Nonlinear Lattice Dynamics of Crystals with Structural Phase Transitions

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Exact periodic solutions are found for three-dimensional lattices with fourth-order on-site electron-ion potentials. Numerical results are presented for ferroelectric SnTe. The coupling of these nonlinear waves with phonons is investigated for phase transitions with finite critical wave vectors. For K_2SeO_4 both the paraelectric-incommensurate and the incommensurate-commensurate ferroelectric transitions are analyzed. The cubic power of the nonlinear force leads to a lock-in transition at the wave vector $2\pi/3$.

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The lattice dynamics of crystals has been treated for a long time in the harmonic approximation. In this paper we show that a systematic extension to nonlinear potentials can be made for crystals exhibiting structural phase transitions.[1] The concept of soft modes[2] is extended to the nonlinear case. In addition to the nonlinear continuum models (e.g., the φ^4 models[3]) we investigate exact periodic solutions on the lattice. The underlying physical ideas connected with ferroelectric phase transitions have been discussed in a recent paper.[4]

First, we compare exact nonlinear solutions for a three-dimensional lattice ("periodons")[4] with the self-consistent phonon approximation (SPA). Ferroelectric SnTe is discussed as an interesting example. Second, we study the coupling between these nonlinear modes and the self-consistent phonons leading to phase transitions with a finite critical wave vector $q_c \neq 0$. The case of K_2SeO_4 is investigated in some detail. Finally, some general aspects of our results are discussed.

We focus on ionic solids, the dynamics of which may be described in terms of dipolar ("shell") models with the harmonic lattice potential

$$\varphi^{(2)} = \varphi_{ii} + \varphi_{ei} + \varphi_{ee}, \tag{1}$$

φ_{ii} denoting the ion-ion interaction, φ_{ee} the electron-electron interaction, and φ_{ei} the electron-ion interaction. We now extend the model by including a local fourth-order anisotropic potential in the electron-ion interaction:

$$\varphi_{ei}^{(4)} = \tfrac{1}{4}\textstyle\sum_{L,\alpha} g_{4,\alpha}(\kappa) w_\alpha^{\,4}(L) \tag{2}$$

with $\vec{w}(L) = \vec{v}(L) - \vec{u}(L)$ and $\alpha = x, y, z$. $\vec{u}(L)$ and $\vec{v}(L)$ are the displacements of the ions and electronic shells at lattice site $L = (l, \kappa)$, respectively. This electron-ion interaction potential leads to ferroelectric phase transitions in many systems[5] at a critical temperature T_c. Such transitions are often treated in the SPA.[6] In our case the SPA corresponds to the following substitution[5]:

$$w_\alpha^{\,3}(L) \cong 3 w_\alpha(L) \langle w_\alpha^{\,2}(L)\rangle_T, \tag{3}$$

with the thermodynamic average $\langle w_\alpha^{\,2}(L)\rangle_T$.

In addition, we consider exact solutions for structural phase transitions at finite wave vectors. Besides the solutions of kink type, obtained in the continuum approximation,[3] we study nonlinear periodic lattice solutions for general three-dimensional (3D) lattices ("periodons").[4] They are obtained from the following *Ansatz* for the displacements ($x = u, v, w$):

$$\vec{x}(L) = \mathrm{Re}\{\vec{X}_1 \exp[i(\omega t - \vec{q}\cdot\vec{R}(L))] + \vec{X}_3 \exp[3i(\omega t - \vec{q}\cdot\vec{R}(L))]\}. \tag{4}$$

$\vec{X}_1$ and $\vec{X}_3$ are determined by the equations of motion.

The dispersion relation for the periodons is given by (see Ref. 4 for the 1D case)

$$\omega_p(\vec{q}) = \tfrac{1}{3}\omega_R(3\vec{q}), \tag{5}$$

where $\omega_R(\vec{q})$ is the dispersion relation in the SPA in the limit where the nonlinearly polarizable ions $(\bar{\kappa})$ are replaced by rigid ions $[g_{4,\alpha}(\bar{\kappa}) \to \infty]$.

