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Thermo-elastic behaviour of grossular garnet at high pressures and temperatures

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ABSTRACT
The thermo-elastic behaviour of synthetic single crystals of grossular garnet (Ca\textsubscript{3}Al\textsubscript{2}Si\textsubscript{3}O\textsubscript{12}) has been studied in situ as a function of pressure and temperature separately. The same data collection protocol has been adopted to collect both the pressure-volume ($P-V$) and temperature-volume ($T-V$) datasets in order to make the measurements consistent with one another. The consistency between the two datasets allows simultaneous fitting to a single pressure-volume-temperature equation of state (EoS), which was performed with a new fitting utility implemented in the latest version of the program EoSFit7c. The new utility performs fully weighted simultaneous fits of the $P-V-T$ and $P-K-T$ data using a thermal pressure Equation of State combined with any PV EoS. Simultaneous refinement of our $P-V-T$ data combined with that of $K^T$ as a function of $T$ allowed us to produce a single $P-V-T-K^T$ equation of state with the following coefficients:

$V_0 = 1664.46(5)$ Å\textsuperscript{3}, $K_0 = 166.57(17)$ GPa and $K^T = 4.96(7)$ $a_{300K,1bar} = 2.09(2)*10^{-5}$ $K^{-1}$ with a refined Einstein temperature ($\theta_E$) of 512K for a Holland-Powell-type thermal pressure model and a Tait 3rd-order EoS. Additionally, thermodynamic properties of grossular have been calculated for the first time from crystal Helmholtz and Gibbs energies, including the contribution from phonons, using density functional theory within the framework of the quasi-harmonic approximation.

Keywords: grossular, high-pressure, high-temperature, diffraction, bulk modulus, P-V-T-K fit, EosFit
1. INTRODUCTION

Stable over a wide range of pressure and temperature conditions, garnets are among the most abundant phases in the Earth’s upper mantle and transition zone. Yet coherent and homogeneous equation of state coefficients to reliably describe their behaviour at simultaneous high pressures and temperatures still have to be determined with sufficient accuracy and precision. Recent papers have shown the importance of a robust and valid description of the elastic behaviour of the most abundant mineral phases for the accurate calculation of host-inclusion entrapment pressures that in turn allow the growth conditions in the Earth to be inferred (e.g. Angel et al. 2014, 2015a, 2015b; Ashley et al. 2015; Milani et al. 2015). However, the determination of a full set of elastic coefficients of a mineral is always challenging because of the limitations in performing simultaneous high-pressure ($P$) and temperature ($T$) experiments on one side and because of the lack of consistent measurements performed separately at high-$P$ and high-$T$. Therefore, a reliable description of the elastic behaviour of minerals at high-$P,T$ with a single set of Equation of State (EoS) coefficients can be extremely challenging.

Pressure-volume EoS are well-developed and are capable of reproducing the isothermal volume or density changes of materials to within the experimental uncertainties. A natural approach to describing the $P$-$V$-$T$ behaviour of a material is therefore to describe how the volume ($V_0T$), bulk moduli ($K_0T$) and its pressure derivatives ($K_0T'$) change with increasing temperature (at room pressure), and then use these parameters to calculate the isothermal compression at the temperature of interest. A potential limitation of this approach is that while the variation of $K_0T$ with $T$ can be measured, the variation of $K_0T'$ with $T$ has been measured very rarely, although it is obvious that it should increase slightly with increasing temperature. As Helffrich and Connolly (2009) pointed out, the common assumption that $K_0T'$ does not change with temperature in combination with the approximation that $\partial K_0T' / \partial T$ is constant, often leads to the prediction of non-physical negative

$^1$ Notation: subscripts on $K$ (e.g. $K_{P,T}$) indicate the reference pressure and temperature to which the bulk modulus is referred; superscripts S or T (e.g. $K^3$ or $K^T$) stand for adiabatic or isothermal quantities.
thermal expansion coefficients at reasonably modest pressures for a large number of materials. An alternative approach is to employ the idea of thermal pressure (e.g. Anderson 1995). Then the total pressure \( P \) at a given \( V \) and \( T \) can be expressed as the sum of two terms:

\[
P(V,T) = P(V,T_{\text{ref}}) + P_{\text{th}}(T)
\]

The function \( P(V,T_{\text{ref}}) \) is the isothermal equation of state for material at the reference temperature, up to the volume at \( P \) and \( T_{\text{ref}} \). As shown in the Figure 1, if \( T > T_{\text{ref}} \), then \( P(V,T_{\text{ref}}) < P(V,T) \). The thermal-pressure \( P_{\text{th}}(T) \) is the pressure that would be created by increasing the temperature from \( T_{\text{ref}} \) to \( T \) at constant volume, which is the isochor of the material passing through the final \( P,T \) point of interest. As shown in Figure 1, the concept of thermal pressure is therefore essentially a way of calculating \( P(V,T) \) along a different path in \( P,T \) space. We can consider that the isothermal compression part that gives us \( P(V,T_{\text{ref}}) \) is well-defined. The slope of the isochor is given by

\[
\frac{\partial P}{\partial T} = \frac{\alpha}{\beta} = aK^T
\]

