Elasticity and Raman and infrared spectra of MgAlO spinel from density functional perturbation theory

Razvan Caracas, Edward J. Banigan

► To cite this version:

Razvan Caracas, Edward J. Banigan. Elasticity and Raman and infrared spectra of MgAlO spinel from density functional perturbation theory. *Physics of the Earth and Planetary Interiors*, 2009, 174 (1-4), pp.113. 10.1016/j.pepi.2009.01.001 . hal-00533034

HAL Id: hal-00533034

<https://hal.science/hal-00533034>

Submitted on 5 Nov 2010

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Accepted Manuscript

Title: Elasticity and Raman and infrared spectra of MgAl_2O_4 spinel from density functional perturbation theory

Authors: Razvan Caracas, Edward J. Banigan

PII: S0031-9201(09)00003-X
DOI: doi:10.1016/j.pepi.2009.01.001
Reference: PEPI 5119

To appear in: *Physics of the Earth and Planetary Interiors*

Received date: 1-10-2007
Revised date: 25-11-2008
Accepted date: 6-1-2009

Please cite this article as: Caracas, R., Banigan, E.J., Elasticity and Raman and infrared spectra of MgAl_2O_4 spinel from density functional perturbation theory, *Physics of the Earth and Planetary Interiors* (2008), doi:10.1016/j.pepi.2009.01.001

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

Elasticity and Raman and infrared spectra of MgAl_2O_4 spinel from density functional perturbation theory

Razvan Caracas^{1,2} and Edward J. Banigan³

1) *Ecole Normale Supérieure de Lyon, Laboratoire de Sciences de la Terre CNRS UMR5570, 46 allée d'Italie Lyon, e-mail: razvan.caracas@ens-lyon.fr*

2) *Bayerisches Geoinstitut, University of Bayreuth, Universitaetstrasse 30, D-95446 Bayreuth, Germany*

3) *University of Pennsylvania, Department of Physics and Astronomy, 209 South 33rd Street, Philadelphia, PA 19104-6396*

Abstract

We determine the elastic constants and the Raman spectra of spinel under pressure using density functional perturbation theory. Like other spinels, MgAl_2O_4 shows an increasing bulk modulus and a weakly varying shear modulus under pressure. The Raman spectrum is dominated by two main peaks whose intensities decrease under pressure. The theoretical Raman spectra of disordered spinel shows a better agreement with measurements on natural samples than the ordered one. We also investigate the high-pressure stability of different structures and find the calcium titanate type to be the stable phase beyond 45 GPa.

1 Introduction

There has been a significant amount of work done on MgAl_2O_4 spinel at high pressure. Notably, various studies have found the equations of state and/or crystal structure up to about 70 GPa (Kruger et al., 1997; Funamori et al., 1998; Wittlinger et al., 1998; Catti, 2001; Fang and De With 2002), while others investigated various minerals having spinel structure and systems involving mixtures of MgAl_2O_4 spinel and similar minerals (Bina and Wood, 1987; Kiefer et al., 1997; Akaogi et al., 1999; Miura et al., 2000).

At ambient pressure and temperature, MgAl_2O_4 spinel is cubic with space group $\text{Fd}\bar{3}\text{m}$ (Kruger et al., 1997, Fang and De With 2002). As pressure is applied, this structure becomes unstable and disassociates into a periclase (MgO) and corundum (Al_2O_3) mixture around 15 GPa (Akaogi et al., 1999).

At about 26-27 GPa, this mixture has been observed to undergo a transition into an orthorhombic calcium ferrite-like structure (Decker and Kasper, 1957; Kruger et al., 1997; Funamori et al., 1998; Akaogi et al., 1999). This phase is stable over a limited pressure range as it was proposed that MgAl_2O_4 undergoes another phase transition above 40 GPa to an orthorhombic calcium titanate-type (space group Cmcm) phase (Bertraut and Blum, 1956; Funamori et al., 1998; Catti 2001). Some experiments show directly the formation of the calcium titanate structure after recombination (Ono et al., 2006).

Several other structures including a hexagonal phase, a tetragonal phase, and additional orthorhombic phases have been linked to spinel and spinel-like materials. For example, it has been shown that MgAl_2O_4 is part of a hexagonal aluminous phase with CaAl_2O_4 , which is particularly significant for studies of the subducted crust and the lower mantle (Akaogi et al. 1999, Miura et al. 2000). Other suggested postspinel phases include a tetragonal structure, which is observed in high pressure NiMn_2O_4 (Martin de Vidales et al., 1994; Åsbrink et al., 1998) and the very dense CaMn_2O_4 -type orthorhombic structure (Giesber et al., 2001).

Here we analyze the behavior and properties of MgAl_2O_4 up to 150 GPa. First we investigate the relative stability of several structures. We find that cubic spinel decomposes into a mixture of oxides around 15 GPa and then recomposes into calcium titanate structure around 45 GPa. This is the most favorable structure up to at least 150 GPa. Then for the cubic structure we compute the elastic constants tensor and the Raman spectra within the density-functional perturbation theory.

2 Methodology

2.1 General

We perform first-principles calculations using the ABINIT implementation (Gonze et al., 2002, Gonze et al., 2005) of the density functional theory (DFT) (Hohenberg and Kohn, 1964, Kohn and Sham, 1965) and the density functional perturbation theory (DFPT) (Gonze et al., 1992, Gonze, 1997, Gonze and Lee, 1997, Baroni et al., 2001, Gonze et al., 2005a) based on planewaves and pseudopotentials.

We use the local density approximation for the exchange-correlation energy. As usual with planewave basis sets, the numerical accuracy of the calculation can be systematically improved by increasing the cut-off kinetic energy of the planewaves and the density of the sampling of the Brillouin zone (Payne

et al., 1992). We use a 38 Ha cut-off energy for the kinetic energy of the planewaves. We sample the reciprocal space using regular grid of special k points according to the Monkhorst-Pack scheme (Monkhorst and Pack 1976). We use two 4x4x4 grids of k-points interpenetrating in a body-centered cubic-way for the elasticity calculations and simple cubic-like grids of 4x4x4 k points for the vibrational calculations. The 4x4x4 grid and the 38Ha cut-off energy yield a precision in total energy on the order of 1mHa/molecule. The Raman spectra are also converged at the 4x4x4 grids with respect to the 6x6x6 grid. The determination of the response function with respect to strains usually requires a better sampling in k-points, hence our choice of using a double dense grid for these calculations. For the structural relaxations we use grids of 4x4x4 k-points or larger until convergence.

