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Microscopic model for the two-phonon Raman spectra of alkali halides

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The second-order Raman-scattering (SORS) cross section of alkali halides has been evaluated by using the Buckingham expansion for the induced polarizability. This *ab initio* approach leads to a microscopic expression of the SORS cross section without free parameters. The first two nonzero contributions of the expansion, namely, the dipole-induced dipole (DID) coming from the first-order dressed polarizability and the *BTQ* (second-dipole hyperpolarizability × dipole propagator × effective charge) coming from the second-dipole–quadrupole polarizability, have been considered. The short-range contribution to the induced polarizability coming from the electronic overlap has not been included in the present work. The SORS spectra are expressed in terms of the dynamical quantities of the crystal (eigenvectors and eigenfrequencies) and in terms of some bare ionic susceptibilities, namely, the ions' bare polarizabilities α^+ and α^- and the second-dipole–quadrupole bare polarizabilities B^+ and B^-. As an example the results are shown in the case of KBr. Considerations on the long-range nature of the DID spectrum and on the short-range nature of the *BTQ* spectrum are made. The relative weights of the two contributions to the SORS in the whole class of alkali halides are also discussed.

I. INTRODUCTION

In the last decades many theoretical and experimental works[1–16] have been devoted to the study of the second-order Raman-scattering (SORS) spectra from alkali halides, as well as from other cubic crystals. Indeed, for such materials the first-order Raman scattering vanishes because atoms are centers of inversion symmetry and the spectra show only features coming from the SORS.

In the literature, the SORS has always been considered as an image of the two-phonon joint density of states. This statement is in some way true, since the most relevant features of the two-phonon joint density of states are indeed evident in SORS spectra. These features have been assigned to couples of phonons coming from high-symmetry points of the first Brillouin zone (BZ), even if no quantitative agreement has been found between the shape of the two-phonon joint density of states and the SORS spectra. At the present stage it is clear that in order to have a full and satisfactory explanation of this spectral shape, a detailed knowledge of the microscopic scattering mechanisms is required.

It is well known that the expression for the Raman-scattering intensity is given in terms of the space-time Fourier transform of the correlation function of the microscopic polarizability of the crystal. The time fluctuations of this tensor are therefore needed to calculate the Raman-scattering spectra. As indicated by Born and Bradburn,[17] whenever the frequency of the exciting radiation is much less than the lowest electronic transition frequency, the crystal polarizability can be expanded in a power series of the atomic displacements, which in turn can be expressed in terms of phonon coordinates. In particular, in dealing with SORS, the quantities involved in determining the spectral shape are the second-order derivatives of the crystal polarizability with respect to the atomic coordinates (a fourth-rank tensor) and a suitable combination of four phonon field operator correlation functions.

Hence the problem of calculating SORS splits in two parts: (i) the determination of the phonon properties (eigenvalues and eigenfrequencies) and (ii) the determination of the effects which all couples of phonons have in modulating the lattice polarizability.

At the present time, with the help of computers, a huge number of dynamical models have been developed. The one most used for alkali halides is the shell model (SM), that allows one to perform lattice dynamics calculations which show very good agreement with the experimental data. Since a very large bibliography on the subject is available[18–22] we will not go into further details.

If on one side the solution of the dynamical problem is well established in the current literature, on the other side, the calculation of the Raman tensor is much more intriguing. At this time, a reliable microscopic theory does not exist that will predict the relative values of the various tensor elements as well as the absolute spectral intensities.

Since the early seventies, an approach based on the Buckingham expansion[23] for the effective atomic polarizability has been successfully used for the quantitative calculation of the Raman spectral shape of gases and liquids.[24] Within this approach the macroscopic polarizability of the system is expressed as the sum of the atomic-effective polarizabilities, which in turn are the sums of the bare (or in vacuo) atomic polarizabilities plus a collision-induced term. This last term depends on the relative distance between all the atoms of the system and is expressed via the multipolar expansion of the local electric fields. The main underlying hypothesis in this approach is that the electronic wave functions of the system are so well localized around the scattering entities (ions in the present case), that they can be considered as isolated in the zero-order approximation, and the effect of all the surrounding entities can be treated as an electromagnetic perturbation.

This scheme has been applied to crystalline systems and, as far as SORS is concerned, it has been used by

Werthamer and co-workers[25,26] for calculating the spectral shape in the case of rare-gas crystals. In these works the authors consider the crystals of He, Ne, and Ar as being composed of point polarizable atoms and consider only the leading term in the Buckingham expansion, i.e., the dipole-induced dipole (DID) term. In dealing with the DID contribution to the effective atomic polarizability, two main approximations have been used in those papers, i.e., the exchanged wave vector was considered negligible and the self-consistent equation for the effective atomic polarizability was truncated at the first order. In the following we will discuss the consequences of these approximations.

To our knowledge, the application of the Buckingham expansion to other systems has been adopted only by Mahan and Subaswamy[27] on alkali halides. In their work, these authors take into account the contribution at the SORS as coming from the second hyperpolarizability and from the second-dipole–quadrupole polarizability ($\bar{\bar{\gamma}}$ and $\bar{\bar{\mathbf{B}}}$, respectively, in the Buckingham notations). The reason for this choice is clearly explained by the authors. In the limit that only first derivatives of the local electric field are taken into account only the $\bar{\bar{B}}$ terms contribute to SORS. On the other hand, the DID terms will participate in SORS if we include second derivatives of the local electric field.

In this paper we propose a microscopic model for the calculation of the SORS spectra in alkali halides, which accounts for both the DID and the second-dipole–quadrupole polarizability contributions. The model is described by *BTQ*, the tensor product of the second-dipole hyperpolarizability *B*, the dipole propagator *T*, and the effective charge *Q*.

Our model adopts the Born-Bradburn separation of the polarizability from the dynamical problem, together with the Buckingham expansion for the effective atomic polarizability. The leading terms of the multipolar expansion are retained, and the resulting self-consistent equation for the effective polarizability is rigorously solved, overcoming the generally employed first-order approximation. Moreover, it will be shown that the effects of neglecting the finite value for the wave vector exchanged by the radiation in the scattering process are not negligible, and therefore the expression for the SORS cross section will be calculated taking into account the $|\mathbf{q}|$ value, even if small.

In Sec. II the expression for the SORS cross section is derived following this scheme and in Sec. III we will discuss, as an example, the results for the KBr SORS spectral shape showing the effects of the various approximations when introduced.