(where \( \alpha \) is the volume thermal expansion and \( \beta \) is the compressibility of the material) so the thermal pressure is

\[
P_{\text{th}} = \int_{T_{\text{ref}}}^{T} (aK^T) \, dT
\]

In order to use a thermal-pressure EoS one then has to know, or to make an assumption, about how the product \( aK^T \) varies along the isochor. For many materials and \( P,T \) ranges of interest (e.g. Figure 1) the temperatures are in the region of the Debye temperature, so the isochor is linear and thus \( aK_T \) is a constant. In this case

\[
P_{\text{th}} = (aK^T) \, (T - T_{\text{ref}})
\]

A number of other assumptions or models of the behaviour of the material can be made, including the Debye and similar models which make assumptions about the vibrational and hence thermal behaviour of materials. Holland and Powell (2011) noted that the form of \( aK^T \) against temperature should have the shape of a heat capacity function and developed an approximation for the integral of \( aK^T \) that involves an Einstein function, as follows:
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\[
P_{th} = \alpha_0 K_{00} \left( \frac{\theta_E}{\xi_0} \right) \left( \frac{1}{\exp(\frac{\theta_E}{T}) - 1} - \frac{1}{\exp(\frac{\theta_E}{T_{ref}}) - 1} \right)
\]

with \( \xi_0 \) being the same as in the thermal expansion equation of Kroll et al. (2012). This thermal-pressure model has the physically-correct properties that the product \( \alpha K^T \) becomes constant at high temperatures while it decreases to zero at low temperatures. This means that both the bulk modulus \( K_{0T} \) and the thermal expansion become constant at low temperatures, and both have an approximately linear variation with temperature above \( \theta_E \). The exact expressions for thermal expansion and bulk modulus as a function of temperature depend on the choice of isothermal equation of state, but at \( T_{ref} \) and zero pressure \( \alpha = \alpha_0 \) (Holland and Powell 2011). In this study we used the Holland and Powell (2011) model of thermal pressure in combination with the Tait isothermal EoS (so as to maintain compatibility with Thermocalc, Holland and Powell 2011) to determine the EoS of grossular (Ca\(_3\)Al\(_2\)Si\(_3\)O\(_{12}\)) garnet. We show that the thermal pressure approach allows the full \( P-V-T \) EoS to be determined by fitting simultaneously measurements of the volume and bulk modulus over a range of temperature but only at room pressure. Additional separate measurements of the volume compression curve at high-\( P \) can be used to provide either an independent test of the EoS parameters, or be used to further constrain them in simultaneous global fits of all available data. This approach has the advantage of not requiring data from simultaneous high-\( P \), high-\( T \) measurements which remain challenging with respect to both the control and accurate measurement of \( P \) and \( T \), and with respect to the precision in volume measurements. A comparison with previous literature data (e.g. Skinner 1956; Isaak et al. 1992; Thieblot et al. 1998; Kono et al. 2010; Gwanmesia et al. 2014; Du et al. 2015 etc..) is provided together with a further crosscheck of our experimental data against the results obtained by density functional theory (DFT) ab-initio simulation. Thermodynamic properties of grossular have been calculated for the first time from crystal Helmholtz and Gibbs energies, including the contribution from phonons, using density functional theory within the framework of the quasi-harmonic approximation.
2. METHODS

2.1 Sample synthesis and characterization

Synthetic single crystals of pure end-member grossular (Gr$_{100}$) garnets were synthesized at high pressures with a multi-anvil apparatus at the Bayerisches Geoinstitut. Stoichiometric mixtures of CaO (prepared by decarbonation of CaCO$_3$), Al(OH)$_3$ and SiO$_2$ were packed into platinum capsules of 3.5 mm length and 2 mm diameter. Samples were synthesized at 6 GPa and 1300°C. The experimental sample was heated in 23 mins and the temperature was kept at 1300°C for 40 mins. Each multi-anvil experiment was performed with Cr-doped MgO octahedra of 18 mm edge length combined with tungsten carbide cubes of 11 mm truncation-edge lengths. For all the experiments a graphite heater was employed. Experiments were quenched by cutting the electrical power supply to the furnace. Single-crystals of up to ca. 100 μm in diameter were recovered from the capsules. The compositions of the crystals have been determined by electron microprobe at the University of Padova using a Cameca CAMEBAX-micro operating at 15 nA and 15 kV with standards of andradite for Si, spinel for Al and diopside for Ca. Results from the chemical analyses are reported in Table 1. Two crystals (with size ca. 80 x 30 x 30 μm) were selected for the X-ray diffraction study based on the absence of twinning and visible inclusions and on the quality of their diffraction peak profiles (FWHM not greater than 0.15°).