The Born effective charges, the dielectric tensors and the dynamical matrices were computed using the DFPT. In DFPT the energy is analytically expanded as a Taylor series, built around small perturbations, λ :

$$E[\lambda] = E^{(0)} + \sum_i \frac{\delta E}{\nabla \lambda_i} \lambda_i + \frac{1}{2} \sum_{i,j} \frac{\delta^2 E}{\nabla \lambda_i \nabla \lambda_j} \lambda_i \lambda_j + \frac{1}{6} \sum_{i,j,k} \frac{\delta^3 E}{\nabla \lambda_i \nabla \lambda_j \nabla \lambda_k} \lambda_i \lambda_j \lambda_k + \dots (1)$$

The perturbations can be atomic displacements, electric fields, lattice strains, etc. or any combination thereof. Each term of the series can be related to a physical property and is obtained calculating the appropriate derivative of the total energy with respect to these perturbations.

The first term of the series represents the standard ground-state energy. If the perturbation λ represents the atomic displacements then the first term corresponds to the forces on the atoms. This term is null at equilibrium. In this case the next term, the second derivative of the energy with respect to atomic displacements, is a matrix of size 3xN by 3xN where N is the number of atoms per unit cell and whose entries represent the interatomic force constants. By diagonalization this matrix yields the phonon frequencies and the phonon eigenvectors, their corresponding displacements. When one considers the interatomic forces between all the atoms within the same unit cell the diagonalization gives the frequencies of the phonon modes visible in Raman (*g*-modes) and infrared (*u*-modes) and of the silent modes. The remaining terms correspond to different higher-order effects, like anharmonicities.

The formalism behind DFPT has been extensively described elsewhere in much detail (Gonze, 1997, Gonze and Lee, 1997, Baroni et al., 2001, Gonze et al., 2005a) and thus we will not describe it any further. We primarily want to stress that DFPT offers an elegant, analytical and straightforward way to obtain physical properties which can be expressed as derivatives of the energy with respect to specific perturbations.

In the following we apply DFPT to compute the elasticity and the Raman spectra of cubic MgAl_2O_4 spinel. Alternatively, both of these properties can be computed from finite differences methods, as done previously (Karki et al., 2001). But DFPT offers a more straightforward and elegant approach with several useful physical properties computed on-the-fly.

We also study the effect of Mg-Al order/disorder on the properties of cubic spinel. The classical method to address this type of problem is the cluster expansion model. According to this approach the properties of the disordered solid may be inferred using the computed results for only several supercells with different representative atomic configurations and making use of statistical physics. This model is straightforward and it can be applied to any type of disordered structure or solid solution, but the results are highly dependent on the quality of the sampling. Each individual calculation is more tedious because of larger system sizes and possible losses of symmetry due to the specific atomic configuration.

Here we adopt an alternative approach, the virtual crystal approximation (Bel-laiche and Vanderbilt, 2000). For each of the disordered sites we construct one *alchemical* pseudopotential mixing the atoms that participate in the solid solution in the appropriate amounts (Giantomassi et al, 2005, Cohen, 2007). This approach uses small simulation cells and preserves the symmetry, but the mixing should be realized between chemically similar atoms. In practice the *alchemical* pseudopotentials are obtained as follows: the local potentials of the original pseudopotentials are linearly mixed, the form factors of the non-local projectors are all preserved, and all considered to generate the alchemical potential, the scalar coefficients of the non-local projectors are multiplied proportionally and the core charge cutoff radius and functions are linear combinations of respectively the radii and the functions of the original pseudopotentials.

2.2 Elasticity

In the DFPT approach the elastic constants tensor is obtained analytically, considering the strains as the perturbation. The theoretical basis has been put forth a few decades ago (Baroni et al., 1987, Gonze et al., 1992, Baroni et al. 2001) with further developments and implementations emerging recently (Hamann et al., 2005). Notably in the ABINIT implementation (Hamann et al., 2005) the perturbation with respect to the strains is described using the metric of the point group. Solving the perturbation expansion in a reduced coordinate framework rather than a cartesian one has the advantage of being universal and symmetry independent. The bare second-order energy derivative with respect to two strains η_i and η_j for fixed atomic positions, namely the

derivative without taking into account the atomic rearrangements due to the strain itself ($s = 0$), yields the clamped-ion elastic constants:

$$\overline{C}_{ij} = \frac{1}{\Omega} \frac{dE^2}{d\eta_i d\eta_j} \quad (2)$$

where Ω is the unit cell volume, and the energy is normalized to one unit cell.

The relaxed-ion elastic constants are obtained by correcting the above clamped-ion elastic constants as follows:

$$C_{ij} = \overline{C}_{ij} - \frac{1}{\Omega} \Lambda_{mi} (K^{-1})_{mn} \Lambda_{nj} \quad (3)$$

where Λ is the energy derivative with respect to atomic displacements, dr and strains, $d\epsilon$, and K are the interatomic force constants, $K = d^2E/dr^2$.

These terms ensure that the coupling between different perturbations through first order derivatives of the total energy is correctly taken into account. The corrections applied to the clamped tensors are straightforward. The full theoretical derivation of these formulas and the implementation in ABINIT have been detailed in the original paper (Hamann et al., 2005) and will not be reproduced here again.

