Raman scattering due to disorder-induced polaritons

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Abstract

The selection rules for dipole and Raman activity can be relaxed due to local distortion of a crystalline structure. In this situation a dipole-inactive mode can become simultaneously active in Raman scattering and in dipole interaction with the electromagnetic field. The later interaction results in disorder-induced polaritons, which could be observed in first-order Raman spectra. We calculate scattering cross-section in the case of a material with a diamond-like average structure, and show that there exists a strong possibility of observing the disorder induced polaritons.

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1 Introduction

The effects of a resonance linear interaction between excitations of different nature are well known and their importance for properties of crystalline materials has been appreciated for a long time. One could mention, for instance, such phenomena as magneto-elastic resonance [1], or various kinds of the polariton resonance [2]. The former refers to resonance interaction between spin and elastic waves that results in mixed excitations carrying both
magnetic and elastic types of energy. The latter term is used to refer to 
excitations arising as a result of interaction between electromagnetic 
waves and excitations of crystals such as phonons, excitons, plasmons, and so on. In 
spite of significant differences between all the cited examples, they share one 
common feature. In the absence of interaction the dispersion curves of the 
participating excitations cross each other at a certain point. This crossing is 
actually responsible for the resonance nature of the interaction, which lifts 
the degeneracy of the initial excitations at the crossing point and gives rise 
to the mixed states.

In a recent paper [3] the effect of crossing resonance has been studied 
in systems with a random interaction between participating excitations. It 
was shown that even a random coupling parameter with zero mean value 
can, under certain conditions, result in the strong coupling between interacting 
waves, leading to a lifting of the degeneracy at the crossing point. The 
mixed excitations arising in this model of disorder-induced crossing resonance 
(DICR), however, differ significantly from the respective excitations in the 
deterministic case. First of all, excitations that are actually mixed together 
are coherent excitations of one nature with nonzero average amplitude and 
non-coherent scattered excitations of the other nature with average amplitude 
equal to zero. Correspondingly, one has to consider two such mixed excita-
tions, and each of them can result in dispersion laws split at the crossing point 
in two branches. It is possible, therefore, to have three or even four different 
dispersion curves describing averaged properties of the system. Recently 
the model of DICR was developed further to include nonzero mean value of 
the random coupling parameter [4]. It was shown in Ref.[4] that transition 
between the completely disordered case with zero mean to the nonrandom 
situation occurs in a nontrivial way. The idea of the DICR was first applied 
to the magnetoelastic resonance in amorphous zero-mean-magnetostriction 
alloys [5]. In magnetoelastic case it is possible to perform a direct observation 
of elastic and magnetic susceptibilities modified due to DICR. The relation-
ship between maxima of the susceptibilities and solutions of the dispersion 
equations for magnetoelastic resonance was studied in Ref. [6] 

In Ref.[7] it was suggested that DICR can also occur for the polariton 
resonance in disordered materials if one considers the interaction of electromagnetic 
waves with phonon or exciton excitations that would be dipole-
inactive in the absence of disorder (disorder-induced polaritons). Polariton 
dispersion curves in ideal crystals can be experimentally studied by means of 
Raman scattering (see, for example, Ref. [8]). It was also suggested in Ref.[9]
that polaritons arising due to retardation effects in the electromagnetic interaction between local impurity vibrations can also be observed in Raman scattering. It seems natural, therefore, to explore whether it is possible to use the Raman effect to observe the disorder-induced polaritons. In this paper we present calculations of the first order Raman scattering cross-section from forbidden polaritons arising in a simple cubic diamond-like structure due to local structural distortions.

2 Intensity of Raman scattering from disorder-induced polaritons. General expression

The polarization, $P$, of a dielectric medium subjected to an external electromagnetic field, $E_{in}$, with frequency $\omega_{in}$ can be expressed by means of a susceptibility tensor $\chi_{ij}$ as

$$P_i = \chi_{ij} E_{in}^j.$$  \hspace{1cm} (1)

In the frequency region of our interest, susceptibility can be divided into two major contributions: ion susceptibility $\chi_{ij}^{\text{ion}}$ and electron susceptibility $\chi_{ij}^{\text{el}}$. The former part of the susceptibility arises due to the coherent motion of ions caused by the incident electromagnetic wave and is responsible for a modification of the wave’s velocity (real part) and for its absorption (imaginary part). The electron contribution $\chi_{ij}^{\text{el}}$ reflects the contribution of electron transitions in the dipole moment of the atoms constituting crystal. For frequencies far enough from those of electron transitions and in the linear approximation $\chi_{ij}^{\text{el}}$ can be considered as a frequency independent constant. However, if one takes into account nonlinear corrections such as an interaction between electrons and ionic vibrations, the electron contribution becomes modulated by thermal ionic vibrations giving rise to the inelastic scattering of light known as Raman scattering. As a result of this scattering the frequency, $\omega_{in}$, and wave number $k_{in}$, of the incident wave changes. In the case of scattering from an ideal crystal, frequencies and wave numbers of the incident and scattered waves obey well-known kinematic relations that reflect energy and momentum conservation laws:

$$\omega_{in} - \omega_s = \pm \Omega$$

$$k_{in} - k_s = \pm K$$

3
Here \( \omega_s \) and \( k_s \) are the frequency and wave number of the scattered field, and \( \Omega \) and \( K \) are the frequency and wave number of the excitations of the medium responsible for scattering. The signs + and − correspond to processes of emission and absorption of the excitations respectively giving rise to Stokes and anti-Stokes components of the scattered field. In the presence of disorder the second of the equations (2) does not hold any more since disordered systems lack translational invariance.

