

AperTO - Archivio Istituzionale Open Access dell'Università di Torino

**Elasticity of Grossular-Andradite Solid Solution: An Ab initio Investigation.**

**This is the author's manuscript**

*Original Citation:*

Elasticity of Grossular-Andradite Solid Solution: An Ab initio Investigation. / V. Lacivita; A. Erba; R. Dovesi; Ph. D'Arco. - In: PHYSICAL CHEMISTRY CHEMICAL PHYSICS. - ISSN 1463-9076. - STAMPA. - 16(2014), pp. 15331-15338.

*Availability:*

This version is available <http://hdl.handle.net/2318/157220> since 2016-09-10T10:18:55Z

*Terms of use:*

Open Access

Anyone can freely access the full text of works made available as "Open Access". Works made available under a Creative Commons license can be used according to the terms and conditions of said license. Use of all other works requires consent of the right holder (author or publisher) if not exempted from copyright protection by the applicable law.

(Article begins on next page)

# Elasticity of Grossular-Andradite Solid Solution: An *Ab initio* Investigation.

V. Lacivita,<sup>1,2</sup> A. Erba,<sup>3</sup> R. Dovesi,<sup>3</sup> and Ph. D'Arco<sup>2,4, a)</sup>

<sup>1)</sup> Sorbonne Universités, UPMC Univ Paris 06, Institut Calcul et Simulation, F-75005, Paris (France)

<sup>2)</sup> Sorbonne Universités, UPMC Univ Paris 06, UMR 7193, Institut des Sciences de la Terre Paris (iSTeP), F-75005 Paris, (France)

<sup>3)</sup> Dipartimento di Chimica and Centre of Excellence NIS (Nanostructured Interfaces and Surfaces), Università di Torino, via Giuria 5, IT-10125 Torino (Italy)

<sup>4)</sup> CNRS, UMR 7193, Institut des Sciences de la Terre Paris (iSTeP), F-75005 Paris, (France)

(Dated: 3 April 2014)

*Ab initio* simulations of the elastic properties of the silicate garnet grossular-andradite solid solution,  $\text{Ca}_3\text{Fe}_{2-2x}\text{Al}_{2x}(\text{SiO}_4)_3$ , are performed, using an all-electron local basis set of Gaussian-type orbitals and the hybrid B3LYP density functional. The dependence of the bulk modulus (obtained by fitting energy-volume data to an equation-of-state) on composition  $x$  is investigated over the whole range  $0 \leq x \leq 1$ . The bulk modulus is also computed following an independent approach, from elastic tensor calculations: results almost coincide with those of the equation-of-state scheme, thus confirming the high numerical accuracy of all the adopted algorithms. Contrary to what previously conjectured from a number of “heterogeneous” experimental measurements, a rather linear trend is predicted for the bulk modulus as a function of  $x$ , up to 20 GPa. The largest deviation from linearity is about 0.5 GPa at ambient conditions; it progressively reduces to less than 0.2 GPa at  $P = 20$  GPa.

## I. INTRODUCTION

The characterization of the deep structure of the Earth is essentially based on seismic surveys and relies on the knowledge of the elastic properties of its individual constituents. Silicate garnets are among the most important rock-forming minerals of the upper mantle and transition zone, between 400 km and 670 km depth.<sup>78</sup>

Different compositional models of the mantle have been proposed, starting from the known elastic behavior of various minerals. In particular, Anderson and Bass<sup>79,80</sup> have proposed a chemically heterogeneous model according to which the transition region is richer in calcium than the upper mantle, containing Ca-bearing silicate garnets, such as grossular,  $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_3$ , and andradite,  $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$ . At geophysical conditions, grossular and andradite naturally occur as a solid solution, *grandite*  $\text{Ca}_3\text{Fe}_{2-2x}\text{Al}_{2x}(\text{SiO}_4)_3$ , displaying a range of compositions  $x$  on which its elastic properties certainly depend. By combining the few available experimental bulk moduli of *grandite* solid solutions,<sup>81–83</sup> a significant deviation from linearity seems to turn out, as discussed by O'Neill *et al.*,<sup>83</sup> at variance with the linear composition-modulus trend observed for the pyrope-almandine-spessartine (*pyralspite*) series,  $(\text{Mg,Fe,Mn})_3\text{Al}_2\text{Si}_3\text{O}_{12}$ . However, uncertainty and non-homogeneity of the measurements still leave room for further insights.

Some of the present authors have recently demonstrated that *ab initio* simulations do represent an effective and reliable tool for investigating the elastic properties

(elastic constants, bulk, shear and Young moduli, directional seismic wave velocities, elastic anisotropy index, Poisson's ratio, etc.) of the end-members of this class of materials at ambient pressure<sup>84,85</sup> and at geophysical pressures up to 60 GPa,<sup>86</sup> by comparing with available experimental data.<sup>87–102</sup> Assuming a linear transferability of the computed *ab initio* elastic properties from end-members to solid solutions also provided accurate estimates for a set of 32 solid solutions of *pyralspite*,<sup>96</sup> whose end-members have bulk moduli relatively close to one another.<sup>87,93,103</sup> The *grandite* solid solution appears as a more complex system where relatively large deviations from linearity of its bulk modulus as a function of chemical composition have been experimentally reported. As a consequence, the sole theoretical characterization of the elastic properties of the two end-members seems not enough, in this case. An explicit treatment of the compositional effect on its bulk modulus is required.

In this paper we undertake an explicit *ab initio* theoretical study of the elastic properties of the *grandite* solid solution,  $\text{Ca}_3\text{Fe}_{2-2x}\text{Al}_{2x}(\text{SiO}_4)_3$ , as a function of its composition  $x$ . A structural model which refers to the 8 available sites for substitution in the end-member primitive cell is adopted. The whole composition range,  $0 \leq x \leq 1$ , is investigated; in particular, apart from the two end-members, other seven intermediate compositions are considered ( $x = 0.125, 0.25, 0.375, 0.5, 0.625, 0.75$  and  $0.875$ ). Each intermediate composition is represented by a number of independent atomic configurations efficiently selected through a symmetry-adapted sampling of the configuration space<sup>104</sup> recently developed by Mustapha *et al.*<sup>105</sup> and D'Arco *et al.*<sup>106</sup>

Calculations are performed with the CRYSTAL14 program for *ab initio* quantum chemistry and physics of the solid state,<sup>104,107</sup> which features a general, fully au-

---

<sup>a)</sup> Electronic mail: philippe.d'arco@upmc.fr

tomated procedure for computing elastic properties of periodic systems of any symmetry.<sup>84,108</sup> The fully periodic implementation of the hybrid B3LYP<sup>109,110</sup> functional and all-electron Gaussian basis sets are used. The same computational approach has already been successfully applied to the investigation of structural, electronic, vibrational (Infrared and Raman), magnetic and optical properties of silicate garnets.<sup>111–117</sup>

The structure of the paper is as follows: Section II illustrates the theoretical methodology adopted for the determination of the equation of state (EOS), the calculation of the bulk modulus via elastic constants and the definition of a structural model of the solid solution; computational parameters are given in Section III; calculated bulk moduli are discussed in Section IV; conclusions are drawn in Section V.

