

Nonperturbative anharmonic phenomena in crystal lattice dynamics

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Abstract. Slow dynamics of energy transfer between different phonon modes under the resonance conditions is considered. It may result in new effects in the inelastic and quasielastic neutron scattering spectra.

INTRODUCTION

Crystal lattice dynamics [1, 2] is a prototype theory for many-body physics as a whole. In this case all principal approximations and concepts can be justified accurately on the basis of adiabatic (Born-Oppenheimer) approximation of quantum mechanics. Due to the smallness of typical atomic displacements in crystals \bar{u} in comparison with interatomic distances d one can pass rigorously from a problem of strongly interacting *particles* (atoms, ions, or molecules) to a problem of *weakly* interacting *quasiparticles* (phonons). In the leading order in the smallness parameter $\eta = \bar{u}/d$ the crystal lattice dynamics and thermodynamics can be described in terms of an *ideal* phonon gas (harmonic approximation) [1, 2]. With the temperature T increase the parameter η increases as well, however, due to a semiempirical Lindemann criterion (see, e.g., [2, 3] and Refs. therein) $\eta \simeq 0.1$ at the melting point $T = T_m$ so higher-order (*anharmonic*) contributions to thermodynamic properties are usually small up to the melting temperature [4, 5]. This statement is true for the most of *average* characteristics. At the same time, for some *peculiar* modes anharmonicity can be crucially strong, especially in the vicinity of some structural transformations (see, e.g., computational results for Ba [6] and Zr [7, 8], as well as inelastic neutron scattering data for A15 structure compounds [9] and for high-temperature bcc phases of Ti, Zr, and Hf [10]). For these cases a standard phonon picture is not adequate, for instance, additional non-phonon peaks in the dynamical structural factor may appear [11]. A “slow” (low-frequency) lattice dynamics in the form of a “central peak” in quasielastic neutron scattering is also typical for these strongly anharmonic modes [9, 12, 13].

Phonon picture can be broken for these modes since the corresponding effective potential $V(u)$ turns out to

be essentially nonparabolic [6, 7, 11, 13, 14]. In the vicinity of structural phase transitions (e.g., ferroelectric transitions [13] or martensitic transformations in metals [6, 14]) this potential normally has several minima corresponding to several competing phases, the height of the barrier being much smaller than a typical cohesion energy. It is not surprising that the harmonic approximation is an extremely poor starting point to describe this situation. Here we discuss the following issue: is the phonon picture always adequate in a *generic* case when $\eta \ll 1$ for all phonon modes? To answer this question it is instructive to consider a crystal from the point of view of a contemporary theory of dynamic systems rather than from that of statistical thermodynamics [14]. According to the KAM (Kolmogorov-Arnold-Moser) theory [15] a system of noninteracting oscillators (that is, an ideal phonon gas) is stable with respect to small interphonon interactions (anharmonicity) except the cases of the resonance where the ratio of phonon frequencies is close to the ratio of small enough integer numbers. One can expect that this exceptional case is a situation where even small anharmonicities can lead to essentially nonperturbative effects in the lattice dynamics [14, 16, 17].

RESONANCE PHENOMENA IN PHONON SUBSYSTEM

The well-known Fermi resonance in the Raman molecular spectra under the conditions of integer ratio of phonon frequencies [18, 2] is a prototype example of these nonperturbative resonance phenomena. It was first discovered for CO₂ molecule where the ratio of two molecular vibration frequencies ω_1 and ω_2 is close, by accident, to 1:2. This leads to a quasidegeneracy of the states with energies $\hbar\omega_1$ and $2\hbar\omega_2$. As a result the first harmonic of

the first mode is strongly coupled with the second harmonic of the second mode which leads to the violation of symmetry-induced selection rules and appearance of additional lines in the Raman spectra. Fermi resonance is typical for many organic compounds, especially containing CH group, and is well investigated by molecular spectroscopists [19]. The theory of the Fermi resonance is rather simple since the ultraquantum limit $T \ll \hbar\bar{\omega}$ (where $\bar{\omega}$ is a mean phonon frequency) is typical for all these cases and therefore there are only few states which are involved in the resonance.

