PHYSICAL REVIEW B VOLUME 43, NUMBER 3 15 JANUARY 1991-II

Intrinsic localized modes in a monatomic lattice with weakly anharmonic nearest-neighbor force constants

S. R. Bickham and A. J. Sievers
Laboratory of Atomic and Solid State Physics and Materials Science Center, Cornell University, Ithaca, New York 14853-2501

(Received 7 March 1990)

The frequencies of anharmonic local modes in one-, two-, and three-dimensional lattices have been obtained analytically by combining the rotating-wave approximation with some of the formalism used previously to characterize defect modes in harmonic crystals. For weak anharmonicity these modes become delocalized, while they take on the vibrational pattern of a small molecule when the anharmonicity becomes large. The first-order corrections to the rotating-wave approximation are found to be small for any anharmonicity parameter, verifying that this approximate method of analysis can be used to separate the equations of motion. This identification of the weak-anharmonicity limit permits us for the first time to address the question of the existence of anharmonic local modes in real crystals. With anharmonic parameters similar to those found in alkali-metal halide crystals, the energy needed to produce these modes in all three dimensions is estimated. We find that thermal motion alone does not provide enough amplitude to support these modes in a lattice with the anharmonicity of pure LiF. On the other hand, at some defect sites the requirements could be less severe, and anharmonic modes might be generated by a nonthermal process such as an optical excitation of the *F* center, which introduces an energy equivalent of ~40-Debye phonons into the lattice. The large anharmonicities found in solid He and near ferroelectric systems should provide more friendly environments for these modes.

I. INTRODUCTION

The possibility of intrinsic localized modes in pure anharmonic crystals for sufficiently strong quartic anharmonicity[1-3] has been confirmed by numerical simulation studies[4,5] in one and two dimensions. In some ways the results are reminiscent of the defect-induced local modes. For example, simulations for a one-dimensional (1D) diatomic anharmonic lattice show that intrinsic local modes appear both in the gap between the optic and acoustic plane-wave spectrum as well as above the optic branch,[5] similar to the spectrum generated by a point defect in a harmonic diatomic lattice.[6] Although the original analytical study[1] focused on the odd-parity vibrational mode, which in one dimension has essentially the amplitude pattern of a simple triatomic molecule, both the simulations[4,5] and the recent analytical work by Page[7] have shown that an unusual even-parity mode with the vibrational pattern of a diatomic molecule also exists. So far all efforts have been directed at characterizing and understanding the large-anharmonicity regime.

Here we study analytically an experimentally relevant problem: the influence of hard but *small* quartic anharmonicity on the vibrational spectrum of a monatomic lattice with nearest-neighbor force constants.[8] We find that both odd and even localized modes are possible for all values of the anharmonicity parameter, but the odd mode is determined to be the fundamental intrinsic localized excitation. With a first-order correction to the rotating-wave approximation, we also demonstrate that the frequency of the odd mode at ω_L as a function of the anharmonicity parameter is red-shifted by a few percent due to the presence of a higher-frequency local mode at $3\omega_L$. In all cases the amplitude at $3\omega_L$ is a small fraction of the amplitude at ω_L so that the response from still-higher-frequency components at $5\omega_L$, etc., can be ignored. Finally, we demonstrate that in larger dimensional lattices it becomes increasingly difficult to produce an intrinsic localized mode with realistic anharmonic parameters, such as those for the alkali-metal halide crystals. For example, with parameters appropriate to LiF, we find that, within the framework of our model, sufficient thermal motion does not exist to support these modes even near the melting point; however, the vibrational amplitude in the *F*-center excited state is found to be the right order of magnitude to produce such modes in one and two dimensions but is only marginal in three. The general conclusion is that solids with larger anharmonicity should be examined to search for these new localized modes.

In the next section, general approximate analytical expressions are found for the odd and even local-mode frequency and range in the lattice for one dimension and then the results are extended to higher dimensions. The section ends with a derivation of the small red shift for the odd local mode produced by higher harmonics of the local mode. In Sec. III the dependence of the square of the local-mode frequency on anharmonicity parameter is determined in all three dimensions: the dependence is quadratic for small values and linear for large ones. Next the connection between the size of the quartic potential and existence of the modes is examined in some detail.

Both thermal and nonthermal processes are considered. The findings are summarized in Sec. IV.

II. DERIVATION OF LOCAL-MODE FREQUENCIES

An analogy has already been made between the eigenvectors of defect harmonic local modes and intrinsic anharmonic local modes.[1-3] To bring out the similarities and differences in a direct manner, we demonstrate here that the frequency of an intrinsic odd-symmetry anharmonic local mode can be obtained to a good approximation by combining the rotating-wave approximation to linearize the nonlinear equations of motion and then apply essentially the same formalism that, in the past, has been used to characterize defect modes in harmonic lattices.[9] We use a monatomic lattice (N atoms) with only nearest-neighbor harmonic and anharmonic (quartic) force constants that have equal transverse and longitudinal components to identify, in the simplest manner, the dependence of the local-mode frequency on anharmonicity in one, two, and three dimensions. The resulting separable potential energy for the three-dimensional system is

$$U=\sum_{\sigma}\sum_{l,n,m}\left\{\frac{K_2}{2}[(u^{\sigma}_{l,m,n}-u^{\sigma}_{l+1,m,n})^2+(u^{\sigma}_{l,m,n}-u^{\sigma}_{l,m+1,n})^2+(u^{\sigma}_{l,m,n}-u^{\sigma}_{l,m,n+1})^2]\right.$$
$$\left.+\frac{K_4}{4}[(u^{\sigma}_{l,m,n}-u^{\sigma}_{l+1,m,n})^4+(u^{\sigma}_{l,m,n}-u^{\sigma}_{l,m+1,n})^4+(u^{\sigma}_{l,m,n}-u^{\sigma}_{l,m,n+1})^4]\right\}\;, \tag{1}$$

where K_2 and K_4 are the harmonic and quartic potential constants, respectively, and $u^{\sigma}_{l,m,n}$ identifies the σth component of the displacement at site (l,m,n).

