DE GRUYTER Z. Kristallogr. 2019; 234(2): 129–140

Ross J. Angel*, Mara Murri, Boriana Mihailova and Matteo Alvaro

Stress, strain and Raman shifts

https://doi.org/10.1515/zkri-2018-2112
Received July 3, 2018; accepted August 23, 2018; published online September 18, 2018

Abstract: The concept of the phonon-mode Grüneisen tensor is reviewed as method to determine the elastic strains across crystals from the changes in the wavenumbers of Raman-active phonon modes relative to an unstrained crystal. The symmetry constraints on the phonon-mode Grüneisen tensor are discussed and the consequences for which combinations of strains can be determined by this method are stated. A computer program for Windows, stRAinMAN, has been written to calculate strains from changes in Raman (or other phonon) mode wavenumbers, and vice-versa. It can be downloaded for free from www.rossangel.net.

Keywords: mode Grüneisen tensor; Raman spectroscopy; strain tensor; stRAinMAN program.

Introduction

The measurement of elastic strains in crystals has many applications, including the determination of thermal expansion coefficients and compressibilities, the characterisation of structural phase transitions and crystals under non-hydrostatic stress states inside diamond-anvil cells (DACs), as well as the stress states of individual crystal grains within a rock or ceramic composite. When the sample crystal is uniformly stressed, for example when it is under hydrostatic pressure inside a fluid pressure medium, then the strains are uniform across the sample, and they can be determined by measuring the unit-cell parameters of the crystal and comparing them to those of an unstrained reference crystal. This is the basis of using diffraction measurements to determine the thermal expansion and equations of state of minerals.

However, if a crystal is surrounded by other solid material it is subjected to strains imposed upon it by the thermal expansion and compressibility of the host material. The simplest case to consider is a spherical or ellipsoidal-shaped single crystal trapped as an inclusion inside an elastically-isotropic host crystal. When the pressure (P) or the temperature (T) changes, the host crystal will impose a uniform isotropic strain on the inclusion. If the inclusion crystal is elastically anisotropic it will therefore develop different normal stresses in different directions. Therefore, the inclusion will not be under hydrostatic pressure. This deviatoric stress state will be the same at all points within the inclusion [1], and there will be no strain gradients across the inclusion. The strain in such inclusions can therefore be measured by conventional X-ray diffraction (XRD) techniques. However, when the same inclusion is faceted, the edges and corners act as stress concentrators and the stress and strain will change across the inclusion volume [e.g. 2–4]. Strain gradients also exist across crystals in DACs when the pressure medium becomes non-hydrostatic. In both cases, the strain gradients give rise to broadening of Bragg reflections in the diffraction pattern [e.g. 5, 6], and the measured unit-cell parameters are some average of all of the various strained unit cells within the part of the sample that is within the X-ray beam. To follow the strain gradients it is therefore necessary to reduce the probed sample volume. This can be done with synchrotron-based XRD where the intensity of the source allows small volumes of the sample to be probed [e.g. 7, 8]. However, synchrotron XRD is a rather expensive method and cannot be routinely applied to the many grains or inclusions that must be measured in even a single geological study of one small field area. Raman spectroscopy provides a practical alternative which is economically-accessible to most laboratories. Raman spectrometers coupled to microscopes can obtain spectra from volumes of just a few μm^3 of individual minerals within polished sections and allow the Raman shifts of multiple lines to be mapped across the volume of an inclusion a few 10's of microns across [e.g. 2, 9].

The Raman shifts from inclusions are normally interpreted as the result of the inclusion being under a hydrostatic pressure. Consequently, the Raman shifts measured from inclusions are directly converted into a hydrostatic pressure [e.g. 10], using pressure-wavenumber calibration curves established from hydrostatic DAC experiments. However, it is a common misconception implicit in such

---

***Corresponding author: Ross J. Angel,** Department of Earth and Environmental Sciences, University of Pavia, Via A. Ferrata 1, I-27100 Pavia, Italy, E-mail: rossjohnangel@gmail.com
Mara Murri and Matteo Alvaro: Department of Earth and Environmental Sciences, University of Pavia, Via A. Ferrata 1, I-27100 Pavia, Italy
Boriana Mihailova: Department of Earth Sciences, University of Hamburg, Grindelallee 48, Hamburg D-20146, Germany

an analysis that Raman shifts directly measure stress or pressure, as can be easily illustrated. First, let us assume that the change $\Delta\omega^m$ in the wavenumber of a phonon mode m is indeed proportional to the applied normal stresses as:

$$\Delta\omega^m = a_1^m\sigma_1 + a_2^m\sigma_2 + a_3^m\sigma_3 \quad (1)$$

With the a_i^m representing coefficients of proportionality that depend on the mode m and the direction in the crystal, but not on the magnitude of any of the stresses σ_i. This approach implicitly assumes that the effects of three simultaneous stresses along the X, Y, and Z axes is equal to the sums of the effects of the individual uniaxial stresses. Basic physical insight shows that this cannot be true. A uniaxial stress along X leads to expansion in Y and Z for normal materials with positive Poisson ratio, whereas simultaneous compression along X and Y must lead to shortening along both X and Y which is a completely different physical state. Therefore, the structural effect of compression along X and Y simultaneously is not the sum of compression along X and Y separately. As phonon modes of a crystal depend on the structure and bonding within the crystal, it is clear that these two different stress states must give rise to different Raman shifts, in contradiction to the premise behind Equation (1).

Second, at ambient pressure, heating a crystal does not change its stress state but its strain state; therefore, the observed changes of the Raman peak positions at different temperatures are the direct result of the strain tensor $\boldsymbol{\varepsilon}$ induced by temperature change ΔT. Similarly, in *in situ* high-pressure experiments the observed changes in the phonon wavenumbers are the direct result of strain, which is induced by pressure P. Further, for many modes in many minerals, the phonon-wavenumber changes induced by reducing the temperature or increasing the pressure are the same for the same decrease in volume. For example, if the shifts of the most intense Raman peak of quartz at ca. 464 cm^{-1} are plotted against the unit-cell volume, then both the high-pressure and the low- and high-temperature data fall on a single trend [2]. This clearly demonstrates that the wavenumber of this Raman-active mode of quartz is determined *not* directly by the pressure or the temperature, but is *solely a function of the strains* induced by changes in P or T. The effects of P and T on the Raman peak positions are therefore indirect; a change in P or T changes the unit-cell parameters and volume and this change (or strain) determines the change in the wavenumber of the Raman-active mode.

The concept was first established by Grüneisen [11] for isotropic solids. He defined what is now known as the thermal or thermodynamic Grüneisen parameter which relates the change in internal energy of an isotropic solid to the change in its pressure along an isochor. From an atomistic point of view, the Grüneisen parameter represents the response of lattice dynamics (atomic vibrations) as opposed to the response of lattice statics (atomic equilibrium positions) to temperature change or stress, and it is determined by the anharmonicity of the crystal potential due to phonon-phonon interactions [12]. If the anharmonicity in the potential is relatively small then the Grüneisen parameter remains approximately constant with either P or T. Grüneisen was clearly aware that the thermodynamic Grüneisen parameter was a tensor quantity in non-isotropic solids related to the anisotropic thermal expansion, the heat capacity and the elastic moduli. The details are laid out in [13] and discussed for the mineral olivine, for example, in [14]. Since the entropy of a solid depends explicitly on the lattice vibrations (phonon modes) [e.g. 12, 15, 16] it is possible to relate the macroscopic thermodynamic Grüneisen parameter to the microscopic phonon-mode Grüneisen tensors that define the relative wavenumber changes induced by the tensorial strain imposed on the crystal. In this paper we apply this idea to the specific problem of determining the strains in a crystal by measuring changes in the Raman shifts compared to those in an unstrained crystal. We first review the concept of the phonon-mode Grüneisen tensor and introduce a new approach to uniquely determine strains in crystals by measurements of Raman shifts. This has an immediate application, for example, in the measurement of strains in natural inclusions in order to provide estimates of the P and T at which they were entrapped deep within the Earth [e.g. 10, 17, 18]. The final section describes a new computer program, stRAinMAN, which is freely available and can be used to calculate strains of crystals from measured Raman shifts and vice-versa.

