Kurtz (private communication).
[q] K. Hojendahl, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. **16**, 66 (1938); this work is quoted by N. F. Mott and R. W. Gurney, in *Electronic Processes in Ionic Crystals* (Dover Publications, Inc., New York, 1964).
[r] Value predicted on basis of trends noted in text; experimental data are not firm.

the worst variation in lattice constant among skew-tetrahedrally-coordinated crystals for which firm values of $\epsilon_1(0)$ have been obtained is the 5% variation between CdS and AlSb, the crystal CdS being 2% lower than expected and AlSb 3% higher.

To take account of what variation there is, we scale the r_α's to the lattice constant that is actually observed. Thus if $a_{\alpha\beta}$ is the observed lattice constant and $a_{\alpha\beta}'$ is the geometric mean of the $a_{\alpha,\gamma}$'s, we define r_α by

$$r_\alpha=\tfrac{1}{2}d_{\alpha,\gamma}(a_{\alpha\beta}/a_{\alpha\beta}'). \tag{4.2}$$

When (4.1) and (4.2) are used to compute the values of C for row 1 and rows 3 and 4 (see Fig. 1), one finds that the agreement with experiment is qualitative. However, (4.1) represents the average antisymmetric potential of bare ions, whereas the actual antisymmetric potential includes the effects of valence electron screening.

The simplest treatment of valence electron screening is obtained from the Thomas-Fermi theory. This yields a linearized screening wave number k_s which may be expressed as[24]

$$k_s=(4k_f/\pi a_0)^{1/2}, \tag{4.3}$$

where k_f is the Fermi wave number of the valence electron gas,

$$k_f{}^3=3\pi^2N, \tag{4.4}$$

and N corresponds to eight electrons per diatomic volume.

When this screening is included, (4.1) is replaced by

$$C_{\alpha\beta}=b(Z_\alpha/r_\alpha-Z_\beta/r_\beta)e^{-k_sR}, \tag{4.5}$$

where $R=\tfrac{1}{2}(r_\alpha+r_\beta)$, r_α and r_β are as defined in (4.2), and b is a dimensionless constant, which is of order unity. The exponential screening factor varies from 0.14 to 0.07 from row 1 to 4.

In common with (4.1), the screened expression (4.5) yields $C_{\alpha\beta}\propto|Z_\alpha-Z_\beta|$ when α and β belong to the same row. However, because of the exponential factor, (4.5)

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[24] N. F. Mott and H. Jones, *Theory of the Properties of Metals and Alloys* (Dover Publications, Inc., New York, 1958).

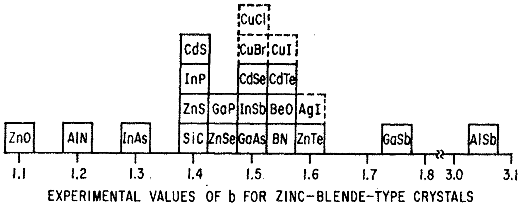

FIG. 4. Frequency histogram for zinc-blende- and wurtzite-type crystals of the parameter b in Eq. (4.5), which determines the mean ionic potential C.

differs from (4.1) in that the former is not in general transitive. Thus $C_{\alpha\beta}$ cannot be expressed as the difference of two terms, one depending only on α and the other only on β.

Physically (4.5) says that the electronegativity difference is proportional to the screened electrostatic potential difference of α and β at a point that might loosely be taken to be their point of contact or bond site; i.e., a distance r_α from α toward atom β. (Indeed scaling r_α has insured that the actual nearest-neighbor distance is $r_\alpha+r_\beta$.) The dielectric screening is represented by the exponential, which is the geometric mean of the factors $e^{-k_s r_\alpha}$ and $e^{-k_s r_\beta}$, the screening factors for the ion core potential at the bond site in the simple, linearized Thomas-Fermi model. Note that no allowance has been made for d-state effects; C is a property relevant to the bonding sites which are outside the core.

At this point in the development of our theory we refer to the experimental dielectric constants for a second time. We calculate the value of C necessary to give the most reliable experimental value of $\epsilon_1(0)$ (the underlined value in Table III), for all zinc-blende and wurtzite crystals, except those containing noble metals, for which reliable experimental data is known to the author (18 crystals in all). (We noted the anomalous behavior of CuBr and AgI in Fig. 1 and will discuss the noble metals later.) With this value of C and Eq. (4.5) we find the corresponding value of b, the prefactor in (4.5). The b's are plotted in a frequency histogram, Fig. 4.

