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# Uniaxial-Stress Dependence of the Raman-Active Phonons in TiO$_2$[†]

P. S. Peercy
*Sandia Laboratories, Albuquerque, New Mexico 87115*

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The uniaxial-stress derivatives of the $B_{1g}$, $E_g$, and $A_{1g}$ Raman-active phonon-mode frequencies of rutile were measured at room temperature. The measurements were combined with previous measurements of the temperature dependences of these three modes to evaluate precisely the anharmonic contributions to the phonon self-energies. Results of the separation of the isobaric frequency shifts of the phonon modes into pure-volume and pure-temperature contributions are compared with similar results based on a cubic approximation. We conclude that the cubic approximation is valid to ∾ 10% for the Raman-active modes in this material.

## I. INTRODUCTION

Anharmonic interactions among the phonons are known to be important in the lattice dynamics of crystals.[1,2] Effects of these anharmonicities are observed in the temperature dependences of the normal-phonon-mode frequencies and linewidths. The temperature dependences of the frequencies arise from two different contributions: (i) There is a pure-volume contribution associated with the thermal expansion of the crystal; (ii) there is a pure-temperature contribution which would occur even if the volume of the crystal were held constant. Measurement of the isobaric temperature dependence of the phonons yield frequency shifts produced by a combination of these two effects.

Recently there has been considerable work in the area of separating the isobaric frequency shifts into their pure-volume (thermal expansion) and pure-temperature ("higher-order anharmonic") contributions. The procedure used is to combine measurements of the isobaric temperature dependences of the phonon frequencies with measurements of the hydrostatic pressure dependences of the same phonon frequencies along with the volume thermal expansivity and isothermal volume compressibility. The results are then compared with perturbation calculations such as those by Maradudin and Fein[1] and by Cowley[2] in an attempt to determine the origin of the higher-order (cubic or quartic) anharmonicities.

While this procedure is valid for cubic or isotropic symmetry, difficulties are encountered in applying a procedure appropriate to cubic (or isotropic) symmetry to crystals of lower symmetry. This difficulty was noted by Samara and Peercy[3] in measurements of the dielectric constants and Raman-active phonons in rutile (TiO$_2$) which has tetragonal symmetry (space group $P\,4/mmm$) and was recently considered in greater detail by Fritz[4] in the analysis of elastic-constant measurements in rutile. While Samara and Peercy[3] made arguments (based on the fact that the changes in $c/a$ with either temperature or pressure were small compared with the corresponding changes in volume) that equations appropriate to cubic symmetry were a reasonable approximation for rutile, calculations by Fritz[4] demonstrated that, in principle, the error made in using such an approximation could be appreciable. We have, therefore, measured the *uniaxial* stress dependences of the Raman-active-phonon frequencies to evaluate the anharmonic contributions to the phonon self-energies more precisely and to determine the magnitude of the error introduced by assuming the validity of the cubic approximations for rutile.

## II. THEORETICAL CONSIDERATIONS

In a cubic or isotropic system an isobaric phonon-frequency shift arises from two contributions: (i) a frequency shift which arises from a change in density i.e., an explicit volume contribution, and (ii) a frequency shift which would occur even if the volume of the crystal were held constant, i.e., an explicit temperature contribution. Writing $\omega = \omega(V, T)$ yields

$$\left(\frac{\partial \ln\omega}{\partial T}\right)_P = \left(\frac{\partial \ln\omega}{\partial \ln V}\right)_T \left(\frac{\partial \ln V}{\partial T}\right)_P + \left(\frac{\partial \ln\omega}{\partial T}\right)_V$$

$$= -\frac{\beta_v}{\kappa_v}\left(\frac{\partial \ln\omega}{\partial P}\right)_T + \left(\frac{\partial \ln\omega}{\partial T}\right)_V \,, \qquad (1)$$

where $\beta_v$ is the volume thermal-expansion coefficient and $\kappa_v$ is the volume compressibility. Measurements of the isobaric frequency shifts and the hydrostatic pressure derivatives combined with $\beta_v$ and $\kappa_v$ therefore yield the pure-temperature $[(\partial\ln\omega/\partial T)_V]$ and pure volume $[-(\beta_v/\kappa_v)(\partial\ln\omega/\partial P)_T]$ contributions. As indicated above, however, Eq. (1) is not valid for the present tetragonal system since $\omega$ is also a function of $c/a$. Alternatively, we may write $\omega = \omega(a, c, T)$ and application of the standard chain rule for differentiation yields[4]

