PHYSICAL REVIEW B VOLUME 7, NUMBER 6 15 MARCH 1973

d-Electron Effects on Bond Susceptibilities and Ionicities

B. F. Levine
Bell Laboratories, Murray Hill, New Jersey 07974

(Received 17 August 1972)

We have been able to extend the dielectric theory of ionicity to include such *d*-electron systems as the noble-metal halides (e.g., CuCl, AgBr, etc.), *A B* transition-metal compounds (e.g., ScN, MnS, FeO, NiO, etc.), A_mB_n crystals (e.g., ZrF_4, TiO_2, Cr_2O_3, Fe_2O_3), and multibond compounds (e.g., $LiNbO_3$, $LiTaO_3$, $CuGaS_2$, $CuInS_2$, $AgGaSe_2$, $AgInSe_2$). This characterization of the ionicity and other bond parameters should be useful in some of the wide variety of problems to which the non-*d*-electron theory has already been successfully applied, e.g., the calculation of nonlinear optical susceptibilities.

I. INTRODUCTION

The dielectric theory of electronegativity[1-3] has been successfully used in a wide variety of physical problems.[4] Since the compounds considered by Phillips and Van Vechten[2] (PV) only include the simple *AB* crystals, it seems worthwhile to extend these fruitful ideas. In a forthcoming paper[3] (hereafter referred to as I) we succeeded in generalizing this dielectric theory of PV for systems devoid of strong *d*-electron effects (i.e., not containing noble- or transition-metal atoms). This generalized theory encompasses a wide range of both simple and complex (e.g., multibond) structures spanning the entire ionicity range (from $f_i = 0$ up to $f_i > 0.97$ in BaF_2). We have been able to evaluate the bond ionicities and other associated parameters for such varied compounds as the 10-electron Ge, Sn, and Pb chalcogenides; the 16-electron quartz, fluorite, antifluorite, and MgF_2 structures; the 24-electron corundum structure, Al_2O_3; various multibond structures, e.g., $LiGaO_2$, $ZnGeP_2$, $AlPO_4$, etc.; the highly anisotropic compounds HgS, Se, and Te; and various miscellaneous structures, e.g., Cd_3As_2 and Si_3N_4, to mention only a partial list. The comparison with Pauling's ionicity scale showed it to be generally in agreement with our dielectric analysis. We also found simple and interesting trends between structural parameters such as the coordination number N_c and the Thomas–Fermi screening factor which enters into the ionic gap C.

In this paper we extend these ideas to include crystals containing noble or transition metals with their important *d*-electron effects (e.g., CuCl, FeO, TiO_2, Cr_2O_3, $CuInS_2$, $LiNbO_3$, $LiTaO_3$, etc.). The goal of our analysis is to obtain some of the *average* properties characterizing these systems (such as the effective number of *d* electrons, the average optical energy gap, the bond susceptibilities, the ionicity, etc.) by generalizing I using the minimum number of additional assumptions. This determination and systemization of the *average* properties is complementary to the more rigorous treatments[5] of the detailed band structure which has been done for some of these *d*-electron compounds. It seems likely that our simple analysis will prove to be useful for understanding some of the wide variety of problems to which the non-*d*-electron dielectric theory has been fruitfully applied.[4] For example, we have successfully used these ideas to calculate the second-order nonlinear optical susceptibility[6] for such compounds as CuCl, AgI, $CuInS_2$, $CuGaSe_2$, $AgGaS_2$, $LiNbO_3$, $Ba_2NaNb_5O_{15}$, $LiTaO_3$, etc.

II. REVIEW

Before discussing the *d*-electron materials it is useful to list some of the results of I that will be needed later.

If a crystal is composed of different types of bonds (labeled μ) then the total low-frequency electronic susceptibility χ can be resolved into contributions χ^μ from the various types of bonds[7]:

$$\chi = \sum_\mu F^\mu \chi^\mu = \sum_\mu N_b^\mu \chi_b^\mu , \tag{1}$$

$$\chi^\mu = \frac{1}{4\pi} \frac{(\hbar\Omega_p^\mu)^2}{(E_g^\mu)^2} , \tag{2}$$

where χ^μ is the total macroscopic susceptibility which a single crystal composed entirely of bonds of type μ would have (including local-field effects), F^μ is the fraction of bonds of type μ composing the actual crystal, χ_b^μ is the macroscopic susceptibility of a single bond of type μ, and N_b^μ is the number of bonds per cm^3. Equation (2) defines the appropriate average energy gap for the type-μ bonds, E_g^μ. The plasma frequency Ω_p^μ, in this relation, is obtained from the number of valence electrons of type μ per cm^3, N_e^μ, using

$$(\hbar\Omega_p^\mu)^2 = (4\pi N_e^\mu e^2/m) D^\mu A^\mu \equiv (\hbar\omega_p^\mu)^2 D^\mu A^\mu , \tag{3}$$

where D^μ and A^μ are correction factors of order unity.[2] See I for a detailed discussion of these and the following results.

The fractional ionicity f_i^μ and covalency f_c^μ of the individual bonds can be determined by separating the average gap $(E_g^\mu)^2$ into homopolar $(E_h^\mu)^2$ and heteropolar $(C^\mu)^2$ parts using

$$(E_g^\mu)^2 = (E_h^\mu)^2 + (C^\mu)^2 \tag{4}$$

and

$$f_i^\mu = (C^\mu)^2/(E_g^\mu)^2 , \quad f_c^\mu = (E_h^\mu)^2/(E_g^\mu)^2 . \tag{5}$$

The expressions for C and E_h (for an A_mB_n compound where $n > m$) are given by

$$E_h^\mu = 39.74/(d^\mu)^{2.48} \text{ eV} , \tag{6}$$

$$C^\mu = 14.4 b^\mu e^{-k_s^\mu r_0^\mu}\left(\frac{Z_\alpha^\mu}{r_0^\mu} - \frac{n}{m}\frac{Z_\beta^\mu}{r_0^\mu}\right) \text{ eV} , \tag{7}$$

$$r_0^\mu = \tfrac{1}{2} d^\mu , \tag{8}$$

where d is the nearest-neighbor distance, Z_α is the number of valence electrons on the cation, and $e^{-k_s r_0}$ is the Thomas–Fermi screening factor. For convenience we have written Eqs. (6) and (7) so that when d^μ or r_0^μ is expressed in Å, E_h and C will be in eV.

The physical interpretation of Eq. (7) is that the antisymmetric energy gap C^μ is given by the difference between the screened Coulomb potentials produced by the two atoms composing the bond. Because the true screening behavior of a solid is more complex than this simple Thomas–Fermi description, a correction factor b^μ of order unity is necessary. It is shown in I that a close relationship exists between this screening factor and the average coordination number N_c of the crystal, i.e.,

$$b \simeq 0.089 \bar{N}_c^2 . \tag{9}$$

Finally it was found[2,3] that special care was required for the Ca, Sr, and Ba salts, since they contain low-lying *conduction*-band d levels only $\Delta E_c = 1.7$, 1.8, and 0.6 eV above the ground states in Ca^+, Sr^+, and Ba^+, respectively. These d levels increase the polarizability since the valence electrons can make transitions to them. We accounted[3] for these transitions by generalizing Eqs. (2), (4), and (7) as follows:

$$\chi^\mu = \frac{1}{4\pi}\,\frac{(\hbar\omega_p^\mu)^2 A^\mu D^\mu}{(E_g^{\mu\prime})^2} , \tag{10}$$

$$\frac{1}{(E_g^{\mu\prime})^2} = \frac{1}{(E_g^\mu)^2} + \frac{1}{(E_g^\mu + \Delta E_c^\mu)^2} , \tag{11}$$

$$(E_g^{\mu\prime})^2 = (E_h^\mu)^2 + (C^{\mu\prime})^2 , \tag{12}$$

$$C^{\mu\prime} = 14.4 (b^{\mu\prime}) e^{-k_s^\mu r_0^\mu}\left(\frac{Z_\alpha^\mu}{r_0^\mu} - \frac{n}{m}\frac{Z_\beta^\mu}{r_0^\mu}\right) , \tag{13}$$

where the effective gap $E_g^{\mu\prime}$ now includes these conduction-band d levels.