In the finite difference approach we first relax the structure minimizing the energy, the forces and the residual stresses. Next we apply different strains, $\boldsymbol{\eta}$, and for each of these we relax at fixed cell geometry the positions of the atoms, minimizing the energy and the residual forces. We compute the resulting stresses, $\boldsymbol{\epsilon}$. Finally we apply the linear relation between the stresses, $\boldsymbol{\epsilon}$ and the strains, $\boldsymbol{\eta}$ to extract the complete elastic constants tensor, $\mathbf{C}$: $\boldsymbol{\epsilon} = \mathbf{C}\boldsymbol{\eta}$. Despite the large amount of calculations required for the low-symmetry systems, this procedure has been applied with much success over the years (see *e.g.* Karki et al, 2001).

2.3 Raman intensities

The Raman intensity for an xy-oriented single-crystal depends on the frequency of the incident laser ω_L , on temperature, T , which are user-defined parameters, on the frequency of the Raman mode ω_i and on the xy element of the Raman tensor, α_{xy} (*e.g.* Cardona, 1982):

$$I_{xy} \sim C\alpha_{xy}^2 \quad (4)$$

where the prefactor C is

$$C \sim (\omega_L - \omega_i)^4 \frac{1 + n(\omega_i)}{30\omega_i} \quad (5)$$

The temperature dependence is given by the Bose occupancy factor, $n(\omega)$:

$$1 + n(\omega_i) = [1 - \exp(-\hbar\omega_i/kT)]^{-1} \quad (6)$$

The Raman tensors are defined as:

$$\alpha_{xy} = \sqrt{\Omega} \sum_{\alpha\tau} \frac{\partial \chi_{xy}}{\partial r_{\alpha\tau}} \quad (7)$$

where Ω is the unit cell volume, the atom τ moves along direction α , and χ_{xy} is the macroscopic dielectric tensor:

$$\chi_{xy} = \frac{\epsilon_{xy}^{\infty} - \delta_{xy}}{4\pi} \quad (8)$$

The derivative of the macroscopic dielectric tensor is computed with respect to the atomic displacements, $r_{\alpha\tau}$, corresponding to the phonon eigenvector.

The Raman tensors are the key ingredients needed to calculate the Raman spectra. They can be computed either from finite differences, as the change of the dielectric tensor due to infinitesimal atomic displacements, or from perturbation theory, as the derivative of the energy with respect to electric fields and atomic displacements (Baroni and Resta, 1986, Dal Corso and Mauri, 1994, Lazzeri and Mauri, 2003, Veithen et al., 2005). In this study we use the second approach as in the ABINIT implementation (Veithen et al., 2005).

For this we need to calculate the third order derivative of the energy with respect to two electric fields and one atomic displacements. The derivatives with respect to electric fields yields the dielectric tensor and the derivative with respect to the atomic displacements yields the change in dielectric tensor as the atoms vibrate according to a certain phonon eigenvector. Computing these high-order terms of the Taylor expansion is possible based on the previous availability of the lower-order terms with some limited amount of extra-coding and computing (Veithen et al., 2005).

This approach gives us the Raman susceptibility tensors for each phonon mode for a single crystal. As most experimental spectra from high-pressure diamond-anvil cell experiments are recorded on powders, we report here the Raman spectra for crystalline powders. For this we neglect the surface reconstruction

and the grain size effects and we perform integrals over all possible orientations of ideal bulk crystals. These integrals are reduced to the following three rotational invariants (Prosandeev et al., 2005, Placzek, 1934, Hayes and Loudon, 1978):

$$G^{(0)} = \frac{\sum_{ii,i=x,y,z} (\alpha_{ii})^2}{3} \quad (9)$$

$$G^{(1)} = \frac{\sum_{ij,i,j=x,y,z} (\alpha_{ij} - \alpha_{ji})^2}{2} \quad (10)$$

$$G^{(2)} = \sum_{ij,i,j=x,y,z} \frac{(\alpha_{ij} + \alpha_{ji})^2}{2} + \frac{(\alpha_{ii} - \alpha_{jj})^2}{3} \quad (11)$$

The intensities of the two polarized components of the powder spectra, parallel and perpendicular, and the resulting total powder spectra are :

$$I_{\parallel}^{powder} = C(10G^{(0)} + 4G^{(2)}) \quad (12)$$

$$I_{\perp}^{powder} = C(5G^{(1)} + 3G^{(2)}) \quad (13)$$

$$I_{tot}^{powder} = I_{\parallel}^{powder} + I_{\perp}^{powder} \quad (14)$$

We have successfully applied this approach to several other phases (Caracas and Cohen, 2006; Caracas, 2007) under pressure and obtained excellent agreement between calculations and experimental data.

Using the formalism described above one computes the total intensity of the Raman peaks, but not the width of the peaks. This latter quantity comes from anharmonic effects that correspond to even higher-order terms of the Taylor expansion, which are not yet implemented within DFPT.

3 Results

3.1 Elasticity

Table ?? and Figure ?? show the computed elastic constants tensor at several pressures. For one pressure (20GPa) we compute the elastic constants using both methods, DFPT and finite differences. We see an excellent agreement

between the DFPT approach and the finite differences approach as well as between the computed values and the experimental data.

With pressure the C_{11} and C_{12} elastic constants increase by respectively 59 GPa and 81 GPa over 0-20 GPa theoretical pressure range, corresponding to dC_{11}/dP and dC_{12} slopes of 3.55 and 4.05 (Table ?? and Figure . This increase is reflected in the bulk modulus $K'=4.27$. The tetragonal shear defined as $(C_{11}-C_{12})/2$ decreases by 11GPa over the 0-30GPa pressure range: from 65GPa at 0GPa pressure down to 54GPa at 30GPa pressure. The C_{44} elastic constant increases by only about 12 GPa in the 0-20 GPa pressure range, which corresponds to a $dC_{44}/dP=0.6$ and to a roughly constant shear modulus.

Our results are in good agreement with the previous experimental (Yoneda, 2000, Suzuki et al., 2000, Reichmann and Jacobsen, 2006) measurements at ambient conditions of pressure and temperature or with various other calculations employing LDA or GGA approximations for the exchange-correlation and pseudopotential and all-electron implementations (Wdowik et al., 2006, Khenata et al., 2000, Li et al., 2007), all of which are summarized in Table ?. These studies show a linear dependence of C_{11} and only a weak dependence of C_{12} and C_{44} with Mg/Al disorder (Li et al., 2007). The elastic constants C_{11} , C_{12} and C_{44} decrease linearly with temperature by respectively 32, 12 and 12 GPa between room temperature and 1200K (Suzuki et al., 2000).