II. THEORY

A. Scattering equation

We will indicate with $(\partial^2\sigma/\partial\omega\,\partial\Omega)_\Gamma$ the cross section for light scattering in a given "scattering configuration" Γ;

$$\left[\frac{\partial^2\sigma}{\partial\omega\,\partial\Omega}\right]_\Gamma=\frac{\omega_i\omega_f^3}{c^4}\sum_{\alpha\beta\gamma\delta} I_{\alpha\beta\gamma\delta}(\omega,\mathbf{q})\hat{m}_\alpha\hat{n}_\beta\hat{m}_\gamma\hat{n}_\delta \; . \tag{1}$$

The scattering configuration $\Gamma\equiv(\hat{n},\hat{m},\mathbf{k}_i\mathbf{k}_f)$ is defined by the polarization unit vector $\hat{n}$ ($\hat{m}$), and the wave vector $\bar{k}_i$ ($\bar{k}_f$), of the incident (scattered) radiation. The axes of the reference frame are chosen to be coincident with the crystallographic axes of the cubic crystal. Moreover $\omega=\omega_f-\omega_i$, with $\omega_i=c|\mathbf{k}_i|$ and $\omega_f=c|\mathbf{k}_f|$, is the Raman shift and $\mathbf{q}=\mathbf{k}_f-\mathbf{k}_i$ is the exchanged wave vector. The terms $I_{\alpha\beta\gamma\delta}(\omega,\mathbf{q})$ are the elements of the scattering tensor which are the space-time Fourier transform of the macroscopic polarizability density tensor correlation functions.

$$I_{\alpha\beta\gamma\delta}(\omega,\mathbf{q})=\frac{1}{2\pi N}\int dt\, e^{i\omega t}\int d\mathbf{r}_1 d\mathbf{r}_2 e^{-i\mathbf{q}\cdot(\mathbf{r}_1-\mathbf{r}_2)} \times\left\langle \Pi_{\alpha\beta}(\mathbf{r}_1,t)\,\Pi_{\gamma\delta}(\mathbf{r}_2,0)\right\rangle \; . \tag{2}$$

If the system is composed of entities (say atoms, ions, or molecules) whose eigenfunctions are localized on a dimension much smaller than the wavelength of the incident light, it is useful to carry out the microscopic description of the scattering process by writing the macroscopic polarizability tensor in terms of local properties of each entity, i.e.,

$$\Pi_{\alpha\beta}(\mathbf{r},t)=\sum_{l\lambda}\pi_{\alpha\beta}^{l\lambda}(t)\delta[\mathbf{r}-\mathbf{R}^{l\lambda}(t)] \; . \tag{3}$$

In Eq. (3), $\pi_{\alpha\beta}^{l\lambda}(t)$ is the "effective" polarizability tensor of the entity λ in the lth unit cell ($\lambda=1,2,\ldots,r$, with r being the number of entities belonging to the basis of the crystal, and $l=1,\ldots,N$) and $\mathbf{R}^{l\lambda}(t)$ is the instantaneous position of the ($l\lambda$) entity. The latter quantity can be written as

$$\mathbf{R}^{l\lambda}(t)=\mathbf{r}^{l\lambda}+\mathbf{u}^{l\lambda}(t)=\mathbf{x}^l+\mathbf{a}^\lambda+\mathbf{u}^{l\lambda}(t) \; , \tag{4}$$

where $\mathbf{u}^{l\lambda}(t)$ is the displacement from the equilibrium position $\mathbf{r}^{l\lambda}$, $\mathbf{x}^l$ individuates the lth cell, and $\mathbf{a}^\lambda$ is the basis vector for the λth entity in the unit cell. By expanding the effective atomic polarizability $\pi_{\alpha\beta}^{l\lambda}(t)$ in a series of atomic displacements and by writing the atomic displacements in terms of phonons, Eq. (2) becomes

$$I_{\alpha\beta\gamma\delta}(\omega,\mathbf{q})=\frac{\hbar^2}{16N}\sum_{jj'}\sum_{\mathbf{k}}F_{jj'\mathbf{k}}(\omega,\mathbf{q})\chi_{\alpha\beta}(\mathbf{k},\mathbf{q};\;jj')\chi_{\gamma\delta}(-\mathbf{k},-\mathbf{q};\;jj') \; , \tag{5}$$

where the coupling amplitude $\chi_{\alpha\beta}(\mathbf{k},\mathbf{q};jj')$ is defined as

$$\chi_{\alpha\beta}(\mathbf{k},\mathbf{q};\;jj')=\sum_{\mu\nu}\sqrt{1/M_\mu M_\nu}\sum_{\eta\theta}e_\eta(\mu|j\mathbf{k})e_\theta(\nu|j'\mathbf{q}-\mathbf{k})^{(2)}P_{\alpha\beta\eta\theta}^{\mu\nu}(\mathbf{k},\mathbf{q}) \tag{6}$$

and

$$\begin{aligned}F_{jj'\mathbf{k}}(\omega,\mathbf{q})=[\omega_j(\mathbf{k})\omega j'(\mathbf{q}-\mathbf{k})]^{-1}\{&\delta[\omega+\omega_j(\mathbf{k})+\omega_{j'}(\mathbf{k}-\mathbf{q})]n(\mathbf{k},j)n(\mathbf{k}-\mathbf{q},j')\\&+\delta[\omega+\omega_j(\mathbf{k})-\omega_{j'}(\mathbf{k}-\mathbf{q})]n(\mathbf{k},j)[n(\mathbf{k}-\mathbf{q},j')+1]\\&+\delta[\omega-\omega_j(\mathbf{k})+\omega_{j'}(\mathbf{k}-\mathbf{q})][n(\mathbf{k},j)+1]n(\mathbf{k}-\mathbf{q},j')\\&+\delta[\omega-\omega_j(\mathbf{k})-\omega_{j'}(\mathbf{k}-\mathbf{q})][n(\mathbf{k},j)+1][n(\mathbf{k}-\mathbf{q},j')+1]\}\ ,\end{aligned}\qquad(7)$$

where $n(\mathbf{k},j)$ is the Bose population factor for the $(\mathbf{k},j)$ mode. In Eq. (6) ${}^{(2)}P^{\mu\nu}_{\alpha\beta\eta\theta}(\mathbf{k},\mathbf{q})$ is defined as

$${}^{(2)}P^{\mu\nu}_{\alpha\beta\eta\theta}(\mathbf{k},\mathbf{q})=\sum_{mn}e^{i(\mathbf{k}-\mathbf{q}/2)\cdot(\mathbf{x}^{m\mu}-\mathbf{x}^{n\nu})}\sum_{\lambda}{}^{0}[\partial^2\pi^{0\lambda}_{\alpha\beta}/\partial u_{\eta}^{m\mu}\partial u_{\theta}^{n\nu}]e^{i\mathbf{q}/2\cdot(\mathbf{x}^{m\mu}+\mathbf{x}^{n\nu})}\ ,\qquad(8)$$

moreover $\omega_j(\mathbf{k})$ and $e_\eta(\mu|j\mathbf{k})$ are, respectively, the eigenvalues and the eigenvectors for the $(\mathbf{k},j)$ mode, and ${}^{0}[\ ]$ indicates that the term included in the brackets is taken in the equilibrium position $\mathbf{u}^{l\lambda}(t)=0$.

Equation (5) is an "easy to read" result for the two-phonon Raman-scattering intensity. Indeed, it states that there are contributions to the scattered intensity from all the couples of phonons $(j,\mathbf{k})$ or $(j',\mathbf{k}')$ for which $\mathbf{k}+\mathbf{k}'+\mathbf{q}=0$, and that this contribution is proportional to the inverse of the phonons' frequency, to a suitable thermal population factor, and to the square of the coupling amplitude $\chi_{\alpha\beta}(\mathbf{k},\mathbf{q};jj')$.

