Strongly localized anharmonic modes in perfect and imperfect crystals

V.Hizhnyakov\textsuperscript{1,3}, D.Nevedrov\textsuperscript{1,2}, E.Sigmund\textsuperscript{3}

\textsuperscript{1}Institute of Theoretical Physics, University of Tartu, Tähe 4, Tartu EE2400, Estonia.

\textsuperscript{2}Institute of Physics, University of Tartu, Riia 142, Tartu EE2400, Estonia.

\textsuperscript{2}NORDITA, Blegdamsvej 17, Copenhagen DK-2100, Denmark.

\textsuperscript{3}Brandenburgische Technische Universität Cottbus, Karl-Marx-Str. 17, D-03044 Cottbus, Germany.

Localized modes of large amplitudes in nonlinear lattices are considered.

The applied method allows the reduction of nonlinear problem to a linear inverse problem of phonons scattering on a local potential. The method is efficient in the case of strongly localized modes. Analytical description of such modes in monatomic chain is given. Results of numerical calculations of anharmonic local vibrations of light ions in pure and impure alkali halide crystal are presented. It is found that, in the case of amplitudes $\tilde{\alpha} > 0.5\text{Å}$, the vibrations depend very strongly on the crystallographic directions.

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I. INTRODUCTION

Recent studies of nonlinear vibrational dynamics lead to observation of long-living localized vibrations in perfect anharmonic lattices\textsuperscript{1,6} (see also review\textsuperscript{7} and references therein). The methods, which have been used so far for studying of these novel excitations, are based on direct numerical integration of classical equations of motions, being here the nonlinear differential equations. Due to the fast growth of the number of numerical operations and computational time with increase of the number degrees of freedom, the research is mainly focused on simple models, such as one-dimensional one- and two-atom lattices; only little have been done for real 3D crystals\textsuperscript{7}. On the contrary, in harmonic approximation calcu-
lations can be performed also for macroscopically large pure and locally distorted crystals. Here we present a method which makes use of harmonic approximation results for calculations of the anharmonic local modes (ALM). The developed techniques allow one to reduce the nonlinear problem of ALMs to a properly formulated problem of linear local dynamics. It is applicable for lattices of arbitrary dimension, being especially efficient in the case of strongly localized modes, when it allows to obtain analytical solutions. The consideration is based on classic mechanics; account of quantum effects is given in [1–12].

The starting points for the method are the stability conditions of an ALM with respect to small fluctuations:

- all frequencies of the spectrum of these fluctuations should be real and positive,
- spectrum of fluctuations should contain also the basic frequency \( \omega_l \) of the ALM, i.e. there should be harmonic local mode (HLM) with the same frequency \( \omega_l \); the same holds for the higher harmonics of the mode,
- the ratios of the amplitudes of atoms of the HLM should coincide with that of corresponding ALM.

The physical meaning of the condition a) is obvious: the configuration of the crystal lattice with the ALM must be stable (not metastable). The conditions b) and c) ensure that a solution, which describes an ALM are stable with respect to infinitesimal changes of the ALM phase. The last two conditions allow the self-consistent calculation of the ALMs. Indeed local mode of finite amplitude in anharmonic lattice causes local perturbation of the dynamical matrix of small vibrations. Therefore, knowing (or choosing as a trial parameters) the amplitudes of the ALM on different atoms, we can determine the changes of the elastic springs, caused by the ALM. Then, by applying the Lifschitz formula of local dynamics in harmonic approximation, the expressions for the HLM (and ALM) may be obtained, both for its frequency and amplitudes of contributing atoms. These expressions allow the obtaining of the self-consistency conditions, being the set of of equations for the parameters of the ALM. Thus, the method reduces the nonlinear problem of calculation of an ALM to a kind of a linear inverse problem of phonons scattering on a local scattering potential for small
vibrations (phonons). If the ALM is strongly localized, then the procedure is simple while one needs to calculate only few amplitudes. This can be done analytically. The method is applicable for lattices of different dimensions. Besides, it can be also used for calculations of anharmonic local modes of defects.

To illustrate, how the method works, we will apply it first to the ALMs in monatomic chain with hard quartic anharmonicity. We will show that one gets analytical results which, in the limiting case of high frequency, coincide with known solutions. Then we will calculate odd ALMs in pure and impure alkali halide crystals with light and heavy ions and with account of quartic anharmonicity (the ALMs under consideration are almost fully localized on the light atoms). Frequency spectra in these crystals are calculated in the shell model. Anharmonic constants are determined from the Born-Coulomb-Mayer potentials.

II. GENERAL

Let us consider a vibrational system with the potential energy

$$V = \frac{1}{2} \sum_{n_1n_2} V^{(2)}_{n_1n_2} U_{n_1} U_{n_2} + \frac{1}{3} \sum_{n_1n_2n_3} V^{(3)}_{n_1n_2n_3} U_{n_1} U_{n_2} U_{n_3} + \ldots,$$

where $U_n$ are the Cartesian displacements of atoms situated at the site $n$, $V^{(2)}$, $V^{(3)}$, \ldots are harmonic and anharmonic springs. The displacements $U_n$ satisfy the following equations of motion

$$-M_n \ddot{U}_n = \sum_{n_1} V^{(2)}_{nn_1} U_{n_1} + \sum_{n_1n_2} V^{(3)}_{n_1n_2n_3} U_{n_1} U_{n_2} + \ldots,$$

