Solid Earth Discuss.,
https://doi.org/10.5194/se-2020-180-AC2, 2021

Solid Earth Discussions
Open Access
EGU

Interactive comment on "Analytical solution for residual stress and strain preserved in anisotropic inclusion entrapped in isotropic host" *by* Xin Zhong et al.

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Received and published: 8 January 2021

We thank the workers for posting this interesting comment on the symmetry breaking issue. Below, we provide our replies to the comments. Our replies are given in blue and the original comments from the commenters are in black.

The analysis developed in this manuscript to calculate the Raman shifts developed in ellipsoidal inclusions is correct under the assumption that the symmetry of the inclusion crystal is not broken by the strains imposed by the host crystal. Under these circumstances, it agrees with the extensive analyses published in both the materials science and geological literature.

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With an isotropic host crystal (and we agree that normal metamorphic silicate garnets can be treated as being elastically isotropic for these purposes) the Eshelby solution for inclusion stress and strain shows that the symmetry of an ellipsoidal inclusion crystal will be broken when the crystallographic axes of the inclusion crystal do not coincide with the principal axes of its ellipsoidal shape. The manuscript is also correct in stating that the symmetry of faceted inclusion crystals will be also be broken; this is the consequence of stress and strain concentration at corners and edges of the inclusion, as well as of the orientation of the crystallographic axes of the inclusion with respect to the shape. Such symmetry breaking of the inclusion crystal must also affect the values of the components of the phonon-mode Grüneisen tensor which determine its Raman shifts arising from the strains applied to the inclusions. These Grüneisen tensors have only been determined for a limited number of crystals. Recent DFT calculations of these Grünesien tensors (Murri et al. 2018 for quartz; Stangarone et al. 2019 for zircon, Musiyachenko et al. 2020 for rutile) explicitly assume that the symmetry of the crystal is preserved. That means that the unit-cell strains are constrained as e1 = e2 to preserve the equivalence of the a- and b-axes of these uniaxial crystals. Therefore, these tensors cannot be applied to strain states where the e1 component is different from e2, or those with non-zero shear components, which will arise from the mechanical states presented in Figures 4 and 5 of this manuscript.

The magnitude of the effect of symmetry-breaking on the Grüneisen tensors of minerals has not been calculated in recent DFT simulations. But there is direct experimental evidence that it can be significant compared to the shifts without symmetry breaking (e.g. Briggs and Ramdas, 1977, on quartz). If symmetry-breaking was not an issue, then the Raman peaks of cubic host minerals such as diamond and garnets would not exhibit any change in the deviatoric strain fields around inclusions (e.g. Angel et al. 2019). But the Raman shifts in diamond (e.g. Nasdala et al., 2005) and garnets (Campomenosi et al., 2020) around inclusions have been measured and are significant. They are correlated with the symmetry-breaking visible in thin sections as optical birefringence haloes. Therefore, the calculations in the current manuscript of Raman

shifts of inclusions whose symmetry is broken is not correct. The magnitude of the error is unknown. In summary, for the cases in which the symmetry of the inclusion crystal is not broken, this manuscript provides results that are in agreement with previous studies with a variety of methods. For inclusions whose symmetry is broken, this manuscript does not allow for the additional Raman shifts that will arise from the symmetry breaking. This means that Figures such as 4 and 5 should not be used to interpret the Raman shifts in quartz inclusions trapped in garnets and the authors should clearly identify in the manuscript all of their examples and calculations in which the inclusion symmetry is broken.

We agree with the commenters that deviatoric stresses will generally impose an effect of the physical properties of minerals. The commenters also correctly point out that the DFT calculation performed by Murri et al. (2018) embeds the property of e1=e2, which mimics the D3 symmetry of quartz. We presume that the commenters argue that when our model predicts e1$\neq$e2, the existing parameterization of the Gruneisen tensor by Murri et al. (2018) should not be applied as the assumption taken before is violated.

First, we want to clarify that the stress-induced symmetry breaking and related impact on physical properties have no adverse effect on the proposed analytical solution based framework to studying inclusion-host mechanics. In our view there are two aspects of the problems: 1) the applicability of the analytical solution and the stress field associated with loads due to inclusion eigenstrain (the main target of the work) and 2) the impact of potential symmetry breaking on the calculated Raman shift. The commenters are mainly concerned about the second part. However, the main outcome of our work, which is the proposed analytical solution framework, is largely unaffected by the stress-induced symmetry-breaking effects. Regarding the symmetry breaking issue, it is not only the Gruneisen tensor that is affected by the symmetry breaking effects due to the presence of general (deviatoric) stress states, when for example shear stress components along the principal crystallographic axes do not necessarily vanish. Any physical property such as elastic stiffness, viscosity and thermal expansivity