III. IMPORTANCE OF *d* ELECTRONS

Owing to the relatively small binding energy[8] and the significant delocalization[5,9–12] of the d electrons in unfilled inner shells (i.e., transition metals) or newly completed shells (i.e., noble metals), such d electrons can influence crystal properties to a substantial degree. For this reason a large body of work (see, for example, Refs. 5, 9–12, and references therein) has been devoted to understanding these interesting compounds. This partial delocalization (indicated by the substantial p-d overlap and hybridization[5,9–12]) is an important reason for the large d-electron effects on the band structure,[5,9–12] optical spectra,[5,9–12] transport properties[5] (e.g., the metallic or insulating nature of the rocksalt transition-metal oxides), and nonlinear optical susceptibilities.[6,13] The d-electron influence is especially clear for the latter phenomenon since the sign of the nonlinear susceptibility in the noble-metal halides is anomalous,[14] being opposite to all the other *similar* crystals devoid of such d electrons. The major importance of these d states is thus evident, since in order to reverse this sign they must make a contribution larger than that of the s and p electrons.

The work of Wemple and DiDomenico,[15] on the dispersion of the linear susceptibility, lends further support to the significant influence of these d states. These authors found it necessary to include all the d electrons when evaluating the effective number of valence electrons, Z_α, for the noble- or transition-metal atoms, e.g.,

$$Z_{\mathrm{Cu,Ag}} = 11 , \quad Z_{\mathrm{Ti}} = 4 , \tag{14}$$

etc. This means that in the noble-metal halides, for example, the plasma frequency Ω_p in Eq. (3) should be evaluated by using an N_e corresponding to $11 + 7 = 18$ electrons per formula unit N_F, instead of $1 + 7 = 8$, i.e.,

$$N_F(\text{noble-metal halides}) = 18 \tag{15a}$$

and

$$N_F(\mathrm{TiO_2}) = 16, \text{ etc.} \tag{15b}$$

This increase of the plasma frequency, owing to the d electrons, by the factor $(\frac{18}{8}) = 2.25$ [in Eq. (15a)] seems quite reasonable since it has been shown that, even relatively tightly bound, d-core states can significantly enhance Ω_p by as much as a factor of ~1.5.[16]

The reason for these large d-electron effects is that the d electrons of Cu are weakly bound[8] unlike the usual tightly bound d-core states of, say, Zn (which is the following element in the Periodic Table). The $3d^9 4s^2$ configuration in Cu (which is the lowest excited state) is only $\Delta E_v = 1.38$ eV above the $3d^{10} 4s^1$ valence-electron ground state.[8] Since the average gap E_g in CuCl is 14 eV, we see that ΔE_v is only 10% of the average energy gap. In contrast $\Delta E_v \simeq E_g$ for the tightly bound d levels of the isoelectronic Zn^+ in ZnS. Because of this ease of promoting a d electron in Cu to the valence band, the d electrons can make a large contribution to the susceptibility.

As a severe test of Eq. (14) we can consider the compound Cu_2O. This is an especially interesting crystal since a very large fraction (20 out of 28) of its valence electrons are d electrons. Suppose we attempt to calculate f_i using only the eight s and p electrons per formula unit ($N_e = N_F/v_F = 8/v_F$, where v_F is the formula unit volume); then Eqs. (2)–(8) together with $\epsilon = 6.25^{17}$ result in the *impossible* situation of a negative ionicity

$$f_i < 0 \ .$$

This proves that the d electrons *must* be included in N_F and the plasma frequency Ω_p. If we take $Z_{\mathrm{Cu}} = 11$, then $N_F = 8 + 20 = 28$, and Eqs. (2)–(8) lead to the reasonable result

$$f_i(\mathrm{Cu_2O}) = 0.56 \ . \tag{16}$$

Returning to the noble-metal halides (e.g., CuCl), and using $Z_{\mathrm{Cu}} = 11$ (i.e., $N_F = 18$), yields the ionicities and ionic gaps C listed in Table I. It is instructive to compare this approach with that of Phillips[1] and Van Vechten[2] (PV) who use $N_F = 8$ and assume that the d electrons make only a small (~9%) contribution to the plasma frequency in, say, CuCl (i.e., $D = 1.09$). PV find $f_i = 0.75$ for CuCl, to be compared with our result $f_i = 0.88$. It may be of interest to point out that our ionicity is in good agreement with that of Coulson, Redei, and Stocker,[18] $f_i(\mathrm{CuCl}) = 0.85$. Although PV's ionicity may appear similar to ours, it should be noted that the covalencies $f_c = 1 - f_i$ actually differ by over a factor of 2.

Further evidence supporting our larger ionicities can be obtained from Martin's[19] work on the elastic constants of diamond, zinc-blende, and wurtzite crystals. Martin showed that the reduced shear modulus follows a clear trend when plotted against the ionicity; the only AB crystals that deviate significantly are CuCl, CuBr, and CuI. Assuming these Cu halides do follow this trend, and that it is the PV ionicity scale that is incorrect (for these d-electron crystals), results in $f_i \sim 0.8$–0.9, which is in good agreement with our ionicity determination.

TABLE I. Bond parameters for some zinc-blende(z) and rocksalt(r) noble-metal halides.

Crystal	ϵ	N_F	Z_α^*	σ	C (eV)	E_h (eV)	f_i
CuCl(z)	3.7[a]	18	15.8	1.44	13.2	4.82	0.882
CuBr(z)	4.2[a]	18	15.5	1.41	11.1	4.14	0.877
CuI(z)	5.1[a]	18	14.8	1.35	9.04	3.66	0.859
AgCl(r)	4.0[b]	18	15.3	1.39	15.8	3.17	0.961
AgBr(r)	4.8[b]	18	13.1	1.20	10.4	2.87	0.930
AgI(z)	4.2[b,c]	18	16.4	1.49	9.34	3.08	0.902

[a] D. Chemla, P. Kupecek, C. Schwartz, C. Schwab, and A. Goltzene, IEEE J. Quantum Electron. QE-7, 126 (1971).

[b] Reference 17.

[c] B. F. Levine, W. A. Nordland, and J. W. Shiever, IEEE J. Quantum Electron. (to be published).

Our ionicity for tetrahedral CuCl is greater than the critical ionicity for which a phase change to octahedral coordination is supposed to occur. However, as discussed in I, this is not in disagreement with the PV theory since the latter is only applicable to eight-electron systems. It is, however, significant that the rocksalt crystals AgCl and AgBr are more ionic (see Table I) than the zinc-blende CuCl, CuBr, CuI, and AgI.

