PRESSURE DEPENDENCE OF LONG-WAVELENGTH OPTICAL PHONONS IN IONIC CRYSTALS*

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The purpose of this note is to report measurements on the effect of pressure on the $\vec{k}\sim 0$ lattice vibrational modes of ionic crystals. We believe no such experimental results have been reported before. In fact, except for measurements of the pressure dependence of long-wavelength acoustic phonon frequencies of some crystals and a recent indirect measurement[1] on the zone-boundary phonons of Ge, no data seem to be available on the effect of pressure on lattice vibrations. Yet such data are extremely useful in the understanding of anharmonic interactions in solids, especially to distinguish between the purely volume-dependent contribution and the contribution from the various anharmonic terms in the crystal Hamiltonian[2] to the observed shift of phonon frequencies with temperature. The volume dependence of the optic modes also contributes significantly to the coefficient of thermal expansion of a crystal, even though at low temperatures these modes play an unimportant role in determining the specific heat.[3]

Measurements were made with a Perkin-Elmer Model-301 double-beam far-infrared spectrophotometer in conjunction with a modified 6× beam condenser and a high-pressure diamond cell.[4] The experimental arrangement has been described elsewhere.[5] Crystals studied were formed from finely powdered material in the diamond cell by the slow applying of relatively low pressure of up to 1 to 10 kbar and then leaving the material under that pressure for some time (usually between 0.5 and 12 h, depending on the compressibility and flow characteristics of the material). Polycrystals were readily formed (although quite often single crystals were formed) the boundaries of which eventually coalesced into one large crystal, entirely covering the exposed area of the diamond windows. Crystals used in our measurements were about 500 μm in diameter and about 1 μm thick.

The highly convergent and oblique incidence of radiation encountered in the beam condenser enabled one to record the $\vec{k}\sim 0$ longitudinal optic mode (LO) due to Berreman effect,[6] in addition to the $\vec{k}\sim 0$ transverse optic mode (TO). Infrared-transmission measurements were made in the pressure range of about 1 to 50 000 atm. Total absence of any uniaxial-stress-induced splitting confirmed the earlier contention of Weir, Van Valkenburg, and Lippincott[7] that the diamond pressure cells of the type used in this investigation chiefly produce hydrostatic pressure. A typical spectrum is shown in Fig. 1. Figure 2 gives the data on the TO and LO modes of NaF, and the TO modes of ZnS and LiF. The peak positions of the infrared bands are accurate to within ±2 cm^{-1}, whereas the pressure calibration is presumed to be correct to within ±5 %. All measurements were made at 298°K. No hysteresis was noted. Once the crystals formed, results were reproducible within the limits of experimental accuracy independent of the direction of approach of the pressure. The measured phonon frequen-

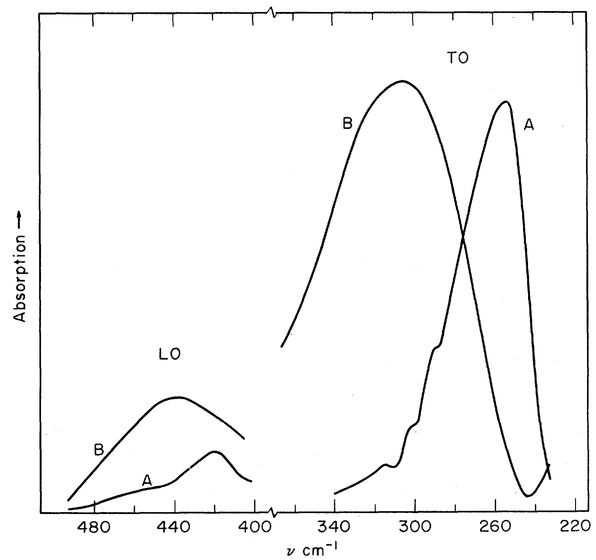

FIG. 1. Infrared-active lattice vibrations of NaF showing absorption due to long-wavelength LO and TO modes at two pressures: *A*, 1.5 kbar; *B*, 42.5 kbar.