The coupling amplitude is in turn written [see Eqs. (6)–(8)] in terms of the eigenvectors of the system, $\mathbf{e}(\mu|j\mathbf{k})$, and the efficiency through which the displaced atoms modulate the appropriate spatial Fourier component of the crystal polarizability i.e., ${}^{(2)}P^{\mu\nu}_{\alpha\beta\gamma\delta}(\mathbf{k},\mathbf{q})$.

If we take the $\mathbf{q}=0$ limit of Eq. (5), the equations of Hardy and Karo are easily recovered by identifying the term $P_{\alpha\beta\eta\theta}(n-m|\mu\nu)$ in Eq. (12) of Ref. 10 with the quantity $\sum_{l\lambda}{}^{0}[\partial^2\pi^{l\lambda}_{\alpha\beta}/\partial u_{\eta}^{m\mu}\partial u_{\theta}^{n\nu}]$.

It is worth noting that in our expression we let $\mathbf{q}\neq0$. The reason for keeping a finite value for the exchanged light wave vector will be clear as we will go further in the calculations.

In order to give a microscopical description of the phenomenon we are dealing with, we need to evaluate the quantities ${}^{(2)}P^{\mu\nu}_{\alpha\beta\gamma\delta}(\mathbf{k},\mathbf{q})$, which is the goal of the following sections.

B. Effective polarizability

In condensed systems, different approaches have been used to write an explicit expression for the effective atomic polarizability. For dielectric materials (or in any case for all condensed systems, where the lowest electronic absorption frequency is much bigger than $\hbar\omega_i$), the Buckingham-like series[23] have been widely used. In this formulation, one starts writing the effective instantaneous dipole moment on a given (l,λ) entity in terms of the local electric fields $\mathbf{E}^{l\lambda}$ acting on it.

$$\begin{aligned}\tilde{\mu}^{l\lambda}_{\alpha}={}^{0}\mu^{\lambda}_{\alpha}&+\sum_{\beta}\alpha^{\lambda}_{\alpha\beta}E^{l\lambda}_{\beta}+\frac{1}{2}\sum_{\beta\gamma}\beta^{\lambda}_{\alpha\beta\gamma}E^{l\lambda}_{\beta}E^{l\lambda}_{\gamma}\\&+\frac{1}{6}\sum_{\beta\gamma\delta}\gamma^{\lambda}_{\alpha\beta\gamma\delta}E^{l\lambda}_{\beta}E^{l\lambda}_{\gamma}E^{l\lambda}_{\delta}+\frac{1}{3}\sum_{\beta\gamma}A^{\lambda}_{\alpha\beta,\gamma}\nabla_{\beta}E^{l\lambda}_{\gamma}\\&+\frac{1}{3}\sum_{\beta\gamma\delta}B^{\lambda}_{\alpha\beta,\gamma\delta}E^{l\lambda}_{\beta}\nabla_{\gamma}E^{l\lambda}_{\delta}+\cdots\ ,\end{aligned}\qquad(9)$$

where higher-order effective multipole contributions have been neglected. In this equation the quantities α^{λ}, β^{λ}, γ^{λ}, A^{λ}, and B^{λ} are electrical "bare" properties (susceptibility tensors); more precisely $\alpha^{\lambda}_{\alpha\beta}$ is the polarizability, $\beta^{\lambda}_{\alpha\beta\gamma}$ and $\gamma^{\lambda}_{\alpha\beta\gamma\delta}$ are the first and the second hyperpolarizabilities, and $A^{\lambda}_{\alpha\beta,\gamma}$ and $B^{\lambda}_{\alpha\beta,\gamma\delta}$ are the first and second dipole-quadrupole polarizabilities, respectively. An explicit expression for these susceptibilities in terms of electronic wave functions can be found in Ref. 23.

This description takes into account only the electromagnetic disturbance to the isolated entities and it completely neglects the contribution to the effective dipole moments coming from both electronic overlap and exchange effects. This implies that all the previous quantities are time independent. If electronic overlap and exchange effects are to be introduced, this can be done separately (see Ref. 45).

In the case of atoms or ions (as in our crystal), we can reduce the terms appearing in Eq. (9). Indeed, for spherically symmetric entities, it results[23] in the following:

$$\begin{aligned}&{}^{0}\mu^{\lambda}_{\alpha}=\beta^{\lambda}_{\alpha\beta}A^{\lambda}_{\alpha\beta,\gamma}=0,\quad \alpha^{\lambda}_{\alpha\beta}=\alpha^{\lambda}\delta_{\alpha\beta}\ ,\\&\gamma^{\lambda}_{\alpha\beta\gamma\delta}=\tfrac{1}{3}\gamma^{\lambda}(\delta_{\alpha\beta}\delta_{\gamma\beta}+\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma})\ ,\\&B^{\lambda}_{\alpha\beta,\gamma\beta}=B^{\lambda}[\tfrac{3}{4}(\delta_{\alpha\gamma}\delta_{\beta\delta}+\delta_{\alpha\delta}\delta_{\beta\gamma})-\tfrac{1}{2}\delta_{\alpha\beta}\delta_{\gamma\delta}]\ .\end{aligned}\qquad(10)$$

The local electric field "felt" by each entity is given by the sum of the incident laser field $\mathcal{E}^{l\lambda}=\mathcal{E}_0e^{i\mathbf{k}_i\cdot\mathbf{r}^{l\lambda}}$ and by the field propagating from all the other (effective) multipoles of the system, i.e.,

$$\begin{aligned}E^{l\lambda}_{\alpha}=\mathcal{E}^{l\lambda}_{\alpha}&+\sum_{l'\lambda'}T^{(1)}_{\alpha}[\mathbf{R}^{l\lambda}(t)-\mathbf{R}^{l'\lambda'}(t)]Q^{\lambda'}\\&+\sum_{\beta}\sum_{l'\lambda'}T^{(2)}_{\alpha\beta}[\mathbf{R}^{l\lambda}(t)-\mathbf{R}^{l'\lambda'}(t)]\tilde{\mu}^{l'\lambda'}_{\beta}+\cdots\ ;\end{aligned}\qquad(11)$$

here Q^{λ} is the charge of the ions of species λ and the tensor $T^{(n)}_{\alpha_1\cdots\alpha_n}(\mathbf{R})$ is the n-pole electric-field propagator, given by

$$T^{(n)}_{\alpha_1\cdots\alpha_n}(\mathbf{R})=(-1)^n\nabla_{\alpha_1}\cdots\nabla_{\alpha_n}\frac{1}{|\mathbf{R}|}\ .\qquad(12)$$

Equations (9)–(12) provide a complete description of the electric fields inside a crystal if the electrical susceptibilities of the various ions are well-defined quantities, i.e., if the electronic wave functions of different entities do not overlap, which is the approximation we are working with.