To make further progress we generalize Eq. (7) to take these d electrons into account:

$$C^\mu = 14.4\left(S^\mu \frac{Z_\alpha^\mu}{r_0^\mu} - \frac{n}{m} b^\mu e^{-k_s^\mu r_0^\mu} \frac{Z_\beta^\mu}{r_0^\mu}\right)$$

$$= 14.4 b^\mu e^{-k_s^\mu r_0^\mu} \left(\frac{Z_\alpha^{\mu *}}{r_0^\mu} - \frac{n}{m}\frac{Z_\beta^\mu}{r_0^\mu}\right) \ , \tag{17}$$

where we have for convenience defined an effective unscreened noble- or transition-metal core charge

$$Z_\alpha^* \equiv Z_\alpha (S/be^{-kr}) \equiv \sigma Z_\alpha \ , \tag{18}$$

and where Z_α is the number of noble- or transition-metal valence electrons, S is the appropriate noble- or transition-metal-core screening factor (including all the s, p, and d electrons), and be^{-kr} is the usual Thomas–Fermi screening factor for the anion β which *only* includes the s and p electrons (the d electrons are mostly near the metal atom). That is, although the d electrons are more highly delocalized in Cu than in, say, Zn, as indicated by the significant overlap of the noble d electrons with the anion p electrons (i.e., substantial p-d hybridization[5,9–12]), it still seems appropriate to have them mostly situated around the noble- or transition-metal atom, with a maximum reasonable radius of something like $\sim r_0$. This d-electron radius is approximately three times larger than the usual d-core radii[20] (~20 times larger volume) and is consistent with our expectation of their significant delocalization.

Since we have already determined C experimentally (listed in Table I) we can now use Eq. (17) to find Z_α^*. We do this by first obtaining b from Eq. (9) using $\bar{N}_c = 4$ for the tetrahedral zinc-blende (z) crystals and $\bar{N}_c = 6$ for the octahedral rocksalt (r) crystals. These values are $b = 1.42$ and $b = 3.20$ for the z and r, respectively. Using these b's results in the σ and Z_α^* parameters given in Table I.[21] The values $\sigma \sim 1.4$ show that the noble-metal screening factor S is similar to but somewhat higher than the usual s- and p-electron Thomas–

Fermi screening. The effective noble-metal core charge Z_α^* is relatively constant, which is satisfying in view of the similarity of these noble-metal halides. Our value $Z_\alpha^* \sim 15$ should be compared with the very different assumption made by PV, namely, $Z_\alpha^* = 2$. Since in our case $Z_\alpha^* > Z_\beta$ whereas PV have $Z_\alpha^* < Z_\beta$, the *sign* of C is opposite in the two approaches. We have already mentioned several reasons for preferring our larger Z_α^*; this sign difference provides an additional strong reason. As we have demonstrated,[6,13] the anomalous negative sign of the nonlinear optical coefficient in CuCl and CuBr as well as the small value of Millier's Δ in the noble-metal chalcopyrites are completely explained by this sign reversal of C.

IV. *AB* TRANSITION-METAL COMPOUNDS

In order to treat the transition-metal compounds, further care is required since they also possess *unfilled* d shells. The empty conduction-band d levels this implies must be included in addition to the loosely bound valence d electrons, since transitions to these empty d levels will increase the susceptibility. This situation is rather similar to the previously considered[2,3] Ca, Sr, and Ba crystals. Thus, in analogy with Eqs. (10) and (11), we suggest

$$4\pi\chi = (\hbar\omega_p)^2 A\left(\frac{1}{E_g^2} + \frac{\Gamma}{E_d^2}\right) , \tag{19}$$

where Γ is the fraction of empty d levels, i.e., the number of holes in the d shell per formula unit divided by the total number valence electrons per formula unit (includes s, p, and d electrons). For future reference,

$$\Gamma = \frac{\text{number of } d \text{ holes}}{\text{number of valence electrons}} . \tag{20}$$

That is, Γ describes the fractional increase in oscillator strength relative to $\hbar\Omega_p$. For example, in CuCl, $\Gamma = 0$; in FeO, there are 14 valence electrons (two s and six d electrons from Fe and two s and four p electrons from O) and four d holes per formula unit making $\Gamma = \frac{4}{14}$; for TiO_2, $\Gamma = \frac{8}{16}$, etc.

We also need to know E_d, the average gap to these conduction-band d levels. The weak binding energy of the d electrons in these transition-metal atoms suggests the simple estimate

$$E_d \simeq E_g . \tag{21}$$

Note that this is similar to the situation in Ca, Sr, and Ba for which $\Delta E_c \ll E_g$ in Eq. (11). Since the d-electron contributions enter Eq. (19) as Γ/E_d^2 the errors in our simplified d-electron picture tend to cancel; i.e., we have probably slightly overestimated their importance in both Γ and E_d.

For convenience we rewrite Eq. (19) as

$$4\pi\chi = (\hbar\omega_p)^2 A(1+\Gamma)/E_g^2 . \tag{22}$$

Since $(1+\Gamma) \geq 1$ we see that, as expected, these conduction-band d levels also increase the susceptibility, as do the previously discussed [i.e., Eq. (15)] valence d electrons which enhance ω_p. In analogy with Eqs. (12) and (13) we may now define an ionic gap C' and prescreening factor b', which are modified by these *conduction*-band d levels. Thus,

$$(E_g^{\mu\prime})^2 = (E_h^\mu)^2 + (C^{\mu\prime})^2 , \tag{23a}$$

$$(E_g^{\mu\prime})^2 = (E_g^\mu)^2/(1+\Gamma) , \tag{23b}$$

$$C^{\mu\prime} = 14.4(b^{\mu\prime})e^{-k_s^\mu r_0^\mu}\left(\frac{Z_\alpha^{\mu *}}{r_0^\mu} - \frac{n}{m}\frac{Z_\beta^\mu}{r_0^\mu}\right) . \tag{23c}$$

A useful relationship between the primed and unprimed quantities can be easily obtained from the above, namely,

$$b = b'\left(\frac{1+\Gamma}{1-\Gamma f_c/f_i}\right)^{1/2} . \tag{24}$$

This shows, for example, that when there are no conduction-band d levels as in the noble metals then $\Gamma = 0$ and $b = b'$; as Γ increases so does the difference between the primed and unprimed quantities.

We can now obtain the desired bond parameters for these transition-metal compounds. For example, we can obtain C, E_h, E_g, f_i, f_c from Eqs. (1)–(6). We show in I that for conduction-d-band compounds (e.g., Ca, Sr, and Ba crystals) the primed prescreening factor b' is closely given by Eq. (9), i.e.,

$$b' \simeq 0.089\bar{N}_c^2 . \tag{25}$$

Thus, the other bond parameters such as b, Z_α^*, etc., can now be obtained with the aid of Eqs. (24) and (25). These parameters are given in Table II for some of the interesting zinc-blende and rocksalt transition-metal compounds.

TABLE II. Bond parameters for some zinc-blende(z) and rocksalt(r) transition-metal compounds.