The key idea that allows one to separate the coupled harmonic problem into orthogonal homogeneous and inhomogeneous wave solutions makes use of the very different amplitudes of excursion in each kind of mode. For a plane-wave mode the excursion of each atom is $\sim O(N^{-1/2})$, with N a large number, whereas the excursion of an atom for a localized mode is $\sim O(1)$, with $N\sim 1$. In the former case the homogeneous plane-wave solutions can be obtained by ignoring the K_4 potential term in Eq. (1) so that the dispersion relation simplifies to the standard one,

$$M\omega^2=2K_2\sum_{\sigma}[1-\cos(q_{\sigma}a)] \tag{2}$$

with real wave-vector components, q_{σ}.

When an anharmonic local mode exists, the full potential given by Eq. (1) must be employed. However, far from the local-mode site, the excursion in that particular mode is again small, so in this region of the crystal the quartic term can be neglected when determining the asymptotic properties of the solution. An inhomogeneous wave solution is characterized by a complex wave vector with components

$$q^{*}_{\sigma}=q_{\sigma}\pm iq'_{\sigma}=(2j_{\sigma}+1)\pi/a\pm iq'_{\sigma}\;, \tag{3}$$

where j_{σ} is an integer and the sign of the second term on the right is chosen so that the solution decays with increasing distance from the local-mode center. The form of the first term on the right comes from the requirement that the inhomogeneous wave solution has a frequency larger than the maximum plane-wave value $\omega_m^2=4dK_2/M$, where d is the dimension of the lattice.[9] In general, new frequencies appear for complex wave vectors, but the most confined modes, those localized in d dimensions in this cubic system ($q'_x=q'_y=q'_z=q'$), satisfy the equation

$$\left[\frac{\omega}{\omega_m}\right]^2=\tfrac{1}{2}[1+\cosh(q'a)] \tag{4}$$

independent of dimension. We assume that far from the mode center all anharmonic localized modes must obey this expression.[9] Because of the inversion symmetry of the problem, the modes can be classified, in the electric-dipole sense, as either odd ($u^{\sigma}_{l,m,n}=u^{\sigma}_{-l,-m,-m}$; $u^{\sigma}_{0,0,0}=\alpha$) or even ($u^{\sigma}_{l,m,n}=-u^{\sigma}_{-l,-m,-n}$;$u^{\sigma}_{0,0,0}=0$).

A. Odd-symmetry local mode in one dimension

To identify q' in Eq. (4) for the one-dimensional case, we must introduce the equations of motion for the central atom and its neighbors. Although we are only interested in presenting enough constraints to specify the mode, namely the $n=0$ and $n=1$ equations of motion, there is some value in temporarily retaining the index n. The acceleration equation becomes

$$M\frac{d^2u_n}{dt^2}=-K_2(2u_n-u_{n-1}-u_{n+1})$$
$$-K_4[(u_n-u_{n-1})^3+(u_n-u_{n+1})^3]\;. \tag{5}$$

To eliminate the time dependence, we introduce the rotating-wave approximation

$$u_n=\xi_n\cos(\omega_0 t)\;; \tag{6}$$

set $\omega_m^2=4K_2/M$ and the lattice constant $a=1$ to obtain

$$\left[\frac{\omega_0}{\omega_m}\right]^2\xi_n=\tfrac{1}{4}(2\xi_n-\xi_{n-1}-\xi_{n+1})$$
$$+\frac{3K_4}{16K_2}[(\xi_n-\xi_{n-1})^3+(\xi_n-\xi_{n+1})^3]\;. \tag{7}$$

For the conditions $\xi_0=\alpha,\xi_n=\xi_{-n},\xi_n=\alpha A(-1)^n e^{-nq'}$ for $n>0$, and with the anharmonicity parameter $\Lambda\equiv K_4\alpha^2/K_2$, Eq. (7) becomes

$$\left[\frac{\omega_0}{\omega_m}\right]^2=\tfrac{1}{2}(1+Ae^{-q'})+\frac{3\Lambda}{8}(1+Ae^{-q'})^3 \tag{8}$$

for the central atom ($n=0$) and

$$\left[\frac{\omega_0}{\omega_m}\right]^2 Ae^{-q'}=\tfrac{1}{4}(2Ae^{-q'}+1+Ae^{-2q'})+\frac{3\Lambda}{16}[(Ae^{-q'}+1)^3+A^3e^{-3q'}(1+e^{-q'})^3] \tag{9}$$

for the nearest neighbor ($n=1$). Note that $Ae^{-q'}$ is the amplitude of the nearest-neighbor atom with respect to the center atom in this odd mode, and the amplitude α of the center atom is defined by the particular excitation experiment. We anticipate that this grafting together of the close-in eigenvector of the anharmonic localized mode with the farther out inhomogeneous wave appropriate to a harmonic localized mode should provide a good description both for strong and weak anharmonicity but would be a less valid approximation for intermediate values.