Intensity of the field scattered at a given direction within a certain frequency interval is determined by the differential cross-section \( \frac{d^2 \sigma}{d\Omega d\omega} \), where \( d\Omega \) is a differential of a solid angle at a given direction. In general the cross section can be presented as

\[
\frac{d^2 \sigma}{d\Omega d\omega} = \text{const} \times e_s^* e_s^l e_{in}^* e_{in}^l <\delta \chi_{ik}(\Omega, K) \delta \chi_{jl}(\Omega, K) \rangle
\]  

(3)

where \( e_s^s \) and \( e_{in}^s \) are polarization vectors of the scattered and the incident fields respectively, and the \( \text{const} \) in front of the whole expression is a combination of such parameters as volume of the scattering region of the sample, frequency of the incident wave, etc., which are not significant for the purpose of our consideration. Double angular brackets \( <\cdot \cdot \cdot \rangle \) denote two types of averaging: thermodynamical average over statistical ensemble, and the average over realizations of the random inhomogeneities of the system.

Modulation of the susceptibility \( \delta \chi_{ik}(\Omega, K) \) can be found if one expands the electronic susceptibility into a power series with respect to the amplitudes of excitations responsible for the scattering. In the case of scattering due to polaritons, the electronic susceptibility is modulated by both ionic displacements \( W_\sigma \) and electric field \( E \) associated with those displacements. Therefore, \( \delta \chi_{ik}(\Omega, K) \) is the sum of two terms

\[
\delta \chi_{ik}(\Omega, K) = \sum_\sigma \int d^3q W^*_\sigma(\Omega, q) h_{ik}^\sigma(K - q) + \int d^3q E^*_m(\Omega, q) g^{ikm}(K - q),
\]  

(4)

where \( W_\sigma \) represents an amplitude of \( \sigma \)-th normal mode of the ionic vibrations, \( h_{ik}^\sigma \) is the tensor of mechano-optic coefficients, and \( g^{ikm} \) represents electro-optic coefficients of the system, wave number \( K \) is determined by the Eq.(2), and an additional integration over \( q \) reflects the inhomogeneous nature of the considered system and the lack of the translational invariance. For this reason susceptibility derivatives \( h_{ik}^\sigma \) and \( g^{ikm} \) should be considered
as random functions. Within the phenomenological approach utilized in this paper we have to make additional assumptions about the properties of these functions based upon some general arguments. We begin with separating out mean parts of these functions and represent them in the following form:

\[ h_{i\sigma}^{jk}(K - q) = < h_{i\sigma}^{jk} > \delta(K - q) + \tilde{h}_{i\sigma}^{jk}(K - q) \]  
\[ g_{ikm}(K - q) = < g_{ikm} > \delta(K - q) + \tilde{g}_{ikm}(K - q). \]  

According to this representation the scattering cross-section has two different contributions: the coherent one, resulting from averaged parts of the coefficients \( h \) and \( g \), and the non coherent contribution due to inhomogeneous parts of the tensors. The main physical difference between these contributions is that the former conserves momentum (this is reflected by the presence of the \( \delta \)-function in the respective term of Eq. (5)), and the latter does not. The properties of the mean parts of the susceptibility derivatives is determined by the average symmetry of the system. We assume the cubic average symmetry of the crystal structure that preserves central symmetry, and that the normal vibrational mode of the system is a triply degenerate (in the absence of interaction with electromagnetic field) mode of even parity. (An example of such a system can be the \( \Gamma^\uparrow_5 \) mode in a diamond-like structure). This mode is dipole inactive on average and its coupling to the electromagnetic field occurs only due to random deviations of structure from the average one. This assumption ensures that we actually deal with the disorder-induced polaritons, and at the same time it guarantees that \( < h_{i\sigma}^{jk} > \) is not equal to zero since it is well known \[10\] that infra-red activity and Raman activity are mutually exclusive in the crystals with a center of inversion. The tensor structure of \( < h_{i\sigma}^{jk} > \) in the case of a diamond like structure can be presented in the following form \[10\]

\[ < h_{i\sigma}^{jk} > d_{ij}^{\sigma} = h|\epsilon_{ikm}| \]  

where \( d_{ij}^{\sigma} \) is a polarization vector of a given mode, and \( |\epsilon_{ikm}| \) is the Levi-Civita symbol.

The question about properties of the electro-optical coefficient in our model is more subtle. In the regular case of crystalline materials these coefficients come into play only in the case of vibrational modes of odd parity, because only in this case does there exist an electromagnetic field associated with the vibrations. Then a third-rank tensor \( g_{ikm}^{jk} \) in such a situation is equal to zero in crystals with central symmetry, therefore, the whole issue of
the properties of the electro-optical coefficients in crystalline materials arises only in non-centro-symmetrical crystals. In our situation of disorder-induced polaritons the mode one deals with has even parity. Therefore, symmetry arguments do not forbid nonzero value of the tensor $g^{ikm}$ even in materials with central-symmetry average structure. Therefore we can assume for the tensor structure of $g^{ikm}$ the same form as in Eq.(6).

We can conclude, therefore, that the coherent contribution in the scattering cross-section consists of two terms

$$
\frac{d^2\sigma^{coh}}{d\omega d\Omega} = \text{const} \times [n(\Omega) + 1](I_W^{coh} + I_E^{coh}),
$$

where the vibrational contribution $I_W^{coh}$ is

$$
I_W^{coh} = h^2|\epsilon_{ikm}|^2 \epsilon_{jip} e_j^s e_k^i \sum_{\sigma} e_{m}^{\sigma} e_{p}^{\sigma} \text{Im} \left[ \eta_W^{\sigma}(\Omega, K) \right],
$$

and the electromagnetic contribution $I_E^{coh}$ is given by the similar expression

$$
I_E^{coh} = g^2|\epsilon_{ikm}|^2 \epsilon_{jip} e_j^s e_k^i \sum_{\sigma} e_{m}^{\sigma} e_{p}^{\sigma} \text{Im} \left[ \eta_E^{\sigma}(\Omega, K) \right].
$$

Writing down these expressions we make use of the fluctuation-dissipation theorem and express the vibrational and electric field correlation functions in terms of thermodynamical Bose-factor $n(\Omega) + 1$, and the respective vibrational and electromagnetic linear-response functions $\eta_W^{\sigma}(\Omega, K)$ and $\eta_E^{\sigma}(\Omega, K)$.