## II. THEORETICAL METHOD

### A. Equations of State

An approach that is commonly adopted for computing the bulk modulus of a crystalline material is via so-called Equations of State (EOS). A “cold” EOS is an energy-volume (or pressure-volume) relation which describes the behavior of a solid under compression and expansion, at  $T = 0$  K, that is the case of standard *ab initio* simulations. Universal, *i.e.* not specific of particular materials, EOS are usually expressed as analytical functions of a limited set of parameters (equilibrium energy  $E_0$ , equilibrium volume  $V_0$ , equilibrium bulk modulus  $K_0 = -V\partial P/\partial V$  and pressure derivative of equilibrium bulk modulus  $K'_0 = \partial K_0/\partial P$ ) for ease of interpolation, extrapolation and differentiation, and are quite used in solid state physics and geophysics.<sup>118,119</sup>

Energy-volume data are numerically fitted to the analytical  $E(V)$  functional form of the EOS. From  $P = -\partial E/\partial V$ , the  $P$ - $V$  connection is established. In principle, an advantage of this approach would be the possibility of predicting the high-pressure behavior of a solid from low-pressure or even equilibrium properties: the explicit dependence of the bulk modulus on volume (or pressure from  $P$ - $V$ ), is then given by  $K(V) = V\partial^2 E/\partial V^2$ .

A number of universal EOS have been proposed so far.<sup>118,120–125</sup> All of them are phenomenological and can behave quite differently from each other as regards extrapolation at high pressure. Comprehensive reviews and comparisons of different EOS are available in the literature.<sup>126–130</sup> Four EOS are currently implemented in the CRYSTAL14 program: the original third-order Murnaghan’s,<sup>120</sup> the third-order Birch’s,<sup>121,122</sup> the logarithmic Poirier-Tarantola’s,<sup>125</sup> and the exponential Vinet’s.<sup>123</sup>

### B. Elastic Constants and Related Properties

The elements of the fourth-rank elastic tensor  $\mathbf{C}$  for 3D systems are usually defined as second energy density derivatives with respect to pairs of deformations:<sup>131</sup>

$$C_{vu} = \frac{1}{V} \left. \frac{\partial^2 E}{\partial \eta_v \partial \eta_u} \right|_0, \quad (1)$$

where  $\boldsymbol{\eta}$  is the symmetric second-rank pure strain tensor and Voigt’s notation is used according to which  $v, u = 1, \dots, 6$  ( $1 = xx$ ,  $2 = yy$ ,  $3 = zz$ ,  $4 = yz$ ,  $5 = xz$ ,  $6 = xy$ ). The elastic  $\mathbf{C}$  tensor exhibits, in general, 21 independent elements that reduce to 3 (*i.e.*  $C_{11}$ ,  $C_{12}$  and  $C_{44}$ ) for crystals with cubic symmetry, as in the case of silicate garnet end-members. Tensor  $\mathbf{S} \equiv \mathbf{C}^{-1}$  is the so-called compliance tensor. A fully-automated and general procedure for computing elastic tensors under pressure, photoelastic constants and seismic velocities of crystals of any symmetry has recently been implemented in the CRYSTAL program.<sup>84,86,132–138</sup>

Elastic properties of isotropic polycrystalline aggregates can be computed from the elastic and compliance constants defined above via the Voigt-Reuss-Hill averaging scheme.<sup>139</sup> For crystals of any symmetry, an average bulk modulus  $\bar{K} = 1/2[K_V + K_R]$  can be defined between Voigt upper bound

$$K_V = \frac{1}{9}[C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23})],$$

and Reuss lower bound

$$K_R = [S_{11} + S_{22} + S_{33} + 2(S_{12} + S_{13} + S_{23})]^{-1}.$$

For cubic crystals, these two bounds coincide and the bulk modulus  $\bar{K}$  simply reduces to:

$$\bar{K} = \frac{1}{3}(C_{11} + 2C_{12}). \quad (2)$$

### C. Structural Model for Solid Solution

Reference is made to the primitive unit cell of the end-members (cubic space group  $\mathcal{G} \equiv Ia\bar{3}d$ ), which counts  $|\mathcal{G}| = 48$  symmetry operators and 4 formula units  $\text{Ca}_3\text{Y}_2(\text{SiO}_4)_3$ . The structure displays dodecahedral (Ca), tetrahedral (Si) and octahedral (Y) crystallographic sites. There are 8 Y sites involved for substitutions. Solid solutions are obtained from andradite by progressively replacing  $\text{Fe}^{3+}$  with  $\text{Al}^{3+}$  cations. Apart from the two end-members, andradite ( $x = 0$ ) and grossular ( $x = 1$ ), other seven compositions are explicitly considered:  $x = 0.125, 0.25, 0.375, 0.5, 0.625, 0.75$  and  $0.875$ .

For each composition  $x$ ,  $n_{\text{Al}} = 8x$  aluminum atoms are present that correspond to  $8!/[n_{\text{Al}}!(8 - n_{\text{Al}})!]$  different substitutional configurations, *i.e.* cation distributions among the Y sites. Altogether, the configurations sum up

to 256 over the whole range of compositions. Following the symmetry analysis recently proposed by Mustapha *et al.*,<sup>105</sup> these configurations can be partitioned into 23 distinct symmetry independent classes (SIC). Each class  $L$  consists of  $\mathcal{M}_L \equiv \mathcal{M}_l^x = |\mathcal{G}|/|\mathcal{H}_L|$  configurations that belong to a symmetry subgroup of order  $|\mathcal{H}_L|$  of the aristotype symmetry, where  $l$  is a relative index of the classes within a given composition  $x$ .

Since all the configurations of a given SIC are equivalent to each other, the number of calculations to be actually performed reduces to one *per* SIC, that is, to a total of 23.  $\mathcal{M}_L$  can then be interpreted as the multiplicity of class  $L$ . Only the highest spin ferromagnetic configurations will be considered, as the difference between ferromagnetic and anti-ferromagnetic energies was shown to be extremely small.<sup>140</sup>

A list of all the configurations studied, along with their symmetry and multiplicity, is given in Table I. The two end-members are described by a single cubic class with  $\mathcal{M}_L = 1$ . Compositions  $x = 0.125$  and  $x = 0.875$  can be described by a single trigonal class ( $L = 2$  and  $L = 22$ , respectively) with  $\mathcal{M}_L = 8$  equivalent atomic configurations. For describing compositions  $x = 0.25$  and  $x = 0.75$ , three classes are required, one of trigonal symmetry with a multiplicity of 4 and two of monoclinic symmetry with a multiplicity of 12. Three classes are also required for modeling the  $x = 0.375$  and  $x = 0.625$  compositions: one trigonal and two triclinic with multiplicities of 8 and 24, respectively. The middle composition  $x = 0.5$  is represented by seven classes: one cubic, one orthorhombic, one tetragonal, one trigonal, two monoclinic, and one triclinic, which, in Table I, are sorted in terms of decreasing symmetry and increasing multiplicity.