etc. is affected as well, and, in general, resulting in substantial challenges as experimental measurements under different level of deviatoric stress need to be performed and fit all the physical properties as a function of individual stress components. To our knowledge, there is no such data related to e.g. quartz in garnet system. As we are not specialists in experiments, there may be technical difficulties associated with such experiments, which the commenters may know better. However, the proposed analytical approach is capable of incorporating an arbitrary stiffness tensor for the inclusion phase, and in particular the cases of oblique crystallographic orientations with respect to the principal geometric axes of the inclusion. The model, in its incremental form, can also embed stress-induced changes to the stiffness tensor, including the effect due to symmetry-breaking (please see below). In fact, the non-linearity of stiffness tensor (both inclusion and host) due to deviatoric stress has not been addressed in any of the available mechanical models relevant to Raman elastic thermobarometry. The analytical framework described in this work has a capacity to deal with this problem for the inclusion phase (however admittedly not for the host phase), and experimental parametrizations of the non-linear dependence of the mineral stiffness tensor components on general (deviatoric) stress states would be greatly appreciated in this context.

The key question is how large the effects due to symmetry-breaking could be in minerals. The commenters referenced the paper of Briggs and Ramdas (1977), where they applied uniaxial stress on single quartz crystal along x, y and z direction to fit the experimental deformation potential (same as Gruneisen tensor components). When the uniaxial force F is along the x or y direction, the symmetry is reduced from D3 to C2 (or C1 if F has arbitrary orientation). In this case, the commenters argue that the Gruneisen tensor should significantly vary. Below, we summarize the experimentally (uniaxial stress) calibrated Gruneisen components with symmetry broken ($e1 \neq e3$) and the HF/DFT ab-initio results from Murri et al. (2019). For comparison purpose, we present the ratio between the Gruneisen components along the crystallographic a and c directions. (EXP represents the experimental value from Briggs and Ramdas 1977

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Raman bands	a/c (EXP)	a/c (DFT)
464 (A1)	0.542	0.504
206 (A1)	0.889	0.693
360 (A1)	-0.550	-0.689
1080 (A1)	0	0.06

and DFT represents the ab-initio results from Murri et al. 2019). Only A1 vibration mode is reported here.

Although the exact ratio is different, they are still quite comparable and we need to also note that one set is experimental and the other is ab-initio, which is already in good agreement. The experimental data is obtained under uniaxial stress with symmetry broken while the DFT is based on symmetry preserving condition. It is our speculation that the effect of deviatoric stress may not be significant to the Raman shift (also the second-order effect of shear modulus as a function of deviatoric stress). It is also noted that quartz in garnet system has been successfully in numerous literatures cited in the manuscript, showing that the deviatoric stress effect is not so significant at least for quartz case.

We agree that by breaking the mineral symmetry due to applied deviatoric stress, all physical properties, including the Gruneisen and stiffness tensors, may be affected but the amount of the effect is unknown yet due to the lack of experimental data. We would argue that the symmetry breaking effects can be viewed as a subset of a wider class of effects due to stress-induced (non-linear) changes of physical properties. We agree that these effects should be thoroughly studied and the resulting new parameterization could be directly used in improved mechanical models such as the one proposed in this study.

We have added a new paragraph in the manuscript to speculate about the effect of

symmetry breaking. We also would like to point out that we are primarily focused how large the departure of Raman shift is from a spherical case by assuming that the phonon coefficients in front of the e1 and e2 terms are still the same even if e1 is not equal to e2. This is a first-order estimate that is taken here and clarified in the main text. We would be very happy to apply the new calibrations for symmetry broken situation, if they are available, thus we will keep track of the updates of the commenters' research.

References

Angel RJ, Murri M, Mihailova B, Alvaro M (2019) Stress, strain and Raman shifts.Zeitschrift für Kristallographie, 234, 129-140.

Briggs RJ, Ramdas AK (1977) Piezospectroscopy of the Raman spectrum of a-quartz.Physical Review B, 16, 3815-3826.

Campomenosi N, Mazzucchelli ML, Mihailova B, Angel RJ, Alvaro M (2020) Using-polarized Raman spectroscopy to study the stress gradient in mineral systems with-anomalous birefringence. Contributions to Mineralogy and Petrology, 175:16.

Murri, M., Mazzucchelli, M.L., Campomenosi, N., Korsakov, A. V., Prencipe, M., Mihailova, B.D., Scambelluri, M., John, A.R., Matteo, A., Angel, R.J., Alvaro, M., (2018) Raman elastic geobarometry for anisotropic mineral inclusions. Am. Mineral. 103, 1869–1872.

Musiyachenko KA, Murri M, Prencipe M, Angel RJ, Alvaro M (2020) A new Grüneisen tensor for rutile and its application to host-inclusion systems. American Mineralogist, submitted.

Nasdala, L., Hofmeister, W., Harris, J.W., and Glinnemann, J. (2005) Growth zoningand strain patterns inside diamond crystals as revealed by Raman maps. American Mineralogist, 90, 745–748.

Stangarone C, Alvaro M, Angel R, Prencipe M, Mihailova BD (2019) Determination ofthe phonon-mode Grüneisen tensors of zircon by DFT simulations. European Jour-

nalof Mineralogy, 31, 685-694

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