Crystal	ϵ	N_F	Z_α^*	σ	C (eV)	E_h (eV)	f_i
ScN(r)	11[a]	8	3.9	1.30	7.98	5.50	0.678
MnS(z)	6.4[b]	13	10.7	1.53	8.41	4.42	0.784
MnO(r)	4.6[b]	13	10.0	1.43	15.4	5.48	0.887
FeO(r)	4.9[b]	14	9.9	1.24	15.5	5.92	0.873
CoO(r)	5.3[c]	15	9.8	1.09	15.0	6.09	0.858
NiO(r)	5.7[c]	16	9.7	0.97	14.7	6.40	0.841

[a] G. Harbeke, E. Meier, and J. P. Dismukes, Optics Commun. 4, 335 (1972).

[b] Reference 17.

[c] P. J. Gielisse, J. N. Plendl, L. C. Mansur, R. Marshall, S. S. Mitra, R. Mykolajewycz, and A. Smakula, J. Appl. Phys. 36, 2446 (1965).

As previously noted for the noble-metal halides the screening factors for all of these systems are significantly larger than the usual s- and p-electron screening factor (i.e., $S > be^{-kr_0}$). This seems reasonable in view of the intermediate delocalization of these d electrons (i.e., although they are significantly more delocalized than the usual d-core states in non-noble-metal and non-transition-metal atoms, they are nevertheless more localized than the s- and p-valence electrons). This means that these d electrons tend to have more atomiclike properties than the s and p electrons. Since the atomic screening (i.e., the Slater screening[22]) is less effective than the free-electron screening (i.e., the Thomas-Fermi screening be^{-kr_0}), it seems reasonable that $S > be^{-kr_0}$. To be more specific we consider as an example ZnS, in which the Zn core electrons are very tightly bound (not at all like the loosely bound d electrons in, say, Cu). For these Zn d electrons the Slater screening produced by each of the other nine d electrons is 0.35, yielding an effective one-electron core charge of $Z_{\text{eff}} = 12 - (0.35)(9) = 8.85$. Thus, the screening $S = 8.85/12 = 0.74$ is not very effective as can be seen from $\sigma \equiv S/be^{-kr_0} = 5.9$, which is much larger than the σ values in Tables I and II. Of course, these d electrons are very tightly bound ($\Delta E_v \simeq E_g$ for ZnS) and do not contribute significantly to chemical bonding or to the susceptibility. Thus, the observation that $\sigma \gtrsim 1$ in Tables I and II seems perfectly reasonable and the fact that this ratio is relatively close to unity (typically $\sigma \sim 1.3$ compared to $\sigma \sim 6$ for the tightly bound Zn) shows that, as expected, these noble-metal and transition-metal d electrons are not very atomiclike; i.e., they are relatively delocalized and contribute substantially to the susceptibility.

In Fig. 1 we have plotted Z^* for the third-row elements. As would be expected there is a general increase in Z^* from K to Cu; however, between Ni and Cu there is a rather sharp increase. This is due to the fact that Cu has a filled d shell and hence the d electrons are more tightly bound than those in Ni. Hence, as indicated by our previous discussion on the tightly bound d states in Zn, σ will be greater than unity ($\sigma = 1.44$ for CuCl), and thus $Z^* > 11$. In Ni the d electrons have an unusually small binding energy[8] (the separation of the s and d levels is less than 0.1% of E_g for NiO), σ will be close to unity, and thus $Z^* \simeq 10$ as expected.

As we go across the row from Ni to Mn, the binding energy[8] of the d electrons increases; hence, σ also increases. Since Mn possesses a half-filled d shell, these electrons are more tightly bound than usual, and $\sigma = 1.43$, which is similar to the value in CuCl. This increase in the screening factor σ from Ni to Mn compensates for the decrease in the number of d electrons; consequently, Z^* remains relatively constant.

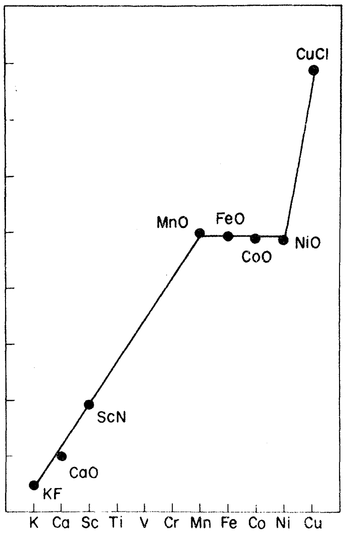

FIG. 1. Plot of the effective charge Z^* of the noble- or transition-metal atom for atoms in the third periodic row. The compounds which were used to determine Z^* are indicated.

As a check on the basic reasonableness of this idea, we plot (in Fig. 2) σ against $(\Delta E_v/E_g)$, where ΔE_v is the magnitude of the energy separation between the s and d atomic levels (e.g., $3d^8 4s^2$ and $3d^9 4s$ in Ni). Since σ may well depend on other variables in addition to $\Delta E_v/E_g$, we have tried to minimize the effects of these other parameters by choosing the similar transition-metal oxides NiO, CoO, FeO, and MnO. There is a clear upward trend in Fig. 2 as anticipated, starting from $\sigma \simeq 1$ when $\Delta E_v/E_g \simeq 0$. This suggests the reasonable conclusion that in these simple compounds the screening for the s and d electrons is similar when they are close in energy.

As an example of the use of these bond parameters (ionicity, effective core charge Z^*_α, ionic gap, etc.) we will now discuss the very interesting problem of the metallic or insulating nature of the transition-metal oxides. This important problem has received a lot of attention and a great deal of progress has been made towards a rigorous fundamental understanding of the details of the band structure[5] in these materials. However, owing to the difficulty of treating the d electrons properly, this behavior is not completely understood; e.g., some of these transition-metal oxides are predicted to be metals whereas in fact they are excellent insulators.[5]

It is interesting to speculate about this difficult problem from the viewpoint of our highly simplified model for the average bond properties. Since, as Table III shows, the metallic and insulating na-

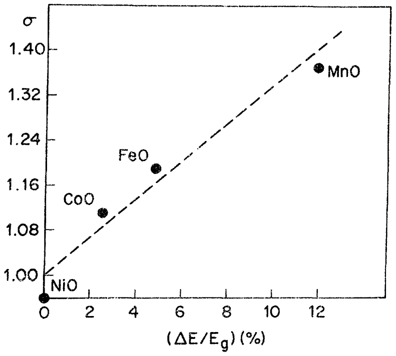

FIG. 2. Plot of $\sigma = Z^*/Z$ against the energy separation of the atomic *s* and *d* levels, for the rocksalt transition-metal oxides.

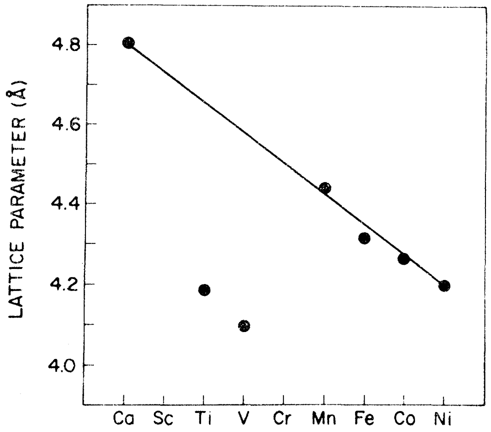

FIG. 3. Trends in the nearest-neighbor distances for the rocksalt transition-metal oxides.

ture of these oxides follows a simple and symmetrical pattern, it is conceivable that a detailed band theoretical approach may not be necessary. If we consider the effective charge Z_α^* for Mn in MnO ($Z_\alpha^* = 10.0$), we note that $Z_\alpha^* > Z_\beta$ (for oxygen $Z_\beta = 6$). However, as we go across this transition row (Mn, Cr, V, Ti, Sc, Ca, and K), Z_α^* decreases until for Ca($Z_\alpha = 2$) $Z_\alpha^* < Z_\beta$. Thus, between CaO and MnO a point is reached when $Z_\alpha^* \simeq Z_\beta$, implying $C \simeq 0$ and $f_i \simeq 0$. In fact, as Fig. 1 shows, the line drawn between K and Mn crosses 6 between Ti and V; hence, for TiO and VO, we expect that $f_i \simeq 0$.