### III. COMPUTATIONAL DETAILS

Calculations are performed with the CRYSTAL14 program.<sup>104</sup> The B3LYP one-electron Hamiltonian is adopted, which contains a hybrid Hartree-Fock/Density-Functional exchange-correlation term. The valence open-shell of  $\text{Fe}^{3+}$  ( $d^5$ ) requires a spin-polarized solution. All-electron atom-centered Gaussian-type-function (GTF) basis sets are adopted. Oxygen, silicon, aluminum and calcium atoms are described in order by (8s)-(411sp)-(1d), (8s)-(6311sp)-(1d), (8s)-(611sp)-(1d) and (8s)-(6511sp)-(21d) contractions of primitive GTFs. For iron, a (8s)-(64111sp)-(411d) contraction of GTFs is used, augmented with a further  $f$ -type polarization function as reported into details in previous works.<sup>112,113,141</sup>

In CRYSTAL, the truncation of infinite lattice sums is controlled by five thresholds, which are set to 7, 7, 7, 8, 16.<sup>107</sup> Reciprocal space is sampled according to a sublattice with shrinking factor 2, which corresponds to a number of irreducible  $\mathbf{k}$ -points in the first Brillouin zone between 3 and 8, depending on the symmetry of the configuration. The DFT exchange-correlation contribution is evaluated by numerical integration over the cell vol-

TABLE I. The 23 symmetry independent classes of atomic configurations used to model the *grandite* solid solution at nine compositions  $x$  are listed and labeled with the absolute index  $L$  and a relative index  $l$  within each composition. The symmetry of the corresponding lattice and multiplicity of each class are also reported.

| $x$   | $L$ | $l$ | Lattice      | $\mathcal{M}_L \equiv \mathcal{M}_l^x$ |
|-------|-----|-----|--------------|--|
| 0.    | 1   | 1   | Cubic        | 1                                      |
| 0.125 | 2   | 1   | Trigonal     | 8                                      |
|       | 3   | 1   | Trigonal     | 4                                      |
| 0.25  | 4   | 2   | Monoclinic   | 12                                     |
|       | 5   | 3   | Monoclinic   | 12                                     |
| 0.375 | 6   | 1   | Trigonal     | 8                                      |
|       | 7   | 2   | Triclinic    | 24                                     |
|       | 8   | 3   | Triclinic    | 24                                     |
| 0.5   | 9   | 1   | Cubic        | 2                                      |
|       | 10  | 2   | Orthorhombic | 6                                      |
|       | 11  | 3   | Tetragonal   | 6                                      |
|       | 12  | 4   | Trigonal     | 8                                      |
|       | 13  | 5   | Monoclinic   | 12                                     |
|       | 14  | 6   | Monoclinic   | 12                                     |
|       | 15  | 7   | Triclinic    | 24                                     |
| 0.625 | 16  | 1   | Trigonal     | 8                                      |
|       | 17  | 2   | Triclinic    | 24                                     |
|       | 18  | 3   | Triclinic    | 24                                     |
| 0.75  | 19  | 1   | Trigonal     | 4                                      |
|       | 20  | 2   | Monoclinic   | 12                                     |
|       | 21  | 3   | Monoclinic   | 12                                     |
| 0.875 | 22  | 1   | Trigonal     | 8                                      |
| 1.    | 23  | 1   | Cubic        | 1                                      |

ume: radial and angular points of the atomic grid are generated through Gauss-Legendre and Lebedev quadrature schemes, using an accurate predefined pruned grid (keyword XLGRID). The convergence threshold on energy for the self-consistent-field (SCF) step of the calculations is set to  $10^{-9}$  hartree.

Equilibrium and strained configurations are optimized calculating analytical energy gradients with respect to both atomic coordinates and unit-cell parameters or atomic coordinates only.<sup>142-144</sup> A quasi-Newtonian technique is used, combined with the BFGS algorithm for Hessian updating.<sup>145-148</sup> Convergence is checked on both gradient components and nuclear displacements; the corresponding tolerances on their root mean square are chosen to be 10 times more severe than the default values for simple optimizations: 0.00003 a.u. and 0.00012 a.u., respectively.

As regards EOS calculations, five hydrostatic compressions (up to 14 % in volume) and five hydrostatic expansions (up to 8 % in volume) are applied to each configuration and a constant-volume optimization is performed at each step. Energy-volume data are then fitted to a third-order Birch-Murnaghan EOS<sup>121,122</sup> for the determination of the corresponding bulk modulus,  $K_{\text{EOS}}$ .

For the elastic constants calculation, two strained

configurations are considered for each symmetry-independent strain (two for cubic and six for triclinic crystals), with a dimensionless strain amplitude of 0.01.

#### IV. RESULTS AND DISCUSSION

Before illustrating our theoretical results on the elastic behavior of the grossular-andradite solid solution series, let us summarize the main findings of previous studies. In Figure 1, we collect the outcomes of experimental measurements on the evolution of the bulk modulus  $K$  of *grandite* as a function of composition  $x$ . Available experimental data are represented by solid symbols.<sup>81,82,149–153</sup>

Two values are reported at  $x \approx 1$ , which represent the grossular end-member (natural single crystal samples pure to 97 % and 99 %, respectively): an ultrasonic measurement by Halleck<sup>149</sup> (triangle) provided  $K = 171.4 \pm 1.7$  GPa, and a Brillouin scattering experiment performed by Bass<sup>151</sup> (square) yielded  $K = 168.4 \pm 0.7$  GPa. As regards andradite, two values are reported as determined by Brillouin spectroscopy:  $K = 157 \pm 2$  GPa by Bass<sup>82</sup> (circle) and  $K = 154.5 \pm 0.6$  GPa by Jiang *et al.*<sup>153</sup> (inverted triangle). Let us stress that, even for the two end-members, different experimental determinations of their bulk moduli can hardly be considered compatible with each other on the grounds of the corresponding uncertainties (see the error bars reported in Figure 1). Experimental uncertainties become even larger for most of the intermediate compositions, as we shall discuss below.

The main experimental investigation of the elastic properties of intermediate compositions of the *grandite* solid solution has been performed by Babuska *et al.* in 1978<sup>81</sup> by means of the rectangular parallelepiped resonance method. They analyzed four specimens of three different composition:  $\text{Gr}_{79.9}\text{An}_{14.2}$ ,  $\text{Gr}_{76.1}\text{An}_{22.1}$ , and  $\text{An}_{70.4}\text{Gr}_{22.2}$ . The corresponding bulk moduli are represented as rhombi in Figure 1. The three grossular-rich samples provide  $K$  in the range 161–164 GPa. The andradite-rich sample showed a bulk modulus of  $147.3 \pm 3.4$  GPa. More recently, in 2004, Jiang *et al.*<sup>152</sup> performed Brillouin spectroscopy on a grossular-rich garnet of composition  $\text{Gr}_{87}\text{An}_9\text{Py}_2\text{Al}_2$  (Py stands for pyrope, Al for almandine), for which they obtained  $K = 165.8 \pm 0.5$  GPa (pentagon).

The dashed line in Figure 1 represents the bulk modulus trend as a function of composition  $x$  which was proposed by O’Neill *et al.*<sup>83</sup> in 1989, on the grounds of available experimental data at that time. Nowadays, having at hand also more recent determinations of  $K$ , we can see how the proposed pronounced deviation from linearity is mainly dominated by the sole value at about  $x = 0.22$ . The solid line in the figure represents our theoretical results, to be discussed into detail in what follows, which clearly shows a quasi-linear behavior of the elastic response of the *grandite* solid solution as a function of its chemical composition.

