Pressure-Induced Phonon Frequency Shifts Measured by Raman Scattering

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Pressure shifts of long-wavelength LO and TO phonons of a number of diamond-, zinc-blende-, and wurtzite-type crystals as functions of hydrostatic pressure have been investigated by Raman-scattering measurements. The measured Grüneisen parameters appear to correlate with ionicity. The E_2 modes of CdS and ZnO have also been studied.

ONLY a few attempts have been made so far to investigate the effect of pressure on lattice vibrations: (i) hydrostatic pressure measurements on long-wavelength ($k\sim0$) acoustic phonons[1] by ultrasonic methods, (ii) Brillouin-zone boundary acoustic phonons of RbI[2] and Pb[3] and along the acoustic (00ρ) branches in Ne[4] by neutron scattering, (iii) the shift of optic and acoustic phonons of Ge at the L critical point (CP) under uniaxial stress by tunneling spectroscopy,[5] and (iv) the pressure dependence of long-wavelength optic phonons of ionic crystals measured by infrared transmission of thin crystals held in a high-pressure diamond cell.[6] Inelastic neutron-scattering methods provide, in principle, a versatile technique for measuring phonon energies, but the relatively low resolution limits their use in making quantitative measurements of small energy shifts. The infrared method, although capable of measurements up to 100 kbar, has been limited primarily to $k\sim0$ transverse optic (TO) phonons of ionic crystals with the only exception being the longitudinal optic (LO) phonon of NaF. The reported pressures were approximately hydrostatic with large pressure gradients across the faces of the diamond windows and associated calibration problems.

In this paper, we report the shift of certain phonon frequencies measured by Raman scattering in single crystals under calibrated hydrostatic pressures. The method is general, reliable, and is readily applicable to a variety of solids with Raman-active $k\sim0$ optic modes. Under certain circumstances, it is also capable of measuring the pressure dependence of zone-boundary phonon frequencies from both optic and acoustic branches, e.g., by studying certain polytypes and by measuring multiphonon spectra. Use of cw lasers in the excitation of Raman scattering has made such measurements feasible. The crystals were immersed in a transparent oil contained in an optical pressure cell having perpendicular scattering geometry. The experimental details have been reported in a recent paper[7] describing measurements on phase transitions.

The pressure dependence of the optic phonons of diamond, ZnO, ZnS, ZnSe, ZnTe, CdS, GaP, and SiC has been measured. Diamond belongs to the O_h^7 space group with only one (triply degenerate at $k\sim0$) optic phonon which is Raman-active. ZnS, ZnSe, ZnTe, GaP, and SiC have zinc-blende structure (T_d^2). They are partially ionic with the resultant splitting of the LO and TO branches. Phonons from both of these branches near the center of the Brillouin zone (TCP) are Raman-active. Since these experiments were done with a He-Ne laser, we could only record[8] the LO phonon of ZnS. Both LO and TO phonons of the other zinc-blende–type crystals were studied as functions of pressure. CdS and ZnO belong to the wurtzite structure (C_{6v}^4). With our experimental set up we could only measure the long-wavelength LO and the low-frequency E_2-type phonons of CdS, and the high- and low-frequency E_2 branches of ZnO. The resulting frequency shifts are shown in Fig. 1, where each point represents the average of at least five different measurements. Within the limits of experimental accuracy, no change in half-width with pressure could be detected. The pressure determination is believed to be accurate to ±0.1 kbar and the frequency shift measurement

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within ± 0.1 to ± 0.2 cm^{-1}. The frequency-versus-pressure curves appear linear except for the TO phonon of SiC and the high-frequency E_2 phonon of ZnO.

We shall discuss the pressure dependence of a normal mode frequency in terms of a so-called "mode Grüneisen parameter" defined by $\gamma_i(\mathrm{k}) \equiv -d \ln \nu_i(\mathrm{k})/d \ln V$, where $\nu_i(\mathrm{k})$ is the mode frequency and V is the crystal volume. Within the limitations of the quasiharmonic-oscillator model, $\gamma_i(\mathrm{k})$ is expected to be independent of temperature. The Grüneisen parameter can be determined from the pressure-dependent frequency shift provided the isothermal compressibility χ_T is known:

$$\gamma_i(\mathrm{k}) = \frac{1}{\chi_T \nu_i(\mathrm{k})} \left(\frac{\partial \nu_i(\mathrm{k})}{\partial P} \right)_T . \qquad (1)$$