The three equations can be simplified by introducing the definitions

$$\kappa=e^{-q'} \text{ and } \Delta-1=Ae^{-q'}=A\kappa\ . \tag{10}$$

Equation (4) then becomes

$$\left[\frac{\omega_0}{\omega_m}\right]^2=\frac{(1+\kappa)^2}{4\kappa}\ , \tag{11}$$

Eq. (8) becomes

$$\left[\frac{\omega_0}{\omega_m}\right]^2=\frac{\Delta}{2}\left[1+\frac{3\Lambda\Delta^2}{4}\right]\ , \tag{12}$$

and Eq. (9) becomes

$$\left[\frac{\omega_0}{\omega_m}\right]^2=\frac{1}{4(\Delta-1)}\left[\Delta+(\Delta-1)(1+\kappa)+\frac{3\Lambda}{4}[\Delta^3+(\Delta-1)^3(1+\kappa)^3]\right]\ . \tag{13}$$

Hence for a given Λ, Eqs. (11)–(13) can be solved simultaneously for κ, Δ, and $(\omega_0/\omega_m)^2$. A complete discussion of this solution is deferred to Sec. III A.

B. Even local mode in one dimension

An analysis similar to that given above can be carried out for the even-mode case where $u_n^\sigma=-u_{-n}^\sigma$; $u_0^\sigma=0$ and although solutions are found, computer simulations[10] show that such even modes are in fact unstable. This even mode breaks up into pairs of odd modes that are then repelled from each other.[11] These modes will not be considered here.

Earlier simulations[5] and analytical work[7] have demonstrated the stability of another type of localized vibration which is symmetric about the point halfway between two adjacent sites. This even-symmetry mode has the displacement pattern $u_n^\sigma=u_{-n}^\sigma$ where $n>0$. The odd-symmetry case ($u_n^\sigma=u_{-n}^\sigma$) is uninteresting because there is no relative displacement of the center two atoms. In the strongly localized limit, the even mode corresponds to the stretch-mode vibration of a diatomic molecule with the next neighbors also having some small amplitude. Here we find the necessary conditions for this type of even mode, the analog of a force constant defect mode.[12]

Following the notation used in the preceding section, the atom amplitudes of the even mode are labeled $\xi_{\pm n}$, where $n>0$, and the displacement pattern satisfies $\xi_{-n}=-\xi_n$. With $\xi_1=\alpha$ and $\xi_n=\alpha A(-1)^{n-1}e^{-(n-1)q'}$ for $n>1$, the condition for the $n=1$ atom becomes

$$\left[\frac{\omega_0}{\omega_m}\right]^2=\tfrac{1}{4}(2+\Delta)+\frac{3\Lambda}{16}(8+\Delta^3)\ . \tag{14}$$

For the $n=2$ atom, the condition reduces to Eq. (13) given above, since its nearest neighbors have the same amplitude pattern. The far-field condition, Eq. (4) [or (11)] remains unchanged for these modes. Again a discussion of the solution is deferred to Sec. III A.

C. Odd and even modes in higher dimensions

Because of the simplicity of the potential given by Eq. (1), higher-dimensional cases can be treated in the same way as for the one-dimensional case, but with the one added feature that more neighbors must be counted in the mode. As we shall demonstrate in Sec. III B, the increased number of neighbors with increased dimension plays an important role in defining the minimum anharmonicity value consistent with anharmonic local-mode production.

For small values of the anharmonicity parameter Λ, approximate analytic expressions can be found for the local-mode frequency for both the odd- and even-mode cases. We summarize the results below. Let d identify the dimension of the lattice. Then for the odd-mode case

$$\left[\frac{\omega_0}{\omega_m}\right]^2=1+\frac{9(1+2d)^2\Lambda^2}{[(2d-2)(\sqrt{2}-1)+1]^2} \tag{15}$$

and the nearest-neighbor amplitude relative to the amplitude of the central atom, $|\xi_1/\xi_0|=1-6\Lambda$, independent of dimension. For the even mode we find

TABLE I. Local-mode parameters in the weak-anharmonicity limit. For the odd mode $|\xi_1/\xi_0|=\Delta-1=Ae^{-q'}$, which is called NN here, while for the even mode this quantity is equal to $|\xi_2/\xi_1|$. The local-mode frequency dependence for small Λ is $(\omega_0/\omega_m)^2=1+(C\Lambda)^2$.

Symmetry	Dimension	NN	C
odd	1	1-6Λ	9
odd	2	1-6Λ	8.20
odd	3	1-6Λ	7.91
even	1	1-12Λ	12
even	2	1-24Λ/3	8.75
even	3	1-36Λ/5	8.13

TABLE II. Local-mode parameters in the strong-anharmonicity limit. For the odd mode $|\xi_1/\xi_0| = \Delta - 1 = Ae^{-q'}$, which is called NN here, while for the even mode this quantity is equal to $|\xi_2/\xi_1|$. The limiting slope $=(\omega_0/\omega_m)^2/\Lambda$. As $d \rightarrow \infty$, all slopes $\rightarrow 0.375$.