We calculate next the isotropic compressional (V_p) and shear (V_s) wave velocities for homogeneous polycrystalline aggregates as:

$$V_p = \sqrt{\frac{K + \frac{4}{3}G}{\rho}}, V_s = \sqrt{\frac{G}{\rho}} \quad (15)$$

considering the Voigt-Reuss-Hill scheme for the bulk and shear moduli, $K = (C_{11} + 2C_{12})/3$ and $G = (G_v + G_r)/2$, where :

$$G_v = \frac{C_{11} - C_{12} + 3C_{44}}{5}, G_r = \frac{5(C_{11} - C_{12})C_{44}}{4C_{44} + 3(C_{11} - C_{12})} \quad (16)$$

The bulk modulus obtained from the above equation is $K=205$ GPa in excellent agreement with the bulk modulus obtained from fitting a 3rd order Birch-Murnaghan equation of state on the pressure-volume theoretical results for spinel, which gives $K=202$ GPa. The values obtained for the seismic wave velocities as well as the densities as a function of pressure are listed in Table ?. The compressional wave velocity increases with pressure and the shear wave velocity decreases with pressure; the computed velocities scale with pressure as:

$$V_p = 9.824 + 0.021 P \text{ [in km/s]}$$

and

$$V_s = 5.518 - 0.014 P \text{ [in km/s]}$$

This behavior reproduces the experimental observations for spinel (Yoneda, 1990). It is also observed in other spinel structures, like magnetite (Reichmann and Jacobsen, 2004) and gahnite (Reichmann and Jacobsen, 2006). However gahnite shows a slightly positive increase in V_s , while we obtain a slightly negative variation in V_s for spinel.

The large anisotropy of the elastic properties of spinel is reflected in the anisotropy ratio, defined for the cubic crystals as the ratio between the shear modulus and the tetragonal shear. At ambient pressure the anisotropy is 1.72, but it increases to 1.79 at 10 GPa, 1.89 at 20 GPa to reach 2.04 at 30 GPa. This increase is almost linear up to 20 GPa and then it slightly deviates upwards.

The weak variation of the C_{44} with pressure is a general characteristic of the oxide spinels. It can be explained based on the coupling between atomic displacements and shear strains. In DFPT we obtain two types of elastic constants: for clamped ions and for non-clamped ions. In the first case the internal coordinates of freedom are not allowed to vary. In other words the atoms are fixed inside the distorted unit cell, so the coordination polyhedra do not distort to accommodate the strain. These elastic constants have a stronger variation with pressure: C_{44} changes from 189 GPa at 0 GPa to 205 GPa at 10 GPa and up to 220 GPa at 20 GPa. In the case of non-clamped ions, the atoms are allowed to relax and thus the octahedral distortion is adjusted to better accommodate the shear deformation. As a result the elastic stiffness of the structure is decreased. Similarly, the fact that variation of C_{44} and G with pressure is smaller for oxide spinels than for silicate spinels can be explained from the difference in the softness of the octahedra; the octahedra in the oxides are softer, whereas those in the silicates are stiffer.

3.2 Vibrational spectroscopy

According to group theory, the 39 optical zone-center vibrational modes in cubic spinel decompose as $A_{1g} + E_g + 3T_{2g} + T_{1g} + 2B_{1u} + 2E_u + 2T_{1u} + 4T_{2u}$. All the u modes are infrared active and the g modes are Raman active, except for T_{1g} , which is silent. The frequencies of all these modes are obtained from the interatomic force constants matrix as described in Section 2.

The variation with pressure of the u -modes is shown in Figure ???. The B_{1u} , E_u and T_{1u} modes do not show a LO-TO splitting, while the T_{2u} modes

show an increasingly large LO-TO splitting at high frequencies. In general the low-frequency modes show a weak dependence with pressure. The same features were observed in silicate spinels (Hofmeister and Mao, 2001). The lower frequency B_{1u} and E_u modes correspond to off-centering displacements of the Al, the higher frequency B_{1u} and E_u modes to bending of respectively the O-Al-O and the O-Mg-O angles. The T_{1u} modes correspond to off-center displacements of Al inside the AlO_6 octahedra associated with displacements of parts of the O sublattice. The low-frequency T_{2u} mode corresponds to off-center displacements of the Mg atoms in the MgO_4 tetrahedra and all the other T_{2u} modes to different off-center displacements of the Al atoms in the AlO_6 octahedra.

For the Raman-active g -modes we compute the Raman susceptibility tensors. The symmetry of the Raman tensors is shown in Table ???. They determine the selection rules: which modes are visible in what geometry in Raman measurements on single-crystals (Cardona, 1982). For powders we consider all possible orientations of the crystals performing an average over all Euler angles that would rotate the Raman tensors. The three resulting constants as equivalent of an isotropic medium are given by Equations (8)-(10). The computed Raman spectra for cubic spinel are shown in Figure ?? with both peak positions and intensities. The spectra are computed for ideal powders, where the surface, size and preferred orientation effects are neglected. We show the intensities for parallel polarization, for cross-polarization and for unpolarized spectra (total intensity).

The powder Raman spectra are dominated by the E_g mode. There is one intense T_{2g} mode, the two other T_{2g} modes being much weaker. The relative difference between the intensities of the E_g and the highest T_{2g} modes increases with pressure. The low-frequency T_{2g} mode corresponds to out-of-phase off-centering of Mg inside the tetrahedra such that the total polar moment remains null. The E_g mode corresponds to bending of the O-Mg-O angles and the A_{1g} to bending of the O-Al-O angles. The higher-frequency T_{2g} modes are breathing modes of the octahedra. The silent T_{1g} modes are rotations of the octahedra. Figure ?? shows that under pressure all the modes harden.