Theory

Strains

Strains describe the change in shape and size of a physical object relative to an initial undeformed reference state. In this paper we are concerned with small elastic strains in crystals. ‘Elastic’ means that when the external field or force creating the strains, such as pressure, temperature or stress, is removed then the single crystal returns to its original size and shape. Plastic deformation and brittle failure, which both lead to permanent changes in size or shape, are explicitly excluded from this analysis. Elastic strains fall into two types, normal strains related to changes in length, and shear strains which do not change linear dimensions of the sample.

For crystals it is easiest to define strains in terms of the changes in their unit-cell parameters. The exact relationships between the strains and the cell parameters depend on the orientation with respect to the crystal axes of the Cartesian axes used to describe the strains. The conventional orientation for crystal classes of orthorhombic or higher symmetry is the natural one of having the Cartesian axes parallel to the crystallographic axes, thus **X**//**a** and **Z**//**c**. Then (except for the hexagonal system) the infinitesimal normal strain components ε_{11}, ε_{22} and ε_{33} define the changes in the cell parameters a, b, and c, for example $\varepsilon_{11}=da/a$, where da is a very small change in the a cell parameter. The shear strains are related to changes in unit cell angles, for example ε_{13} is related to the change in angle between the a and c axes. In monoclinic and triclinic systems there are several widely-used different conventions for orienting the Cartesian axes of the tensor relative to the crystal axes, and the expressions for the strain components in terms of the unit-cell parameters are different in each case. Explicit equations for different conventions are given in [19] and [20], and general equations in [21] and [22], for example. The strain tensor by definition excludes rigid-body rotations [23] so it is symmetric, $\varepsilon_{ij}=\varepsilon_{ji}\ i, j=1, 2, 3$.

Phonon-mode Grüneisen tensor

The fractional change in the wavenumber, $\frac{-\Delta\omega^m}{\omega_0^m}$ of a phonon mode m in a crystal as a result of a strain $\boldsymbol{\varepsilon}$ is determined by a second-rank symmetric tensor, the phonon-mode Grüneisen tensor $\boldsymbol{\gamma^m}$ [12, 15, 16]:

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

The “:” in Equation (2) indicates a double-scalar product between the two tensors, which can be written out in a full form as:

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

Both tensors are symmetric and therefore $\varepsilon_{ij}=\varepsilon_{ji}$ and $\gamma_{ij}^m=\gamma_{ji}^m$ for each pair of non-diagonal elements, so:

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

For ease of notation 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 [24] convention used here for strains, 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 ε_4, ε_5, ε_6 are one-half of the values of the corresponding tensor components ε_{23}, ε_{13}, ε_{12}. Therefore, if we set γ_4^m, γ_5^m and γ_6^m equal to the values of the corresponding tensor components γ_{23}, γ_{13}, γ_{12}, we obtain:

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

The introduction of a factor of ½ into the strain vector components and not into the Grüneisen vector components avoids factors of two appearing for the terms with subscripts $i=4, 5, 6$ in the matrix version (5) of the tensor Equation (2). The same convention works for the vector expression for the elastic energy of a solid [23]. The values of γ_i^m are different for different modes, indicated here by the superscript m. In general, each phonon mode is characterized by its wavenumber ω, wavevector **k**, and polarization [transverse optical (TO) vs. longitudinal optical (LO)]. However, only modes at the Brillouin-zone center can be measured by Raman spectroscopy and therefore m represents in fact the wavenumber of non-polar modes (e.g. A_1 in quartz) as well as the wavenumber of the corresponding TO and LO components of a polar mode (e.g. ETO and ELO in quartz). Thus γ_1^{464} for quartz relates the wavenumber of the 464 cm^{-1} mode of quartz to the applied ε_1 strain.

This relationship means that the changes in the Raman peak positions depend on all of the strains in three dimensions experienced by the crystal, not just the volume change. The negative sign on the left-hand side of Equations 2–5 is a convention introduced to make the values of γ_i^m positive for most phonon modes in most materials [e.g. 12]. With this convention, Equation (5) predicts that positive strains normally lead to a decrease in the phonon wavenumbers, and vice-versa. This is consistent with the general observation that, in the absence of phase transitions, Raman shifts increase with increasing hydrostatic pressure due to the development of negative strains and decrease with increasing temperature due to the development of positive strains.

The changes in phonon-mode wavenumbers induced by a temperature change ΔT can be calculated from (5) by recalling that in matrix form the strain is related to the thermal expansion tensor by:

$$\alpha_i \Delta T = \varepsilon_i \tag{6}$$

So that we can write (5) as:

$$\frac{-\Delta\omega^m}{\omega_0^m} = (\gamma_1^m\alpha_1 + \gamma_2^m\alpha_2 + \gamma_3^m\alpha_3 + \gamma_4^m\alpha_4 + \gamma_5^m\alpha_5 + \gamma_6^m\alpha_6)\Delta T \tag{7}$$

Or, similarly, the direct effect of pressure on phonon mode wavenumbers can be written directly in terms of the compressibility $\beta_i = -\varepsilon_i/\Delta P$:

$$\frac{\Delta\omega^m}{\omega_0^m} = (\gamma_1^m\beta_1 + \gamma_2^m\beta_2 + \gamma_3^m\beta_3 + \gamma_4^m\beta_4 + \gamma_5^m\beta_5 + \gamma_6^m\beta_6)\Delta P \tag{8}$$

Note that this means the phonon wavenumbers are not expected to be linear in either *T* or *P*, because the values of the thermal expansion and compressibility of a crystal change with *T* and *P*, respectively. In the absence of strong anharmonicity in the crystal interatomic potentials one can assume that γ_i^m = constant for each $i = 1, \ldots, 6$. That means that the response of lattice dynamics (phonons) follows the response of the static lattice (atomic equilibrium positions) to changes in temperature or pressure. In this case, the use of the phonon-mode Grüneisen parameters has several advantages over using empirical polynomial functions in *P* and *T* to describe the variation in peak shifts [e.g. 25, 26]. First, the phonon-mode Grüneisen tensor has a sound physical basis and reflects the underlying physics that Raman shifts due to changes in *P* and *T* are not independent from each other. Second, they account for deviatoric strains as required, for example, in the analysis of host-inclusion systems, with the same approach as used for hydrostatic pressure. Third, quite often less coefficients are needed to describe the phonon wavenumbers than are required for higher-order polynomials in *P* and *T*.