where $M_n$ are the masses of atoms. We suppose that a ALM is excited at the site $n = 0$ and its nearest neighbors. This excitation is the solution of the equations of motion with exponentially decreasing $|U_n|$ with $|n| \to \infty$. As it is known, a solution, which corresponds to the ALM with the frequency $\omega_l$ has the form $U_n(t) = A_n \cos(\omega_l t) + \xi_n + O(\omega_l)$, where $O(\omega_l)$ is the sum of small terms of the frequencies $3\omega_l, 5\omega_l, \ldots$ (i.e. the higher order harmonics; these harmonics are neglected below). The amplitudes $A_n$ and the shifts $\xi_n$ can be found by equating the coefficients before the terms with the same time dependence. The corresponding equations are
\[ M_n \omega_l^2 U_n = \sum_n V^{(2)}_{nn_1} U_{n_1} + 2 \sum_{n,n_2} V^{(3)}_{nn_1n_2} U_{n_1} \xi_{n_2} + 3 \sum_{n,n_1,n_2,n_3} V^{(4)}_{nn_1n_2n_3} \left( \frac{1}{4} U_{n_1} U_{n_2} + \xi_{n_1} \xi_{n_2} \right) U_{n_3} + \ldots, \] (3)

\[
\sum_n V^{(2)}_{nn_1} \xi_{n_1} + \sum_{n,n_2} V^{(3)}_{nn_1n_2} \left( \frac{3}{2} U_{n_1} U_{n_2} + \xi_{n_1} \xi_{n_2} \right) + \ldots = 0.
\]

To take into account small fluctuations we present the displacements in the form \( \bar{U}_n = U_n + q_n / \sqrt{M_n} \), where \( q_n \) stands for the reduced small displacement. The equations for \( q_n \) are obtained from (3) and read:

\[ \ddot{q}_n = \sum_{n'} (V_{2nn'} + W_{2nn'}) q_{n'}, \] (4)

where \( V_{2nn'} \) is the dynamical matrix in harmonic approximation,

\[
W_{2nn'} = \frac{2}{\sqrt{M_n M_{n'}}} \left( \sum_{n' n_1} V^{(3)}_{nn' n_1} \xi_{n_1} + \frac{3}{4} \sum_{n_1 n_2} V^{(4)}_{nn'n_1n_2} (U_{n_1} U_{n_2} + 2 \xi_{n_1} \xi_{n_2}) + \ldots \right),
\] (5)

describes anharmonic renormalization of the dynamic matrix due to the ALM (time-dependent terms \( \sim \cos k\omega_l t, \ k = 0, 1, 2, \ldots \) are neglected here; these terms are important in quantum mechanical description of fluctuations: they lead to multi-phonon decay of the ALM). In the case of strongly localized modes one can include into consideration only small number \( N \) of amplitudes \( U_n \). Then \( \{W_{2nn'}\} \) is the \( N \times N \)-matrix of the local springs of the lattice.

Hamiltonian, which corresponds to the equations of motions (4), equals \( H_{ph} = H_{0,ph} + \tilde{V}_2 \), where

\[
H_{0,ph} = \frac{1}{2} \sum_n \dot{q}_n^2 + \frac{1}{2} \sum_{nn'} V_{2nn'} q_n q_{n'} = \frac{1}{2} \sum_i (\dot{x}_i^2 + \omega_i^2 x_i^2)
\] (6)

is the phonon Hamiltonian of the harmonic lattice, \( x_i = \sum_n e_{in} q_n \) are the normal coordinates of the lattice (in a perfect lattice \( e_{in} \sim e^{i\vec{k} \vec{n}} \)),

\[
\tilde{V}_2 = \frac{1}{2} \sum_{nn'} W_{2nn'} q_n q_{n'}
\]

describes the effect of the ALM on the phonons, \( W_{2nn'} \) are corresponding local distortions of the elastic springs, given by (5).
The HLMs, induced by the interaction $\tilde{V}_2$, are determined by the poles of the spectral Greens functions

$$G_{nn'}(\omega) = -i \int_0^\infty e^{i\omega t - et} G_{nn'}(t)$$

on the real axis of $\omega$; $G_{nn'}(t) = \Theta(t) \sum_i \tilde{e}_{in} \tilde{e}_{in} \sin(\omega_i t)$ is the retarded matrix-Green’s function of phonons, $\tilde{e}_{in} = e_{in}/\omega_i$. This matrix-function can be found by applying Lifshitz formula

$$G_{nn'} = G_{nn'}^{(0)} + \sum_{n_1n_2} G_{nn_1}^{(0)} W_{2n_1n_2} G_{n_2n'},$$

(7)

where $G_{nn'}^{(0)}(\omega)$ are the Green’s functions of the harmonic lattice. These functions can be calculated by standard methods of lattice dynamics. To find the frequency and shape of the HLM (and ALM) let us introduce the configurational coordinates

$$Q_\nu = \sum_n S_{\nu n} q_n, \quad \tilde{Q}_\mu = \sum_\nu s_\mu(\omega) Q_\nu.$$

The first transformation $S$ is chosen to diagonalize the perturbational quadratic form $\tilde{V}_2$:

$$\tilde{V}_2 = \sum_\nu \eta_\nu Q_\nu^2/2.$$

The second transformation $s(\omega)$ diagonalizes the dimensionless Green’s function matrix $\tilde{G}_{\nu\nu'} = \sqrt{\eta_\nu \eta_{\nu'}} \tilde{G}_{\nu\nu'}^{(0)}$:

$$\tilde{G}_{\mu\mu'} = \delta_{\mu\mu'} \sum_{\nu\nu'} s_{\mu\nu} s_{\mu'\nu'} \tilde{G}_{\nu\nu'} = \delta_{\mu\mu'} \sum_{nn'} R_{\mu n} R_{\mu' n'} G_{nn'}^{(0)}.$$

Here $\tilde{G}_{\nu\nu'}^{(0)}(\omega)$ are the lattice Greens functions in $Q_\nu$-space, $R_{\mu n}(\omega) = \sum_\nu s_{\mu\nu}(\omega) \sqrt{\eta_\nu} S_{\nu n}$. In the $\tilde{Q}_\mu$-representation the Lifshitz formula takes the form $\tilde{G}_{\mu\mu}(\omega) = \tilde{G}_{\mu\mu}^{(0)}(\omega)(1 - \tilde{G}_{\mu\mu}(\omega))$.

