

Lattice dynamics of ZnAl_2O_4 and ZnGa_2O_4 under high pressure

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This article is dedicated to Manuel Cardona.

In this work we present a first-principles density functional study of the vibrational properties of ZnAl_2O_4 and ZnGa_2O_4 as function of hydrostatic pressure. Based on our previous structural characterization of these two compounds under pressure, herewith, we report the pressure dependence on both systems of the vibrational modes for the cubic spinel structure, for the CaFe_2O_4 -type structure (*Pnma*) in ZnAl_2O_4 and for marokite (*Pbcm*) ZnGa_2O_4 . Additionally we report a second order phase transition in ZnGa_2O_4 from the marokite towards the CaTi_2O_4 -type structure (*Cmcm*), for which we also calculate the pressure dependence of the vibrational modes at the Γ point. Our calculations are complemented with Raman scattering measurements up to 12 GPa that show a good overall agreement between our calculated and measured mode frequencies.

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1 Introduction

AB_2O_4 compounds are ceramics with many interesting mechanic, electric, magnetic and optical properties. Many of these oxides crystallize in the cubic spinel structure (*Fd $\bar{3}m$*) exemplified by MgAl_2O_4 . In particular, ZnAl_2O_4 and ZnGa_2O_4 have gained recent interest for their applications as phosphors because they combine a wide direct band-gap above 3.5 eV, transparent and electroconductive properties, high thermal stability, low acidity, and hydrophobic behavior to be used in many different new dispositives [1–3].

Little is known about the pressure dependence of the mechanical, electrical, and optical properties of ZnAl_2O_4 and ZnGa_2O_4 spinels. High pressure X-ray diffraction studies of these two compounds have shown that while ZnAl_2O_4 does not undergo any phase transition till 43 GPa [4], ZnGa_2O_4 undergoes two phase transitions towards the tetragonal spinel (*I4 $_1$ /amd*) and marokite (*Pbcm*) structures around 34 and 55 GPa, respectively [5]. Recently, S. López et al. have performed first principles calculations to study the stability of the spinel structures of ZnAl_2O_4 and ZnGa_2O_4 under high pressure and phonon frequencies in the Γ point at zero pressure [6, 7]. It has been predicted that ZnAl_2O_4 should undergo a pressure-induced

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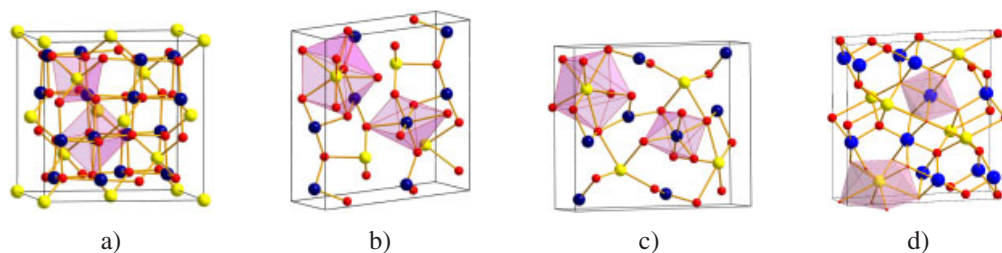


Fig. 1 (online colour at: www.ann-phys.org) Unit cell of the AB_2O_4 structures a) cubic spinel, b) marokite-type, c) CaFe_2O_4 -type, and d) CaTi_2O_4 structure. The atom color palette for $A(\text{Zn})$, $B(\text{Ga or Al})$, and O are yellow, blue, and red, respectively.

phase transition from the cubic spinel towards the orthorhombic CaFe_2O_4 -type ($Pnma$) structure around 38.5 GPa while ZnGa_2O_4 should undergo a pressure-induced phase transition from the cubic spinel towards the orthorhombic CaMn_2O_4 -type (marokite) structure around 33.4 GPa. However, the theoretical study has suggested that a possible phase transition from the cubic spinel towards the tetragonal spinel structure can be explained by the presence of non-hydrostatic conditions. This transition had already been observed in ZnMn_2O_4 [8] and NiMn_2O_4 [9]. Figure 1 shows the unit cells of the cubic spinel, marokite, CaFe_2O_4 and CaTi_2O_4 phases.

In this paper, we report a lattice dynamics study of ZnAl_2O_4 and ZnGa_2O_4 spinels as function of hydrostatic pressure. We report the theoretical pressure dependence of the vibrational modes for the cubic spinel structure for both compounds and for the $Pnma$ and $Pbcm$ phases in ZnAl_2O_4 and ZnGa_2O_4 , respectively. In addition we report a new calculated second order phase transition in ZnGa_2O_4 compound from $Pbcm$ towards $Cmcm$ (CaTi_2O_4 -type structure) phase for which we also report the pressure dependence of the vibrational modes. Our calculations are complemented with Raman scattering measurements in both spinels up to 12 GPa.

2 Computational details

Total energy calculations were done within the framework of the density functional theory (DFT) and the projector-augmented wave (PAW) [10, 11] method using the Vienna *ab initio* simulation package (VASP) [12–15]. The exchange and correlation energy was described within the local density approximation (LDA) [16]. We use a plane-wave energy cutoff of 500 eV to ensure a high precision in the calculations. Monkhorst-Pack scheme was employed for the Brillouin-zone (BZ) integrations [17] with meshes of $4 \times 4 \times 4$, $3 \times 9 \times 3$, $8 \times 4 \times 4$, and $8 \times 4 \times 4$, which corresponds to a set of 10, 20, 16 and 16 special k -points in the irreducible Brillouin-zone, for structures: cubic spinel ($Fd\bar{3}m$), and the orthorhombic structures with space groups $Pbcm$, $Pnma$ and $Cmcm$ respectively. In the relaxed equilibrium configuration, the forces are less than $0.9 \text{ meV}/\text{\AA}$ per atom in each of the cartesian directions. The highly converged results on forces are required for the calculations of the dynamical matrix using the direct force constant approach (or supercell method), as implemented in the PHONON program [18]. The construction of the dynamical matrix at the Γ point is particularly simple and involves separate calculations of the forces in which a fixed displacement from the equilibrium configuration of the atoms within the unit cell is considered. Symmetry aids by reducing the number of such independent distortions to a six independent displacements in the cubic spinel phase. Diagonalization of the dynamical matrix provides both the frequencies of the normal modes and their polarization vectors. It allows us to identify the irreducible representation and the character of the phonon modes at the zone center. The phonon dispersion curves were calculated along several high symmetry directions in the BZ. We use a supercell $2 \times 2 \times 2$ times the conventional unit cell which consist of four primitive unit cells. The phonon density of states (PDOS) was obtained by integration of the

phonon frequencies with a very high number of k -points. The specific heat of both spinels were obtained from the calculated PDOS within the harmonic approximation.

