Pis'ma v ZhETF, vol.66, iss.12, pp.817 - 822

INTERACTION OF OPTICAL PHONONS WITH ANISOTROPIC IMPERFECTIONS

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Submitted 13 November 1997

Inelastic (Raman) light scattering by phonons interacting with anisotropic imperfections has been investigated. Three different kind of disorder-induced defects (point, linear and planar) have been considered. The optical phonon width and lineshape are found to be essentially dependent on the dimension of the imperfections. There is a close correspondence between the scale of the imperfection and the phonon lineshape observed in the Raman scattering experiments. Dependence of the phonon frequency shift and width on the defect concentrations is calculated and critical concentrations are defined under which the optical phonon cannot be observed anymore.

PACS: 63.20.Mt

1. Many problems encountered in disorder systems have well known theoretical explanations. In particular, the dynamics of impurities in crystals has been described in [1, 2], where both the density of states and frequency of local vibrations have been specially considered. The influence of impurities on the vibrational Raman scattering has been examined in [3, 4] but, so far, there has been no relevant interpretation of the optical phonon interaction with anisotropic imperfections. This is done in present work. Let us emphasize the peculiarities of this phenomenon.

First, the different type of imperfections (e.g. impurities, vacancies, dislocations, crystallite boundaries) have different space structure. The dislocations are an example of line defects. In the case of ion implantation, the defects are certainly more elongated in the normal direction to the surface than they are in the tangent one. Finally, the boundaries of crystallites or pores are plane defects. In this work, we focus on the interaction of optical phonons with three main kind of disorder-induced defects: *(i)* point defects, *(ii)* line defects, and *(iii)* a random set of plane defects. Both the optical phonon width and lineshape are found to be essentially dependent on the dimension of the imperfections.

Second, because the optical phonons are usually observed in the inelastic (Raman) light scattering, the momentum transfer k (which is of the order of the incident light momentum $\omega^{(i)}/c$) is much smaller than the cutoff value $k^{(w)} = \sqrt{\omega_o \Gamma}/s$ determined by the phonon width $\Gamma \simeq 5\ \mathrm{cm}^{-1} \simeq 10^{12}\mathrm{s}^{-1}$, the frequency $\omega_o \simeq 5 \times 10^2 \mathrm{cm}^{-1} \simeq 10^{14}\mathrm{s}^{-1}$ and the dispersion parameter $s \simeq 10^6 \mathrm{cm/s}$ which is of the order of the sound velocity. Therefore, the condition $k \ll k^{(w)}$ is valid and we have to calculate the width in the vicinity of a branch extremum, taking into account self-consistently the phonon width and shift which result from the interaction of phonons with disorder. The size $1/k^{(w)}$ is moderately large in the atomic scale $a = \pi s/\omega_o$: $1/k^{(w)}a = \sqrt{\omega_o/\Gamma}/\pi$ and this is the existence of this large (on the microscopic scale) parameter $1/k^{(w)}$ that provides justification for the present theory.

Third, since the optical phonons are bosons, they can be excited or emitted singly in the process of interaction with light. Then the Raman cross section of the first order

is determined by the phonon Green function averaged over the distribution of imperfections. Therefore, a simple theory can be advanced using Dyson's equation with a squared phonon–imperfection potential as transition probability. A similar technique has been recently applied to the problem of strain relaxation near semiconductors hetero-interfaces [5], except that averaging over the distribution of imperfections can be performed now in an explicit form. We obtain the phonon shift and width (i.e. the phonon self-energy) in the case of the various imperfection geometry. The phonon lineshape i.e. the frequency dependence of the inelastic light scattering cross section (which is proportional to the imaginary part of the averaged Green function) becomes asymmetric and conditioned by the parameter $r_o k^{(w)} = \pi r_o/a\sqrt{\omega_o/\Gamma} \simeq 0.1\, r_o/a$ for the set of values listed before, where r_o is the domain size where phonons can be scattered by the imperfection. Before closing this series of introductory remarks, it may be be useful to notice that this asymmetry has no connection to the well known Fano resonance in conducting systems. Indeed, the Fano resonance results from a contribution of the electron loop in the photon-phonon vertex while, in our case, the asymmetric phonon line shape originates from the phonon density of final states when one considers the scattering of phonons by the imperfections.