The experimental measurements confirm our theoretical findings. Slotznik and Shim (2008) measured the Raman spectra of different synthetic and natural samples of spinel and found at ambient pressure and temperature peak frequencies in the $305\text{-}312\text{ cm}^{-1}$ for the most intense T_{2g} mode, in the $666\text{-}681\text{ cm}^{-1}$ for the high-frequency T_{2g} mode with the third T_{2g} mode not visible, frequencies of $407\text{-}411\text{ cm}^{-1}$ for the E_g mode and of $765\text{-}770\text{ cm}^{-1}$ for the A_{1g} mode. All the modes soften quasi-linearly with temperature up, but show changes in the $800\text{-}1200\text{K}$ range. The same tendency is observed by Cynn et al. (1992), who report the T_{2g} modes at 307 cm^{-1} and 670 cm^{-1} , the E_g mode at 407 cm^{-1} and the A_{1g} mode at 768 cm^{-1} . One natural sample and one syn-

thetic show a weak peak at 726 cm^{-1} that may correspond to our computed third T_{2g} mode. This peak vanishes after annealing from 1234K.

Previous first-principles calculations (de Wijs, 2002) yield the T_{2g} modes at 319, 570 and 682 cm^{-1} , the E_g mode at 426 cm^{-1} and the A_{1g} mode at 776 cm^{-1} . The full Raman spectra were previously fully computed at ambient pressures for both order and partially disordered spinel (Lazzeri and Thibaudau, 2006) and show a similar pattern to our results.

3.3 Raman spectra of the disordered structure

Next we study the disordered structure of spinel. We allow the cations to intermix; some of Al to occupy the cubic positions and some of the Mg to occupy the octahedral position, resulting in the general formula $(\text{Mg}_{1-x}\text{Al}_x)(\text{Mg}_{2x}\text{Al}_{1-2x})_2\text{O}_4$. We want to see what is the effect of the disorder on the Raman spectra. We consider one term in the solid solution with $x = 0.2$ corresponding to $(\text{Mg}_{0.8}\text{Al}_{0.2})(\text{Al}_{0.9}\text{Mg}_{0.1})_2\text{O}_4$. We build the appropriate *alchemical* pseudopotentials based on the algorithm described above and the corresponding atomic concentrations. We use these pseudopotentials and we relax the cubic structure of spinel at 0, 10 and 20 GPa. For the relaxed structures we compute the dynamical properties in the zone-center and the Raman susceptibilities.

The Raman peaks in the spectra of the disordered structure are softened with respect to the ordered one. This shift can be attributed to a slight variation of the volume due to disorder and change of pseudopotentials. The influence of the disorder is clearly seen on the change in intensity of the peaks. The intensity of the E_g modes, which correspond to bending of the O-Mg-O angles is almost tripled by allowing some Al atoms to replace the Mg on the tetrahedral sites. This is due to an enhanced polarizability associated with the presence of the p electrons of Al that hybridize with the O p orbitals more than the Mg s orbitals, which rather tend to lose their electrons. The effect on the most intense T_{2g} mode is less important. The relative ratio between the intensity of these two main modes is in better agreement with the experimental measurements for the disordered structure than for the ordered one.

3.4 Structural stability

We investigate the relative stability of the spinel and post-spinel structures. In the cubic $Fd3m$ structure the Mg, Al and O atoms are respectively on the $8a(1/8\ 1/8\ 1/8)$, $16d(1/2\ 1/2\ 1/2)$ and $32e(x\ x\ x)$ Wyckhoff positions. The Mg atoms are fourfold coordinated and sit in the middle of tetrahedra and Al

are six-fold coordinated and sit in the middle of octahedra. In natural samples often there is some disorder between the cations.

From enthalpy calculations we observe that under pressure the ordered spinel cubic $Fd3m$ structure decomposes into a mixture of oxides at 15 GPa, in agreement with previous observations (Akaogi et al., 1999) and calculations (Catti, 2001). $MgAl_2O_4$ recombines at about 50 GPa into a $CaTi_2O_4$ type structure with $Cmcm$ space group (Figure ??), the same trend being observed in other calculations with advanced approximations for the exchange-correlation term, like B3LYP (Gracia et al., 2002). The failure to observe the Ca-ferrite type structure, like in certain experimental studies (Irifune et al., 1991) might be due to the static approximation present in our calculations, where entropic effects due to both order-disorder and to lattice contributions are neglected.

We test several other structures common to AB_2O_4 compounds: $CaFe_2O_4$ type with $Pnma$ symmetry (Decker and Kasper, 1957), a $CaMn_2O_4$ type with $Pbcm$ symmetry (Giesber et al., 2001), an orthorhombic $Imma$ structure, a hexagonal P-6 structure (Miura et al., 2000) and a tetragonal $I4_1/amd$ phase (Martin de Vidales et al., 1994). None of these structures have a lower enthalpy than the calcium titanate one at 0K (Figure ??). Contrary to some experimental studies we do not obtain the calcium ferrite type structure ($Pnma$) lower in enthalpy than the calcium titanate type ($Cmcm$) above the recombination pressure. However, there are experiments that confirm our theoretical findings (e.g. Ono et al., 2006). The pressure that we obtain for the transition to the calcium titanate structure is consistent with other computational study, performed using both LDA and more advanced formalisms, like B3LYP (Catti, 2001, Fang and de With, 2002). The discrepancies between these different studies can be assigned to temperature or reaction kinetics effects, as the two structures have similar enthalpies, on the order of 2 mHa/molecule or less above 50 GPa. Moreover, there are strong structural similarities between the two phases. We also observe that the calcium manganate structure relaxes into the calcium titanate structure and the tetragonal $I4_1/amd$ structure relaxes into the cubic spinel in our calculations.

For each of the investigated structures we fit Vinet equation of states on the pressure-volume data. The results are summarized in Table ?? and Figure ?. The $Cmcm$ phase has the largest bulk modulus and the largest density. The theoretical bulk modulus of the cubic structure, 202 GPa, is slightly larger than the experimental one, 198 GPa. The discrepancy can be attributed to the 2% volume underestimation in our calculations of the experimental volume at ambient pressure because of LDA.