Table I in [6] provides the calculated and experimental parameters of the spinel structure of both ZnAl_2O_4 and ZnGa_2O_4 spinels at ambient pressure. An agreement better than 1% is found between theory and experiment for the calculated parameters. Besides, calculated parameters for the tetragonal spinel and CaMn_2O_4 and CaFe_2O_4 structures are also provided in Table IV of [6].

3 Experimental details

ZnAl_2O_4 (ZnGa_2O_4) powder was synthesized by a solid state reaction at high temperature by mixing appropriate quantities of ZnO and Al_2O_3 (Ga_2O_3) precursors and firing at 1400 °C (1100 °C) for 24 h [19, 20]. Chemical and structural analysis have shown the stoichiometric composition of ZnAl_2O_4 and ZnGa_2O_4 and the presence of traces of impurities (α - Al_2O_3 and β - Ga_2O_3 , less than 1% by volume, and ZnO , less than 0.2% by volume). Raman scattering measurements were carried out in powder samples at room temperature (RT) in a JobinYvon LabRAM UV HR microspectrometer using an exciting laser line of 532.12 nm with resolution below 3 cm^{-1} and a power below 10 mW on the sample. Raman measurements under high pressures up to 12 GPa were performed with a diamond-anvil cell (DAC) using a 4:1 methanol-ethanol mixture as pressure-transmitting medium [21] and ruby grains for pressure determination [22].

4 Results and discussion

4.1 Cubic spinel ZnAl_2O_4 and ZnGa_2O_4

Gahnite (ZnAl_2O_4) and zinc gallate (ZnGa_2O_4) crystallize at ambient pressure in a diamond-type cubic spinel structure with space group $Fd\bar{3}m$ (227) and have two formula units per primitive unit cell, see Fig. 1. The A cations are tetrahedrally coordinated and the B cations are in BO_6 octahedra. The Zn atoms are located at the Wyckoff positions, 8a ($1/8, 1/8, 1/8$) tetrahedral sites, while Al (or Ga) atoms are located on the 16d ($1/2, 1/2, 1/2$) octahedral sites and the oxygen atoms at 32e (u, u, u). The spinel crystal structure is characterized only by the lattice parameter a and the internal parameter u .

According to group theory, cubic spinels have the following phonon modes at the Γ point [23]

$$\Gamma = A_{1g}(R) + E_g(R) + T_{1g} + 3T_{2g}(R) + 2A_{2u} + 2E_u + 5T_{1u}(IR) + 2T_{2u}$$

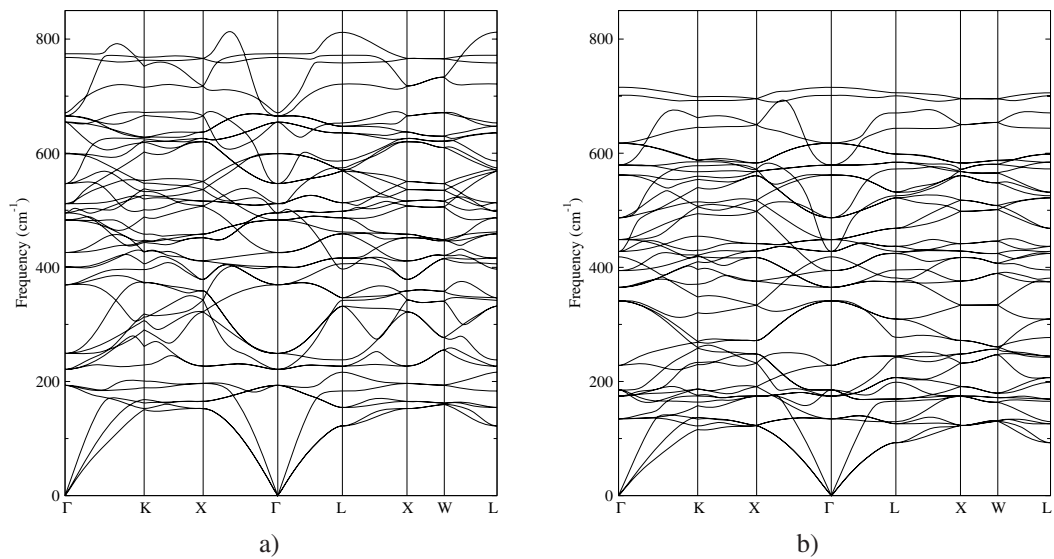
where R and IR corresponds to Raman- and infrared-active modes, respectively, and where one triply degenerated T_{1u} correspond to acoustic modes. Figure 2 shows the calculated phonon dispersion curves along high symmetry directions in both ZnAl_2O_4 and ZnGa_2O_4 spinels at ambient pressure and the corresponding phonon density of states (PDOS) are show in Fig. 3.

For the PDOS of ZnAl_2O_4 the low-frequency motions are mainly due to Zn ions ($<250\text{ cm}^{-1}$), while the phonon modes with frequencies over 250 cm^{-1} are due to O and Al, with a major contribution of O than Al. As we can see from Fig. 3, the PDOS over 729 cm^{-1} are predominantly due to O motions. In the case of ZnGa_2O_4 , frequencies below 362 cm^{-1} are dominated by the motion of Zn and Ga atoms (with a higher contribution of Ga ions from 261 to 362 cm^{-1} , while higher frequencies are dominated by the motion of O ions, as in ZnAl_2O_4). The main difference between the two compounds is due to the fact that Ga atoms are heavier than Al atoms. In the case of ZnAl_2O_4 we found a good agreement with the phonon spectrum and PDOS calculated in [24].

