OPTICAL PHONONS IN FINITE CRYSTALS*

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(Received 19 April 1966)

Because of the long-range nature of the dipole-dipole interaction, optical phonons with wavelengths comparable to the specimen size become size and shape dependent. The spatial variation and the frequencies for these phonons were derived for some special cases.[1,2] In this Letter we give a unified treatment covering a wide class of crystal shapes.

For long wavelengths the short-range contribution to the optical phonon spectrum is flat. Also, the sum over the dipole-dipole interactions may be replaced by an integral and the equation of motion for an optical phonon in a diatomic, rigid ionic lattice is[3] (with neglect of retardation)

$$Kf_\alpha(\vec{r}) = \int dV'\left[\frac{\partial}{\partial r_\alpha}\frac{\partial}{\partial r_\beta'}\frac{1}{|\vec{r}-\vec{r}'|} - \frac{4\pi}{3}\delta(\vec{r}-\vec{r}')\delta_{\alpha\beta}\right]f_\beta(\vec{r}'). \qquad (1)$$

The eigenfunctions $f_\alpha(\vec{r})$ are phonon amplitudes regarded as functions of the continuous variable of the position $\vec{r} = r_\alpha$ ($\alpha = 1, 2, 3,$); the eigenvalues are $K = \mu v(\omega^2 - \omega_0^2)/Z^2e^2$ (in words, the reduced mass of the ions times the volume of the unit cell times the squared frequency counted from a convenient zero, divided by the square of the ionic charges). The integration in (1) is over the volume of the body. The second term in the integrand subtracts off the self-interaction of the dipoles.

Operating on (1) by div and curl in succession, and using $\nabla^2|\vec{r}-\vec{r}'|^{-1} = -4\pi\delta(\vec{r}-\vec{r}')$, one obtains $(K - 8\pi/3)\operatorname{div}\vec{f} = 0$ and $(K + 4\pi/3)\operatorname{curl}\vec{f} = 0$.

Accordingly, either $K = 8\pi/3$ and $\operatorname{curl}\vec{f} = 0$, or $K = -4\pi/3$ and $\operatorname{div}\vec{f} = 0$, or $\operatorname{div}\vec{f} = \operatorname{curl}\vec{f} = 0$. The first two possibilities give the usual longitudinal and transverse frequencies in the infinite crystal.[4] Only the third alternative yields frequencies which depend on the size and shape of the crystal.[5] These frequencies are derivable from (1), once a set of orthonormal eigenfunctions is found.

Explicit solutions representing surface phonons will now be given for a somewhat restricted class, namely, those solids whose macroscopic boundary surface may be regarded as the surface or surfaces $\xi_1 =$ constant, where the curvilinear coordinates $\xi_1\xi_2\xi_3$ are such that $|\vec{r}-\vec{r}'|^{-1}$ can be expanded in the vicinity of the boundary surface in the form[6]

$$|\vec{r}-\vec{r}'|^{-1} = -4\pi\,\frac{h_1}{h_2h_3}\rho(\xi_2', \xi_3')\sum_q W_q(\xi_2', \xi_3') \times W_q(\xi_2, \xi_3)\frac{1}{\Delta(\xi_1')}\,y_{1q}(\xi_1)y_{2q}(\xi_1').$$

Here h_i are the scale factors, ρ is the weight function, y_1 and y_2 are two independent solutions of the "radial" differential equation, $\Delta(\xi_1')$ is the Wronskian evaluated at ξ_1', and W are essentially surface harmonics in the two quasiangular coordinates ξ_2, ξ_3.

Two cases must now be distinguished:

(a) The solid is bounded externally by a single surface $\xi_1 = \xi^0 =$ constant. Suppose that y_1 is the solution regular within the solid. Then (un-normalized) solutions of (1) are

$$\vec{f}_q(\vec{r}) = \operatorname{grad}[W_q(\xi_2, \xi_3)y_{1q}(\xi_1)]$$

and

$$K_q + \frac{4\pi}{3} = -4\pi\left[\frac{d}{d\xi_1}y_{1q}(\xi_1)\right]_{\xi^0}\frac{y_{2q}(\xi^0)}{\Delta(\xi^0)}$$

Thus, for a spherically shaped ionic solid of arbitrary finite radius[7]

$$\vec{f}_{lm}(\vec{r}) = \operatorname{grad}[Y_l^m(\theta, \varphi)r^l]$$

and

$$K_l + \frac{4\pi}{3} = 2\pi\frac{l}{l+\frac{1}{2}}.$$

For a long circular cylinder of radius ρ^0,

$$\vec{f}_{m,k}(\vec{r}) = \operatorname{grad}[e^{im\varphi + ikz}I_m(kr)]$$

and

$$K_{mk} + 4\pi/3 = 4\pi k\rho^0 I_m'(k\rho^0)K_m(k\rho^0).$$

In both these cases the eigenvalues fall in the lower half of the gap.

