its variation with x, and its invariance with grain size are in quantitative agreement with theory.[4] The increase in ρ_0 with annealing is attributed to a decrease in the number density of grains.

Finally we point out that certain device applications require stable, high-resistance films with a low temperature coefficient of resistivity. This combination of properties, unattainable in most materials, is readily achieved in our films for $x \simeq 0.47$.

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Mechanisms That Determine the Electronic Dielectric Constants of Ionic Crystals*

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The very old and widely accepted theory for the electronic dielectric constants of ionic crystals assumes that intra-ionic excitations dominate in the crystal whereby polarizabilities of individual ions may be identified and tabulated. It is shown here that this assumption is unfounded and leads to inconsistencies and unphysical results. In turn I present theoretical and experimental evidence that the mechanism determining the dielectric constants is in fact the extreme opposite, namely strictly interionic excitations, whereby the concept of polarizability of ions in solids is physically meaningless.

The classical picture of an ionic crystal is a collection of positive and negative ions held together by Coulomb forces. Long before the advent of quantum theory, expressions were obtained for the electronic dielectric constants ϵ_∞ of these crystals by taking the ions to be *independently* polarizable. This allows one to write the polarizability of the crystal as the sum of the polarizabilities of the ions, or, equivalently, the susceptibility χ as

$$\chi = N_+\alpha_+ + N_-\alpha_- , \tag{1}$$

where N_+ (N_-) and α_+ (α_-) are the density and polarizability of positive (negative) ions, respectively. The simplest expression for ϵ_∞ is

$$\epsilon_\infty = 1 + 4\pi\chi . \tag{2}$$

When "local fields" are included in the calculation of ϵ_∞, more complicated expressions arise,[1] the simplest of which is the Clausius-Mossotti form

$$(\epsilon_\infty - 1)/(\epsilon_\infty + 2) = \tfrac{4}{3}\pi\chi . \tag{3}$$

By using such expressions, many workers attempted to obtain empirical values for ionic polarizabilities. These attempts have continued until very recent times and by now several "polarizability tables" exist which are used in various problems.[2-4] The details of the approach may be found in most standard textbooks which treat ionic crystals.[5]

Quantum mechanically, the polarizability of a free atom or ion is of course determined by virtual excitations of the ground-state electrons to empty eigenstates of the system. Thus the treatment of the ionic crystal as a collection of independently polarizable ions, as described above, is equivalent to assuming that the virtual excitations that determine the value of χ or ϵ_∞ are predominantly, if not strictly, *intra-ionic* in nature. Clearly, if *interionic* excitations were to play an important role in the crystal, one would not even be able to ascribe a well-defined meaning to the quantities α_+ and α_-. In any case, sizable interionic contributions would invalidate the simple expression (1) so that finding unique and consistent values of the α's for large classes of materials would become impossible.

The purpose of this Letter is to show that the assumption of independently polarizable ions, or, equivalently, the assumption that the ϵ_∞'s of ionic crystals are determined exclusively by intra-ionic excitations, is in fact invalid. In turn, I will present conclusive proof that *the opposite extreme limit, namely strictly interionic transitions, is the mechanism that actually determines the value of* ϵ_∞. I intend to carry out this task in three steps: First, I will show that there exists no evidence in support of the classical picture and that it actually leads to internal inconsistencies and unphysical results. Second, I will present theoretical and experimental evidence that disproves the validity of the classical assumption of strictly intra-ionic excitations and instead suggests the opposite limit of interionic excitations. Finally, I will present theoretical and experimental evidence that this latter limit is the one that indeed obtains.