When we consider Fermi-resonance-like phenomena for crystals we immediately face several difficulties which make the problem much less trivial [14, 16, 17]. First, the classical limit $T > \hbar\bar{\omega}$ is interesting now and it turns out to be much more complicated than the ultraquantum one since here we have an infinite number of relevant states. Second, now we have to satisfy the resonance conditions not only for the frequencies but also for the phonon wave vectors \mathbf{q} . Then, there is a continuum of nonresonant phonons which is nevertheless also important working as a thermal bath and leading to the phonon damping and ‘‘Brownian motion’’ fluctuations. The most important point is the occurrence of essentially new phenomenon in the classical case, namely, a low-frequency dynamics due to energy transfer between the modes participating in the resonance; this effect is exponentially small at low temperatures (ultraquantum regime) when the corresponding modes are not excited. This ‘‘slow’’ dynamics corresponds to transitions between the states split by the anharmonic interaction under the Fermi resonance conditions. In this sense it relates to the Fermi resonance like the electron paramagnetic resonance relates to the Zeeman effect. Experimentally it may result in the appearance of low-energy peaks in the quasielastic neutron scattering spectra [14, 16, 17].

These new phenomena result from a correlated character of atomic displacements corresponding to different phonon branches under the Fermi resonance conditions. In a generic case the smallness of adiabatic parameter justifies the applicability of the perturbation theory for the consideration of anharmonic effects [20, 2]. From the technical point of view, it means the decoupling of the higher-order phonon correlators according to the Wick’s theorem, or, in classical terms, we suppose that the initial phases of the interacting phonons are random. This is a standard approximation which is used to calculate the temperature dependence of phonon frequencies and dampings [21, 22, 23]. However, when the phonon frequency ratio turns out to be integer (and provided that some symmetry conditions are satisfied) a well-known nonlinear effect, the ‘‘phase locking’’, appears [24] and the perturbation theory fails. In particular, it leads to an essential enhancement of multiphonon contributions to the dynamical structure factor in comparison with the

perturbative treatment, and to the appearance of quasistatic atomic displacements. This is a consequence of subtle phase coherence phenomena which are completely ignored by a standard perturbative treatment. The situation is similar to the Anderson localization in disordered systems which also cannot be described by any consideration of the *average* Green function [25].

To illustrate general mechanisms consider first the simplest case of the resonance, namely, phonons with the wave vector $\mathbf{q}_0 = (\frac{2}{3}, \frac{2}{3}, \frac{2}{3})$ and the frequency ratio 1:2 [16, 17]. It corresponds to BCC phases of alkali and alkaline earth metals (for instance, for potassium the frequencies of longitudinal and transverse phonons in this point at $T = 4.2K$ are 0.27 ± 0.01 and 0.55 ± 0.01 of ionic plasma frequency, respectively). Transverse phonons are double degenerate, however, microscopic estimations of the corresponding anharmonic coupling constants [16] show that only one transverse branch participates in the resonance since the coupling constant for another one is four orders of magnitude smaller. So we can consider a simplified model with the interaction of one longitudinal branch (with the displacement field $u(\mathbf{r}, t)$) and one transverse one (with the displacement field $v(\mathbf{r}, t)$). Taking into account only resonant interaction term $V = \lambda \int d\mathbf{r} uv^2$ one can write a set of equations of motion,

$$\begin{cases} \ddot{u} + \omega^2(-i\nabla)u + 2\gamma(-i\nabla)u + \lambda v^2 = 0 \\ \ddot{v} + \Omega^2(-i\nabla)v + 2\Gamma(-i\nabla)v + 2\lambda uv = 0 \end{cases} \quad (1)$$