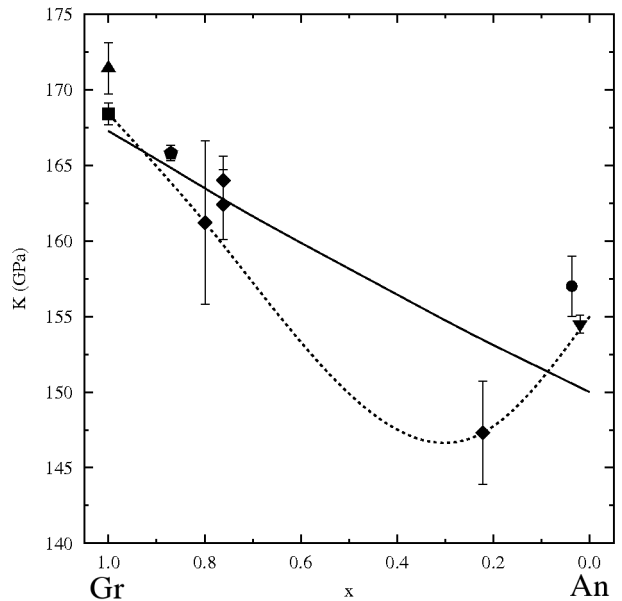


FIG. 1. Variation of the bulk modulus  $K$  of the *grandite* solid solution  $\text{Ca}_3\text{Fe}_{2-2x}\text{Al}_{2x}(\text{SiO}_4)_3$  as a function of composition  $x$ . The solid line shows the quasi-linear trend of our calculated values, whereas the dashed curve is drawn to provide an approximate fit to the experimental data, as suggested by O’Neill *et al.*<sup>83</sup> Experimental data are from Halleck<sup>149</sup> ( $\text{Gr}_{97.4}$ , triangle), Babuska *et al.*<sup>81</sup> (intermediate compositions, rhombi), Bass<sup>82</sup> ( $\text{An}_{96}\text{Gr}_{3.7}\text{Py}_{0.3}$ , circle), Bass<sup>151</sup> ( $\text{Gr}_{99.2}$ , square), Jiang *et al.*<sup>152</sup> ( $\text{Gr}_{87}\text{An}_9\text{Py}_2\text{Al}_2$ , pentagon) and Jiang *et al.*<sup>153</sup> ( $\text{Gr}_2\text{An}_{98}$ , triangle). Here, Gr stands for grossular, An for andradite, Py for pyrope, and Al for almandine. When available, error bars are also shown.

For each composition  $x$  and each symmetry independent class, we have computed the equation of state of a representative atomic configuration, according to the procedure described in Section III. The calculated bulk moduli  $K_{\text{EOS}}$  are reported in Table II. As regards the two end-members, computed values are found to be in agreement with experimental data within 1 % for grossular and 3 % for andradite.

The numerical accuracy of the EOS determinations of the bulk moduli is checked by comparison with the analytical bulk moduli  $K_V$ ,  $K_R$  and  $\bar{K}$  calculated from the elastic tensor  $\mathbf{C}$  of equation (1), according to Voigt-Reuss-Hill averaging scheme. These three elastic determinations of the bulk modulus are also reported in Table II. The following considerations can be made: i) the agreement between  $\bar{K}$  and  $K_{\text{EOS}}$  is excellent (within 0.9 %) in the whole composition range, which confirms the extremely high numerical accuracy of all the algorithms involved; ii) the values of  $K_{\text{EOS}}$  obtained for polymorphic classes are very close to one another, with differences never larger than 0.1 %; iii)  $K_V$  and  $K_R$  essentially coincide with each other within any class, regardless of the

TABLE II. For each symmetry independent class, labeled by the absolute index  $L$  and relative index  $l$  within each composition  $x$ , the bulk modulus  $K$  (GPa) is reported as computed with an EOS approach,  $K_{\text{EOS}}$ , and from the elastic constants following Voigt's,  $K_V$ , Reuss's,  $K_R$ , and Hill's,  $\bar{K}$ , prescriptions.  $\Delta E = E_l^x - E_{\text{min}}^x$  (in mHa) is the difference between the energy of configuration  $l$  at composition  $x$ ,  $E_l^x$ , and the energy of the most stable configuration with the same composition,  $E_{\text{min}}^x$ .<sup>a</sup>

| $x$   | $L$ | $l$ | $\Delta E$ | $K_{\text{EOS}}$ | $K_V$ | $K_R$ | $\bar{K}$ |
|-------|-----|-----|------------|------------------|-------|-------|-----------|
| 0.    | 1   | 1   | -          | 150.0            | 149.7 | 149.7 | 149.7     |
| 0.125 | 2   | 1   | -          | 151.9            | 150.8 | 150.8 | 150.8     |
|       | 3   | 1   | 2.335      | 153.9            | 153.6 | 153.6 | 153.6     |
| 0.25  | 4   | 2   | 1.634      | 154.0            | 153.2 | 153.2 | 153.2     |
|       | 5   | 3   | -          | 153.9            | 153.8 | 153.8 | 153.8     |
|       | 6   | 1   | 3.002      | 156.0            | 156.3 | 156.3 | 156.3     |
| 0.375 | 7   | 2   | 1.721      | 156.0            | 154.6 | 154.6 | 154.6     |
|       | 8   | 3   | -          | 156.0            | 155.1 | 155.1 | 155.1     |
|       | 9   | 1   | 5.925      | 158.3            | 157.8 | 157.8 | 157.8     |
|       | 10  | 2   | 3.053      | 158.1            | 157.4 | 157.4 | 157.4     |
|       | 11  | 3   | -          | 158.1            | 157.6 | 157.6 | 157.6     |
| 0.5   | 12  | 4   | 1.267      | 158.2            | 157.2 | 157.2 | 157.2     |
|       | 13  | 5   | 1.541      | 158.1            | 158.2 | 158.1 | 158.2     |
|       | 14  | 6   | 1.946      | 158.1            | 158.0 | 157.9 | 158.0     |
|       | 15  | 7   | 3.289      | 158.2            | 157.3 | 157.3 | 157.3     |
|       | 16  | 1   | 3.259      | 160.3            | 160.1 | 160.1 | 160.1     |
| 0.625 | 17  | 2   | 1.382      | 160.3            | 160.2 | 160.2 | 160.2     |
|       | 18  | 3   | -          | 160.3            | 159.3 | 159.3 | 159.3     |
|       | 19  | 1   | 2.131      | 162.4            | 162.6 | 162.6 | 162.6     |
| 0.75  | 20  | 2   | 1.954      | 162.6            | 162.5 | 162.5 | 162.5     |
|       | 21  | 3   | -          | 162.6            | 161.8 | 161.7 | 161.8     |
| 0.875 | 22  | 1   | -          | 164.9            | 163.9 | 163.9 | 163.9     |
| 1.    | 23  | 1   | -          | 167.3            | 167.1 | 167.1 | 167.1     |

<sup>a</sup>  $E_{\text{min}}^{0.0} = -25329.246886$  Ha,  $E_{\text{min}}^{0.125} = -24308.149454$  Ha,  $E_{\text{min}}^{0.25} = -23287.054557$  Ha,  $E_{\text{min}}^{0.5} = -22265.958966$  Ha,  $E_{\text{min}}^{0.375} = -21244.865171$  Ha,  $E_{\text{min}}^{0.625} = -20223.769247$  Ha,  $E_{\text{min}}^{0.75} = -19202.676027$  Ha,  $E_{\text{min}}^{0.875} = -18181.582403$  Ha,  $E_{\text{min}}^{1.0} = -17160.490459$  Ha

specific symmetry of the corresponding lattice. Since  $K_V$  and  $K_R$  are expected to coincide only for cubic systems, their equality appears consistent with the pseudo-cubic metric attributed to *grandite* solid solutions by both experimental and theoretical investigations. Details about the minimum energy structures of the different classes, as obtained with B3LYP geometry optimizations, are reported in Ref. 154. All the calculated cells are pseudo-cubic, with the three lattice parameters differing from each other by less than 0.01 Å, and angles that deviate by less than 0.4° from right angles.