Symmetry constraints

We explore the symmetry constraints on the Grüneisen tensor in some detail because they have significant consequences for which individual strains can, and which cannot, be determined through the measurements of the shifts of Raman active modes of a crystal. These limitations arise because we are using scalars $\frac{\Delta\omega^m}{\omega_0^m}$ to determine the values of the components of a strain tensor via a property tensor. This is in contrast to measurements to determine, for example, strains from the applied stresses via elasticity theory. In elasticity, the relevant property tensor is the compliance tensor, s_{ijkl}, and if the stresses σ_{ij} are known, then the strains can be calculated directly from the tensor equation relating stress to strain. The closer analogy in elasticity for the Grüneisen concept would be to determine the strains from the known stresses by measuring the work done on the system dW, which is the double scalar product of the stress and the change in strains, $d\varepsilon_{ij}$, thus $dW = \boldsymbol{\sigma}\mathbf{:}\, d\boldsymbol{\varepsilon} = \sigma_{ij} d\varepsilon_{ij}$ [23].

The reformulation of Equation (5) in terms of the thermal expansion and compressibility tensors (Equations 7, 8) indicates that the phonon-mode Grüneisen tensor is subject to the same symmetry constraints on its component values as other second-rank property tensors. This can be proved algebraically by requiring that $\frac{\Delta\omega^m}{\omega_0^m}$ does not change when the symmetry operators of the crystal are applied as a transformation. The physical picture is that if symmetry-equivalent strains are applied separately to a crystal, one must obtain the same shift in mode wavenumbers: a strain ε_1 applied to a tetragonal crystal must result in the same $\frac{\Delta\omega^m}{\omega_0^m}$ as a strain ε_2. If this were not true, the symmetry-equivalent *a*- and *b*-axes of the tetragonal crystal could be distinguished by experiment. For convenience, the constraints imposed by the symmetry on the components of the phonon-mode Grüneisen tensor are summarized in Table 1. For triclinic crystals all six components γ_i^m can be non-zero and have different values. For monoclinic crystals with the diad axis set along the *y*-axis, $\gamma_4^m = \gamma_6^m = 0$, so:

$$\frac{-\Delta\omega^m}{\omega_0^m} = \gamma_1^m\varepsilon_1 + \gamma_2^m\varepsilon_2 + \gamma_3^m\varepsilon_3 + \gamma_5^m\varepsilon_5 \tag{9}$$

In all crystals with orthorhombic symmetry or higher, $\gamma_4^m = \gamma_5^m = \gamma_6^m = 0$, and the wavenumber shifts become governed by:

$$\frac{-\Delta\omega^m}{\omega_0^m} = \gamma_1^m\varepsilon_1 + \gamma_2^m\varepsilon_2 + \gamma_3^m\varepsilon_3 \tag{10}$$

The Grüneisen tensor concept can also be used to predict the consequences for Raman spectra of small strains imposed on a crystal that break its symmetry. For example, a shear strain ε_5 applied to an orthorhombic crystal will cause the β unit-cell angle to deviate from 90°, thereby breaking the orthorhombic lattice symmetry. However, if ε_5 is close to zero, such a symmetry change will only have a very small effect on the relative wavenumber shifts because the additional "monoclinic term" $\gamma_5^m\varepsilon_5$ will be negligibly small with respect

Tab. 1: Symmetry constraints on the phonon-mode Grüneisen tensor in vector notation.

Crystal system	Vector	
	Independent values	Constraints
Triclinic	$\gamma_1^m, \gamma_2^m, \gamma_3^m, \gamma_4^m, \gamma_5^m, \gamma_6^m$	None
Monoclinic, *b*-unique	$\gamma_1^m, \gamma_2^m, \gamma_3^m, \gamma_5^m$	$\gamma_4^m = \gamma_6^m = 0$
Monoclinic, *c*-unique	$\gamma_1^m, \gamma_2^m, \gamma_3^m, \gamma_6^m$	$\gamma_4^m = \gamma_5^m = 0$
Orthorhombic	$\gamma_1^m, \gamma_2^m, \gamma_3^m$	$\gamma_4^m = \gamma_5^m = \gamma_6^m = 0$
Tetragonal, trigonal, hexagonal	γ_1^m, γ_3^m	$\gamma_1^m = \gamma_2^m$ $\gamma_4^m = \gamma_5^m = \gamma_6^m = 0$
Cubic	γ_1^m	$\gamma_1^m = \gamma_2^m = \gamma_3^m$ $\gamma_4^m = \gamma_5^m = \gamma_6^m = 0$

to the "orthorhombic one" given by Equation (10). Therefore $\Delta\omega^m \sim 0$ for small symmetry-breaking strains. However, if the symmetry-breaking strain exceeds a certain threshold value, then the wavenumber change of the lower-symmetry phase will become different from that predicted by the Grüneisen tensor of the higher-symmetry phase. This "pseudo-symmetry" approach certainly holds under conditions where the Grüneisen tensor components do not depend on strains. This is completely analogous to the concept of infinitesimal strains and constant coefficients used in linear elasticity theory [e.g. 23] in which the elastic compliance tensor conforms to the original symmetry of the undeformed crystal, but can predict the strains arising from small stresses that break the symmetry. For Grüneisen tensors, as for elasticity, it remains for experiments to determine the range of strains for which the linear approximation represented by this approach (Equations 5–10) remains valid. This approach is not expected to apply to structural phase transitions, where the associated anharmonicity may change the values of the γ_i^m significantly.

For all uniaxial crystals (tetragonal, trigonal, hexagonal) in the standard setting $\gamma_1^m = \gamma_2^m$ and the relationship (10) is further reduced to:

$$\frac{-\Delta\omega^m}{\omega_0^m} = \gamma_1^m(\varepsilon_1 + \varepsilon_2) + \gamma_3^m \varepsilon_3 \qquad (11)$$

Note that in a uniaxial crystal even if the strains ε_1 and ε_2 are not equal, the change in phonon wavenumbers depends only on their sum $\varepsilon_1 + \varepsilon_2$ and not their individual values. Conversely, a measurement of the change in the Raman shift of two vibrational modes of a uniaxial crystal can be used to determine $\varepsilon_1 + \varepsilon_2$ and ε_3, if the values of the γ_i^m are known. Measurement of further vibrational modes can only reduce the uncertainty in the values of $\varepsilon_1 + \varepsilon_2$ and ε_3, but cannot ever allow the value of ε_1 to be determined separately from ε_2.

For cubic crystals and isotropic materials $\gamma_1^m = \gamma_2^m = \gamma_3^m$, and the other components are zero. Further, for small strains, the sum of the normal strains $\varepsilon_1 + \varepsilon_2 + \varepsilon_3$ is the fractional volume change, or the volume strain $\frac{\Delta V}{V_0}$. Thus, for cubic crystals, the Raman shift depends only upon the total volume change and *not* the values of the individual strain components:

$$\frac{-\Delta\omega^m}{\omega_0^m} = \gamma_1^m(\varepsilon_1 + \varepsilon_2 + \varepsilon_3) = \gamma_1^m \frac{\Delta V}{V_0} \qquad (12)$$

It follows that the measurement, for example by Raman spectroscopy, of the change in the wavenumber of a single vibrational mode in a cubic crystal is sufficient to determine the volume change of the crystal. However, by analogy with the case of uniaxial crystals, if a cubic crystal is under unequal strains with $\varepsilon_1 \neq \varepsilon_2 \neq \varepsilon_3$, the symmetry of the phonon-mode Grüneisen tensor means that it is not possible to determine the individual strain components (Equation 12), no matter how many Raman lines are measured. Equation (12) also predicts that if the strains of a cubic crystal are purely deviatoric so that $\varepsilon_1 + \varepsilon_2 + \varepsilon_3 = 0$, there will be no change in the phonon wavenumbers, provided that the strains are infinitesimal.