In order to describe non-coherent contributions in the cross-section we have to make assumptions regarding correlation properties of the susceptibility derivatives $h^{ik}_{\sigma}$ and $g^{ikm}$. It is natural to assume that their fluctuations are both homogeneous and isotropic. These assumptions allow one to introduce the spectral densities (spatial Fourier-transforms) of the corresponding correlation functions and present them in the following form

$$
< h^{ik}_{\sigma}(k_1) h^{jl}_{\sigma}(k_2) > = H^{ikjl}(k_1) \delta(k_1 - k_2)
$$

and

$$
< g^{ikm}(k_1) g^{jnl}(k_2) > = G^{ikm,l}_{jnl}(k_1) \delta(k_1 - k_2)
$$

where $S(k)$ is a scalar spectral density of the structural inhomogeneities, $H^{ikjl}$ and $G^{ikm,l}_{jnl}$ are isotropic tensors with a structure reflecting properties of coefficients $h^{ik}_{\sigma}$ and $g^{ikm}$.

6
Calculations of the non-coherent contributions in the cross-section requires averaging of the expressions like
\[
\langle \langle W_\sigma(k_1) W_\sigma^*(k_2) \tilde{h}_{ik}^\sigma(K - k_1) \tilde{h}_{jl}^{\sigma\star}(K - k_2) \rangle \rangle
\]. Doing so we use the simplest decoupling of the correlators of this from as follows:
\[
\langle \langle W_\sigma(k_1) W_\sigma^*(k_2) \tilde{h}_{ik}^\sigma(K - k_1) \tilde{h}_{jl}^{\sigma\star}(K - k_2) \rangle \rangle \simeq \langle \langle W_\sigma(k_1) W_\sigma^*(k_2) \rangle \rangle \langle \langle \tilde{h}_{ik}^\sigma(K - k_1) \tilde{h}_{jl}^{\sigma\star}(K - k_2) \rangle \rangle \]

This approximation is justified in the case of sufficiently weak inhomogeneities, which is assumed throughout the paper. Within this approximation the non-coherent cross-section can again be separated into two terms \( I_{ncoh}^W \) and \( I_{ncoh}^E \) with quantities \( I \) having the meaning similar to that in Eq.(7). It is natural to assume isotropy of the correlation tensors \( H^{ikjl} \) and \( G^{ikmn}_{jnl} \) with additional symmetry properties following from the symmetries of the initial mechano-optical and electro-optical coefficients. For the vibrational contribution \( I_{ncoh}^W \) in the non coherent scattering one then has
\[
I_{ncoh}^W = [H_1 + H_2(\epsilon_s^e \epsilon_m^i)] \sum_\sigma \int d^3q \text{Im} [\eta^W_\sigma(\Omega, q)] S(K - q), \tag{10}
\]
where \( H_1 \) and \( H_2 \) are the only independent elements of the tensor \( H^{ikjl} \). An expression for the non-coherent electromagnetic contribution is somewhat more cumbersome because of more complicated tensor structure of \( G^{ikmn}_{jnl} \):
\[
I_{ncoh}^E = [G_1 + G_2(\epsilon_s^e \epsilon_m^i)] \int d^3q \text{Im} [\eta^E_{ii}(\Omega, q)] S(K - q) +
\]
\[
[G_3 (\epsilon_i^{in} \epsilon_j^{in} + \epsilon_i^s \epsilon_j^s) + G_4 (\epsilon_i^s \epsilon_j^{in} + \epsilon_i^{in} \epsilon_j^s)] \int d^3q \text{Im} [\eta^E_{ij}(\Omega, q)] S(K - q). \tag{11}
\]

3 \hspace{1em} Linear-response functions for disorder-induced polaritons

This section of the paper concerns with linear response functions \( \eta^W_\sigma(\Omega, q) \) and \( \eta^E_{ij}(\Omega, q) \), which determine Raman scattering cross-section in our system. We start from dynamical equations describing ionic vibrations in the
following form
\[ m_\alpha \frac{\partial^2 U_\alpha^i}{\partial t^2} + \sum_{\beta, r_1} D_{\alpha \beta}^{ij}(r, r_1)U_\beta^j(r_1) = e_\alpha E^i(r). \] (12)

This equation must be complemented by Maxwell’s equations
\[ \frac{\partial^2 E}{\partial t^2} + c^2 \nabla \times \nabla \times E = -4\pi \frac{\partial^2 P}{\partial t^2} \] (13)

with polarization density \( P \) defined as
\[ P = \frac{1}{V} \sum_\alpha e_\alpha U_\alpha + \chi_{el} E. \] (14)

Indices \( \alpha, \beta \) label ions within one elementary cell, \( U^i \) is a Cartesian component of a displacement vector, \( D_{\alpha \beta}^{ij}(r, r_1) \) is a dynamical matrix describing interaction between ions of masses \( m_\alpha \) and charges \( e_\alpha \). For given radius-vectors \( r, r_1 \) the dynamical matrix can be diagonalized with respect to sub-cell and Cartesian indices. If \( c_{\alpha \sigma}^i(r) \) is a matrix that diagonalizes the dynamical matrix, the equation of motion (12) and the equation for polarization (14) can be rewritten in the following form
\[ \frac{\partial^2 W_\sigma^i}{\partial t^2} + \sum_{r_1} D_\sigma^{ij}(r, r_1)W_\sigma^j(r_1) = Z_\sigma(r)d_\sigma^i E^i(r) \] (15)
\[ P = \frac{1}{V} \sum_\sigma Z_\sigma(r)d_\sigma W_\sigma + \chi_{el} E, \]

where normal mode \( W_\sigma^i(r) \) and its effective charge \( Z_\sigma(r) \) are determined according to
\[ U_\alpha^i(r) = \sum_\alpha c_{\alpha \sigma}^i(r) \frac{e_\alpha}{\sqrt{m_\alpha}} W_\sigma(r) \] (16)
\[ Z_\sigma(r)d_\sigma^i = \sum_\alpha c_{\alpha \sigma}^i(r) \frac{e_\alpha}{\sqrt{m_\alpha}}. \]

