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Volume Dependence of the Grüneisen Parameter of Alkali Halides[†]

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The parameter $q=(\partial \ln\gamma/\partial \ln V)_T$ which describes the volume variation of the Grüneisen parameter has been calculated by the following two independent methods: (a) a macroscopic calculation using a thermodynamic formula and carefully selected thermodynamic data; (b) a microscopic calculation using a six-parameter pressure-dependent lattice-dynamical shell model. The first method has been applied to twelve alkali halides and the second to only six alkali halides for which experimental data on the second-order pressure dependence of the elastic constants are available. Typical values of q have been found to be equal to about 1.5. The low-temperature limit of q has been investigated by using an acoustic-continuum model. It was found that q increases sharply at low temperatures.

I. INTRODUCTION

The parameter $q=(\partial \ln\gamma/\partial \ln V)_T$, which describes the volume dependence of the Grüneisen parameter $(\gamma=V\beta B_T/C_V)$ emerges frequently in discussions of the thermoelastic properties of solids. Since no theoretical microscopic calculations of q have been performed in the past, except for a recent work on inert-gas crystals,[1] some simple assumptions about its numerical value have usually been made. Most often, q appears in relations which also involve the Anderson-Grüneisen parameters, which describe the temperature dependence of the bulk moduli and are defined by[2,3]

$$\delta_S=-\frac{1}{\beta}\left(\frac{\partial \ln B_S}{\partial T}\right)_P , \tag{1}$$

$$\delta_T=-\frac{1}{\beta}\left(\frac{\partial \ln B_T}{\partial T}\right)_P . \tag{2}$$

Here, B_S and B_T are the adiabatic and the isothermal bulk moduli, respectively, and β is the coefficient of volume expansion. Some formulas for δ_S, which have been given in the past,[4] were based on the assumption that $q \ll 1$, which does not hold for the alkali halides, as will be shown later. Anderson,[3] on the other hand, after giving expressions for δ_S and δ_T which involve q, employed the more reasonable approximation that $q=1$. The assumption that γ is proportional to the volume (which implies $q=1$) seems to be the most popular. It has been used in theories of shock-wave propagation[5] and also in various discussions of equations of state.[6,7] Another approach has been adopted by Rice[8] in his discussion of the alkali metals. By making the assumption that the Grüneisen parameter, as well as the adiabatic bulk modulus, is a function of volume only, he was able to derive a simple explicit expression for the dependence of γ on volume. In terms of the parameter q, his relation is $q=\gamma+1$.

A significant feature of the parameter q is that it can be calculated directly from lattice-dynamical models. A calculation of this type, based on a six-parameter shell model, is presented in Sec. III. The results are compared with q values obtained in Sec. II from room-temperature ultrasonic and thermodynamic data. The low-temperature behavior of q is discussed in Sec. IV.

II. EVALUATION OF q FROM THERMODYNAMIC AND ULTRASONIC DATA

The most convenient expression for q in terms of available experimental quantities is

$$q=1+(1+T\beta\gamma)\delta_S-B_S'+\gamma+T\left(\frac{\partial \ln\gamma}{\partial T}\right)_V , \tag{3}$$

where $B'_S = (\partial B_S/\partial P)_T$. This equation, which is exact, has been derived by Bassett *et al.*[9] by using standard thermodynamic identities. An equivalent expression for q is

$$q = 1 + \delta_T - B'_T - \left(\frac{\partial \ln C_V}{\partial \ln V}\right)_T , \tag{4}$$

where $B'_T = (\partial B_T/\partial P)_T$. This equation is of less practical value than Eq. (3), but will be of interest in later discussion.

The values of q at 295 °K, which were obtained from Eq. (3), as well as the values of closely related quantities, are given in Table I. The ultrasonic values of B'_S were taken from two recent papers, one on the sodium and potassium halides[10] and another on the rubidium halides.[11] The values of β and γ were also taken from Refs. 10 and 11. The last term on the right-hand side of Eq. (3) is negligible in the high-temperature region to which all the calculations of this section refer. This point will be discussed below.

