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Refractive index of the alkali halides. I. Constant joint density of states model

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The electronic contribution to the imaginary part of the dielectric function of the alkali halides is assumed to be proportional to E^{-2} above the onset of optical absorption, which is equivalent to the assumption of a constant joint density of states (CJDOS) model. In this approach the electronic contribution to the refractive index can be described by two parameters, the long-wavelength limit of the refractive index n_∞ and the frequency of the onset of optical absorption E_{x0}. Various fits of the corresponding model function to experimental dispersion data show that E_{x0} is closely related to the frequency of the lowest exciton. Exciton absorption and interband transitions from the *p* valence bands to *s* and *d* conduction bands make the main contributions to the imaginary part of the dielectric function. The relative shifts of the *s* and *d* bands with respect to the *p* bands with density have different signs, and make different contributions to the photoelastic behavior. The CJDOS model is extended to account for the different behavior of *s* and *d* bands, and it is shown that the available literature data for the density dependence of the refractive index can be related to the energies of the *s* and *d* bands, derived from optical spectra and band-structure calculations. Shock data for LiF and NaCl are discussed, as well as low-pressure results for KCl, KBr, and KI. Recent high-pressure results for CsI show a strong nonlinear density dependence of the refractive index, in contrast to the almost linear behavior of the lighter alkali halides. Within the CJDOS model, this nonlinear behavior can be related to the closure of the band gap in CsI. [S0163-1829(97)06011-6]

I. INTRODUCTION

In the optics of alkali halide (AH) crystals, the density or stress dependence of the refractive index (RI) has long been of interest.[1,2] This interest has been caused largely by the fact that AH's can be regarded as prototypes of ionic materials, and the RI is a fundamental property, which depends on the interatomic distances. Thus, the comparison of atomistic-model calculations with respect to experimental data can serve as a critical test of the respective model. Numerous papers have appeared which relate the density dependence of the RI to changes in the ionic polarizabilities within the Clausius-Mosotti model (Ref. 3, and references therein). But it was noted[4] that the model of deformable ions[5] is not very well suited for the description of the photoelastic properties of AH's, and, furthermore, the Clausius-Mosotti model has been questioned.[6]

The alternative description, which has been used in the literature, relates the RI to an average gap.[7–9] However, the connection between the characteristic properties of the dielectric function (DF), such as excitons and critical points, and the average gap seems to be loose and nonpredictive.[10,11] Up to now, there seems to have been no successful attempt to relate the density dependence of the RI to changes in the actual band structures of the AH's. This might be due to the general opinion that the methods, which have been developed to describe the RI of semiconductors in the band picture, are not applicable in the case of ionic materials.[12]

Beside this fundamental interest in AH's with respect to their model character, a number of experimental and theoretical papers appeared which were stimulated by the interest in the effect of pressure on the optical properties of different window materials. On the one hand, it was noted that in high power laser applications the photoelastic behavior of optical components in the light path contributes to the distortion of laser beams.[13,14] On the other hand, the interest in the photoelastic behavior of AH's resulted from their utility as window materials in shock experiments.[15–17] The present paper intends to give the theoretical background for the interpretation of recent high-pressure data.[18]

The fundamental characteristics of band structures have been clarified by a number of calculations for most of the AH's and it is possible to derive the imaginary part of the DF by Brillouin-zone integration.[19–22] Such calculations, however, involve a further step of sophistication, and to our knowledge have not been performed in full detail for the AH's up to now. Thus the empirical approach of the present paper is justified and helps to clarify the fundamental contributions to the photoelastic properties of AH's.

II. CJDOS MODEL

The band structures of most AH's are very similar. The valence band is predominantly built up by the *p* electrons of the halides. The lowest conduction band has an *s* symmetry, with minima at the Γ and X points of the Brillouin zone. Above the *s* band there is a group of *d* bands, partly crossing the *s* band, and nearly degenerate at the Γ point.[23–28] LiF and NaF and the three cesium halides with CsCl-type ($B2$) structure are different with respect to these general trends. In the two fluorides the constituent ions have no low-lying *d* levels, and there are thus no *d* bands in the vicinity of the band gap.[23,26] In the cesium halides, on the other hand, two of the *d* bands are nearly degenerate with the *s* band.[29,30]

The imaginary part ε_2 of the DF is generally a complicated function of the photon energy. Besides interband transitions, the optical spectra of the AH's are dominated by excitons which are usually attributed to the Γ and X points. Other pronounced structures in the ε_2 spectra are caused by transitions in those parts of the Brillouin zone where valence and conduction bands are almost parallel.[31–35]