The vector \( d_\sigma^i \) is a polarization vector of \( \sigma \)-th mode. In a crystal with cubic symmetry all modes can be classified as longitudinal or transverse ones, making the direction of the polarization vector independent of the orientation of
the elementary cell. Therefore, we can assume that local inhomogeneities, entering Eq. (14) through the \( r \)-dependence of the diagonalizing matrix \( c_{i\sigma}^f(r) \), result in fluctuations of the effective charge \( Z_\sigma(r) \), leaving the directions of the polarization vectors without change. According to our basic assumption all triply degenerate modes contributing to the scattering have even parity, so the mean value of the effective charge is equal to zero. Correlation properties of the inhomogeneous effective charge are specified by means of the autocorrelation function \( K(r) = \langle Z_\sigma(r)Z_\sigma(0) \rangle \) or its spectral density \( S(k) = \int d^3r K(r) \exp(ikr) \). In what follows we assume that the correlation function, \( K(r) \), and spectral density \( S(k) \) are given as

\[
K(r) = \langle Z_\sigma^2 \rangle \exp(-rk_c) \\
S(k) = \langle Z_\sigma^2 \rangle \frac{k_c}{\pi^2 (k^2 + k_c^2)^2},
\]

where \( \langle Z_\sigma^2 \rangle \) is an rms fluctuation of the effective charge, and \( k_c \) is a correlation wave number, which is the inverse of a correlation radius and set the spatial scale of the inhomogeneities. We will also assume that the diagonalized dynamic matrix \( D^\alpha(r, r_1) \) is nonrandom, so that the mechanical properties of the system are not affected by the disorder.

### 3.1 Vibrational response function

Linear response functions \( \eta^W_\sigma(\Omega, \mathbf{q}) \) and \( \eta^E_{ij}(\Omega, \mathbf{q}) \) can be found from the solutions of Eq. (15) and Eq. (13) with appropriate source terms on the right hand side of the equations. We will start by determining the mechanical response function \( \eta^W_\sigma(\Omega, \mathbf{q}) \). For this purpose we add an external force \( \mathbf{F} \) to the right hand side of the equation Eq. (13), and our aim is to find an equation for the averaged over the disorder amplitude, \( \langle W_\sigma(\Omega, \mathbf{K}) \rangle \). Carrying out the calculations with the use of a perturbation approach with respect to the rms fluctuation of the effective charge, \( d^2 \), discussed in detail, for instance, in Ref. [6], we can find with the accuracy to the first nontrivial correction (Bourret approximation)

\[
(\Omega^2 - \varepsilon^2_K) \langle W_\sigma(\Omega, \mathbf{K}) \rangle - \\
\frac{4\pi}{\varepsilon_{\infty}V^2} \sum_{\alpha} \langle W_\alpha(\Omega, \mathbf{K}) \rangle \int d^3q S(K - q) d^\alpha_\sigma(K - q) d^\alpha_{ij}(K - q) G^\alpha_{em}(q) = F_K.
\]
We introduce here an initial dispersion law of the vibrations, $\varepsilon_K^2$, describing triply degenerate (in the absence of interaction with electromagnetic field) mode. In the long wavelength limit the dispersion law assumes the form $\varepsilon_K^2 = \omega_0^2 + v^2 K^2$. Tensor $G^{ij}_{em}(q)$ in Eq.(18) is the Green’s function of Maxwell’s equation (13) in the absence of the coupling with the vibrations

$$G^{ij}_{em}(q) = \frac{1}{\Omega^2 - c^2 q^2} (\delta_{ij} - \frac{q_i q_j}{q^2}) + \frac{1}{\Omega^2} \frac{q_i q_j}{q^2}. \tag{19}$$

High-frequency dielectric constant $\varepsilon_\infty$ takes into account the electronic contribution into the polarization, and speed of light $c$ in the previous equation is corrected for $\varepsilon_\infty$. Nondiagonal terms (with respect to the polarization indices $\alpha, \sigma$) in Eq.(18) can be shown to vanish after the integration over $q$, so we only have to evaluate $\eta^W_L$ for the longitudinal mode and $\eta^W_T$ for transverse modes. Evaluating the integral in Eq.(18) one has to take into account that typical values of the correlation wave number $k_c$ determining the scale of the inhomogeneities can be of the order of magnitude between $10^6 cm^{-1}$ and $10^8 cm^{-1}$ while the value of polariton wave numbers is of the order of $10^3 cm^{-1}$ or $10^4 cm^{-1}$. Another important observation is that the frequency $\omega_c = c k_c$ corresponding to the correlation wave number is much greater than all other characteristic frequencies of the system. Therefore, one can neglect any effects of retardation, which are of the order of $(\Omega / \omega_c)^2$, and evaluating all the remaining integrals with the accuracy to $(K/k_c)^2$, obtain longitudinal and transverse vibrational response functions in the following form

$$\eta^W_{L,T}(\Omega, K) = \frac{1}{\Omega^2 - \varepsilon^2_{L,T}(K) - 2i\Omega \Gamma_{in}}, \tag{20}$$

where

$$\varepsilon^2_L = \omega_0^2 + \Lambda^2 + (v^2 - \frac{1}{6} \frac{\Lambda^2}{k_c^2}) K^2, \quad \varepsilon^2_T = \omega_0^2 + (v^2 + \frac{1}{6} \frac{\Lambda^2}{k_c^2}) K^2. \tag{21}$$

The parameter $\Gamma_{in}$ takes into account initial damping of the vibrations, which is not related to the interaction with the field and is determined by intrinsic relaxation processes such as, for instance, anharmonism. This parameter can also include some effects of an additional scattering due to inhomogeneities that are intrinsic to the ion system, for example, spatial fluctuations of the dynamical matrix. Parameter $\Lambda$ introduced above is an effective coupling
parameter defined as

$$\Lambda^2 = \frac{4\pi \langle Z_2^2 \rangle}{V \varepsilon_\infty}.$$ 

It can be seen from these expressions that the vibrational response function does not contain effects of the disorder-induced interaction between vibrations and transverse electromagnetic field. This happens because the effective relaxation parameter $ck_c$, which is responsible for the scattering of the phonons into electromagnetic waves, is much greater than the effective coupling parameter $\Lambda$. Therefore, according to the general results obtained in Ref. [3], the coupling is ineffective and phonon properties are practically unaffected by the interaction.