The values of q are typically 1.5 for the sodium and the potassium halides. The largest values of about 2.0 occur in the rubidium halide sequence. An accuracy of 0.3 was assigned to the values of q in Table I on the basis of the uncertainty in the input data.

The values of δ_S and δ_T that are given in Table I are based on the same set of thermodynamic and ultrasonic data. These parameters, which are closely related to q through Eqs. (3) and (4), have often been estimated theoretically, starting from various approximations and equations of state,[12–14] with rather poor agreement among the results of different methods. The presented values of the Anderson-Grüneisen parameters are believed to be superior to previous compilations since they are based on experimental data that have been carefully selected[10,11] with special emphasis on a smooth variation in each halide sequence as the halogen ion is changed.

III. LATTICE-DYNAMICAL CALCULATION OF q

To derive q directly from a lattice-dynamical model, we begin with the quasiharmonic model expression for the Grüneisen parameter in terms of the microscopic mode γ's:

$$\gamma = \sum c_i \gamma_i \Big/ \sum c_i , \tag{5}$$

where c_i is the Einstein specific heat of the ith mode. Differentiation with respect to volume gives the relation

$$q = \left[\sum c_i \left(\frac{\partial \gamma_i}{\partial \ln V}\right)_T + (\gamma_i - \gamma)\left(\frac{\partial c_i}{\partial \ln V}\right)_T\right] \Big/ \sum c_i \gamma_i . \tag{6}$$

The summations over the $3N$ normal modes have been evaluated by using the volume-dependent lattice-dynamical model which has been previously employed[15] to calculate γ from Eq. (5). For this we have expressed all quantities appearing in Eq. (6) in terms of the mode frequencies ω_i and their first and second pressure derivatives:

$$\gamma_i = B_T \left(\frac{\partial \ln \omega_i}{\partial P}\right)_T , \tag{7}$$

$$\left(\frac{\partial \gamma_i}{\partial \ln V}\right)_T = -\frac{B_T}{\omega_i}\left[B'_T\left(\frac{\partial \omega_i}{\partial P}\right)_T + B_T\left(\frac{\partial^2 \omega_i}{\partial P^2}\right)_T - \frac{B_T}{\omega_i}\left(\frac{\partial \omega_i}{\partial P}\right)^2\right], \tag{8}$$

$$c_i = \frac{k x^2 e^x}{(e^x - 1)^2} , \qquad x = h\omega_i/kT , \tag{9}$$

$$\left(\frac{\partial c_i}{\partial \ln V}\right)_T = \gamma_i c_i (x \coth x - 2) . \tag{10}$$

The lattice-dynamical shell model used has six parameters which were determined, through well-known relations,[16] from the following six macroscopic quantities: the dielectric constants ϵ_0 and ϵ_∞, the infrared absorption frequency ω_{TO}, and the three adiabatic elastic constants C_{11}, C_{12}, and C_{44}. For the pressure dependence of the dielectric constants, the data given by Jones[17] and by Barsch and Achar[18] have been used. For the second-order pressure dependence of the elastic constants, we were able to find experimental data for NaI, KI,[19] KCl,[20] RbCl, RbBr, and RbI.[21] We have performed the lattice-dynamical calculation for only these six materials. The values for the transverse optical frequencies ω_{TO} were taken from data by Martin.[22] Their dependence on volume was estimated from a Born-Mayer potential of the form

$$U = -\alpha e^2/r + a e^{-r/\rho} . \tag{11}$$

The first volume derivative of ω_{TO} or, equivalently, the γ of this mode is then given by[23]

$$\gamma_{\mathrm{TO}} = \frac{\frac{1}{6}\alpha(\sigma^2 - \sigma - 2) - \pi}{\alpha(\sigma - 2) - 2\pi} , \tag{12}$$

TABLE I. Thermodynamic values of q and related quantities. All thermodynamic data are from Refs. 10 and 11.