From Fig. 4 we see that 13 of the 18 experimental values of b fall between 1.4 and 1.6, i.e., within 7% of 1.5. Because of the discrepancies in the experimental values recorded in Table III, we believe that 7% is about the level of experimental accuracy. The five cases in which the experimental b is more than 7% away from 1.5 are InAs (1.3), AlN (1.2), ZnO (1.1), GaSb (1.75), and AlSb (3.05). We have already noted that AlSb has an unexpectedly large lattice constant, indeed only BeO (for which the experimental $b=1.55$) varies more from our predicted value. ZnO is also unusual because its wurtzite structure is distorted so that one neighbor is substantially nearer than the other three.[25]

Now consider the noble metals, Cu, Ag, and Au. These have often been a source of trouble in electronegativity theories.[2,23,26] Chemically they show a propensity to assume an effective valence greater than the value of 1 that we would expect from their $d^{10}s^1$ ground-state configuration. Indeed, reference to their atomic-energy levels[22] shows that the d^9s^2 configuration is the lowest excited state in Cu and Au, only 1.38 and 1.13 eV, respectively, above $d^{10}s^1$, and in Ag d^9s^2 is only slightly higher than $d^{10}p^1$ at 3.7 eV. The d^9s^2 configuration would indicate an effective valence of 2 instead of 1. We noted in Fig. 1 that when CuBr and AgI are placed on the extrapolation of the $1/\chi$-versus-$(\Delta Z)^2$ lines for rows 3 and 4, their observed dielectric constants indicate values of $(\Delta Z)^2$ of 26 and 29, respectively. These values are closer to the value 25, which would be obtained by assigning valence 2 to the noble metals[26] than to the value 36, which would be obtained if they have valence 1.

When we calculate the experimental value of b for the four zinc-blende crystals containing a noble metal for which an experimental value of $\epsilon_1(0)$ has been obtained, we find (Fig. 4) that all four values fall within 7% of 1.5, provided we assume $Z=2$ for these metals. (However, we have continued to assume eight electrons per diatomic volume when calculating ω_p and E_f.) Therefore, we will assume that $Z=2$ for these metals in further calculations.

V. ROCK-SALT STRUCTURE

All diatomic compounds which are composed of elements from the first four rows of the periodic table and which have a saturated valence band (i.e., have eight valence electrons per diatomic unit) are found in stable crystals either in the NaCl structure or in the diamond, zinc-blende, or wurtzite structures, which

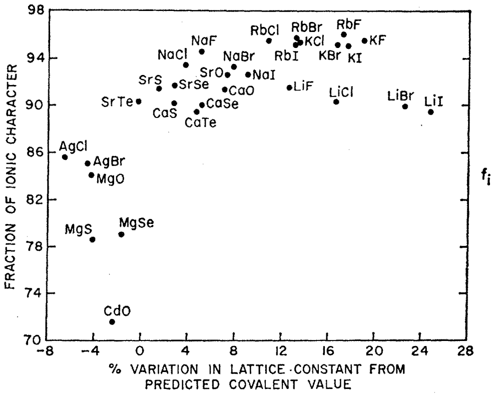

FIG. 5. For NaCl-type crystals the fraction of ionic character is plotted against the deviation of observed lattice constant from the value predicted by taking the mean of the lattice constants of the group-IV crystals of the rows to which the two elements of the compound belong.

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[25] See the u-parameter table [R. W. G. Wyckoff, *Crystal Structures* (Wiley-Interscience, Inc., New York, 1963), Vol. I, p. 112]; ZnO has the greatest distortion of any wurtzite crystal listed there.

[26] See Guggenheimer, Ref. 20.

have already been discussed. By extending our calculations to include the NaCl-type crystals we will be able to treat all diatomic compounds to which the simple Penn model applies, and for which we have fixed values for the r, Δ, and δ parameters. Note that a characteristic feature of the Penn model is the absence of structure factors S_G which would distinguish between zinc-blende and rock-salt structures. Therefore to the extent that a continuum model is applicable to strongly ionic systems, the Penn model can be used to extrapolate the dielectric properties of semiconductors to I–VII ionic crystals.

As in zinc-blende crystals, the NaCl structure is fcc, diatomic, and contains eight atoms per unit cell. Thus the translational symmetry is the same, and crystals of the same atomic density will have the same lattice constant a in the two structures. However, NaCl has coordination number 6, whereas zinc-blende has 4, and the nearest-neighbor distance is $\frac{1}{2}a$ instead of $\frac{1}{4}\sqrt{3}a$. For crystals of the same atomic density, each ion in the NaCl structure will have 50% more of the oppositely charged ions as nearest neighbors, but they will be about 15% further away. If one thought of the atoms as hard spheres, one might expect the NaCl structure to yield denser crystals than the zinc-blende structure.