2. The inelastic light scattering cross section is determined by the Green function of optical phonons $D_{ij}(\mathbf{r},\mathbf{r}',\omega)$ which obey the equation

$$\left(H - i\omega\Gamma^{(int)} + V(\mathbf{r}) - \omega^2\right) D(\mathbf{r},\mathbf{r}',\omega) = \delta(\mathbf{r}-\mathbf{r}'),$$

where the matrix $H_{ij} = \omega_o^2\delta_{ij} + \mu_{ijlm}\partial^2/\partial x_l \partial x_m$ represents the long-wave expansion of the dynamical matrix near a extremum of the branch. The damping parameter $\Gamma^{(int)}$ describes the intrinsic phonon width caused by the phonon - phonon and electron - optic phonon interactions [6] and the matrix

$$V_{ij}(\mathbf{r}) = \sum_n v_{ij}(\mathbf{r}-\mathbf{r}_n) \tag{1}$$

is the interaction with imperfections located at points $\mathbf{r}_n$. In the case of a substitutional defect of mass m_v instead of m, the interaction may be simply estimated as $v_{ij}(\mathbf{r}-\mathbf{r}_n) = \delta_{ij}\delta(\mathbf{r}-\mathbf{r}_n)\omega_o^2 a^3(m-m_v)/M$, where M and a^3 are the mass and volume of the lattice cell. For a line defect, $(\mathbf{r}-\mathbf{r}_n)$ is a two-dimensional vector. It becomes one-dimensional for a plane defect. The phonon degeneracy has been taken into account by using the subscript i. For instance, in a cubic crystal, there are three optical phonons at the Γ-point with a triple degenerate frequency ($i = 1,2,3$). The long-range Coulomb forces split this degeneracy in such a way that the LO phonon has a higher frequency than the two-times degenerate TO one.

The Green function has to be averaged over defects distributed randomly. Using the diagram technique and summing diagrams with the averages $< V_{ij} >$ and $< \delta V_{ij}(\mathbf{r})\delta V_{lm}(\mathbf{r}_1) >= W_{ijlm}(\mathbf{r}-\mathbf{r}')$, where $\delta V = V - < V >$, we obtain the Dyson equation for the averaged Green function. Near the branch maximum, we search for its solution

$$D_{jj}^{-1}(\mathbf{k},\omega) = \omega_j^2(\mathbf{k},\omega) - s_j^2 k^2 - i\omega\Gamma_j(\mathbf{k},\omega) - \omega^2 \tag{2}$$

and arrive at a system of coupled integral equations

$$\omega_j^2(\mathbf{k},\omega) - \omega_j^2 - i\omega(\Gamma_j(\mathbf{k},\omega) - \Gamma_j^{(int)}) - < V_{jj} >=$$

$$= -\sum_m \int \frac{d^3k_1}{(2\pi)^3} \frac{W_{jmmj}(\mathbf{k}_1-\mathbf{k})}{\omega_m^2(\mathbf{k}_1,\omega) - s^2k_1^2 - i\omega\Gamma_m(\mathbf{k}_1,\omega) - \omega^2} \tag{3}$$

where the unknown functions are $\Gamma_j(\mathbf{k},\omega)$ and $\omega_j(\mathbf{k},\omega)$.

The conditions of validity for Dyson's equation (3) should be outlined here. The line shape on the wings ($|\omega-\omega_o|>\Gamma$) can be obtained using the perturbation theory (Born's approximation) when $\omega_m^2(\mathbf{k}_1,\omega)-i\omega\Gamma_m(\mathbf{k}_1,\omega)$ is substituted in the right-hand side (i.e. in the phonon self-energy) for its unperturbeted value $\omega_o^2-i\omega\Gamma_m^{(int)}$. At the center of the line, the diagrams with intersections of the correlator lines make contribution of the order of the leading diagram and a more sophisticated theory is needed.