where γ, Γ are corresponding phonon damping parameters. We try the solutions of Eq.(1) in the form

$$\begin{cases} u = A(\mathbf{r}, t) \exp i[\mathbf{q}_0\mathbf{r} - \omega(\mathbf{q}_0)t] + \\ B(\mathbf{r}, t) \exp i[\mathbf{q}_0\mathbf{r} + \omega(\mathbf{q}_0)t] + c.c. \\ v = C(\mathbf{r}, t) \exp i[\mathbf{q}_0\mathbf{r} + \omega(\mathbf{q}_0)t/2] + \\ D(\mathbf{r}, t) \exp i[\mathbf{q}_0\mathbf{r} - \omega(\mathbf{q}_0)t/2] + c.c. \end{cases} \quad (2)$$

Amplitudes A, B, C, D are slowly varying in space and time functions. It is important that the wave vector \mathbf{q}_0 is equivalent to $-2\mathbf{q}_0$ since $\exp(3i\mathbf{q}_0\mathbf{r}) = 1$ for the crystal lattice sites. Substituting Eq.(2) into Eq.(1), taking into account only resonant terms and only leading approximations in the anharmonic smallness parameter (for more details, see Ref. [17])

$$\begin{cases} \frac{\partial A}{\partial t} + \left(\frac{\partial \omega}{\partial \mathbf{q}}\right)_0 \nabla A - \frac{i}{4\omega_0} \left(\frac{\partial^2 \omega^2}{\partial q_\alpha \partial q_\beta}\right) \frac{\partial^2 A}{\partial x_\alpha \partial x_\beta} \\ + \gamma_0 A + i\Lambda C^{*2} = 0 \\ \frac{\partial C}{\partial t} - \frac{1}{2} \left(\frac{\partial \omega}{\partial \mathbf{q}}\right)_0 \nabla C + \frac{i}{8\omega_0} \left(\frac{\partial^2 \omega^2}{\partial q_\alpha \partial q_\beta}\right)_0 \frac{\partial^2 C}{\partial x_\alpha \partial x_\beta} \\ + \left(\Gamma_0 + \frac{i\nu_0}{2}\right) C - 4i\Lambda A^* C^* = 0 \end{cases} \quad (3)$$

where $\omega = 2\Omega + \nu$ ($\nu \ll \omega$), $\Lambda = \lambda/2\omega_0$ and subscript ‘‘0’’ means $\mathbf{q} = \mathbf{q}_0$. Equations for B and D differ from Eq.(3) by the replacement $v \rightarrow -v, \Lambda \rightarrow -\Lambda$.

One can demonstrate [17] that at small enough ν (realistic estimations for alkali metals show that ‘‘small’’

means 5-7% of ω) purely sine waves $A, B, C, D = \text{const}$ turn out to be unstable with respect to a self-modulation and the solitons of the envelopes can form. This modulation is connected with a slow (in comparison with a characteristic phonon times) dynamics of energy transfer between longitudinal and transverse phonons. Numerical simulations of the thermal noise effects [26, 27] show that the latter do not suppress this slow dynamics. It appeared that there are *two* limit circles in this system (which correspond to two phase locking regimes with different relative phases for A and C waves) and this energy transfer dynamics can be described as a stochastic resonance between these two limit circles [27].

Similar phenomena can be also considered for acoustic (long-wavelength) phonons as an energy transfer between two ultrasound waves with different polarization vectors and integer ratio of sound velocities [28]. Alkali metals near the melting point (1:3 ratio for different transverse sound waves propagating into $\langle 110 \rangle$ direction) or $\text{W}_{1-x}\text{Re}_x$, $\text{Mo}_{1-x}\text{Re}_x$ alloys (1:1 ratio for the same sound waves) might be an interesting examples. Computer simulations [28] demonstrate that, depending on the initial phases of the waves, this energy transfer may be both chaotic and quasiperiodic. It would be interesting to check this prediction experimentally.