Although no clear distinction has yet been made between ionic and covalent compounds, those which are generally considered to be most ionic, e.g., KI, are found in the NaCl structure and those which are considered most covalent, e.g., diamond, are found in the diamond, zinc-blende, or wurtzite structures. Indeed, covalency is commonly thought to be concomitant with tetrahedral coordination. To some extent this idea may arise from the fact that many tetrahedrally coordinated crystals have an average of four valence electrons per atom and the notion of a covalent bond as a shared, localized, pair of electrons between the atoms involved. This notion of the bond is certainly naive for there are many tetrahedrally coordinated crystals in the diamond and zinc-blende structures which do not have four valence electrons per atom,[27] e.g., Ga_2Se_3, and there are NaCl-type crystals, e.g., LiH, which are thought to be substantially covalent on the basis of analysis of the charge distribution[28] and measurement of the dipole moment.[29] Some compounds, such as MgS and MgSe, will condense from the gas phase in the wurtzite structure and then undergo a slow phase change to a stable NaCl structure.[27,30]

In Fig. 5 a plot is shown of the fraction of ionic character, f_i, as defined by (1.6), versus the deviation of the lattice constant from the "normal covalent value," i.e., the value we would predict for a zinc-blende crystal of the same compound using our covalent radii for 30 NaCl-type crystals. (We do not use any of the well-known ionic radii tables.) We note that all the Li, Na, K, Rb, and Ca salts have a lattice constant up to about 28% greater than that predicted. The Mg, Ag, and Cd compounds in the NaCl structure are more dense than the author would predict, but in no case is the observed lattice constant as much as half the 15%-less value that a hard-sphere model would indicate.

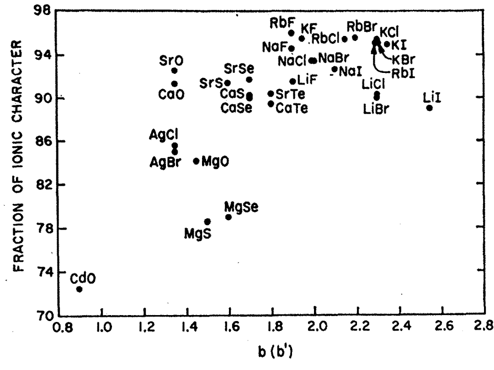

FIG. 6. Fraction of ionic character versus the b parameter of Eq. (4.5) or for Ca and Sr salts the b' parameter of (5.3).

In Fig. 6 a plot is presented of f_i versus the value of b in Eq. (4.5) which is necessary to obtain the experimental value of $\epsilon_1(0)$ from (2.8′)—except as noted below for Ca and Sr salts—when, as noted earlier, we continue to obtain E_h from the extrapolation of the diamond and Si values[31] as a function of the actual nearest-neighbor distance (3.6), and D from (3.11).

Special note must be taken of the calculation for the group IIa compounds, i.e., the Ca and Sr alkali earths. In contrast to the group IIb elements Zn and Cd, the elements Ca, and Sr have no d core so that $D=1.0$ and (3.11) should not be used. However, reference to the atomic-energy levels[22] shows that the d-states lie just 1.7 and 1.8 eV, respectively, above the ground state for Ca^+ and Sr^+, so that these levels should not be neglected. One method of including the effect of the conduction-band d levels is as follows: We assume total ionicity so that in the valence level the electrons are localized about the group-VI atom and that in the

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[27] N. A. Goryunova, *The Chemistry of Diamond-like Semiconductors* (Chapman and Hall, London, 1965), pp. 42–57.

[28] R. S. Calder, W. Cochran, D. Griffiths, and R. D. Lowdee, J. Phys. Chem. Solids **23**, 621 (1962).

[29] M. Brodsky and E. Burstein, J. Phys. Chem. Solids **28**, 1655 (1967).

[30] H. Mittendorf, Z. Physik **183**, 113 (1965).

[31] It is possible to test the validity of the extrapolation method of determining E_h by examining the cases in which (1) there are no d states present in the cores and (2) the value of C as predicted by (4.5) is too small to have much effect on the value of E_g. The latter condition obtains when $Z_\alpha/Z_\beta \sim r_\alpha/r_\beta$. The zinc-blende-type crystal BP satisfies these conditions, and we calculate that $\epsilon_1(0)$ should be 8.6. Unfortunately, we do not know of any firm experimental determination. However, Goryunova (Ref. 27, p. 93), gives a tentative value of 9. The NaCl-type crystal LiH is also expected to satisfy these conditions. Although we have not yet fixed a characteristic covalent radius for H, we conclude from the fact that the lattice constant of LiH ($7.720a_0$) is about 1% larger than that of LiF ($7.592a_0$), that the radius for H should be about the same as that of the first row elements. (Of course, Z is 1 for both Li and H.) If we take $C=0$, we calculate $E_h=6.8$ eV and $\epsilon_1(0)=3.9$. Brodsky and Burstein (Ref. 29) found $\epsilon_1(0)=3.6$. That value would indicate that the true value of C should be about 2.3 eV.