The simplest approach to describe the energy dependence of the DF which goes beyond a single oscillator description, assumes a constant joint density of states (JDOS) above the onset of optical absorption E_{x0}. This leads to the following expression for the electronic contribution:

$$\varepsilon_2^{\mathrm{el}}(E)=C\,\frac{P^2 z}{E^2}. \tag{1}$$

Thereby P represents an average transition matrix element, z the JDOS, and C a proportionality constant. Below E_{x0} the imaginary part is assumed to be zero. The same expression has been used for the description of two-dimensional critical points in semiconductors,[36–38] and similar ideas were applied to a background DF in Ref. 7. The band gap represents a three-dimensional critical point, but the contributions of the excitons are much stronger as, e.g., in semiconductors, and the assumption of a constant JDOS seems to be a reasonable description for both the interband transitions and the exciton contributions. Figure 1 shows the comparison of the experimental[35] and the model dielectric function of KCl. The model parameter E_{x0} for the onset of optical absorption (derived in Sec. III) is more closely related to an observable quantity, namely, the energy of the lowest exciton, than the average gap parameters E_0 (Ref. 7) and E_g.[8]

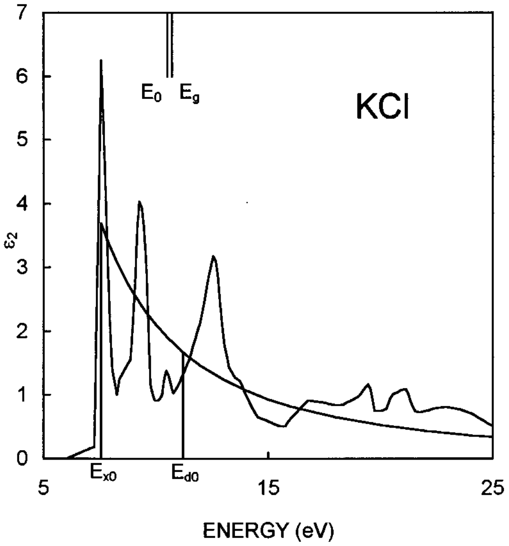

FIG. 1. Imaginary part of the dielectric function of KCl (Ref. 35) and the approximation in the CJDOS model. E_0 is the average gap (Ref. 7), and E_g the Phillips gap parameter (Ref. 8), E_{x0} is the CJDOS parameter for the onset of optical transitions, and E_{d0} the lower bound of transitions to the d bands, described later in the text.

III. DISPERSION OF THE REFRACTIVE INDEX

The electronic contribution to the real part of the DF can be obtained by a Kramers-Kronig transformation of Eq. (1),

$$\Delta\varepsilon_1^{\mathrm{el}}(E)=-(n_\infty^2-1)\,\frac{E_{x0}^2}{E^2}\,\ln\left|1-\frac{E^2}{E_{x0}^2}\right|, \tag{2}$$

with $n_\infty^2-1=CP^2z/(\pi E_{x0}^2)$. Function (2), which contains the two adjustable parameters n_∞ and E_{x0}, has been fitted to the available dispersion data.[39–41] In the low-frequency region an additional term, which takes into account the contribution of the optical phonons, has to be added:

$$\Delta\varepsilon_1^{\mathrm{TO}}(E)=(\varepsilon_0-n_\infty^2)\,\frac{E_{\mathrm{TO}}^2}{E_{\mathrm{TO}}^2-E^2}. \tag{3}$$

The RI is thus

$$n(E)=\sqrt{1+\Delta\varepsilon_1^{\mathrm{TO}}(E)+\Delta\varepsilon_1^{\mathrm{el}}(E)}. \tag{4}$$

The RI dispersion has not been experimentally determined in the total transparent region for every substance of the 20 AH's. Different numerical approaches are thus necessary to fit Eq. (4) to the available experimental data. For a first group of eight AH's, the RI is known from the far IR, the regime of the optical phonons, up to nearly the onset of electronic absorption. For these eight substances the results of least-

TABLE I. Results of the three parameter fits of Eq. (4) to experimental refractive index data (Ref. 39). Additional literature data are also given for comparison.

	n_∞[a]	E_{x0}[a] (eV)	ε_0[a]	σ[a] (10^{-3})	n_∞[b]	E_{x0} (eV)		ε_0[c]	E_{TO}[d] (meV)
LiF	1.3878	12.074	8.919	1.4	1.386[e]	12.5[f]		9.00	37.9
NaF	1.3210	10.873	5.134	1.7	1.3188	10.56[g]		5.08	30.5
NaCl	1.5278	7.577	6.035	3.3	1.5252	7.97[g]	7.78[h]	5.90	20.3
KCl	1.4751	7.541	5.126	6.6	1.4770	7.78[g]	7.63[h]	4.84	17.6
KBr	1.5367	6.710	4.792	0.2	1.5332	6.75[g]	6.53[h]	4.90	14.2
KI	1.6275	5.650	4.980	0.8	1.6238	5.86[g]	5.61[h]	5.09	12.6
CsBr	1.6686	6.667	6.586	0.2	1.6676	6.81[g]		6.66	9.12
CsI	1.7428	5.651	6.410	0.1	1.7378	5.77[g]		6.54	7.69

[a] Present work.
[b] Reference 40.
[c] Reference 44.
[d] Reference 45.
[e] Calculated (Ref. 41).
[f] Reference 32.
[g] Transmission (10 K, Ref. 42).
[h] Reflection (RT, Ref. 43).