The correlation function $W_{jmmj}(\mathbf{k}_1-\mathbf{k})$ has the meaning of a transition probability $(j,\mathbf{k})\to(m,\mathbf{k}_1)$. In order to find the averages $<V>$ and $<\delta V(\mathbf{r})\delta V(\mathbf{r}')>$, let us write the Fourier transform in Exp. (1) for the point defects

$$V_{ij}(\mathbf{r})=\sum_n\int\frac{d^3q}{(2\pi)^3}v_{ij}(\mathbf{q})e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}_n)}. \tag{4}$$

Averaging, i.e. performing an integration over all positions of the defects in the large (to the microscopic scale) volume V_o we get immediately $<V_{ij}(\mathbf{r})>=n_v v_{ij}(\mathbf{q}=0)$ where n_v is the volume concentration of defects.

The contribution in the two-points correlation function comes from the terms which, in the product of two sums (4), involve the same defect :

$$<\delta V_{im}(\mathbf{r})\delta V_{lj}(\mathbf{r}')>=n_v\int\frac{d^3q}{(2\pi)^3}v_{im}(\mathbf{q})v_{lj}(\mathbf{q})e^{i\mathbf{q}(\mathbf{r}-\mathbf{r}')}. \tag{5}$$

Exp. (5) gives the Fourier transform $W_{imlj}(\mathbf{q})$ of the potential-potential correlation function for points defects. If the defects are line, we obtain $W_{imlj}(\mathbf{q})=2\pi n_s\delta(q_z)v_{im}(\mathbf{q}_\perp)v_{lj}(\mathbf{q}_\perp)$, where $\mathbf{q}_\perp$ is the two-dimensional vector in the plane perpendicular to the set of line imperfections and n_s is their concentration per unit area. A similar expression (with 2D $\delta-$function) can be found for plane imperfections with concentration n_ℓ per unit line.

3. For simplicity, let us consider only the case of phonon singlet. We will discuss the interband phonon transitions in the conclusion. In this case the subscripts in D_{ij} and V_{ij} take only one value ($j=1$) and we will omit them. The poles of the phonon Green function give the phonon dispersion law. In the absence of imperfections, using (2) and (3) we get near the maximum of the branch $\omega^2(\mathbf{k})=\omega_o^2-s^2k^2-i\omega_o\Gamma^{(int)}$, where the parameter s depends on the $\mathbf{k}$-direction. This is not essential for the following.

One point should be noticed. When applied to Raman scattering, the momentum $\mathbf{k}$ and frequency ω in Eqs. (3) have the sense of momentum and frequency transfers from light. Then the values $k_1\le k^{(w)}=\sqrt{\omega_o\Gamma}/s$ are essential, in the denominator (3), if one is interested in the vicinity $|\omega_o-\omega|\simeq\Gamma$ of the phonon frequency ω_o. The size $1/k^{(w)}$ is large in atomic scale $a=\pi s/\omega_o$: $1/k^{(w)}=a\sqrt{\omega_o/\Gamma}/\pi\simeq 10\,a$. On the other hand, the phonon momentum transfer $(\mathbf{k}_1-\mathbf{k})$ in the interaction with an imperfection is determined by the domain size r_o where the imperfection relaxes. The two values $k^{(w)}$ and $1/r_o$ maybe of the same magnitude, but they are much more larger than the small momentum transfer $k\simeq\omega^{(i)}/c$ from incident light. Then $\mathbf{k}$ can be omitted in the integrand, i.e. the unknown functions $\omega_1(\mathbf{k},\omega)$ and $\Gamma(\mathbf{k},\omega)$ can be regarded as $\mathbf{k}-$independent. But these functions depend essentially on ω because of the square root singularity of the phonon density of states at the extremum of branches. This dependence is responsible for the nonlorentzian shape of the phonon mode (of course, the asymmetric broadening and line shift are much more pronounced for the short-range disorder $r_ok^{(w)}\le 1$). Finally, if we put (for the

correlation function only) the Fourier component $v(q) = v(q = 0)$ in the region $q < r_o^{-1}$ and equal to zero elsewhere, all integrals can be done analytically and one obtains the system of coupled algebraic equations for $\Gamma(\omega)$ and $\omega_1(\omega)$.