Determining phonon-mode Grüneisen components

For cubic crystals the single symmetrically-independent value $\gamma_1^m = \gamma_2^m = \gamma_3^m$ for each mode can be determined from the change of the mode wavenumber with pressure if the bulk modulus $K = -V\frac{\partial P}{\partial V}$ is known:

$$\gamma_1^m = K.\frac{1}{\omega^m}\frac{\partial \omega^m}{\partial P} \qquad (13)$$

Note that K is not a constant, but is a function of P and T. Therefore, a more correct approach is to plot the wavenumber of the phonon mode against volume, and to use Equation (12) to determine the value of γ_1^m. For non-cubic crystals, one can define a similar quantity, the volume Grüneisen parameter γ_V^m of a mode:

$$\gamma_V^m = \frac{-\Delta\omega^m}{\omega_0^m} / \frac{\Delta V}{V_0} \tag{14}$$

This can be determined from the measured shift in wavenumber with pressure, $\frac{1}{\omega^m}\frac{\partial\omega^m}{\partial P}$, known as the 'phonon compressibility' [27], and the measured volume change with pressure. Consideration of Equation (8) shows that values of γ_V^m are related to the values of the components of the phonon-mode Grüneisen tensor by:

$$\gamma_V^m = K(\gamma_1^m\beta_1 + \gamma_2^m\beta_2 + \gamma_3^m\beta_3 + \gamma_4^m\beta_4 + \gamma_5^m\beta_5 + \gamma_6^m\beta_6) \tag{15}$$

with the appropriate simplifications for symmetries higher than triclinic.

In crystals of lower than cubic symmetry the determination of the components of the phonon-mode Grüneisen tensor for even a single vibrational mode is not easy to achieve experimentally, because it requires different strain states to be imposed on a crystal. It is therefore not sufficient to measure the Raman shifts under hydrostatic pressure, because this generates a single strain state. Consider a uniaxial crystal, like quartz. The symmetry constraints reduce Equation 8 to:

$$\frac{\Delta\omega^m}{\omega_0^m} = (2\gamma_1^m\beta_1 + \gamma_3^m\beta_3)\Delta P \tag{16}$$

If the change in mode wavenumber $\Delta\omega^m$ is measured as a function of pressure change ΔP, then all that can be determined is $\frac{\Delta\omega^m}{\Delta P} = (2\gamma_1^m\beta_1 + \gamma_3^m\beta_3)\omega_0^m$. Even if the values of the compressibilities β_1 and β_3 are known, it is not possible to determine the *two* values of γ_1^m and γ_3^m from the *just one* value of $\frac{\Delta\omega^m}{\Delta P}$. Only if $\gamma_1^m = \gamma_3^m$, which is the case in cubic minerals, can their values be determined from hydrostatic compression experiments. An equation exactly analogous to (16) can be written for a temperature change ΔT at constant pressure, with the implication that the values of γ_1^m and γ_3^m cannot be determined independently.

Therefore, in order to determine the values of γ_i^m in non-cubic crystals it is necessary to generate several different sets of strain conditions. This has been done successfully on quartz, by applying uniaxial stresses of up to 0.5 GPa, to determine both phonon-mode Grüneisen components for various Raman active modes [16, 28]. The limited fracture strength of silicate crystals however limits the deviatoric stress and strain levels that can be applied to quite low levels, limiting the precision with which the values of γ_i^m can be determined. And, such experiments cannot be performed under significant tension, except via shock wave techniques [29]. One possibility is that reproducible deviatoric stress at GPa levels can be applied to single crystals by using non-hydrostatic pressure media [30], and this is an avenue currently under exploration.

A practical alternative is to use computer simulations of the crystal based on density-functional theory (DFT) to calculate the Raman spectra [e.g. 31, 32] under a range of deviatoric strains [2]. The strains applied in the simulations are not limited by the physical fragility of the crystal and can be arbitrarily large, and any combination of strains both positive in tension and negative in compression can be applied provided that the structure remains dynamically stable. If the simulations are performed over a grid of strains, then a contour plot of the phonon wavenumber on this grid immediately indicates the relationship between the phonon-mode shift and the strains. An example is provided by Figure 1a, for the 969 cm^{-1} Raman line of zircon, which illustrates several important principles about Raman shifts in minerals. First, the contour lines are parallel and equally-spaced, which means that the phonon-mode Grüneisen components are independent of the strains and their values can be determined from fitting a planar surface to the calculated shifts. Second, the contour lines of constant Raman shift are not parallel to the isochors, which for tetragonal zircon would be lines of constant $2\varepsilon_1 + \varepsilon_3$. Therefore, in contrast to cubic minerals, but in agreement with Equation (11), the shift of the 969 cm^{-1} line of zircon does not indicate the volume strain. Figure 1b is the same map replotted as a function of stress rather than strain, using the room *P*, *T* elastic tensor of zircon [33] and shows that the contours are not parallel to lines of constant mean stress, $(2\sigma_1 + \sigma_3)/3$. Therefore, the Raman shift of this line does not provide a measurement of mean stress. Lastly, the contour maps for different phonon modes have very different patterns of contour lines. As an extreme example, Figure 1c is a map of the 223 cm^{-1} mode whose contour lines have positive slopes indicating that one of the two mode Grüneisen components is negative. A fit of this data with Equation (11) yields $\gamma_1^{223} = -0.27$ and $\gamma_3^{223} = 1.32$. A similar analysis of DFT simulations of quartz [2] gave values of the phonon-mode Grüneisen tensor components that are in good agreement with those obtained by direct Raman spectroscopic measurements of uniaxially stressed quartz crystals [16, 28] and that correctly predict Raman shifts from the strains of inclusion crystals in natural garnet crystals measured by XRD [2].