TABLE II. Results of the two parameter fits of Eq. (4) to experimental refractive index data (Ref. 39). Additional literature data are also given for comparison.

	n_∞ [a]	E_{x0} [a] (eV)	σ [a] (10^{-3})	n_∞ [b]	E_{x0} (eV)		ε_0 [c]	E_{TO} [d] (meV)
NaBr	1.6126	6.492	1.6	1.611	6.70[e]		6.27	16.6
KF	1.3545	10.580	0.3	1.360[f]	9.86[e]		5.50	24.0
RbCl	1.4723	7.385	2.4	1.4765	7.54[e]	7.41[g]	4.89	14.4
RbBr	1.5232	6.517	2.2	1.5283	6.62[e]	6.41[g]	4.86	10.9
RbI	1.6050	5.602	2.0	1.6061	5.74[e]	5.50[g]	4.91	9.36
CsCl	1.6190	7.494	0.6	1.6209	7.84[e]		6.95	12.3

[a] Present work.
[b] Reference 40.
[c] Reference 44.
[d] Reference 45.
[e] Transmission (10 K, Ref. 42).
[f] Calculated (Ref. 41).
[g] Reflection (RT, Ref. 43).

squares fits are shown in Table I, and compared with literature data.[32,39–44] n_∞, E_{x0}, and ε_0 have been taken as adjustable parameters for these fits, while for the frequency of the optical phonon the values of Ref. 45 have been used and are given in the last column of the table. The results for the adjusted parameters are given in columns 2–4 of Table I. The fifth column contains the standard deviation σ for each fit. Room-temperature (RT) values for the energy of the lowest exciton (column eight) are not available for every substance, thus values obtained at 10 K are also given. These are about 0.2 eV higher than the respective RT values.

The accuracy of the experimental data differs for different sets of data, and is usually estimated by the authors to be of the order of 10^{-3}–10^{-4}. The standard deviations σ show about the same value for most of the substances. Therefore, the fits can be regarded as reasonable analytical representations of the experimental data. For both NaCl and KCl the standard deviations are unusually large.

The values for n_∞ (second column) can be considered more reliable than the literature values,[40] which had been extrapolated only from three values of the RI. The results for the parameter E_{x0} are very close to the energies of the lowest exciton. Finally, the values for ε_0 are also in good agreement with the literature data.[44]

For a second group of six AH's the RI has not been measured in the IR. Thus the fits for these substances have been performed with only two adjustable parameters, and the results are given in Table II. Experimental accuracies for these substances have been estimated by the authors to be 10^{-3}. The standard deviations of the fits have about the same magnitude. Here again, the values of n_∞ should be more reliable than the literature data,[40] and the values of E_{x0} are very close to the experimentally observed energies of the excitons.

For the rest of the AH's, the RI is only known for a few energy values. For these substances only n_∞ has been fitted, while for E_{x0} the respective values of the exciton energies have been used; Table III shows the results. With respect to the few input data, it is not useful to give values for the standard deviations. For LiI no value for the exciton energy is known. The value given in the table has been estimated from the rule of Hilsch and Pohl.[47] These authors showed that this energy can be derived from the Madelung energy with a correction for the difference between the affinity of the halide and the ionization energy of the alkali atom.

Figure 2 shows the fitted dispersion curves for the potassium halides together with the respective experimental data. In Sec. VI the density dependence of the RI of LiF, NaCl, and CsI will be discussed in more detail. The fitted dispersion curves for these substances are shown in Fig. 3. In the scale of the two figures the agreement between the experimental data and the curves, corresponding to the constant JDOS model, is almost perfect. In Sec. IV the JDOS will be decomposed into different contributions, arising from transitions to the s- and d-conduction bands, respectively.

TABLE III. Long-wavelength limit of the refractive index n_∞ calculated from the limited number of available data (Refs. 40 and 41).

	n_∞ [a]	n_∞ [b]	E_{x0} (eV)	ε_0 [c]	E_{TO} [d] (meV)
LiCl	1.6463	1.658[e]	8.75[f]	11.86	25.1
LiBr	1.7520	1.778[e]	7.23[g]	13.23	21.5
LiI	1.9065	1.949[e]	6.20[h]	11.03[h]	17.6
NaI	1.7305	1.706[e]	5.62[g]	7.28	14.4
RbF	1.3873	1.388	9.52[g]	6.48	19.6
CsF	1.4672	1.469	9.24[g]	8.08	15.7

[a] Present work.
[b] Reference 40.
[c] Reference 44.
[d] Reference 45.
[e] Calculated (Ref. 41).
[f] Reflection (55 K, Ref. 46).
[g] Transmission (10 K, Ref. 42).
[h] Estimated (see text).