2.2 Thermal expansion behaviour by single crystal X-ray diffraction experiments

The high-temperature single-crystal X-ray diffraction experiments were performed at the University of Pavia with a HUBER four-circle point detector diffractometer operating at 50 kV and 30 mA (MoKα radiation) and equipped with a 0.8 mm short collimator and automated with the SINGLE software (Angel and Finger 2011). This diffractometer is equipped with a newly designed...
micro-furnace controlled by a Eurotherm temperature regulator (Alvaro et al. 2015). For the high-$T$ experiments, one single crystal of grossular was placed inside a thin-walled quartz vial (0.3 mm inner diameter and 26 mm long) and held in position by means of quartz wool. The vial was then mounted on a metal goniometer head on the diffractometer. During the high-temperatures experiments the effects of the crystal offsets and the diffractometer aberrations were compensated by using the eight-position centring method (King and Finger 1979) before starting the high-$T$ measurement. The unit-cell parameters (Table 2 and Figure 2) were determined at 23 different temperatures from room-$T$ up to 1020 K using only 4-position centring because of the spatial restrictions described in Alvaro et al. (2015). A further 7 measurements were then made on cooling back to room temperature. Each individual measurement took about 12 hours, and the high-temperature experiment lasted for a total of 14 days. Unconstrained unit-cell parameters confirmed the cubic symmetry within 1 e.s.d. Therefore, only constrained unit-cell parameters obtained by vector least-squares fit (Ralph and Finger 1982) are reported in Table 2. Unit-cell parameters determined on the heating and cooling cycles are indistinguishable.

The low-temperature single-crystal X-ray diffraction experiment was performed on the very same crystal used for the high-$T$ experiment still mounted inside its quartz vial. The experiment was carried out at the Institut für Mineralogie und Kristallographie at the University of Wien using a Stoe StadiVari diffractometer equipped with an Incoatec $\mu$S microsource (Mo-target, with multi-layer mirror optics, operating at 50kV and 0.1mA) and a Pilatus 300K area detector. Low temperatures were achieved using an Oxford Cryojet system that allows measurements to be performed between 100 and 500 K. Full intensity data collections up to 110° 2θ (with a coverage of 99% and redundancy higher than 4) were performed at 10 different temperatures from room-$T$ down to 100 K. Correction of the crystal offsets from the goniometer center were made by first performing a short data collection and adjusting the crystal position to make the frame scale factors flat. Unconstrained unit-cell parameters confirmed the cubic symmetry within 1 e.s.d.; therefore, only constrained unit-cell parameters are reported in Table 2 and Figure 2 together with those
obtained at high-T.

2.3 Compressibility behaviour by single crystal X-ray diffraction experiments

High-pressure single-crystal X-ray diffraction experiments for the grossular garnet were carried out with a Huber four-circle diffractometer at the Bayerisches Geoinstitut. The diffractometer operates at 50 kV and 40 mA (MoKα radiation), is equipped with a point detector and is automated by SINGLE software (Angel and Finger 2011). The sample was loaded in a ETH-type diamond-anvil cell (DAC, Miletich et al. 2000) using a steel gasket, pre-indenteted to 100 μm thickness and with a hole diameter of 250 μm. Methanol:ethanol mixture 4:1 was used as pressure transmitting medium, which remains hydrostatic up to about ~ 9.5 GPa (Angel et al. 2007; Klotz et al. 2009). A single crystal of quartz was loaded in the DAC together with the sample and used as a pressure standard (Angel et al. 1997). During the centring procedure, the effects of crystal offsets and diffractometer aberrations were eliminated from the refined peak position by the eight-position centring method (King and Finger 1979). Unconstrained unit-cell parameters were obtained by vector least-squares fit (Ralph and Finger 1982) on not less than 20 reflections up to 20 = 29°. The symmetry-unconstrained unit-cell edges show deviations smaller than 1 e.s.d. from the constrained ones thus confirming the cubic symmetry within 1 e.s.d.. Therefore, only the constrained unit-cell parameters have been reported in Table 3 and Figure 3.