If $C = 0$ for a crystal in the *rocksalt* structure it will be metallic[2] (this is *not* necessarily true for other structures). Consequently we would expect VO and TiO to be metals, and the crystals $Z_\alpha^* = 3$ (ScO) and $Z_\alpha^* = 6$ (CrO) to have small C values and therefore be unstable. Finally we would expect that CaO, MnO, FeO, CoO, and NiO, which all have large ΔZ (i.e., $Z_\alpha^* - Z_\beta$) and C values, to be stable insulators. Thus, this behavior of the fundamental core charge Z_α^* can explain the trends in the metallic-insulator phases given in Table III for the *similar*[23] set of transition-metal oxides.

A related problem is the anomalously small lattice constant[5] of VO and TiO as shown in Fig. 3. We suggest the following explanation. Since ΔZ and hence f_i are small in these two oxides, the lattice constant will be anomalously small as it is well known that covalent bonds tend to be shorter than ionic ones. For example, both the lattice constant (9.833 Å) and the ionicity (0.790) of MgS are smaller than these quantities in NaCl (10.639 Å and 0.936).

TABLE III. Rocksalt transition-metal oxides formed from the second row of the Periodic Table. The behavior (I = insulator, U = unstable, M = metal) of these compounds is indicated.

CaO	ScO	TiO	VO	CrO	MnO	FeO	CoO	NiO
I	U	M	M	U	I	I	I	I

V. COMPLEX STRUCTURES

Since we have been reasonably successful in treating some of the cubic *AB* transition-metal and noble-metal compounds, it is natural to wonder whether these ideas will be fruitful in more complex systems. We first consider ZrF_4 and HfF_4 for two reasons. They have four anions per cation (the largest previously studied ratio was 3 : 1, e.g., $NaClO_3$ in I) enabling us to examine further the validity of our generalizations, and second, $|\Delta Z| \simeq 4(7) - 4 = 24$ is determined almost entirely by the four F atoms, making any deviation of Zr or Hf from our estimate $Z^* \simeq 4$ rather unimportant.

The resulting parameters for these crystals are quite reasonable. The ionicities are both large ($f_i = 0.93$, 0.94) as expected from the very large ΔZ, and the experimental prescreening factors ($b' = 0.81$, 0.87) are in good agreement with the value $b' = 0.91$ calculated from Eq. (25).

Rutile, TiO_2, is interesting since it is a prototype for several ferroelectrics (e.g., $BaTiO_3$). The results for rutile [assuming $b'(TiO_2) = b(GeO_2)$ for these isomorphic crystals] are shown in Table IV. It is noteworthy that the ionicity of $TiO_2 = 0.69$ is rather close to that of GeO_2 (0.73). This is satisfying since both Ti and Ge are in the same row and have approximately four valence electrons. Thus, TiO_2 is a significantly covalent crystal, which explains its relatively large index of refraction.

Another interesting set of crystals is Cr_2O_3 and Fe_2O_3 since we can directly compare their properties with the isomorphic corundum crystal Al_2O_3. The ionicity values for these two transition-metal crystals are quite reasonable, lying close to that for Al_2O_3. The b' values for Cr_2O_3 and Fe_2O_3 ob-

TABLE IV. Bond properties for some A_mB_n transition-metal compounds. If available, data for isomorphic non-*d*-electron crystals (e.g., GeO_2, Al_2O_3) are also presented. For the latter crystals $b = b'$.

	ϵ	$\bar{N}_c$	N_F	Γ	b'	Z_α^*	C (eV)	E_h (eV)	f_i
ZrF_4	2.2[a]	$\frac{16}{5}$	32	0.25	0.81	$\simeq 4$	23.4	6.3	0.932
HfF_4	2.1[a]	$\frac{16}{5}$	32	0.25	0.87	$\simeq 4$	24.6	6.2	0.940
GeO_2	4.0[a]	4	16	0.0	1.16	···	13.6	8.30	0.730
TiO_2	6.1[b]	4	16	0.5	1.16	7.1	11.1	7.51	0.686
Al_2O_3	3.1[b]	$\frac{24}{5}$	24	0.0	1.87	···	15.7	7.93	0.796
Cr_2O_3	5.3[a]	$\frac{24}{5}$	30	0.333	2.05	5.1	13.4	7.17	0.777
Fe_2O_3	7.3[a]	$\frac{24}{5}$	34	0.235	2.05	5.8	10.5	7.26	0.677

[a] Reference 17.

[b] *American Institute of Physics Handbook*, 2nd ed., edited by D. E. Gray (McGraw-Hill, New York, 1963).

tained from Eq. (25) result in the Z_α^* values given in Table IV. These effective core charges, Z_α^*, are reasonably close to the expected values of $Z_\alpha = 6$ and 8 for Cr and Fe, respectively; however, $Z_\alpha^* \lesssim Z_\alpha$ for these compounds whereas the simpler systems considered previously had $Z_\alpha^* > Z_\alpha$. In view of the relative complexity of these systems, this difference in screening behavior is not very surprising.

VI. $LiNbO_3$ AND $LiTaO_3$

Because of the very low covalency and susceptibility[24] of the Li-O bond relative to the Ta-O or Nb-O bond, we can simplify the treatment of $LiNbO_3$ and $LiTaO_3$ by assuming that essentially all of the susceptibility resides in the transition-metal–oxygen bond. Of course, the Li-O bond cannot be completely neglected since it occupies a substantial fraction of the unit-cell volume. Using the methods described in I [i.e., $v_b \propto d^3$] we can readily determine that the volume of the Nb-O bond is $v_b = 3.935$ Å^3. To determine the other bond parameters it should be remembered that only one-half of the oxygen atoms are bonded to the transition-metal atoms; i.e., the formula $LiNbO_3$ can be thought of as $(LiO_{3/2})(NbO_{3/2})$. For example, the total number of s, p, and d electrons in the Nb-O bonds per formula unit is $N_F = 5 + 6(\frac{3}{2}) = 14$, the number of s and p electrons per Nb-O bond is $n_v = [1 + 6(\frac{3}{2})]/6 = \frac{10}{6}$, and the s- and p-electron density $(N_e)_{sp}$ to be used in evaluating the Thomas–Fermi screening factor $e^{-k r_0}$ is $(N_e)_{sp} = n_v / v_b$, etc. For clarity all of the relevant bond parameters for $LiNbO_3$ and $LiTaO_3$ are given in Table V. It can be seen that these two isomorphic crystals have rather similar properties. Their ionicities seem quite reasonable, being significantly more covalent than SrO or BaO[2,3] ($f_i = 0.93$), which might have been expected from the ferroelectricity (i.e., acentricity) of the niobate and tantalate. Also their effective core charges $Z_\alpha^* \simeq 5$ are close to the value expected.

