Grüneisen tensors of quartz

A comment on 'Quartz under stress: Raman calibration and applications to geobarometry of metamorphic inclusions' by Reynard and Zhong,
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Motivation

The manuscript by Reynard and Zhong describes measurements of the changes in the frequencies of Raman lines of quartz under hydrostatic pressure and also non-hydrostatic stress in two different experiments. These measurements are potentially valuable for the interpretation of the Raman shifts of quartz inclusions trapped inside other mineral hosts in terms of the stress state of the inclusion, from which the entrapment conditions of the inclusion can be constrained (e.g. Kohn 2014; Angel et al. 2017; Zhong et al. 2020; Gilio et al. 2021). It has previously been proposed that the Raman shifts of minerals under deviatoric stress can be interpreted in terms of the phonon-mode Grüneisen tensors (e.g. Angel et al. 2019), and that the values of the components of the tensors can be determined by conducting ab initio Hartree-Fock/ Density Functional Theory (HF/DFT) simulations of crystal structures under different stress/strain conditions (Murri et al. 2019; Stangarone et al. 2019; Musiyachenko et al. 2021).

Reynard and Zhong conclude from their work that the values of the components of the phonon-mode Grüneisen tensors of quartz obtained from HF/DFT are incorrect and further conclude that the use of these tensors to describe the shift in Raman frequencies under stress is not appropriate. In this comment I will clearly separate and discuss two distinct issues:

1) Whether or not the phonon-mode Grüneisen tensor is the correct physical description of the change in Raman frequencies of a crystalline solid under deviatoric stress, and what its known limitations are.

2) Whether or not the values of the components of the phonon-mode Grüneisen tensors determined by HF/DFT or by experiment agree, and if these values are correct.

Phonon-mode Grüneisen tensors

Phonon-mode Grüneisen tensors are simply the anisotropic generalisation of the concept of phonon-mode Grüneisen parameters which are well-established as the appropriate description of the relationship between the change in the wavenumbers of phonon modes with strain. Each phonon mode *m* with a wavenumber ω^m is associated with a volume Grüneisen parameter γ_V^m defined as:

$$\gamma_V^m = \frac{-V}{\omega^m}\frac{d\omega^m}{dV} \qquad (1)$$

Thus, the values of the volume phonon-mode Grüneisen parameters can be determined from an experiment in which wavenumbers of phonons are measured, for example by Raman spectroscopy, while the volume of the crystal is changed, for example in a high-pressure experiment or an experiment in which the temperature of the crystal is changed.

The anisotropic extension of equation (1) requires that instead of considering the volume strain $\frac{dV}{V}$, the change in the shape of a crystal must be considered. This is described by the strain tensor, ε_{ij}, which is a symmetric second rank tensor (Nye 1957). Because the wavenumber ω^m of a phonon mode is a scalar, the volume phonon-mode Grüneisen parameter must be replaced in (1) by a second-rank symmetric tensor, so that:

$$\frac{-d\omega^m}{\omega_0^m} = \boldsymbol{\gamma^m} : \boldsymbol{\varepsilon} \tag{2}$$

The ":" in Equation (2) indicates a double-scalar product between the two tensors, which can be written out in terms of their components as:

$$\begin{aligned}\frac{-d\omega^m}{\omega_0^m} = \gamma_{11}^m\varepsilon_{11} + \gamma_{22}^m\varepsilon_{22} + \gamma_{33}^m\varepsilon_{33} + +\gamma_{23}^m\varepsilon_{23} + \gamma_{32}^m\varepsilon_{32} + +\gamma_{13}^m\varepsilon_{13} \\ + \gamma_{31}^m\varepsilon_{31} + \gamma_{12}^m\varepsilon_{12} + \gamma_{21}^m\varepsilon_{21}\end{aligned} \tag{3}$$