It is worthwhile to note that for the case of 1:2 frequency ratio considered above the resonance conditions for phonon wave vectors can be satisfied only in some peculiar points of the Brillouin zone. For the case of 1:3 resonance they can be satisfied in a generic case; for high-symmetry directions the number of waves participating in the resonance coupling can be very large. FCC La is an interesting example of such resonance (below we follow our work [29]). The lattice dynamics of FCC La is characterized by a drastic nonmonotonicity of the dispersion curves $\omega(\mathbf{q})$ for transverse phonons in $\mathbf{q} \parallel \langle 111 \rangle$ direction and by a significant temperature dependence of their frequencies, i.e. by strong anharmonic interactions [30]. As it was discussed in Ref. [30] this behavior can be accounted for by the electron-phonon interaction (Kohn anomalies). One can see from these experimental data that the ratio of longitudinal to transverse phonon frequencies in $\langle 111 \rangle$ direction varies around the integer ratio $\frac{\omega_2(\mathbf{q}_0)}{\omega_1(\mathbf{q}_0)} = 3$, the value of wave vector \mathbf{q}_0 varying with the temperature within sufficiently wide limits. This makes it possible to shift the resonance watching simultaneously the change in the lattice dynamics behavior.

Let us set up the simplest model to describe the resonance effects under consideration in the lattice dynamics of FCC La. We shall proceed with the equations of motion for the amplitudes of longitudinal (u) and transverse (v) phonons allowing only for the ‘‘resonance’’ anharmonic interaction $V = \lambda \int d\mathbf{r} u v^3$:

$$\begin{cases} \ddot{u} + \omega^2 u + \lambda v^3 = 0 \\ \ddot{v} + \Omega^2 v + 3\lambda u v^2 = 0 \end{cases} \quad (4)$$

Because of the FCC lattice symmetry we should consider phonons propagating in four equivalent directions $\langle 111 \rangle, \langle 1\bar{1}\bar{1} \rangle, \langle \bar{1}1\bar{1} \rangle, \langle \bar{1}\bar{1}1 \rangle$; the relevant wave vectors meeting condition $\omega(\mathbf{q}) = 3\Omega(\mathbf{q})$ will be denoted as \mathbf{q}_j ($j = 0, 1, 2, 3$). Similarly to Ref. [17] we try the solutions of the equations (4) as

$$\begin{cases} u = \sum_{j=0}^3 (A_j \exp i(\mathbf{q}_j \mathbf{r} - \omega t) + B_j \exp i(\mathbf{q}_j \mathbf{r} + \omega t)) + c.c. \\ v = \sum_{j=0}^3 (C_j \exp i(\mathbf{q}_j \mathbf{r} - \Omega t) + D_j \exp i(\mathbf{q}_j \mathbf{r} + \Omega t)) + c.c. \end{cases} \quad (5)$$

where A_j, B_j, C_j, D_j are slowly varying (due to λ smallness) functions of \mathbf{r} and t , i.e. the envelopes of the phonons under consideration. Substituting Eqs. (5) into Eqs. (4) and neglecting the second time derivatives of the envelopes as well as the nonresonance terms we obtain the following set of equations

$$\begin{cases} \dot{A}_0 + i\Lambda(6D_1^* D_2^* D_3^* + 3C_0^2 D_0^* + 6C_0 \sum_{j=1}^3 C_j D_j^*) = 0 \\ \dot{B}_0 - i\Lambda(6C_1^* C_2^* C_3^* + 3D_0^2 C_0^* + 6D_0 \sum_{j=1}^3 D_j C_j^*) = 0 \\ \dot{C}_0 + 9i\Lambda(2B_1^* C_2^* C_3^* + 2B_2^* C_1^* C_3^* + 2B_3^* C_1^* C_2^* + \\ 2A_0 \sum_{j=0}^3 C_j^* D_j + 2D_0 \sum_{j=1}^3 A_j C_j^* + \\ D_0^2 B_0^* + 2D_0 \sum_{j=1}^3 D_j B_j^*) = 0 \\ \dot{D}_0 - 9i\Lambda(2A_1^* D_2^* D_3^* + 2A_2^* D_1^* D_3^* + 2A_3^* D_1^* D_2^* + \\ 2B_0 \sum_{j=0}^3 D_j^* C_j + 2C_0 \sum_{j=1}^3 B_j D_j^* + \\ C_0^2 A_0^* + 2C_0 \sum_{j=1}^3 C_j A_j^*) = 0; \end{cases} \quad (6)$$