VII. $A^{\text{I}}B^{\text{III}}C_2^{\text{VI}}$—e.g., $AgGaS_2$

So far we have discussed d-electron compounds in which the susceptibility of only one type of bond was important. It seems worthwhile to see whether multibond systems with several different types of contributing bonds can also be treated. The magnitude of the d-electron effects in these more complex crystals is comparable to that occurring in the simpler cyrstals already considered. This is clearly demonstrated by recent electroreflectance work[25] on $CuGaS_2$, $AgGaS_2$, and other related compounds, which shows that the uppermost valence bands are ~20% d-like in Ag compounds and ~40% d-like in Cu compounds. Further support for the importance of these d electrons can be obtained from the anomalously small value of the nonlinear optical susceptibility in these compounds,[26] e.g., $\Delta(CuInS_2) \simeq 0.2\Delta(CdS)$. By including the large d-electron contribution to this nonlinearity, this behavior can be quantitatively explained.[6,13]

In I we demonstrated a method for decomposing non-d-electron crystals such as $A^{\text{I}}B^{\text{III}}C_2^{\text{VI}}$, e.g., $LiGaO_2$, $A^{\text{II}}B^{\text{IV}}C_2^{\text{V}}$, e.g., $ZnGeP_2$, and $A^{\text{III}}B^{\text{V}}C_4^{\text{VI}}$, e.g., $AlPO_4$, into their constituent bond properties. In order to obtain these individual bond variables, we need to know the susceptibility χ^μ for each type of bond. Since from Eq. (1) we only know the total net crystal χ, this separation is not trivial. The procedure demonstrated in I involves plotting $(4\pi\chi)^{-1}$ against $(\Delta Z)^2$ as shown in Fig. 4, for the Ga-S bond in, say, $AgGaS_2$. Note that the known AB crystals (filled circles) are composed of atoms in the same row of the Periodic Table as the unknown Ga-S bond. By reading off the χ appropriate to $\Delta Z = 3$, we can directly obtain $4\pi\chi(\text{Ga-S}) = 5.84$.

Because of the presence of the noble-metal d electrons, we do not know ΔZ *a priori* for, say, the Ag-S bond as we do for the non-d-electron bonds such as Ga-S. Therefore, we cannot simply obtain $\chi(\text{Ag-S})$ from a plot such as in Fig. 4. However, this does not really present a problem since we can determine it from Eq. (1), i.e.,

$$\chi(ABC_2) = \tfrac{1}{2}[\chi(A-C) + \chi(B-C)] . \qquad (26)$$

For example, Eq. (26) says that in $AgGaS_2$,

$$\chi(AgGaS_2) = \tfrac{1}{2}[\chi(\text{Ag-S}) + \chi(\text{Ga-S})] . \qquad (27)$$

Since we already know $\chi(\text{Ga-S})$ and the total mea-

TABLE V. Properties of the Nb-O and Ta-O bonds in $LiNbO_3$ and $LiTaO_3$. The prescreening factor b' is obtained from Eq. (25).

	$LiNbO_3$ (Nb-O bond)	$LiTaO_3$ (Ta-O bond)
ϵ	4.4^{a}	4.0^{a}
$\bar{N}_c$	$\frac{21}{4}$	$\frac{21}{4}$
N_b (10^{24} cm^{-3})	0.1131^{b}	0.1135^{c}
χ_b (Å^3)	2.39	2.10
n_v	$\frac{10}{6}$	$\frac{11}{6}$
v_b (Å^3)	3.935	3.761
e^{-kr_0}	0.0941	0.0911
N_F	14	14
ω_p (eV)	28.6	29.3
Γ	0.429	0.500
b'	2.45	2.45
b	3.07	3.14
Z_α^*	5.3	4.8
$(Z_\alpha^* + (n/m)Z_\beta)$	14.3	13.8
C (eV)	15.5	17.4
E_h (eV)	7.12	7.30
f_i	0.825	0.850

[a] See, for example, S. Singh, in *Handbook of Lasers* (Chemical Rubber Co., Cleveland, Ohio, 1971).

[b] S. C. Abrahams, J. M. Reddy, and J. L. Bernstein, J. Phys. Chem. Solids 27, 997 (1966).

[c] S. C. Abrahams, W. C. Hamilton, and A. Sequeira, J. Phys. Chem. Solids 28, 1693 (1967).

sured crystal susceptibility $\chi(AgGaS_2)$, we can easily obtain χ(Ag-S).

The $CuGaS_2$ crystal requires some further discussion since the sample in which the susceptibility was measured[26] was actually *nonstoichiometric*, having a formula $Cu_{0.88}Ga_{1.04}S_2$, and the randomness introduced by this disorder will change C, E_g, f_i, and other properties. We treat this complication in the simplest possible way by assuming a hypothetical crystal with a lowered Cu-S susceptiblity due to the fewer number of such bonds, and a higher χ'(Ga-S) due to the larger number of bonds. That is, we take the adjusted $Ga_{1.04}S$ bond susceptibility $4\pi\chi'(\text{Ga-S}) = 6.07$ to be 4% higher than for the stoichiometric compound since there are 4% more Ga-S bonds. Owing to the small departure from stoichiometry for this bond, the disorder is small and this correction should be accurate enough. The effective lower susceptibility for the $Cu_{0.88}S$ bonds, χ'(Cu-S), is then obtained from the total measured susceptibility using Eq. (26), i.e.,

$$\chi(Cu_{0.88}Ga_{1.04}S_2) = \tfrac{1}{2}[\chi'(\text{Cu-S}) + \chi'(\text{Ga-S})] \ . \qquad (28)$$

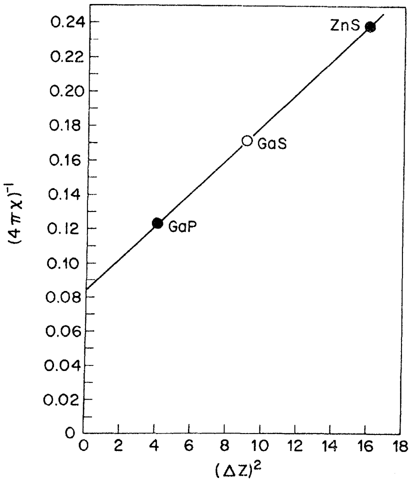

FIG. 4. Inverse susceptibility against $(\Delta Z)^2$ for AB compounds formed from the second and third periodic rows (i.e., GaP and ZnS). From this plot the susceptibility of Ga-S can be determined.

This yields $4\pi\chi'(\text{Cu-S}) = 4.43$, which is in reasonable agreement with 88% of the stoichiometric value of $4\pi\chi(\text{CuS}) = 5.52$, i.e., $4\pi\chi'(\text{Cu-S}) = (0.88)(5.52) = 4.86$. This comparison shows that there is only a relatively small (~ 10%) change from one crystal to another. The $CuGaS_2$ bond parameters f_i, C, and E_h can now be obtained using the values $4\pi\chi'(\text{Cu-S}) = 4.43$ and $4\pi\chi'(\text{Ga-S}) = 6.07$, and they are given in Table VI along with the other noble-metal chalcopyrites considered.