However, the interaction between phonons and a longitudinal macroscopic field modifies their properties. In particular, even zero-mean random effective charge lifts the degeneracy between longitudinal and transverse phonon modes giving rise to the same $LT$-splitting that occurs in regular ideal crystals. It is more interesting that disorder also modifies the parameter $v$, which is responsible for the sign and strength of the spatial dispersion of the modes. The correction $\frac{1}{6} \frac{\Lambda^2}{k_c^2}$ has opposite signs for longitudinal and transverse modes, and its order of magnitude can be comparable to the initial parameter $v$. In ideal crystals the longitudinal electrostatic field is uniform and exerts an equal force upon ions at different sites, resulting in the uniform lift of the longitudinal mode. In the presence of disorder, however, the field is not uniform anymore giving rise to certain corrections to the inter-ion potential. These corrections finally manifest themselves as modification of the parameter of the spatial dispersion $v$, and can be of the same order of magnitude as the initial potential causing substantial modification of the initial spectrum.

### 3.2 Electromagnetic response function.

In order to evaluate the electromagnetic response function $\eta_{ij}^E(\Omega, K)$ one has to insert a source term into the Maxwell equation (13). According to the fundamentals of the linear response theory this source term should have the form of an external polarization [11]. Taking the source term into account and averaging the equations over the disorder in the same manner as above we finally arrive at the following equation for the average amplitude of the
The electromagnetic response function $\eta_{E}^{ij}(\Omega, K)$ is usually determined as \[ \eta_{E}^{ij}(\Omega, K) = \frac{4\pi\Omega^2}{\epsilon_{\infty}} \beta_{ij}(\Omega, K), \] (22)

where $\beta_{ij}(\Omega, K)$ is the inverse matrix for the left-hand side matrix of Eq. (21) and is given as usual by the sum of the transverse and longitudinal parts

\[
\beta_{ij}(\Omega, K) = \beta_{T}(\delta_{ij} - \hat{K}_{i}\hat{K}_{j}) + \beta_{L}\hat{K}_{i}\hat{K}_{j}, \tag{23}
\]

where $\hat{K}$ is a unit vector in the direction of $K$. The integral with the spectral density given by Eq. (17) can be easily calculated to yield the following expression for $\beta_{T}$

\[
\beta_{T} = \frac{\Omega^2 - \epsilon^2_{K} - \chi^2(\Omega) - 2i\Omega(\Gamma_{in} + \Gamma_{s})}{(\Omega^2 - c^2K^2) (\Omega^2 - \epsilon^2_{K} - \chi^2(\Omega) - 2i\Omega(\Gamma_{in} + \Gamma_{s})) - \Lambda^2\Omega^2}, \tag{24}
\]

where

\[
\chi^2(\Omega) = v^2k_{c}^2 - 2vk_{c}\Omega \left[ \left( 1 - \frac{\omega^2_{\ominus}}{\Omega^2} \right)^2 + \frac{4\Gamma^2_{in}}{\Omega^2} \right]^{1/4} \sin \left[ \frac{1}{2} \arctan \left( \frac{2\Omega\Gamma_{in}}{\Omega^2 - \omega^2_{\ominus}} \right) \right],
\]

\[
\Gamma_{s}(\Omega) = vk_{c} \left[ \left( 1 - \frac{\omega^2_{\ominus}}{\Omega^2} \right)^2 + \frac{4\Gamma^2_{in}}{\Omega^2} \right]^{1/4} \cos \left[ \frac{1}{2} \arctan \left( \frac{2\Omega\Gamma_{in}}{\Omega^2 - \omega^2_{\ominus}} \right) \right], \tag{25}
\]

and we again introduced an initial phonon damping $\Gamma_{in}$. The poles of the function $\beta_{T}$ corresponds to the dispersion law of the transverse electromagnetic waves modified due to the random interaction with the phonons. The equation for the poles

\[
(\Omega^2 - c^2K^2) (\Omega^2 - \epsilon^2_{K} - \chi^2(\Omega) - 2i\Omega(\Gamma_{in} + \Gamma_{s})) - \Lambda^2\Omega^2 = 0 \tag{26}
\]
resembles, as it was pointed out in Ref. [3], an equation for eigen frequencies of two waves propagating in a deterministic "effective" medium. The functions $\kappa^2(\Omega)$ and $\Gamma_s(\Omega)$ describe a renormalized dispersion law of phonons in this medium and their damping respectively. Actually, this equation describes the interaction of the coherent (average) electromagnetic wave with non coherent (scattered) ion vibrations, and its solutions give a dispersion law for the coherent component of the electromagnetic waves modified by the disordered coupling with the phonons. An analysis of the simplified version of the Eq.(26) carried out in Ref.[3, 7]) showed that this equation can yield a solution with two well-defined branches of "disorder-induced" polaritons if $\Lambda > \Lambda_{cr}$, where $\Lambda_{cr}$ was estimated in Ref.[4] as $\Lambda_{cr} \simeq v^2k_c^2/\omega_0$ in the model without the initial relaxation $\Gamma_{in}$. However, because of the small value of the parameter $v$ of the phonon spatial dispersion, the initial phonon damping cannot be actually neglected, and a more realistic expression for $\Lambda_{cr}$ can be shown to be $\Lambda_{cr} \simeq \sqrt{(\Gamma_{in}/\Omega)} (vk_c + \sqrt{\Omega \Gamma_{in}})$. Numerically the order of magnitude of $\Lambda_{cr}$ does not differ from the estimate presented in Ref.[7], so the optimistic conclusion of that paper regarding the possibility of observing disorder-induced polaritons in real systems still holds.