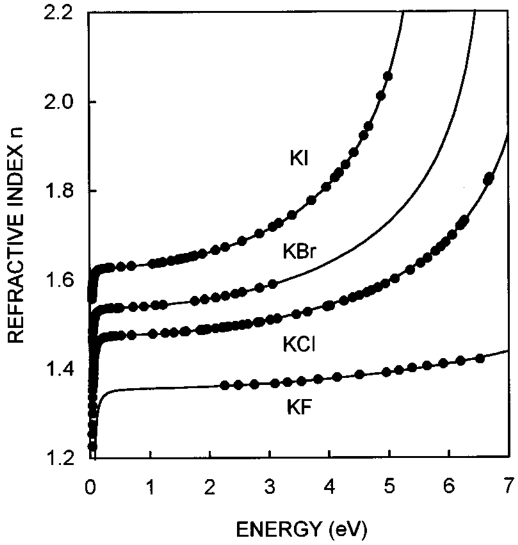

FIG. 2. Dispersion of the refractive index of the potassium halides. For the calculation of the curves. Eq. (4) has been used with the parameters given in Tables I and II. The experimental points (Ref. 39) were used as input data for the fits.

IV. DIFFERENT CONTRIBUTIONS OF *s* AND *d* BANDS

It is interesting to make a rough estimate of the density dependence of the parameters in Eq. 2. For interband transitions, P is proportional to the reciprocal-lattice constant,[36] or $P^2 \propto (\rho/\rho_0)^{2/3}$. The JDOS z can be decomposed into two different contributions: on the one hand the number of states is proportional to density, and on the other hand z is in the reversed ratio to the bandwidths. There is not much information about the density dependence of the bandwidths in the AH's. The calculations for CsI (Ref. 30) suggest that the bandwidths are roughly proportional to density. In this case, the two contributions to the JDOS almost cancel each other, and thus $P^2 z \propto (\rho/\rho_0)^{2/3} \propto E_M^2$, where the Madelung energy E_M has been introduced for convenience. The main contributions to the refractive index may thus be written as $n_\infty^2 - 1 = C' E_M^2 / E_{x0}^2$.

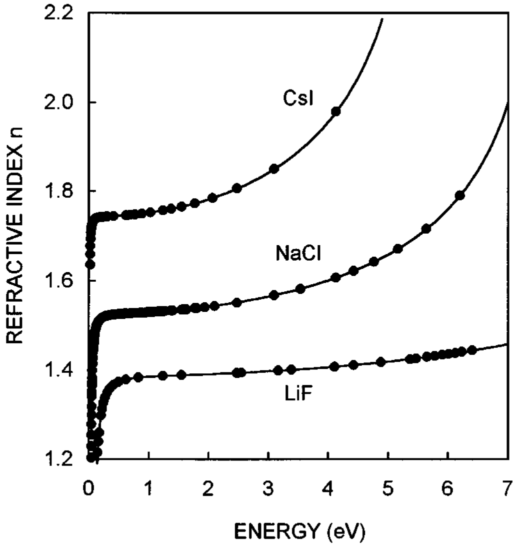

FIG. 3. Dispersion of the refractive index of LiF, NaCl, and CsI. For the calculation of the curves Eq. (4) was used with the parameters given in Table I. The experimental points (Ref. 39) were used as input data for the fits.

TABLE IV. Values for $C' = (n_\infty^2 - 1)\ E_{x0}^2 / E_M^2$. E_{x0} is the CJDOS parameter for the onset of optical transitions of the preceding tables, and E_M is the Madelung energy.

	C'			
	F	Cl	Br	I
Li	0.864	1.336	1.292	1.460
Na	0.747	0.963	0.951	1.040
K	1.055	1.045	1.053	1.038
Rb	1.058	1.094	1.052	1.054
Cs	1.408	1.801	1.705	1.579

Table IV gives the values for C', which have been calculated from the data of the preceding tables. The values for C' cluster around 1 for most of the normal AH's. For LiF and NaF, in which there is a gap between the s and d bands, C' is smaller than 1, while for the cesium halides with overlap of s and d bands, C' is much larger than 1. In order to account for these observations, a separation of the JDOS can be assumed:

$$n_\infty^2 - 1 = \overline{C} E_M^2 \left(\frac{1}{E_{x0}^2} - \frac{1}{E_{c0}^2} + \frac{1}{E_{d0}^2} \right). \qquad (5)$$

E_{c0} represents an upper cutoff energy for s-band transitions and E_{d0} the lower bound for transitions to the d bands. The data of Table IV may then be interpreted in the following way. The average value of C' for the potassium and rubidium halides $C = 1.056$ is taken as a common parameter, and it is assumed that in these substances E_{c0} is equal to E_{d0}. The systematic trends in C'/C can then be interpreted as follows: $C'/C < 1$ indicates a gap between E_{c0} and E_{d0}, while $C'/C > 1$ indicates an overlap of s and d bands. Finally, $C'/C \approx 1$ means that the continuous function Eq. (1) is the appropriate description for the imaginary part of the DF.

The data for the onset of d-band transitions, which can be found in the literature from optical transmission or reflection spectra and band-structure calculations, show a rather large scatter. However, the general trends, which can be derived from these data, indicate that the systematics in C'/C can be understood with the help of Eq. (5). In Sec. V the parameters E_{c0} and E_{d0} will be derived from the additional information about the density dependence of the RI. It will be shown that E_{d0} can in fact be brought into satisfactory agreement with the respective literature data.