The calculated phonon frequencies at ambient pressure in the Γ point are listed in Table 1. Figure 4 a) shows the experimental Raman spectra at room temperature (RT) of ZnAl_2O_4 samples up to 13 GPa. Clearly, two Raman modes out of the five Raman-active modes of the spinel phase have been measured and followed under pressure. They are the E_g mode at 418 cm^{-1} , and the T_{2g} mode at 659 cm^{-1} at ambient pressure. These Raman modes agree in frequency with those observed by Chopelas et al. [23]. We have

Table 1 Calculated vibrational modes (cm⁻¹) for ZnAl₂O₄ and ZnGa₂O₄ at zero pressure in the Γ point [6].

| ZnAl ₂ O ₄ | | | | ZnGa ₂ O ₄ | | | |
|----------------------------------|-----|---------------------|-----|----------------------------------|-----|---------------------|-----|
| T_{2u} | 250 | $T_{1u}(\text{IR})$ | 548 | T_{2u} | 135 | $T_{1u}(\text{IR})$ | 429 |
| $T_{1u}(\text{IR})$ | 222 | T_{2u} | 484 | $T_{1u}(\text{IR})$ | 175 | T_{2u} | 450 |
| $T_{2g}(\text{R})$ | 194 | $T_{2g}(\text{R})$ | 513 | $T_{2g}(\text{R})$ | 186 | $T_{2g}(\text{R})$ | 488 |
| E_u | 402 | E_u | 600 | E_u | 229 | E_u | 563 |
| $T_{1u}(\text{IR})$ | 496 | $T_{1u}(\text{IR})$ | 666 | $T_{1u}(\text{IR})$ | 342 | $T_{1u}(\text{IR})$ | 580 |
| T_{1g} | 371 | $T_{2g}(\text{R})$ | 655 | T_{1g} | 366 | $T_{2g}(\text{R})$ | 618 |
| $E_g(\text{R})$ | 427 | A_{2u} | 769 | $E_g(\text{R})$ | 395 | A_{2u} | 702 |
| A_{2u} | 672 | $A_{1g}(\text{R})$ | 775 | A_{2u} | 419 | $A_{1g}(\text{R})$ | 717 |

**Fig. 2** Calculated phonon-dispersion curves along high-symmetry directions in BZ for a) ZnAl₂O₄ and b) ZnGa₂O₄.

observed other modes at 155, 488, 708 cm⁻¹, but from these modes Chopelas et al. only found the mode near 708 cm⁻¹.

Table 2 summarizes the calculated and experimental Raman modes with their corresponding pressure coefficients and Grüneisen parameters. A good agreement is found between calculated and experimentally measured Raman mode frequencies and pressure coefficients. The T_{2g} mode calculated to be near 194 cm⁻¹ perhaps corresponds to a small peak at 195 cm⁻¹ observed as a shoulder of the broad Raman feature extending from 140 to 200 cm⁻¹, whose peak maximum is around 155 cm⁻¹. The pressure dependence of the small peak at 195 cm⁻¹ has not been measured but the pressure coefficient of the 155-cm⁻¹ peak is around 0.9 cm⁻¹/GPa, which is close to the calculated pressure coefficient for the T_{2g} mode. We have found no clear evidence of the T_{2g} mode calculated to be near 513 cm⁻¹ and experimentally found at 509 cm⁻¹ by Chopelas et al. Similarly, we have not observed the A_{1g} mode calculated to be near 775 cm⁻¹ and experimentally measured around 758 cm⁻¹ by Chopelas et al. Instead, we have found two well defined peaks near 488 and 708 cm⁻¹ that broaden considerably with increasing pressure. These two features shift at rates of around 7 and 3.8 cm⁻¹/GPa, respectively.

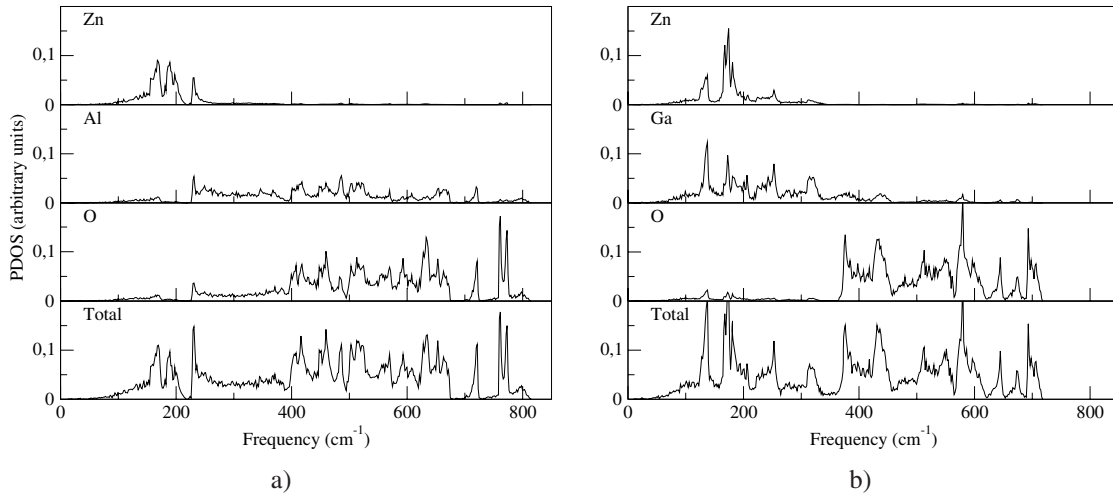


Fig. 3 Partial and total PDOS for a) ZnAl_2O_4 and b) ZnGa_2O_4 cubic spinels.