A Boltzmann average bulk modulus,  $K_{av}^x$ , may be defined for any composition  $x$ :

$$K_{av}^x = \sum_l \mathcal{P}_l^x K_l^x, \quad (3)$$

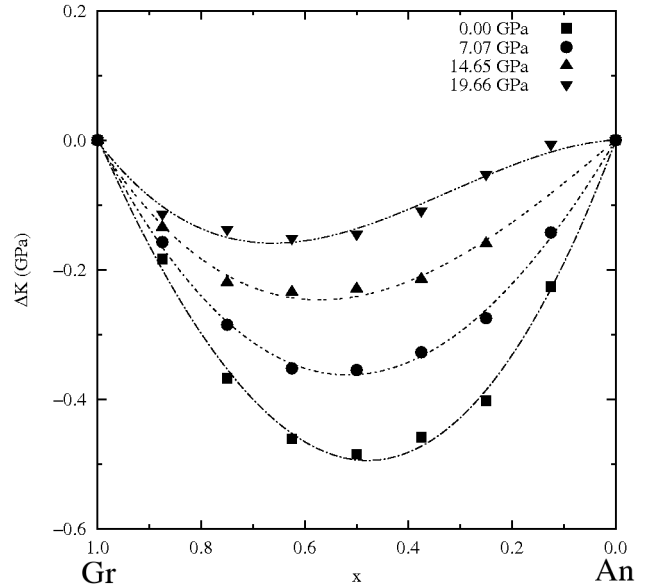


FIG. 2. Deviation from linearity ( $\Delta K$  in GPa) of the Boltzmann average bulk modulus of *grandite*, calculated via the EOS approach, as a function of chemical composition  $x$  and pressure. Temperature  $T$  is fixed at 298 K.

where

$$\mathcal{P}_l^x = \frac{\mathcal{M}_l^x \exp\left(-\frac{\Delta E_l^x}{k_B T}\right)}{\sum_l \mathcal{M}_l^x \exp\left(-\frac{\Delta E_l^x}{k_B T}\right)} \quad (4)$$

is the probability of finding the  $l$ -th class of composition  $x$  at temperature  $T$ . In the expression above,  $\Delta E_l^x = E_l^x - E_{\text{min}}^x$  is the difference between the energy of configuration  $l$  at composition  $x$  and the energy of the most stable configuration with the same chemical composition. These energy differences are reported in Table II, along with the energies of the most stable configurations per each composition  $x$ .

The average bulk moduli for all the considered compositions  $x$  have been computed at  $T = 298$  K via equations (3) and (4), and reported, as a continuous line, in Figure 1 where they are compared with the available experimental data discussed at the beginning of this section. On the scale of that figure, as anticipated before, computed values show an almost linear behavior as a function of the chemical composition of the *grandite* solid solution.

A closer look at the computed data reveals that the dependence of the *grandite* bulk modulus on chemical composition is not perfectly linear. In Figure 2, we report the deviation from linearity of the average bulk modulus,  $\Delta K_{av}$ , as a function of  $x$ . At zero pressure, a maximum deviation of about -0.5 GPa is observed at  $x = 0.5$ .

The EOS approach that we have followed allows to compute the bulk modulus also under increasing hydrostatic pressure. In this respect, an EOS could be used

in two quite different modes: i) to extrapolate at high pressure from small compression data or ii) to interpolate from large compression data. As we recently discussed,<sup>86</sup> mode i) is extremely sensitive to the particular analytical expression adopted for the EOS whereas mode ii) is almost independent of the specific expression of the EOS. In this study we use the latter approach by explicitly computing the energy of each configuration up to volume compressions of 14 %, which roughly correspond to  $P = 25$  GPa. The deviation from linearity of the bulk modulus, as evaluated at about 7 GPa, 15 GPa and 20 GPa, is shown in the figure. It can be seen that the maximum deviation decreases as a function of pressure from about -0.5 GPa at zero pressure to about -0.35 GPa at 7 GPa, -0.23 GPa at 15 GPa and -0.15 GPa at 20 GPa of pressure. Within the explored pressure interval, the deviation from linearity of the bulk modulus decreases as pressure increases.

## V. CONCLUDING REMARKS

Periodic B3LYP quantum-chemical simulations have been performed on the elastic properties of the *grandite* solid solution,  $\text{Ca}_3\text{Fe}_{2-2x}\text{Al}_{2x}(\text{SiO}_4)_3$ , at various compositions  $x$  in the whole range  $0 \leq x \leq 1$ . The bulk modulus of 23 symmetry-independent atomic configurations has been computed following two independent approaches: from the elastic tensor and from fitting energy-volume data to the Birch-Murnaghan equation-of-state. Discrepancies between the two schemes are negligible, thus demonstrating high numerical accuracy and consistency of the algorithms involved.

While “heterogeneous” experimental measurements were suggesting a pronounced non-linear trend of the bulk modulus of the solid solution as a function of its chemical composition (with a maximum deviation of about 7 GPa), the present theoretical results reveal a quasi-linear behavior. A slight deviation from linearity is reported at low pressure, with a maximum value of 0.5 GPa, which is then further reduced under increasing pressure, up to 20 GPa.

The present findings contribute to the definition of a homogeneous frame according to which all the solid solutions of the most abundant silicate garnets (*pyrospite* and *grandite*) exhibit linear elastic properties as a function of their chemical composition. Linearity of *pyrospite* is well-known since long whereas the presumed non-linearity of the *grandite* system has been here demonstrated to be an artifact of heterogeneous experimental measurements.

## ACKNOWLEDGMENTS

This work, partially undertaken within the framework of CALSIMLAB, is supported by the public grant ANR-11-LABX-0037-01 overseen by the French National Re-

search Agency (ANR) as part of the “Investissements d’Avenir” program (reference: ANR-11-IDEX-0004-02). It was granted access to the HPC resources of The Institute for scientific Computing and Simulation financed by Region Ile de France and the project Equip@Meso (reference ANR-10-EQPX-29-01). The CINECA Award N. HP10BLSOR4-2012 is acknowledged for the availability of high performance computing resources and support. Improvements of the CRYSTAL code in its massive-parallel version was made possible thanks to the PRACE proposal no. 2011050810.