In Fig. 1 phonons[7] and periodons are shown for SnTe, a ferroelectric IV-VI material with the rocksalt structure.

The interaction between periodons and phonons may lead to soft modes with transverse polarization and to structural phase transitions at $q = q_c \neq 0$. This mode-mode coupling may be described in a simplified pseudolinear model with one polarizable ion in the unit cell and nearest-neighbor interaction only. The Hamiltonian of the model reads

$$H=\tfrac{1}{2}\sum_n[(M\dot{u}_n^{\,2}+m_{\rm el}\dot{v}_n^{\,2}+f'(u_n-u_{n-1})^2+f(v_n-v_{n-1})^2+g_2(v_n-u_n)^2+\tfrac{1}{2}g_4(v_n-u_n)^4]. \tag{6}$$

The equations of motion are[4]

$$M\ddot{u}_n=g_2w_n+g_4w_n^{\,3}+f'Du_n, \tag{7a}$$

$$m_{\rm el}\ddot{v}_n=-g_2w_n-g_2w_n^{\,3}+fD(w_n+u_n)=0 \quad \text{(adiabatic condition)}, \tag{7b}$$

with $w_n\equiv v_n-u_n$ and the difference operator D defined by $Dx_n\equiv x_{n+1}+x_{n-1}-2x_n$. An exact periodon solution is then

$$w_n=A\sin(\omega t-nqa+\delta), \tag{8}$$

$$u_n=B\sin(\omega t-nqa+\delta)+C\sin 3(\omega t-nqa+\delta), \tag{9}$$

with the dispersion relation

$$M\omega_p^{\,2}(q)=\tfrac{4}{9}(f+f')\sin^2(3qa/2) \tag{10}$$

and the amplitude

$$A^2(q)=\frac{4}{3g_4}\left[-g_2-M\omega_f^{\,2}\left(1-\frac{\omega_f^{\,2}}{\omega_R^{\,2}-\omega_p^{\,2}}\right)\right], \tag{11}$$

where $M\omega_f^{\,2}=4f\sin^2(qa/2)$ and $M\omega_R^{\,2}$ is the rigid-ion limit $[g(T)\to\infty]$ of (12). B and C are functions similar to $A(q)$.[4] The stability of the static periodon, $\omega(2\pi/3)=0$, implies $\sin 3\delta=0$.

The dispersion in the SPA is given by

$$M\omega_s^{\,2}(q)=M\omega_f^{\,2}(q)\{[1+M\omega_f^{\,2}/g(T)]^{-1}+f'/f\} \tag{12}$$

with the thermal average[5]

$$g(T)=g_2+3g_4\langle w_n^{\,2}\rangle_T. \tag{13}$$

To describe the periodon-phonon coupling we make the *Ansatz*

$$w_n=w_{np}+w_{ns},\quad u_n=u_{np}+u_{ns}. \tag{14}$$

The resulting equations of motion can be grouped in the following form:

$$M\ddot{u}_{ns}=(f+f')Du_{ns}+fDw_{ns}, \tag{15a}$$

$$0=[g(T)+3g_4w_{np}^{\,2}]w_{ns}-fD(w_{ns}+u_{ns}), \tag{15b}$$

$$M\ddot{u}_{np}=(f+f')Du_{np}+fDw_{np}, \tag{16a}$$

$$0=g(T)w_{np}+g_4w_{np}^{\,3}-fD(w_{np}+u_{np}). \tag{16b}$$

In Eqs. (15) and (16) we have consistently used the SPA, Eq. (3), for w_{ns}. This results in temperature-dependent periodon amplitudes, obtained by replacing g_2 by $g(T)$ in (11).