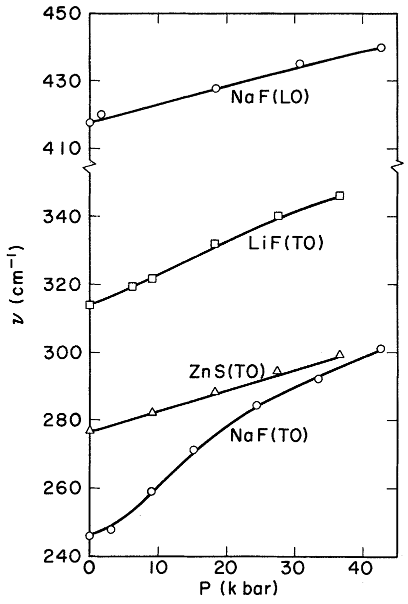

FIG. 2. Effect of pressure on the $\vec{k} \sim 0$ optic mode frequencies of a few ionic crystals.

cies at 1-atm pressure are in agreement with those reported in the literature (LiF,[8,9] NaF,[9] and ZnS[10]). For LiF the measured TO at 1 atm is slightly higher (~8 cm^{-1}) than that obtained by Randall, Fuller, and Montgomery.[9] This discrepancy is not readily understood. However, the small size of the crystal used in the present investigation may be responsible for this slight increase.[11] On the other hand, the agreement for NaF and ZnS is much better.

The volume dependence of $\nu_j(\vec{k})$, the phonon frequency of the jth branch at point $\vec{k}$ in the first Brillouin zone, is given by

$$\gamma_j(\vec{k}) = -\frac{d\ln\nu_j(\vec{k})}{d\ln V}. \tag{1}$$

Within the limits of quasiharmonic oscillator model, the Grüneisen parameter $\gamma_j(\vec{k})$ is expected to be a constant. The Grüneisen parameters for NaF and LiF have been obtained using the P-V data of Drickamer.[12] For ZnS the P-V data of Cline and Stephens[13] were used. Plots of $\ln\nu$ vs $\ln V$ are given in Fig. 3. For NaF, slight deviation from linearity at low pressures may be noted, which may be indicative of a P dependence of $\gamma_j(\vec{k})$. The Grüneisen parameters obtained from the slopes of these lines are given in Table I. One may also obtain an approximate value of γ from isothermal compressibility using the relation

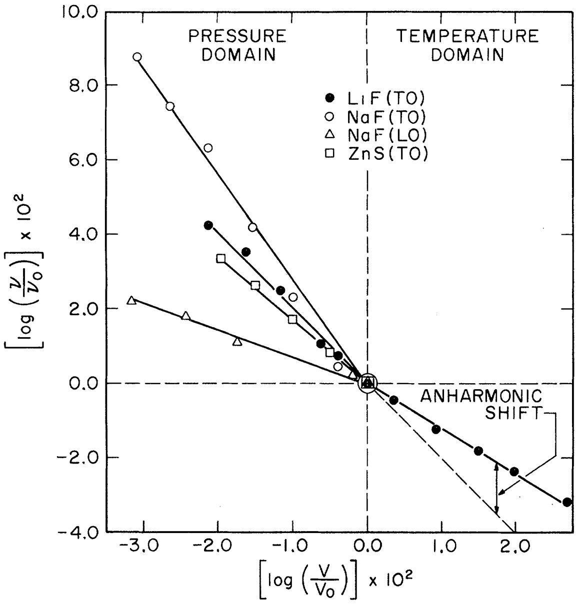

FIG. 3. Plot of $\ln(\nu/\nu_0)$ vs $\ln(V/V_0)$ for a number of optic modes, where ν_0 and V_0 are, respectively, the phonon frequency and volume at 298°K and 1-atm pressure. Data on the left-hand side of the figure are from the present pressure measurements; whereas on the right-hand side, data are from temperature-dependence measurements of Ref. 16.

$$\gamma_j(\vec{k}) = \frac{1}{\chi\nu_j(\vec{k})}\left[\frac{\partial\nu_j(\vec{k})}{\partial P}\right]_T, \tag{2}$$

which is especially suitable when extensive P-V data are not available. γ's obtained from relation (2) are also given in Table I. The experimental values of γ are next compared with those calculated[14] using a rigid-ion model with central forces incorporating repulsion terms of the Born-Mayer $[\exp(-r/p)]$ and inverse-power (r^{-n}) type. Except for ZnS, the agreement is as good as can be expected. The discrepancy in the case of ZnS may be due to the use of a potential which is only valid for an ideally ionic crystal. Bienenstock[3,15] has pointed out that $\gamma_{\rm TO}$ may depend on the coordination number of the crystal. The NaCl structure with a sixfold coordination is thus expected to have a higher $\gamma_{\rm TO}$ than the zincblende structure with a fourfold coordination. It is not unlikely that the γ's for the long-wavelength optic modes may also depend on the ionic character of the crystal. For a homopolar covalent crystal one may not only expect that $\gamma_{\rm TO} = \gamma_{\rm LO}$,

Table I. Observed and calculated Grüneisen parameters for the long-wavelength optic modes.