- <sup>78</sup>H. Jeffreys and K. E. Bullen, *Seismological tables* (British Association for the Advancement of Science, 1940).
- <sup>79</sup>D. L. Anderson and J. D. Bass, *Geophys. Res. Lett.* **11**, 637 (1984).
- <sup>80</sup>D. L. Anderson and J. D. Bass, *Nature* **320**, 321 (1986).
- <sup>81</sup>V. Babuška, J. Fiala, M. Kumazawa, I. Ohno, and Y. Sumino, *Physics of the Earth and Planetary Interiors* **16**, 157 (1978).
- <sup>82</sup>J. D. Bass, *J. Geophys. Res.* **91**, 7505 (1986).
- <sup>83</sup>B. O’Neill, J. D. Bass, J. R. Smyth, and M. T. Vaughan, *J. Geophys. Res.* **94**, 17819 (1989).
- <sup>84</sup>A. Erba, A. Mahmoud, R. Orlando, and R. Dovesi, *Phys. Chem. Minerals* **41**, 151 (2014).
- <sup>85</sup>A. Erba, A. Mahmoud, R. Orlando, and R. Dovesi, *Phys. Chem. Minerals* **41**, 161 (2014).
- <sup>86</sup>A. Erba, A. Mahmoud, D. Belmonte, and R. Dovesi, *J. Chem. Phys.* **140**, 124703 (2014).
- <sup>87</sup>D. G. Isaak and E. K. Graham, *J. Geophys. Res.* **81**, 2483 (1976).
- <sup>88</sup>L. J. Bonczar, E. K. Graham, and H. Wang, *J. Geophys. Res.* **82**, 2529 (1977).
- <sup>89</sup>B. J. Leitner, D. J. Weidner, and R. C. Liebermann, *Phys. Earth Planet. Int.* **22**, 111 (1980).
- <sup>90</sup>B. O’Neill, J. D. Bass, J. R. Smyth, and M. T. Vaughan, *J. Geophys. Res.* **94**, 17819 (1989).
- <sup>91</sup>B. O’Neill, J. D. Bass, G. R. Rossman, C. A. Geiger, and K. Langer, *Phys. Chem. Miner.* **17**, 617 (1991).
- <sup>92</sup>S. V. Sinogeikin and J. D. Bass, *Phys. Earth Planet. Int.* **120**, 43 (2000).
- <sup>93</sup>T. S. Duffy and D. L. Anderson, *J. Geophys. Res.* **94**, 1895 (1989).
- <sup>94</sup>G. Chen, J. A. Cooke, G. D. Gwanmesia, and R. C. Liebermann, *Am. Miner.* **84**, 384 (1999).
- <sup>95</sup>A. Chopelas, H. J. Reichmann, and L. Zhang, in *Mineral Spectroscopy*, edited by M. D. Dyar, C. McCammon, and M. W. Schaefer (Geochem. Soc., Washington, D.C., 1996), p. 229.
- <sup>96</sup>Z. Wang and S. Ji, *Am. Miner.* **86**, 1209 (2001).
- <sup>97</sup>C. Lu, Z. Mao, J.-F. Lin, K. K. Zhuravlev, S. N. Tkachev, and V. B. Prakapenka, *Earth and Planetary Science Letters* **361**, 134 (2013).
- <sup>98</sup>J. D. Bass, *J. Geophys. Res.* **94**, 7621 (1989).
- <sup>99</sup>Y. Sumino and L. O. Anderson, in *Handbook of Physical Properties of Rocks*, edited by R. S. Carmichael (CRC Press, Boca Raton, Florida, 1982), p. 39.
- <sup>100</sup>P. M. Halleck, Ph.D. dissertation p. 82 (1973).
- <sup>101</sup>J. D. Bass, *J. Geophys. Res.* **91**, 7505 (1986).
- <sup>102</sup>F. Jiang, S. Speziale, S. R. Shieh, and T. S. Duffy, *J. Phys.: Cond. Matter* **16**, S1041 (2004).
- <sup>103</sup>A. Yeganeh-Haeri, D. J. Weidner, and E. Ito, *Geophys. Res. Lett.* **17**, 2453 (1990).
- <sup>104</sup>R. Dovesi, R. Orlando, A. Erba, C. M. Zicovich-Wilson, B. Civalleri, S. Casassa, L. Maschio, M. Ferrabone, M. De la Pierre, P. D’Arco, et al., *Int. J. Quantum Chem.* (2014), doi:10.1002/qua.24658.
- <sup>105</sup>S. Mustapha, Ph. D’Arco, M. De La Pierre, Y. Noël, M. Ferrabone, and R. Dovesi, *J. Phys.: Condens. Matter* **25**, 105401 (2013).