2.4 Fitting of the pressure-volume-temperature-modulus data using EoSFit7c

All fits described in this manuscript have been performed with the EosFit7c program (Angel et al. 2014). Previous versions of this program were able to fit isothermal EoS, thermal expansion models and the thermal-pressure EoS of Holland and Powell (2011) to P-V, V-T or P-V-T data, by the method of least-squares. We have now extended the capabilities of EosFit-7c to also fit all of these forms of EoS to bulk and linear moduli, either alone or in combination with volume or unit-cell parameter data. Fits are performed by weighted non-linear least squares to minimise the
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residuals $P_{\text{obs}} - P_{\text{calc}}$, using the effective variance method (Orear 1982) to convert the experimental
uncertainties in volume and bulk moduli, pressure and temperature of each datum into an effective
uncertainty in $P$ (Angel 2000). Input bulk moduli can be either adiabatic ($K^s$) or isothermal values
($K^T$), but in either case they must be Reuss values, corresponding to the response of the material
under hydrostatic pressure. The Voigt and Reuss bulk moduli of a material quantify its volume
response to the application of uniform strain and uniform stress (hydrostatic pressure) respectively.
When uniform stress is applied to a cubic material, it undergoes isotropic (i.e. uniform) strain.
Therefore, the Voigt and Reuss bulk moduli of a cubic material are identical. We remind the reader
that this is not true for materials of lower symmetry and therefore the use of Voigt values, or Voigt-
Reuss-Hill averages, in Equations of state of crystals with symmetry lower than cubic is
inconsistent with the theory underlying equations of state under hydrostatic conditions, and will
lead to incorrect results (e.g. Angel et al. 2009).

If the input moduli to EosFit7c are isothermal, no further conversion is made, and the
observational equations for such data in the least-squares are simply the expression for the bulk
modulus in terms of pressure for each EoS. These expressions are direct for invertible EoS such as
the Murnaghan or Tait EoS (Freund and Ingalls 1989; Holland and Powell 2011; Angel et al. 2014).
For non-invertible EoS the procedure used is to calculate the compression ratio $V/V_0$ corresponding
to the observed $K$ and then use the $P-V$ expression of the EoS to calculate the corresponding
pressure. If adiabatic moduli are provided as input data, they are converted to isothermal values by
$K^s = (1 + \alpha_v \gamma T)K^T$ where the value of thermal expansion ($\alpha_v$) is taken from the current EoS at the
pressure and temperature of interest. The Grüneisen parameter $\gamma$ can be expressed in terms of
measurable quantities, for example $\gamma = \frac{\alpha_v K^s}{C_p} = \frac{\alpha_v K^T}{C_v}$. However, since heat capacity data is not
available at elevated pressures, in EosFit7c we use the simple approximation (Anderson 1996) that
$\gamma(P,T) = \gamma_0 \left(\frac{V(P,T)}{V_0}\right)^q$, with the value of $q$ close to 1 for ‘normal’ solids under modest $P,T$
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ditions. Only Boehler and Ramakrishnan (1980) and Boehler (1982) appear to have attempted to
measure the value of $q$, showing that it scales with volume. This means that the Grüneisen
parameter scales with volume, increasing with increasing temperature and decreasing upon
compression, which when considered as a measure of the pressure-dependence of the frequencies of
vibrational modes, is reasonable. This will break down when the material becomes very
anharmonic, near to structural phase transitions, but should not be a problem for materials such as
the grossular garnet in this study. The value of $\gamma_0$ (i.e. $\gamma$ value at the reference conditions) and of $q$
can be set by the user in Eosfit7c.

For linear moduli that describe the variation of the unit-cell parameters with pressure as

$$M_i^T = -\alpha_i \frac{\partial P}{\partial a_i},$$

the procedure is analogous to that used for linear dimensions in EosFit7 (Angel et al., 2014). Internally the linear moduli are converted to volume-like bulk moduli as $K_i = \frac{M_i}{3}$ and

for the conversion of adiabatic to linear moduli, we use the relationship

between isothermal and adiabatic compressibilities $\beta_i^T = \beta_i^S + \frac{\alpha_i \alpha_i T}{C_p}$ which can be derived from

the fundamental relationship between isothermal and adiabatic elastic compliances

$$s_{ijkl} = s_{ijkl}^S + \frac{\alpha_i \alpha_i T}{C_p}$$

with the $C_p$ in units of $Jm^{-3}K^{-1}$ (Nye 1985). The substitution $\frac{\gamma}{K^S} = \frac{\alpha_y}{C_p}$ gives

$$\beta_i^T = \beta_i^S + \frac{\alpha_i \gamma T}{K^S} = \beta_i^S \left(1 + \frac{\alpha_i \gamma T \beta_i^S}{\beta_i^S}ight)$$

which can be rewritten in terms of moduli as

$$M_i^S = \left(1 + \alpha_i \gamma T \frac{M_i^S}{K^S}\right)M_i^T.$$ 

It is important to notice that for cubic materials $\alpha_i = \alpha_y / 3$ and $\frac{M_i^S}{K^S} = 3$

so that only for cubic materials this can be written as $M^S = \left(1 + \alpha_y \gamma T\right)M^T$ which is the same

relation as for the bulk moduli.