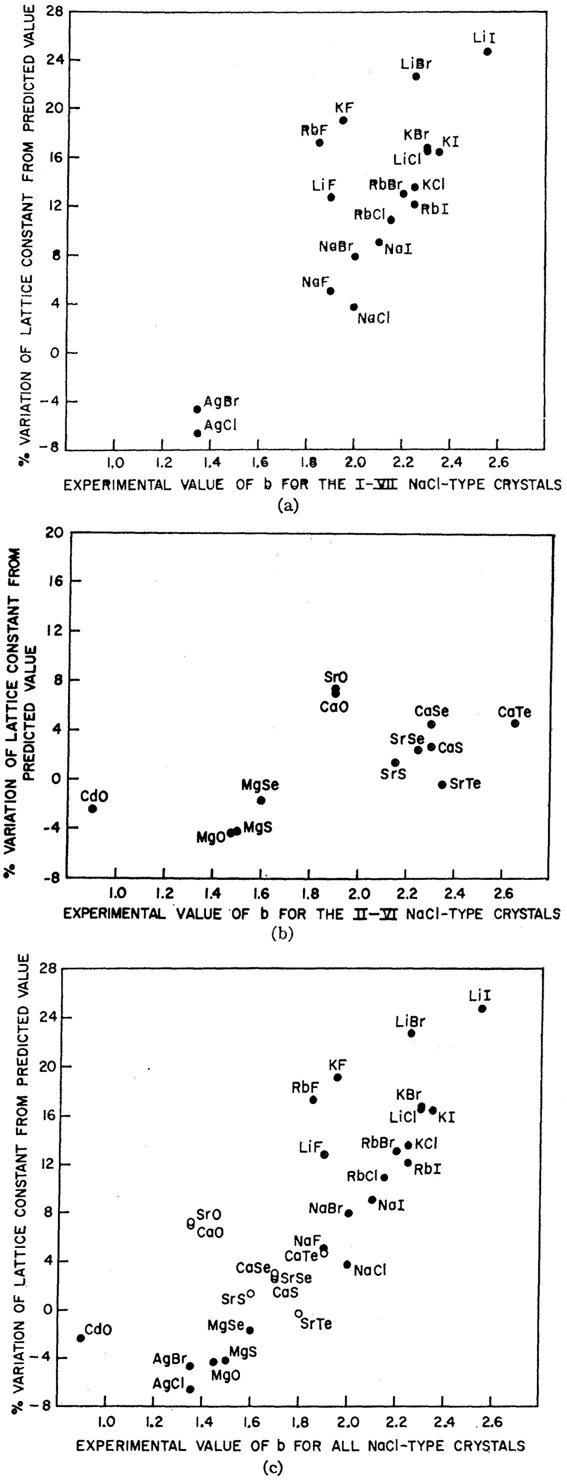

FIG. 7(a). Deviation of lattice constant versus b parameter for the alkali halides and noble-metal halides in the NaCl structure. (b) Deviation of lattice constant versus b parameter for II-VI and IIa-VI compounds in the NaCl structure. Note that the b parameter, which is appropriate to the actual model energy gap, and not b', which is appropriate to the charge redistribution, is used for the IIa-VI compounds. (c) Deviation of lattice constant versus b for all NaCl-type crystals except the IIa-VI compounds for which b' is used instead.

lowest conduction band they are localized about the group-IIa atom. Then, in addition to this lowest conduction band, we add d bands 1.7 and 1.8 eV higher for Ca and Sr, respectively. The p electrons in the valence band can make transitions to the d level as well as to the normal conduction band. Such transitions increase the dielectric constant. Instead of (2.8′) we have

$$\epsilon_1(0)=1+(\hbar\omega_p)^2[1/E_g^2+1/(E_g+\Delta E)^2]A\,, \tag{5.1}$$

where $A=1-B+\frac{1}{3}B^2$ and ΔE is the difference in energy between the ground state and the first-excited d state of the IIa$^+$ ion, i.e., 1.7 or 1.8 eV for Ca or Sr.

There is a clear analogy between the effect described by (5.1) and the effect of adding resistances in parallel. As with resistances, the relevant physical quantity may be either the actual energy gaps E_g and $E_g+\Delta E$ or the effective energy gap defined by

$$1/E_g'^2=1/E_g^2+1/(E_g+\Delta E)^2\,, \tag{5.2}$$

depending on the application.

The value of b used in Fig. 6 is not that which yields the experimental value of E_g for (5.1), i.e., the b which gives the actual E_g and which is appropriate to discussions of the actual interband transition energies. One may also define an effective b value b' and an effective ionic potential C' which gives the effective E_g, E_g' by

$$E_g'^{\,2}=E_h^2+C'^2\,. \tag{5.3}$$

Because the bond charge in the Phillips theory of covalent bonding[32] is inversely proportional to the dielectric constant, which is determined by E_g', the quantity b' is more appropriate than b for discussions of the charge distribution. Thus we use b' for the Ca and Sr salts in Fig. 6.