Table 2 *Ab initio* calculated and experimental zero pressure frequencies ω (cm^{-1}), Grüneisen parameters γ , and pressure coefficients ($\text{cm}^{-1}/\text{GPa}$) of the Raman modes in the cubic spinel structure of ZnAl_2O_4 and ZnGa_2O_4 . Where superscripts refer to ^athis work, ^b [24], ^c [23], ^d [25].

| Mode | ZnAl_2O_4 | | | | | | | ZnGa_2O_4 | | | | | |
|----------|---------------------------|------------|------------------------|------------|------------|------------------------|------------|---------------------------|------------|------------------------|------------|------------------------|------------|
| | Theory | | | | Exp. | | | Theory | | | Exp. | | |
| | ω^a | γ^a | $\frac{d\omega^a}{dP}$ | ω^b | ω^a | $\frac{d\omega^a}{dP}$ | ω^c | ω^a | γ^a | $\frac{d\omega^a}{dP}$ | ω^a | $\frac{d\omega^a}{dP}$ | ω^d |
| T_{2g} | 194 | 0.9 | 0.6 | 197 | | | 196 | 186 | 1.0 | 0.7 | | | |
| E_g | 427 | 1.2 | 2.0 | 442 | 418 | 2.2 | 417 | 395 | 1.2 | 1.8 | | | 638 |
| T_{2g} | 513 | 1.5 | 3.0 | 520 | | | 509 | 488 | 1.8 | 3.4 | 465 | 3.5 | 467 |
| T_{2g} | 655 | 1.4 | 3.4 | 665 | 659 | 3.8 | 658 | 618 | 1.5 | 3.4 | 608 | 3.7 | 611 |
| A_{1g} | 775 | 1.3 | 3.8 | 785 | | | 758 | 717 | 1.5 | 4.0 | 710 | 4.4 | 714 |

Table 2 also summarizes the experimental and theoretical results for the Raman modes of ZnGa_2O_4 . In this compound, we have also found three out of the five Raman-active modes. There is a good agreement between the experimental and calculated frequencies and pressure coefficients. Our measured and calculated frequencies at zero pressure are also in good agreement with those measured by Van Gorkom et al. [25]. For completeness, Table 3 summarizes the frequencies and pressure coefficients of the IR-active modes in both cubic spinels. Our calculated IR-active mode frequencies compare reasonably well with those experimentally measured by Van Gorkom et al. and Chopelas et al. We have not found any reference in the literature about the pressure dependence of the IR-active modes in both cubic spinels. It is interesting to note that the low-frequency mode associated to vibrations of the octahedral BO_6 units has a considerable smaller pressure coefficient than the other modes not only in ZnAl_2O_4 and ZnGa_2O_4 but also in ZnFe_2O_4 and ZnCr_2O_4 [26, 27]. Another systematic behavior we would like to stress is that the high-frequency stretching mode of the ZnO_4 tetrahedral groups has larger pressure coefficients than the bending modes associated to these groups. The first feature is related to the fact that Zn-O bonds are shorter than the B-O bonds in all spinel oxides, the second one suggest that in spinels bond stretching has larger force constants than bond bending.

Table 3 *Ab initio* calculated and experimental zero pressure frequencies ω (cm⁻¹), Grüneisen parameters γ , and pressure coefficients (cm⁻¹/GPa) of the IR modes in the cubic spinel structure of ZnAl₂O₄ and ZnGa₂O₄. Where superscripts refer to ^athis work, ^b[24], ^c[23], ^d[25]. Frequencies from [23,24] are listed as TO(LO).

| Mode | ZnAl ₂ O ₄ | | | | Exp. ω^c | ZnGa ₂ O ₄ | | | |
|----------|----------------------------------|------------|------------------------|------------|--------------------|----------------------------------|------------|------------------------|--------------------|
| | Theory | | | ω^b | | Theory | | | Exp. ω^d |
| | ω^a | γ^a | $\frac{d\omega^a}{dP}$ | | | ω^a | γ^a | $\frac{d\omega^a}{dP}$ | |
| T_{1u} | 222 | 0.44 | 0.34 | 226(240) | 220(231) | 175 | 0.06 | 0.00 | 175 |
| | 496 | 1.44 | 2.72 | 507(528) | 440(533) | 342 | 1.26 | 1.63 | 328 |
| | 548 | 1.32 | 2.74 | 562(648) | 543(608) | 429 | 1.54 | 2.52 | 420 |
| | 666 | 1.57 | 4.01 | 675(832) | 641(838) | 580 | 1.89 | 4.30 | 570 |

A curious feature is that our calculations suggest a non-linear behavior of the Raman and IR active modes under pressure in both spinels (see Fig. 5). The non-linear behavior under pressure is very clear in the second IR T_{1u} mode of ZnAl₂O₄ and the first IR T_{1u} mode of ZnGa₂O₄. From Fig. 5 it is observed that there is a subtle change in slope of the frequencies around 20 GPa in ZnAl₂O₄ and around 10 GPa in ZnGa₂O₄.

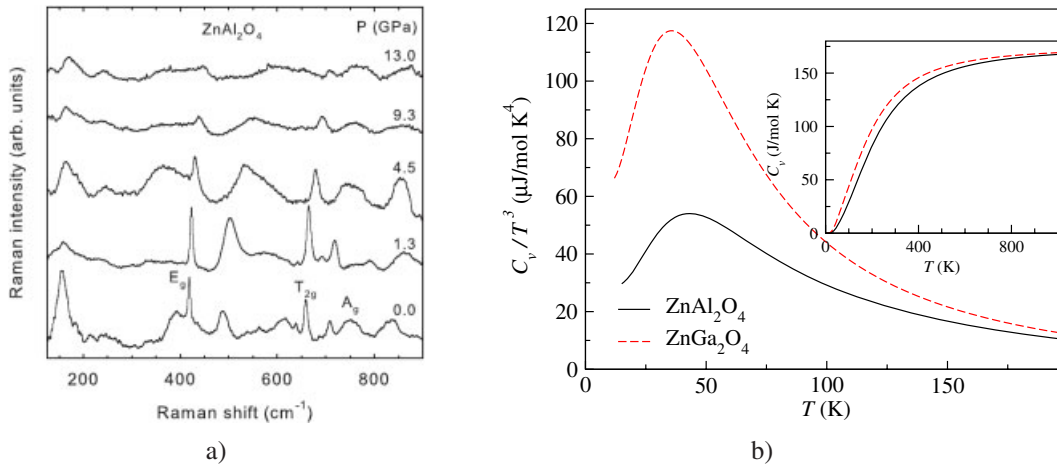


Fig. 4 (online colour at: www.ann-phys.org) a) RT Raman scattering spectra of ZnAl₂O₄ up to 13 GPa; b) Temperature dependence of C_v/T^3 per f.u. of ZnAl₂O₄ and ZnGa₂O₄ of $Fd\bar{3}m$ phase, the inset corresponds to the specific heat vs temperature up to 900 K.