Symmetry	Dimension	NN	Slope
odd	1	0.520	1.317
odd	2	0.256	0.744
odd	3	0.169	0.599
even	1	0.166	1.797
even	2	0.114	1.139
even	2	0.090	0.904

$$\left[\frac{\omega_0}{\omega_m}\right]^2 = 1 + \frac{144 d^4 \Lambda^2}{(2d-1)^2[(2d-2)(\sqrt{2}-1)+1]^2} \tag{16}$$

and the relative amplitude $|\xi_2/\xi_1| = 1 - (12\Lambda d)/(2d-1)$. Note that as $d \rightarrow \infty$, Eqs. (15) and (16) become degenerate, reducing to

$$\left[\frac{\omega_0}{\omega_m}\right]^2 = 1 + \frac{9\Lambda^2}{(\sqrt{2}-1)^2} \tag{17}$$

with the relative amplitude in both the odd and even modes becoming the same, namely $1-6\Lambda$. The appropriate numerical coefficient for one, two, and three dimensions are given in Table I.

For the large Λ limit the analytic expression for relative displacement of the nearest neighbor $(\Delta-1)$ of the odd mode in dimension d is

$$2d(\Delta-1)\Delta^3 = \Delta^3 + (2d-1)(\Delta-1)^3 \ . \tag{18}$$

The solution is inserted into Eq. (12) to obtain a linear relation between $(\omega_0/\omega_m)^2$ and Λ. For the even mode where $|\xi_2/\xi_1| = (\Delta-1)$, the corresponding equation for the relative displacement is

$$(\Delta-1)[8+(2d-1)\Delta^3] = \Delta^3 + (2d-1)(\Delta-1)^3 \ , \tag{19}$$

which together with

$$\left[\frac{\omega_0}{\omega_m}\right]^2 = \frac{1}{4d}\{2+(2d-1)\Delta + \Lambda[8+(2d-1)\Delta^3]\} \tag{20}$$

defines the local-mode frequency dependence on the anharmonicity parameter. The relative amplitude in each mode and the limiting slopes for one, two, and three dimensions are presented in Table II.

D. Correction to the rotating-wave approximation

In developing the local-mode solution, it was assumed above that the system only responded at the fundamental driving frequency. Because of the quartic potential, response at 3ω, 5ω, etc., should also be present, and we investigate here the influence of the 3ω term on the value of the fundamental local-mode frequency. To do this, we generalize the rotating-wave approximation for the displacements to

$$u_n = \xi_n(1-\beta)\cos(\omega_1 t) + \xi_n \beta \cos(3\omega_1 t) \tag{21}$$

using an obvious notation. Substitution of Eq. (21) into the equation of motion yields

$$\left[\frac{\omega_1}{\omega_m}\right]^2 [(1-\beta)\cos(\omega_1 t) + 9\beta\cos(3\omega_1 t)] = [(1-\beta)\cos(\omega_1 t) + \beta\cos(3\omega_1 t)] f(\Delta,\kappa) + [\tfrac{3}{4}(1-2\beta)\cos(\omega_1 t) + \tfrac{1}{4}(1+3\beta)\cos(3\omega_1 t)]\Lambda g(\Delta,\kappa) + O(\beta^2, 5\omega_1, \ldots) \ , \tag{22}$$

where $f(\Delta,\kappa)$ and $g(\Delta,\kappa)$ depend on the site, dimensionality, and the type of excitation being considered. Matching coefficients and keeping terms to $O(\beta^2)$ gives

$$\beta = \frac{\Lambda g(\Delta,\kappa)}{32 f(\Delta,\kappa) + 25\Lambda g(\Delta,\kappa)} \tag{23}$$

and

$$\left[\frac{\omega_1}{\omega_m}\right]^2 = f(\Delta,\kappa) + \tfrac{3}{4}\Lambda g(\Delta,\kappa)\left[\frac{32 f(\Delta,\kappa) + 23\Lambda g(\Delta,\kappa)}{32 f(\Delta,\kappa) + 24\Lambda g(\Delta,\kappa)}\right] . \tag{24}$$

Equation (23) restricts the range of β to $0 \le \beta < \frac{1}{25}$ while the correction factor for Λ is between 1 and $\frac{23}{24}$. Since this factor is less than or equal to unity, ω_1 will be less than the value predicted without the third-harmonic term. The relative difference between the squares of these two frequencies lies in the range

$$0 \le \frac{\omega_0^2}{\omega_1^2} - 1 < \frac{1}{23} \ . \tag{25}$$

This difference is small, so the higher-order terms in Eqs. (21) and (22) can be ignored. For values of $\Lambda \ll 1$, the correction to Eq. (24) is negligible, and the single-frequency rotating-wave approximation given by Eq. (6) is quite accurate.

III. DISCUSSION

A. Mode behavior versus anharmonicity parameter

By solving Eqs. (11)–(13) numerically, we can determine how the local-mode frequency ω_0 and the nearest-neighbor amplitude $\Delta-1$ vary with the anharmonicity parameter Λ for the one-dimensional case. The results are shown in Fig. 1. Over most of the interval the solid line shows that $(\omega_0/\omega_m)^2 \propto \Lambda$ while the dashed line indicates that the nearest-neighbor amplitude is the same as the central atom for small Λ, but approaches roughly half its value for large Λ. In the small-Λ limit, the mode is delocalized since neighbors have nearly the same amplitude, while for large Λ the second neighbor has extremely small amplitude so the triatomic molecule results with the central atom having amplitude 1 and the two neigh-