For the solution of (15) we have to insert $w_{np}^{\,2}$. We distinguish between a low-temperature regime which is governed by the static periodon, $\omega_p=0$ at $q\neq 0$, and a high-temperature regime with self-consistent phonons in a fluctuating periodon field. For low temperatures this yields a site-dependent electron-ion coupling [cf. Eqs. (8), (11), (14), and (15b)]

$$g(T)+3g_4w_{np}^{\,2}(2\pi/3)=\begin{cases} g(T), & n\equiv 0\ (\mathrm{mod}\,3)\\ -2g(T)-\dfrac{9}{1/f+1/f'}, & n\equiv 1 \text{ or } 2\ (\mathrm{mod}\,3)\end{cases} \tag{17}$$

and causes a tripling of the lattice constant. Here, the change of force constants has been neglected in a first approximation. For high temperatures the fluctuating periodons are approximated by a time-averaged solution, which yields a q-dependent coupling[8] $[\langle\sin^2(\omega t-nqa)\rangle_t=\tfrac{1}{2}]$:

$$g(T)+3g_4w_{np}^{\,2}(q)=g(T)+\tfrac{3}{2}g_4A_T^{\,2}(q) \tag{18}$$

with $A_T^{\,2}(q)$ from (11) and g_2 replaced by $g(T)$.

In Figs. 2 and 3 the results for K_2SeO_4 of Axe, Iizumi, and Shirane[9] and Iizumi *et al.*,[10] respectively, are compared with calculations based on our simple model. While $g(T)$ determines the temperature dependence of the commensurate part of the phase transition, $f'(T)$ describes the incommensurate intersite elastic coupling which shifts the minimum of $\omega(q)$ away from $qa=2\pi/3$ to a higher value.[11] The extrapolation of $f'(T)$ and $g(T)$ to zero values (Fig. 4) shows that $g(T)$ governs the second-order phase transition at 127 K ($T=T_i$) while the lock-in phase transition at 93 K ($T=T_c$) can only take place after vanishing of the coupling parameter f'.

The description of both the temperature-dependent coupled phonon-periodon mode in the paraelectric regime (Fig. 2) and of the three split modes in the ferroelectric regime at 40 K (Fig. 3) is satisfactory in view of the rather complex lattice dynamics of K_2SeO_4.[12]

In addition, we have found that the phonon anomalies in $TaSe_2$ and $NbSe_2$ (Ref. 13) may be easily described in terms of our simple model.[14]

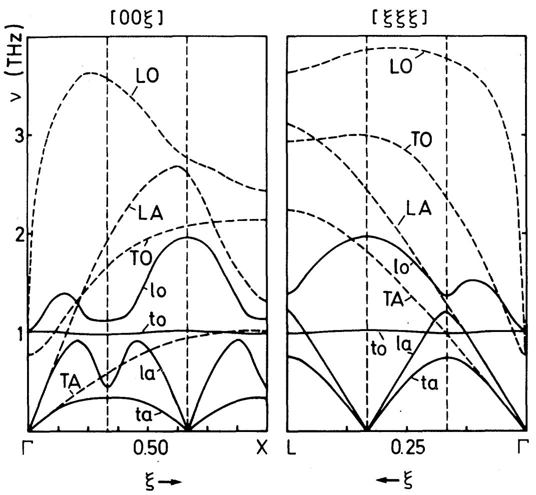

FIG. 1. Dispersion curves of phonons (Ref. 8) (dashed lines) and periodons (solid lines) in SnTe at 100 K. Capital (small) letters denote polarization of phonons (periodons). Parameters are taken from Ref. 7.

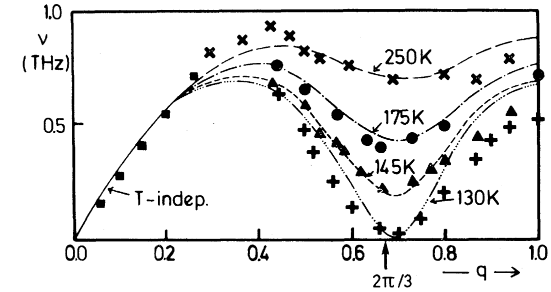

FIG. 2. Dispersion of coupled phonon-periodon mode in the paraelectric regime ($T > T_c = 127$ K) of K_2SeO_4. Parameters: $f + f' = 0.9$ $(\mathrm{THz})^2\times$ (mass unit); f', g: Refer to Fig. 4.