In some cases the adiabatic compressibility obtained from elastic constant data was more reliable.[9] Since the small difference between the adiabatic and isothermal compressibility is much less than the limit of experimental accuracy, in many cases the former was used without correction.[10] Single-crystal compressibility data[11] were used for all crystals except for SiC. For the latter, measurements have only been made on polycrystalline materials.[12] However, a theoretical calculation by Tolpygo[13] gives values of elastic constants of SiC which were consistent with the polycrystalline values and are used here. The Grüneisen parameters obtained from Eq. (1) are shown in Fig. 2. In many cases the inaccuracy in χ exceeds that of the present experimental error, consequently introducing a large additional uncertainty in γ_i. For example, for the $\mathrm{k} \sim 0$ optic mode of diamond, one obtains $\gamma_i = 0.94 \pm 0.10$ using elastic constant data, while $\gamma_i = 1.20 \pm 0.10$, using χ_T from P-V data.[14] These γ_i values may be compared to a value of 1.29 calculated for Ge by Bienenstock[15] and to 1.23 also for Ge calculated by Dolling and Cowley.[16] On the other hand, a tunneling measurement by Payne[5] for phonons of Ge at the L CP gives $\gamma_{TO}(L) = 0.9$ and $\gamma_{LO}(L) = 1.2$, and these are substantially lower than those calculated by Cowley for the L CP.

The present data indicate three conclusions: (i) The value of γ_{LO} is approximately the same for all compounds investigated; (ii) $\gamma_{TO} \geq \gamma_{LO}$; and (iii) the ratio γ_{TO}/γ_{LO} increases with increasing ionicity as measured by the Szigeti effective charge per valence electron (q^*/Ze). These points are evident from Fig. 2 in which are also shown infrared values[6] for γ_{TO} and γ_{LO} of NaF and γ_{TO} of LiF and ZnS. Conclusion (ii) indicates that as the crystal is compressed, there is a decrease

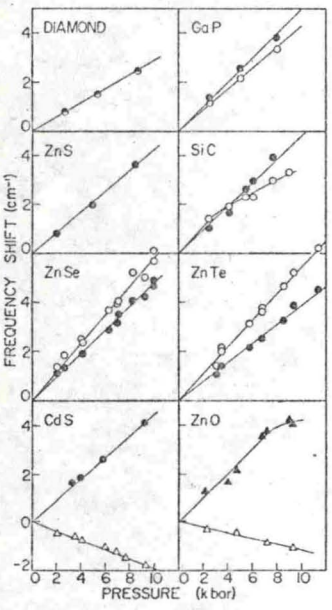

FIG. 1. Frequency shift as a function of pressure for $k \approx 0$ phonons: ⊖, triply-degenerate optic mode; ●, LO mode; ○, TO mode; ▲, high-frequency E_2 mode; △ low-frequency E_2 mode. [The frequencies (in cm^{-1}) at 1-atm pressure are diamond: 1332; GaP: LO=402, TO=364; ZnS: LO=351; SiC: LO=971, TO=795; ZnSe: LO=252, TO=206; ZnTe: LO=206, TO=179; CdS: LO=305, E_2=42; ZnO: E_2=438, 99.]

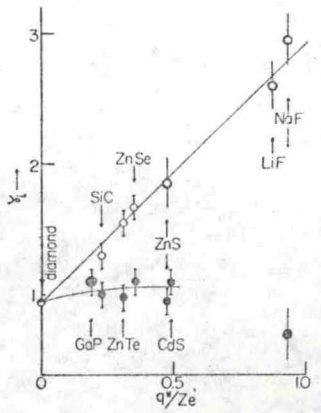

FIG. 2. Optic-mode Grüneisen parameters versus the effective charge per electron. Full and empty circles represent LO and TO modes, respectively; vertical lines show the experimental error; the dotted circles are the infrared values of Ref. 6(a) (the experimental error is not determined, but is estimated to be higher than that of the present measurements).

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in the ratio of LO to TO mode frequencies at k$\sim$0. The Lyddane-Sachs-Teller relation yields the following for the ratio of frequencies: $\nu_{LO}/\nu_{TO}=(\epsilon_0/\epsilon_\infty)^{1/2}$, where ϵ_0 and ϵ_∞ are the low- and high-frequency dielectric constants, respectively. Our results then may be interpreted as indicating that the general "stiffening" of the structure with compression reduces the relative contribution of ionic displacements to the low-frequency dielectric constant. Further, the increase of the ratio γ_{TO}/γ_{LO} with increasing effective charge would follow from the observation that the contribution of ionic motion to ϵ_0 is relatively more important in compounds having higher ionicity.