4 Conclusions and perspectives

We have studied MgAl_2O_4 under pressure. Based on enthalpy calculations, we show that the phase transition sequence at low temperatures consists of cubic spinel decomposing into a mixture of oxides at 15 GPa and recombination of the oxides into the calcium titanate-type structure at 50 GPa.

We obtain the calcium-ferrite structure as competitive but unstable with respect to calcium titanate type. For the cubic structure we computed the elastic constants tensor and the Raman susceptibilities using the perturbation approach to the density functional theory in the ABINIT implementation. We also calculate the Raman spectra for one term along the ideal $(\text{Mg,Al})(\text{Al,Mg})_2\text{O}_4$ solid solution. We showed that we obtain a better agreement in relative intensities between computed and measured Raman spectra if we allow for Mg-Al exchange between the two crystallographic sites of the cations in the structure.

We also find that the values of the elastic constants computed using the perturbative approach are within a few GPa of the values obtained from the finite-differences approach and the experimental values. In Raman spectroscopy the positions of the theoretical peaks are found to lie within a few cm^{-1} and within a few tens of cm^{-1} of the experimentally recorded peaks in the best and worst cases, respectively. The theoretical dominant Raman peaks and their relative intensities agree well with experiments.

The advantages of the perturbation approach over the finite differences approach are the analytical solutions, faster and fewer calculations and the availability of a whole set of related supplementary properties that are obtained through combinations of perturbations. Moreover these advantages become increasingly more important with decreasing the symmetry of the crystal. Thus, our calculations illustrate the high precision that is now attainable with density functional perturbation theory.

5 Acknowledgements

Part of the calculations were performed on the IBM Zeus at CINES, grant stl2816. RC acknowledges financial support from the Alexander von Humboldt foundation that made possible the realization of this project. EB acknowledges the Carnegie Institution of Washington and the Bayerisches GeoInstitut for financial support.

References

- [1] Akaogi, M., Y. Hamada, T. Suzuki, M. Kobayashi, and M. Okada. High pressure transitions in the system MgAl_2O_4 - CaAl_2O_4 : a new hexagonal aluminous phase with implication for the lower mantle. *Physics of the Earth and Planetary Interiors*, 115, 67-77, 1999.
- [2] Åsbrink, S., A. Waskowska, J. Staun Olsen, L. Gerward. High-pressure phase of cubic spinel NiMn_2O_4 . *Physical Review B*, 57, 4972-4974, 1998.
- [3] Baroni, S., Resta, R., 1986. Ab initio calculation of the low-frequency Raman cross section in silicon, *Phys. Rev. B*, 33, 5969-5971.
- [4] Baroni, S., Giannozzi, P., Testa, A., 1987. Greens-function approach to linear response in solids, *Phys. Rev. Lett.*, 58, 1861-1864.
- [5] Baroni, S., de Gironcoli, S., Dal Corso, A., Giannozzi, P., 2001. Phonons and related crystal properties from density-functional perturbation theory, *Rev. Mod. Phys.*, 73, 515-562.
- [6] Bellaiche, L., and Vanderbilt, D., 2000. Virtual crystal approximation revisited: Application to dielectric and piezoelectric properties of perovskites, *Phys. Rev. B* 61, 7877-7882.
- [7] Bertaut, E.F. and P. Blum. Determination de la structure de Ti_2CaO_4 par la methode self-consistante d'approche directe. *Acta Crystallographica*, 9, 121-126, 1956.
- [8] Bina, C.R., and B.J. Wood. Olivine-spinel transitions: experimental and thermodynamic constraints and implications for the nature of the 400-km seismic discontinuity. *Journal of Geophysical Research*, 92, 4853-4866, 1987.
- [9] Cardona, M., 1982. *Light Scattering in Solids II: Basic Concepts and Instrumentation*, vol. 50, *Topics in Applied Physics*, edited by M. Cardona and G. Guntherodt, pp. 19-168, Springer, New York.
- [10] Caracas, R., 2007. Raman spectra and lattice dynamics of cubic gauche nitrogen, *J. Chem. Phys.*, 127, 144510.
- [11] Caracas, R., Cohen, R.E. 2006. Theoretical determination of the Raman spectra of MgSiO_3 perovskite and post-perovskite at high pressure, *Geophys. Res. Lett.*, 33, L12S05, doi:10.1029/2006GL025736.
- [12] Catti, M. High-pressure stability, structure and compressibility of $\text{Cmcm-MgAl}_2\text{O}_4$: an ab initio study, 2001. *Phys Chem Minerals*, 28, 729-736.
- [13] Cohen, M.L., 2007, *Quantum alchemy* in Chemistry for the 21st century, Eds. E. Keinan and I. Schechter. Wiley-VCH.
- [14] Cynn, H., S.K. Sharma, T.F. Cooney, and M. Nicol, 1992. High-temperature Raman investigation of order-disorder behavior in MgAl_2O_4 spinel.