This emphasizes the interrelation of our mode-coupling treatment to the description of these systems in terms of charge-density waves.[12,15]

We have checked the stability of our solutions by a mapping procedure.[16] They turn out to be elliptically stable for the parameter regime $3 \leq |g|(f^{-1}+f'^{-1}) \leq 4$. Our fitted values yield 4.3 which is sufficient for the linear stability of periodons and phonons. There exist other static periodon solutions (e.g., antiferroelectric, etc.) stable for other nonoverlapping parameter regimes.[17] Our treatment shows relations to the current discussions of discommensuration,[18] of details of the phase transitions,[19] and of fractionally charged solitons.[20] They will be discussed in forthcoming papers.[8,21]

In conclusion, we have shown that systems with structural phase transitions such as SnTe and K_2SeO_4 may be treated in terms of coupled modes, one of which is a self-consistent phonon while the other is a periodon, i.e., a nonlinear periodic lattice wave. The magnitude of the wave vector $\vec{q}_c$ of the static periodon $[\omega(\vec{q}_c c) = 0]$ describing the commensurate part of the phase transition at $(\vec{q}_c \cdot \vec{a}/2\pi)^{-1} = 3$ is determined by the cube of $\vec{w}(L)$ in the nonlinear electron-ion force, $-d\varphi_{ei}^{(4)}/d\vec{w}(L) \propto [\vec{w}(L)]^3$. In general, a power $n+1$ of $\vec{w}(L)$ in the electron-ion potential may cause a static periodon at $(\vec{q}_c \cdot \vec{a}/2\pi)^{-1} = n$.

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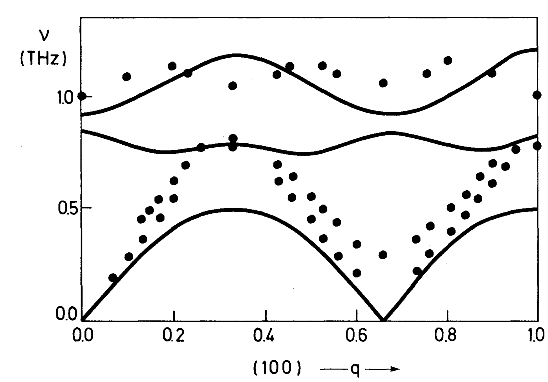

FIG. 3. Tripling of the transverse acoustic coupled mode in the ferroelectric regime of K_2SeO_4 at $T = 40$ K. Parameters: $f = 0.3$, $f' = 0.4$, and $g = -0.75$ [all in $(\mathrm{THz})^2\times$ (mass unit)].

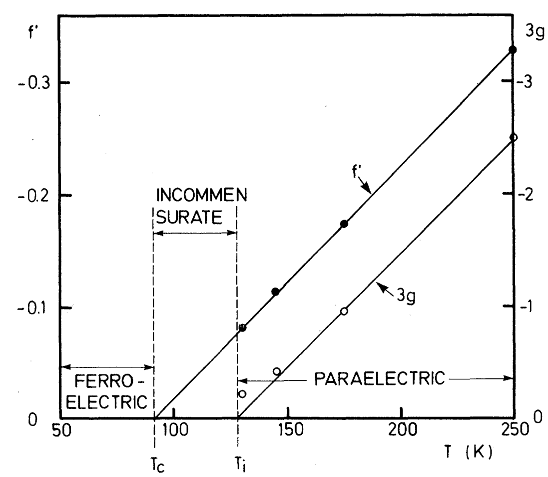

FIG. 4. Temperature dependence of coupling parameters $g(T)$ and $f'(T)$ in the paraelectric and incommensurate regimes (units: 10^2 g s^{-2}).

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[1]See, e.g., *Structural Phase Transitions I,* Topics in Current Physics, edited by K. A. Müller and H. Thomas (Springer, Berlin, 1981).

[2]W. Cochran, Adv. Phys. 9, 387 (1960); P. W. Anderson, in *Fizika Dielektrikov*, edited by G. I. Skamari (Akad. Nauk SSSR, Fizicheskii Inst. Lebedeva, Moscow, 1960).