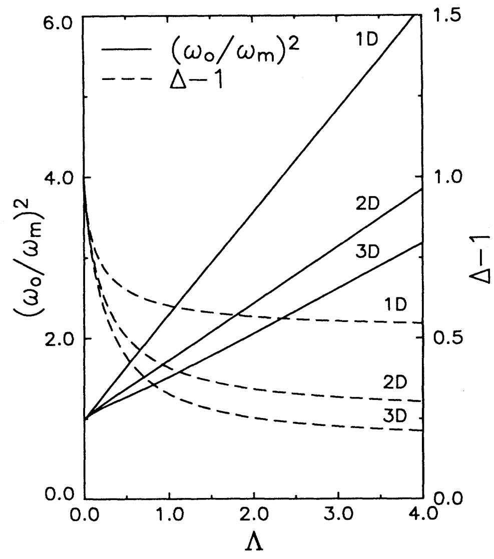

FIG. 1. Local-mode frequency and nearest-neighbor amplitude vs anharmonicity parameter Λ for the odd-symmetry case. For one, two, and three dimensions the solid curves give the calculated frequencies and the dashed curves show the relative amplitudes.

bors oppositely directed with amplitude $\sim\frac{1}{2}$.[13] (See Table II for the precise values.) The results for two and three dimensions are also shown in Fig. 1. To obtain a given local-mode frequency, a larger anharmonicity parameter is required with increased dimension. Although the nearest-neighbor amplitude is smaller in the higher-dimensional cases, there are more neighbors, so for a fixed Λ the mode becomes less localized as the dimension increases.

The frequency and amplitude dependences on Λ of the even mode are shown in Fig. 2. Here the relative amplitude $\Delta-1=|\xi_2/\xi_1|=Ae^{-q'}$. Inspection of this figure shows that the results are qualitatively similar to those for the odd mode presented in Fig. 1. A quantitative difference is that for a given Λ the even-mode frequency is higher than the odd mode in all three cases, even though this mode involves more neighbors than the odd one.

This mode, which does not obey the same symmetry as the odd mode, can be viewed as a vibrational exciton. It can be constructed, approximately, by superimposing two odd modes (described in the preceding section) with opposite phase on next-neighbor sites. The phase is the analogue of charge. Odd modes with opposite phase attract while those with the same phase on near-neighbor sites repel each other. Presumably, this low-symmetry mode must actually move in the lattice to restore the point symmetry of the crystal.

In Sec. II D we found the local odd mode frequency ω_0 is corrected to a new lower-frequency value ω_1 if the third-harmonic response is taken into account in the solution. In Fig. 3 we show the magnitude of the shift on the odd mode solution by plotting both the corrected and uncorrected positions in all three dimensions. As might be expected, the correction term grows with increasing anharmonicity parameter but it remains a small contribu-

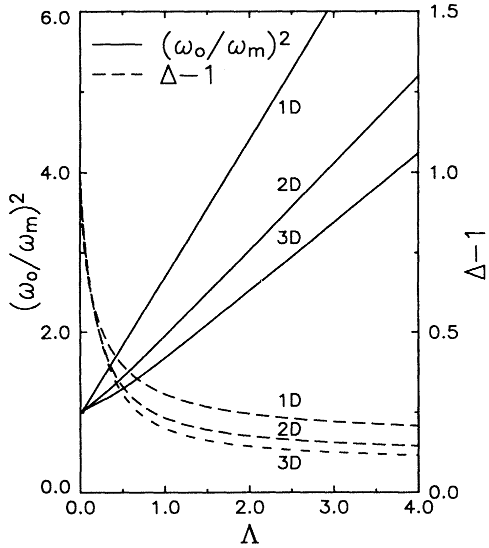

FIG. 2. Local-mode frequency and nearest-neighbor amplitude vs anharmonicity parameter Λ for the vibrational exciton-like mode. For one, two, and three dimensions the solid curves give the calculated frequencies and the dashed curves show the relative amplitudes.

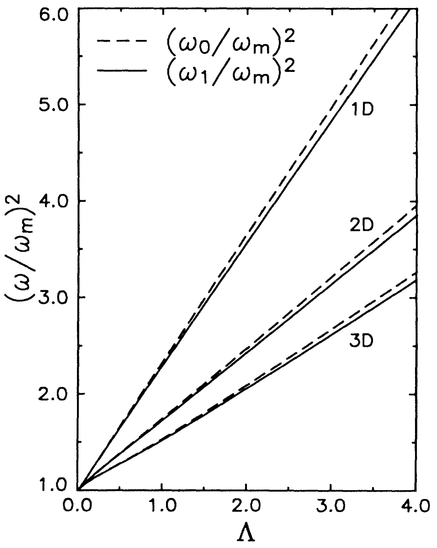

FIG. 3. Local-mode frequency vs Λ as calculated by two different rotating-wave approximations. The dashed curve follows from the single-frequency rotating-wave approximation while the solid curve includes an additional contribution from the third-harmonic term.

tion over the entire parameter range of interest. This figure confirms the idea that the simple rotating-wave approximation [Eq. (6)] is a valid method for identifying anharmonic localized modes.

B. Connection between the size of the quartic potential and mode existence

It would appear from the figures presented so far, which show mode existence at small values of the anharmonicity parameter, that anharmonic local modes could exist for arbitrarily small quartic anharmonicity, but we show here that this is not the case. Although Λ may appear to be a natural variable in this problem, the difficulty in using results presented as a function of Λ is that this variable involves both the quartic anharmonicity and the mode amplitude. As $\omega_0 \rightarrow \omega_m$, Figs. 1 and 2 show that in all dimensions the mode becomes delocalized. The involvement of more atoms ensures that the mean-square amplitude at each site is smaller. Our derivation has already used the fact that if the mean-square amplitude is small enough, then only the harmonic part of the potential is important and a plane-wave spectrum results. So far the physical constraint expressed here is missing from the model.