Both tensors are symmetric (Nye 1957; Angel et al. 2019) and therefore $\varepsilon_{ij} = \varepsilon_{ji}$ and $\gamma_{ij}^m = \gamma_{ji}^m$ for each pair of non-diagonal elements, so:

$$\frac{-d\omega^m}{\omega_0^m} = \gamma_{11}^m\varepsilon_{11} + \gamma_{22}^m\varepsilon_{22} + \gamma_{33}^m\varepsilon_{33} + 2\gamma_{23}^m\varepsilon_{23} + 2\gamma_{13}^m\varepsilon_{13} + 2\gamma_{12}^m\varepsilon_{12} \tag{4}$$

We can reduce these tensors to a vector form in which the double-scalar product in Equation (2) becomes a scalar product of two vectors that represent the $\boldsymbol{\gamma^m}$ and the $\boldsymbol{\varepsilon}$ tensors. Under the Voigt convention, the normal strain components are equal in magnitude to the diagonal components of the tensor, e.g. $\varepsilon_1 = \varepsilon_{11}$, while the shear strains $\varepsilon_4, \varepsilon_5, \varepsilon_6$ are one-half of the values of the corresponding tensor components $\varepsilon_{23}, \varepsilon_{13}, \varepsilon_{12}$. Therefore, if we set γ_4^m, γ_5^m and γ_6^m equal to the values of the corresponding tensor components $\gamma_{23}, \gamma_{13}, \gamma_{12}$, we obtain an expression exactly equivalent to (4):

$$\frac{-d\omega^m}{\omega_0^m} = \gamma_1^m\varepsilon_1 + \gamma_2^m\varepsilon_2 + \gamma_3^m\varepsilon_3 + \gamma_4^m\varepsilon_4 + \gamma_5^m\varepsilon_5 + \gamma_6^m\varepsilon_6 \tag{5}$$

The introduction of a factor of ½ into the strain vector components and not into the Grüneisen vector components avoids factors of 2 appearing for the terms with subscripts *i* = 4,5,6 in the matrix version (5) of the tensor equation (2).

Because the phonon-mode Grüneisen tensors are properties of the crystal they are subject to the symmetry of the crystal. For this reason, the trigonal symmetry of quartz means that $\gamma_1^m = \gamma_2^m$ and $\gamma_4^m = \gamma_5^m = \gamma_6^m$ for each mode, so that each mode in quartz has only two unique non-zero components of its phonon-mode Grüneisen tensor, $\gamma_1^m \neq \gamma_3^m$. and thus equation (5) is reduced for quartz to:

$$\frac{-d\omega^m}{\omega_0^m} = \gamma_1^m(\varepsilon_1 + \varepsilon_2) + \gamma_3^m\varepsilon_3 \quad (6)$$

Both the validation of this description for how the Raman frequencies of quartz change with stress or temperature, and the values of the components γ_1^m and γ_3^m for quartz can only be determined by experimental measurements or ab-initio simulations of quartz.

Is the Grüneisen approach correct in principle?

Both the isotropic (equation 1) and the anisotropic version (equations 3-5 in general, and 6 for quartz) predict that the changes in Raman mode shifts are linear with strain. For small strains, $\varepsilon_1 + \varepsilon_2 + \varepsilon_3 = \frac{dV}{V}$, so the isotropic and anisotropic approaches are consistent in this prediction. A further implication of this approach is that the phonon frequencies are a function of the strains of the crystal alone, and not of temperature or pressure. Therefore, if the Grüneisen approach is correct, a plot of any Raman frequency against the volume should lie on a single trend that is linear in volume, and this is observed for many modes of many crystals, including quartz (e.g. Murri et al. 2018).