2.5 Ab-initio DFT (Density Functional Theory)
Ab-initio calculations have been performed in order to crosscheck our experimental results at simultaneous high-$P$ and $T$. Thermodynamic properties of grossular have been calculated from crystal Helmholtz and Gibbs energies, including the contribution from phonons, using density functional theory (DFT) within the framework of the quasi-harmonic approximation (QHA). Periodic DFT calculations were performed with the plane-wave VASP package (Kresse and Furthmüller 1996) within GGA approximation, with projector-augmented waves (PAW, Blöchl 1994) and the PBEsol functional (Perdew et al. 2008). A plane-wave cutoff of 520 eV (1.3 x default VASP value) was used as recommended in the VASP package. Energy convergence was tested for two k-meshes 2x2x2 and 4x4x4. Since the denser mesh did not lead to any significant reduction in energy ($\Delta E<0.001$ eV) the 2x2x2 mesh was used both for unit cell optimization and subsequent calculation of interatomic forces. The cell was optimized at 17 pressure points within the range [-8 to 8GPa] with step of 1 GPa. The threshold for electronic and ionic convergence was set to $10^{-8}$ and $10^{-6}$ eV, respectively. The atomic forces were converged to $10^{-5}$ eV/Å. Phonon frequencies at constant cell volumes were calculated in program PHONOPY (Togo and Tanaka 2015) which takes advantage of the direct method of Parlinsky et al. (1997). The force constants used to construct the dynamical matrices (input for PHONOPY) were calculated in the VASP package using density functional perturbation theory (DFPT, Baroni et al. 2001) and taking into account symmetries of the conventional body-centered cell of the garnet, containing 160 atoms. The results obtained with DFT-GGA commonly overestimate cell volume values of ionic solids by up to 9.5% with respect to experimental results while PBEsol functional brings the discrepancy down to 2% (Perdew et al. 2008). In our case, the DFT calculations yielded volume values of 1664.6 Å³ (static DFT), 1681.9 Å³ (zero-point vibration included) and 1687.3 Å³ (T=290 K) which agree with experimental values of 1664.3 Å at room $P$ and $T$, (0.0001 GPa and 300 K) within 0.0 %, 1.1% and 1.4% respectively. This volume overestimation amounts to about -2 GPa, on the pressure scale, with respect to the experimental datum.
3. RESULTS

3.1 Temperature-volume data

The room-PT unit-cell volumes \( (V_{00}) \) of grossular as determined in this study, agree with one another to better than 1 e.s.d. thus confirming the reliability of the unit-cell lattice determination with different instruments and measurement protocols. Therefore, we combined the high-\( T \) measurements together with those at low-\( T \) in a single dataset without any normalization or re-scaling. The evolution of the unit-cell volume with temperature is reported in Figure 2 and Table 2 where the low-\( T \) and the high-\( T \) data are reported together. A continuous increase of the unit-cell volume is observed as a function of temperature with no evidence of any irreversible change in the crystal occurred up to the maximum temperature reached in this study. Data collected both with increasing and decreasing temperature overlap within experimental error, thus indicating good experimental reproducibility. The temperature-volume data for the entire range of \( T \) studied were fit using the software EoSFit7c (Angel et al. 2014) using a Kroll-type EoS (Kroll et al. 2012) allowing for refinement of the Einstein temperature \( (\theta_E) \) but not refining \( K' \) value that was kept fixed to 5 (i.e. the value from compressibility data, see the following sections). The thermal expansion coefficients obtained were \( \alpha(298K, \text{1 bar}) = 2.08(2)*10^{-5} \text{ K}^{-1} \), \( V_{00} = 1664.45(7) \text{ Å}^3 \) with \( \theta_E = 515(20) \text{ K} \).

We compared our \( T-V \) for grossular with those from Isaak (1992) determined by dilatometry. Isaak et al. (1992) measured physical expansions, and converted such values to volume expansions \( Yv(\text{obs}) \). Conversion of Isaak et al. (1992) data (taken from their Table 2) to unit-cell volumes has been performed according to \( V = V_0(1 + Yv_{\text{obs}}) \). In order to ensure that our measurements and those by Isaak et al. (1992) were on the same volume scale we used our \( V_{00} \) at the same reference temperature of 293K used by Isaak et al. (1992). A plot of the two datasets (see Figure 2) shows that they agree within their mutual uncertainties.