From symmetry considerations one can chose the configurational coordinate $\tilde{Q}_\mu$ which corresponds to the ALM under investigation. The frequency $\omega_l$ of the local mode is given by the position of the pole of the Green’s function $\tilde{G}_{\mu\mu}(\omega)$ on the real axis $\omega$, i.e. satisfies the relation

$$\tilde{G}_{\mu\mu}^{(0)}(\omega_l) = 1;$$

(8)

the relative amplitude of the $n'$ atom in the mode is given by the formula: $a_\mu = R_{\mu n}(\omega_l) \sqrt{\pi/|G_{\mu\mu}^{(0)}(\omega_l)|}$, where $G_{\mu\mu}^{(0)}(\omega) = dG_{\mu\mu}^{(0)}(\omega)/d\omega$. Taking into account that the relative amplitudes satisfy the normalization condition $\sum_n a_{\mu n}^2 = 1$, we obtain:
\[ a_{\mu n} = \frac{R_{\mu n}(\omega_l)}{\sqrt{\sum_{\nu} S^{2}_{\mu \nu}(\omega_l) \eta_{\nu}}} \]

The relations (9) give the set of equations for \( a_{\mu n} \). In combination with (8) they allow one to find the amplitudes \( A_n \) of the ALM of given frequency \( \omega_l \). The method works better for strongly localized ALMs with high frequency, when the number of contributing amplitudes \( A_n \) (and equations to be solved) is small.

In the case of high frequency of the ALM (\( \omega_l \gg \omega_M \), \( \omega_M \) is maximal phonon frequency) the non-diagonal elements of the \( G_{nn'}^{(0)}(\omega_l) \) are much smaller than the diagonal ones. Then \( \tilde{G}_{\nu \nu'}^{(0)}(\omega_l) \approx \delta_{\nu \nu'} G_{00}^{(0)}(\omega_l) \), i.e. the Greens-function matrix diagonalizes simultaneously with \( \tilde{V}_2 \). In this case the normalized amplitudes of the ALM can be determined by simple self-consistency condition \( a_n = S_{\nu n} \); absolute amplitudes one can find from the relation \( G_{\nu \nu}(\omega_l) = \eta_{\nu}^{-1} \).

If the limited number of atomic displacements is taken into consideration then the quadratic form \( \tilde{V}_2 \) does not depend on the totally-symmetric coordinate, being the common displacement (the sum of equal displacements of all accounted atoms). This means that all modes, which contribute to the diagonalized quadratic form \( \tilde{V}_2 \), are orthogonal to this displacement. Evidently, the same holds for the linear combination of shifts, which give contributions to the ALM. Otherwise, the sum of displacements of all atoms, which contribute to the ALM, should be equal zero:

\[ \sum_n A_n = 0. \]  

The same holds for the sum of momenta of atoms at any time-moment. This property of the ALMs may be called as immobility condition.

III. EVEN AND ODD ALMS IN MONATOMIC CHAIN

We apply the method to description of ALMs in monatomic chain. The potential energy of the chain with account of the nearest-neighbor interactions has the form

\[ V = \sum_n \sum_r \frac{V^{(r)}(U_{n+1} - U_n)^r}{r}. \]
In harmonic approximation \((V^{(2)} > 0, V^{(r)} = 0, r \geq 3)\) for \(\omega/\omega_M > 1\) the Green’s functions of the chain equal:

\[
G^{(0)}_{nn'}(\omega) = \frac{(-\rho)^{|n-n'|}\omega_M/\omega}{4\omega_M\sqrt{\omega^2 - \omega_M^2}},
\]

\(\omega_M = 2\sqrt{V^{(2)}/M_0}\) is the top phonon frequency; \(\rho = (\omega/\omega_M - \sqrt{\omega^2/\omega_M^2 - 1})^2 < 1\). In the limit of strong amplitudes and high frequency one gets two strongly localized ALMs:

1. the odd mode with \(A_n = -A_{-n}\), \(A_1 \approx -A_0/2\), \(|A_n| \ll |A_1|\), \(n \geq 1\) and
2. the even mode with \(A_{n+1} = -A_{-n}\), \(|A_{n+1}| \ll |A_0|\), \(n \geq 1\).

For \(n \gg 1\) we have \(A_{|n|+1} \approx -\rho A_{|n|}\). For smaller frequency the wings (tails) of the mode are stronger. Below we give analytical description of strongly localized ALMs, having remarkable \(\omega_l/\omega_M - 1\), in the chain with quartic anharmonicity \((r = 4)\). Note that in the opposite limit of very small \(\omega_l/\omega_M - 1\) there exists an analytical solution of the problem, which describes the ALM of large size.