	β (10^{-4} °K^{-1})	γ	B'_S	δ_S	δ_T	q
NaF	0.96	1.51	5.21	3.75	5.84	1.22
NaCl	1.19	1.61	5.30	3.87	5.97	1.40
NaBr	1.26	1.64	5.27	4.13	6.30	1.75
NaI	1.37	1.71	5.38	4.16	6.43	1.77
KF	1.02	1.52	5.25	4.12	6.13	1.57
KCl	1.11	1.49	5.35	4.41	6.33	1.77
KBr	1.16	1.50	5.39	4.05	5.87	1.37
KI	1.23	1.53	5.48	3.98	5.86	1.26
RbF	0.94	1.40	5.57	5.05	6.83	2.07
RbCl	1.03	1.39	5.48	5.02	6.79	2.14
RbBr	1.08	1.42	5.45	4.81	6.61	1.99
RbI	1.23	1.56	5.44	4.53	6.54	1.91

where $\sigma = r_0/\rho$ and r_0 is the nearest-neighbor distance. For the volume derivative of γ_{TO}, the following relation is obtained:

$$\frac{\partial \gamma_{\mathrm{TO}}}{\partial \ln V} = 2\gamma_{\mathrm{TO}}^2 - \frac{\frac{1}{18}\alpha(\sigma^3 - 3\sigma^2 - 2\sigma - 2) - \pi}{\alpha(\sigma - 2) - 2\pi} . \tag{13}$$

The values of σ as well as those of γ_{TO} derived from Eq. (12) have already been given in Ref. 15. The values of $\partial\gamma_{\mathrm{TO}}/\partial \ln V$ obtained from Eq. (13) are given in the first column of Table II.

Finally, the pressure dependence of the unit-cell volume must be specified and was assumed to be given by Murnaghan's equation of state[24]

$$V/V_0 = [1 + B_T'(P/B_T)]^{-1/B_T'} . \tag{14}$$

This equation is exact to the second order in pressure[25] and is therefore adequate for our purpose of calculating second-order pressure derivatives.

The phonon frequencies for 1000 wave vectors in the Brillouin zone were obtained at zero pressure and at closely spaced higher pressures. The first and second derivatives of the individual mode frequencies with respect to pressure were evaluated numerically at $P = 0$ and q was obtained from Eqs. (6)–(10). The lattice dynamical results are presented in Table II together with the corresponding thermodynamic values of q.

The shell-model results are senstive to changes in the values of the second pressure derivatives of the elastic constants, which were used as input data and which are known only to low accuracy (especially $\partial^2 C_{12}/\partial P^2$). In view of this we regard the overall agreement between the thermodynamic and the lattice-dynamical values of $(\partial \ln\gamma/\partial \ln V)_T$ as satisfactory.

IV. LOW-TEMPERATURE LIMIT OF q

The magnitude of q at very low temperatures is determined by the volume dependence of the nondispersive acoustic-mode frequencies and may therefore be calculated using elastic data. At low enough temperatures, i.e., in the T^3 region of the specific heat, the summations in Eqs. (5) and (6) may be replaced by integrations over solid angle. The low-temperature value of the Grüneisen parameter is given by[26]

$$\gamma_L = \sum_{i=1}^{3} \int \gamma_i C_i^{-3/2}\, d\Omega \Big/ \sum_{i=1}^{3} \int C_i^{-3/2}\, d\Omega , \tag{15}$$

where the remaining summations are over the three acoustic modes. The element of solid angle is denoted by $d\Omega$. The C_i are the three adiabatic elastic constants associated with the acoustic branches in a given direction, and the γ_i, the corresponding mode γ's, are given by[26]

$$\gamma_i = -\frac{1}{6} + \frac{B_T}{2C_i}\left(\frac{\partial C_i}{\partial P}\right)_T . \tag{16}$$

Since for some of the alkali halides γ becomes very small (or even negative) at low temperatures, q will increase sharply (or even have a singularity) at these temperatures. We have therefore calculated the low-temperature limit of the quantity $\gamma q = (\partial\gamma/\partial \ln V)_T$, which varies rather smoothly with temperature.