Returning to Figs. 5 and 6 we note that there is considerable scatter in both plots but both suggest that the deviations remain small until f_i reaches about 0.90. Then the plots seem to turn over in an intermediate region extending perhaps to 0.93 and then the deviations increase rapidly with f_i. This behavior suggests to the author that a fairly rapid transition from "covalent" behavior to "ionic" behavior occurs in this range of f_i. We also note that there is a substantial amount of clustering in both figures. There appears to be a "normal value "of b for the most ionic crystals in the NaCl structure ($f_i\geq 0.93$) of about 2.25. This would be the normal value for b for the zinc-blende structure, i.e., 1.5, times the ratio of the coordination numbers of the two structures, i.e., 6 to 4. This would say that the average ionic potential is proportional to the number of oppositely charged ions surrounding a given ion. We also note that compounds containing an ion with the neon configuration, i.e., O, F, or Na, have a b value of about 80% of this normal value and that all crystals which are more dense than the covalent prediction have the same b value that we would expect in

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[32] J. C. Phillips, Phys. Rev. 166. 832 (1968).

a zinc-blende structure except for CdO, which exhibits an anomalously small value of b.

In Fig. 7 we simply plot the variation of lattice constant versus the b or b' values. Figure 7(a) shows only the I–VII compounds. Figure 7(b) shows the plot for the II–VI compounds if the b values, instead of b' as in Fig. 6, are used for the Ca and Sr salts. In Fig. 7(c) we plot all NaCl-type crystals using the b' values for the Ca and Sr salts.

Figure 7 suggests that the b value increases with deviation in lattice constant. Although there is substantial scatter, the figure suggests that a linear correlation may exist, and that we should prefer the presentation in Fig. 7(c) to that of Figs. 7(a) and 7(b). (The latter distinction would support our assumption that it is the charge distribution and not the interband energy gaps which is most directly involved in these effects.) To pursue this point we consider the effect of hydrostatic pressure on $\epsilon_1(0)$.

VI. PRESSURE DEPENDENCE OF DIELECTRIC CONSTANT

Photoelastic effects in crystals have been the subject of much experimental and theoretical investigation during the last century.[33] Virtually all theoretical approaches have begun by considering alkali-halide crystals, which were assumed to be totally ionic. There has been substantial variation in treatment among these approaches. Mueller[34] assumed the Lorentz local-field equation

$$\mathbf{E}_{\mathrm{loc}}=\mathbf{E}+\tfrac{4}{3}\pi\mathbf{P}, \qquad (6.1)$$

where $\mathbf{E}_{\mathrm{loc}}$ is the local atomic field $\mathbf{E}$ is the macroscopic average field, and $\mathbf{P}$ is the polarization. This assumption leads to the Clausius-Mossotti model.[10] Mueller demonstrated that in order to explain the pressure dependence of $\epsilon_1(0)$ for the alkali halides, it is necessary to assume that the polarizability of the ions decreases with pressure because the increase in $\epsilon_1(0)$ is generally less rapid than would be predicted by considering only the derivative with respect to atomic density.

Mott and Littleton[35,36] argued that the overlap of the ions in a crystal would invalidate the Lorentz equation (6.1) and suggested replacing it with

$$\mathbf{E}_{\mathrm{loc}}=\mathbf{E}+\tfrac{4}{3}\pi\gamma\mathbf{P}, \qquad (6.2)$$

where γ is a parameter which describes the effect of the overlap. Agreement with experiment is obtained for γ approximately equal to 0 for most alkali halides. Thus (6.2) leads to a model which is approximately equivalent to assuming the Drude equation. When the crystal is compressed the degree of ionic overlap increases and γ must be assumed to decrease still further to account for the pressure dependence of $\epsilon_1(0)$.

Yamashita[37] has developed a quantum-mechanical approach to the calculation of $\epsilon_1(0)$ for ionic crystals which he was able to carry out with fair success for LiF. By introducing empirical parameters, he has been able to extend[38] his method to describe the pressure dependence of $\epsilon_1(0)$ for all the alkali halides.

All the above theories have difficulty with the case of MgO because for this NaCl-type crystal, $\epsilon_1(0)$ decreases with hydrostatic pressure.[39] The Mott-Littleton approach is inapplicable as their γ parameter is found to be imaginary for MgO.[40] Mott[35] argues that the failure of the Cauchy relation among the elastic coefficients C_{ij}

$$8.7=C_{12}\neq C_{44}=14.8(10^{11}\ \mathrm{dyne/cm^2}) \qquad (6.3)$$

in the case of MgO [41] demonstrates the importance of noncentral, covalent forces in this material. Because noncentral forces are important, no theory based on ionic interactions should be applicable to MgO.