Let us now present the results. We will denote the phonon self-energy, i.e. the right-hand side of Eq. (3), by $\Sigma(\omega)$. Then our main equation will take the form

$$\omega_1^2(\omega) - \omega_o^2 - i\omega(\Gamma(\omega) - \Gamma^{(int)}) - < V >= \Sigma(\omega). \tag{6}$$

We see that the linear term $< V >$ gives only *uniform* shift for the squared phonon frequency $\omega_1^{(un)2} = \omega_o^2 + < V >$ which is always linear in the concentration of defects, but can have an arbitrary sign. The additional *inhomogeneous* shift and broadening result from the bilinear (with respect to the imperfection potential) term Σ. To find them, we have to solve Eq. (6).

i. Point imperfections. The imaginery and real parts of (6) with

$$\Sigma(\omega) = A\left(2b - (a_1 - ia_2)\left(\frac{1}{2}\log\frac{x_1^2+1}{x_2^2+1} + i\arctan x_1 + i\arctan x_2\right)\right) \tag{7}$$

give the system of two coupled equations for the unknown functions $\omega_1(\omega)$ and $\Gamma(\omega)$ where $x_1 = (b + a_1)/a_2$, $x_2 = (b - a_1)/a_2$, $a_1 = (\omega_1^2(\omega) - \omega^2 + \Omega^2(\omega))^{1/2}$, $a_2 = (-\omega_1^2(\omega) + \omega^2 + \Omega^2(\omega))^{1/2}\mathrm{sign}(\omega)$, $\Omega^4(\omega) = (\omega_1^2(\omega) - \omega^2)^2 + \omega^2\Gamma^2(\omega)$, $b = \sqrt{2}s/r_o$ and $A = n_v v^2(q = 0)/4\sqrt{2}\pi^2 s^3$.

Let us write $v(q = 0) = g r_o^3 \omega_o^2$ for estimates (where $g \simeq 1$ if the force constants change around imperfections). Then the linear term $< V >$ in (6) gives $g n_v r_o^3 \omega_o^2/2$ and the second order term in (7) $A = g^2 n_v r_o^3 \omega_o (r_o\omega_o/s)^3/4\sqrt{2}\pi^2$. For the above-mentioned example of a substitutional defect, the Fourier component $v(q) = \omega_o^2 a^3(m - m_v)/M$ and we need to cut off the real part of integral (3) at $1/a$ instead of $1/r_o$.

The numerical solution to the coupled system (6) - (7) as a function of the frequency transfer, together with the Raman cross section which is proportional to Im $D(\omega)$, is shown in Fig. 1 for several values of the interaction constant A and $r_o = 3.5\ a$. One find clearly that the lineshape is asymmetric. The resonance curve drops more slowly on the low-frequency side of the peak and, as already said, this comes simply because the density of phonon states increases below the maximum. The center of the line (renormalized phonon frequency) is determined by the equation $\omega_1(\omega) = \omega$ (see Eq. (2) with $k = 0$). Using Eqs. (6) and (7) at the center of the line, one can find easily the phonon width Γ and the defect-induced shift $(\omega_1 - \omega_o)$.

ii. Line imperfections. In this case,

$$\Sigma(\omega) = B\left(\frac{1}{2}\log\frac{(s^2/r_o^2 + \omega^2 - \omega_1^2(\omega))^2 + \omega^2\Gamma^2(\omega)}{(\omega^2 - \omega_1^2(\omega))^2 + \omega^2\Gamma^2(\omega)} - \right. \tag{8}$$
$$\left. -i\arctan\frac{\omega_1^2(\omega) - \omega^2}{\omega\Gamma(\omega)} - i\arctan\frac{s^2/r_o^2 - \omega_1^2(\omega) + \omega^2}{\omega\Gamma(\omega)}\right),$$

where $B = n_s v^2(q_\perp = 0)/4\pi s^2$ and $v(q_\perp = 0) = g r_o^2 \omega_o^2$.