1. Even mode

Let us consider first the even mode. With account of four central atoms displacements the contribution of the ALM to the potential energy of phonons has the form

\[
\tilde{V}_2 = K_4 A_0^2 b((q_2 - q_1)^2 + (q_0 - q_{-1})^2) + (q_1 - q_0)^2],
\]

where \(K_4 = 6V^{(4)}/M_0\), \(b = (1 + \beta)^2/4\), \(\beta = A_2/A_0\). Two following even modes contribute to the \(\tilde{V}_2\) and ALM:

\(y_1 = q_0 - q_1\sqrt{2}\), \(y_2 = q_2 - q_{-1}\sqrt{2}\).

In the strong localization limit the main contribution is given by \(y_1\). Contribution of \(y_2\) depends on the \(\omega_l\) being larger for smaller \(\omega_l\). Our task is to describe the last dependence. In \(y_1, y_2\)–subspace \(\tilde{V}_2 = K_4((2 + b)y_1^2 - 2by_1y_2 + by_2^2)\). This quadratic form is diagonalized in the rotated basis \(Q_1 = y_1 \cos \phi + y_2 \sin \phi\), \(Q_2 = -y_1 \sin \phi + y_2 \cos \phi\) with \(\tan(2\phi) = b\). In the limit of high frequency \(\omega_l\) the self-consistency condition reads

\[
\sin \phi = \beta \approx \frac{b}{2} = \frac{(1 + \beta)^2}{8}.
\]
One gets $\beta \approx 1/6$ in agreement with the corresponding calculation of $\beta$ on the basis of the nonlinear equations of motion\(^\text{[1]}\). To describe $\omega_l$-dependence of $\beta$ we should find coordinates $\tilde{Q}_{1,2}$ which diagonalize the Green’s function matrix $\tilde{G}_{\nu\nu'}^{(0)} = G_{00}^{(0)}(\sqrt{\eta_\nu \eta_{\nu'} g_{\nu\nu'}}), \nu, \nu' = 1, 2$, $\eta_{1,2} = K_4 A_0^2 (1 + b \pm \sqrt{1 - b^2})$,

$$g_{11} = \rho_{11} \cos^2 \phi + \rho_{22} \sin^2 \phi + \rho_{12} \sin (2\phi),$$
$$g_{22} = \rho_{11} \sin^2 \phi + \rho_{22} \cos^2 \phi - \rho_{12} \sin (2\phi),$$
$$g_{12} = -\rho_{12} \cos (2\phi) + \frac{1}{2} (\rho_{11} - \rho_{22}) \sin (2\phi),$$

where $\rho_{11} = 1 + \rho$, $\rho_{22} = 1 + \rho^3$, $\rho_{12} = \rho (1 + \rho)$. The diagonalization is achieved by rotating of the coordinates $Q_{1,2}$ on the angle $\alpha$ with

$$\tan (2\alpha) = \frac{2\sqrt{\eta_1 \eta_2 g_{12}}}{(\eta_1 g_{11} - \eta_2 g_{22})}. \quad (11)$$

The self-consistency condition now is

$$\beta = \sin (\alpha + \phi). \quad (12)$$

This is equation for $\beta(\omega_l)$, which can be easily solved numerically or (approximately) analytically. E.g. in the strong localization limit, when both, $\alpha$ and $\phi$ are small, one gets

$$\beta \approx \frac{1}{6} + \frac{5\rho}{12\sqrt{2}(1 + \rho)}. \quad (13)$$

The dependence of the dimensionless frequency of the mode $\Omega_l = \omega_l/\omega_M$ on the amplitude $A_l$ is given by the equation (8) with $\nu = 1$:

$$\tilde{G}_{11}^{(0)}(\omega_l) = K_4 A_0^2 G_{00}^{(0)}(\omega_l) \left(1 + b + \sqrt{1 - b^2} \right) \left[g_{11} \cos^2 \alpha + g_{22} \eta_2 \sin^2 \alpha + g_{12} \sqrt{\eta_2} \sin (2\alpha)\right] = 1. \quad (14)$$

For $\omega_l > 1.15\omega_M$ given formulas describe the ALM rather well: the contributing amplitudes of the next nearest atoms is less than $10^{-2}$, thereat their contribution to the energy of the ALM is less than $10^{-4}$.

2. **Odd mode**

Let us consider now the odd ALM with account of displacements of five atoms. The mode under consideration satisfies the parity and immobility conditions $A_n = A_{-n}$, $A_2 +
$A_1 + A_0 + A_{-1} + A_{-2} = 0$, which give $A_1 = -A_0(1/2 + \beta)$, $\beta = A_2/A_0$. The contribution of the ALM to the potential energy of phonons equals

$$\tilde{V}_2 = K_4 A_0^2 [\tilde{b}((q_2 - q_1)^2 + (q_{-2} - q_{-1})^2) + (q_1 - q_0)^2 + (q_{-1} - q_0)^2],$$

where $K_4 = 9V^{(4)}(1 + 2\beta/3)^2/8$, $\tilde{b} = (1 + 4\beta)^2/(3 + 2\beta)^2$. Two odd modes, which give contributions to the ALM read:

$$y_1 = \frac{1}{\sqrt{6}}(2q_0 - q_1 - q_{-1}), \quad y_2 = \frac{1}{\sqrt{30}}(3q_2 + 3q_{-2} - 2q_0 - 2q_1 - 2q_{-1}).$$

In the $y_{1,2}$-space $\tilde{V}_2 = K_4[3+\tilde{b}/3)y_1^2 - (2\sqrt{5}/3)\tilde{b}y_1y_2 + (5/3)\tilde{b}y_2^2]$. This quadratic form is also diagonalized in the rotated basis with $\sin (\phi) \approx b/2$, where $b = 2\sqrt{5\tilde{b}}/(9 - 4\tilde{b})$. In the limit of large $\omega_l/\omega_M$ the main contribution to the ALM is given by the $y_1$-mode; contribution of the $y_2$-mode is given by the self-consistency condition $\beta \approx 3\sin (\phi)/2\sqrt{5} \approx \tilde{b}/6$. Taking $\tilde{b} \approx 1/9$ one gets the value $\beta = 1/54$ in agreement with\[9\]. A more accurate approximation is $\beta \approx 3/131$.