Table VI shows that $f_i(\text{Ag-S}) > f_i(\text{Cu-S})$ and that $f_i(\text{In-S}) > f_i(\text{Ga-S})$; this is as expected since[2] $f_i(\text{AgCl}) > f_i(\text{CuCl})$ and $f_i(\text{InP}) > f_i(\text{GaP})$. A further noteworthy point is that, as expected, the b values

TABLE VI. Decomposition of some terniary chalcopyrites $A^{I}B^{III}C_2^{VI}$ into their constituent bond properties. Bond lengths d were estimated from covalent radii tables (Refs. 20) with corrections for the fact that $n_v \neq 8$.

Crystal	ϵ	d (Å)	b	E_h (eV)	C (eV)	f_i	Z_α^*
$CuGaS_2$	6.25^{a}						
Cu-S	5.43	2.389	1.87	4.58	9.95	0.825	11.1
Ga-S	7.07	2.324	1.87	4.91	5.60	0.565	···
$CuInS_2$	6.76^{a}						
Cu-S	6.53	2.416	2.13	4.46	8.52	0.785	9.9
In-S	6.99	2.485	2.13	4.16	5.49	0.636	···
$CuGaSe_2$	7.40^{b}						
Cu-Se	6.76	2.492	1.82	4.13	7.87	0.784	10.5
Ga-Se	8.04	2.407	1.82	4.50	5.10	0.563	···
$AgGaS_2$	5.76^{a}						
Ag-S	4.68	2.559	1.87	3.87	9.87	0.867	11.9
Ga-S	6.84	2.280	1.87	4.90	5.64	0.570	···
$AgGaSe_2$	6.66^{b}						
Ag-Se	5.28	2.642	1.80	3.57	8.56	0.852	11.6
Ga-Se	8.04	2.421	1.80	4.43	5.02	0.561	···
$AgInSe_2$	6.97^{b}						
Ag-Se	5.53	2.670	1.94	3.48	8.15	0.846	11.1
In-Se	8.41	2.572	1.94	3.82	4.71	0.604	···

[a] G. D. Boyd, H. Kasper, and J. H. McFee, IEEE J. Quantum Electron. QE-7, 563 (1971).

[b] G. D. Boyd, H. M. Kasper, J. H. McFee, and F. G. Storz, IEEE J. Quantum Electron. QE-8, 900 (1972).

for Ga-S and In-S are rather similar (1.87 and 2.13, respectively) and are also close to those found[3] in the analogous $A^{I}B^{III}C_2^{VI}$ compound $LiGaO_2$ [i.e., from I we obtain b(Li-O) = 1.91 and b(Ga-O) = 2.34].

Now that we have the noble-metal-bond C parameters, we could use Eq. (17) to obtain Z_α^* for these bonds if we knew the b parameters. This can be done by comparison with a similar crystal as was previously done for TiO_2, Cr_2O_3, and Fe_2O_3 (Table IV). That is, we can compare the noble-metal $A^{I}B^{III}C_2^{VI}$ compounds with the non-noble metal $A^{I}B^{III}C_2^{VI}$ compounds (e.g., $LiGaO_2$). We previously noted the similarity of the b's for the bonds in $LiGaO_2$, i.e., b(Li-O) $\simeq b$(Ga-O), which suggests the simple approximation

$$b(A^{I}\text{-}C^{VI}) \simeq b(B^{III}\text{-}C^{VI}) \tag{29}$$

for the noble-metal $A^{I}B^{III}C_2^{VI}$ compounds. The Z_α^* values obtained from this are given in Table VI. These effective core charges seem reasonable being close to the value $Z_\alpha^* \simeq 11$ expected [i.e., Eq. (14)]. They are a little less than those found in the noble-metal halides (Table I) but as we previously noted for Cr_2O_3 and Fe_2O_3, these more complex structures may well have slightly different screening behavior. Thus, for all the systems we have considered the d-electron screening is within a factor of ~2 (usually much closer) of the s- and p-electron Thomas-Fermi screening factor.

VIII. SUMMARY

In view of the successes achieved by the dielectric theory of electronegativity for the simple AB crystals considered by Phillips and Van Vechten, it was felt worthwhile to generalize these ideas to more complex systems. In I we succeed in treating a wide range of crystal structures spanning virtually the entire ionicity range. In this paper these ideas have been extended to include the important d-electron contributions in noble- and transition-metal crystals. These extensions should prove useful in understanding a number of interesting physical problems. (See Ref. 4 for an indication of the wide variety of problems in which the PV dielectric theory has been used.) As an example we have used these ionicities and other bond parameters to give a quantitive understanding of the nonlinear optical susceptibility for all the acentric crystals discussed in this paper as well as in I.[6,13]

---

[1] J. C. Phillips, Phys. Rev. Lett. **20**, 550 (1968); Rev. Mod. Phys. **42**, 317 (1970); *Chicago Lectures in Physics* (University of Chicago Press, Chicago, 1969).

[2] J. A. Van Vechten, Phys. Rev. **182**, 891 (1969); Phys. Rev. **187**, 1007 (1969).

[3] B. F. Levine (unpublished), hereafter referred to as I.

[4] See, for example, J. A. Van Vechten, in *Proceedings of the Tenth International Conference on the Physics of Semiconductors, Cambridge, Mass., 1970,* edited by S. P. Keller, J. C. Hensel, and F. Stern (U. S. Atomic Energy Commission, Oak Ridge, Tenn, 1970), p. 602; J. A. Van Vechten and T. K. Bergstresser, Phys. Rev. B 1, 3351 (1970); G. B. Stringfellow, J. Phys. Chem. Solids 33, 665 (1971); R. M. Martin, Phys. Rev. B 1, 4005 (1970); P. Lawaetz, Phys. Rev. Lett. 26, 697 (1971); J. C. Phillips and J. A. Van Vechten, Phys. Rev. Lett. 23, 1115 (1969); J. C. Phillips and J. A. Van Vechten, Phys. Rev. B 2, 2147 (1970); P. Lawaetz, Phys. Rev. B 4, 3460 (1971); P. Y. Yu, M. Cardona, and F. H. Pollak, Phys. Rev. B 3, 340 (1971); I. P. Kaminow and E. H. Turner, Phys. Rev. B 5, 1564 (1972); Chr. Flytzanis, Phys. Rev. Lett. 23, 1336 (1969); J. P. Walter and M. L. Cohen, Phys. Rev. B 4, 1877 (1971); A. Baldereschi and J. J. Hopfield, Phys. Rev. Lett. 28, 171 (1972); B. F. Levine, Phys. Rev. Lett. 22, 787 (1969); Phys. Rev. Lett. 25, 440 (1970); J. C. Phillips and J. A. Van Vechten, Phys. Rev. 183, 709 (1969); D. A. Kleinman, Phys. Rev. B 2, 3139 (1970).

[5] See, for example, D. Adler, in *Solid State Physics*, edited by F. Seitz, D. Turnbull, and H. Ehrenreich (Academic, New York, 1968); L. F. Mattheiss, Phys. Rev. B **5**, 290 (1972); Phys. Rev. B **5**, 306 (1972); Phys. Rev. B **5**, 315 (1972), and references therein.

[6] B. F. Levine, Phys. Rev. B 7, 2600 (1973) (following paper).

[7] For bond polarizabilities in organic systems see, for example, C. G. Le Fevre and R. J. W. Le Fevre, Rev. Pure Appl. Chem. **5**, 261 (1955).

[8] R. B. Bacher and S. Goudsmit, *Atomic Energy States* (McGraw-Hill, New York, 1932).

[9] M. Cardona, Phys. Rev. **129**, 69 (1963).