$$\left(\frac{\partial \ln\omega}{\partial T}\right)_P = 2\left(\frac{\partial \ln\omega}{\partial \ln a}\right)_{c,T}\left(\frac{\partial \ln a}{\partial T}\right)_P$$

$$+\left(\frac{\partial \ln\omega}{\partial \ln c}\right)_{a,T}\left(\frac{\partial \ln c}{\partial T}\right)_{P}+\left(\frac{\partial \ln\omega}{\partial T}\right)_{V}\ . \qquad (2)$$

In general, Eqs. (1) and (2) are not equivalent. Adding a term $\alpha$ to the right-hand side of Eq. (1) to correct this expression for the $c/a$ dependence, equating the resulting expression to the right-hand side of Eq. (2), and noting that

$$\left(\frac{\partial \ln\omega}{\partial P}\right)_{T}=2\left(\frac{\partial \ln\omega}{\partial \ln a}\right)_{c,T}\left(\frac{\partial \ln a}{\partial P}\right)_{c,T}+\left(\frac{\partial \ln\omega}{\partial \ln c}\right)_{a,T}\left(\frac{\partial \ln c}{\partial P}\right)_{a,T} \qquad (3)$$

yields[4]

$$\alpha=\frac{2(\beta_a\kappa_c-\beta_c\kappa_a)}{\kappa_v}\left[\left(\frac{\partial \ln\omega}{\partial \ln a}\right)_{c,T}-\left(\frac{\partial \ln\omega}{\partial \ln c}\right)_{a,T}\right]\ . \qquad (4)$$

In Eq. (4), $\beta_a$, $\beta_c$ and $\kappa_a$, $\kappa_c$ are the axial thermal expansivities and compressibilities, respectively. In principle, $|\alpha|$ can be appreciable compared to $|(\beta_v/\kappa_v)(\partial \ln\omega/\partial P)_T|$. Hence, to evaluate precisely the pure-temperature contribution, the uniaxial stress derivatives are required.

If a uniaxial stress $-\sigma_3$ is applied along the $c$ axis, the resulting strains $\epsilon_i$ for $D_{4h}$ symmetry are

$$\epsilon_1=\epsilon_2=-s_{13}\sigma_3\ ,\quad \epsilon_3=-s_{33}\sigma_3\ ;$$

similarly, the resulting strains for a compressive stress $-\sigma_1$ along an $a$ axis are

$$\epsilon_1=-s_{11}\sigma_1\ ,\quad \epsilon_2=-s_{12}\sigma_1\ ,\quad \epsilon_3=-s_{13}\sigma_1\ ,$$

where the $s_{ij}$ are the compliances. If no torques are introduced by the experimental arrangement, $\epsilon_4=\epsilon_5=\epsilon_6=0$. Again, applying the chain rule for differentiation and using these values for the strain, we have

$$\left(\frac{\partial \ln\omega}{\partial \sigma_3}\right)_{T}=-2s_{13}\left(\frac{\partial \ln\omega}{\partial \ln a}\right)_{c,T}-s_{33}\left(\frac{\partial \ln\omega}{\partial \ln c}\right)_{a,T} \qquad (5)$$

and

$$\left(\frac{\partial \ln\omega}{\partial \sigma_1}\right)_{T}=-(s_{11}+s_{12})\left(\frac{\partial \ln\omega}{\partial \ln a}\right)_{c,T}-s_{13}\left(\frac{\partial \ln\omega}{\partial \ln c}\right)_{a,T}\ . \qquad (6)$$