The $\omega_l$-dependence of $\beta$ and $A_0$-dependence of $\omega_l$ can be found in the same way as for the even mode. In this case

$$\eta_{1,2} = \frac{K_4 A_0^2}{2\sqrt{5} + 4b}(3\sqrt{5} + 15b + (3\sqrt{5} + 9b)(1 + \pm\sqrt{1 - b^2}).$$

For small $\beta$ one gets

$$\eta_1 \approx K_4 A_0^2\left(\frac{8}{3} - \frac{40\beta}{18}\right), \quad \eta_2 \approx \eta_1\left(\frac{1}{16} + \frac{27\beta}{64}\right).$$

The factors $g_{\nu \nu'}$ are also determined by the same expressions as in the even ALM case but with the following $\rho_{\nu \nu'}$:

$$\rho_{11} = 1 + \frac{4\rho}{3} + \frac{\rho^2}{3},$$

$$\rho_{22} = 1 + \frac{4\rho}{15} - \frac{8\rho^2}{15} + \frac{4\rho^3}{5} + \frac{3\rho^4}{5},$$

$$\rho_{12} = \sqrt{5}\rho\left(\frac{1}{3} + \frac{8\rho}{15} + \frac{3\rho^2}{15}\right).$$

The self-consistency condition in this case is:

$$\beta = \frac{3\sin (\phi + \alpha)}{2\sqrt{5}\cos (\phi + \alpha) - 2\sin (\phi + \alpha)}, \quad (15)$$
where $\alpha$ is determined by (11); thereat expressions for $\eta_1, 2$ and for $\rho_{\nu\nu}'$ are also determined by the same formulae as in the even ALM case. In the case $\beta \ll 1$ one gets

$$\sin(\alpha) \approx \tilde{\rho}\sqrt{\eta_2/5\eta_1}$$

where $\eta_1 \approx 3 - \bar{b}/3$, $\eta_2 \approx 5\bar{b}/3$, $\tilde{\rho} = \rho(5 - 3\rho)/(3 - \rho)$. This gives

$$\beta \approx \frac{0.023 + \tilde{\rho}/9}{1 - \frac{4\tilde{\rho}/9}{1}}.$$  

(16)

The dependence of the frequency of the mode is given by equation (6) If $\omega_l > 1.15\omega_M$ then the odd ALM is well localized ($\beta < 0.065$), more than 99.98 percent of energy of the mode come from 4 central atoms.

The calculated dependences of $\Omega_l$ and $\beta$ on amplitude for even and odd modes are plotted on Fig.1.

IV. ALMS IN ALKALI HALIDES

We present here calculations of odd local modes associated with light impurity and host ions in alkali-halide crystals. In these cases the ALM is almost fully localized on the light ion and the problem reduces to calculation of the frequency of the mode in dependence on its amplitude.

Within the approximation of the nearest neighbors interaction the potential operator has the form

$$\hat{V} = \sum_{\alpha} \sum_{\vec{n}} \sum_{m=1}^{\infty} \frac{1}{2m} \hat{V}_{\vec{n}_{\alpha}}^{(m)} (\hat{R}_{\vec{n}_{\alpha}})^m,$$

(17)

where $\vec{\alpha} = \pm x, \pm y, \pm z$ are the directions to the nearest neighbors, $\vec{n} = (n_x, n_y, n_z)$ is the vector of the lattice sites, $\vec{n}_{\alpha}$ is the vector of the site nearest to $\vec{n}$ in $\vec{\alpha}$ direction, $V_{\vec{n}_{\alpha}}^{(m)} = V_m$ is the $m$-th derivative of the pair potential between atoms (ions) $\vec{n}$ and $\vec{n}_{\alpha}$ at their mean distance $R_{0\vec{n}_{\alpha}}$, $\hat{R}_{\vec{n}_{\alpha}} = [(R_{0\vec{n}_{\alpha}} + \hat{r}_{\alpha\vec{n}_{\alpha}})^2 + \hat{r}_{\alpha\vec{n}_{\alpha}}^2 - \hat{r}_{\alpha\vec{n}_{\alpha}}^2_{\vec{n}_{\alpha}}]^{1/2} - R_{0\vec{n}_{\alpha}}$ is the operator of distance between the nearest neighbors in the $\alpha$-direction, $\hat{r}_{\beta\vec{n}_{\alpha}} = q_{\beta\vec{n}} - q_{\beta\vec{n}_{\alpha}}$, $q_{\beta}$ is the $\beta$-component of the displacement vector $\hat{q}_{\vec{n}}$ of the atom $\vec{n}$, $\alpha, \beta = x, y, z$, $\hat{r}_{\vec{n}_{\alpha}}^2 = \hat{r}_{\vec{n}_{\alpha}}^2 + \hat{r}_{\vec{n}_{\alpha}}^2 + \hat{r}_{\vec{n}_{\alpha}}^2$. By expanding $\hat{V}$ in the power series of displacement operators $\hat{r}_{\alpha\vec{n}_{\alpha}}$ one gets