[10] K. S. Song, J. Phys. (Paris) **28**, 195 (1967); J. Phys. Chem. Solids **28**, 2003 (1967).

[11] J. B. Anthony, A. D. Brothers, and D. W. Lynch, Phys. Rev. B **5**, 3189 (1972).

[12] S. Kono, T. Ishii, T. Sagawa, and T. Kobayasi, Phys. Rev. Lett. **28**, 1385 (1972).

[13] R. C. Miller, W. A. Nordland, S. C. Abrahams, J. L. Bernstein, and C. Schwab, Phys. Rev. (to be published); B. F. Levine, C. G. Bethea, V. G. Lambrecht, Jr., and M. Robbins, IEEE J. Quan. Elec. QE-9, Feb. 1973. B. F. Levine, W. A. Nordland, and J. W. Shiever, IEEE J. Quan. Elec. QE-9, Apr. 1973 (to be published).

[14] R. C. Miller, S. C. Abrahams, R. L. Barns, J. L. Bernstein, W. A. Nordland, and E. H. Turner, Solid State Commun. **9**, 1463 (1971).

[15] S. H. Wemple and M. DiDomenico, Jr., Phys. Rev. B **3**, 1338 (1971).

[16] In Ref. 2 it is shown that the d-core correction factor D for Sn is 1.46. It should be noted that for crystals not containing noble or transition d electrons, the *d-core* states modify the plasma frequency Ω_p through the *core* correction factor $D > 1$ (N_F is unaffected by the tightly bound core states), whereas noble and transition metal d electrons enhance N_F (any *d-core* effects are negligible by comparison, i.e., $D = 1$). For example, Cu does not even have a d core, while the 3d core of Ag is very tightly bound indeed.

[17] Landolt-Börnstein, *Zahlenwerte und Functionen* (Springer, Berlin, 1962), Vol. II, Pt. 8.

[18] C. A. Coulson, L. B. Redei, and D. Stocker, Proc. R. Soc. Lond. **270**, 352 (1962).

[19] R. M. Martin, Phys. Rev. B 1, 4005 (1970); Phys. Rev. B 6, 4546 (1972) (see Fig. 2.).

[20] J. A. Van Vechten and J. C. Phillips, Phys. Rev. B **2**, 2160 (1970).

[21] Although there is a sign ambiguity in the experimental determination of C (and ΔZ), this usually presents no

difficulty as only one of the two possible Z^*_α values is reasonable.

[22] J. C. Slater, Phys. Rev. **36**, 57 (1930).

[23] This similarity is important, since varying the type of anion (e.g., MnS) or crystal structure (e.g., TiO_2) will complicate the simple regularities exhibited in Table III.

[24] C. R. Jeggo and G. D. Boyd, J. Appl. Phys. **41**, 2741 (1970).

[25] J. L. Shay, B. Tell, H. M. Kasper, and L. M. Schiavone, Phys. Rev. B **5**, 5003 (1972).

[26] G. D. Boyd, H. Kasper, and J. H. McFee, IEEE J. Quantum Electron. **7**, 563 (1971).

PHYSICAL REVIEW B VOLUME 7, NUMBER 6 15 MARCH 1973

Bond-Charge Calculation of Nonlinear Optical Susceptibilities for Various Crystal Structures

B. F. Levine

Bell Laboratories, Murray Hill, New Jersey 07974

(Received 17 August 1972)

A simple localized-bond-charge model for the calculation of nonlinear optical susceptibilities is presented. We find that there are three important contributions to the nonlinearity, namely, the bond ionicity, the difference in atomic radii of the bonded atoms, and d-electron contributions. By including these effects we are able with one simple theory to accurately treat a wide variety of different types of compounds including $A^{\rm III}B^{\rm V}$ (e.g., GaAs, GaP, InSb), $A^{\rm II}B^{\rm VI}$ (e.g., ZnS, ZnO, BeO), $A^{\rm I}B^{\rm VII}$ (e.g., CuCl, CuBr, CuI), $A^{\rm IV}B_2^{\rm VI}$ (e.g., SiO_2), multibond crystals [e.g., $A^{\rm I}B^{\rm III}C_2^{\rm VI}$ ($LiGaO_2$, $AgGaS_2$, $CuInS_2$, $CuGaSe_2$), $A^{\rm II}B^{\rm IV}C_2^{\rm V}$ ($CdGeP_2$, $CdGeAs_2$, $ZnGeP_2$), $A^{\rm III}B^{\rm V}C_4^{\rm VI}$ ($AlPO_4$), also KH_2PO_4], highly anisotropic crystals (e.g., HgS, Se, Te), as well as ferroelectrics (e.g., $LiNbO_3$, $Ba_2NaNb_5O_{15}$, $LiTaO_3$).

I. INTRODUCTION

There has been a substantial effort[1–35] devoted to understanding the origin of the linear[1,2] χ_{ij} and nonlinear optical susceptibility d_{ijk}, defined as

$$P_i(t)=\chi_{ij}E_j(t)+2d_{ijk}E_j(t)E_k(t)\,, \tag{1}$$

where P is the time-dependent polarization produced by an oscillating electric field $E(t)=E\cos\omega t$. Part of this interest in d_{ijk} has been motivated by the large nonlinearities observable with high-power lasers, which lead to such practical devices as efficient harmonic generators, optical mixers, and tunable parametric oscillators.[36] This nonlinearity d_{ijk} is also of great fundamental interest since it is sensitive to the asymmetric part of the charge distribution. That is, d_{ijk} vanishes for a free isolated atom, and hence its magnitude and sign in a crystal are strongly related to atomic interactions in solids, e.g., chemical bonding.

There have been many types of theoretical calculations of the nonlinear optical susceptibility. One approach starts with a perturbation expansion which expresses d_{ijk} in terms of complex sums of matrix elements and energy denominators.[3–10] This first-principles method is appealing since if one knew the complete band structure of the solid, one could directly evaluate d_{ijk} using no adjustable parameters. It is important to note that, since the many terms in the perturbation expressions tend to cancel one another, highly accurate wave functions are necessary (except in the x-ray region where an exact evaluation of the dominant term is possible).[11]

An important advance in greatly simplifying these complex-matrix-element sums was made by Robinson,[12] who related the nonlinear susceptibility to the octupole moment of the ground-state charge distribution. A similar approach using tetrahedral bonding orbitals for the ground-state wave function was later used by Jha and Bloembergen.[13] Flytzanis and Ducuing[14] did a more accurate calculation along these lines, using molecular orbitals determined from a four-parameter variational procedure. Another approach to the problem of simplifying the complex expressions for the nonlinear susceptibility is the constant-matrix-element approximation.[15–17] As shown by Aspnes[16] and Bell[17] contributions to the nonlinearity from a number of different points in the Brillouin zone must be included, with the result depending strongly on the various energy gaps involved. Coulomb interactions (related to local-field effects) have also been shown to be important.[16]

Other simple models for acentric solids include Miller's rule,[18] the free-electron model,[19] the anharmonic-oscillator model,[20–24] experimentally determined bond nonlinearities,[25–27] electric-field-induced energy-band shifts in ferroelectrics,[28] a charge-transfer model,[29] a relationship between the nonlinearity and the polarization in polar materials,[30] a two-band model using the Phillips and Van Vechten dielectric theory,[31,32] and the bond-charge model.[33–35]

This paper discusses the latter approach, which gives better experimental agreement than previous