- [15] Dal Corso, A., Mauri, F., 1994. Wannier and Bloch orbital computation of the nonlinear susceptibility, *Phys. Rev. B*, 50, 5756-5759.
- [16] Decker, B.F., and J.S. Kasper. The structure of calcium ferrite. *Acta Crystallographica*, 10, 332-337, 1956.
- [17] Fang, C.M., and G. De With. Crystal structure and chemical bonding of the high-pressure phase of MgAl_2O_4 from first-principles calculations. *Philosophical Magazine A*, 82, 2885-2894, 2002.
- [18] Funamori, N., R. Jeanloz, J.H. Nguyen, A. Kavner, W. Caldwell, K. Fujino, N. Miyajima, T. Shinmei, and N. Tomioka. High-pressure transformations in MgAl_2O_4 . *Journal of Geophysical Research*, 103, 20813-20818, 1998.
- [19] Giantomassi, M., Boeri, L., and Bachelet, G.B., 2005. Electrons and phonons in the ternary alloy $\text{CaAl}_{2-x}\text{Si}_x$ as a function of composition, *Phys. Rev. B*, 72, 224512.
- [20] Giesber, H.G., W.T. Pennington, and J.W. Kolis. Redetermination of CaMn_2O_4 . *Acta Crystallographica*, C57, 329-330, 2001.
- [21] Gonze, X., 1997. First-principle responses of solids to atomic displacements and homogeneous electric fields: Implementation of a conjugate-gradient algorithm, *Phys. Rev. B*, 55, 10, 33710, 354.
- [22] Gonze, X., Allan, D.C., Teter, M.P., 1992. Dielectric tensor, effective charges and phonon in α -quartz by variational density-functional perturbation theory, *Phys. Rev. Lett.*, 68, 3603-3606.
- [23] Gonze, X., Lee, C., 1997. Dynamical matrices, born effective charges, dielectric permittivity tensors, and interatomic force constants from density-functional perturbation theory, *Phys. Rev. B*, 55, 1035510368.
- [24] Gonze, X., J.M. Beuken, R. Caracas, F. Detraux, M. Fuchs, G.M. Rignanese, L. Sindic, M. Verstraete, G. Zerah, F. Jollet, M. Torrent, A. Roy, M. Mikami, Ph. Ghosez, J.Y. Raty, D.C. Allan. First-principles computation of material properties: the ABINIT software project. *Computational Materials Science*, 25, 478-492, 2002.
- [25] Gonze, X., G.M. Rignanese, M. Verstraete, J.M. Beuken, Y. Pouillon, R. Caracas, F. Jollet, M. Torrent, G. Zerah, M. Mikami, P. Ghosez, M. Veithen, V. Olevano, L. Reining, R. Godby, G. Onida, D. Hamann, and D.C. Allan. A brief introduction to the ABINIT software package. *Zeitschrift für Kristallographie*, 220, 558, 2005.
- [26] Gonze, X., Rignanese, G.-M., Caracas, R., 2005a. First-principles studies of the lattice dynamics of crystals, and related properties, *Z. Kristallogr.*, 220, 458472.
- [27] Gracia, L. A. Beltran, J. Andres, R. Franco, and J.M. Recio, 2002. Quantum-mechanical simulations of MgAl_2O_4 under high pressure, *Phys. Rev. B*, 66, 224114.

- [28] Hayes, W., Loudon, R., 1978. *Scattering of Light by Crystals*, 113 pp., John Wiley, Hoboken, New Jersey.
- [29] Hamann, D., Wu, X., Rabe, K.M. and Vanderbilt D., Metric tensor formulation of strain in density-functional perturbation theory, *Phys. Rev. B* 71, 035117 (2005).
- [30] Hofmeister, A., and H.J. Mao, 2001. Evaluation of shear moduli and other properties of silicates with the spinel structure from IR spectroscopy, *Amer. Mineral.*, 86, 622-639.
- [31] Hohenberg, P., and W. Kohn. Inhomogeneous electron gas. *Physical Review*, 136, 864B-871B, 1964.
- [32] Irifune, T., K. Fujino, and E. Ohtani, 1991. A new high-pressure form of MgAl_2O_4 , *Nature*, 349, 409-411.
- [33] Karki, B.B., Stixrude, L., Wentzcovitch, R.M., 2001. Elastic properties of major materials of Earth's mantle from first principles, *Rev. Geophys.*, 39, 507-534.
- [34] Khenata, R., M. Sahnoun, H. Baltache, M. Rerat, A.H. Reshak, Y. Al-Douri, and B. Bouhafs, 2005. Full-potential calculations of structural, elastic and electronic properties of MgAl_2O_4 and ZnAl_2O_4 compounds, *Phys. Lett. A*, 344, 271-279.
- [35] Kiefer, B., L. Stixrude, and R.M. Wentzcovitch. Calculated elastic constants and anisotropy of Mg_2SiO_4 spinel at high pressure. *Geophys. Res. Lett.*, 24, 2841-2844, 1997.
- [36] Kohn, W., and L.J. Sham. Self-consistent equations including exchange and correlation effects. *Physical Review*, 140, 1133A-1138A, 1965.
- [37] Kruger, M.B., J.H. Nguyen, W. Caldwell, and R. Jeanloz. Equations of state of MgAl_2O_4 spinel up to 65 GPa. *Physical Review B*, 56, 1-4, 1997.
- [38] Lazzeri, M., Mauri, F., 2003. First-principles calculation of vibrational Raman spectra in large systems: signature of small rings in crystalline SiO_2 , *Phys. Rev. Lett.*, 90, 036401.
- [39] Li, L., P. Carrez, and D. Weidner, 2007. Effect of cation ordering and pressure on spinel elasticity by ab initio simulation. *Amer. Mineral.*, 92, 174-178.
- [40] Martin de Vidales, J.L., R.M. Rojas, E. Vila, and O. Garcia-Martinez. Low temperature synthesis of tetragonal nickel manganite spinels: thermal behaviour and reactivity. *Materials Research Bulletin*, 29, 1163-1173, 1994.
- [41] Miura, H., Y. Hamada, T. Suzuki, M. Akaogi, N. Miyajima, and K. Fujino. Crystal structure of $\text{CaMg}_2\text{Al}_6\text{O}_{12}$, a new Al-rich high pressure form. *American Mineralogist*, 85, 1799-1803, 2000.
- [42] Monkhorst, H.J., Pack, J.D., 1976. Special points for Brillouin-zone integrations, *Phys. Rev. B*, 13, 5188-5192.