The expression for the low-temperature limit of $(\partial\gamma/\partial \ln V)_T$ may be obtained from the volume differentiation of Eq. (15). The result is

$$\frac{\partial \gamma_L}{\partial \ln V} = \sum_{i=1}^{3} \int \left(3\gamma_i^2 + \frac{\partial \gamma_i}{\partial \ln V}\right) C_i^{-3/2}\, d\Omega \Big/ \sum_{i=1}^{3} \int C_i^{-3/2}\, d\Omega - 3\gamma_L^2 , \tag{17}$$

where

$$\frac{\partial \gamma_i}{\partial \ln V} = -\frac{B_T}{2C_i}\left(\frac{\partial B_T}{\partial P}\right)_T \left(\frac{\partial C_i}{\partial P}\right)_T + \frac{1}{2}\left(\frac{B_T}{C_i}\right)^2 \left(\frac{\partial C_i}{\partial P}\right)_T^2 - \frac{B_T^2}{2C_i}\left(\frac{\partial^2 C_i}{\partial P^2}\right)_T , \tag{18}$$

which follows from Eq. (16).

Since the second pressure derivatives of the elastic constants that appear in Eq. (18) are available for only six alkali halides, we have evaluated $\partial\gamma_L/\partial \ln V$ for these six crystals only. For the elastic constants and their first and second pressure derivatives, the same (295 °K) data as in Sec. III were used when evaluating γ_i and $\partial\gamma_i/\partial \ln V$ from Eqs. (16) and (18). This involves the assumption that these mode parameters do not exhibit a strong temperature dependence. For the C_i in Eq. (17), the low-temperature experimental values of Refs. 27–29 have been used. The summations and integrations necessary to evaluate $\partial\gamma_L/\partial \ln V$ from Eq. (17) were performed numerically using an extended

Table II. (a) Volume dependence of γ_{TO} calculated from Eq. (13); (b) q values calculated from the lattice-dynamical shell model; (c) q values calculated from Eq. (3); (d) $(\partial\gamma_L/\partial \ln V)$ calculated from Eq. (17); (e) $(\partial\gamma/\partial \ln V)_T = \gamma q$ from the shell model, Eqs. (5) and (6); and (f) $T(\partial \ln\gamma/\partial T)_V$ calculated from the shell model.

	$\left(\frac{\partial\gamma_{\mathrm{TO}}}{\partial \ln V}\right)$	$\left(\frac{\partial \ln\gamma}{\partial \ln V}\right)_T$ at 295 °K		$\left(\frac{\partial\gamma}{\partial \ln V}\right)_T$		$T\left(\frac{\partial \ln\gamma}{\partial T}\right)_V$
	(a)	(b)	(c)	(d)	(e)	(f)
		Lattice dynamics	Thermodynamic data	$T = 0$ °K	$T = 295$ °K	$T = 295$ °K
NaI	4.92	1.44	1.77	4.51	2.72	0.001
KCl	4.85	1.64	1.77	5.13	2.64	0.011
KI	4.79	1.37	1.26	4.66	2.25	0.005
RbCl	4.78	1.82	2.14	9.24	2.84	0.010
RbBr	4.77	1.86	1.99	9.26	2.90	0.006
RbI	4.77	1.93	1.91	8.59	3.05	0.004