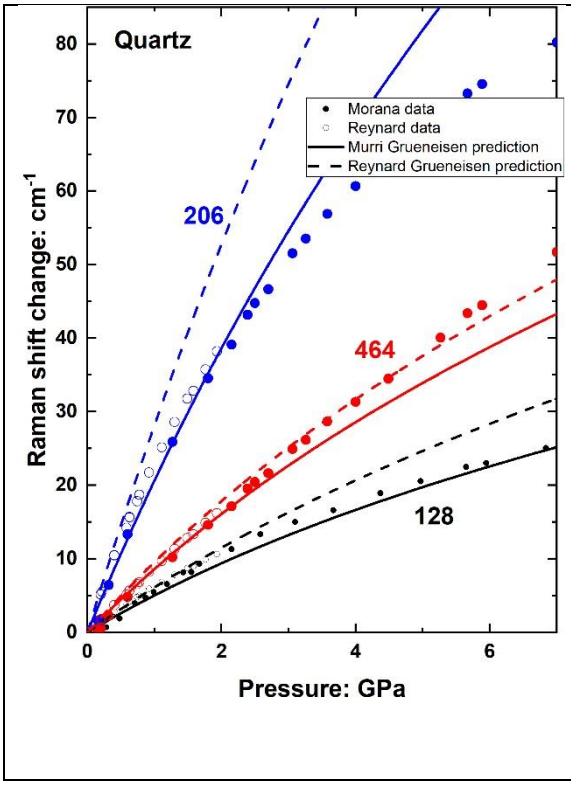

Figure 1. Symbols show the measured changes in Raman shift under hydrostatic pressure from the experimental data of Morana et al. (2020) and Reynard and Zhong. The lines are the predicted shifts calculated from the measured unit-cell parameters of quartz under pressure (Scheidl et al. 2016) and the published Grüneisen tensor components of Murri et al. (2019) as solid lines and Reynard and Zhong (their Table 1) as dashed lines.

Note that the two sets of experimental data are very similar, as are the predicted shifts for the 128 and 464 lines which agree with the measured data up to ca. 2 GPa, a pressure greater than that found in quartz inclusions. The prediction of the 206 line from Reynard and Zhong does not describe the measured pressure evolution of this mode.

For small stresses, within the linear elastic regime where the strains are related to the applied stresses σ_j (again in Voigt notation) by the elastic compliance matrix s_{ij} as $\varepsilon_i = s_{ij}.\sigma_j$, the Raman shifts are predicted to change linearly with applied stress, as shown by Reynard and Zhong (their Fig 3c) and others (e.g. Tekippe et al. 1973; Briggs and Ramdas 1977; Barron et al. 1982). At high pressures, such as achieved in a DAC, the strains are no longer linearly proportional to the applied stress and instead the stress-strain relationship is described by non-linear equations of state. Thus, the Grüneisen approach implicitly predicts that Raman shifts will change non-linearly with pressure because of the non-linearity of strains with

pressure, even if the Grüneisen parameters or tensor components remain invariant with pressure. This is what is commonly observed in measurements of Raman shifts of crystals under hydrostatic pressure in diamond-anvil cells, including those of Reynard and Zhong (Fig. 1).

Further, for quartz and zircon, the mode Grüneisen parameters determined from HF/DFT simulations predict, in combination with the measured strains as a function of pressure, the experimentally measured changes in Raman frequencies with pressure (see my Fig. 1 for quartz). This agreement extends to volumes strains of ca. 4 % in both quartz (Murri et al. 2019) and zircon (Stangarone et al. 2019), corresponding to pressures of, respectively, 2 and 8 GPa. The mode Grüneisen parameters calculated for the 128 and 464 modes by Reynard and Zhong also show the same agreement (Fig. 1).

This brief discussion shows that there is substantial experimental evidence to indicate that the principles behind the Grüneisen approach are valid.

Potential limitations of the Grüneisen approach

We now consider possible limitations to the *extent* of its applicability, because if Grüneisen theory is found to be a valid description of the behaviour of minerals in the range of stresses and strains found in natural inclusions, as Figure 1 suggests, then it will be a useful tool in geology.

The first potential limitation is that it assumes a linear relationship between the phonon frequencies and the strains of the crystal. This may break down for several reasons. The first is already illustrated by Figure 1, that shows for pressures above ca. 2 GPa for quartz, the Raman shifts diverge from the prediction of the phonon-mode Grüneisen tensors. As noted above, this corresponds to about 4% in volume compression, and about 1.3% in linear strains. The same limiting strain value is found for zircon (Stangarone et al. 2019). This is not a breakdown of the Grüneisen approach, but simply requires an extension to non-linear relationships. This would be entirely analogous to the fact that the linear relationship between stress and strain breaks down at quite modest stresses (pressures) and the relationship must be described by non-linear EoS. But this is not a limitation to the method for interpreting Raman spectra of natural quartz inclusions as they exhibit pressures of less than 1.5 GPa.