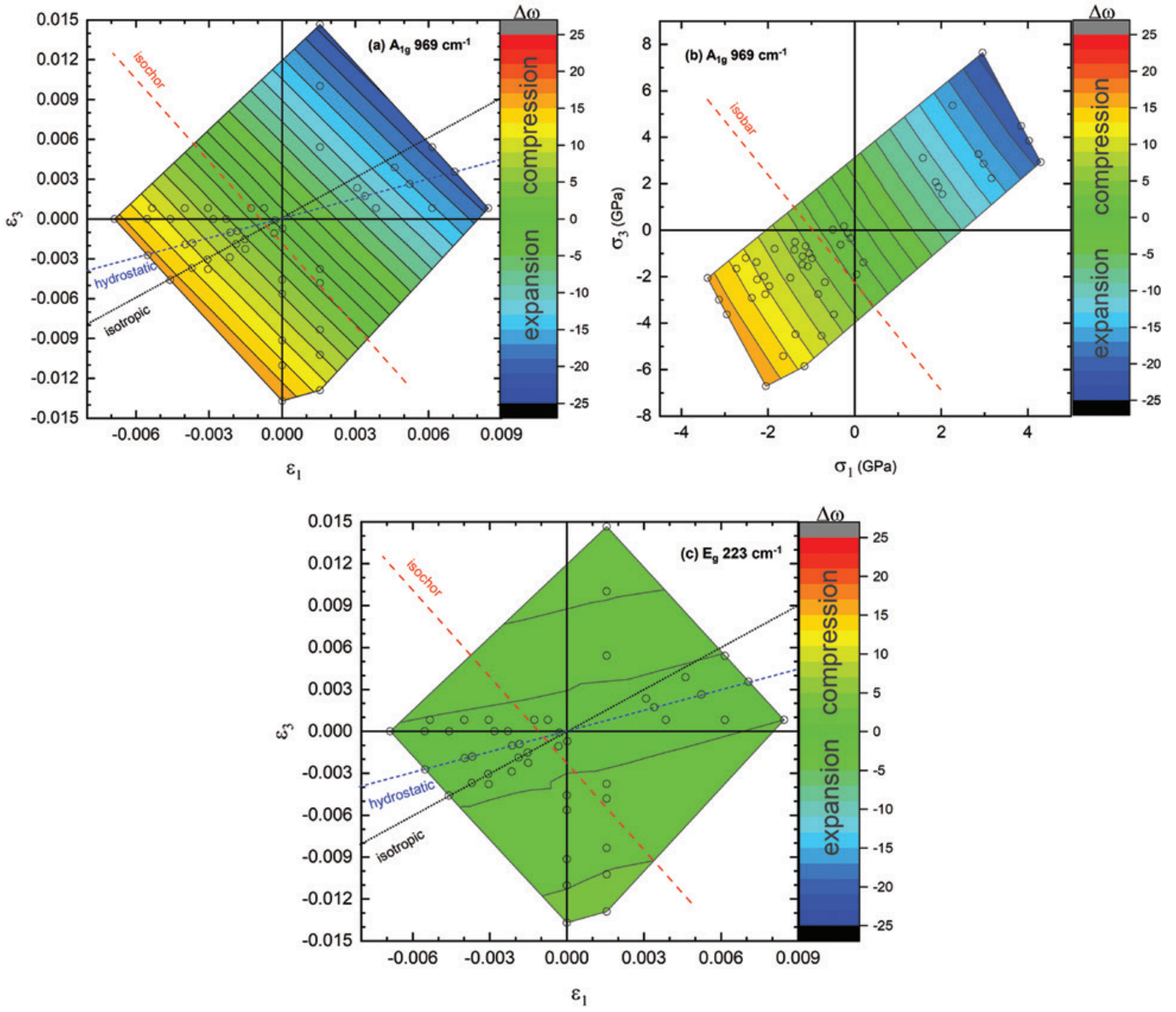
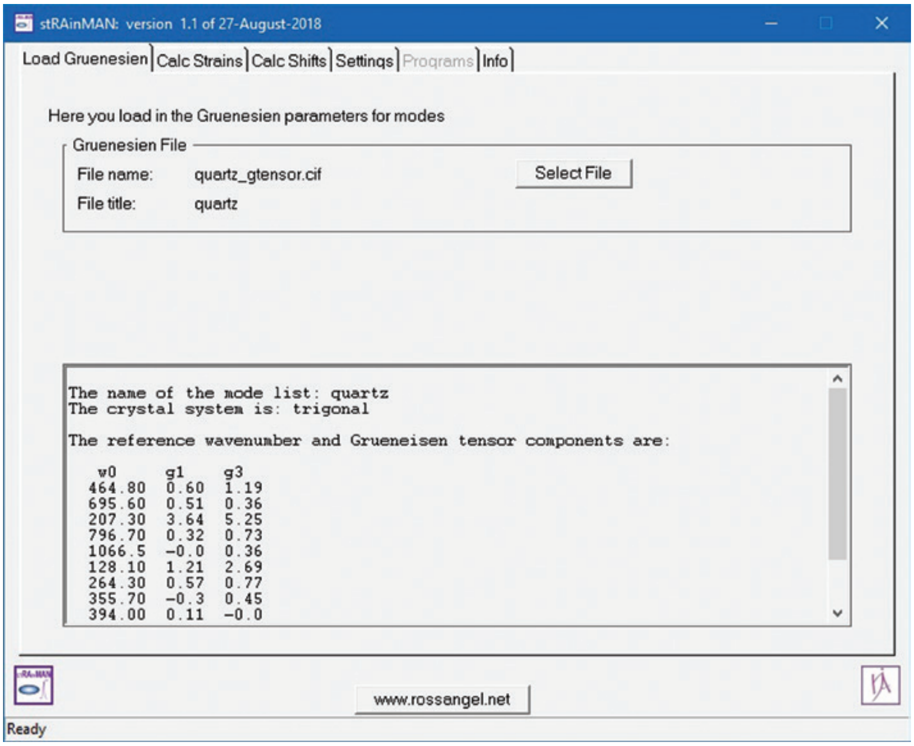


Fig. 1: Variation of Raman shift of phonon modes of zircon, calculated by HF-DFT simulations. (a) The 969 cm⁻¹ mode plotted as a function of strains exhibits parallel, equally-spaced contours indicating that components $\gamma_1^{969} = 1.17$ and $\gamma_3^{969} = 1.26$ of the mode Grüneisen tensor are constant. The contours are not parallel to isochors. (b) Neither are the iso-shift contours parallel to isobars, lines of equal mean stress $(2\sigma_1+\sigma_3)/3$. (c) A contour plot of the 223 cm⁻¹ mode which has $\gamma_1^{223} = -0.27$ and $\gamma_3^{223} = 1.32$.

Implementation

We have written a computer program, stRAinMAN, that calculates the changes in phonon wavenumbers from strains as well as the strains from measured changes in phonon wavenumbers, by applying Equation (5) with the symmetry constraints that we have described above. The program name emphasizes its most important application, which is the determination of strains in crystals by using Raman spectroscopy to measure changes in phonon wavenumbers relative to an unstrained crystal. However, the program can be used for any phonon mode in a crystal whether or not it is Raman- or infrared-active.

The program has a graphical user interface (GUI) consisting of a number of tabs (Figure 2), most of which are comprised of an upper area for user input and a lower information window which displays results as well as warning and error messages from the program. Tabs for calculations only become active when the necessary information about the phonon-mode Grüneisen parameters have been loaded to the program. These are loaded from a file via a file browser launched from the *Load Grueneisien* tab (Figure 2). The structure of the input file follows that of *crystallographic information files* (*cif*), because it is a very flexible text file format which allows information to be explicitly labeled by text flags [e.g. 34] making it



Here you load in the Gruenesien parameters for modes

File name: quartz_gtensor.cif
File title: quartz

```
The name of the mode list: quartz
The crystal system is: trigonal

The reference wavenumber and Grueneisen tensor components are:

   w0      g1     g3
 464.80  0.60   1.19
 695.60  0.51   0.36
 207.30  3.64   5.25
 796.70  0.32   0.73
 1066.5  -0.0   0.36
 128.10  1.21   2.69
 264.30  0.57   0.77
 355.70  -0.3   0.45
 394.00  0.11   -0.0
```

Fig. 2: A screen shot of the stRAinMAN GUI showing the *Load Gruenesien* tab after a mode list for quartz has been loaded from the Grüneisen file listed in Table 3. Not all of the mode list is visible, but it can be accessed with the scroll bar on the right-side of the output window.