- [43] Ono, S., T. Kikegawa, and Y. Ohishi, 2006. The stability and compressibility of MgAl_2O_4 high-pressure polymorphs. *Phys. Chem. minerals* 33, 200-206.
- [44] Payne, M.C., M.P. Teter, D.C. Allan, T.A. Arias, and J.D. Joannopoulos, 1992. Iterative minimization techniques for ab initio total-energy calculations: molecular dynamics and conjugate gradients. *Reviews in Modern Physics*, 64, 1045-1097.
- [45] Placzek, G. (1934), Rayleigh-Streuung und Raman-Effekt, in *Handbuch der Radiologie*, vol. 6, edited by G. Marx, pp. 205-374, Akademische, Frankfurt-Main, Germany.
- [46] Prosandeev, S.A., Waghmare, U., Levin, I., Maslar, J., 2005. First-order Raman spectra of $\text{AB}'_{1/2}\text{B}''_{1/2}\text{O}_3$ double perovskites, *Phys. Rev. B*, 71, 214307.
- [47] Reichmann, H.J., and S.D. Jacobsen, 2004. High-pressure elasticity of a natural magnetite crystal, *Amer. Mineral.* 89, 1061-1066.
- [48] Reichmann, H.J., and S.D. Jacobsen, 2006. Sound velocities and elastic constants of ZnAl_2O_4 spinel and implications for spinel-elasticity systematics, *Amer. Mineral.* 91, 1049-1054.
- [49] Slotznick, S.P., and S.-H. Shim, 2008. In situ Raman spectroscopy measurements of MgAl_2O_4 spinel up to 1400C, *Amer. Mineral.*, 93, 470-476.
- [50] Suzuki I., I. Ohno, and O.L. Anderson, 2000. Harmonic and anharmonic properties of spinel MgAl_2O_4 , *Amer. Mineral.*, 85, 304-311.
- [51] Veithen, M., Gonze, X., Ghosez, P., 2005. Nonlinear optical susceptibilities, Raman efficiencies, and electro-optic tensors from first-principles density functional perturbation theory, *Phys. Rev. B*, 71, 125107.
- [52] Wdowik, U.D. K. Parlinski, and A. Siegel, 2006. Elastic properties and high-pressure behavior of MgAl_2O_4 from ab initio calculations, *J. Phys. Chem. Sol.*, 67, 1477-1483.
- [53] de Wijs, G.A., C.M. Fang, G. Kresse and G. de With, 2002. First-principles calculation of the phonon spectrum of MgAl_2O_4 spinel. *Phys. Rev. B*, 65, 094305.
- [54] Wittlinger, J., S. Werner, and H. Schulz, 1998. Pressure-induced order-disorder phase transition of spinel single crystals. *Acta Crystallographica*, B54, 714-721.
- [55] Yoneda, A., 1990. Pressure derivatives of elastic constants of single crystal MgO and MgAl_2O_4 . *J. Phys. Earth*, 38, 19-55.

Table 1

Parameters of the Vinet equation of state fitted on pressure-volume data for all the MgAl_2O_4 polymorphs considered in this study.

Structure	V_0 ($\text{\AA}^3$)	K_0 (GPa)	K'
Fd3m	62.339	202	4.27
Cmcm	56.207	221	4.26
Pnma	56.494	216	4.74
Imma	61.086	215	4.15
P -6	64.350	121	4.23

Table 2

Elastic constants of cubic MgAl_2O_4 as computed from density functional perturbation theory. Elastic constants computed using finite differences and the linear relation between strains and stresses are denoted by "s-s". Comparison to previous studies are as follows: Experimental data measured at ambient conditions: [1] Yoneda (1990); [2] Suzuki et al. (2000); Theoretical results: [3] Wdowik et al. (2006).; [4] Khenata et al., (2000); [5] Li et al. (2007).

P (GPa)	C_{11}	C_{12}	C_{44}	K	G	ρ (g/cm ³)	V _p	V _s
0	292	162	161	205	112	3.654	9.9	5.5
10	328	202	167	244	113	3.962	10.0	5.3
20	363	243	173	283	113	4.116	10.3	5.2
30	391	283	176	319	110	4.255	10.5	5.1
s-s								
20	370	251	172	291	113	4.116	10.3	5.2
exp.								
(1)	283	155	155	198	110	3.578	9.8	5.5
(2)	281	155	155	198	108	3.585	9.8	5.5
(3)	293	157	150	203	109	3.652	9.8	5.5
(4)	378	140	124	219	122	3.582	10.3	5.8
(5)	317	107	130	177	120	3.48	9.8	5.9

Table 3

Symmetry of the Raman tensors.

A_{1g}			E_g			E_g			T_{2g}		
a	0	0	b	0	0	$-3^{1/2}b$	0	0	0	0	0
0	a	0	0	b	0	0	$3^{1/2}b$	0	0	0	d
0	0	a	0	0	$-2b$	0	0	0	0	d	0

Fig. 1. Pressure variation of the elastic constants of MgAl_2O_4 spinel. Isolated data points are obtained from finite differences calculations and the connected data points from linear response calculations.

Fig. 2. Pressure dependence of the u modes in ordered cubic spinel. The B_{1u} , E_{1u} and T_{1u} mode represented in (a) by respectively circles, triangles and squares have a null LO-TO splitting. The LO and TO components of the T_{2u} modes are represented by respectively solid and open circles in (b). Lines are guide for the eyes.

Fig. 3. Raman spectra of cubic spinel at several pressures. The spectra are computed for powders with the three averages for parallel polarization (upper row), cross-polarization (middle row) and total intensity (bottom row) at pressures of 0 GPa (left column), 10GPa (middle column) and 20 GPa (right column).

Fig. 4. Pressure dependence of the g modes in ordered cubic spinel. Lines are guide for the eyes.

Fig. 5. Pressure dependence of the enthalpy differences with respect to the calcium titanate phase (Cmcm) of the different MgAl_2O_4 polymorphs considered in this study. This diagram shows that the sequence of phase transitions is: cubic spinel - oxide mixture - Cmcm structure.

Fig. 6. Equation of state of several polymorphs of MgAl_2O_4 .

Figure 1
[Click here to download Figure\(s\): fig1_elasticity.eps](#)

Figure 3
[Click here to download Figure\(s\): fig3_raman.eps](#)

Figure 4

[Click here to download Figure\(s\): fig4_gmodes.eps](#)

Figure 6
[Click here to download Figure\(s\): fig6_EOS.eps](#)