From Eq. (9), the effective ionic polarizability, which enters into the light-scattering intensity expression, can be calculated as[23]

$$\pi_{\alpha\beta}^{l\lambda}=\left[\frac{\partial\tilde{\mu}_{\alpha}^{l\lambda}}{\partial\mathcal{E}_{\beta}^{l\lambda}}\right]_{\mathcal{E}_0=0} . \tag{13}$$

By inserting Eqs. (11) and (9) in (13), retaining only the leading terms and keeping in mind that $\mathcal{E}^{l\lambda}=\mathcal{E}^{l'\lambda'}e^{i\mathbf{k}_i\cdot(\mathbf{r}^{l\lambda}-\mathbf{r}^{l'\lambda'})}$ one obtains

$$\pi_{\alpha\beta}^{l\lambda}(t)=\alpha^{\lambda}\delta_{\alpha\beta}+\alpha^{\lambda}\sum_{\gamma}\sum_{l'\lambda'}T_{\alpha\gamma}^{(2)}[\mathbf{R}^{l\lambda}(t)-\mathbf{R}^{l'\lambda'}(t)]e^{-i\mathbf{k}_i\cdot(\mathbf{r}^{l\lambda}-\mathbf{r}^{l'\lambda'})}\pi_{\gamma\beta}^{l'\lambda'}(t)+\frac{1}{6}\sum_{\gamma\delta}\gamma_{\alpha\beta\gamma\delta}^{\lambda}\left[\sum_{l'\lambda'}T_{\gamma}^{(1)}[R^{l\lambda}(t)-\mathbf{R}^{l'\lambda'}(t)]Q^{\lambda'}\right]$$
$$\times\left[\sum_{l'\lambda'}T_{\delta}^{(1)}[\mathbf{R}^{l\lambda}(t)-\mathbf{R}^{l'\lambda'}(t)]Q^{\lambda'}\right]-\frac{1}{3}\sum_{\delta\epsilon}B_{\alpha\beta\delta\epsilon}^{\lambda}\left[\sum_{l'\lambda'}T_{\delta\epsilon}^{(2)}[\mathbf{R}^{l\lambda}(t)-\mathbf{R}^{l'\lambda'}(t)]Q^{\lambda'}\right]+\cdots . \tag{14}$$

This equation states that in systems composed of isotropic scattering particles (atoms or ions), the effective polarizability is mainly given by the sum of three terms, beyond the bare polarizability $\alpha^{\lambda}\delta_{\alpha\beta}$.

The first one represents the dipole-induced dipole contribution ($\alpha T\alpha$ or DID). This term, which is the only nonvanishing one in systems composed of neutral atoms ($Q^{\lambda}\equiv 0$), is always present in dense systems and is responsible for the appearance of the Lorenz-Lorentz relation.[28] As is evident from Eq. (14), the DID contribution to the effective polarizability is defined through a self-consistent equation.

In the first-order DID approximation (which has been considered by many authors[29]) the term $\pi_{\gamma\beta}^{l'\lambda'}(t)$ in the second term on the right-hand side of Eq. (14) is replaced by $\alpha^{\lambda'}\delta_{\gamma\beta}$. This approximation leads directly to a simple expression for $\pi_{\alpha\beta}^{l\lambda}$. In a recent paper[30] it has been shown that in perfect crystals, the self-consistent DID equation can be explicitly solved without any approximation. Throughout this paper we will adopt the same procedure in order to solve the problem without any approximation. In Sec. III we will show what sort of effects the rigorous result has on both the spectral shape and intensity of the scattered light, when compared with that of the first-order approximation.

One of the two terms left in Eq. (14) depends on the second hyperpolarizability γ (γTQ) and is called the charge-induced dipole (CID).[31] As already pointed out by Mahan *et al.*[27] in cubic crystals this term gives no contribution to the SORS due to the vanishing value of both static electric fields and electric-field gradients at the lattice sites.

This is not true for the last term in Eq. (14), the BTQ term, which gives a contribution depending on the third spatial derivative of the static electric fields, which is a nonvanishing quantity. This last term has already been treated by Mahan *et al.*[27] A comparison of the relative intensities of DID and BTQ contributions will be performed in the last section.

C. Summary of the theoretical results for the DID case

If one deals with the self-consistent equation for $\pi_{\alpha\beta}^{l\lambda}(t)$ in the DID framework, writing Eq. (14) as

$$\pi_{\alpha\beta}^{l\lambda}(t)=\alpha^{\lambda}\delta_{\alpha\beta}+\alpha^{\lambda}\sum_{\gamma}\sum_{l'\lambda'}T_{\alpha\gamma}^{(2)}[\mathbf{R}^{l\lambda}(t)-\mathbf{R}^{l'\lambda'}(t)]\pi_{\gamma\beta}^{l'\lambda'}(t)e^{-i\mathbf{k}_i\cdot[\mathbf{r}^{l\lambda}-\mathbf{r}^{l'\lambda'}]} , \tag{15}$$

after straightforward but lengthy algebra, the quantities ${}^{(2)}P_{\alpha\beta\eta\theta}^{\mu\nu}(\mathbf{k},\mathbf{q})$ are

$${}^{(2)}P_{\alpha\beta\eta\theta}^{\mu\nu}(\mathbf{k},\mathbf{q})=\left[\frac{\epsilon+2}{3}\right]^{2}{}^{(2)}P_{\alpha\beta\eta\theta}^{\mu\nu}(\mathbf{k},\mathbf{0}) , \tag{16}$$

with

$${}^{(2)}P_{\alpha\beta\eta\theta}^{\mu\nu}(\mathbf{k},\mathbf{0})|_{\mathrm{DID}}=-\alpha^{\mu}\alpha^{\nu}[{}^{(4)}\hat{B}_{\alpha\beta\eta\theta}^{\mu\nu}(\mathbf{k})+{}^{(4)}\hat{B}_{\alpha\beta\eta\theta}^{\mu\nu}(\mathbf{k})]+\delta_{\mu\nu}\sum_{\lambda}\alpha^{\lambda}\alpha^{\mu}[{}^{(4)}\hat{B}_{\alpha\beta\eta\theta}^{\mu\lambda}(\mathbf{0})+{}^{(4)}\hat{B}_{\alpha\beta\eta\theta}^{\lambda\mu}(\mathbf{0})] \tag{17}$$

and

$$
{}^{(4)}\hat{B}^{\mu\nu}_{\alpha\eta\eta\theta}(\mathbf{k})={}^{(4)}A^{\mu\nu}_{\alpha\beta\eta\theta}(\mathbf{k})+\sum_{\lambda}\alpha^{\lambda}\sum_{\gamma}{}^{(3)}A^{\mu\lambda}_{\alpha\gamma\eta}(\mathbf{k}){}^{(1)}P^{\lambda\nu}_{\gamma\beta\theta}(\mathbf{k},\mathbf{0})\ . \qquad (18)
$$