3.2 Temperature-volume-bulk modulus data
Isaak et al. (1992) also determined the adiabatic bulk modulus of grossular by RUS measurements and then used measured heat capacity data and their own thermal expansion data to also calculate the isothermal bulk modulus at each measurement temperature by means of

\[ K^S = (1 + \alpha_T \gamma T)K^T \]

using the value of the Grüneisen parameter \( \gamma = \frac{\alpha_T K^S}{C_p} \). The reliability of the heat capacity \( (C_p) \) data by Isaak et al. (1992) has been confirmed by comparison with the more recent data by Bosenick et al. (1996) (see Figure 4). The \( C_p \) values determined by Isaak et al. (1992) fall well within the scatter of the data determined by Bosenick et al. (1996) and are also in good agreement with those we have obtained from the DFT calculations.

Using \( K \) and \( V \) data as a function of \( T \) it is obviously possible to refine \( V_{00}, \alpha_0, \theta_E \) and \( K_{00} \). But in addition it is possible and required to refine \( K' \) because this affects the results when using the thermal pressure model as it appears in the isothermal EoS \( P(V, T_{ref}) \), and at room pressure

\[ P(V, T_{ref}) = -P_{th}(T). \]

Simultaneous refinement of our \( T-V \) data and the \( T-K^S \) data from Isaak et al. (1992) for grossular using \( \gamma_0=1.22 \) and \( q=0 \) (i.e. \( \gamma=\gamma_0 \)) yielded identical results as to those obtained from fitting the \( T-V-K^T \) data (see Table 4\(^2\)). This shows that the assumption that \( \gamma \) is constant is a reasonable approximation for grossular. This observation is also in agreement with Isaak et al. (1992) who calculated that \( \gamma \) drops by 0.1(± 0.05) over the temperature range from 300K to 1200K and with our results from DFT calculations as shown in Figure 4 according to which \( \gamma \) drops to 1.24 at 650K and then it assumes constant values (e.g. changes of about 2 at the 3\(^{rd}\) decimal place) above 650K.

3.3 Pressure-volume data

The unit-cell volume decreases smoothly with increasing pressure, as shown in Figure 3 and reported in Table 2, up to the maximum hydrostatic pressure reached in this study of ~7.5 GPa.

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\(^2\) The Equation of State coefficients reported in Table 4c representing the best fit of our data have been deposited as supplementary material in the form of .eos files (that can be read with EoSFit7c). They are also available directly from the authors.
Such pressure covers the stability pressure range for upper mantle garnets. Fit of the \(P-V\) data alone using a 3\textsuperscript{rd} order Tait EoS yielded the following coefficients: \(V_{00} = 1664.36(7) \text{ Å}^3\), \(K_{00} = 167.45(1.04)\text{ GPa}\) and \(K_{00}^\prime = 4.93(31)\) also reported in Table 4a. The goodness of the fit results was confirmed by the low \(\Delta P_{\text{max}}\) value (calculated as \(|P_{\text{obs}} - P_{\text{calc}}|\)) of 0.010 GPa. The equation of state coefficients obtained with this method agree with those obtained by \(T-V-K\) fitting to better than 1 e.s.d. thus confirming the reliability of the results from the two fitting approaches.

### 3.4 P-V-T-K and PVT Equation of State

The remarkably good agreement between the lattice parameters as determined with different experimental settings and that of the EoS coefficients obtained with different procedures allowed us to perform a simultaneous refinement of the entire set of EoS coefficients by combining our pressure-volume and temperature-volume data together with those of temperature-bulk modulus (Isaak et al. 1992) into a single dataset. Fully weighted simultaneous fit of the \(P-V-T-K\) data has been performed using a thermal pressure Equation of State with a 3\textsuperscript{rd} order Tait EoS, allowing simultaneous refinement of \(V_{00}, K_{00}, K_{00}^\prime, \alpha_0\) and \(\theta_E\). As expected, the resulting coefficients \(V_{00} = 1664.46(5) \text{ Å}^3; K_{00}=166.57(17)\text{ GPa}; K_{00}^\prime=4.96(7); \alpha_{(298K, 1bar)} = 2.09(2)*10^{-5} \text{K}^{-1}\), with \(\theta_E= 512(19)\text{K}\) (\(\gamma_0=\gamma=1.22\)) agree within 2 \(\sigma\) to those from \(P-V\) and \(T-V-K\) separately (see Table 4). At this point it is important to point out that the main difference between the \(P-V-T-K\) and \(T-V-K\) fits can be seen in the description of the bulk moduli as a function of \(T\) (Figure 5a). It should be clear from Figure 5a that while in the thermal regime between room-\(T\) and the maximum temperature reached with the experiments the bulk moduli calculated from the \(T-V-K\) and \(P-V-T-K\) Equations of State agree within mutual uncertainties, in the low-\(T\) regime much larger discrepancies are observed. These discrepancies are due to the different values of \(\theta_E\) in the two EoS.