Two branches of the disorder-induced polaritons can manifest themselves as two maxima on the frequency dependence of the transverse component of electromagnetic response function $\eta^E_{ij}(\Omega, K)$. Detailed study of the relationship between maxima of response functions and solutions of the dispersion equations was carried out in Ref.[3] in the case of the disorder-induced magnetoelastic resonance. Applying the general results obtained in Ref.[3] to our situation we can conclude that two maxima appear on $\eta^E_{ij}(\Omega, K)$ when a gap between two solutions of the dispersion equation (26) at the crossing point becomes greater than $\Lambda_{cr}$. Since $\Lambda_{cr}$ is the inversed decay time for the solutions at the resonance, the stated condition for two maxima to appear has a clear physical meaning - the frequency interval between two peaks must be greater than their width.

Though qualitatively the conclusions drawn from the simplified model of Ref. [3] remain valid for our more complicated situation, there is an important difference. The effective damping parameter in our case is frequency dependent. This fact leads to an asymmetrical form of the frequency dependence of the respective response function. From Eq.(25) one can see that parameter $\Gamma_s$ decreases with the increase of frequency. One can expect, therefore, that the low frequency maximum of the response function will be lower and wider than the maximum corresponding to the upper polariton.
branch. The plots presented in the subsequent section of the paper support this conclusion.

The fact that vibrational and electromagnetic response functions demonstrate such a different behavior is typical for systems with disorder induced crossing resonances. The simple qualitative interpretation of this fact was given in Ref. [6], where the concept of two effective media was introduced. According to this concept, averaging over the disorder results in two different effective media for each of the interacting waves. The most important difference between the media is in their relaxation properties. The order of magnitude of the effective relaxation parameters is determined, among other things, by the slope of the initial dispersion curves and the correlation radius of the disorder. The former in the case of electromagnetic waves is just speed of light and is much greater than the corresponding parameter $v$ for phonons. As a result, a dispersion law for coherent phonons is determined by the interaction with electromagnetic waves propagating in strongly absorbing effective media; the modification of the initial dispersion law is negligibly small in this situation. As for coherent electromagnetic waves, their dispersion law is modified due to the coupling with phonons in the effective media with rather weak absorption. The coupling is much more effective in this situation. Therefore, the initial dispersion curve splits at the resonance resulting in two maxima on the electromagnetic response function.

4 Frequency dependence of the scattering cross section

The response functions presented in the previous section can be used to study Raman scattering cross-section in our system. The results for the coherent part of the cross-section are obtained by a substitution of imaginary parts of Eq. (19) into Eq. (8) for the ionic contribution into the coherent cross-section, and the imaginary part of Eq. (22) into Eq. (9) for the electromagnetic contribution. As a result, the ionic contribution is

$$ I_{W}^{coh} = 2\hbar^2 |\epsilon_{ikm}| |\epsilon_{jlp}| e_i^s e_j^s e_k^i e_l^i \Omega \Gamma_{in} \times $$

$$ \left\{ \frac{\hat{K}_m \hat{K}_p}{[\Omega^2 - \varepsilon_L^2(K)]^2 + 4\Omega^2 \Gamma_{in}^2} + \frac{2 \left( \delta_{mp} - \hat{K}_m \hat{K}_p \right)}{[\Omega^2 - \varepsilon_T^2(K)]^2 + 4\Omega^2 \Gamma_{in}^2} \right\} $$  

(27)
and electromagnetic part of the cross-section has the following form

\[
I_{E}^{\text{coh}} = g^2 |\epsilon_{ikm}| |\epsilon_{jpq}| e_i^* e_j^* e_k^* e_l^* \frac{8\pi \Omega \Lambda^2 (\Gamma_{in} + \Gamma_s)}{V \epsilon_{\infty}} \times \\
\left[ 2 \left( \delta_{mp} - \hat{K}_m \hat{K}_p \right) \text{Im} \beta_T' (\Omega, K) + \hat{K}_m \hat{K}_p \text{Im} \beta_L' (\Omega, K) \right].
\]

(28)

The Im\beta_T' (\Omega, K) term in Eq.(28) represents the contribution due to scattering from transverse modes

\[
\text{Im} \beta_T' = \frac{2\Omega^4}{[(\Omega^2 - c^2 K^2)(\Omega^2 - \varepsilon_K^2) - \Lambda^2 \Omega^2]^2 + 4\Omega^2 (\Omega^2 - c^2 K^2)^2 (\Gamma_{in} + \Gamma_s)^2},
\]

(29)

whereas the second term corresponds to the scattering due to the longitudinal mode

\[
\text{Im} \beta_L' = \frac{1}{(\Omega^2 - \varepsilon_K^2 - \Lambda^2)^2 + 4\Omega^2 (\Gamma_{in} + \Gamma_s)^2},
\]

(30)

where we neglect the term \varkappa_2(\Omega) defined in Eq.(28), which can be shown to be small.

The polarization dependence of the coherent scattered intensity is mostly determined by the symmetry of the underlying structure, therefore we shall be focused upon a frequency profile of the intensity, which has more universal significance. We would like to note, however, that the suggested average symmetry of the system results in vanishing of both coherent contributions when the polarization of the scattered wave coincides with the polarization of the incident wave. This feature of the considered structure can be used to separate the coherent contribution from the non coherent one. In what follows we restrict our consideration to the perpendicular polarization geometry. In this case the angular dependent factors in Eqs.(28,27) take the form \(1 - \hat{K}_{in}^2\) for the transverse component , and \(\hat{K}_{in}^2\) for the longitudinal one, where \(\hat{K}_{in}\) is a component of \(\hat{K}\) in the direction of propagation of the incident wave, \(\hat{K}_{in} \approx \sin(\theta/2)\), where \(\theta\) is an angle between wave vectors of the incident and scattered waves.