Thermodynamics properties of the crystal at constant volume are determined by the phonons. Calculations of the C_v were performed by integrating the phonon DOS with the standard method [18] (in the region of our interest $C_p \approx C_v$). Figure 4 b) shows the temperature dependence of C_v/T^3 per f.u. of ZnAl₂O₄ and ZnGa₂O₄ in the $Fd\bar{3}m$ phase while the inset shows the C_v evolution with temperature. According to Fig. 4 b) the specific heat C_v at room temperature is 117.16 J/mol·K for ZnAl₂O₄, in good agreement with the theoretical value of 116.2 J/mol·K obtained in [24], while the C_v for ZnGa₂O₄ is 128.65 J/mol·K. Our results show that the maximum of C_v/T^3 plot is of 53.8 $\mu\text{J}/\text{mol}\cdot\text{K}^4$ for ZnAl₂O₄ and 117.4 $\mu\text{J}/\text{mol}\cdot\text{K}^4$ for ZnGa₂O₄. Both compounds have the maximum around the value of 43 and 36 K, respectively, showing the clear dependence of the maximum value with the cation. To our knowledge no experimental data are

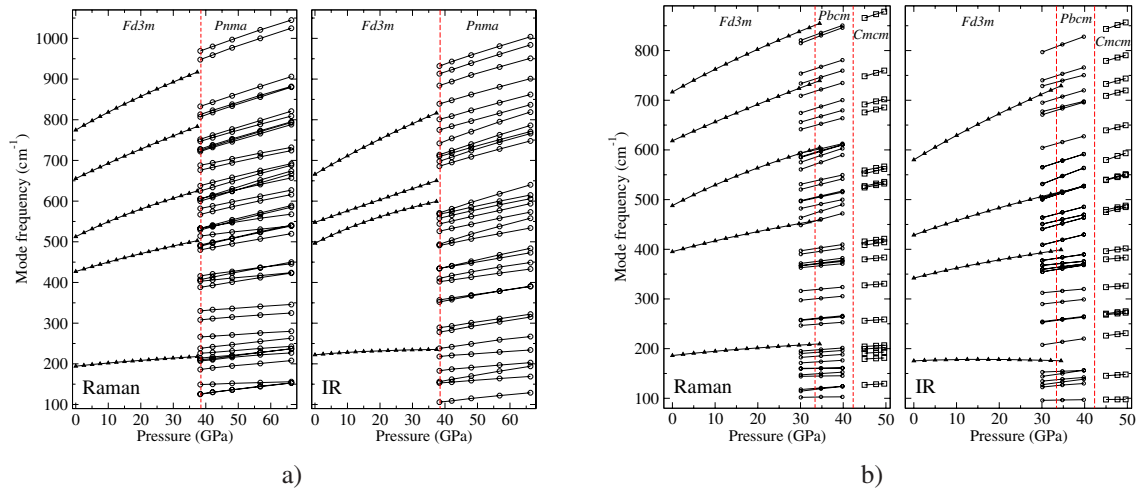


Fig. 5 (online colour at: www.ann-phys.org) Pressure dependence of Raman and IR active modes of space groups a) $Fd\bar{3}m$ and $Pnma$ of $ZnAl_2O_4$, and b) $Fd\bar{3}m$, $Pbcm$, and $Cmcm$ of $ZnGa_2O_4$.

available, but recent works from Cardona et al. [28,29] found a good agreement between experimental data and similar *ab initio* results in binary compounds.

4.2 High-pressure phases

According to our previous calculations [6, 7], a phase transition in $ZnAl_2O_4$ from the cubic spinel towards the $CaFe_2O_4$ -type structure ($Pnma$) should occur at 38.5 GPa. Similarly, a phase transition in $ZnGa_2O_4$ from the cubic spinel towards the $CaMn_2O_4$ -type structure ($Pbcm$) should occur at 33.4 GPa. In the previous results we found that $Pbcm$ structure is very competitive energetically with the $CaTi_2O_4$ -type structure ($Cmcm$) due to the close group-subgroup relation between $Cmcm$ and $Pbcm$ space groups. In this work we found that phonon frequencies from $Pbcm$ phase of $ZnGa_2O_4$ have a remarkable change at 42.5 GPa. Due to the close competition of $CaMn_2O_4$ - and $CaTi_2O_4$ -type structure we think that the $CaTi_2O_4$ -type structure becomes more stable than $CaMn_2O_4$ -type structure at this pressure. These results suggest a possible second order phase transition with no change in volume at the phase transition pressure. In this transition there is not a change in coordination in Zn and Ga cations (i.e. the $ZnGa_2O_4$ are made up of GaO_6 distorted octahedra and ZnO_8 zinc-centered distorted polyhedra, see Fig. 1). The transition from the $Pbcm$ to $Cmcm$ phase in ABO_4 compounds has been observed previously in $CaMn_2O_4$ at 35 GPa [30]. In the light of these results we also include the vibrational properties of the $CaTi_2O_4$ -type structure of the $ZnGa_2O_4$ compound.

The high pressure phase of $ZnGa_2O_4$, the $CaMn_2O_4$ -type structure (SG: $Pbcm$), is characterized by the Wyckoff positions (WPs) $4d(x, y, 1/4)$ for Zn atom, $8e(x, y, z)$ for Ga atom, and $4c(x, 1/4, 0)$, $4d$ and $8e$ for O atoms. On the other hand, the $CaTi_2O_4$ -type structure (SG: $Cmcm$) is characterized by the following WPs: Zn atoms in $4c(0, y, 1/4)$, Ga atoms in $8f(0, y, z)$, and O atoms in $4b(0, 1/2, 0)$, $4c$ and $8f$. Group theory predicts the following vibrations at the Γ point in the $Pbcm$ and $Cmcm$ phases, respectively

$$\begin{aligned} \Gamma(Pbcm) &= 11A_g(R) + 9A_u + 12B_{1g}(R) + 10B_{1u}(IR) \\ &\quad + 10B_{2g}(R) + 12B_{2u}(IR) + 9B_{3g}(R) + 11B_{3u}(IR) \\ \Gamma(Cmcm) &= 6A_g(R) + 3A_u + 4B_{1g}(R) \\ &\quad + 8B_{1u}(IR) + 2B_{2g}(R) + 8B_{2u}(IR) + 6B_{3g}(R) + 5B_{3u}(IR) \end{aligned}$$

In the CaFe₂O₄-type structure of ZnAl₂O₄ the Zn, Al and O atoms occupy the WP 4c ($x, 1/4, z$), in which Al and O atoms have two and four different 4c WPs, respectively. Group theory predicts the following vibrations at the Γ point in the *Pnma* phase

$$\Gamma(Pnma) = 14A_g(R) + 7A_u + 7B_{1g}(R) \\ + 14B_{1u}(IR) + 14B_{2g}(R) + 7B_{2u}(IR) + 7B_{3g}(R) + 14B_{3u}(IR)$$

In Table 4 appears the mechanical representation of the phonon modes of the space groups *Pbcm*, *Pnma*, and *Cmcm* in which is clearly depicted the corresponding modes to each Wyckoff position.