(1) The only evidence offered for the validity of the classical assumption has been *ex post facto,* namely, the relative success achieved in obtaining unique values for ionic polarizabilities from the observed values of the dielectric constants.[3,4] Closer scrutiny of this claim, however, reveals that only the alkali halides have been fitted successfully. For all other materials no unique values for the α's have been possible. For example, Tessman, Kohn, and Shockley[3] list α for O^{--} ranging from 0.5 to 3.2. For Fe^{++} they list $\alpha = -1$, a physical impossibility. For Mg^{++}, the two crystals MgF_2 and $MgCl_2$ yielded $\alpha = +0.63$ and -0.34, respectively, when $\alpha(F)$ and $\alpha(Cl)$ obtained from the alkali halides were used! Finally, even in the case of the alkali halides, for which a consistent fit is obtained,[3,4] the results turn out to be unphysical: For example, $\alpha(Rb^+) = 1.98$ and $\alpha(F^-) = 0.64$ imply that the dielectric constant of RbF is due 3 times more to the polarizability of the deep core electrons on the Rb's than to the polarizability of the valence electrons which reside on the F's!

(2) Next we check whether the underlying assumption of the classical picture, namely that of strictly intra-ionic excitations, is in agreement with experiments other than measurements of ϵ_∞'s. We do this by noting that the virtual transitions that determine the value of ϵ_∞ are the very same ones that are observed during an ultraviolet absorption or reflectance experiment. Such spectra do exist for many ionic crystals and their interpretation is beyond reasonable doubt[6,7]: The lowest and strongest excitations are those of valence p electrons (residing on *anions*) to an s-like exciton or to the lowest conduction bands which are also s-like. Both the exciton and the bands are formed predominantly from the lowest empty s state of the *cations.* When the cation has low-lying d states (Na, K, Rb, but *not* Li) the s excitations are followed by well-identified d resonances. Particularly impressive data are on alloys[7] such as $NaCl_xBr_{1-x}$ or $Na_xK_{1-x}Cl$ and also the core x-ray spectra.[8] The clear indication is that the excited states of these crystals are in fact primarily determined by the *cations,*[9] whereby the primary excitations are *interionic* in nature. This has often been referred to as the charge-transfer model. Theoretical band calculations are in agreement with this.[6]

(3) We will now proceed by assuming that *all* important excitations are *interionic* in nature, in particular excitations of the valence p electrons residing on anions to exciton and band states formed from cation orbitals, and follow through with the consequences.

The quantum-mechanical expression for ϵ_∞ is

$$\epsilon_\infty = 1 + \frac{8\pi N^2 \hbar^4}{m^2} \sum_{jj'} \frac{|\langle j|\nabla|j'\rangle|^2}{(E_{j'} - E_j)^3}, \tag{4}$$

where $|j\rangle$ are the occupied one-electron states and $|j'\rangle$ are the excited states, both bands and excitons. N is the density of the valence electrons.[10] The reasoning then proceeds as follows: In all the rocksalt-type compounds, the valence bands are formed from the outer p electrons on the anions which form an fcc lattice. I recently showed[11] that hybridization is negligible because of the large band gaps and obtained a universal set of valence bands for all such compounds, scaled only by the interatomic spacing d. The assumption of interionic excitations then means that these p electrons polarize via virtual excitations to states formed from cation *orbitals.*

Thus, as long as we consider same-cation compounds, say the sodium halides, we expect the excitation energies to be only a simple function of d. Only when we change the cation do we introduce a qualitatively different set of excited states (for example, the lowest excited states in the Li halides arise from Li $2s$ and $2p$ orbitals, but in the Na halides they arise from Na $3s$, $3p$, *and* $3d$ orbitals). This cation dependence has already been found to be true for typical excitation energies, such as the optical band gaps E_g which obey the relation

$$E_g = \eta_g \hbar^2 d^{-2}/m , \tag{5}$$

where the dimensionless constants η_g depend only on the cation.[11] This is the same d^{-2} dependence found to be obeyed by excitation energies in the tetrahedral semiconductors.[12-14] Thus, if a simple power-law dependence on d holds for the excitation energies in (4), we are immediately led to the simple formula

$$\epsilon_\infty = 1 + Ad^s , \tag{6}$$

where the exponent s may be expected to be universal for ionic crystals *and the constant A depends only on the cation.* In a sense, A contains in a capsule all the necessary information about the excited states that a given cation may generate in an ionic crystal. Of course it is possible that the matrix elements $\langle j|\nabla|j'\rangle$, and hence A, depend on d in a complicated way, instead of a simple power law, whereby (6) would not be very useful. However such matrix elements were found in the tetrahedral materials to be actually independent of material.[15] If that turns out to be true for ionic crystals as well, A would be independent of d, and (4) would allow us to predict the value of the exponent s to be 3.