There is also evidence from HF/DFT simulations (Murri et al. 2019) that at large strains some modes, and especially those involved in soft mode phase transitions such as the α–β transition in quartz, become non-linear in strain. Leaving aside other considerations, the physical properties of a mineral such as quartz change rapidly as the α–β transition is approached; for example the bulk modulus of quartz drops to zero at the transition (Lakshtanov et al. 2007) and other properties such as the heat capacity and thermal expansion coefficient diverge towards infinite values (e.g. Carpenter et al. 1998; Murri and Prencipe 2021). Given that the thermal expansion and heat capacity depend on the phonon frequencies, it would be entirely expected that the relationship between those frequencies and the cell parameters and strain may also become non-linear near to the phase transition.

The phonon-mode wavenumbers depend upon the interactions between the atoms within the crystal, which depend in part on the distances between them. One can associate the changes in phonon-mode wavenumbers with changes in the inter-atomic distances. For simple

structures, such as the rock salt structure in which all of the atoms have fixed coordinates within the unit cells, changes in inter-atomic distances are determined by the change in the unit-cell parameters alone. Therefore, there is good reason to expect a direct linear relationship between phonon-mode wavenumbers and unit-cell strains. However, in more complex structures such as quartz, the atom coordinates within the unit cell are independent variables. Therefore, there is no a-priori physical reason why the strains (fractional length changes) of inter-atomic distances or bonds should scale with the unit cell strains; indeed certain structural elements such as SiO_4 tetrahedra have much higher bulk moduli than the mineral structures that they form. Experimental determinations of bond lengths by diffraction methods is challenging because of both the small changes involved and the role of correlated thermal motion that prevents diffraction returning true local bond lengths (e.g. Busing and Levy 1964; Downs et al. 1992) especially in open framework structures such as quartz (Kihara 1990; 2001; Kimizuka et al. 2003; Murri et al. 2019). On the other hand, HF/DFT simulations do suggest that at low temperatures away from the $\alpha-\beta$ transition, that the real inter-atomic distances scale approximately linearly with the unit-cell strains (Murri et al. 2019). The same was found for zircon (Stangarone et al. 2019). Therefore, the internal degrees of freedom in mineral structures do not appear to create a significant limitation to the Grüneisen approach.

The Grüneisen relationship in terms of stress

For linear elasticity the Grüneisen relationships, both isotropic and anisotropic, can be written directly in terms of stress, by using the linear relationship between stress and strain, as Reynard and Zhong do. This is not wrong, but has two major disadvantages:

First: that it is not immediately obvious from the components of the stress tensor whether or not the symmetry of the crystal has been broken. This is important, because when the symmetry of the crystal is broken by the stress, then the forces and distances between the atoms are changed and the symmetries and frequencies of the phonon modes therefore change. Since the phonon-mode Grüneisen tensor is a property tensor and is therefore subject to the symmetry of the crystal (Eqn. 6) it only describes the changes in phonon-mode wavenumbers when the symmetry of the crystal is preserved. Therefore, a phonon-mode Grüneisen tensor of quartz calculated for trigonal symmetry is not expected to predict the wavenumber shifts of a quartz crystal whose symmetry has been broken by applied stress (Murri et al. 2022), and this is a problem in the analysis of Reynard and Zhong. They describe two non-hydrostatic stress experiments, one with stress applied along the c-axis of quartz, and the second with the stress applied perpendicular to the c-axis. In the first case, the only non-zero component of the stress vector is σ_3. For the second case Reynard and Zhong provide insufficient information about crystal orientations and the Cartesian axis convention used to determine the values of σ_1 and σ_2. What is however certain is that in this experiment the non-zero components of the stress field are some combination of σ_1 and σ_2, but they are not required to be equal (note this contradicts the statement made on lines 154-155 of Reynard and Zhong). In neither case is it obvious what is the symmetry of the quartz crystal under these stresses. If we convert these stresses into strains, then the answer is obvious. The first stress field induces strains $\varepsilon_1 = \varepsilon_2 \neq \varepsilon_3$ and the symmetry is preserved. The second, if the stress is just $\sigma_1 \neq 0$, $\sigma_2 = \sigma_3 = 0$, will produce a compressive strain along the Cartesian X axis, and expansion along the Cartesian Y and Z axes. Therefore, if we assume that the Cartesian X-axis is aligned along the crystallographic a-axis, the a-axis will be