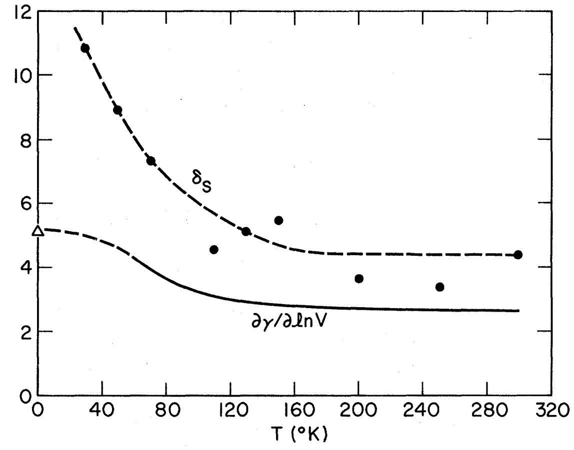

FIG. 1. Temperature variation of $(\partial\gamma/\partial \ln V)_T$ for KCl as calculated from shell model (full curve). Triangle denotes the low-temperature limiting value obtained from Eq. (17). Full circles denote values of δ_S obtained from Eq. (1) using experimental data (Refs. 28 and 30) on β and B_S.

version of the computer program described by Schuele and Smith.[26]

The low-temperature limit of $(\partial\gamma/\partial \ln V)_T$ as calculated from Eq. (17) is given in Table II, column (d), where the room-temperature values of the same quantity are also shown for comparison, column (e). The latter are the product of $(\partial \ln\gamma/\partial \ln V)_T$ given in column (b) and γ given by Eq. (5). It can be seen that for the six alkali halides discussed, $(\partial\gamma/\partial \ln V)_T$ increases in magnitude at low temperatures. Since for these alkali halides γ decreases as the temperature is lowered, this implies a much sharper increase in the magnitude of q at low temperatures.

The result that $(\partial\gamma/\partial \ln V)_T$ increases at low temperatures can be supported by an additional calculation which will provide a link to the shell-model calculation of Sec. III. By assuming that the γ_i as well as the $\partial\gamma_i/\partial \ln V$ do not vary with temperature, it follows from Eq. (6) that the only temperature dependence of q and of $(\partial\gamma/\partial \ln V)_T$ arises through the coefficients c_i. We can therefore obtain $(\partial\gamma/\partial \ln V)_T$ as a function of temperature by using the room-temperature values of γ_i and $\partial\gamma_i/\partial \ln V$ that were calculated in Sec. III from the shell model. The solid curve in Fig. 1 shows the calculated value of $(\partial\gamma/\partial \ln V)_T$ for KCl. The method of calculation is applicable only down to moderately low temperatures, since the number of excited modes in our sample of the Brillouin zone becomes too small at lower temperatures. The increase in $(\partial\gamma/\partial \ln V)_T$ as the temperature is lowered is, however, clearly noticeable. The triangle at $T = 0$ °K denotes the value of $\partial\gamma_L/\partial \ln V$ calculated from Eq. (17).

The sharp increase in the magnitude of q at low temperatures implies that the parameter δ_S will exhibit a corresponding increase. This can be seen from Eq. (3). The only term on the right-hand side of this equation which is sufficiently temperature dependent to account for the large increase in q is δ_S. In order to verify this conclusion we have calculated δ_S directly from Eq. (1), using experimental data for the temperature dependence of the adiabatic bulk modulus[28] and of the thermal expansion coefficient[30] of KCl. δ_S, given by the broken curve of Fig. 1, indeed shows the expected increase as low temperatures are approached. A plot of δ_S vs temperature for RbI was also constructed from available temperature data on B_S and β. The resulting values of δ_S exhibit a much sharper increase at low temperatures than in the case of KCl. The parameter δ_T appearing in Eq. (4) has a temperature dependence which closely resembles that of δ_S.