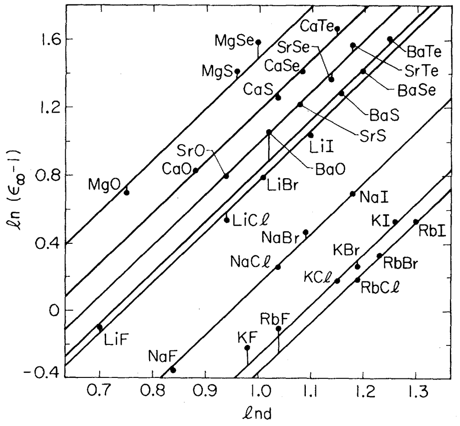

FIG. 1. Plot of $\ln(\epsilon_\infty - 1)$ versus $\ln d$ verifying Eq. (6). The values of the constants A extracted from this plot are listed in Table I. The deviations seen for KF, RbF, and BaO are probably due to contributions from polarizable cation electrons with energies close to or overlapping the anion p-electron valence bands.

I test all this for the alkali halides and the alkaline-earth chalcogenides, all of which have the rocksalt structure, by plotting $\ln(\epsilon_\infty - 1)$ against $\ln d$ (Fig. 1). The verification of (6) with $s = 3$ (the slope of all solid lines is 3) is indeed impressive. The constant A does depend only on the cation as expected (values extracted from Fig. 1 are listed in Table I), and (6) is valid for a very wide range of materials.

I will conclude by furnishing an additional and crucial test that will fully establish the validity of all the assumptions that led to (6). I turn to the cross compounds for which the classical approach of independently polarizable ions did particularly poorly (recall the case of MgF_2 and $MgCl_2$). Most of these compounds crystallize in the fluorite (CaF_2) or so-called antifluorite (representative compound: Li_2O) structure. They consist of *three* interpenetrating fcc lattices, one for each element in the chemical formula. If the present picture of ionic crystals is valid, we would have the following: The valence bands of these materials are again formed from the p electrons of the negative anions and the excited states are formed from orbitals of the cations.[16] The same d^{-2} bond-length dependences ought to obtain. Let us now compare Li_2O with, say, LiF, each of which has a set of p valence bands. Both systems have Li excited states, but Li_2O has twice as many for each p electron. Thus the present picture would predict that the constant A for Li_2O is *twice* that of LiF; once A is fixed, ϵ_∞ for Li_2O, Li_2S, Li_2Se, and Li_2Te would be given by (6). Similarly for the other antifluorite-type compounds. By the same token, when we compare CaF_2 with, say, CaO, we would predict that A for CaF_2 is *half* that of CaO since there

TABLE I. The values of the constants A as extracted from Fig. 1 for alkali halides.

Cation	A ($Å^{-3}$)	Cation	A ($Å^{-3}$)
Li	0.108	Mg	0.230
Na	0.059	Ca	0.162
K	0.038	Sr	0.132
Rb	0.034	Ba	0.113

TABLE II. Theoretical and experimental (from Ref. 3) values of ϵ_∞ for compounds of the fluorite and antifluorite structure. d is the anion-cation spacing.

Crystal	d(Å)	ϵ_∞(th)	ϵ_∞(exp)	Crystal	d(Å)	ϵ_∞(th)	ϵ_∞(exp)
MgF_2[a]	2.00	1.92	1.90	Li_2O	2.00	2.73	2.70
$MgCl_2$[a]	2.54	2.88	2.81	Li_2S	2.48	4.29	...
$MgBr_2$[a]	2.70	3.26	...	Li_2Se	2.60	4.80	...
MgI_2[a]	2.94	3.92	...	Li_2Te	2.82	5.84	...
CaF_2	2.36	2.06	2.06	Na_2O	2.41	2.65	...
$CaCl_2$[a]	2.73	2.65	2.56	Na_2S	2.82	3.65	...
$CaBr_2$[a]	...	...	...	Na_2Se	2.95	4.03	...
CaI_2[a]	3.04	3.28	...	Na_2Te	3.17	4.76	...
SrF_2	2.51	2.04	2.07	K_2O	2.79	2.65	...
$SrCl_2$	3.02	2.82	2.72	K_2S	3.20	3.49	...
$SrBr_2$[a]	3.30	3.37	...	K_2Se	3.33	3.81	...
SrI_2[a]	...	...	...	K_2Te	3.54	4.37	...
BaF_2	2.68	2.09	2.18	Rb_2O	2.92	2.69	...
$BaCl_2$	3.18	2.82	2.99	Rb_2S	3.32	3.49	...
$BaBr_2$	...	...	...	Rb_2Se	...	...	...
BaI_2	...	...	...	Rb_2Te	...	...	...