V. DENSITY DEPENDENCE
OF THE REFRACTIVE INDEX

The possibility of a decomposition of the JDOS into contributions arising from transitions to s and d bands is important for the description of the density dependence of the RI, because s and d bands show different relative shifts with respect to the p valence band with density.

Theoretical studies[48–52] predict that p-d gaps become smaller at high densities. This effect is, e.g., responsible for the observed closing of the band gap in CsI (see below). As the d bands make an important contribution to the JDOS for most of the AH's, the effect of the closure of the p-d gap should also show up in the behavior of the RI.

In the following discussion of the density dependence of the different energy parameters the usual definition $\gamma_i = \partial \ln E_i / \partial \ln \rho$ is used. For the density dependence of the exciton energy E_x, a value of $\gamma_x = \frac{1}{3}$ can be assumed.[47,53,54] For the density dependence of E_c the assumption about the density dependence of the bandwidths $\gamma_B = 1$ gives $\gamma_c = 1 - 2E_{x0}/(3E_{c0})$. There is only little information about γ_d. For CsI it has been found that the value of γ_d is nearly the same as γ_x, but with the opposite sign.[29,55] Thus in the following discussion $\gamma_d = -\frac{1}{3}$ is assumed. With the help of the relations

$$\frac{C'}{\bar{C}} = 1 - \frac{E_{x0}^2}{E_{c0}^2} + \frac{E_{x0}^2}{E_{d0}^2} \tag{6}$$

and

$$\rho \frac{\partial n_\infty}{\partial \rho} = \frac{n_\infty^2 - 1}{2 n_\infty} \left[\left(1 - 2 \frac{E_{x0}}{E_{c0}} \right) \frac{E_{x0}^2}{E_{c0}^2} + 4 \frac{E_{x0}^2}{E_{d0}^2} \right], \tag{7}$$

the parameters E_{c0} and E_{d0} can be calculated from the data of Table IV and a knowledge of the density derivative of the RI. The density and energy dependence of the electronic contribution to the DF is

$$\Delta\varepsilon_1^{\mathrm{el}}(E,\rho) = -(n_\infty^2 - 1) \frac{\bar{C}}{C'} \frac{E_{x0}^2}{E^2} \left(\frac{\rho}{\rho_0} \right)^{2/3} \left[\ln\left| 1 - \frac{E^2}{E_x^2(\rho)} \right| - \ln\left| 1 - \frac{E^2}{E_c^2(\rho)} \right| + \ln\left| 1 - \frac{E^2}{E_d^2(\rho)} \right| \right]. \tag{8}$$

The phonon contribution is

$$\Delta\varepsilon_1^{\mathrm{TO}}(E,\rho) = (\varepsilon_0 - n_\infty^2) \frac{E_{\mathrm{TO}}^2(\rho_0)}{E_{\mathrm{TO}}^2(\rho) - E^2} \frac{\rho}{\rho_0}. \tag{9}$$

Equation (4) can thus be extended to include the density dependence

$$n(E,\rho) = \sqrt{1 + \Delta\varepsilon_1^{\mathrm{TO}}(E,\rho) + \Delta\varepsilon_1^{\mathrm{el}}(E,\rho)}.$$

VI. EXAMPLES

Shock wave data on LiF (Refs. 15–17) led to the conclusion that a linear density dependence of the RI is an excellent description for normal solids up to a relative density change of $\Delta\rho/\rho_0 \leq 0.75$.[56] Some care is of course necessary for the interpretation of shock data, because of temperature effects. It has been shown, however, that the temperature derivative at constant pressure is dominated by the density change, and that additional temperature effects are negligible for the AH's.[57] It may thus be concluded that temperature plays a minor role in shock experiments on the RI.

Table V gives the density derivative of the RI (Refs. 17 and 58–61) and constant JDOS (CJDOS) parameters. The value for E_{d0} is somewhat higher than the value obtained from band-structure calculations.[26] Figure 4 shows the imaginary part of the DF (Ref. 32) and the approximation in the CJDOS model. Figure 5 presents the variation of the RI with density, together with the results of the shock wave experiments.[17,15] One can notice that the density variation is almost, but not perfectly, linear.

TABLE V. Density derivative of the refractive index and the CJDOS parameters for LiF.

$\rho\partial n/\partial\rho$			E_{c0} (eV)	E_{d0} (eV)
0.126[a]	0.13[b]	0.129[c]		30.6[d]
0.124[e]	0.11[f]	0.125[g]	23.4[g]	38.7[g]

[a] Reference 59.
[b] Reference 60.
[c] Reference 61.
[d] Reference 26 (calc.)
[e] Reference 58.
[f] Reference 17.
[g] This work.

Table VI gives experimental values for $\rho\partial n/\partial\rho$,[17,58,60,62,63] and the results of band-structure calculations for the $\Gamma_{15} \rightarrow \Gamma'_{25}$ transition in NaCl, which range from 12.7 up to 17.6 eV.[23,26,28,64–66] Experimental values are 13.2 eV (Ref. 31) and 15.2 eV (Ref. 33) (Table VI). The present CJDOS model predicts 14.3 eV, and is thus in very good agreement with the literature data.