	Experimental				Calculated[a]			
	From Eq. (1) and Fig. 3		From Eq. (2)[b]		Born-Mayer[c]		r^{-n} repulsion[d]	
Crystal	γ_{TO}	γ_{LO}	γ_{TO}	γ_{LO}	γ_{TO}	γ_{LO}	γ_{TO}	γ_{LO}
LiF	2.15		2.59		2.44	0.88	3.46	0.84
NaF	2.80	0.74	2.95	0.64	2.43	0.86	3.00	0.95
ZnS	1.75		1.85				2.43	0.98

[a] Calculated for rigid ions using repulsive potentials of the Born-Mayer $\exp(-r/\rho)$ and r^{-n} type. For LiF and NaF equations obtained by Mitra (Ref. 14) and for ZnS, those of Bienenstock (Ref. 15) are used.

[b] Estimated approximately from Eq. (2). Isothermal compressibility for LiF and NaF are from M. Born and K. Huang, Dynamical Theory of Crystal Lattices (Oxford University Press, London, 1954), p. 52; for ZnS from Ref. 13.

[c] Potential constants are from M. Born and K. Huang, op. cit., p. 26.

[d] Potential constants are from F. Seitz, Modern Theory of Solids (McGraw-Hill Book Company, New York, 1940, pp. 80-83.

but perhaps that their value be somewhere in between those for an ionic crystal like LiF. For ZnS with a structure closely related to that of diamond and some covalent character in its binding, it is thus not surprising to find its γ_{TO} somewhat smaller than that of LiF or NaF.

For the understanding of the temperature dependence of $\nu_j(\vec{k})$, Eq. (1) is not sufficient, because in addition to the purely volume-dependent part obtainable from the Grüneisen equation of state, one needs to consider[2] the contribution from the various anharmonic (cubic and higher) terms in the potential energy of the lattice. Often the directions of shifts arising from the two effects may be opposite thus resulting in a smaller apparent temperature dependence. The temperature dependence of the TO frequency of LiF has recently been reported by Jasperse, Kahan, Plendl, and Mitra.[16] Their high-temperature data are plotted on a volume scale[17] in the right-hand side of Fig. 3. As is evident from the figure, the straight line extrapolated from the pressure domain does not coincide with the line obtained from temperature measurements. The difference may thus be attributed to a purely anharmonic contribution to the frequency shift, steadily increasing with increasing temperature. It is not known if γ_{TO} and γ_{LO} are temperature dependent in violation of the quasiharmonic approximation.[18] Measurements of the pressure dependence of the long-wavelength optical phonon frequencies at temperatures other than 298°K may thus be interesting and may provide more reliable experimental values for the anharmonic contribution to the temperature shift of these phonons.

Our preliminary measurements on KBr show the expected transition at the onset of CsCl structure. Experimental values for the anharmonic shifts for this crystal are also being obtained for comparison with semiempirical calculations of Cowley.[19] The details of these and related work will be published elsewhere.

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[1] R. T. Payne, Phys. Rev. Letters 13, 53 (1964).

[2] A. A. Maradudin, Phys. Status Solidi 2, 1493 (1963); A. A. Maradudin and A. E. Fein, Phys. Rev. 128, 2589 (1962).

[3] A. Bienenstock, Phil. Mag. 9, 755 (1964).

[4] C. F. Weir, E. R. Lippincott, A. Van Valkenburg, and E. N. Bunting, J. Res. Nat. Bur. Std. 63A, 55 (1959); E. R. Lippincott, F. E. Welsh, and C. E. Weir, Anal. Chem. 33, 137 (1961).

[5] J. R. Ferraro, S. S. Mitra, and C. Postmus, Inorg. Nucl. Chem. Letters 2, 269 (1966).

[6] D. W. Berreman, Phys. Rev. 130, 2193 (1963).

[7] C. E. Weir, A. Van Valkenburg, and E. R. Lippincott in Modern Very High Pressure Techniques, edited

by R. H. Wentorf, Jr. (Butterworths Scientific Publications, Ltd., London, 1962), p. 51.

[8] M. Gottlieb, J. Opt. Soc. Am. 50, 343 (1960).

[9] C. M. Randall, R. M. Fuller, and D. J. Montgomery, Solid State Commun. 2, 273 (1964).