To introduce the connection between the number of atoms in the mode and the mean-square amplitude per atom, we make use of the virial theorem for a harmonic oscillator, namely, $2U=E$, where U is the potential energy and E is the total energy of the mode under consideration.[14] Since we are only interested in the fundamental connection between the number of particles in a mode and the mean-square amplitude, anharmonicity is not explicitly considered here. For the one-dimensional case this energy expression can be written as

$$m\omega_0^2 \sum_n u_n^2 = m\omega_0^2 N_{\mathrm{eff}} \alpha^2 = \frac{\hbar\omega_0}{2} \coth\left[\frac{\hbar\omega_0}{2kT}\right] + S\hbar\omega_m , \tag{26}$$

where N_{eff} is defined by the first equality and, on the far right, the first term accounts for the thermal energy and the second term describes energy introduced into the mode by some external means. These two terms are assumed to add incoherently. This second term, for example, could arise from the recoil energy of the nucleus in a Mössbauer transition. It is written as a multiple S of the zone-boundary phonon energy for convenience. Multiplying both sides of Eq. (26) by K_4/K_2 and using the definition $\Lambda \equiv K_4\alpha^2/K_2$ gives another condition for the existence of a local mode, namely,

$$\frac{K_4}{K_2} = N_{\mathrm{eff}} \Lambda \left\{ \left[\frac{\hbar}{m\omega_m}\right] \left[\frac{\omega_m}{\omega_0}\right] \left[\tfrac{1}{2}\coth\left[\frac{\Theta_{\mathrm{D}}}{2T}\frac{\omega_0}{\omega_m}\right] + S\frac{\omega_m}{\omega_0} \right] \right\}^{-1} , \tag{27}$$

where $\Theta_D = \hbar\omega_m / k_B$.

To estimate N_{eff}, the number of atoms with mean-square amplitude α^2 in one dimension, we note that in terms of the model parameters

$$N_{\mathrm{eff}} = 1 + 2[(A\kappa)^2 + (A\kappa^2)^2 + (A\kappa^3)^2 + \cdots] = 1 + \frac{2(A\kappa)^2}{1-\kappa^2} . \tag{28}$$

The values of A, κ, (ω_0/ω_m), N_{eff} can all be calculated for any given value of Λ, hence K_4/K_2 can be found for specified values of Λ, T, and S.

For two and three dimensions, a value of N_{eff} has been estimated by summing over a finite number of crystal directions, making sure that all atoms within seven lattice spacings of the central atom are included. Although this approximation is not valid as $\Lambda \rightarrow 0$, it is still accurate down to $\Lambda \approx 0.02$, the lower limit to the extent of Λ that we considered here.

For the even-mode calculation the N_{eff} can be related to that for the odd mode cases. We find the following relations:

$$N_{\mathrm{eff}}(\mathrm{even},1) = N_{\mathrm{eff}}(\mathrm{odd},1) + 1 \quad (\text{for 1D}) ,$$
$$N_{\mathrm{eff}}(\mathrm{even},2) = N_{\mathrm{eff}}(\mathrm{odd},2) + N_{\mathrm{eff}}(\mathrm{odd},1), \quad (\text{for2D}) , \tag{29}$$

and

$$N_{\mathrm{eff}}(\mathrm{even},3) = N_{\mathrm{eff}}(\mathrm{odd},3) + N_{\mathrm{eff}}(\mathrm{odd},2) \quad (\text{for 3D}) ,$$

hence the even modes are always more delocalized than the odd ones and the first anharmonic mode to be allowed as a function of increasing K_4/K_2 will be an odd one.

To obtain some idea of the magnitude of K_4/K_2 available in solids for the production of anharmonic localized modes, we apply alkali-metal halide parameters appropriate to a diatomic face-centered-cubic lattice to our one atom per unit cell, simple cubic lattice with nearest-neighbor force constants. Admittedly, this is a zeroth-order approximation and only qualitative conclusions can be obtained. We now demonstrate that the model improvements one might imagine are irrelevant since the values of K_4/K_2 are so small for alkali-metal halide crystals compared to what is required to produce anharmonic local modes that such refinements cannot make up the difference. The first row of Table III gives theoretical values of K_4/K_2 for different alkali-metal halide crystals with the potential parameters taken from Table 12 of

TABLE III. Some theoretical and experimental parameters for alkali-metal halide crystals.

Parameter	LiF	NaCl	KCl	KBr	KI
K_4/K_2 (Å^{-2})[a]	5.50	2.42	0.71	0.95	0.09
Θ_D (K)[b]	730	321	231	173	131
S[c]	41	42	31	51	54

[a] Reference 14.

[b] N. W. Ashcroft and N. D. Mermin, *Solid State Physics* (Holt, Rinehart and Winston, New York, 1976), p. 549.

[c] B. Henderson and G. F. Imbush, *Optical Spectroscopy of Inorganic Solids* (Clarendon, Oxford, 1989), p. 323.