easily-read by both humans and computer programs, and editable by the simplest text editors. For the stRAinMAN program we have introduced a new set of *cif* data names to describe the parameters of phonon-mode Grüneisen tensors, which are listed in Table 2. An example file with the phonon-mode Grüneisen tensor components of quartz is given in Table 3. By using the *cif* syntax and structure we are also able to make use of standard *cif* data names to specify the crystal system of the mineral, and the file can be read by any program that is *cif*-compliant. If the crystal system is specified, then the stRAinMAN program applies the appropriate symmetry constraints to the components of the Grüneisen tensor that we have described above. For the example of trigonal quartz (Table 3), the program will set $\gamma_2^m = \gamma_1^m$ and $\gamma_4^m = \gamma_5^m = \gamma_6^m = 0$ for all the modes input. If any tensor components listed in the Grüneisen file violate the symmetry constraints, or if a symmetry-required component is not listed, then a warning is issued to the user. The input file must also contain the value of ω_0^m for each mode because Equation (5) defines the fractional change of the wavenumber of the mode, not the absolute value of the shift. The units used for wavenumbers are not defined by Equation (5), and therefore any units can be used in the program. However, the input and output formats in stRAinMAN are designed to optimally display wavenumbers in the most commonly-used units for Raman spectroscopy, namely cm^{-1}.

Tab. 2: Data names used to describe modes in Grüneisen files for stRAinMAN.

Data name	Definition
_mode_name	Name of mode, text
_mode_w0	Value of ω_0^m, of a mode in cm^{-1}
_mode_gamma_1	Value of γ_1^m of a mode, if not give assumed 0
_mode_gamma_2	γ_2^m
_mode_gamma_3	γ_3^m
_mode_gamma_4	γ_4^m
_mode_gamma_5	γ_5^m
_mode_gamma_6	γ_6^m
_mode_symm	Symmetry label of a mode, e.g. A1g

All of these data names can be used together in a *cif* loop_ structure as shown in Table 3.

It is not required to list all of the modes of a crystal in the Grüneisen file, nor even all of the Raman-active modes. Only the modes of interest need be listed, but other modes can also be listed even if they are not employed in calculations. Thus, a single file can be kept

Tab. 3: Example of a Grüneisen file for quartz.

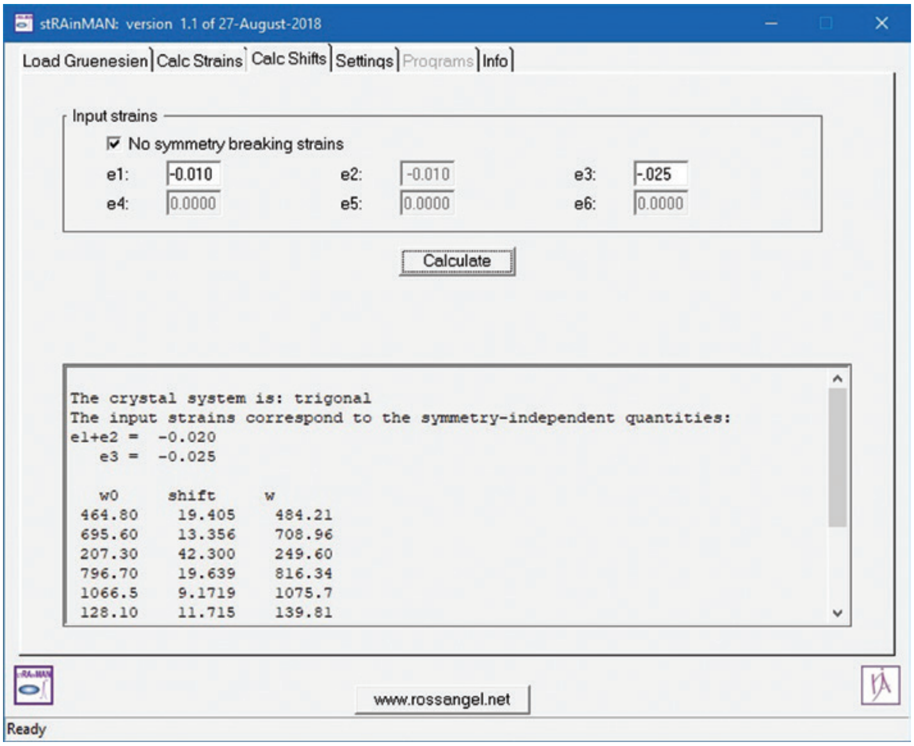
File contents				**Explanation**
data_quartz_modes				Start of data block (only the first datablock is used by stRAinMAN)
_chemical_name_mineral			quartz	Optional name for data
_space_group_crystal_system			trigonal	Crystal system: required
loop_				Standard *cif* loop header structure.
_mode_w0				Data will contain ω_0^m, γ_1^m and γ_3^m for each mode
_mode_gamma_1				
_mode_gamma_3				_mode_symm and _mode_name could also be used
464.8	0.60	1.19		
695.6	0.51	0.36		
207.3	3.64	5.25		One line for each mode, with ω_0^m, γ_1^m and γ_3^m in the same order as specified in the loop header
796.7	0.32	0.73		
1066.5	−0.02	0.36		
128.1	1.21	2.69		
264.3	0.57	0.77		Modes can appear in any order
355.7	−0.31	0.45		
394	0.11	−0.05		
449.7	0.55	0.69		
1082.1	0.02	0.33		
1161.3	−0.05	−0.09		

for each mineral, and used for all subsequent calculations without any need to edit it. When a valid set of Grüneisen tensor components has been loaded into stRAinMAN, the calculation tabs become active (Figure 2). The *Calc Shifts* tab allows mode wavenumber shifts to be calculated from strains input by the user. There is the option to limit the input strains to only those allowed by the symmetry of the crystal (Figure 3). The output window contains the calculated change in wavenumber of each mode (the 'shift') for the input strains, calculated following Equation (5) as:

$$\Delta\omega^m = -\omega_0^m \gamma_i^m \varepsilon_i \tag{17}$$

where $\gamma_i^m \varepsilon_i$ follows the Einstein summation convention and means the sum over all components $i = 1-6$. It is important in this calculation to use the value of ω_0^m that was used to determine the values of γ_i^m, as their values depend on the value of ω_0^m. If the measured wavenumber of a mode in an unstrained crystal, say $\omega_{0,\mathrm{exp}}^m$, is slightly different from ω_0^m, the calculated change $\Delta\omega^m$ can be added to the measured $\omega_{0,\mathrm{exp}}^m$ to obtain the wavenumber $\omega_{\mathrm{exp}}^m = \omega_{0,\mathrm{exp}}^m + \Delta\omega^m$ expected from an experimental measurement.