- <sup>106</sup>Ph. D'Arco, S. Mustapha, M. Ferrabone, Y. Noël, M. De La Pierre, and R. Dovesi, *J. Phys.: Condens. Matter* **25**, 355401 (2013).
- <sup>107</sup>R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, K. Doll, N. M. Harrison, B. Civalieri, I. J. Bush, et al., *CRYSTAL14 User's Manual*, Università di Torino, Torino (2014), <http://www.crystal.unito.it>.
- <sup>108</sup>W. F. Perger, J. Criswell, B. Civalieri, and R. Dovesi, *Comput. Phys. Commun.* **180**, 1753 (2009).
- <sup>109</sup>A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- <sup>110</sup>C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
- <sup>111</sup>Ph. D'Arco, F. Freyria Fava, R. Dovesi, and V. R. Saunders, *J. Phys.: Condens. Matter* **8**, 8815 (1996).
- <sup>112</sup>R. Dovesi, M. De La Pierre, A. M. Ferrari, F. Pascale, L. Maschio, and C. M. Zicovich-Wilson, *Am. Mineral.* **96**, 1787 (2011).
- <sup>113</sup>C. M. Zicovich-Wilson, F. J. Torres, F. Pascale, L. Valenzano, R. Orlando, and R. Dovesi, *J. Comput. Chem.* **29**, 2268 (2008).
- <sup>114</sup>A. Meyer, F. Pascale, C. M. Zicovich-Wilson, and R. Dovesi, *Int. J. Quantum Chem.* **110**, 338 (2010).
- <sup>115</sup>L. Valenzano, A. Meyer, R. Demichelis, B. Civalieri, and R. Dovesi, *Phys. Chem. Minerals* **36**, 415 (2009).
- <sup>116</sup>L. Valenzano, F. Pascale, M. Ferrero, and R. Dovesi, *Int. J. Quantum Chem.* **110**, 416 (2010).
- <sup>117</sup>V. Lacivita, Ph. D'Arco, R. Orlando, R. Dovesi, and A. Meyer, *Phys. Chem. Minerals* **40**, 781 (2013).
- <sup>118</sup>A. B. Alchagirov, J. P. Perdew, J. C. Boettger, R. C. Albers, and C. Fiolhais, *Phys. Rev. B* **63**, 224115 (2001).
- <sup>119</sup>R. E. Cohen, O. Gülseren, and R. J. Hemley, *Am. Mineral.* **85**, 338 (2000).
- <sup>120</sup>F. D. Murnaghan, *Proc. Natl. Acad. Sci. USA* **30**, 244 (1944).
- <sup>121</sup>F. Birch, *Phys. Rev.* **71**, 809 (1947).
- <sup>122</sup>F. Birch, *J. Geophys. Res.* **83**, 1257 (1978).
- <sup>123</sup>P. Vinet, J. Ferrante, J. R. Smith, and J. H. Rose, *J. Phys. C* **19**, 467 (1986).
- <sup>124</sup>W. B. Holzapfel, *Rep. Prog. Phys.* **59**, 29 (1996).
- <sup>125</sup>J.-P. Poirier and A. Tarantola, *Physics of the Earth and Planetary Interiors* **109**, 1 (1998).
- <sup>126</sup>O. L. Anderson, *Equations of State of Solids for Geophysicists and Ceramic Science* (Oxford University Press, New York, 1995).
- <sup>127</sup>T. S. Duffy and Y. Wang, *Mineralogical Society of America Reviews in Mineralogy* **37**, 425 (1998).
- <sup>128</sup>J. Hama and K. Suito, *J. Phys.: Cond. Matter* **8**, 67 (1996).
- <sup>129</sup>F. Stacey, B. Brennan, and R. Irvine, *Geophys. Surveys* **4**, 189 (1981).
- <sup>130</sup>R. J. Angel, in *High-Pressure and High-Temperature Crystal Chemistry*, edited by R. Hazen and R. Downs (Mineralogical Society of America, 2000), pp. 35–59.
- <sup>131</sup>J. F. Nye, *Physical properties of crystals* (Oxford University Press, Oxford, 1957).
- <sup>132</sup>A. Erba, M. Ferrabone, J. Baima, R. Orlando, M. Rérat, and R. Dovesi, *J. Chem. Phys.* **138**, 054906 (2013).
- <sup>133</sup>V. Lacivita, A. Erba, Y. Noël, R. Orlando, Ph. D'Arco, and R. Dovesi, *J. Chem. Phys.* **138**, 214706 (2013).
- <sup>134</sup>A. Erba, K. E. El-Kelany, M. Ferrero, I. Baraille, and M. Rérat, *Phys. Rev. B* **88**, 035102 (2013).
- <sup>135</sup>J. Baima, A. Erba, R. Orlando, M. Rérat, and R. Dovesi, *J. Phys. Chem. C* **117**, 12864 (2013).
- <sup>136</sup>A. Erba and R. Dovesi, *Phys. Rev. B* **88**, 045121 (2013).
- <sup>137</sup>A. Mahmoud, A. Erba, K. E. El-Kelany, M. Rérat, and R. Orlando, *Phys. Rev. B* **89**, 045103 (2014).
- <sup>138</sup>K. E. El-Kelany, A. Erba, P. Carbonnière, and M. Rérat, *J. Phys.: Cond. Matter* (2014), in press.
- <sup>139</sup>R. Hill, *J. Mech. Phys. Solids* **11**, 357 (1963).
- <sup>140</sup>A. Meyer, F. Pascale, C. M. Zicovich Wilson, and R. Dovesi, *Int. J. Quantum Chem.* **110**, 338 (2010).
- <sup>141</sup>F. Pascale, C. Zicovich-Wilson, R. Orlando, C. Roetti, P. Ugliengo, and R. Dovesi, *J. Phys. Chem. B* **109**, 6146 (2005).
- <sup>142</sup>K. Doll, *Comput. Phys. Commun.* **137**, 74 (2001).
- <sup>143</sup>K. Doll, V. Saunders, and N. Harrison, *Int. J. Quantum Chem.* **82**, 1 (2001).
- <sup>144</sup>B. Civalieri, Ph. D'Arco, R. Orlando, V. R. Saunders, and R. Dovesi, *Chem. Phys. Lett.* **348**, 131 (2001).
- <sup>145</sup>C. G. Broyden, *IMA J. Appl. Math.* **6**, 76 (1970).
- <sup>146</sup>R. Fletcher, *Comput. J.* **13**, 317 (1970).
- <sup>147</sup>D. Goldfarb, *Mathematics of Computation* **24**, 23 (1970).
- <sup>148</sup>D. F. Shanno, *Mathematics of Computation* **24**, 647 (1970).
- <sup>149</sup>P. Halleck, *The Compression and Compressibility of Grossular Garnet: A Comparison of X-ray and Ultrasonic Methods* (University of Chicago, Department of the Geophysical Sciences, 1973).
- <sup>150</sup>D. G. Isaak and E. K. Graham, *J. Geophys. Res.* **81**, 2483 (1976).
- <sup>151</sup>J. D. Bass, *J. Geophys. Res.* **94**, 7621 (1989).
- <sup>152</sup>F. Jiang, S. Speziale, and T. S. Duffy, *J. Geophys. Res.* **109**, B10210 (2004).
- <sup>153</sup>F. Jiang, S. Speziale, S. R. Shieh, and T. S. Duffy, *J. Phys.: Condens. Matter* **16**, S1041 (2004).
- <sup>154</sup>M. De La Pierre, Y. Noël, S. Mustapha, A. Meyer, Ph. D'Arco, and R. Dovesi, *Am. Mineral.* **98**, 966 (2013).
- <sup>78</sup>H. Jeffreys and K. E. Bullen, *Seismological tables* (British Association for the Advancement of Science, 1940).
- <sup>79</sup>D. L. Anderson and J. D. Bass, *Geophys. Res. Lett.* **11**, 637 (1984).
- <sup>80</sup>D. L. Anderson and J. D. Bass, *Nature* **320**, 321 (1986).
- <sup>81</sup>V. Babuška, J. Fiala, M. Kumazawa, I. Ohno, and Y. Sumino, *Physics of the Earth and Planetary Interiors* **16**, 157 (1978).
- <sup>82</sup>J. D. Bass, *J. Geophys. Res.* **91**, 7505 (1986).
- <sup>83</sup>B. O'Neill, J. D. Bass, J. R. Smyth, and M. T. Vaughan, *J. Geophys. Res.* **94**, 17819 (1989).
- <sup>84</sup>A. Erba, A. Mahmoud, R. Orlando, and R. Dovesi, *Phys. Chem. Minerals* **41**, 151 (2014).
- <sup>85</sup>A. Erba, A. Mahmoud, R. Orlando, and R. Dovesi, *Phys. Chem. Minerals* **41**, 161 (2014).
- <sup>86</sup>A. Erba, A. Mahmoud, D. Belmonte, and R. Dovesi, *J. Chem. Phys.* **140**, 124703 (2014).
- <sup>87</sup>D. G. Isaak and E. K. Graham, *J. Geophys. Res.* **81**, 2483 (1976).
- <sup>88</sup>L. J. Bonczar, E. K. Graham, and H. Wang, *J. Geophys. Res.* **82**, 2529 (1977).
- <sup>89</sup>B. J. Leitner, D. J. Weidner, and R. C. Liebermann, *Phys. Earth Planet. Int.* **22**, 111 (1980).
- <sup>90</sup>B. O'Neill, J. D. Bass, J. R. Smyth, and M. T. Vaughan, *J. Geophys. Res.* **94**, 17819 (1989).
- <sup>91</sup>B. O'Neill, J. D. Bass, G. R. Rossman, C. A. Geiger, and K. Langer, *Phys. Chem. Miner.* **17**, 617 (1991).
- <sup>92</sup>S. V. Sinogeikin and J. D. Bass, *Phys. Earth Planet. Int.* **120**, 43 (2000).
- <sup>93</sup>T. S. Duffy and D. L. Anderson, *J. Geophys. Res.* **94**, 1895 (1989).
- <sup>94</sup>G. Chen, J. A. Cooke, G. D. Gwanmesia, and R. C. Liebermann, *Am. Miner.* **84**, 384 (1999).
- <sup>95</sup>A. Chopelas, H. J. Reichmann, and L. Zhang, in *Mineral Spectroscopy*, edited by M. D. Dyar, C. McCammon, and M. W. Schaefer (Geochem. Soc., Washington, D.C., 1996), p. 229.
- <sup>96</sup>Z. Wang and S. Ji, *Am. Miner.* **86**, 1209 (2001).
- <sup>97</sup>C. Lu, Z. Mao, J.-F. Lin, K. K. Zhuravlev, S. N. Tkachev, and V. B. Prakapenka, *Earth and Planetary Science Letters* **361**, 134 (2013).
- <sup>98</sup>J. D. Bass, *J. Geophys. Res.* **94**, 7621 (1989).
- <sup>99</sup>Y. Sumino and L. O. Anderson, in *Handbook of Physical Properties of Rocks*, edited by R. S. Carmichael (CRC Press, Boca Raton, Florida, 1982), p. 39.
- <sup>100</sup>P. M. Halleck, Ph.D. dissertation p. 82 (1973).
- <sup>101</sup>J. D. Bass, *J. Geophys. Res.* **91**, 7505 (1986).
- <sup>102</sup>F. Jiang, S. Speziale, S. R. Shieh, and T. S. Duffy, *J. Phys.:Cond. Matter* **16**, S1041 (2004).
- <sup>103</sup>A. Yeganeh-Haeri, D. J. Weidner, and E. Ito, *Geophys. Res. Lett.* **17**, 2453 (1990).