Simultaneous refinement of the \(P-V-T\) data alone yielded the following coefficients \(V_{00} = 1664.44(6) \text{ Å}^3; K_{00}=166.19(1.25)\text{ GPa}; K_{00}^\prime=5.14(40); \alpha_{(298K, 1bar)} = 2.09(2)*10^{-5} \text{K}^{-1}, \) with \(\theta_E= 512\text{K}\) (not refined). Standard deviations on the bulk modulus \((K_0T)\) and its first derivative \((K^'\) obtained...
from the $P$-$V$-$T$ fitting are 6-8 times larger than those from the $P$-$V$-$T$-$K$ ones and, when considered, the resulting coefficients from the $P$-$V$-$T$ fit agree within 1 sigma with those obtained from the $P$-$V$-$T$-$K$ fits. The $P$-$V$-$T$ results are not showed in Figure 5a for sake of clarity, however, the resulting bulk moduli as a function of $T$ agrees with the experimental data within 1 $\sigma$.

4. DISCUSSION

4.1 Thermal expansion: comparison with literature data

The measured room temperature-pressure volumes ($V_{00}$) reported in this study are in good agreement with those previously reported in literature by several authors (see Table 4a and b). So far, only few X-ray diffraction thermal expansion data are available for grossular garnet (e.g. Skinner 1956; Bosenick and Geiger 1997; Thieblot et al. 1998; Du et al. 2015) and most of them have been obtained by means of powder X-ray diffraction. Data from Du et al. (2015) and those by Skinner (1956) have been re-fitted to their entire temperature range 296 K - 859 K (excluding two outliers at 393 K and 477 K) and 284 K -980 K, respectively. On the other hand, data from Thieblot et al. (1998) have been fitted from 300 K to 1453 K (i.e. well below the decomposition temperature) excluding a few outliers at 607 K, 724 K, and 1241 K. The results of all the extrapolations at 300 K are reported in Table 4b and shown Figure 2. As shown in Table 4b, there are considerable differences between our data and those available in literature. These can be most likely ascribed to the compositional differences between the various samples and/or to the uncertainties given by the different experimental methods. For example, both Skinner (1956) and Thieblot et al. (1998) used grossular-rich samples for their investigation. For sake of comparison, regardless the compositional differences, these literature data have been re-fitted to Fei-type EoS (Fei 1995). Results from the fitting are reported in Table 4b, and Figure 2.

As shown in Figure 2, our data for the low-$T$ regime are in good agreement with those reported by Bosenick and Geiger (1997) if their most scattered data (e.g. 195, 220 and 295 K) are not considered.
The thermal expansion coefficients at 300 K from both Skinner (1956) and Du et al. (2015) are smaller than those calculated from our fitting. The discrepancies between our dataset and that by Skinner (1956) could be ascribed to the differences in composition as their sample referred to as a ‘grossularite’ has not been properly characterized. The thermal coefficient value obtained fitting the data by Du et al. (2015) is not reliable as demonstrated by the negative thermal expansion at high-\(T\) (regardless of the Equation of State model chosen). The same is true also for the data reported by Thieblot et al. (1998), where the thermal expansion value decreases with increasing temperature. Our datasets, ranging from 100 K to about 1000 K, allowed fitting of a Kroll-type EoS (Kroll et al. 2012), leading to a much more reliable description of the thermal behaviour of grossular. The reliability of the Einstein temperatures used (\(\theta_E=569(13)\) K) have been confirmed by comparison with the saturation temperature (where \(T_{sat}\approx \theta_E/2\)) obtained from the fitting of the low-\(T\) data alone (\(T_{sat}=270(6)\) K) using a Salje-type EoS (Salje et al. 1991). The agreement within 1 sigma is also achieved when comparing with the \(\theta_E\) from the \(P-V-T-K\) fit \([\theta_E=512(19)\) K, see Table 4c]\.

\subsection*{4.2 Compressibility: comparison with literature data}

The elastic coefficients for grossular have been determined in several studies using different methods (e.g. ultrasonic wave velocity, static compression experiments in diamond-anvil cell, ab-initio calculations) as summarised in Table 4a. For purpose of comparison with the literature data, the adiabatic bulk modulii \((K^S)\) obtained by means of ultrasonic wave velocity techniques have been converted to \(K^T\).