In Eq. (18) ${}^{(n)}A^{\mu\nu}_{\alpha_1\cdots\alpha_n}(\mathbf{k})$ are lattice sums defined by

$$
{}^{(n)}A^{\mu\nu}_{\alpha_1\cdots\alpha_n}(\mathbf{k})=\frac{1}{N}\sum_{ll'}T^{(n)}_{\alpha_1\cdots\alpha_n}(\mathbf{r}^{l\lambda}-\mathbf{r}^{l'\lambda'})e^{i\mathbf{k}\cdot(\mathbf{r}^{l\lambda}-\mathbf{r}^{l'\lambda'})} \qquad (19)
$$

and ${}^{(1)}\hat{P}^{\mu\nu}_{\alpha\beta\eta}(\mathbf{k},\mathbf{0})$ is given by the self-consistent equation

$$
{}^{(1)}\hat{P}^{\mu\nu}_{\alpha\beta\eta}(\mathbf{k},\mathbf{0})={}^{(3)}A^{\mu\nu}_{\alpha\beta\eta}(\mathbf{k})+\sum_{\lambda}\alpha^{\lambda}\sum_{\gamma}{}^{(2)}A^{\mu\lambda}_{\alpha\gamma}(\mathbf{k}){}^{(1)}\hat{P}^{\lambda\nu}_{\gamma\beta\eta}(\mathbf{k},\mathbf{0})\ . \qquad (20)
$$

D. Contribution from the *BTQ* term

Following Mahan and Subbaswamy[27] in dealing with the *BTQ* term one must consider as a starting equation the following approximation to Eq. (14):

$$
\pi^{l\lambda}_{\alpha\beta}(t)=-\frac{1}{3}\sum_{\delta\epsilon}B^{\lambda}_{\alpha\beta,\delta\epsilon}\left[\sum_{l'\lambda'}T^{(2)}_{\delta\epsilon}[\mathbf{R}^{l\lambda}(t)-\mathbf{R}^{l'\lambda'}(t)]Q^{\lambda'}\right]\ . \qquad (21)
$$

by using the expression $B^{\lambda}_{\alpha\beta,\gamma\delta}$ for the case of spherical particles [Eq. (10)] and remembering that $\sum_{\alpha}T^{(2)}_{\alpha\alpha}[\mathbf{R}(t)]=0$, one obtains

$$
\pi^{l\lambda}_{\alpha\beta}(t)=-\tfrac{1}{2}B^{\lambda}\sum_{l'\lambda'}Q^{\lambda'}T^{(2)}_{\alpha\beta}[\mathbf{R}^{l\lambda}(t)-\mathbf{R}^{l'\lambda'}(0)]\ . \qquad (22)
$$

Since Eq. (22) is a closed equation, one can then easily perform the second derivative and the calculation of ${}^{(2)}P^{\mu\nu}_{\alpha\beta\eta\theta}(\mathbf{k},\mathbf{0})$, defined in Eq. (8), which in this case leads to

$$
{}^{(2)}\hat{P}^{\mu\nu}_{\alpha\beta\eta\theta}(\mathbf{k},\mathbf{0})|_{BTQ}=[B^{\mu}Q^{\nu}/2\ {}^{(4)}A^{\mu\nu}_{\alpha\beta\eta\theta}(\mathbf{k})+B^{\nu}Q^{\mu}/2\,{}^{(4)}A^{\nu\mu}_{\alpha\beta\eta\theta}(\mathbf{k})]-\delta_{\mu\nu}\sum_{\lambda}[B^{\lambda}Q^{\mu}/2\,{}^{(4)}A^{\lambda\mu}_{\alpha\beta\eta\theta}(\mathbf{0})+B^{\mu}Q^{\lambda}/2\,{}^{(4)}A^{\mu\lambda}_{\alpha\beta\eta\theta}(\mathbf{0})]\ . \qquad (23)
$$

Equation (23) can be easily compared with Eq. (17) which gives the same quantity for the DID case. Indeed, by substituting $-B^{\lambda}Q^{\lambda'}/2$ with $\alpha^{\lambda}\alpha^{\lambda'}$, the two equations appear identical once the $\mathbf{q}\equiv 0$ limit has been considered for the DID case.

In the following we will consider

$$
{}^{(2)}P^{\mu\nu}_{\alpha\beta\eta\theta}(\mathbf{k},\mathbf{0})=\xi_1\,{}^{(2)}P^{\mu\nu}_{\alpha\beta\eta\theta}(\mathbf{k},\mathbf{0})|_{\mathrm{DID}}+\xi_2\,{}^{(2)}P^{\mu\nu}_{\alpha\beta\eta\theta}(\mathbf{k},\mathbf{0})|_{BTQ} \qquad (24)
$$

and we will compute the spectra alternatively with $\xi_1=1$, $\xi_2=0$ (DID spectrum), with $\xi_1=0$, $\xi_2=1$ (BTQ spectrum), and with $\xi_1=\xi_2=1$ (total spectrum).

III. DISCUSSION

To compute the SORS spectra from Eqs. (16)–(20) and (23) one needs the values of α^{+}, α^{-}, B^{+}, B^{-}, Q^{+}, and Q^{-}; namely, the bare polarizabilities, the bare second-dipole–quadrupole polarizabilities, and the effective charges of both ions. These values are summarized in Table I for a large class of alkali halide crystals, as derived from current literature.

The values for the effective charges $Q^{+}=-Q^{-}$ are those employed in the shell model calculations,[32] where Q^{+} was used as a free parameter.

The whole cell polarizability $\alpha=\alpha_{+}+\alpha_{-}$ values are determined from the measured dielectric constant at optical frequencies, making use of the Lorentz-Lorenz relation. As far as the separate anions and cations polarizabilities are concerned, no direct experimental determination is possible. However, many indirect measurements[33–37] as well as theoretical calculations[38–40] have been performed. The values we report in Table I are those taken from Ref. 40.

To our knowledge no experimental determination of B^{+} and B^{-} is available so that in Table I we reported only some theoretical predictions.[41–43] Exhaustive work on the calculation of the $\bar{\bar{B}}$ tensor in the entire class of alkali halides was made by Johnson *et al.*[41] using the spherical model approximation in the framework of the time-dependent local-density approximation (TDLDA). It is worthwhile to note that the values of the second-dipole–quadrupole polarizability reported in Table I are three times smaller with respect to those computed in Ref. 41 because of the different definition of the $\bar{\bar{B}}$ tensor.[44]

Let us now discuss the results of our calculations. Roughly speaking, i.e., considering only the effect of the first neighbors in the induction of polarizability, the intensity of the *BTQ* contribution to the light scattering is determined by the factor $(B^{+}Q^{-}/2a^{5}+B^{-}Q^{+}/2a^{5})^{2}$, where a is the nearest-neighbor distance. At the same level of approximation, the intensity of the DID contribution is determined by

$$
(\alpha^{+}\alpha^{-}/a^{5}+\alpha^{-}\alpha^{+}/a^{5})^{2}=(2\alpha^{-}\alpha^{+}/a^{5})^{2}\ .
$$

As can be seen from Table I, B^{+} is always negligible with respect to B^{-}; therefore the value of the ratio $(4\alpha^{+}\alpha^{-}/B^{-}Q^{+})$ when squared gives a rough estimate of the relative intensity of the DID to the *BTQ* contribution. This quantity is reported in the last column in Table I. As can be seen, the *BTQ* term is predominant in the spectra of lithium and sodium halides while the DID term is the major one responsible for the potassium and rubidium halides. The two terms have, however, comparable relevance (the ratios are not greater than two) in the NaF, NaCl, KBr, and KI alkali halides.