- <sup>104</sup>R. Dovesi, R. Orlando, A. Erba, C. M. Zicovich-Wilson, B. Civalleri, S. Casassa, L. Maschio, M. Ferrabone, M. De la Pierre, P. D'Arco, et al., *Int. J. Quantum Chem.* (2014), doi:10.1002/qua.24658.
- <sup>105</sup>S. Mustapha, Ph. D'Arco, M. De La Pierre, Y. Noël, M. Ferrabone, and R. Dovesi, *J. Phys.: Condens. Matter* **25**, 105401 (2013).
- <sup>106</sup>Ph. D'Arco, S. Mustapha, M. Ferrabone, Y. Noël, M. De La Pierre, and R. Dovesi, *J. Phys.: Condens. Matter* **25**, 355401 (2013).
- <sup>107</sup>R. Dovesi, V. R. Saunders, C. Roetti, R. Orlando, C. M. Zicovich-Wilson, F. Pascale, K. Doll, N. M. Harrison, B. Civalleri, I. J. Bush, et al., *CRYSTAL14 User's Manual*, Università di Torino, Torino (2014), <http://www.crystal.unito.it>.
- <sup>108</sup>W. F. Perger, J. Criswell, B. Civalleri, and R. Dovesi, *Comput. Phys. Commun.* **180**, 1753 (2009).
- <sup>109</sup>A. D. Becke, *J. Chem. Phys.* **98**, 5648 (1993).
- <sup>110</sup>C. Lee, W. Yang, and R. G. Parr, *Phys. Rev. B* **37**, 785 (1988).
- <sup>111</sup>Ph. D'Arco, F. Freyria Fava, R. Dovesi, and V. R. Saunders, *J. Phys.: Condens. Matter* **8**, 8815 (1996).
- <sup>112</sup>R. Dovesi, M. De La Pierre, A. M. Ferrari, F. Pascale, L. Maschio, and C. M. Zicovich-Wilson, *Am. Mineral.* **96**, 1787 (2011).
- <sup>113</sup>C. M. Zicovich-Wilson, F. J. Torres, F. Pascale, L. Valenzano, R. Orlando, and R. Dovesi, *J. Comput. Chem.* **29**, 2268 (2008).
- <sup>114</sup>A. Meyer, F. Pascale, C. M. Zicovich-Wilson, and R. Dovesi, *Int. J. Quantum Chem.* **110**, 338 (2010).
- <sup>115</sup>L. Valenzano, A. Meyer, R. Demichelis, B. Civalleri, and R. Dovesi, *Phys. Chem. Minerals* **36**, 415 (2009).
- <sup>116</sup>L. Valenzano, F. Pascale, M. Ferrero, and R. Dovesi, *Int. J. Quantum Chem.* **110**, 416 (2010).
- <sup>117</sup>V. Lacivita, Ph. D'Arco, R. Orlando, R. Dovesi, and A. Meyer, *Phys. Chem. Minerals* **40**, 781 (2013).
- <sup>118</sup>A. B. Alchagirov, J. P. Perdew, J. C. Boettger, R. C. Albers, and C. Fiolhais, *Phys. Rev. B* **63**, 224115 (2001).
- <sup>119</sup>R. E. Cohen, O. Gülseren, and R. J. Hemley, *Am. Mineral.* **85**, 338 (2000).
- <sup>120</sup>F. D. Murnaghan, *Proc. Natl. Acad. Sci. USA* **30**, 244 (1944).
- <sup>121</sup>F. Birch, *Phys. Rev.* **71**, 809 (1947).
- <sup>122</sup>F. Birch, *J. Geophys. Res.* **83**, 1257 (1978).
- <sup>123</sup>P. Vinet, J. Ferrante, J. R. Smith, and J. H. Rose, *J. Phys. C* **19**, 467 (1986).
- <sup>124</sup>W. B. Holzapfel, *Rep. Prog. Phys.* **59**, 29 (1996).
- <sup>125</sup>J.-P. Poirier and A. Tarantola, *Physics of the Earth and Planetary Interiors* **109**, 1 (1998).
- <sup>126</sup>O. L. Anderson, *Equations of State of Solids for Geophysicists and Ceramic Science* (Oxford University Press, New York, 1995).
- <sup>127</sup>T. S. Duffy and Y. Wang, *Mineralogical Society of America Reviews in Mineralogy* **37**, 425 (1998).
- <sup>128</sup>J. Hama and K. Suito, *J. Phys.: Cond. Matter* **8**, 67 (1996).
- <sup>129</sup>F. Stacey, B. Brennan, and R. Irvine, *Geophys. Survveys* **4**, 189 (1981).
- <sup>130</sup>R. J. Angel, in *High-Pressure and High-Temperature Crystal Chemistry*, edited by R. Hazen and R. Downs (Mineralogical Society of America, 2000), pp. 35–59.
- <sup>131</sup>J. F. Nye, *Physical properties of crystals* (Oxford University Press, Oxford, 1957).
- <sup>132</sup>A. Erba, M. Ferrabone, J. Baima, R. Orlando, M. Rérat, and R. Dovesi, *J. Chem. Phys.* **138**, 054906 (2013).
- <sup>133</sup>V. Lacivita, A. Erba, Y. Noël, R. Orlando, Ph. D'Arco, and R. Dovesi, *J. Chem. Phys.* **138**, 214706 (2013).
- <sup>134</sup>A. Erba, K. E. El-Kelany, M. Ferrero, I. Baraille, and M. Rérat, *Phys. Rev. B* **88**, 035102 (2013).
- <sup>135</sup>J. Baima, A. Erba, R. Orlando, M. Rérat, and R. Dovesi, *J. Phys. Chem. C* **117**, 12864 (2013).
- <sup>136</sup>A. Erba and R. Dovesi, *Phys. Rev. B* **88**, 045121 (2013).
- <sup>137</sup>A. Mahmoud, A. Erba, K. E. El-Kelany, M. Rérat, and R. Orlando, *Phys. Rev. B* **89**, 045103 (2014).
- <sup>138</sup>K. E. El-Kelany, A. Erba, P. Carbonnière, and M. Rérat, *J. Phys.: Cond. Matter* (2014), in press.
- <sup>139</sup>R. Hill, *J. Mech. Phys. Solids* **11**, 357 (1963).
- <sup>140</sup>A. Meyer, F. Pascale, C. M. Zicovich Wilson, and R. Dovesi, *Int. J. Quantum Chem.* **110**, 338 (2010).
- <sup>141</sup>F. Pascale, C. Zicovich-Wilson, R. Orlando, C. Roetti, P. Ugliengo, and R. Dovesi, *J. Phys. Chem. B* **109**, 6146 (2005).
- <sup>142</sup>K. Doll, *Comput. Phys. Commun.* **137**, 74 (2001).
- <sup>143</sup>K. Doll, V. Saunders, and N. Harrison, *Int. J. Quantum Chem.* **82**, 1 (2001).
- <sup>144</sup>B. Civalleri, Ph. D'Arco, R. Orlando, V. R. Saunders, and R. Dovesi, *Chem. Phys. Lett.* **348**, 131 (2001).
- <sup>145</sup>C. G. Broyden, *IMA J. Appl. Math.* **6**, 76 (1970).
- <sup>146</sup>R. Fletcher, *Comput. J.* **13**, 317 (1970).
- <sup>147</sup>D. Goldfarb, *Mathematics of Computation* **24**, 23 (1970).
- <sup>148</sup>D. F. Shanno, *Mathematics of Computation* **24**, 647 (1970).
- <sup>149</sup>P. Halleck, *The Compression and Compressibility of Grossular Garnet: A Comparison of X-ray and Ultrasonic Methods* (University of Chicago, Department of the Geophysical Sciences, 1973).
- <sup>150</sup>D. G. Isaak and E. K. Graham, *J. Geophys. Res.* **81**, 2483 (1976).
- <sup>151</sup>J. D. Bass, *J. Geophys. Res.* **94**, 7621 (1989).
- <sup>152</sup>F. Jiang, S. Speziale, and T. S. Duffy, *J. Geophys. Res.* **109**, B10210 (2004).
- <sup>153</sup>F. Jiang, S. Speziale, S. R. Shieh, and T. S. Duffy, *J. Phys.: Condens. Matter* **16**, S1041 (2004).
- <sup>154</sup>M. De La Pierre, Y. Noël, S. Mustapha, A. Meyer, Ph. D'Arco, and R. Dovesi, *Am. Mineral.* **98**, 966 (2013).