The resonance line appears wider than it was in case (i) because of the more important frequency-dependence of the line shift.

iii. Plane imperfections. We obtain

$$\Sigma(\omega) = C\left(\frac{1}{2}\log\frac{x_1^2+1}{x_2^2+1} + \arctan x_1 + i\arctan x_2\right)/(-a_1 + ia_2), \tag{9}$$

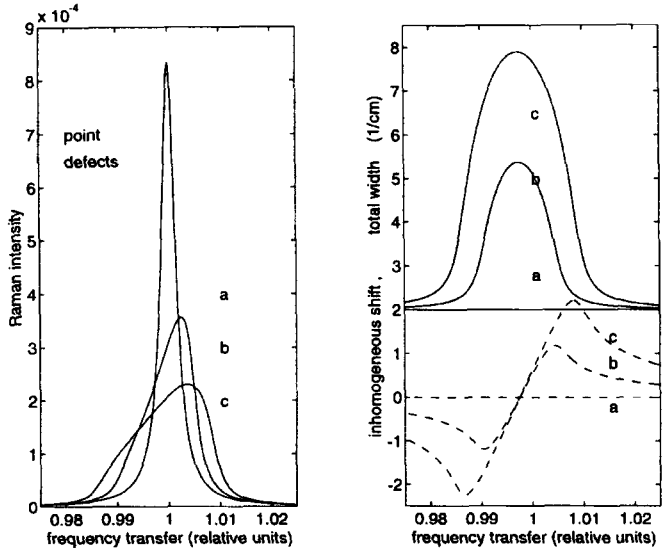


Fig.1. Theoretical Raman intensity (imaginary part of the phonon Green function, the left panel), phonon width (top of the right panel) and shift (dotted lines) plotted as a functions of the frequency transfer in the case of point defects with a potential of the small radius $r_o = 3.5\ a$ in atomic units a. The intrinsic phonon width is taken 2 cm^{-1} but three different values of the interaction dimentionless constant $A_d = A/\omega_o$ have been used in Eq. (7) and the corresponding total widths Γ (cm^{-1}) obtained at the center of lines : (a) perfect crystal, $A_d = 0, \Gamma = 2$ (b) $A_d = 0.075, \Gamma = 4.84$ (c) $A_d = 0.187, \Gamma = 7.40$

where notations are the same as in (7), $C = n_\ell v^2(q_z = 0)/\sqrt{2}\pi s$, the one-dimensional Fourier component $v(q_z = 0) = g\omega_o^2 r_o$ and n_ℓ is the linear concentration of scattering planes. In other words $(n_\ell a)^{-1}$ is the average crystallite or pore size measured in atomic units.

It is interesting to remark that one obtains the same frequency-dependence of the Raman cross section in the limiting case of the very large potential radius $r_o k^{(w)} \gg 1$ for all dimensions. This case describes simply the small-angle scattering of phonons by imperfections and, as a consequence, the phonon cannot "see" really the geometry of the imperfections. As an example, we show the case of the line defects in Fig. 2 for long-range disorder. Although our final results have been written for a single phonon mode, the basic Dyson equation (3) may be applied to the generate phonon. In this case, the phonon scattering by the anisotropic imperfections implies as well damping as splitting of the degenerate phonon mode.

4. In Fig. 3 the inhomogeneous shift (the uniform shift is not included) and width are shown as functions of the defect concentration for different imperfections dimensions. They would be the linear functions if we use the standard perturbation theory. For imperfections of the atomic scale $r_o \sim a$, one can obtain from Eqs. (7) - (9) the rough estimates $\Gamma - \Gamma^{(int)} = g^2 n_v a^3 (\omega_o \Gamma)^{1/2}$ for the point defects, $\Gamma - \Gamma^{(int)} = g^2 n_s a^2 \omega_o$ for the line defects and $\Gamma - \Gamma^{(int)} = g^2 n_\ell a \omega_o (\omega_o/\Gamma)^{1/2}$ for the plane defects where $g \simeq 1$ is a dimensionless coupling of phonons with imperfections.