$$\hat{V} = \frac{1}{4} \sum_{\alpha,\vec{n}} \left[ V_2 \hat{r}_{\alpha\vec{n}}^2 + V_2' (\hat{r}_{\alpha\vec{n}}^2 - \hat{r}_{\alpha\vec{n}}^2_{\vec{n}_{\alpha}}) + 1 \right] \frac{V_3 \hat{r}_{\alpha\vec{n}}^3 + V_3' \hat{r}_{\alpha\vec{n}} (\hat{r}_{\alpha\vec{n}}^2 - \hat{r}_{\alpha\vec{n}}^2_{\vec{n}_{\alpha}})}{12} V_4 \hat{r}_{\alpha\vec{n}}^4 +$$
\[ \frac{1}{2} V'_4 \hat{r}^2_{\alpha n} (\hat{r}^2_{\alpha} - \hat{r}^2_{\alpha n}) + \frac{1}{4} V''(\hat{r}^2_{\alpha} - \hat{r}^2_{\alpha n})^2 + \ldots \right], \quad (18) \]

where

\[ V'_2 = V_1 R_0^{-1}, \quad V'_3 = (V_2 - V'_2) R_0^{-1}, \]
\[ V'_4 = R_0^{-1} V_3 - 2 R_0^{-2} (V_2 - V'_2), \quad V''_4 = R_0^{-2} (V_2 - V'_2). \quad (19) \]

\( V_2, V_3 \) and \( V_4 \) make account of the central, while \( V'_2, V'_3, V'_4 \) and \( V''_4 \) of the non-central forces. The potential considered does not take account of the covalent interaction which leads to the chemical bonding. This (covalent) interaction can, however, be easily included in calculations by introducing additional terms of the type \( V_2, V_3 \) and \( V_4 \).

As it is known, harmonic non-central springs \( V'_2 \) are normally 5 to 10 times smaller than the central springs \( V_2 \). Our calculations of \( V_3 \) and \( V'_3 \) for alkali halides show that \( V'_3/V_3 \) is even smaller than \( V'_2/V_2 \) (\( V'_3 \) is twenty-thirty times smaller than \( V_3 \)). The same holds also for quartic and higher order anharmonic terms: the higher order anharmonicity the smaller are corresponding non-central interactions as compared to central ones. Therefore, as a first step, only central forces may be accounted. One can show (see Appendix) that the main effect of the non-central anharmonic interactions to the static local dynamics consists in renormalization of central elastic constants: \( U^2 V_4 \) is replaced by \( U^2 (V_4 + 6 V'_4) \). This allows one to improve the central-force approximation by replacing \( V_4 \) by \( \tilde{V}_4 = V_4 + 6 V'_4 \).

We calculate a strong local vibration of light impurity or host atom (ion) situated at the origin of our reference frame. In this case solutions of classical equations of motion, corresponding to the local mode, satisfy the conditions: \( |A_0| \gg |A_n| \). This allows one to suppose that the mode is well localized on the atom at the site \( n = 0 \). Then in the approximation of central forces 9 coordinates of atoms contribute to perturbation of the dynamical matrix: 3 coordinates of the central atom and 6 directed to this atom coordinates of the nearest neighbor atoms. We chose coordinates according to Fig. 4. In this representation the impurity induced change of the dynamical matrix \( \tilde{V}_2 \) is

\[
V = \begin{pmatrix}
w_x & 0 & 0 \\
0 & w_y & 0 \\
0 & 0 & w_z
\end{pmatrix}, \quad w_\alpha = \begin{pmatrix}
\beta_\alpha & -\gamma_\alpha & -\gamma_\alpha \\
-\gamma_\alpha & \gamma_\alpha & 0 \\
-\gamma_\alpha & 0 & \gamma_\alpha
\end{pmatrix}.
\]
In harmonic approximation $\beta$ and $\gamma$ do not depend on $\alpha$: $\gamma = \Delta V_2$ is the change of the magnitude of the central elastic constants due to defect atom, $\beta = 2\gamma + \omega^2(1 - M/M_0)$, $\omega$ is the frequency of the normal mode, $M/M_0$ is the ratio of impurity and host atom masses. Quartic anharmonicity leads to amplitude dependent corrections of elastic constants and to their dependence of $\alpha$:

$$
\beta_\alpha = \omega^2 \left(1 - \frac{M}{M_0}\right) + 2\gamma_\alpha, \quad \gamma_\alpha = \Delta V_2 + \frac{1}{2} V_4 A^2_\alpha, \quad (20)
$$

$A_\alpha$ is the $\alpha$'s Cartesian component of the amplitude of the local mode. Perturbed Green’s functions are

$$
G = \begin{pmatrix}
G_x & 0 & 0 \\
0 & G_y & 0 \\
0 & 0 & G_z
\end{pmatrix}, \quad G_\alpha = \begin{pmatrix}
G_{\alpha 11} & G_{\alpha 12} & G_{\alpha 12} \\
G_{\alpha 12} & G_{\alpha 22} & 0 \\
G_{\alpha 12} & 0 & G_{\alpha 22}
\end{pmatrix},
$$

where

$$
G_{\alpha n n'} = ([I - G^{(0)}(\omega)]^{-1} G^{(0)})_{n n'},
$$

$$
G^{(0)}_{n n} = \sum_{\nu \vec{k}} \frac{e_{n \nu \vec{k}}^2}{\omega^2 - \omega_{\nu \vec{k}}^2}, \quad G^{(0)}_{12} = \sum_{\nu \vec{k}} \frac{e_{1 \nu \vec{k}} e_{2 \nu \vec{k}} \cos (k_x d)}{\omega^2 - \omega_{\nu \vec{k}}^2}, \quad (21)
$$

are Green’s functions of perfect lattice, $d$ is the lattice constant, $\vec{k}$ is the wave vector of phonon, $\nu$ is the phonon branch, $\omega_{\nu \vec{k}}$ is the frequency of phonon, $e_{n \nu \vec{k}}$ is the projection of the polarization vector of phonon onto $x$-component of the atom. We use for the Green’s functions $G^{(0)}$ their values calculated within shell model\cite{14}.