Ref. 15. Of this group, LiF is the most anharmonic.[16] (The connection between our notation and that of Ref. 15 is $K_2=f$ and $6K_4=h$, so that $K_4/K_2=h/6f$.) With the Debye temperature obtained from the second row of Table III, we plot in Fig. 4 the dependence of the anharmonicity parameter on K_4/K_2 at two temperatures, $T=0$ and near the melting temperature of LiF, $T=1100$ K. The solid, dashed, and dot-dashed lines identify the solutions for one, two, and three dimensions. For sufficient K_4/K_2 the intersections with the two- and three-dimensional curves are double valued. Since the most localized mode will have the highest configurational entropy, the higher-frequency mode is assumed to be the only physically relevant solution in this region.

There is some value in showing the different dimensional results in Fig. 4. We have assumed throughout our derivation that the transverse spring constant is equal to the longitudinal one, but the smaller the transverse is with respect to the longitudinal, the more one dimensional the mode appears and the smaller the required K_4/K_2 value. However, even at temperatures near the melting point, the values of K/K_2 given in Table III are too small to intersect the curve for the (most favorable) one-dimensional case. So within the framework of our simple model, thermal energy is not sufficient to produce anharmonic localized modes for realistic anharmonic potentials in pure alkali-metal halide crystals. We anticipate that this stringent condition would be relaxed somewhat near small defects that are known to produce a softening of the net small amplitude restoring force due to an accidental cancellation of the electronic polarization terms with the harmonic nearest-neighbor force constant.[7]

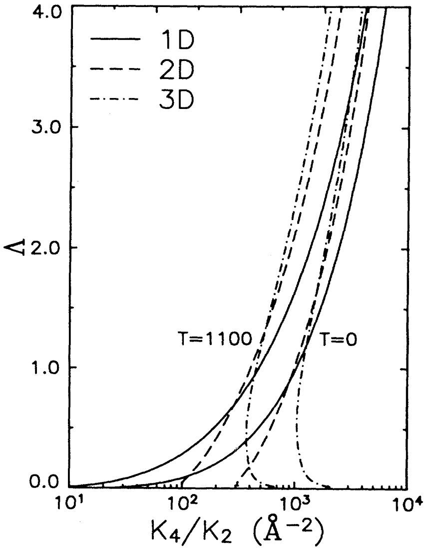

FIG. 4. Parametric curves defining the existence of an anharmonic odd-parity localized mode for LiF-like parameters at two temperatures. The curves identify the values of K_4/K_2 needed to produce a specific value of Λ and hence a local mode. The curves on the right correspond to zero point motion, while those on the left correspond to thermal motion near the melting point. The room-temperature value for LiF parameters is $K_4/K_2=5.5$ Å^{-2}, which is off scale, so no local mode can occur.

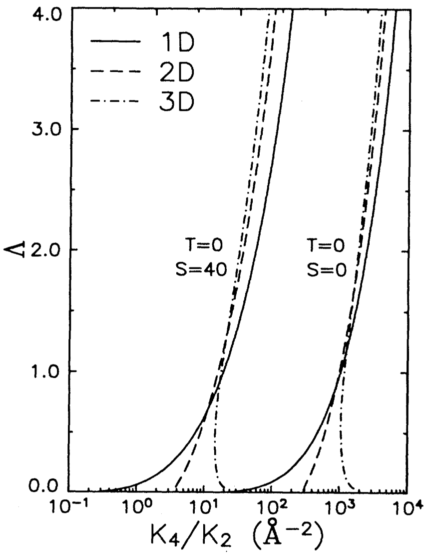

FIG. 5. Parametric curves defining the existence of an anharmonic odd-parity localized mode for LiF-like parameters for two different excitation energies. The curves identify the values of K_4/K_2 needed to produce a specific value of Λ and hence a local mode. The curves on the right correspond to zero point motion, while those on the left, with $S=40$, correspond to a process involving an energy equivalent to 40 Debye phonons. The minimum values of K_4/K_2 with $S=40$, for one, two, and three dimensions, are 0.27, 3.9, and 14.5 Å^{-2}, respectively. For $K_4/K_2=5.5$ Å^{-2}, a local mode exists in one and two dimensions but not in three.

We now turn to the possibility of putting energy directly in the mode by a nonthermal means such as a Mössbauer recoil or an optical transition. We consider the optical process here because it provides the largest energy transfer. Row three of Table III gives the measured S values for the excited state of an F center for the different alkali-metal halides.[18] Using a value of $S=40$ (appropriate to LiF) the connection between the anharmonicity parameter Λ and K_4/K_2 is obtained and graphed in Fig. 5. Now for $K_4/K_2=5.5$ Å^{-2} a mode is allowed in both one and two dimensions and the curves are within a factor of 3 of being allowed in three dimensions (with the unfavorable condition of equal transverse and longitudinal force constants). Vibrational energy transfer into the lattice equivalent to a 40-phonon process appears to be the correct order of magnitude for the generation of anharmonic localized modes in alkali-metal halide crystals. A more realistic lattice model which included the F center would be required to test this prediction further.

Our calculations indicate that only extremely anharmonic crystals will provide a suitable habitat for anharmonic localized modes. Systems such as soft mode ferroelectrics and antiferroelectrics or solid helium might provide the proper environment. It has already been recognized that some ferroelectric materials show glasslike thermal properties at low temperatures[19] and a linear term in the specific heat of solid helium observed in early measurements is still unexplained.[20] A recent model indicates that under the proper conditions diffusing localized modes can produce such glasslike thermal properties.[21]

IV. SUMMARY

In this paper we have shown that when the nearest-neighbor potentials include hard quartic anharmonicity, localized modes can be generated in a perfect monatomic lattice in any dimension for any anharmonicity parameter Λ. The character of these modes undergoes a smooth evolution from a homogeneous plane-wave state when $\Lambda=0$ to an inhomogeneous wave that has the vibrational pattern of a small molecule for large Λ. The local symmetry around a particle dictates that both odd- and even-symmetry modes may exist but our study shows that even modes are unstable; hence, the fundamental building block for describing anharmonic localized vibrational excitations appears to be the odd-symmetry mode. An even mode that does not satisfy the same site symmetry can be constructed from two odd modes by placing them side by side with opposite phase; the result is a vibrational exciton.