Polariton effects manifest themselves in Raman scattering only at small scattering angles, corresponding to small wave numbers \(K\). The main contribution into the coherent scattering in this situation comes from the transverse components, which depends upon the scattering angle as \(\cos^2(\theta/2)\), while the
contributions from the longitudinal components is small as \( \sin^2(\theta/2) \). The frequency profile of the spectrum is determined by the sum of two parts of the scattering cross-section: ionic contribution Eq.(27) and electromagnetic contribution Eq.(28). The former component of the cross-section does not contain any traces of polariton effects as was explained in the previous sections of the paper. Its frequency dependence has a simple form with one maximum, which is situated at the frequency of TO phonons. Due to weak phonon dispersion, position of this maximum almost independent of scattering angle \( \theta \). Effects of disorder-induced polaritons can appear in the scattering spectrum only due to the electromagnetic contribution to the cross-section. If the system under study allows for disordered polaritons to arise, the transverse response function \( \text{Im} \beta_T \) has two peaks at the polariton frequencies, which are shifted with respect to the TO frequency. The resulting coherent intensity has, in this situation, three peaks: one in the center due to the ionic contribution, and two others due to the disorder-induced polaritons (see Fig.1, where electro-optical and mechanical coherent intensity are plotted together. A small bump on the electro-optical spectrum corresponds to a small longitudinal contribution at LO frequency.) Positions and height of polariton peaks significantly depend upon polariton wave number \( K \), which in turn is determined by the scattering angle. These dependence can be obtained on the bases of the general analysis of susceptibilities presented in Ref.[6]. At \( K \) much smaller than the resonance value, one can observe only one wide peak of \( \text{Im} \beta_T \) at LO frequency. The total coherent spectrum in this case will consist of two maxima corresponding to LO and TO phonons. Upon increasing \( K \) the original LO maximum will start shifting toward high frequencies while becoming narrower and taller. Simultaneously an additional maximum will emerge at frequencies below the frequency of TO phonons. The overall picture in resonance region, hence, will contain three maxima with the central one corresponding to TO phonons, and two others resulting from disorder-induced polariton excitations. According to the general results of the theory of disorder-induced crossing resonance [3] the width of the polariton peaks allows for tracking the dependence between location of the peak and polariton wave number \( K \), i.e. the dispersion law of the disorder-induced polaritons. If the crossing resonance does take place one would observe in this case the parts of two polariton branches described in Ref.[3, 4]. Increasing \( K \) beyond the resonance value will move the higher frequency maximum toward even higher frequency while making it sharper. The low frequency maximum at the same time will be approaching TO frequency and broadening. Finally
the upper polariton branch will become invisible, and the lower one will be indistinguishable from TO phonons. At the same time the contribution from longitudinal cross-section will rise, therefore one will again observe the spectrum with two maxima at LO and TO frequencies.

If the effective coupling parameter $\Lambda$ is too small for the disorder-induced crossing resonance to occur, then all one could observe is a two maximum spectrum whose shape only weakly depends upon the scattering angle.

Now let us consider non coherent scattering. Substituting Eq.(19) for the vibrational response function in Eq.(10) for the non coherent cross-section, and evaluating the integral with the spectral density given by Eq.(17), one arrives at the following expression for $I_{W}^{\text{coh}}$

$$I_{W}^{\text{coh}} = 2[H_{1} + H_{2}(e^{*}e^{in})^{2}]\Omega \times$$

\[
\left\{ \frac{\Gamma_{L}^{\text{eff}}(\Omega)}{(\Omega^{2} - \omega_{L}^{2})^{2} + 4\Omega^{2}\left[\Gamma_{L}^{\text{eff}}(\Omega)\right]^{2}} + \frac{\Gamma_{T}^{\text{eff}}(\Omega)}{(\Omega^{2} - \omega_{T}^{2})^{2} + 4\Omega^{2}\left[\Gamma_{L}^{\text{eff}}(\Omega)\right]^{2}} \right\},
\]

(31)

where $\omega_{T}^{2} = \omega_{0}^{2} + v_{T}^{2}k_{c}^{2}$, $\omega_{L}^{2} = \omega_{0}^{2} + v_{L}^{2}k_{c}^{2} + \Lambda^{2}$ and

$$\Gamma_{L,T}^{\text{eff}}(\Omega) = \Gamma_{in} + v_{L,T}k_{c}\left[\left(1 - \frac{\omega_{L,T}}{\Omega}\right)^{2} + \frac{4\Gamma_{in}^{2}}{\Omega^{2}}\right]^{1/4} \times$$

$$\cos \left[\frac{1}{2} \arctan \left(\frac{2\Omega\Gamma_{in}}{\Omega^{2} - \omega_{L,T}^{2}}\right)\right],
\]

(32)

and $v_{T,L}^{2} = (\nu^{2} \pm \frac{1}{6}\Lambda^{2}/k_{c}^{2})$ are the phonon dispersion parameters modified due to the interaction with the electromagnetic field (see Eq.(20)). we have neglected here $K$-dependence of the phonon dispersion laws. Eq.(31) has a structure similar to the expression for the coherent vibrational intensity except for its independence from the scattering angle. Therefore, transverse and longitudinal components have equal weights. The positions and the widths of the both peaks, however, differ from the coherent scattering. Fluctuations of the mechano-optical coefficients result in a shift of the transverse and longitudinal frequencies by $v_{T,L}^{2}k_{c}$ respectively, and cause an increase in the width given by the second term in Eq.(32). This expression is similar to Eq.(25), which determines the widths of the maxima of the coherent electromagnetic contribution, with the obvious replacement of the parameters.
The analysis of the non-coherent electromagnetic scattering is somewhat more cumbersome because of the more complicated polarization dependence. We would like to point out two simplifying details. First, a contribution from the transverse part of the electromagnetic response function has the order of \((\Omega/k_c)^3\) and can be neglected. Second, we can neglect \(K\)-dependence in the corresponding integrals. As a result, the expression for non coherent electromagnetic part of the scattering intensity takes the following form

\[
I_{E}^{\text{ncoh}} = \left[ \tilde{G}_1 \tilde{G}_2 (e^* e^{in})^2 \right] \frac{4\pi\Lambda^2}{V\epsilon_{\infty}} \frac{\Omega(\Gamma_{in} + \Gamma_s)}{(\Omega^2 - \omega_0^2 - \Lambda^2)^2 + 4\Omega^2(\Gamma_{in} + \Gamma_s)^2}, \tag{33}
\]

where \(\tilde{G}_1\) and \(\tilde{G}_2\) are certain combinations of the original coefficients \(G\). One can see that the non coherent electromagnetic contribution is identical to the coherent longitudinal contribution.