The trends shown in Fig. 2 can be qualitatively understood from a rigid ion model, in spite of the fact that such a model is only moderately successful for predominantly ionic crystals. For such crystals it can be shown[17] that

$$\gamma_{TO}=\left(-\frac{V_a}{Z^2}\frac{\partial f}{\partial V_a}-\frac{4\pi}{3}\frac{e^{*2}}{V_a}\right)\Big/\left(\frac{2f}{Z^2}-\frac{8\pi}{3}\frac{e^{*2}}{V_a}\right) \quad (2)$$

and

$$\gamma_{LO}=\left(-\frac{V_a}{Z^2}\frac{\partial f}{\partial V_a}+\frac{8\pi}{3}\frac{e^{*2}}{V_a}\right)\Big/\left(\frac{2f}{Z^2}+\frac{16\pi}{3}\frac{e^{*2}}{V_a}\right), \quad (3)$$

where f is the nearest-neighbor force constant, V_a is the unit cell volume, and $e^*=q^*/Z$ is the effective ionic charge per valence electron. Since the nearest-neighbor force constant primarily depends on overlap forces expressible by an inverse-power-type potential, it is expected that f/Z^2 and $(V_a/Z^2)(\partial f/\partial V_a)$ will change relatively only a little from crystal to crystal. For a homopolar crystal like diamond, $e^*=0$, hence $\gamma_{TO}=\gamma_{LO}$, and this value is smaller than γ_{TO} of any crystal with finite effective charge. Since $-\partial f/\partial V_a$ is a positive quantity and $2f$ is larger[18] than $(8\pi/3)\times(e^{*2}/V_a)$, it is obvious that as e^* increases so does γ_{TO}. It does not give a simple explanation[19] to the variation of γ_{LO} with e^*.

The effective ionic charge is expected to remain nearly constant with pressure. In the one extreme case for diamond, both $e^*=0$ and $de^*/dP=0$. In the other extreme case for an ionic crystal like KBr, it may be shown[20] that e^* changes relatively slowly with pressure ($de^*/dP=-0.9\times10^{-3}$ kbar^{-1}). The present data could yield pressure derivations of compressibility and effective charge, provided pressure dependence of low- and high-frequency dielectric constants were available. For diamond, since $e^*=0$, one simply obtains

$$\frac{1}{\nu}\left(\frac{\partial\nu}{\partial P}\right)_T=\frac{(\partial B/\partial P)_T-\frac{1}{3}}{2B}, \quad (4)$$

where B ($=1/\chi$) is the bulk modulus. Using our data for $d\nu/dP$ and a B value of 5.6×10^3 kbar,[14] dB/dP is estimated to be 2.7. This value may be compared to the values 4.35 and 4.16 for Ge and Si, respectively, obtained by Anderson[21] from data on elastic constants.

Finally, a brief comment on the E_2 modes of the wurtzite crystals is in order. For the low-frequency E_2 modes, the Grüneisen parameters are $\gamma=-2.75$ (CdS) and $\gamma=-1.80$ (ZnO). For the high-frequency E_2 mode of ZnO, $\gamma=1.65$. The wurtzite structure is closely related to the zinc-blende structure. The zone-center E_2 modes of the wurtzite structure correspond to the zone-boundary (at the L CP) transverse modes of the zinc-blende structure,[22] the high-frequency branch going over to the TO branch, whereas the low-frequency branch goes over to the transverse-acoustic (TA) branch. The present measurements thus may be regarded as yielding $\gamma_{TA}(L)$ for CdS and ZnO and $\gamma_{TO}(L)$ for ZnO (if these substances were available in the zinc-blende structure). The γ values for the TO branch may not change much with k, thus a value of $\gamma_{TO}=1.65$ for ZnO is quite reasonable when compared with Fig. 2. A negative γ_{TA} at the zone boundary in diamondlike materials is associated with an anomalous negative volume coefficient of thermal expansion.[23] $\gamma_{TA}(L)$ of Ge has also been found[5] to be negative, although considerably smaller (-0.4). For RbI, on the other hand, $\gamma_{TA}(X)$ has been measured[2] to be -3.32. Negative γ values may also indicate a decrease in stiffness of the lattice to a particular mode under compression, preceding a first-order transition.[1] CdS is known to undergo such a transition to NaCl structure around 25 kbar, whereas for ZnO such a transition occurs at much higher pressures (120 kbar). This may be a partial explanation for the fact that γ_i of the low-frequency E_2 mode in CdS has a higher negative value than the corresponding one in ZnO.

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