the rest twelve equations are obtained from (6) by cyclic permutations of the indices. Here $\Lambda = \frac{\lambda}{2\omega}$.

The dynamics of the energy transfer in this system has been investigated in Ref. [29] by numerical simulations. It was shown that depending on the initial phases of the involved phonons this energy transfer can be either regular or chaotic. One can expect from the dimension considerations that a typical frequency of this slow dynamics will be of order of

$$\omega^* \simeq \bar{\omega} \left(\frac{\bar{u}^2}{a^2} \right) \frac{\lambda}{M \bar{\omega}^2 a^6}, \quad (7)$$

Here M is the ion mass, a is the lattice constant, \bar{u}^2 is the average square of atomic displacements. For the room temperature $\omega^* \approx 10^{-3} \bar{\omega}$ can be taken for the estimation. However, it was shown that in reality it is much larger,

$\Delta\omega \simeq 10^2\omega^*$, due to a large number of interacting waves (32 real fields).

Similarly to Ref. [17] (see also above) it can be shown that the account for intermode or non-resonant intramode anharmonicities may result in the appearance of the peaks in quasielastic neutron scattering spectra with a frequency width about $\Delta\omega$. The largest contributions result from the lowest-order (three-phonon) anharmonic processes. For example, the term $V = \mu \int d\mathbf{r}v^3$ in the potential energy leads to the appearance of the “low-frequency” contribution to the transverse phonon field, $\delta v = -3\mu v^2/\Omega^2$. Assuming all the amplitudes A_j and C_j in the equation (5) to be constant we would obtain static contributions to v with the wave vectors $\mathbf{Q}_a = \mathbf{q}_i \pm \mathbf{q}_j + \mathbf{g}$ where \mathbf{g} is a reciprocal lattice vector (which can be, in particular, equal to zero). One can expect therefore the peaks in the quasielastic neutron scattering spectra near the wavevectors \mathbf{Q}_a which reflect the dynamics of the envelopes. In a special case considered above for the frequency ratio 2:1 one of these vectors coincides with the vector \mathbf{q}_i but for the ratio 3:1 it is impossible. The vectors \mathbf{Q}_a for $i = j$ are just the reciprocal lattice vectors but the rest of them should be temperature dependent due to the temperature dependence of the phonon frequencies shifting the Fermi resonance point. It can be important for the experimental verification of the effects under consideration. A similar contribution of order of u^2 appears in the longitudinal phonon field because of the potential energy term $V = v \int d\mathbf{r}u^3$.

CONCLUSIONS

To conclude, we predict a new class of nonperturbative anharmonic phenomena in lattice dynamics under resonance conditions in the phonon system. This resonance results in the instability of phonons and complicated picture of energy transfer between the modes in the resonance. It can be experimentally investigated by inelastic and quasielastic neutron scattering as well as by acoustic methods. There is an interesting open issue what is the role of these phenomena in the development of lattice instabilities of the crystals, in particular, in the melting [14]. This question is motivated by two general remarks: (i) anharmonic effects in a generic case are small up to the melting point and (ii) instability of a generic weakly anharmonic dynamical system, according to the KAM theory, is connected with the resonances. Therefore it might appear that the phenomenon under consideration is not a kind of exotic but important for any crystal.

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