Since the optical phonons are not visible in the Raman scattering if $\Gamma/\omega_o > .01$ roughly, that defines the critical concentrations of the point and line defects $n_v a^3 g^2 \simeq (\Gamma/\omega_o)^{1/2} \simeq .1$ and $n_s a^2 g^2 \simeq \Gamma/\omega_o \simeq .01$, respectively, and the critical crystallite size $(n_\ell g^2)^{-1} \sim a(\omega/\Gamma)^{3/2} \simeq 10^3 a$ above which the Raman line are no longer observed.

Our results show also that there is a definite correspondence between the imperfection scale r_o and the phonon lineshape observed in the Raman scattering. The crossover value r_o^{-1} for the potential radius is determined by the phonon width $k^{(w)} = \sqrt{\Gamma\omega_o}/s$. In the case of the short-range imperfection potential $k^{(w)} r_o \leq 1$, the phonon lineshape

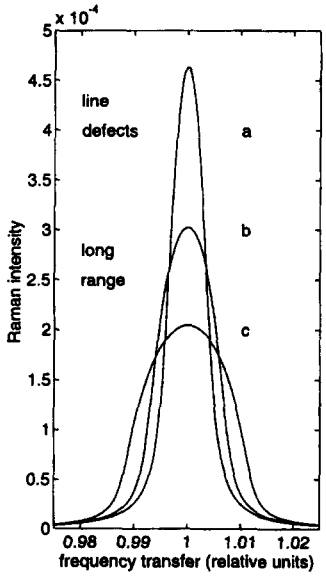
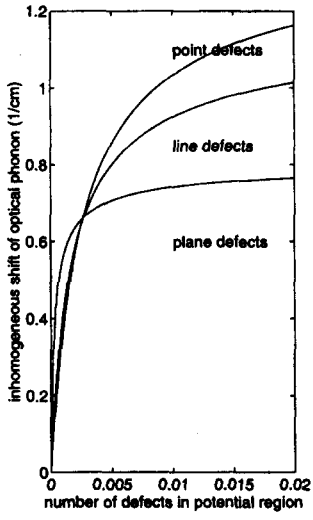


Fig.2. Same as Fig. 1 but for line defects of large radius $r_o = 20\ a$ for three values of the interaction constant B_d: (a) $B_d = 0.063, \Gamma = 3.58$ (b) $B_d = 0.21, \Gamma = 5.5$ (c) $B_d = 0.55, \Gamma = 8.1$



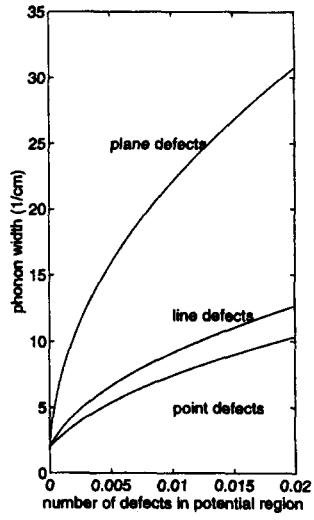


Fig.3. Imperfection concentrations dependence of the inhomogeneous phonon shift and width (at the center of lines) for three kinds of defects. The potential radius $r_o = 3.5\ a$ and the phonon-imperfection coupling $g = 0.5$ are taken for all cases. The concentrations are given by the dimensionless variables $n_v r_o^3, n_s r_o^2, n_l r_o$ for the point, line and plane imperfections, respectively. Solid lines are solutions of Eqs. (6)-(9)

is asymmetric due to influence of the phonon density of state (see Fig. 1). For the imperfections of large radius $k^{(w)} r_o > 1$, the influence of phonon–defect scattering results in the symmetric but nonlorentzian lineshape (see Fig. 2).

This paper appears due to discussions with J. Camassel of his experiments on interfaces and ion implantation. It is my pleasure to thank him for comments and ideas. I am also grateful to V. Fateev for discussions and comments. This work was supported in the framework of INTAS programme 0101–CT93–0023 and also by Russian Foundation for Basic Research (Grant No 97-02-16044).

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