Table 4 Mechanical representation of the phonon modes of the space groups (SG) *Pbcm*, *Pnma*, and *Cmcm*, which correspond to the CaMn₂O₄-, CaFe₂O₄-, and CaTi₂O₄-type structures. Where A_g and B_{xg} are Raman modes and B_{xu} are IR modes.

| SG | WP | A_g | A_u | B_{1g} | B_{1u} | B_{2g} | B_{2u} | B_{3g} | B_{3u} |
|-------------|----|-------|-------|----------|----------|----------|----------|----------|----------|
| <i>Pbcm</i> | 8e | 3 | 3 | 3 | 3 | 3 | 3 | 3 | 3 |
| | 4d | 2 | 1 | 2 | 1 | 1 | 2 | 1 | 2 |
| | 4c | 1 | 1 | 2 | 2 | 2 | 2 | 1 | 1 |
| <i>Pnma</i> | 4c | 2 | 1 | 1 | 2 | 2 | 1 | 1 | 2 |
| <i>Cmcm</i> | 8f | 2 | 1 | 1 | 2 | 1 | 2 | 2 | 1 |
| | 4c | 1 | | 1 | 1 | | 1 | 1 | 1 |
| | 4b | | 1 | | 2 | | 2 | | 1 |

Table 5 summarizes the different modes, frequencies, pressure coefficients and Gruneisen parameters for ZnAl₂O₄ in the *Pnma* structure at 42.1 GPa and ZnGa₂O₄ in the *Pbcm* structure at 34.8 GPa. Correspondingly, Table 6 summarizes the different modes, frequencies, pressure coefficients and Gruneisen parameters for ZnGa₂O₄ in the *Cmcm* structure at 45 GPa. The calculated pressure dependence of the Raman- and IR-active modes of the *Fd3m* and *Pnma* phases in ZnAl₂O₄ and of the *Fd3m*, *Pbcm*, and *Cmcm* in ZnGa₂O₄ are plotted in Figs. 5a) and b), respectively.

According to group theory, there are four types of Raman active modes ($A_g, B_{1g}, B_{2g}, B_{3g}$) and three types of IR active modes (B_{1u}, B_{2u} and B_{3u}) in the *Pbcm*, *Pnma*, *Cmcm* space groups. With the correlation between the Raman active modes of the four point groups (*Fd3m* and *Pbcm*, *Pnma*, *Cmcm*) the A_{1g} and E_g modes in the *Fd3m* representation transform to the A_g modes in the *Pbcm*, *Pnma* and *Cmcm* representation, and the T_{2g} modes transform to the $B_{1g} + B_{2g} + B_{3g}$ modes. The correlation of some of the vibrational modes in the different phases can be followed in our calculations.

For the spinel structure of ZnGa₂O₄, the first T_{2g} Raman mode has a pressure coefficient of 0.66 cm⁻¹/GPa, for *Pbcm* phase the Raman modes below 403 cm⁻¹ (A_g from Table 5) have pressure coefficients between 0.09 and 1.29 cm⁻¹/GPa, and the *Cmcm* phase have pressure coefficients between 0.52 and 1.22 cm⁻¹/GPa for frequencies lower than 416 cm⁻¹ (A_g). For this range of frequency we find that in the *Pbcm* and *Cmcm* phases there are many Raman modes with pressure coefficient values very close to the first mode T_{2g} of cubic spinel. After a frequency of 460 cm⁻¹ pressure coefficients increase from 1.82 to 3.2 and 1.72 to 2.76 cm⁻¹/GPa for *Pbcm* and *Cmcm* phases, respectively. Also, it is observed that there are many Raman modes from orthorhombic phases of ZnGa₂O₄ that have pressure coefficients with values very close to the respective modes of spinel phase. Similar behavior is observed for ZnAl₂O₄ and IR active modes in both compounds.

Table 5 *Ab initio* calculated frequencies ω (cm^{-1}), Grüneisen parameters γ , and pressure coefficients ($\text{cm}^{-1}/\text{GPa}$) of the phonon modes of ZnAl_2O_4 in the *Pnma* structure, and ZnGa_2O_4 in the marokite structure. Frequencies were calculated at 42.1 and 34.8 GPa for ZnAl_2O_4 and ZnGa_2O_4 , respectively. Where A_g and B_{xg} are Raman modes and B_{xu} are IR modes.