The values of $\partial\gamma_i/\partial \ln V$ of nondispersive acoustic modes for crystallographic directions on the boundary of the unit triangle bound by the [100], [110], and [111] corners are shown in Fig. 2 for the case of RbI. The mode parameters shown exhibit considerable anisotropy, as do the corresponding mode γ's.[26] For an isotropic crystal there would be no

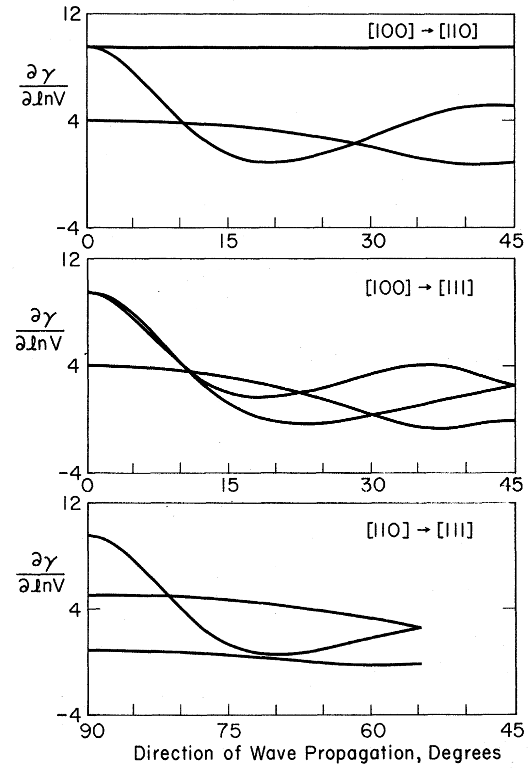

FIG. 2. Illustration of the anisotropy of $(\partial\gamma_i/\partial \ln V)$ for the three acoustic modes in RbI.

TABLE III. Thermodynamic values of q.

	Bassett *et al.* (Ref. 9)	Leadbetter *et al.* (Ref. 31)	Present work
NaF	0.73		1.22
NaCl	1.46	1.10	1.40
KCl	1.70	1.38	1.77
KBr		0.87	1.37
RbI	1.65		1.91

directional dependence and the two shear modes would be degenerate.

V. DISCUSSION

The values of $\partial \ln\gamma/\partial \ln V$ for alkali halides, as derived from thermoelastic data, and also from a detailed shell-model calculation, do not support any of the simplified assumptions (e.g., $q=0$ or $q=1$) which have been employed in the past. As a rough first estimate, the value of $q=1.5$ at room temperature is more appropriate.

To our knowledge, no lattice-dynamical calculation of q for alkali halides has been performed in the past. Some estimates of q values from thermodynamic data have been reported, and these are compared in Table III with the present thermodynamic estimates. The values given by Leadbetter *et al.*[31] are consistently lower than ours, and those of Bassett *et al.*[9] are comparatively low for NaF and RbI and show very good agreement for NaCl and KCl.

In evaluating the room-temperature value of q from Eq. (3), the term $T(\partial \ln\gamma/\partial T)_V$ has been neglected. It can be shown to be much smaller in magnitude than q. Bartels and Schuele[32] have given very rough numerical estimates of $(\partial\gamma/\partial T)_V$ at 295 °K for NaCl (0.5×10^{-4} deg^{-1}) and for KCl (-6.5×10^{-4} deg^{-1}). This gives for $T(\partial \ln\gamma/\partial T)_V$ the values 0.01 for NaCl and -0.13 for KCl, which are less than the uncertainty reported for q. Moreover, it seems that typical values of $T(\partial \ln\gamma/\partial T)_V$ would be closer to the lower value reported for NaCl. This can be shown by differentiating Eq. (5) with respect to temperature, which gives the following relation for the quasiharmonic value of $(\partial\gamma/\partial T)_V$:

$$\left(\frac{\partial\gamma}{\partial T}\right)_V=\sum(\gamma_i-\gamma)(\partial c_i/\partial T)_V/\sum c_i\ . \qquad (19)$$

For the six alkali halides, for which lattice-dynamical calculations have been performed, we have also evaluated $(\partial\gamma/\partial T)_V$ from Eq. (19) as a function of temperature. The room-temperature values of $T(\partial \ln\gamma/\partial T)_V$ are given in the last column of Table II. It can be seen that the quasiharmonic room-temperature values of $T(\partial \ln\gamma/\partial T)_V$ are negligible in comparison with q. The incorporation of anharmonic interactions which are explicitly temperature dependent (and for which the quasiharmonic model does not account) is unlikely to cause a change in the order of magnitude of $T(\partial \ln\gamma/\partial T)_V$.