Figure 6 shows the imaginary part of the DF (Ref. 31) and the approximation in the CJDOS model. Figure 7 illustrates the assumed variation of the three energy parameters. Figure 8 compares the predicted density change of the RI with the shock wave data.[15,17] The relative deviation from a linear density dependence for NaCl is smaller than in LiF, which can be attributed to the influence of the d bands, as the closing of the $p-d$ gap favors a positive sign for the second derivative of the RI (see below).

For KCl, KBr, and KI there is no gap between transitions to the s and d bands in the CJDOS model, because $C'/C \approx 1$ (see Table IV and Fig. 1). However, these substances transform from the NaCl-type ($B1$) to the CsCl-type ($B2$) structure at about 2 GPa.[39] This phase transition is accompanied

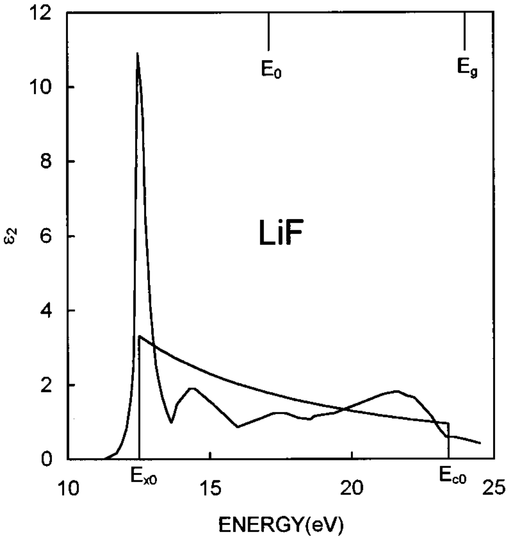

FIG. 4. Imaginary part of the dielectric function of LiF (Ref. 32) and the approximation in the CJDOS model. The average gaps of E_g (Ref. 8) and E_0 (Ref. 7) are also given.

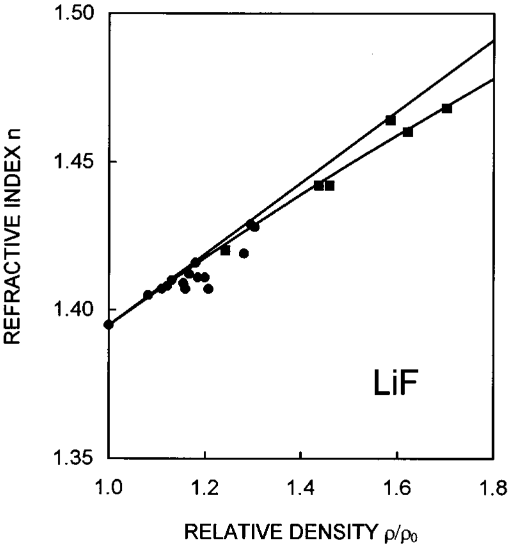

FIG. 5. Refractive index change of LiF. Experimental data points are from shock experiments: circles (Ref. 17), squares (Ref. 15). The straight line represents a linear dependence, and the curve the prediction of the CJDOS model.

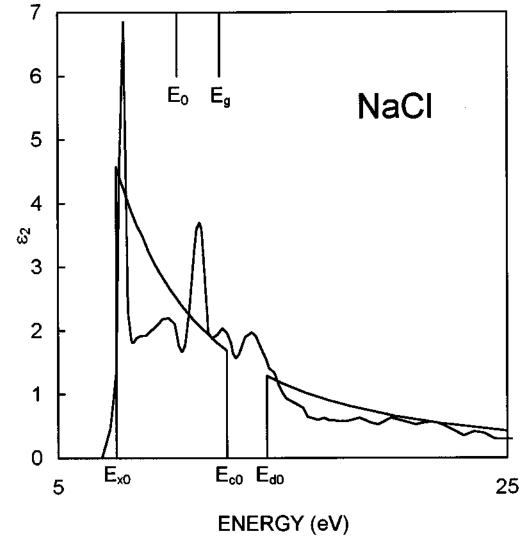

FIG. 6. Imaginary part of the dielectric function (Ref. 31) and the approximation in the CJDOS model for NaCl. The average gaps of E_g (Ref. 8) and E_0 (Ref. 7) are also given.

by a discontinuous change of the RI.[18] The function for the density dependence of the RI with the parameters obtained from low-pressure measurements can thus not be extrapolated over an extended density range.

Table VII gives experimental values for $\rho\,\partial n/\partial\rho$,[14,58–60,62,67] and the results of band-structure calculations for the $\Gamma_{15}\rightarrow\Gamma'_{25}$ transitions,[23,24,26,64] as well as experimental results for these transition energies.[31,33,42,68] The CJDOS parameter E_{d0} is in good agreement with these literature data.