| ZnAl ₂ O ₄ | | | | | | | ZnGa ₂ O ₄ | | | | | | | | |
|----------------------------------|----------|----------------------|-----|-----------------|----------|----------------------|----------------------------------|-----------------|----------------------|-----|----------|-----------------|----------------------|-----|-----|
| ω | γ | $\frac{d\omega}{dP}$ | | ω | γ | $\frac{d\omega}{dP}$ | ω | γ | $\frac{d\omega}{dP}$ | | ω | γ | $\frac{d\omega}{dP}$ | | |
| B _{2u} | - | - | - | A _u | 504 | 1.9 | 2.2 | B _{1u} | - | - | - | B _{1g} | 396 | 1.2 | 1.2 |
| B _{3u} | - | - | - | A _g | 518 | 0.7 | 0.9 | B _{2u} | - | - | - | A _g | 403 | 1.3 | 1.3 |
| B _{1u} | - | - | - | B _{3u} | 533 | 1.3 | 1.7 | B _{3u} | - | - | - | A _u | 417 | 2.0 | 2.1 |
| B _{3u} | 109 | 3.1 | 0.8 | B _{1g} | 537 | 1.6 | 2.0 | A _u | 22 | | | B _{1u} | 419 | 2.0 | 2.1 |
| A _u | 110 | 3.2 | 0.9 | B _{3g} | 541 | 1.6 | 2.0 | B _{1u} | 97 | 0.5 | 0.1 | B _{3u} | 452 | 2.0 | 2.3 |
| B _{1g} | 129 | 3.1 | 1.0 | A _g | 539 | 1.0 | 1.2 | B _{2g} | 103 | 0.4 | 0.1 | B _{3g} | 460 | 2.1 | 2.4 |
| B _{3g} | 130 | 3.1 | 1.0 | B _{3u} | 551 | 1.4 | 1.8 | A _g | 119 | 3.2 | 1.0 | B _{1u} | 460 | 1.6 | 1.9 |
| A _u | 141 | 1.6 | 0.5 | B _{1u} | 565 | 1.3 | 1.7 | B _{1g} | 121 | 2.1 | 0.7 | A _u | 468 | 1.6 | 1.9 |
| A _g | 150 | 0.7 | 0.2 | A _u | 577 | 1.8 | 2.5 | B _{2u} | 127 | 2.3 | 0.7 | A _g | 477 | 2.3 | 2.7 |
| B _{1u} | 155 | 1.6 | 0.6 | B _{2g} | 575 | 1.3 | 1.7 | B _{1u} | 133 | 3.4 | 1.1 | B _{2u} | 474 | 1.9 | 2.2 |
| B _{2u} | 162 | 3.4 | 1.3 | B _{1u} | 574 | 1.2 | 1.7 | A _u | 130 | 1.1 | 0.4 | B _{2g} | 491 | 1.5 | 1.8 |
| B _{3u} | 186 | 1.6 | 0.7 | B _{2u} | 581 | 1.8 | 2.5 | B _{3u} | 138 | 2.2 | 0.8 | A _g | 506 | 1.5 | 1.9 |
| A _g | 190 | 1.7 | 0.8 | A _g | 588 | 1.6 | 1.6 | B _{1g} | 145 | 0.3 | 0.1 | B _{2g} | 507 | 1.5 | 2.0 |
| A _u | 205 | 1.6 | 0.8 | B _{1g} | 609 | 1.6 | 2.4 | B _{2u} | 150 | 3.3 | 1.3 | B _{1u} | 514 | 2.1 | 2.7 |
| B _{2g} | 210 | 1.5 | 0.7 | B _{3g} | 615 | 1.7 | 2.5 | B _{2g} | 150 | 1.5 | 0.6 | B _{2u} | 516 | 1.8 | 2.4 |
| A _g | 213 | 1.9 | 1.0 | B _{2g} | 613 | 1.3 | 1.8 | B _{3u} | 154 | 0.8 | 0.3 | B _{1g} | 531 | 1.6 | 2.2 |
| B _{2g} | 217 | 1.6 | 0.8 | A _g | 634 | 1.5 | 2.3 | A _u | 161 | 1.0 | 0.4 | A _u | 543 | 2.5 | 3.4 |
| B _{2u} | 221 | 1.1 | 0.6 | B _{2g} | 646 | 1.3 | 1.9 | B _{3g} | 160 | 0.3 | 0.1 | B _{3g} | 540 | 1.4 | 1.9 |
| B _{1g} | 228 | 1.2 | 0.6 | A _g | 683 | 1.1 | 1.7 | A _g | 161 | 0.2 | 0.1 | B _{3u} | 547 | 2.4 | 3.3 |
| B _{1u} | 242 | 1.8 | 1.0 | B _{3u} | 695 | 1.3 | 2.2 | A _g | 174 | 1.2 | 0.5 | B _{3g} | 575 | 2.0 | 3.0 |
| B _{2g} | 242 | 1.5 | 0.9 | B _{2g} | 694 | 1.0 | 1.6 | B _{3g} | 185 | 1.3 | 0.6 | B _{3u} | 578 | 1.8 | 2.7 |
| B _{3g} | 268 | 0.8 | 0.5 | B _{1u} | 708 | 1.5 | 2.4 | B _{2g} | 193 | 1.3 | 0.6 | A _g | 589 | 1.9 | 2.8 |
| B _{1u} | 283 | 1.9 | 1.3 | A _u | 716 | 1.3 | 2.2 | B _{1g} | 198 | 1.3 | 0.6 | B _{2g} | 597 | 1.7 | 2.6 |
| B _{3u} | 293 | 1.7 | 1.2 | B _{2u} | 718 | 1.3 | 2.2 | B _{1u} | 214 | 2.4 | 1.3 | B _{1g} | 599 | 1.6 | 2.5 |
| B _{3g} | 311 | 0.8 | 0.6 | B _{1u} | 724 | 1.5 | 2.6 | B _{3g} | 250 | 1.0 | 0.6 | B _{1g} | 602 | 1.2 | 1.9 |
| B _{1g} | 333 | 0.7 | 0.6 | B _{3g} | 732 | 1.3 | 2.3 | B _{2u} | 258 | 1.7 | 1.1 | B _{2u} | 616 | 1.5 | 2.4 |
| B _{3u} | 358 | 1.6 | 1.4 | A _g | 735 | 1.4 | 2.4 | B _{2u} | 259 | 1.6 | 1.1 | A _u | 618 | 1.4 | 2.2 |
| B _{1u} | 362 | 1.4 | 1.2 | B _{1g} | 738 | 1.4 | 2.4 | B _{2g} | 260 | 1.1 | 0.7 | B _{3g} | 652 | 1.4 | 2.3 |
| A _g | 393 | 1.3 | 1.2 | B _{3u} | 754 | 1.5 | 2.7 | B _{1g} | 262 | 1.3 | 0.8 | A _g | 668 | 1.4 | 2.4 |
| B _{3u} | 406 | 1.2 | 1.1 | B _{2g} | 756 | 1.2 | 2.2 | B _{3u} | 294 | 1.3 | 1.0 | B _{1u} | 683 | 1.5 | 2.6 |
| B _{2g} | 406 | 0.8 | 0.7 | A _g | 762 | 1.4 | 2.4 | B _{1g} | 301 | 1.1 | 0.8 | B _{2g} | 687 | 1.5 | 2.6 |
| A _g | 413 | 1.6 | 1.5 | B _{3u} | 784 | 1.2 | 2.2 | B _{1u} | 316 | 1.0 | 0.8 | B _{3u} | 687 | 1.2 | 2.1 |
| B _{1u} | 417 | 1.4 | 1.4 | B _{1u} | 809 | 1.1 | 2.2 | A _g | 320 | 1.0 | 0.8 | B _{2u} | 707 | 1.4 | 2.6 |
| B _{2g} | 421 | 1.1 | 1.1 | A _g | 818 | 1.3 | 2.6 | A _u | 331 | 1.0 | 1.6 | A _g | 722 | 1.5 | 2.7 |
| B _{2u} | 441 | 1.7 | 1.8 | B _{2g} | 823 | 1.3 | 2.5 | B _{3u} | 361 | 1.5 | 1.4 | B _{3u} | 739 | 1.2 | 2.2 |
| B _{1u} | 440 | 1.3 | 1.4 | B _{2g} | 843 | 1.3 | 2.6 | B _{2u} | 365 | 1.2 | 1.1 | B _{1g} | 746 | 1.4 | 2.7 |
| A _u | 456 | 1.7 | 1.8 | B _{1u} | 848 | 1.1 | 2.2 | B _{2g} | 367 | 0.9 | 0.8 | B _{2u} | 753 | 1.4 | 2.7 |
| B _{2g} | 486 | 1.2 | 1.4 | B _{3u} | 894 | 1.1 | 2.4 | B _{3g} | 371 | 0.9 | 0.9 | B _{1g} | 767 | 1.4 | 2.8 |
| B _{3g} | 497 | 1.5 | 1.8 | B _{3u} | 923 | 1.2 | 2.5 | B _{1g} | 372 | 1.1 | 1.1 | B _{1u} | 812 | 1.5 | 3.2 |
| B _{3u} | 497 | 1.3 | 1.5 | B _{1u} | 943 | 1.2 | 2.6 | B _{2u} | 372 | 0.9 | 0.8 | A _u | 813 | 1.4 | 3.0 |
| B _{1g} | 498 | 1.5 | 1.7 | A _g | 959 | 1.2 | 2.7 | A _g | 377 | 1.1 | 1.1 | B _{2g} | 830 | 1.5 | 3.2 |
| B _{2u} | 504 | 1.9 | 2.3 | B _{2g} | 980 | 1.2 | 2.7 | B _{3u} | 384 | 1.3 | 1.3 | B _{3g} | 835 | 1.4 | 3.1 |