It is of interest to compare Eq. (3) with Eqs. (5) and (6). Noting that for the present symmetry $\kappa_a=s_{11}+s_{12}+s_{13}$ and $\kappa_c=s_{33}+2s_{13}$, Eq. (3) yields

$$\left(\frac{\partial \ln\omega}{\partial P}\right)_{T}=-2(s_{11}+s_{12}+s_{13})\left(\frac{\partial \ln\omega}{\partial \ln a}\right)_{c,T}-(s_{33}+2s_{13})\left(\frac{\partial \ln\omega}{\partial \ln c}\right)_{a,T}\ , \qquad (7)$$

which is identical to the result one gets by adding $(\partial \ln\omega/\partial\sigma_3)_T$ from Eq. (5) to $2(\partial \ln\omega/\partial\sigma_1)_T$ from Eq. (6). Therefore, the uniaxial-stress measurements, when combined with $(\partial \ln\omega/\partial T)_P$, give all of the information required to evaluate $(\partial \ln\omega/\partial T)_V$ and the hydrostatic-pressure measurements are superfluous. They do, however, provide a valuable check on the results of the more difficult uniaxial-stress measurements through the relationship pointed out immediately above.

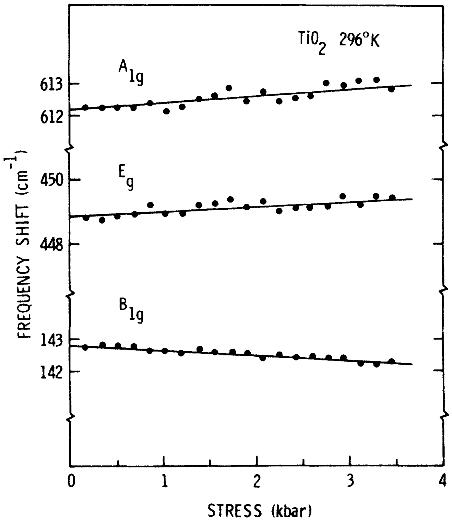

FIG. 1. Frequency shifts for uniaxial stress along the $a$ axis.

TABLE I. Uniaxial-stress and hydrostatic-pressure dependences for the Raman-active modes in TiO$_2$. Also included are the corrections $\alpha$ for these modes.

| Sym | $\omega$ (cm$^{-1}$) | $(\partial \ln\omega/\partial\sigma_3)_{aT}$ ($10^{-3}$/kbar) | $(\partial \ln\omega/\partial\sigma_1)_{cT}$ ($10^{-3}$/kbar) | $(\partial \ln\omega/\partial P)_T$ ($10^{-3}$/kbar) | $\alpha$ ($10^{-5}$/°K) |
|---|---|---|---|---|---|
| $B_{1g}$ | 143 | $-0.2\pm0.1$ | $-1.2\pm0.2$ | $-2.6\pm0.5^{a}$<br>$-2.4\pm0.2^{b}$ | 0.6 |
| $E_g$ | 449 | $0.4\pm0.1$ | $0.4\pm0.1$ | $1.2\pm0.3^{a}$<br>$1.15\pm0.2^{b}$ | 0.4 |
| $A_{1g}$ | 612 | not measured | $0;4\pm0.1$ | ...<br>$0.75\pm0.2^{b}$ | $0.05^{c}$ |

[a] Calculated assuming $(\partial \ln\omega/\partial P)_T=2(\partial \ln\omega/\partial\sigma_1)_{cT}+(\partial \ln\omega/\partial\sigma_3)_{a,T}$.

[b] Reference 3.

[c] Calculated assuming $(\partial \ln\omega/\partial\sigma_3)_{a,T}=0.15\times10^{-3}$/kbar.

## III. EXPERIMENTAL CONSIDERATIONS

The experimental arrangement, with the exception of the pressure system, has been described elsewhere.[3] The uniaxial-stress apparatus was basically very simple: Compressive force is applied by means of a micrometer adjustment to a sample held between two optically flat nickel maraging steel plates and measured on a W. C. Dillon model $U$ force gauge.[5] The micrometer and gauge were contacted to the plates with ball bearings to help assure uniaxial stress and light-weight oil was used between the sample surfaces and the plates in an attempt to relieve any nonuniaxial components of force which build up because of changes in the sample dimensions with pressure.