Yamashita[37] calculated $\epsilon_1(0)-1$ for MgO on the basis of his *a priori* quantum-mechanical theory to be 3.56 as compared to the observed value of 1.95. However, his extended model with three empirically determined parameters[38] is capable of accounting for a decrease in $\epsilon_1(0)$ with increasing pressure if one makes the assumption that the energy due to the overlap of the ions is roughly a constant fraction of the total energy for all crystals.[39] We know of no explanation of the basis of such an assumption nor of any further development along these lines.

The explanation that seems to have been preferred is that based on the Mueller theory. Vedam and Schmidt[38] conclude that the ionic polarizabilities, particularly that of O^{--}, must decrease rapidly enough in MgO to outweigh the increase in atomic density. However, no theory has been advanced to explain this behavior of the ions and it is noted that similar behavior of O^{--} in vitreous silica is not observed.[39]

Although $d\epsilon_1(0)/dV<0$ for all alkali halides, MgO is by no means the only case for which $d\epsilon_1(0)/dV>0$. It is known that for ZnS,[42] diamond,[43] Si,[44] and Ge [44] the quantity $\epsilon_1(0)$ also decreases with pressure.

We propose to approach the problem of the pressure dependence of $\epsilon_1(0)$ by means of our covalent theory for diamond, zinc-blende, and NaCl-type crystals. Let us take the derivative of (2.8′) with respect to $r=r_\alpha+r_\beta$.

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[33] Cf., K. Vedam and S. Ramaseshan, in *Progress in Crystal Physics*, edited by R. S. Krishnan (Wiley-Interscience, Inc., New York, 1958), Vol. I

[34] H. Mueller, Phys. Rev. **47**, 947 (1935).

[35] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Dover Publications, Inc., New York, 1964).

[36] N. F. Mott and M. J. Littleton, Trans. Faraday Soc. **34**, 485 (1938).

[37] J. Yamashita, Progr. Theoret. Phys. (Kyoto) **8**, 280 (1952).

[38] J. Yamashita and T. Kurosawa, J. Phys. Soc. Japan **10**, 610 (1955).

[39] K. Vedam and E. D. D. Schmidt, Phys. Rev. **146**, 584 (1966).

[40] S. Mayburg, Phys. Rev. **79**, 375 (1950).

[41] *Americal Institute of Physics Handbook* (McGraw-Hill Book Co., New York, 1963), 2nd ed.

[42] K. Vedam and E. D. D. Schmidt, Phys. Rev. **150**, 766 (1966).

[43] D. F. Gibbs and G. J. Hill, Phil. Mag. **9**, 367 (1964).

[44] M. Cardona, W. Paul, and H. Brooks, J. Phys. Chem. Solids **8**, 204 (1959).

As $A\equiv 1-B+\frac{1}{3}B^2$ is always approximately 1 because B is always small with respect to 1, we make the approximation $A=\text{const}$ and find

$$\frac{r}{\epsilon_1(0)}\frac{d\epsilon_1(0)}{dt}=2\frac{\epsilon_1(0)-1}{\epsilon_1(0)}\times\left[\tfrac{1}{2}r\frac{dD}{dr}+2.48\frac{E_h{}^2}{E_g{}^2}-\frac{C^2}{E_g{}^2}\left(\frac{r}{C}\frac{dC}{dr}\right)-1.5\right]. \tag{6.4}$$

We first consider the elemental group-IV crystals for which $E_h=E_g$ and $C=0$, so that we need not evaluate dC/dr. Thus (6.4) becomes

$$\frac{r}{\epsilon_1(0)}\frac{d\epsilon_1(0)}{dr}=2\frac{\epsilon_1(0)-1}{\epsilon_1(0)}\left(\tfrac{1}{2}r\frac{dD}{dr}+0.98\right). \tag{6.5}$$

For diamond and Si, the quantity D is always equal to 1, so $dD/dr=0$ and we predict $[r/\epsilon_1(0)]d\epsilon_1(0)/dr$ to be +1.62 and +1.80, respectively. Unfortunately the experimental data are not as conclusive as one might hope. Gibbs and Hill[43] have reported

$$\frac{1}{\epsilon_1(0)}\left(\frac{\partial\epsilon_1(0)}{\partial P}\right)_T=(-1.07\pm0.09)\times10^{-7}\ \text{cm}^2/\text{kg}$$

for a type-IIa diamond (0.02% nitrogen impurity). Cardona, Paul, and Brooks[44] have reported $(1/n)\times(\partial n/\partial P)_T=(-3\pm2)\times10^{-7}$ cm²/kg for Si, where n is the optical index of refraction.