DFT calculations of a P(V) curve, fitted by a third order Birch-Murnaghan EoS, provide a value of 156 GPa for the bulk modulus \(K^T\) at 300K, and a \(K'\) of 4.22. The static (no zero point and thermal effects included) and the athermal (zero point corrected and a temperature of 0K) values are respectively 163.9 and 160.1 GPa (\(K'\) fixed at 4.22: the value we obtained at 300K). These results are in line with the standard performances of DFT-GGA Hamiltonians like PBEsol, as they generally underestimate bulk moduli by about 10 GPa at room temperature. Another DFT study
from the literature (Erba et al. 2014) provided a somewhat higher bulk modulus (171 GPa), but that was a result from a static calculation with a hybrid HF/DFT (B3LYP) Hamiltonian which includes an Hartree-Fock correction to the DFT-GGA electronic exchange functional. Indeed, such correction proved to be crucial to compute bulk moduli (and vibrational frequencies) very close to the experimental data (Prencipe et al. 2009, 2011, 2012, 2014), but it is computationally very costly if a plane-wave basis set is used, as in the present case, and therefore it cannot be afforded. The largest discrepancy in grossular bulk modulus value is with respect to the results obtained by Kawai and Tsuchiya (2012) with a lattice dynamics approach together in combination with a LDA functional. Furthermore, the first derivative of the bulk modulus ($K'$) which we could now reliably refine clearly demonstrates that the correct value must be very close to 5 in agreement with some of the previous studies (see Table 4a).

4.3 Full elastic behaviour ($P$-$V$-$T$-$K$): comparison with literature data

The new utility available in EoSFit7c allowed us to also apply the same method described in the sections above ($P$-$V$-$T$-$K$ fitting) to the available literature data obtained from independent elastic measurements and $PVT$ datasets (Kono et al. 2010; Gwanmesia et al. 2014). It is remarkable the extra constraint given by the simultaneous weighted fit of the $K$ data (see results in Table 4c) which however applied to the literature dataset does not allow to obtain the same quality as for our elastic coefficients due to the lack of data in the low-temperature regime. This combined with the much lower accuracy and precision that in most cases arises by the limitation of the $P$-$V$-$T$ simultaneous measurements (i.e. pressure calibrant, pressure transmitting media etc.) give rise to discrepancies such as those showed in Figure 5b. In this case the discrepancies in bulk modulus values at high-$T$ reach up to 4% (more than 6 GPa at 1400 K). In order to crosscheck the measurements with the DFT results, we performed fitting of the DFT data in the temperature range between 400 and 800K using a thermal pressure equation of state combined with a 3rd order Tait-eos. For purpose of comparison with the other fits, bulk moduli values have been normalized to the
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bulk moduli extrapolated at 0K from the P-V-T-K fit of the experimental data (Fig. 5a, red line).

The trend of the two fits agrees within 1σ thus confirming the reliability of our fitting results via P-V-T-K fits even at the highest temperature where the DFT approach leads to the smallest deviations from the experimental data.

4. CONCLUSIONS AND IMPLICATIONS

It is obvious that pressure-volume or temperature-volume measurements alone do not provide strong constraints on the cross-terms in P-T space (e.g. ∂K/∂T or ∂α/∂P) which are fundamental for the description of the elastic properties of a material at simultaneous high-P and high-T. Limitation in experimental measurements and/or in the description of the pressure-volume-temperature data (e.g. incorrect Equations of State, erroneous mis-use of Voigt, Reuss isothermal or adiabatic bulk moduli) has often in the past lead to inaccurate unreliable or even completely wrong results (e.g. negative thermal expansion, erroneous ∂K/∂T etc…) specially when the EoS are subsequently extrapolated to high-P,T.

Pressure-volume EoS are well-developed and, if correctly used, are capable of reproducing the isothermal volume or density changes of materials to within the experimental uncertainties. Previous versions of the EoSFit program were able to fit isothermal EoS, thermal expansion models and the thermal-pressure (Holland and Powell 2011) to P-V, V-T or P-V-T data, by the method of least-squares. We have now extended the capabilities of EosFit7c to also fit all of these forms of EoS to bulk and linear moduli, either alone or in combination with volume or unit-cell parameter data. With this approach we can now provide a reliable description of the variation of K’ with T thus avoiding mistaken extrapolations leading to non-physical behaviour as often occurs for several materials (Helffrich and Connolly 2009).

The consistency of the results obtained with this new fitting procedure has been shown by comparison of results from using adiabatic and isothermal moduli. It has also been demonstrated the importance of performing fitting with this procedure in terms of both accuracy and precision of the thermoelastic coefficients when the PT cross-terms (∂K/∂T or ∂α/∂P) are extrapolated in PT space.
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(see Figure 5b). Additionally, thermodynamic functions were calculated for grossular using DFT approach within QHA. The obtained results are in fairly good agreement with experiment, when allowing for the known short-comings of the functionals employed in the DFT.

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