In contrast to the band structure of an AH with $B1$ structure, the Γ_{12} states in CsI exhibit a minimum, almost degenerate with the Γ_1 minimum, while the Γ'_{25} states have a higher energy.[29,30,69] In transmission measurements[55] it was observed that the deformation potentials of the Γ_1 and Γ_{12} excitons have opposite signs, leading to a crossover at about 0.7 GPa. At higher compression, the $\Gamma_{15}\rightarrow\Gamma_{12}$ gap closes.[70–77] This behavior of the fundamental gap in the $B2$ structure is thus opposite to the behavior of the gap in AH's with $B1$ structure. With the help of the CJDOS model, it is now possible to study the influence of the gap on the RI.

For the variation of E_d a second-order polynomial $E_d(\rho)=E_{d0}(1+\gamma_d(\Delta\rho/\rho_0)+\delta(\Delta\rho/\rho_0)^2)$ has been fitted to the experimentally observed variation of the gap, with $E_{d0}=6.41$ eV and $\delta=-0.576$. The cutoff parameter is $E_{c0}=10.66$ eV.

Figure 9 compares experimental results of different bandgap measurements with the changes of the three parameters E_x, E_d, and E_c. The most striking difference in the behavior of CsCl, CsBr, and CsI compared to the other AH's, discussed above, is the fact that the RI shows a nonlinear behavior with a positive second derivative.[18] This nonlinearity is of course related to the closure of the band gap.

TABLE VI. Density derivative of the refractive index and $\Gamma_{15}\rightarrow\Gamma_{25}$ transition energies (E_{d0}) of NaCl.

	$\rho\,\partial n/\partial\rho$			E_{d0} (eV)	
0.267[a]	0.28[b]	0.26[c]	13.2[d]	15.2[e]	14.0[f]
0.269[g]	0.255[h]	0.268[i]	13.9[j]	15.7[k]	15.4[l]
			17.6[m]	12.7[n]	14.3[i]

[a] Reference 62.
[b] Reference 60.
[c] Reference 17.
[d] Reference 31 (expt.).
[e] Reference 33 (expt.).
[f] Reference 23 (calc.).
[g] Reference 63.
[h] Reference 58.
[i] This work.
[j] Reference 64 (calc.).
[k] Reference 66 (calc.).
[l] Reference 26 (calc.).
[m] Reference 65 (calc.).
[n] Reference 28 (calc.).

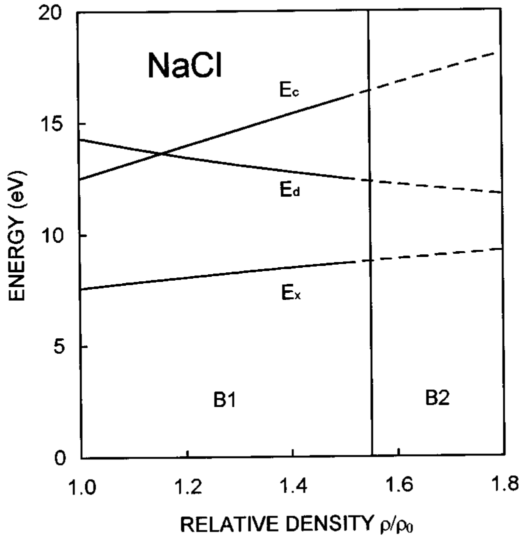

FIG. 7. Evolution of the CJDOS parameters. For a relative density $\rho/\rho_0\approx1.55$ sodium chloride transforms to the CsCl-type ($B2$) structure.

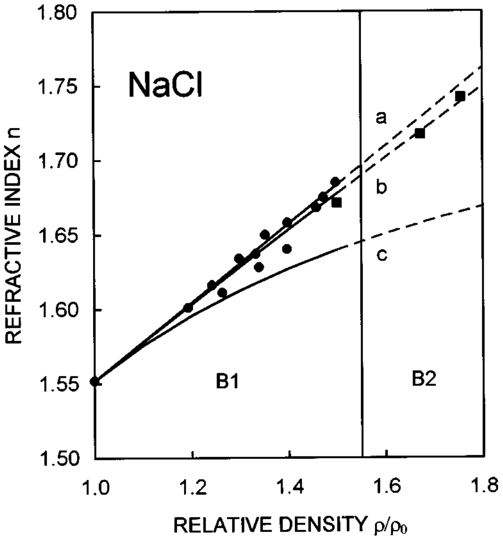

FIG. 8. Density dependence of the refractive index of NaCl at a photon energy of 2.4 eV. For the three curves a value of $\rho \partial n/\partial \rho = 0.263$ for ambient conditions has been assumed. (a) Linear dependence. (b) CJDOS model. (c) Linearity with volume strain (Ref. 63). Data points: shock wave experiments (Refs. 15 and 17).

VII. DISCUSSION

The present CJDOS model reasonably describes the dielectric function of the AH's. The density dependence of the RI can be described by the different behaviors of *s* and *d* bands at high densities. The opening of the *p*-*s* gap leads to a sublinear behavior of the RI with density (e.g., predominantly in LiF), while the closure of the *p*-*d* gap makes a contribution with a positive curvature (e.g., CsI). In NaCl these different contributions nearly cancel each other, resulting in an almost linear density dependence of the RI.

TABLE VII. Density derivative of the refractive index and $\Gamma_{15} \rightarrow \Gamma_{25}$ transition energies (E_{d0}) of potassium halides.