[3]See, e.g., A. R. Bishop, J. A. Krumhansl, and S. E. Trullinger, Physica (Utrecht) 1D, 1 (1980).

[4]H. Büttner and H. Bilz, in *Recent Developments in Condensed Matter Physics*, edited by J. T. Devreese (Plenum, New York, 1981), Vol. I., p. 49.

[5]R. Migoni, H. Bilz, and D. Bäuerle, Phys. Rev. Lett. 37, 1155 (1976); H. Bilz, A. Bussmann, G. Benedek, H. Büttner, and D. Strauch, Ferroelectrics 25, 339 (1980), and to be published.

[6]See, e.g., A. A. Maradudin, in *Ferroelectricity*, edited by F. Weller (Elsevier, Amsterdam, 1967).

[7]G. S. Pawley, W. Cochran, R. A. Cowley, and G. Dolling, Phys. Rev. Lett. 17, 753 (1966); E. R. Cowley, J. K. Darby, and G. S. Pawley, J. Phys. C 2, 1916 (1969).

[8]H. Bilz, H. Büttner, A. Bussmann-Holder, W. Kress, and U. Schröder, to be published; see also H. Büttner, in "Nonlinear Phenomena at Phase Transitions and Instabilities," Proceedings of the NATO Advanced Study Institute at Geilo, 1981 (to be published).

[9]J. D. Axe, M. Iizumi, and G. Shirane, Phys. Rev. B 22, 3408 (1980).

[10]M. Iizumi, J. D. Axe, G. Shirane, and K. Shimaoka, Phys. Rev. B 15, 4392 (1977).

[11]The microscopic origin of f' and its relation to other treatments [A. D. Bruce and R. A. Cowley, J. Phys. C 11, 3609 (1978)] will be discussed in a forthcoming paper (Ref. 8).

[12]M. S. Haque and J. R. Hardy, Phys. Rev. B 21, 245 (1980).

[13]Refer to H. Bilz and W. Kress, *Phonon Dispersion Curves in Insulators* (Springer-Verlag, New York, 1979).

[14]A. Bussmann, H. Bilz, and H. Büttner, in Proceedings of the Fifth International Meeting on Ferroelectricity, University Park, Pa., 17–22 August 1981 (to be published).

[15]H. Fröhlich, Proc. Roy. Soc. London Ser. A 233, 296 (1954); A. W. Overhauser, Phys. Rev. B 3, 3173 (1971); T. M. Rice, in *Festkörperprobleme: Advances in Solid State Physics*, edited by J. Treusch (Vieweg, Braunschweig, 1980), Vol. XX, p. 393.

[16]M. Tabor, Adv. Chem. Phys. 46, 73 (1981); P. Bak, Phys. Rev. Lett. 46, 791 (1981).

[17]H. Büttner and H. Bilz, in Proceedings of the International Conference on Phonon Physics, Bloomington, Ind., 31 August–3 September 1981 (to be published).

[18]V. Heine and J. D. C. McConnell, Phys. Rev. Lett. 46, 1092 (1981).

[19]R. A. Cowley, Adv. Phys. 20, 1 (1980).

[20]W. P. Su and J. R. Schrieffer, Phys. Rev. Lett. 46, 738 (1981).

[21]H. Bilz and H. Büttner, in Proceedings of the Fifth International European Physical Society General Conference, Istanbul, Turkey, 7–11 September 1981 (to be published).

Time-Resolved Optical Transmission and Reflectivity of Pulsed-Ruby-Laser Irradiated Crystalline Silicon

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The time-resolved optical transmission and reflectivity of n^--type crystalline silicon has been observed during and after pulsed-laser irradiation. The transmission goes to zero, and remains at zero, during the period of enhanced reflectivity, contradicting reports of earlier experiments. Our measurements are in quantitative agreement with results of thermal melting model calculations and with known optical properties of molten silicon.

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The effects of pulsed-laser irradiation on semiconductors has recently become a topic of widespread interest, both because of practical applications in device fabrication, and because of a controversy which has arisen regarding the new physical phenomena involved. The thermal-melting model[1-3] of pulsed-laser effects assumes that the absorbed laser energy is transferred from