(b) The solid is bounded by the two surface $\xi_1 = \xi^{\mathrm{I}}$ and $\xi_1 = \xi^{\mathrm{II}}$. Then out of the two solutions y_{1q} and y_{2q} one can construct two orthogonal functions regular within the extent of the solid:

$$\vec{f}_q^{\,\mathrm{I}}(\vec{r}) = \mathrm{grad}\, W_q(\xi_2, \xi_3) y_{1q}(\xi_1),$$

and

$$\vec{f}_q^{\,\mathrm{II}}(\vec{r}) = \mathrm{grad}\, [W_q(\xi_2, \xi_3) y_{2q}(\xi_1)].$$

Substitution of these in (1) yields a matrix whose eigenvalues are

$$K + 4\pi/3.$$

For a spherical shell of outer and inner radii R^{I}, R^{II} two radial functions, r^l and $r^{-(l+1)}$, enter with the same spherical harmonic Y_l^m. The resulting eigenvalues are now[8]

$$K - \frac{2\pi}{3} = \pm \frac{2\pi}{l + \frac{1}{2}} \left[\frac{1}{4} + l(l+1) \frac{R^{\mathrm{II}}}{R^{\mathrm{I}}(2l+1)} \right]^{1/2}$$

The range of K is now twice what it was before: between $-4\pi/3$ and $8\pi/3$.

[*] Work supported by Air Force Materials Laboratory, Research and Technology Division AFSC through the European Office of Aerospace Research, USAF.

[1] H. Fröhlich, Theory of Dielectrics (Clarendon Press, Oxford, England, 1958), pp. 153-5.

[2] R. Fuchs and K. L. Kliewer, Phys. Rev. 140, A2076 (1965.

[3] M. Born and K. Huang, Dynamical Theory of Crystal Lattices, (Clarendon Press, Oxford, England, 1956), Secs. 24.4, 23.3. Our treatment bears a direct, though somewhat lengthy, generalization to many-atomic and polarizable lattices for which Eq. (1) still gives the spatial dependence of the phonons.

[4] T. H. K. Barron, Phys. Rev. 123, 1995 (1961).

[5] The three possibilities appear to give all physically interesting solutions to (1); however, neither the completeness of the solutions nor the bulk modes are treated in this Letter.

[6] P. M. Morse and H. Feshbach, Methods of Theoretical Physics, (McGraw-Hill Book Company, Inc., New York, 1953), p. 831; see also Chap. 5 for discussion on separable coordinates and for notation.

[7] The lowest order nontrivial solution, with $l = 1$, is the one found in Ref. 1.

[8] Regarding the slab as the limiting case of thin spherical shell, this includes the result of Ref. 2.

SOLUBLE EXTENSION OF THE ISING MODEL

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(Received 31 March 1966)

In this note we wish to relate a somewhat trivial, but surprising, soluble extension of the multidimensional Ising model. Our extension was motivated by recent experiments on a real material, dysprosium aluminum garnet (DyAlG), which closely resembles an ideal three-dimensional Ising model,[1] except for what appeared to be one unfortunate detail: The electronic (Ising) spins are connected not just to their electronic neighbors, but also to their own dysprosium nuclei by a fairly large hyperfine interaction. The interacting nuclear isotopes are randomly distributed with a natural abundance of 18.9% for Dy^{161} (hyperfine coupling constant $A = 0.073$°K) and 25% for Dy^{163} ($A = 0.104$°K).[2] This physical system thus corresponds to a model Ising antiferromagnet disturbed by a magnetic field (the hyperfine-coupled nuclear spins) random in magnitude and position. The magnitude of the disturbance is not negligible, considering the low critical temperature of DyAlG ($T_N = 2.5$°K), and is indeed comparable in magnitude with any one of the Ising bonds!

Given this substantial random perturbation of the Ising spins, it is reasonable to expect a drastic effect on thermodynamic properties, especially critical-point phenomena. For example, an estimate on the basis of molecular field theory shows each spin in a different specific environment, and hence a broadening of the transition region. The smallest effect on the thermodynamic properties which one might reasonably expect is a broadening of the lamb-