The bulk modulus k of Si is generally reported to be 9.75×10^{11} dyne/cm².[41,45–47] For diamond there is some question as to what the value of k is, and there may be significant dependence of k on the nitrogen impurity level.[43,45] McSkimin and Bond[48] report $k=57.7\times10^{11}$ dyne/cm², which is 30% higher than earlier values. With these values we calculate the experimental values of

$$\frac{r}{\epsilon_1(0)}\frac{d\epsilon_1(0)}{dr}=\frac{1}{\epsilon_1(0)}\frac{\partial\epsilon_1(0)}{\partial P}(-3k)$$
$$=\frac{2}{n}\frac{dn}{dP}(-3k)$$

to be +1.85 and +1.75 for diamond and Si, respectively. Thus our predicted values of +1.62 and +1.80 are in agreement with observation to within the limits of experimental uncertainty.

Table IV. Pressure dependence of $\epsilon_1(0)$, C, and b.

Crystal	$\frac{r}{\epsilon_1(0)}\frac{d\epsilon_1(0)}{dr}$ if $\frac{dC}{dr}=0$	$\frac{r}{\epsilon_1(0)}\frac{d\epsilon_1(0)}{dr}$ Expt	$\frac{r}{C}\frac{dC}{dr}$ Expt	$\frac{r}{b}\frac{db}{dr}$	Ref.
RbCl	−1.5	−1.44	−0.1	2.3	49
KI	−1.7	−1.57	−0.2	2.2	50
KBr	−1.6	−1.35	−0.2	2.1	50
KCl	−1.5	−0.93	−0.5	1.8	50
NaCl	−1.5	−0.95	−0.5	1.7	50
LiF	−1.2	−0.57	−0.7	1.3	51
MgO	−1.5	+1.07	−2.3	−0.2	39

For the case of Ge, we lack a theoretical prescription for evaluating dD/dr. We might conclude that it is positive by noting that D is larger for Sn than it is for Ge. If we assume we can make a rough estimate of dD/dr by taking

$$\frac{dD}{dr}\sim\frac{D_{\text{Sn}}-D_{\text{Ge}}}{r_{\text{Sn}}-r_{\text{Ge}}}, \tag{6.6}$$

we conclude $rdD/dr\sim1.43$. With this value we would predict from (6.5) $[r/\epsilon_1(0)]d\epsilon_1(0)/dr=+3.20$ for Ge, whereas if we assume $dD/dr=0$, we would predict +1.84. Cardona, Paul, and Brooks[44] reported $(1/n)\times(\partial n/\partial P)=-(7\pm2)\times10^{-7}$ cm²/kg for Ge, and k is generally reported[41,45] to be 7.52×10^{11} dyne/cm². Thus the experimental value of $[r/\epsilon_1(0)]d\epsilon_1(0)/dr$ is +3.16. This result would indicate that dD/dr is indeed positive, and that our rough estimate is approximately correct.

Although the experimental evidence is not sufficient to confirm the validity of our treatment, we note that (6.4) does offer a simple explanation of the fact that $\epsilon_1(0)$ decreases under compression for diamond, Si, Ge, and for the more covalent crystals in general. It is simply that E_h, and thus the bond energy gap, increases with pressure faster than the plasma energy.

For nonelemental crystals, $C\neq0$; thus we need to evaluate dC/dr in order to use (6.4). Taking the derivative of (4.5) we find

$$\frac{r}{C}\frac{dC}{dr}=\frac{r}{b}\frac{db}{dr}-\frac{k_sr}{4}-1. \tag{6.7}$$

The value of k_sr is, in general, between 4 and 6 for the alkali halides. If we assume that we may estimate db/dr, at least for the alkali halides, from the correlation noted in Sec. V [Figs. 7(a) or 7(c)] between the observed lattice constant and the experimental value for b, we conclude that $(r/b)db/dr$ is approximately +2.0 to +2.5. Thus we would conclude from (6.7) that

$$(r/C)dC/dr\sim0 \tag{6.8}$$

for the alkali halides. This is an attractive conclusion because it implies that in the ionic limit the condition that the total energy be a minimum, which determines the equilibrium lattice constant, is equivalent to the condition that the mean ionic potential C be a maximum. Since the Madelung energy makes the dominant contribution to the cohesive energy in alkali halides,

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[45] H. B. Huntington, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1958), Vol. 7.

[46] H. J. McSkimin, J. Appl. Phys. **24**, 988 (1953).

[47] S. C. Prasad and W. A. Wooster, Acata Cryst. **8**, 361 (1955).

[48] H. J. McSkimin and W. L. Bond, Phys. Rev. **105**, 166 (1957).

the equilibrium lattice constant should be that which maximizes the ionicity of the crystal.

Of course, even in the alkali halides we never reach the fully ionic limit, i.e., E_h is never totally negligible. Thus we expect small deviations from the condition $(r/C)dC/dr=0$.