[10] C. Haas and J. P. Mathieu, J. Phys. Radium 15, 492 (1956).

[11] M. Hass, Phys. Rev. Letters 13, 429 (1964).

[12] M. Pagannone and H. G. Drickamer, J. Chem. Phys. 43, 2266 (1965).

[13] C. F. Cline and D. R. Stephens, J. Appl. Phys. 36, 2869 (1965).

[14] S. S. Mitra, Phys. Status Solidi 9, 519 (1965).

[15] A. Bienenstock and G. Burley, J. Phys. Chem. Solids 24, 1271 (1963).

[16] J. R. Jasperse, A. Kahan, J. N. Plendl, and S. S. Mitra, Phys. Rev. 146, 526 (1966).

[17] The thermal expansion data were taken from P. D. Pathak, N. V. Pandya, and M. P. Ghadiali, Indian J. Phys. 37, 293 (1963).

[18] J. C. Slater, Introduction to Chemical Physics (McGraw-Hill Book Company, New York, 1939), Chap. XIII.

[19] R. A. Cowley, Advan. Phys. 12, 421 (1963).

NONLINEAR POLARIZATION OF DIELECTRIC

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Using the relation between polarization $\vec{P}$ and electron displacement $\vec{\xi}$ obtained by Prakash and Vachaspati, it is shown that Adler misses some terms in the polarization due to two simultaneously incident electromagnetic waves because he presumes a linear relation between $\vec{P}$ and $\vec{\xi}$.

It is commonly believed that if the nuclei are too heavy to be disturbed appreciably, the polarization due to electromagnetic field is proportional to the displacement of electrons due to it and one can write[1-3]

$$\vec{P} = -eN_0\vec{\xi}, \tag{1}$$

where $\vec{P} \equiv \vec{P}(\vec{x}, t)$ is the polarization at $\vec{x}$ at time t, $\vec{\xi} \equiv \vec{\xi}(\vec{x}, t)$ is the displacement at $\vec{x}$ at time t, and N_0 is the density of the electrons of charge $-e$. However, it seems obvious that this relation can be true only in first order of approximation because (i) the density of electrons is not constant and its variation should be taken into account, and (ii) there is no a priori reason why $\vec{\xi}(\vec{x}, t)$ should be related to polarization at the original position $\vec{x}$ of the electron and not at its instantaneous position $\vec{x} + \vec{\xi}$. Prakash and Vachaspati[4,5] have recently shown that for a homogeneous dielectric one has

$$P_i = -eN_0\int dt\, [\dot{\xi}_i - (\dot{\xi}_{i,j}\xi_j + \dot{\xi}_i\xi_{j,j}) + \dot{\xi}_i(\xi_{j,j}\xi_{k,k} + \xi_{j,k}\xi_{k,j} + 2\xi_{j,jk}\xi_k) + \dot{\xi}_{i,j}(\xi_j\xi_{k,k} + \xi_{j,k}\xi_k) + \tfrac{1}{2}\dot{\xi}_{i,jk}\xi_j\xi_k + \cdots], \tag{2}$$

where the dot denotes partial differentiation with respect to time, $\xi_{i,j} \equiv \partial\xi_i/\partial x_j$, $\xi_{i,jk} \equiv \partial^2\xi_i/\partial x_j\partial x_k$, etc., and N_0 is the average density of the electrons.

This reduces to Eq. (1) in the first order of approximation. In the second order of approximation, it gives

$$P_i^{(2)} = -eN_0[\xi_i^{(2)} - \int dt\, (\dot{\xi}_{i,j}^{(1)}\xi_j^{(1)} + \dot{\xi}_i^{(1)}\xi_{j,j}^{(1)})] \tag{3}$$

where the superscript gives the order of the quantity. Adler[2] has however used the relation

$$P_i^{(2)} = -eN_0\xi_i^{(2)} \tag{4}$$

to get the second-order terms in $\vec{P}$. He has therefore missed some terms; this can be shown very easily.

If one considers the model of a homogeneous dielectric containing spherically symmetric harmonic oscillators of natural frequency, say ω_0, the polarization due to a field which is in the first order

$$\vec{E} = \sum_i \vec{E}_i \cos\Omega_i, \quad \Omega_i = \omega_i t - \vec{k}_i\cdot\vec{x} \quad (i = 1, 2) \tag{5}$$

$$(|\vec{E}_1| \sim |\vec{E}_2|,\ \vec{E}_i\cdot\vec{k}_i = 0),$$