A sample plot for the total scattering intensity is shown in Fig.2. In generating plots in Fig.1 and Fig.2 we choose parameters typical for the systems under consideration, the most important of which are the coupling parameter, internal phonon damping rate, electro-optical and mechano-optical coefficients. The coupling parameter \(\Lambda\) was chosen to be an order of magnitude smaller than the resonance frequency, and phonon damping was assumed to be two orders of magnitudes smaller than the frequency. The relative value of the electro-optical and mechano-optical parameters was chosen to make respective contributions into the scattering intensity be of the same order of magnitude. One can see that the total scattering retain the three-peak feature of the coherent contribution. The peak at the center is formed as a result of superposition of the mechanical coherent cross-section and all the non coherent contributions. Obviously the width of the non coherent maxima for values of parameters chosen for the plot appears to be to large to reveal different types of non coherent contributions, which formally should have appeared at frequencies shifted with respect to coherent TO and LO frequencies. Since the values of the most parameters required to make more explicit predictions of the shape of the spectra are not known we cannot discuss details of the spectra. The figures presented demonstrate nevertheless that under favorable circumstances non coherent contribution would not mask effects due to disordered polaritons in Raman scattering intensity. We can conclude, therefore, that one could hope to observe the polariton-related effects in materials whose average structure forbid polariton formation by studing the spectra for different scattering angles as explained above.
5 Conclusion

In this paper we develop a theory of Raman scattering of light due to disorder-induced polaritons. We consider a material that on average retains a diamond-like cubic structure. This structure has only one triply degenerate optic phonon mode of even parity, which is dipole-inactive in an ideal structure. Local random distortion of the structure, however, gives rise to a random effective charge of the mode and respectively to an effective random coupling with electromagnetic field. The distortion can be induced by different means such as application of pressure [12], using thin films [13], or amorphization. Among materials with the structure of diamond, for example, Si and Ge exist in amorphous versions. Raman scattering in the systems considered in the paper has an interesting feature, which does not show up in the case of ideal structures. In crystalline materials with center of symmetry there exists an “exclusion rule” for dipole infra-red activity and Raman activity. Dipole-active modes, which form polariton states, do not participate in the first-order Raman scattering. Therefore, in ideal crystals the problem of polariton Raman scattering arises only in structures without a center of symmetry. In our situation we deal with a mode which is, on average, dipole inactive, and is, therefore, Raman active. At the same time this mode is coupled to electromagnetic field due to fluctuating effective charge, and induces random electromagnetic field. This field has zero average amplitude, but its intensity is not zero, and it makes sense to take into account the modulation of the electron polarizability due to this field. Components of the respective tensor of the susceptibility derivatives are, of course, random functions and contribute to the non coherent scattering. The average symmetry of the structure does not forbid, however, this tensor from having non-zero average value. If this is the case, then one can observe coherent electromagnetic component of the scattering cross-section from disorder-induced polaritons. Assuming that the average electro-optical coefficients in our situation do not differ in magnitude from more standard situations we show that polariton contribution into Raman scattering can indeed be observed on the non-coherent background.

Raman spectra of amorphous materials have been studied for many years (see, for example, the latest paper in Ref [14] and references therein). Their interpretation, however, is rather complicated, therefore, it is difficult to determine if the disorder-induced polaritons have been already observed. An accurate identification of disorder-induced polaritons in the spectra requires
special experiments. We considered the behavior of the Raman cross-section under the change of the scattering angle, and determined which features of the spectra are specific for disorder-induced polaritons. On the basis of our analysis we think that comparison of spectra measured at different scattering angles could reveal the effects caused by disorder-induced polaritons. We suggest that crystals with locally distorted structures rather than amorphous materials are the best candidates for disorder-induced polariton experiments. Additional means to interpret experimental Raman spectra are provided by the possibility to compare spectra of disordered materials with their crystalline counterparts. In this case one has to take into account that our model does not explicitly describe the shifting and broadening of the spectra due to inhomogeneities intrinsic to the phonon subsystem. We incorporated the broadening phenomenologically by means of the initial damping parameter $\Gamma_{in}$, and can also assume that initial phonon TO frequency is already corrected for the shift due to the intrinsic phonon scattering. Such consideration is valid if one assumes that intrinsic phonon parameters of the system (density and force constants) fluctuate independently of the phonon-photon coupling parameter. This is a legitimate assumption since a correlator between, for instance, the force constants and the coupling parameters should be the tensor of rank three. Such a tensor must vanish in a system with the average structure displaying a center of symmetry. Therefore, one can say that the central peak of the predicted three-peak spectrum corresponds to the broaden and shifted peak, which would correspond to TO phonon peak in the absence of the polariton effects.

Among other results we would like to mention the modification of phonon dispersion laws due to the fluctuating longitudinal electromagnetic field. Our calculations show that in random systems the longitudinal field modifies both the fundamental frequency of phonons and the slope of their dispersion curves. The last effect means that fluctuating component of longitudinal field contributes into interactions between atoms from different elementary cells. It is interesting, that this contribution is found in transverse as well as in longitudinal modes of the vibrations, but with opposite signs. The fluctuating field weakens longitudinal components of the interatomic forces, and enhances the transverse ones.
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Figure Caption

Fig.1 Double peaked line shows electro-optical contribution to coherent scattering intensity. The single peak line is the coherent mechanical contribution. The frequency on the plot is normalized by the resonance frequency.

Fig.2 Total scattering intensity with three peaks. The left one presents the contribution from the lower polariton branch, the right one from the upper polariton branch. The peak in the middle is the resulting contribution from TO phonons and non-coherent scattering. Upon increase of the non-coherent scattering the left peak will disappear first, and yet the remaining double-peaked structure will present a clear indication on the existence of the disordered polaritons.