The frequency of the ALM, which depends on the amplitude of the mode, is given by the position of the pole of the Greens function $G_{\alpha 00}(\omega)$ on the real axis of $\omega$. Energy of the local mode depends on the amplitude via dependence of the $\omega_l$ and directly:

$$
E_l \simeq \frac{1}{2} M \omega_l^2 A_l^2 + \frac{1}{64} \bar{V}_4 (A_x^4 + A_y^4 + A_z^4) \quad (22)
$$

($A_l^2 = A_x^2 + A_y^2 + A_z^2$).

In a perfect lattice the perturbation matrix $\tilde{V} \sim V_4 A^2_\alpha$. This perturbation can lead to appearance of the ALMs. In three dimensional crystals they appear only if the local perturbation is strong enough. This means that there is an minimal (critical) amplitude of the central atom $A_0$ for appearance of an ALM\cite{17}.
We performed calculation of the ALMs and ILMs associated with light $F^-$ and $Na^-$ ions in different alkali halide crystals. Results of some of our calculations are presented on Figs. 3 and 4. One sees that frequency of the ALM of light ion $F^-$ in KCl rather strongly depends on amplitude of the mode and on the crystallographic direction of the vibration. Thereat the smaller is the distance to the nearest neighbor ($nn$) atom in direction of vibration the larger is effect of anharmonicity at the same amplitude. The reason for this correlation is rather obvious: central anharmonic forces, which dominate in the anharmonic repulsive interactions, are stronger for smaller $nn$ distance. One also sees that the ILM on light host ion $Na^+$ in NaI appear already at rather moderate amplitude $\sim 0.4\AA$. Thereat with increasing of amplitude the mode first appear in (100) direction, then in (110) direction and then in (111) direction. The reason for such directional dependence is given above: anharmonic interaction is stronger for smaller $nn$ distance. Note that the decay time of the modes due to two-phonon emission, as it was shown in also strongly depends on the crystallographic direction.

In conclusion, the method of calculation of anharmonic local modes both, ILMs (in pure crystals) and ALMs (in doped crystals) is proposed. The method allows the reduction of the problem of nonlinear local dynamics to the linear inverse problem of phonons scattering on a local potential, caused by the local mode. New analytical description of the even and odd strongly localized ILMs in the monatomic chain is given. Results of numerical calculations of anharmonic local modes of light ions in pure and impure alkali halide crystals are presented. It is found that the ILM on a light host ion appears already at rather moderate amplitude (e.g $\sim 0.4\AA$ in NaI). Both, ILMs and ALMs in alkali-halide crystals strongly depend on the crystallographic direction.

V. ACKNOWLEDGMENT

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A. Appendix: Non-central forces

Although non-central anharmonic interactions are remarkably weaker than central ones their number is larger. Therefore it is of interest to account them. These interactions switch-on into the perturbation $\tilde{V}_2$ all 21 Cartesian coordinates of the central atom and its 6 nearest neighbors. It is convenient to chose these coordinates as follows (see Fig. 1):

$q_1 = x_0, q_2 = y_0, q_3 = z_0, q_4 = x_1, q_5 = y_1, q_6 = z_1, q_7 = x_{-1}, q_8 = y_{-1}, q_9 = z_{-1}, q_{10} = l_1, q_{11} = x_1, q_{12} = z_1, q_{13} = y_{-1}, q_{14} = x_{-1}, q_{15} = z_{-1}, q_{16} = z_1, q_{17} = x_1, q_{18} = y_1, q_{19} = z_{-1}, q_{20} = x_{-1}, q_{21} = y_{-1} ; U = \sqrt{U_x^2 + U_y^2 + U_z^2}$. In this representation the perturbation matrix of lattice dynamics equals

$$V = \begin{pmatrix}
\begin{bmatrix}
\nu_0 & -\tilde{\nu}_1 & -\tilde{\nu}_2 & -\tilde{\nu}_3 \\
\end{bmatrix}

| & | & |
\end{pmatrix},$$

where $\nu_0 = \tilde{\beta} I_3$ is 3 x 3 matrix, $\tilde{\nu}_{i(i',\nu)} = (1,1) \times \nu_{i(i',\nu)}$ are 3 x 6 matrixes, $\tilde{\nu}_1 = I_2 \times \nu_1$ are 6 x 6 matrixes, $I_n$ is nxn-unit matrix, $\gamma$ and $\gamma'$ are changes of central and non-central elastic springs due to the impure central ion, $\tilde{\beta} = \omega^2 (1 - M/M_0) + 2\gamma + 4\gamma'$,

$$\nu_1 = \begin{pmatrix}
\begin{bmatrix}
\gamma & 0 & 0 \\
0 & \gamma' & 0 \\
0 & 0 & \gamma' \\
\end{bmatrix}

| & | & |
\end{pmatrix}, \quad \nu_2 = \begin{pmatrix}
\begin{bmatrix}
0 & \gamma' & 0 \\
\gamma & 0 & 0 \\
0 & 0 & \gamma' \\
\end{bmatrix}

| & | & |
\end{pmatrix}, \quad \nu_3 = \begin{pmatrix}
\begin{bmatrix}
0 & \gamma & 0 \\
0 & 0 & \gamma' \\
\gamma & 0 & 0 \\
\end{bmatrix}

| & | & |
\end{pmatrix}.$$

In harmonic approximation $\nu_1 = \nu_1' = \nu_2''$. Quartic anharmonicity causes amplitude-dependent renormalization of the elastic springs and leads to the following corrections of (additions to) given above matrixes $\nu$:

1. (100)-direction: $\nu_1' = \nu_1'' = \nu_2'$,

$$\nu_0' = \begin{pmatrix}
\begin{bmatrix}
\zeta_1 & 0 & 0 \\
0 & \zeta_2 & 0 \\
0 & 0 & \zeta_2 \\
\end{bmatrix}

| & | & |
\end{pmatrix}, \quad \nu_1' = \begin{pmatrix}
\begin{bmatrix}
\delta_1 & 0 & 0 \\
0 & \delta_2 & 0 \\
0 & 0 & \delta_2 \\
\end{bmatrix}

| & | & |
\end{pmatrix}, \quad \nu_2' = \begin{pmatrix}
\begin{bmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0 \\
\end{bmatrix}

| & | & |
\end{pmatrix}, \quad \nu_3' = \begin{pmatrix}
\begin{bmatrix}
0 & 0 & 0 \\
0 & 0 & \delta_2 \\
0 & \delta_2 & 0 \\
\end{bmatrix}

| & | & |
\end{pmatrix}.$$
where $\delta_1 = U^2(V_4 + 6V_4')/4, \delta_2 = U^2V_4'/4, \zeta_1 = 2\delta_1, \zeta_2 = 4\delta_2$; energy correction equals $E_i' = U^4(V_4 + 6V_4')/64$;

2. (110)-direction: $\nu'_t = \nu'_1$,

$$
\begin{pmatrix}
\xi_1 & \bar{\sigma} & 0 \\
\bar{\sigma} & \xi_1 & 0 \\
0 & 0 & \xi_2
\end{pmatrix}, \quad
\begin{pmatrix}
\sigma_1 & \sigma_2 & 0 \\
\sigma_2 & \sigma_2 & 0 \\
0 & 0 & \sigma_2
\end{pmatrix}, \quad
\begin{pmatrix}
\sigma_2 & \sigma_2 & 0 \\
\sigma_1 & \sigma_2 & \sigma_2 \\
0 & 0 & 0
\end{pmatrix}, \quad
\begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}, \quad
\begin{pmatrix}
\sigma_2 & 0 & 0 \\
\sigma_2 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}, \quad
\begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}, \quad
\begin{pmatrix}
0 & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
$$

where $\sigma_1 = U^2(V_4 + 7V_4')/8, \sigma_2 = U^2V_4'/8, \bar{\sigma} = 4\sigma_2, \xi_1 = 2\sigma_1 + 6\sigma_2, \xi_2 = 6\sigma_2$; energy correction equals $E_i' = U^4(V_4 + 12V_4')/128$;

3. (111)-direction: $\nu'_t = \nu'_{1''} = \nu'_1$,

$$
\begin{pmatrix}
\phi & f & f \\
f & \phi & f \\
f & f & \phi
\end{pmatrix}, \quad
\begin{pmatrix}
\kappa_1 & \kappa_2 & \kappa_2 \\
\kappa_2 & \kappa_3 & 0 \\
\kappa_2 & 0 & \kappa_3
\end{pmatrix}, \quad
\begin{pmatrix}
\kappa_2 & \kappa_3 & 0 \\
\kappa_1 & \kappa_2 & \kappa_2 \\
\kappa_1 & \kappa_2 & \kappa_2
\end{pmatrix}, \quad
\begin{pmatrix}
\kappa_2 & \kappa_3 & 0 \\
\kappa_2 & \kappa_3 & \delta_2 \\
\kappa_1 & \kappa_2 & \kappa_2
\end{pmatrix}
$$

where $\kappa_1 = U^2(V_4 + 8V_4')/12, \kappa_2 = U^2V_4'/6, \kappa_3 = \kappa_2/2, \phi = 2\kappa_1 + 4\kappa_2, f = 8\kappa_3$; energy correction equals $E_i' = U^4(V_4 + 18V_4')/192$.

Corrections $\sim V_4''$ are neglected; they are at least one order of magnitude smaller than smallest accounted correction $\sim V_4'$. As one sees the main effect of the non-central anharmonic interactions to the local dynamics consists in renormalization of central elastic constants: $A^2V_4$ is replaced by $A^2(V_4 + 6V_4')$. 
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Figure captions

Figure 1. $\beta$ (solid lines) and $A_l$ (dot-dashed lines) vs. $\omega_l$ for even and odd modes. We used for calculations $\omega_M = 1$ and $V^{(4)}/M_0 = 1$.

Figure 2. Atomic displacements, which contribute to the perturbation of the dynamical matrix: a) account of central forces – 9 displacements; b) account of central and noncentral forces – 21 displacements.

Figure 3. Frequency of the localized mode ($w_l/w_m$) vs. amplitude (in Å). $KCl : F$, [100] – solid line, [110] – dashed line, [111] – dot-dashed line.

Figure 4. Frequency of the localized mode ($w_l/w_m$) vs. amplitude (in Å). $NaI$, [100] – solid line, [110] – dashed line, [111] – dot-dashed line.
KCl:F

\[ \omega_L \] vs Amplitude