The accuracy of the rotating-wave approximation has been checked by calculating the influence of the oscillations at $3\omega_1$ produced by the quartic potential. We have shown that the amplitude of the particle displacement at the third harmonic is a small fraction of the amplitude at the fundamental for any Λ. The corrected fundamental frequencies are reduced by at most a few percent so to a good approximation this correction term can be ignored.

Although the equations of motion indicate that anharmonic localized modes can exist for any value of Λ in any dimension, when real system parameters are introduced the possibility is more restricted. With LiF-like parameters it has been found that thermal energy alone is not sufficient to produce localized anharmonic modes due to the relatively small size of the quartic anharmonicity, but these modes may be generated by an optical or other nonthermal process that involves the equivalent of 40 or more Debye phonons. Solids with extremely large anharmonicity would provide a more natural environment for these localized excitations.

ACKNOWLEDGMENTS

Discussions with J. B. Page, J. P. Sethna, and S. Takeno have been extremely helpful. This work has been supported by National Science Foundation (NSF Grant No. DMR-87-14600 and by Army Research Office Grant No. DAAL03-89-K-0053. One of us (S.R.B.) has been supported in part by the NSF.

---

[1] A. J. Sievers, and S. Takeno, Phys. Rev. Lett. **61**, 970 (1988).

[2] S. Takeno and A. J. Sievers, Solid State Commun. **67**, 1023 (1988).

[3] S. Takeno, K. Kisoda, and A. J. Sievers, Prog. Theor. Phys. Suppl. **94**, 242 (1988).

[4] R. Bourbonnais, Ph.D. thesis, L'Université Joseph Fournier, Grenoble, 1989; R. Bourbonnais and R. Maynard, Phys. Rev. Lett. **64**, 1397 (1990).

[5] V. M. Bourlakov, S. A. Kiselev, and V. N. Pyrkov, Solid State Commun. **74**, 327 (1990); V. M. Burlakov, S. A. Kiselev, and V. N. Pyrkov, Phys. Rev. B **42**, 4921 (1990).

[6] A. S. Barker and A. J. Sievers, Rev. Mod. Phys. **47**, Suppl. 2 (1975).

[7] J. B. Page, Phys. Rev. B **41**, 7835 (1990).

[8] The influence of cubic anharmonicity on the results presented in this paper is still to be investigated.

[9] A. Haug, *Theoretical Solid State Physics* (Pergamon, Oxford, 1972), Vol. 2, p. 193.

[10] S. R. Bickham, J. P. Sethna, A. J. Sievers, J. B. Page, and O. F. Sankey (unpublished).

[11] Simulations have shown that this even mode is stable in two dimensions when the transverse and longitudinal force constants are equal and $\Lambda > 1.64$, but it breaks up into an even number of odd modes when these conditions are not satisfied. We expect these criteria to be relaxed in three dimensions.

[12] W. Ludwig, *Recent Developments in Lattice Theory,* Vol. 43 of *Springer Tracts in Modern Physics,* edited by G. Höhler, (Springer-Verlag, Berlin, 1967), p. 152.

[13] In the strong-anharmonicity limit, our solution predicts that the relative amplitude of the second-nearest neighbor in the one-dimensional odd mode should approach zero asymptotically. An exact calculation given in Ref. 7 gives a value of 0.02 for this amplitude, thus eliminating the fictitious center-of-mass motion found in our approximate solution. The results for the even-parity modes and for modes in two and three dimensions are analogous.

[14] W. Hayes and A. M. Stoneham, *Defects and Defect Processes in Nonmetallic Solids* (Wiley, New York, 1985), p. 79.

[15] G. Leibfried and W. Ludwig, in *Solid State Physics, Advances in Research and Applications,* edited by F. Seitz and D. Turnbull (Academic, New York, 1961), p. 401.

[16] Another value for K_4/K_2 was obtained following the method of G. P. Montgomery, W. R. Fenner, M. V. Klein, and T. Timusk, Phys. Rev. B **6**, 3343 (1972). Including contributions to the potential energy from Born-Mayer repulsion, Coulomb interaction, Van der Waals attraction, and a polarization term, we find for LiF that $K_4/K_2=3.93$ Å^{-2}. Since this value and the one given in Table III are within a factor 2 of each other and both are roughly 100 times too small to produce anharmonic localized modes, we can ignore crystal model refinements.

[17] J. A. D. Matthew, Solid State Commun. **3**, 363 (1965).

[18] Note that the modes involved in this optical transition must be even, and that such even symmetry anharmonic localized modes are unstable in one and two dimensions and break up into odd-symmetry modes (see Ref. 11). For the estimates given here, we assume that the odd modes are produced in this way.

[19] Y. Y. De Yoreo, R. O. Pohl, and G. Burns, Phys. Rev. B **32**, 5780 (1985).

[20] D. S. Graywall, Phys. Rev. B **15**, 2604 (1977).

[21] A. J. Sievers and S. Takeno, Phys. Rev. B **39**, 3374 (1989).