shortened, while the crystallographic b and c parameters will be expanded. Unequal strains along the crystallographic a- and b-axes accompanied necessarily by a shear strain thus will result from all uniaxial stresses applied to quartz perpendicular to the c-axis. Therefore, the symmetry will be broken and the use of the trigonal phonon-mode Grüneisen tensors is not valid. Further, such a symmetry reduction does not result in LO-TO splitting of the E modes as claimed by Reynard and Zhong, but the generation of a pair of modes with different wavenumbers from the doubly-degenerate E modes of the parent trigonal structure. If the strained structure has monoclinic symmetry (as would occur for stress applied exactly along the crystallographic a-axis) the parent E mode splits into one A and one B mode. For other stress directions, the strained structure has triclinic symmetry and the E modes of the parent structure split into a pair of A modes (Tekippe et al. 1973; Murri et al. 2022). In both cases, each of these modes has an LO and TO component.

Note also that the LO-TO splitting in general of the E modes in quartz does not require the application of stress. The LO and TO components can be easily resolved in a well oriented crystal under certain scattering geometries, although the scattering geometry used by Reynard and Zhong is not specified. However, the E mode near 128 cm^{-1} is the only one for which the LO-TO splitting cannot be resolved in unstressed quartz. Therefore, the evidence of splitting of this Raman peak into two different peaks requires symmetry breaking; the splitting of the 128 E mode reported by Reynard and Zhong is therefore not the TO-LO splitting of one parent E mode, but two different modes under the broken symmetry, neither of which can be expected to have properties predicted by the trigonal properties and Grüneisen tensors of quartz.

The second problem in using the applied stress as a basis for predicting changes in Raman or other phonon frequencies, as illustrated by the text of Reynard and Zhong, is that it is linear in the stresses (their equation 4, and equation 7 here). As I have stated above, apart from identifying symmetry breaking, under linear elasticity the relationship between mode wavenumbers written in terms of stress is entirely equivalent to that written in terms of strain. However, the changes in wavenumbers with large stress, as illustrated by the experiments under hydrostatic pressure, are non-linear (Fig. 1). If the wavenumber shifts are expressed in terms of pressure, then this requires two separate analyses for small stresses and large stresses, and the cross-over point from one approach to the other is not defined; indeed such an approach suggests that the behaviour of solids under small single stresses and under significant hydrostatic pressure is fundamentally different. This is not correct. In contrast, the expression of wavenumber shifts in terms of strains has the great advantage that the non-linearity of wavenumber shift with high pressures emerges automatically and naturally not as a change in behaviour but simply as a consequence of the non-linearity of strains with pressure (Fig. 1).

Thus, we see that a description of an experiment, and the Grünesien relationship, in terms of strain leads to a clear identification of symmetry-breaking and thus the applicability or otherwise of the phonon-mode Grüneisen tensors. And it unifies the physical description of the response of the Raman modes to both small stresses and large hydrostatic pressure.

Values of the components of the Grüneisen tensors

Having established that there is sufficient experimental evidence that the Grüneisen theory of solids can predict the hydrostatic evolution of the Raman spectra of quartz (my Fig. 1, Murri

et al. 2019), zircon (Stangarone et al. 2019) and rutile (Musiyachenko et al. 2021) up to about 4% compression, we can now address the question as to how to determine the values of the components of the phonon-mode Grüneisen tensors.