At low temperatures, the values of q and of the related Anderson-Grüneisen parameters increase in magnitude for the materials considered. This has some implications regarding the Wachtman-Anderson relation[2] for the temperature dependence of the adiabatic bulk modulus. This relation is based on the assumption that δ_S and γ are independent of temperature. We find that for the alkali halides discussed in the present paper this assumption is applicable only above temperatures of the order of 150 °K.

We have been able to study only six alkali halides with regard to the low-temperature limit of q, and the qualitative conclusions which we have drawn, though probably applicable to most other alkali halides, may not carry over entirely to all of them. The magnitude changes in $q\equiv\partial \ln\gamma/\partial \ln V$ as the temperature is lowered arise due to nearby equal fractional changes in γ (decrease) and in $\partial\gamma/\partial \ln V$ (increase). For those ionic materials for which γ increases as the temperature is lowered (e.g., LiF and MgO) the low-temperature variation of q and δ_S is entirely uncertain.

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Excitonic Effects on Dielectric Properties of Solids in a Uniform Electric Field

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The imaginary part of the dielectric function for excitonic transitions and different types of critical points of a solid in a uniform electric field are presented in a closed form. The time-dependent Schrödinger equation, with a time-dependent gauge for the applied electric field which includes the electron-hole interaction forces is treated within the effective-mass approximation. In the weak fields and using the two-band approximations, the results can be expressed in terms of Airy functions. The peak position of the exciton lines is found to shift to lower energies and then move to higher energies as the electric field increases. The amplitude of the peak decreases as the electric field increases. The electron-hole interaction can be neglected in calculating the electric-field-induced change of the dielectric constant, when the applied electric field is much larger than the effective field of the electron-hole interaction.

I. INTRODUCTION

The electro-optic or Franz-Keldysh effect has been fruitful in identifying energies of solids at which critical points occur.[1] However, the one-electron uniform-electric-field theory can not explain the experimental results.[2] Some authors have pointed out that other effects, such as nonuniformity of the modulating electric field,[3] the Coulomb interaction,[2,4] and collision broadening[5] should be properly included in the theory.

In order to describe the effect of nonuniform fields, Aspnes and Frova[6] have proposed an averaging procedure, based on an approximate solution of Maxwell's equations for inhomogeneous media, and a one-electron theory and an exponentially decaying electric field[7] have been used to derive the field-induced change in dielectric function. This explains the gross features of electroreflectance. The validity of the one-electron approximation for interband transitions is based on the assumption that the Coulomb interaction between electrons and holes is weak. In order to provide an adequate interpretation of the optical experiments, a qualitative discussion by Hamakawa *et al.*[2,8] shows that the broadening of exciton lines by the electric field produces additional peaks in the field-induced change in dielectric function. Duke and Alferieff[9] have used a semiquantitative theory of this effect to discuss the optical absorption in semiconductors. Recently, Penchina, Pribram, and Sak[10] and Rowe and Aspnes[11] used the Koster-Slater model, while Ralph,[12] Dow and Redfield,[13] and Blossey[14] solved the effective-mass equation numerically to discuss the excitonic effects on the optical absorption of solids. Enderlein[15] used the Green's-function approach to solve the problem, but one of his assumptions made his result only valid in the limit of zero electron-hole interaction.[10,16]

We present here a theoretical calculation which includes the electron-hole interaction and is based on the assumptions that include the validity of the effective-mass approximation and the uniform electric field.

II. MODEL OF PROBLEM

A. Wave Functions

We consider a model of an electronic Hamiltonian