Table 6 *Ab initio* calculated frequencies ω (cm⁻¹), Grüneisen parameters γ , and pressure coefficients (cm⁻¹/GPa) of the phonon modes of ZnGa₂O₄ in the *Cmcm* structure at 45 GPa.

| Mode | ω | γ | $\frac{d\omega}{dP}$ | Mode | ω | γ | $\frac{d\omega}{dP}$ |
|-----------------|----------|----------|----------------------|-----------------|----------|----------|----------------------|
| B _{2u} | - | - | - | A _g | 416 | 1.2 | 1.2 |
| B _{1u} | - | - | - | A _u | 438 | 1.9 | 1.9 |
| B _{3u} | - | - | - | B _{3u} | 475 | 2.0 | 2.1 |
| A _u | 31 | | | B _{1u} | 479 | 1.7 | 1.8 |
| B _{1u} | 98 | 0.3 | 0.1 | A _g | 524 | 1.4 | 1.7 |
| B _{1g} | 127 | 1.8 | 0.5 | B _{2g} | 527 | 1.5 | 1.8 |
| B _{3u} | 145 | 1.7 | 0.6 | B _{2u} | 539 | 1.8 | 2.2 |
| A _g | 179 | 1.2 | 0.5 | B _{1u} | 540 | 2.0 | 2.4 |
| B _{3g} | 191 | 1.1 | 0.5 | B _{1g} | 552 | 1.6 | 2.0 |
| B _{2g} | 199 | 1.2 | 0.6 | B _{3g} | 559 | 1.4 | 1.7 |
| B _{1g} | 204 | 1.2 | 0.5 | A _u | 576 | 2.3 | 3.0 |
| B _{1u} | 226 | 2.1 | 1.1 | B _{3u} | 580 | 2.2 | 3.0 |
| B _{3g} | 256 | 1.0 | 0.6 | B _{2u} | 640 | 1.5 | 2.2 |
| B _{2u} | 268 | 1.4 | 0.8 | B _{3g} | 675 | 1.4 | 2.1 |
| B _{2u} | 271 | 1.7 | 1.0 | A _g | 692 | 1.4 | 2.2 |
| B _{1u} | 324 | 0.9 | 0.6 | B _{1u} | 709 | 1.5 | 2.4 |
| A _g | 327 | 0.9 | 0.7 | B _{2u} | 733 | 1.4 | 2.4 |
| B _{3g} | 380 | 0.9 | 0.8 | A _g | 748 | 1.5 | 2.5 |
| B _{2u} | 380 | 0.9 | 0.7 | B _{2u} | 779 | 1.4 | 2.5 |
| B _{3u} | 396 | 1.3 | 1.2 | B _{1u} | 843 | 1.5 | 2.8 |
| B _{1g} | 409 | 1.3 | 1.2 | B _{3g} | 866 | 1.4 | 2.8 |

5 Conclusions

We have calculated by first principles the Raman and IR phonon modes as well as the pressure coefficients and Grüneisen parameters of the spinel structure in the range of pressure from 0 to 35 GPa for ZnAl₂O₄ and ZnGa₂O₄. Additionally we have measured the Raman spectra of these two spinels up to 12 GPa and we have found a good agreement between our experimental and theoretical data and with available data in the literature. Finally, we have calculated the pressure dependence of the Raman and IR active modes in other high-pressure structures (the orthorhombic CaMn₂O₄-, CaFe₂O₄-, and CaTi₂O₄-type structures) of these two spinels and we have found the possibility of a second order phase transition in ZnGa₂O₄ from the CaMn₂O₄- to a CaTi₂O₄-type structure around of 42.5 GPa which was not found in our previous report [6].

We hope that this work will stimulate and help future theoretical and experimental studies of phonon frequencies of AB₂O₄ compounds.

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