The experimental data on the pressure dependence of $\epsilon_1(0)$ for the alkali halides allow a somewhat more rigorous test of these conjectures than was possible for the group-IV crystals. We present the evidence in Table IV.[49–51] First we calculate a predicted value of $[r/\epsilon_1(0)]d\epsilon_1(0)/dr$ from (6.4) under the assumption $dC/dr=0$. (We also have $dD/dr=0$ because the d core states are well below the valence level in Br, I, and Rb and not present in K.) Next we show the experimental value of $[r/\epsilon_1(0)]d\epsilon_1(0)/dr$ and from this, again using (6.4), we obtain an experimental value for $(r/C)dC/dr$. In the last column we give the value of $(r/b)db/dr$ necessary to give the experimental value of $(r/C)dC/dr$ from (6.7).

In view of the cumulative effect of all the experimental uncertainties, as well as the approximations involved, we believe that the results of Table IV support the following: (1) The basic validity of our covalent approach even in the case of the alkali halides and (2) the conjecture that dC/dr is small in ionic crystals.

We have included in Table IV the results of a similar calculation for MgO. The covalent effects noted by Mott are clearly evidenced by the fact that the logarithmic derivative of C is not small but indeed is roughly the same as that of E_h.

On the basis of very sparse experimental data available to us, we suggest that there may be a linear dependence of the value of b (or b' for IIa-VI crystals) on lattice constant for the most ionic crystals. Among NaCl-type crystals only our data on RbCl,[49] LiF,[51] and MgO[39] are recent. In Fig. 8 we have reproduced Fig. 7(c) with lines drawn through RbCl, LiF, and MgO having the slope indicated by the pressure dependence of $\epsilon_1(0)$ for these crystals (see Table IV). It is seen that most of the crystals for which $f_i \gtrsim 0.93$ fall close to the RbCl line. The behavior of MgO and the position of the CaO and SrO points seems to indicate that for the more covalent crystals ($f_i < 0.90$), the value of b is much less dependent on lattice constant. LiF may represent an intermediate case. We note that in LiF the Cauchy relation is also violated[41]:

$$C_{12}=4.20\neq 6.28=C_{44} \text{ in units of } 10^{11} \text{ dyne/cm}^2.$$

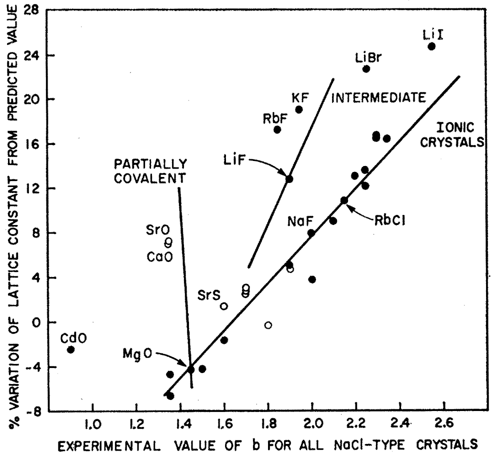

FIG. 8. Lines indicating relation of variation of lattice constant to value of the parameter b as obtained from pressure dependence of $\epsilon_1(0)$ in MgO, LiF, and RbCl. The points are the same as in Fig. 7(c).

Note added in proof. The value of $\epsilon_1(0)$ for CdO shown in Table III, 6.2, is inaccurate because of anomalous dispersion at the frequency at which the refractive index was measured. Although there is still some uncertainty as to the true value, it is known[52] to be approximately 5. If we take $\epsilon_1(0)=5.0$ we calculate $b=1.05$, $c=9.0$ eV, and $f_i=0.78$. This correction brings CdO into line with ZnO and similar skew compounds containing one first row element. Thanks are due to Dr. P. Eisenberger and Dr. H. Finkenrath for bringing this to my attention.

Also new data is now available for the pressure dependence of the dielectric constant of several alkali halides[53] and also of CdS, ZnS, and ZnO.[54] The new alkali halide data is in substantially better agreement with the values calculated in Table IV than is the 1948 data of Ref. 50. The data on CdS and ZnO is within 10% of value calculated in a manner similar to that used for Ge, but for ZnS the experimental value is about $\frac{1}{3}$ the calculated value.

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[49] K. Vedam and E. D. D. Schmidt, J. Mat. Sci. 1, 310 (1966).

[50] E. Burnstein and P. L. Smith, Phys. Rev. 74, 229 (1948).

[51] K. Vedam and E. D. D. Scmhidt, Solid State Commun. 3, 373 (1965).

[52] H. Finkenrath, H. Köhler, and M. Lochmann, Z. Angew. Phys. 21, 512 (1966).

[53] K. Vedam (unpublished).

[54] K. Vedam and T. A. Davis, Phys. Rev. (to be published).