The *Calc strains* tab of the stRAinMAN GUI allows the user to calculate the strains in a crystal from the measured changes in wavenumbers of several modes. In order to obtain accurate values of strains it is essential to measure the mode wavenumbers $\omega_{0,\mathrm{exp}}^m$ in an unstrained crystal of the same material under the same experimental conditions as the sample of interest, and to input $\Delta\omega_{\mathrm{exp}}^m = \omega_{\mathrm{exp}}^m - \omega_{0,\mathrm{exp}}^m$ into the program. The stRAinMAN program checks that the values of $\Delta\omega_{\mathrm{exp}}^m$ of a sufficient number of modes are input to allow the calculation of the symmetry-independent strain quantities of the crystal. Thus, a minimum of one mode is required to determine $\varepsilon_1 + \varepsilon_2 + \varepsilon_3$ in cubic crystals, and two modes to determine the quantities $\varepsilon_1 + \varepsilon_2$ and ε_3 in uniaxial crystals, etc. If exactly this number of modes are input, then only the values of the strain quantities can be determined by the program. If more modes are used, the estimated uncertainties of the strain components are also calculated by linear least-squares inversion of Equation (5) with the symmetry constraints applied, along with the value of χ^2 from the least-squares to indicate the consistency of the measured mode wavenumbers. The measured $\Delta\omega_{\mathrm{exp}}^m$ can be input directly into the GUI (Figure 4) or, for ease of processing large datasets, they can be read from a data file. The data file format is illustrated in Table 4. It consists of two essential header lines, followed by one line of mode shifts for each measurement. The mode shifts can appear in any order, but they must have the same order in every line. The header line labeled 'w0:' defines the order of the data by labeling the columns with the ω_0^m values. These must match (within 1 cm^{-1}) the values of ω_0^m in the file with the phonon-mode Grüneisen tensor components. For reasons of space, when a file is used to input the mode shifts, the uncertainties of calculated strain quantities



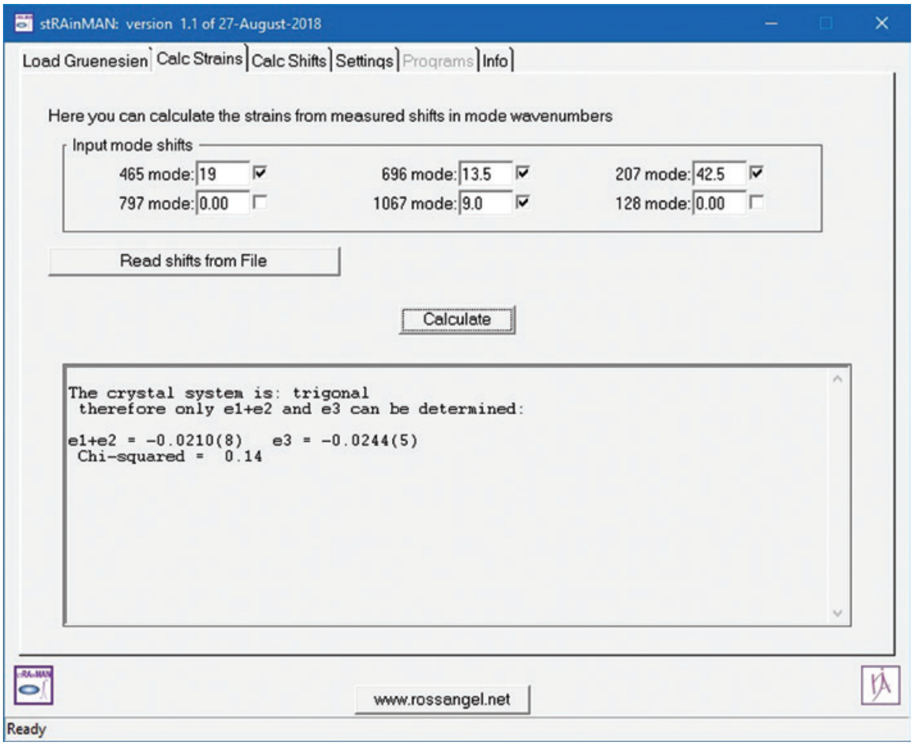
☑ No symmetry breaking strains

e1: -0.010
e2: -0.010
e3: -.025
e4: 0.0000
e5: 0.0000
e6: 0.0000

```
The crystal system is: trigonal
The input strains correspond to the symmetry-independent quantities:
e1+e2 =  -0.020
   e3 =  -0.025

   w0      shift     w
 464.80    19.405    484.21
 695.60    13.356    708.96
 207.30    42.300    249.60
 796.70    19.639    816.34
 1066.5    9.1719    1075.7
 128.10    11.715    139.81
```

Fig. 3: The *Calc Shifts* tab of the stRAinMAN GUI showing the result of a calculation for quartz. By ticking the box labeled 'No symmetry-breaking strains' the value of strain ε_2 is set equal to the value input for ε_1, and the input boxes for the shear strains are de-activated. The output window contains the calculated change in wavenumber of each mode $\Delta\omega^m$ (labeled as 'shift') for the input strains as well as the final value of the wavenumber 'w' assuming that the mode in the unstrained crystal has a wavenumber of ω_0^m.



Here you can calculate the strains from measured shifts in mode wavenumbers

465 mode: 19 ☑
696 mode: 13.5 ☑
207 mode: 42.5 ☑
797 mode: 0.00 ☐
1067 mode: 9.0 ☑
128 mode: 0.00 ☐

```
The crystal system is: trigonal
 therefore only e1+e2 and e3 can be determined:

e1+e2 = -0.0210(8)   e3 = -0.0244(5)
 Chi-squared =   0.14
```

Fig. 4: The *Calc Strains* tab of the stRAinMAN GUI showing the strains calculated from the changes in mode wavenumbers input into four of the boxes in the GUI. Because there are only two independent strain quantities that can be calculated for a uniaxial crystal, inputing data for at least three modes (four in the screenshot) allows the program to calculate the uncertainties in the strains, which are shown in parentheses. The *Read Shifts from File* button allows experimental data of changes in wavenumbers to be read from a list in a text file (Table 4).

Tab. 4: Example of a data file with measured changes in Raman shifts.

File contents	Explanation
title: Quartz shifts for calculating strains	Title of the file
w0: 207 464 696 1067	Value of ω_0^m to identify the mode in this file
shifts:	Start of data
42.3 19.4 13.3 9.2	1 line per spectrum
−43.0 −22.0 −10.0 −15.0	Each line contains measured values of $\Delta\omega^m$ in the order specified by the line labeled 'w0:'
−0.88 2.7 −5.6 8.5	
24.1 9.4 10.4 0.6	The order of the modes in this file does not have to match the order in which they are listed in the Grüneisen file

are not output to the GUI. They can be obtained by first opening a log file under the *Settings* tab of the GUI, which will then contain the results of all calculations that are performed. This provides a useful method by which results of calculations can then be cut and pasted into graphics or spreadsheet programs for further analysis and display.

The stRAinMAN program is written in Fortran-95 using the CrysFML [35] library. The program is free for non-commercial use and does not require any commercial software or libraries other than those provided with the program. It is freely available for download from www.rossangel.net for Windows operating systems, together with phonon-mode Grüneisen parameter files for common minerals, and example input files for illustrating the calculation of strains from measured Raman shifts. Basic help information is provided within the program, and this paper serves as the full description of how the stRAinMAN program operates.

Acknowledgements: Software development and analysis was supported by ERC starting grant 714936 and by the MIUR-SIR grant "MILE DEEp" (RBSI140351) to Matteo Alvaro. We thank Javier Gonzalez-Platas (La Laguna) for continuing collaboration and development of the CrysFML, Greta Rustoni (Bayreuth) for naming stRAinMAN, Nicola Campomenosi and Mattia Mazzuchelli for testing it, and Claudia Stangarone for giving us the data for Figure 1.

References

[1] J. D. Eshelby, The determination of the elastic field of an ellipsoidal inclusion, and related problems. *Proc. R. Soc. Lond. A Math. Phys. Sci.* **1957**, *241*, 376.