Previous work (e.g. Tekippe et al. 1973; Briggs and Ramdas 1977) has used mechanical deformation, as Reynard and Zhong have done. This is a conceptually simple approach but has potential pitfalls. The most serious is that it is assumed that the stress applied to the load cell compressing the sample is applied completely to the sample (unless a friction correction is made), and that the sample is under a uniform homogeneous stress. The obvious problem is that, unless the sample is completely constrained in directions perpendicular to the load axis it will expand in the equatorial plane. If the stress and strain is homogeneous then this can be calculated from the elastic tensors of the crystal. However, an end-loaded sample will in general become barrel shaped; wider at the middle of the sample than at the ends due to friction in contact with the loaded pistons. Therefore, in order to interpret the measured Raman shifts from such an experiment it is necessary to either demonstrate that the stress and strain state is homogeneous across the complete sample, or to independently determine the strain or stress at the point of the Raman measurement (which could be done by simultaneous X-ray diffraction). Reynard and Zhong do not report such measurements, so the actual stress state of their samples could be different from that inferred from the pressure of the load cell.

That may be one contribution to the difference in the Grüneisen parameters determined in the experiments of Reynard and Zhong and those by HF/DFT (Murri et al. 2019), and may also account for the failure of the Grünesien parameters of Reynard and Zhong to predict their own hydrostatic measurements of the 206 mode (Figure 1 above).

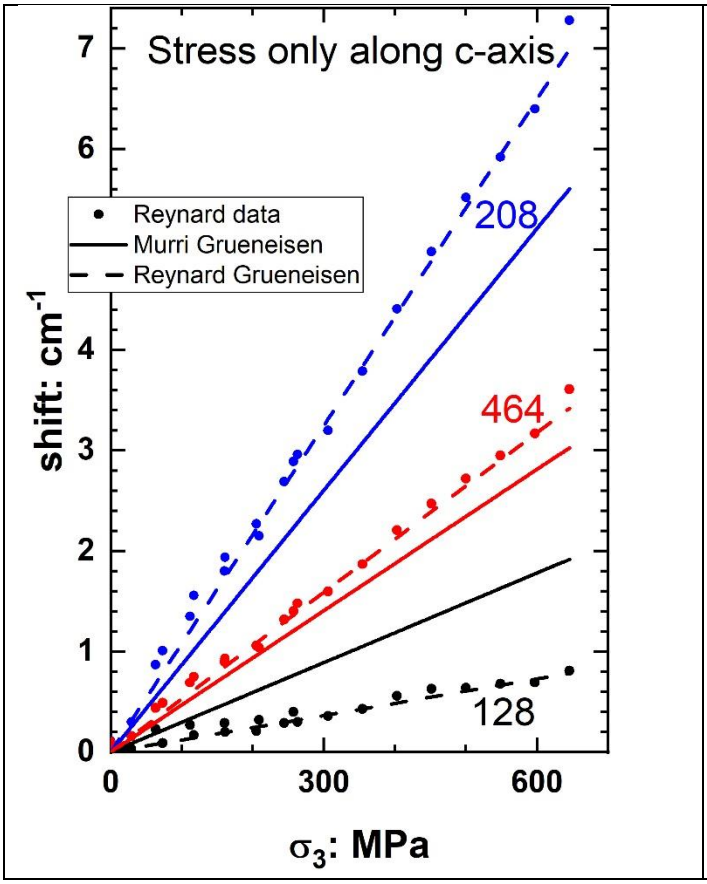

Figure 2: Plot of measured changes in Raman shift under uniaxial stress along the c-axis from Reynard and Zhong. Dashed lines are the fits of Reynard and Zhong to their data.

The solid lines are calculated from the published Grüneisen tensor components of Murri et al. (2019) and the strains calculated from the applied stress and the elastic compliance tensor of quartz at room T (Lakshtanov et al. 2007). Other published measurements of the elastic tensor give very similar results.