[a] These materials crystallize in the rutile or other structures whose coordination is similar to that of fluorite. See Ref. 16.

are only half as many Ca-type excited states per p electron in CaF_2 than in CaO. I put these predictions to test and obtain, with the only input the lattice constants, the ϵ_∞'s for all A_2B- and AB_2-type compounds. The results are shown in Table II. Wherever experiment is available, agreement with it is entirely within the uncertainties of both experiment and theory, thus confirming conclusively the validity of the present picture. Measurements of the remaining ϵ_∞'s would certainly be worthwhile.

The main conclusion of this paper has been that individual-ion polarizabilities in the sense of Refs. 1–5 are not meaningful quantities in terms of which to express the dielectric constant. We might note, furthermore, that the present results, based on opposite assumptions from those of Refs. 1–5, do not constitute a model, such as the well-known single-oscillator models[17-19] which involve "average" quantities that *simulate* the true excitations in the solid. In the present case, the constant A is a quantity in its own right and could be directly calculated. We have simply established that A has the same value in same-cation compounds and thus gained insight into the nature of the true excitations in ionic solids.

The conclusions are valid only in the case of ionic solids whose crystal structure does not allow the construction of true covalent bonds. In fact, one can show that when true covalent bonds may be formed (as in the tetrahedral semiconductors where one can construct directed hybrid orbitals and form bonds[12]) it is the opposite mechanism, namely *intra-ionic* excitations, that primarily determines ϵ_∞.[20] This distinction is absent in the Phillips–Van Vechten ionicity model where it was *postulated* that the mechanisms determining ϵ_∞ in rocksalt-type ionic solids are the same as in the tetrahedral covalent semiconductors (homopolar and ionic average gaps). This *imposed* a complicated dependence of ϵ_∞ on d $\{\epsilon_\infty = 1 + ad^{-3}/[bd^{-4.96} + c(d)]$, where a and b are constants and $c(d)$ is a material-dependent, rather complicated function of d of unknown form[18]$\}$ which cannot be reconciled with the experimental facts of Fig. 1. Further analysis of this and other points, studies, and applications will be given elsewhere.

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Chemical Effect on $K\alpha$ X-Ray Satellites: New Evidence for Interatomic Transitions*

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$K\alpha$ x-ray satellite spectra produced by bombardment with 2.0-MeV/nucleon oxygen and neon ions have been measured for several sulfur compounds. Comparison of the satellite-peak relative-intensity distributions has revealed a dependence on chemical environment. We interpret this effect to be caused by variations in the lifetimes of L-shell vacancies and find evidence that transitions from ligand valence levels play an important role.

Over the past few years it has become increasingly evident that both the energies *and* the widths of core levels in atoms bound in molecular systems are sensitve to the nature of the chemical environment.[1,2] Moreover it has become apparent that a full understanding of Auger and x-ray spectra requires consideration of the effects of *interatomic* transitions in which inner-shell vacancies may be filled by electrons from ligand valence levels.[3] Recently evidence for interatomic Auger transitions was deduced from a study of x-ray photoemission linewidths,[4] but subsequent comparisons of these data with $K\alpha$ x-ray linewidths indicated that an appreciable portion of the photoemission linewidth is instead attributable to phonon broadening.[5,6] As a consequence of phonon-broadening contributions to photoemission linewidths, it now appears that x-ray photoemission