We expect that these systems, where the contributions of DID and BTQ terms have comparable intensity, should show the most interesting feature in the Raman spectra. As an example, and in order to clarify the discussion, we have numerically calculated the spectral shape for a KBr crystal. The shell model parameters used to calculate the dynamics are taken from Ref. 20. Both dynamic quantities and light-scattering spectra have been calculated, sampling the irreducible Brillouin zone (which for the symmetry of the Raman-scattering tensor is $\frac{1}{8}$ of the full zone) over a grid of 10 000 points.

The spectra reported here refer to the VV polarization with the exchanged $\mathbf{q}$ lying in the xy plane and have been calculated at $T=300$ K. Only the Stokes' side has been shown in the figures.

The spectral shape arising from the DID contribution (i.e., $\xi_2=0$) is represented in Fig. 1 (solid line spectrum). The calculation of this contribution deserves some comment.

(i) The finite (even if small) value of the wave vector exchanged by the radiation makes the results of the complete theory somewhat different from that obtained considering $\mathbf{q}=0$ in the scattering equation [Eq. (2)]. Indeed, the finite value of $\mathbf{q}$ is responsible for the presence of the local-field factor, which in this case comes directly in the scattering equations without any *a priori* assumption. The local-field factor by itself, being frequency independent, does not modify the spectral shape but only its intensity. We will see that the finite-$\mathbf{q}$ value also influences the spectral shape if the DID resummation is performed.

(ii) In the present work, the DID effect has been taken into account solving the self-consistent equations, thus overcoming the generally employed first-order approximation in calculating the polarizability tensor components. This approach gives rise to a spectral shape which looks slightly different from that calculated in a first-order approximation. Indeed, the expression for the quantity ${}^{(2)}P^{\nu\mu}_{\alpha\beta\eta\theta}(\mathbf{k},\mathbf{q})$ in the first-order approximation results in

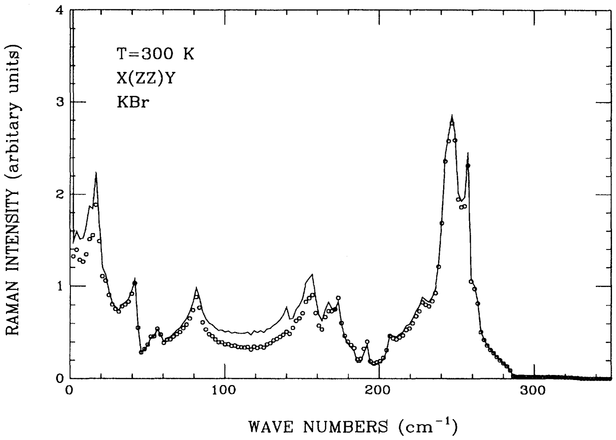

FIG. 1. Calculated DID contribution to SORS for KBr in the $x[zz]y$ configuration ($T=300$ K, Stokes' side). The open circles represent the first-order approximation, while the solid line represents results from the complete calculation.

TABLE I. Calculated polarizabilities and hyperpolarizabilities (TDLDA) for alkali halide crystals from Ref. 40 and effective charges employed in the shell model calculations from Ref. 32.

Crystal (+ −)	α^+ (Å^3)	α^- (Å^3)	B^+ (Å^6/e)	B^- (Å^6/e)	Q (e)	$4\frac{\alpha^+\alpha^-}{B^-Q^+}$
LiF	0.032	0.848	1.15×10^{-3}	0.47	0.902	0.256
LiCl	0.032	2.81	1.17×10^{-3}	2.64	1	0.136
LiBr	0.032	3.86	1.17×10^{-3}	4.46	1	0.111
LiI	0.032	5.67	1.17×10^{-3}	8.34	1	0.087
NaF	0.158	1.13	0.016	0.91	0.907	0.865
NaCl	0.158	3.26	0.016	3.98	0.89	0.582
NaBr	0.158	4.40	0.016	6.40	1	0.434
NaI	0.159	6.37	0.016	11.55	0.89	0.394
KF	0.839	1.28	0.21	1.27	0.961	3.52
KCl	0.838	3.50	0.21	4.93	0.82	2.90
KBr	0.838	4.66	0.21	7.63	0.965	2.12
KI	0.838	6.68	0.21	13.43	0.92	1.81
RbF	1.39	1.38	0.54	1.55	1	4.95
RbCl	1.39	3.68	0.54	5.75	0.79	4.50
RbBr	1.39	4.89	0.53	8.88	0.79	3.88
RbI	1.38	6.95	0.53	15.27	0.87	2.89

$$
{}^{(2)}P^{\mu\nu}_{\alpha\beta\eta\theta}(\mathbf{k},0)=\alpha^{\mu}\alpha^{\nu}[{}^{(4)}A^{\mu\nu}_{\alpha\beta\eta\theta}(\mathbf{k})+{}^{(4)}A^{\nu\mu}_{\alpha\beta\eta\theta}(\mathbf{k})] -\delta_{\mu\nu}\sum_{\lambda}\alpha^{\lambda}\alpha^{\mu}[{}^{(4)}A^{\lambda\mu}_{\alpha\beta\eta\theta}(0)+{}^{(4)}A^{\mu\lambda}_{\alpha\beta\eta\theta}(0)]\ , \quad (25)
$$

which looks quite different from Eq. (17) because of relation (18). In other words, DID resummation implies a different spectral shape with respect to the first-order approximation, but only if the finite **q** value is considered.

To show quantitatively the effect of resummation, the DID contribution calculated in the first-order approximation is also shown in Fig. 1 (open circles) for a comparison with the results of the complete theory (solid line). The first-order DID contribution reported in Fig. 1 has been *ad hoc,* multiplied for the local-field factor.

The spectral shape arising from the *BTQ* contribution alone ($\xi_1=0$) is shown in Fig. 2. Its computation, if compared with the computation of the full DID contribution, is quite simple because of the absence of self-consistency. The field factor here plays only the role of a multiplicative quantity, without any influence on the spectral shape.