Apart from this mode, there is general agreement in the prediction of the hydrostatic evolution of the 128 and 464 modes from both HF/DFT and the experiments of Reynard and Zhong (Figure 1). The agreement between the predictions of HF/DFT and the uniaxial stress measurements is poorer (Figure 2). This may be due inhomogeneities in the stress field in the sample during the experiments. But it may also indicate short-comings in the use of HF/DFT simulations, which is why determinations of the Grüneisen tensors by different methods is so important. Possible explanations for the predictions of HF/DFT being in error centre around the fact that the HF/DFT simulations are performed at 0 K (at the static limit), and the experiments are performed at 300K. Therefore, if there is a significant change in the dynamics of the quartz between 0 K and 300K, for example in the phonon-phonon interactions, then one would expect that the prediction of the Raman shifts at room temperature to be in error. However, then one would also expect that the predicted Raman shifts with pressure at room temperature (Figure 1) would be wrong, but they are actually correct. These discrepancies between mechanical experiments and predictions of HF/DFT can only be resolved by further careful evaluation and cross-comparison of both approaches.

The other point of agreement between the experiments of Reynard and Zhong and HF/DFT is in the sensitivity of the three Raman modes of quartz to non-hydrostatic stress. This can be evaluated from the Grüneisen tensors of quartz (Murri et al. 2019) by calculating the angle in the ε_1- ε_3 strain space between the lines of predicted constant mode wavenumber (the isoshift lines of Murri et al., 2019), and the line of strains expected under hydrostatic stress. The HF/DFT-predicted isoshift line (Murri et al. 2019) of the 206 mode lies at 91^o (i.e. almost perpendicular) to the line of hydrostatically-induced strains, whereas the isoshift lines of the 128 and 464 modes are approximately 80 degrees from the hydrostatic line. The HF/DFT simulations therefore predict that the 206 mode is the least-sensitive to non-hydrostatic stresses, and this appears to be confirmed by the results of Reynard and Zhong.

Summary

It is clear that there is the possibility that the values of the components of the phonon-mode Grüneisen tensors determined by HF/DFT at 0 K are not exactly correct. They are however sufficiently correct that they reproduce the hydrostatic evolution of the Raman modes of quartz up to 2 GPa, the discrepancies being of the same order as the differences (which are unexplained by Reynard and Zhong) between the data of Reynard and Zhong and the previous determinations by Schmidt and Ziemann (2000) and Morana et al. (2020). The Grüneisen tensors also reproduce the expected inclusion pressures of synthetic inclusions from their measured Raman spectra (Bonazzi et al. 2019), and natural inclusions (e.g. Gilio et al. 2022), although I agree with Reynard and Zhong that some inclusions appear to have unreasonably high deviatoric stress calculated by this method. Whether this reflects experimental difficulties in measuring Raman spectra, the high correlation between the ε_1 and ε_3 strains determined from Raman shifts via the phonon-mode Grüneisen tensors, or actually problems with the values of the tensor components determined by HF/DFT, remains to be determined.

Possible reasons for different values of the components of the phonon-mode Grüneisen tensors may lie either in short-comings of applying HF/DFT simulations to experiments at room temperature, or to short-comings in the deformation experiments of quartz. The reasons can only be determined through carefully documented experiments in which the stress or strain state of the sample at the point of Raman measurement is determined. Such experiments can only provide a test of the HF/DFT simulations if they are performed in

orientations and stress states that preserve the symmetry of the quartz crystal. Thus, the second uniaxial stress experiment of Reynard and Zhong with the stress applied perpendicular to the c-axis broke the crystal symmetry of quartz (as evidenced by the splitting of the mode into two modes, not the LO and TO components of one mode), and cannot be used for comparison to the predictions from the HF/DFT simulations of trigonal quartz. Further experiments are clearly required before any conclusions can be drawn about the correctness or otherwise of the component values of Grüneisen tensors calculated by HF/DFT. In any case, whether or not the values are correct, no evidence has yet emerged to disprove the general concept of Grüneisen that the phonon-mode wavenumbers scale with the strains applied to the crystal.

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