TABLE II. Separation of the isobaric frequency shifts into their pure-volume and pure-temperature dependences using the results of the uniaxial-stress measurements and comparison with the corresponding analysis for hydrostatic-pressure results (numbers in parentheses). $\delta(V)$ is the pure-volume contribution.

| Sym. | $\omega$ (cm$^{-1}$) | $(\partial \ln\omega/\partial T)_P =$ (10$^{-5}$/°K) | $\delta(V)$ (10$^{-5}$/°K) | $+ (\partial \ln\omega/\partial T)_V$ (10$^{-5}$/°K) |
|---|---|---|---|---|
| $B_{1g}$ | 143 | 0.6 ± 0.4 | 12.4<br>(11.8)[a] | −11.8<br>(−11.2)[a] |
| $E_g$ | 449 | −6.3 ± 0.4 | −6.1<br>(−5.7)[a] | −0.2<br>(−0.6)[a] |
| $A_{1g}$ | 612 | 0.6 ± 0.4 | −3.7<br>(−3.7)[a] | 4.3<br>(4.3)[a] |

[a] Values assuming a cubic approximation (Ref. 3).

Samples were cut from the same boule as the samples previously used for hydrostatic-pressure measurements of the Raman spectra[3] and elastic constants.[4] The sample dimensions were typically 0.35×0.35×0.15 cm and the stress was applied normal to the large faces which were polished optically flat and parallel. For stress along the *c* axis, the edges were cut 45° to the axes to allow observation of the *xx*-*yy* component of the polarizability tensor ($B_{1g}$ mode). Since the experimental geometry was such that the incident and scattered light propagation directions were normal to each other and both normal to the direction of the stress, the $A_{1g}$ mode was not observed for stress along the *c* axis. The $A_{1g}$ mode was only observed for stress along an *a* axis where the sample faces were cut normal to the crystal axes. The complete measurements consisted of the stress dependence of $\omega(B_{1g})$, $\omega(E_g)$, and $\omega(A_{1g})$ for stress along *a* and $\omega(B_{1g})$ and $\omega(E_g)$ for stress along *c*. No attempt was made to study the weak $B_{2g}$ mode.

## IV. RESULTS AND DISCUSSION

The uniaxial-stress dependences are shown in Fig. 1 for compressive stress along the *a* axis. Results for stress along the *c* axis are similar. There are two points to note about the data. First, the sign of the frequency shift is the same for each mode with stress along either *c* or *a* as it is with hydrostatic pressure which implies that the correction term $\alpha$ will be small in all cases. Second, the frequency shifts are very small. This is not surprising when one considers the implications of Eqs. (5)–(7)—i.e., since all modes have frequency shifts of the same sign with uniaxial stress as with hydrostatic pressure, the uniaxial pressure shifts are expected to be on the order of $\frac{1}{3}$ the magnitude of the hydrostatic-pressure shifts.

The pressure derivatives obtained from a least-squares fit to these data assuming a linear stress dependence are given in Table I. In the two cases ($B_{1g}$ and $E_g$) where both *c* and *a* stress measurements were made, the uniaxial and hydrostatic data agree within the experimental uncertainty. The uncertainty (one standard deviation from the least-squares fit) is rather large for the uniaxial stress measurements because of the small frequency shifts. The values of $\alpha$ which result are also listed in this table. To compute $\alpha$ we have used linear thermal expansivities determined from the measurements of the temperature dependence of the lattice constants by Mauer and Botz of the U. S. National Bureau of Standards and compliances obtained from the elastic constants measured by Fritz[4] on material cut from the same boule as was used in the present measurements. To evaluate $\alpha$ for the $A_{1g}$ mode, it was assumed that $(\partial \ln\omega/\partial P_c)_{a,T}$ could be evaluated from the relation

$$(\partial \ln\omega/\partial P_c)_{a,T} = (\partial \ln\omega/\partial P)_T - 2(\partial \ln\omega/\partial P_a)_{c,T} .$$

The separation of the isobaric frequency shifts of the Raman-active modes into their pure-temperature and pure-volume contributions at room temperature is shown in Table II. The values obtained for these quantities assuming a cubic approximation are included (in parentheses) for comparison. These results indicate that the cubic approximation is valid to ≲10% for each of the modes. This difference is comparable to the uncertainty in the uniaxial-stress measurements. In view of the similarity of the isobaric temperature and hydrostatic pressure dependences between $TiO_2$ and $SnO_2$[6] as well as the isomorphous fluorides[7] $MnF_2$ and $NiF_2$ it is felt that the cubic approximation may also be reasonably valid for the analysis of anharmonicities in the Raman-active modes of these materials; however, no conclusions can be made concerning the validity of the cubic approximation for the elastic constants.

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