A quantitative comparison of Figs. 1 and 2 shows that there is a marked difference between the DID and *BTQ* spectral shapes. This can be explained by considering the difference in the spatial range involved in the DID and *BTQ* polarizability induction mechanism. In order to clarify this point, we report in Fig. 3(a) the spectrum from the *BTQ* term (open circles) together with the same spectrum calculated considering only nearest-neighbor (NN) polarizability interactions (solid line). As can be seen, the *BTQ* contribution is almost completely determined from the NN ions. Roughly speaking, each of the 12 next-nearest-neighbor (NNN) contributions to the spectral intensity is $[B^-Q^-/(\sqrt{2}a)^5]^2$ while the 6 NN contributions read $(B^-Q^+/a^5)^2$. Thus the intensity ratio between the entire contribution coming from the NN and NNN will be

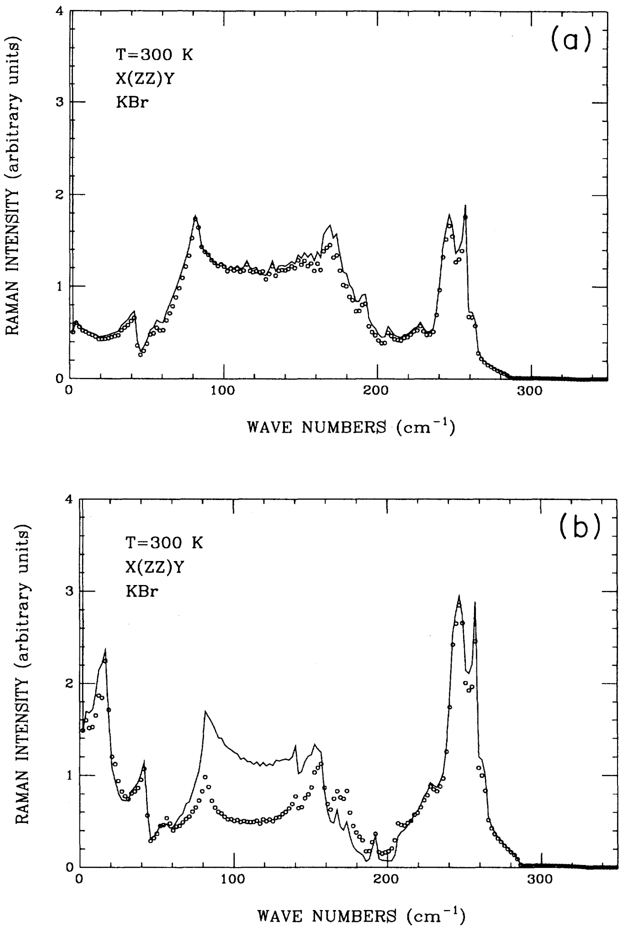

FIG. 3. (a) Calculated *BTQ* contribution to SORS for KBr in the $x[zz]y$ configuration ($T=300$ K, Stokes' side). The solid line is the contribution from the nearest neighbors alone while the spectrum obtained considering the interactions at all distances is shown in open circles. (b) The same as in (a) but for the DID case.

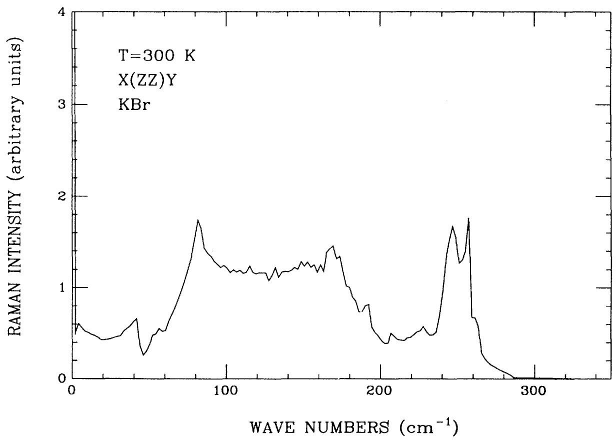

FIG. 2. *BTQ* contribution to SORS for KBr in the $x[zz]y$ configuration ($T=300$ K, Stokes' side). Complete calculation.

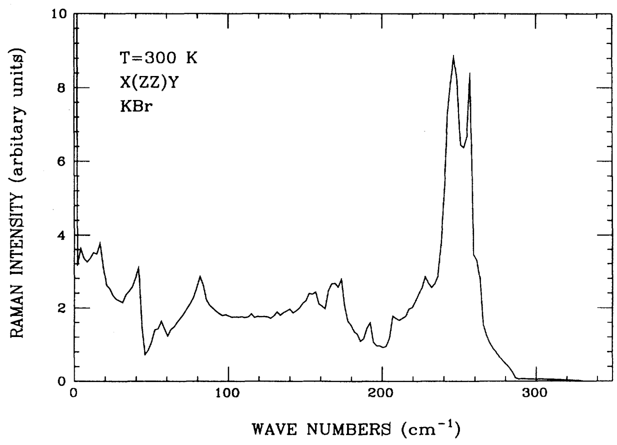

FIG. 4. Calculated SORS for KBr in the $x[zz]y$ configuration ($T=300$ K, Stokes' side). Full *BTQ*+DID spectrum obtained using the electrical values reported in Table I.

$$\frac{12}{6}\left[\frac{1}{\sqrt{2}}\right]^{10}=2^{-4}\simeq 0.06 \ , \qquad (26)$$

i.e., in the BTQ term, the NNN contribution is only 6% of the whole scattered intensity. The situation is quite different for the DID term. In this case, each of the (6+6) couples of NN ions will contribute to $(\alpha^+\alpha^-/a^5)^2$, while the 12 bromine-bromine NNN couples contribute to $[(\alpha^-)^2/(\sqrt{2}a)^5]^2$ (the potassium-potassium contribution is negligible because $\alpha^+/\alpha^-\simeq 0.2$). The relative intensity ratio is therefore

$$\left[\frac{\alpha^-}{\alpha^+}\right]^2\left[\frac{1}{\sqrt{2}}\right]^{10}\simeq\frac{25}{2^5}\simeq 0.75 \ , \qquad (27)$$

i.e., the contributions of the NNN and NN ions in the DID term are of the same order of magnitude. This result is emphasized in Fig. 3(b), where the full DID (open circles) is compared with the NN contribution (solid line). The difference between the DID and BTQ spectral shapes can therefore be explained in view of the different dynamics involved, which are essentially those of the NN in the BTQ and of NN plus NNN in the DID spectra.

In Fig. 4 the total spectrum obtained by Eq. (24) is shown. As can be seen by comparing Figs. 1 (solid line) and 2 with Fig. 4, the full SORS spectrum can be quite well represented as the sum of the two contributions. This means that BTQ and DID cross terms are found to be quite negligible. The spectrum in Fig. 4 can be quantitatively compared very well with the experimental results reported in Ref. 8.

Last but not least, a comment has to be made on the elastic ($\omega=0$) contribution to the spectra. This contribution obviously comes from couples of phonons $(j,\mathbf{k};j\mathbf{k}')$ belonging to the same branch, which satisfy the condition $\omega_j(\mathbf{k})=\omega_j(\mathbf{q}-\mathbf{k}')$. In the framework of a perfect harmonic lattice theory, such a contribution is a δ function (see all the figures). In real spectra this elastic contribution will be broadened by the finite lifetime of the excitations involved due to crystal anharmonicity. This peak is isolated from the remaining spectrum because of its higher intensity with respect to the other contributions. For the harmonic spectrum BTQ+DID (Fig. 4) the ratio of the intensity of the elastic peak to the integrated intensity of the remaining spectrum is 0.184. This characteristic of the spectra can be employed to measure a mean anharmonicity of the crystals at various temperatures.