KCl		KBr		KI	
$\rho \partial n/\partial \rho$	E_{d0} (eV)	$\rho \partial n/\partial \rho$	E_{d0} (eV)	$\rho \partial n/\partial \rho$	E_{d0} (eV)
0.31^{a}	11.4^{b}	0.35^{a}	10.4^{c}		
0.294^{d}	18.0^{e}	0.343^{d}	9.5^{f}		
0.231^{g}	12.2^{h}	0.355^{g}		0.423^{g}	
0.315^{i}	10.7^{j}		9.7^{j}	0.412^{i}	7.7^{j}
0.324^{k}	11.9^{l}	0.365^{k}	10.4^{m}	0.436^{k}	8.7^{j}
0.313^{n}	11.2^{o}	0.353^{n}	9.9^{o}	0.423^{n}	8.2^{o}

[a] Reference 60.
[b] Reference 31 (expt.).
[c] Reference 68 (expt.).
[d] Reference 59.
[e] Reference 33 (expt.).
[f] Reference 42 (expt.).
[g] Reference 58.
[h] Reference 23 (calc.).
[i] Reference 62.
[j] Reference 24 (calc.).
[k] Reference 14.
[l] Reference 64 (calc.).
[m] Reference 26 (calc.).
[n] Reference 67.
[o] This work.

It is generally assumed that the methods that have been derived to described the DF of semiconductors are not very well suited to describe ionic materials.[12] Figure 10 shows the DF's of GaP,[37] a typical semiconductor, and KCl, a normal AH (see also Fig. 1). The main differences are caused by the contributions of the excitons and the *d* bands in the AH's. In semiconductors the excitons have only a very small oscillator strength, and the three-dimensional critical point at the band gap makes only a minor contribution to the DF. The main contribution is caused by the critical points E_1 and E_2, attributed to transitions between the top valence bands and the lowest conduction band. Disregarding these differences, the overall energy dependence of the dielectric function has a $1/E^2$ behavior for both groups of substances.

It would be interesting if the main assumptions about the density dependence of the band parameters in the present

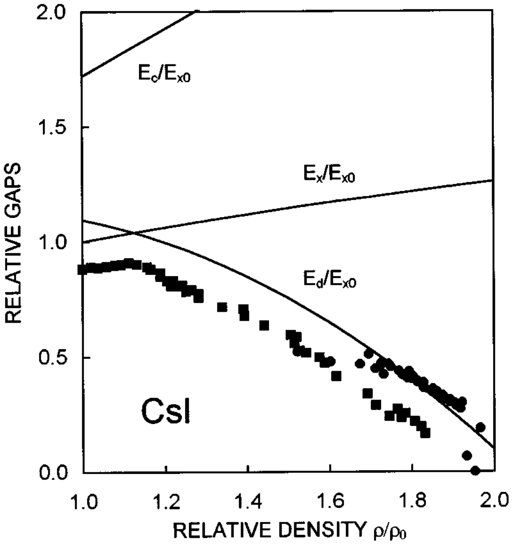

FIG. 9. Variation of the three energy parameters of the CJDOS model for CsI compared to the experimental observed variation of the band gap (Refs. 70–77). The data of Ref. 73 (squares) are low, because a certain threshold energy has been used in this work.

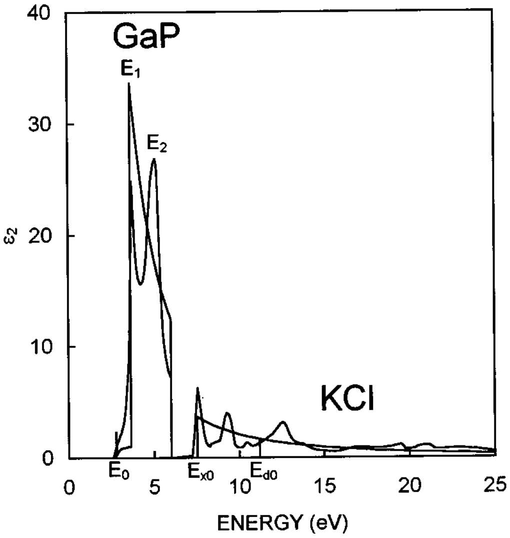

FIG. 10. Comparison of the imaginary part of the dielectric function of GaP (Ref. 37), a typical semiconductor, and KCl (see Fig. 1). The major differences are caused by the excitonic contribution, which is negligible in semiconductors, and the contribution of the *d* bands in the alkali halides.

approach could be confirmed by band-structure calculations. In particular, the deformation potentials of the *d* bands and the band broadening at high densities would provide valuable information for the understanding of the DF of ionic materials.

On the experimental side, high-pressure experiments up to 12 GPa for 11 alkali halides are presented in Ref. 18. The results for NaF, NaBr, and NaI, as well as CsCI, CsBr, and CsI, can satisfactorily be described in the CJDOS model. For the interpretation of high-pressure results on potassium and rubidium halides,[18] additional information about the respective equations of state of the B2 structure is required, and will be discussed in a later paper.

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