[2] M. Murri, M. L. Mazzucchelli, N. Campomenosi, A. V. Korsakov, M. Prencipe, B. Mihailova, M. Scambelluri, R. J. Angel, M. Alvaro, Raman elastic geobarometry for anisotropic mineral inclusions. *Am. Mineral.* **2018**, *103*, in press. DOI: 10.2138/am-2018-6625CCBY.

[3] M. L. Mazzucchelli, P. Burnley, R. J. Angel, S. Morganti, M. C. Domeneghetti, F. Nestola, M. Alvaro, Elastic geothermobarometry: corrections for the geometry of the host-inclusion system. *Geology* **2018**, *46*, 231.

[4] N. Campomenosi, M. L. Mazzucchelli, B. Mihailova, M. Scambelluri, R. J. Angel, F. Nestola, A. Reali, M. Alvaro, How geometry and anisotropy affect residual strain in host inclusion system: coupling experimental and numerical approaches. *Am. Mineral.* **2018**, *103*, in press. DOI: 10.2138/am-2018-6700CCBY.

[5] R. J. Angel, M. Bujak, J. Zhao, G. D. Gatta, S. D. Jacobsen, Effective hydrostatic limits of pressure media for high-pressure crystallographic studies. *J. Appl. Crystallogr.* **2007**, *40*, 26.

[6] J. Zhao, N. Ross, Non-hydrostatic behavior of KBr as a pressure medium in diamond anvil cells up to 5.63 GPa. *J. Phys. Condens. Matter* **2015**, *27*, 185402.

[7] H. O. Sørensen, S. Schmidt, J. P. Wright, G. B. M. Vaughan, S. Techert, E. F. Garman, J. Oddershede, J. Davaasambu, K. S. Paithankar, C. Gundlach, H. F. Poulsen, Multigrain crystallography. *Z. Kristallogr.* **2012**, *227*, 63.

[8] L. E. Levine, C. Okoro, R. Xu, Full elastic strain and stress tensor measurements from individual dislocation cells in copper through-Si vias. *IUCrJ* **2015**, *2*, 635.

[9] V. P. Zhukov, A. V. Korsakov, Evolution of host-inclusion systems: a visco-elastic model. *J. Metamorph. Geol.* **2015**, *33*, 815.

[10] M. J. Kohn, "Thermoba-Raman-try": calibration of spectroscopic barometers and thermometers for mineral inclusions. *Earth Planet. Sci. Lett.* **2014**, *388*, 187.

[11] E. Grüneisen, Zustand des festen Körpers. *Handbuch der Physik* **1926**, *1*, 1.

[12] J. M. Ziman, *Electrons and Phonons: the Theory of Transport Phenomena in Solids*. Oxford University Press, Oxford, p. 469, **1960**.

[13] S. W. Key, Grüneisen tensor for anisotropic materials. *J. Appl. Phys.* **1967**, *38*, 2923.

[14] H. Kroll, A. Kirfel, R. Heinemann, Axial thermal expansion and related thermophysical parameters in the Mg,Fe olivine solid-solution series. *Eur. J. Mineral.* **2014**, *26*, 607.

[15] J. H. Cantrell, Generalized Grüneisen tensor from solid nonlinearity parameters. *Phys. Rev. B* **1980**, *21*, 4191.

[16] T. H. K. Barron, J. F. Collins, T. W. Smith, G. K. White, Thermal expansion, Grüneisen functions and static lattice properties of quartz. *J. Phys. C Solid State Phys.* **1982**, *15*, 4311.

[17] Y. Zhang, Mechanical and phase equilibria in inclusion–host systems. *Earth Planet. Sci. Lett.* **1998**, *157*, 209.

[18] R. J. Angel, M. L. Mazzucchelli, M. Alvaro, P. Nimis, F. Nestola, Geobarometry from host-inclusion systems: the role of elastic relaxation. *Am. Mineral.* **2014**, *99*, 2146.

[19] M. A. Carpenter, E. K. H. Salje, A. Graeme-Barber, Spontaneous strain as a determinant of thermodynamic properties for phase transitions in minerals. *Eur. J. Mineral.* **1998**, *10*, 621.

[20] F. Camara, F. Nestola, R. J. Angel, H. Ohashi, Spontaneous strain variations through the low temperature displacive phase transition of $LiGaSi_2O_6$ clinopyroxene. *Eur. J. Mineral.* **2009**, *21*, 599.

[21] N. Zotov, Review of relationships between different strain tensors. *Acta Crystallogr. A* **1990**, *46*, 627.

[22] J. L. Schlenker, G. V. Gibbs, M. B. Boison, Jr., Strain-tensor components expressed in terms of lattice parameters. *Acta Cryst.* **1978**, *A34*, 52.

[23] J. F. Nye, *Physical Properties of Crystals*. Oxford University Press, Oxford, p. 329, **1957**.

[24] W. Voigt, *Lehrbuch der Kristallphysik*. Teubner, Leipzig, **1910**.

[25] C. Schmidt, M. A. Ziemann, In-situ Raman spectroscopy of quartz: a pressure sensor for hydrothermal diamond-anvil cell experiments at elevated temperatures. *Am. Mineral.* **2000**, *85*, 1725.

[26] K. Ashley, D. W. Barkoff, M. Steele-MacInnis, Barometric constraints based on apatite inclusions in garnet. *Am. Mineral.* **2017**, *102*, 743.

[27] F. A. Pina-Binvignat, T. Malcherek, R. J. Angel, C. Paulmann, J. Schlüter, B. Mihailova, Radiation-damaged zircon under high pressures. *Phys. Chem. Miner.* **2018**. published online.

[28] R. J. Briggs, A. K. Ramdas, Piezospectroscopy of the Raman spectrum of α-quartz. *Phys. Rev. B* **1977**, *16*, 3815.

[29] S. M. Gallivan, Y. M. Gupta, Study of tensile deformation in shocked Z-cut, α-quartz using time resolved Raman spectroscopy. *J. Appl. Phys.* **1995**, *78*, 1557.

[30] J. Zhao, R. J. Angel, N. L. Ross, Effects of deviatoric stresses in the diamond-anvil pressure cell on single crystal samples. *J. Appl. Crystallogr.* **2010**, *43*, 743.

[31] M. Prencipe, Simulation of vibrational spectra of crystals by ab initio calculations: an invaluable aid in the assignment and interpretation of the Raman signals. The case of jadeite ($NaAlSi_2O_6$). *J. Raman Spectrosc.* **2012**, *43*, 1567.

[32] C. M. Zicovich-Wilson, F. Pascale, C. Roetti, V. R. Saunders, R. Orlando, R. Dovesi, Calculation of the vibration frequencies of α-quartz: the effect of Hamiltonian and basis set. *J. Comput. Chem.* **2004**, *25*, 1873.

[33] H. Özkan, J. Jamieson, Pressure dependence of the elastic constants of non-metamict zircon. *Phys. Chem. Miner.* **1978**, *2*, 215.

[34] I. D. Brown, CIF (Crystallographic Information File): a standard for crystallographic data interchange. *J. Res. Natl. Inst. Stand. Technol.* **1996**, *101*, 341.

[35] J. Rodriguez-Carvajal, J. Gonzalez-Platas, Crystallographic Fortran 90 Modules Library (CrysFML): a simple toolbox for crystallographic computing programs. *IUCr Comput. Comm. Newsletter* **2003**, *1*, 50.