IV. CONCLUDING REMARKS

In this paper a microscopic model has been developed to compute in the harmonic approximation, the SORS spectral shape and intensity for alkali halide crystals.

The main source of the SORS in this class of systems has been considered to be the effective ionic polarizability modulation due to all couples of phonons accomplishing the energy-momentum conservation rule.

Following the Buckingham expansion of the effective ionic polarizability, the leading terms which give rise to SORS spectra have been identified in the DID and the BTQ terms. The BTQ contributions are found to be dominated from the first neighbor relative anion-cation dynamics, while in the DID term both NN anion-cation and NNN cation-cation relative dynamics appear at about the same extent. No electric overlap or exchange effects have been introduced, which will probably not be a good approximation for the heavier atoms, similarly to what happens in rare-gas crystals.[45]

The spectral shape of the SORS are predicted to be strongly dependent on the ratio between B^-Q^+ and the ionic polarizabilities product $\alpha^+\alpha^-$. A quantitative analysis of the experimental spectral shape can therefore be a way to measure the B^- values, which up to now are only theoretically evaluated. Experiments are in progress to check our theoretical predictions quantitatively.

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[1] H. L. Welsh, M. F. Crawford, and W. J. Staple, Nature (London) **164**, 737 (1949).

[2] A. M. Karo and J. R. Hardy, Phys. Rev. **141**, 696 (1966).

[3] M. Krauzman, C. R. Acad. Sci. Ser. B **265**, 689 (1967).

[4] G. Raunio and S. Rolandson, Solid State Commun. **7**, 1341 (1969).

[5] J. R. Hardy, A. M. Karo, I. W. Morrison, C. T. Sennett, and J. P. Russel, Phys. Rev. **179**, 837 (1969).

[6] S. L. Cunningham, J. R. Hardy, and M. Hass, in *Light Scattering in Solids,* Proceedings of the Second International Conference on Light Scattering, edited by M. Balkansky (Flammerion, Paris, 1971), p. 257.

[7] A. D. Bruce and R. A. Cowley, J. Phys. C **5**, 595 (1972).

[8] J. E. Potts, C. T. Walker, and I. R. Nair, Phys. Rev. B **8**, 2756 (1973).

[9] M. Krauzman, Solid State Commun. **12**, 157 (1973).

[10] S. L. Cunningham, T. P. Sharma, S. S. Jashwall, M. Hass, and J. R. Hardy, Phys. Rev. B **10**, 3500 (1974).

[11] A. Pasternak, E. Cohen, and G. Gilat, Phys. Rev. B **9**, 4584 (1974).

[12] T. P. Sharma, R. D. Kirby, and S. S. Jaswall, Phys. Rev. B **9**, 1971 (1974).

[13] S. S. Jaswall, G. Wolfram, and T. P. Sharma, J. Phys. Chem. Solids **35**, 571 (1974).

[14] J. A. Taylor, M. S. Haque, J. E. Potts, J. B. Page, and C. T. Walker, Phys. Rev. B **12**, 5969 (1975).

[15] B. S. Agrawal, R. D. Kirby, and J. R. Hardy, Phys. Rev. B **11**, 5153 (1975).

[16] M. H. Grimsditch, Solid State Commun. **25**, 389 (1978).

[17] M. Born and M. Bradburn, Proc. R. Soc. London, Ser. A **188**, 161 (1946).

[18] E. W. Kellerman, Philos. Trans. R. Soc. London, Ser. A **328**, 513 (1940).

[19] A. D. B. Woods, W. Cochran, and B. N. Brockhouse, Phys. Rev. **119**, 980 (1960).

[20] R. A. Cowley, W. Cochran, B. B. Brockhouse, and A. D. B. Woods, Phys. Rev. **131**, 1030 (1963).

[21] J. R. D. Copley, R. W. Macpherson, and T. Timusk, Phys. Rev. **182**, 965 (1969).

[22] G. Raunio and S. Rolandson, Phys. Rev. B **2**, 2098 (1970).

[23] A. D. Buckingam, Adv. Chem. Phys. **12**, 107 (1967).

[24] V. Mazzacurati, G. Ruocco, G. Signorelli, and M. Nardone,

in *Phenomena Induced By Intermolecular Interactions,* edited by G. Birnbaum (Plenum, New York, 1985), p. 567.

[25] N. R. Werthammer, R. L. Gray, and T. T. Koeheler, Phys. Rev. B **2**, 4199 (1970).

[26] N. R. Werthammer, R. L. Gray, and T. T. Koeheler, Phys. Rev. B **4**, 1324 (1971).

[27] C. D. Mahan and K. R. Subbaswamy, Phys. Rev. B **33**, 8657 (1986).

[28] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York, 1976).

[29] Various authors in *Phenomena Induced By Intermolecular Interactions,* edited by G. Birnbaum (Plenum, New York, 1985), p. 567.

[30] V. Mazzacurati and G. Ruocco, Mol. Phys. **61**, 1391 (1987).

[31] V. Mazzacurati, G. Ruocco, G. Signorelli, E. Cazzanelli, A. Fontana, and G. Mariotto, Phys. Rev. B **26**, 2216 (1982).

[32] R. K. Gupta, Phys. Rev. B **12**, 4452 (1975).

[33] J. R. Tessman, A. H. Khan, and W. Shockley, Phys. Rev. **92**, 890 (1953).

[34] L. Pauling, Proc. R. Soc. London, Ser. A **114**, 191 (1927).

[35] M. Born and W. Heisenberg Z. Phys. **23**, 388 (1924).

[36] K. Fajans and G. Joos Z. Phys. **23**, 1 (1924).

[37] J. E. Mayer and M. G. Mayer, Phys. Rev. **43**, 605 (1933).

[38] G. D. Mahan, Phys. Rev. B **34**, 4235 (1986).

[39] S. Petterson and K. R. Subbaswamy, Phys. Rev. B **42**, 5883 (1990).

[40] Gerald D. Mahan and K. R. Subbaswamy, *Local Density Theory of Polarizability* (Plenum, New York, 1990), pp. 153 and 186.

[41] M. D. Johnson, K. R. Subbaswamy, and G. Senatore, Phys. Rev. B **36**, 9202 (1987).

[42] P. W. Fowler and P. A. Madden, Phys. Rev. B **29**, 1035 (1984).

[43] P. W. Fowler and P. A. Madden, Phys. Rev. B **30**, 6131 (1984).

[44] The $\overline{\overline{B}}$ tensor is implicitly defined in the expression for the induced multipole moments in the presence of an external electric field. We followed the Buckingham notation [see our Equations (22) and (3) of Ref. 23)] while Johnson *et al.* used a definition [compare Eq. (2) of Ref. 41 with Eq. (4) of Ref. 23 or Eq. (29) of Ref. 41 with Eq. (13) of Ref. 23] which is compatible with the Buckingham one assuming $\overline{\overline{B}}$ three times greater.

[45] P. Gallo, V. Mazzacurati and G. Ruocco, Mol. Phys. **71**, 97 (1990).