

# QUANTUM-MECHANICAL MODELING AND STUDY OF THE ELASTIC AND STRUCTURAL PROPERTIES OF MINERAL PHASES OF GEOLOGICAL INTEREST

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## INTRODUCTION

The study of the minerals at extreme pressure and temperature conditions is extremely important as the major fraction of minerals in the solid Earth has high-pressure origin. Studies of high-pressure (and high-temperature) physical and chemical properties of minerals are the key for understanding global geophysics and geochemistry

Nowadays, the main source of information concerning the structure and the dynamic of the Earth's interior is given by the collection of seismic waves that travel across the Earth, which are analysed within the framework of geophysical models which strongly rely upon data concerning the thermoelastic behavior of the mineralogical phases present at different depths (Deschamps & Trampert, 2004; Hama & Suito, 2001); in absence of such data the seismic data themselves can not be interpreted. Consequently the knowledge of the properties of the minerals of the lower mantle at extreme pressure and temperature (P/T) conditions is of crucial importance. To date the main problems in geophysics, are either the estimation of the iron content in these phases, or its impact on their thermoelastic properties, especially at the level of the D" layer that is likely very Fe-rich. Such determinations are very important for the correct interpretation of the seismic data and, in turn, for the consistency of the geophysical model relying upon them.

For these reasons, in this thesis I decided to study in detail the properties of the ferropericlasite, the magnesium-rich MgO-FeO solid solution (NaCl structure type - space group  $Fm\bar{3}m$ , whose structure is stable all along the P/T ranges of the lower mantle. In particular I focused on the determination of the elastic (static cell volume  $V_0$ , static bulk modulus  $K_0$ ), thermoelastic (cell volume  $V_T$ , bulk modulus  $K_T$ , thermal expansion coefficient  $\alpha$ ) and thermodynamic properties (heat capacity  $C_V$  and  $C_P$ , entropy  $S$ ) as a function of P, T and iron content (X), to obtain the P/T/X dependence of these properties for the conditions of the lower mantle (up to 135 GPa and 2450 K, simultaneously). The study of the X dependence was one of the main aim of this work as the exact concentration of iron in this phase is still not known exactly (the FeO content of ferropericlasite in the lower mantle is supposed to be around from 15 to 20 mole%; Fei *et al.*, 2007).

The method followed to derive the P/T/X dependence of the thermo-elastic properties is computational and, precisely, it is a fully *ab-initio* quantum-mechanical approach, that works within the framework of the quasi-harmonic approximation (QHA) (see Anderson, 1995 for a detailed description of the approximation). In detail the ground state wave functions, the corresponding energies at the static limit, the optimized geometries and the vibrational frequencies were calculated from first principles, at different cell volumes, by means of the CRYSTAL09 code (Dovesi *et al.*, 2009) which implements the LCAO Hartree-Fock and Kohn-Sham SCF method for the study of periodic systems (see Pisani, 1996 for details). It has demonstrated its ability to correctly reproduce experimental data obtained at ambient conditions, and it is largely confirmed by the literature concerning the properties of crystalline compounds (Karki *et al.*, 2000; Oganov & Dorogokupets, 2003, 2004; Ottonello *et al.*, 2008, 2009, 2010a, 2010b; Prencipe & Nestola, 2005; Prencipe *et al.*, 2011; Prencipe, 2012; Scanavino *et al.*, 2012; Wu *et al.*, 2008). Moreover this methodology has also demonstrated to be reliable under simultaneous HP and HT conditions (Oganov & Dorogokupets, 2003; Ottonello *et al.*, 2008, 2009, 2010a, 2010b; Prencipe *et al.*, 2011; Scanavino *et al.*, 2012; Ungureanu *et al.*, 2010, 2012). The reliability under simultaneous HP and HT conditions represents one of the main advantages of such methodology as it is extremely difficult to experimentally obtain the same data (*e.g.*, by X-ray diffraction) due to the required very high P/T conditions at which the measurements must be performed. In laboratory we are nowadays able to reach

pressures, at room temperature, comparable with those of the lower mantle (Matsui *et al.*, 2012) but the same can not be said at high temperatures. This means that it is very difficult, and sometimes even impossible, to experimentally obtain the necessary P(V,T) data. This remarks the importance of this work.

In this respect, in this work intrinsic anharmonic effects (Oganov & Dorogokupets, 2004) were not taken into account, though they could play a role in determining frequencies and Grüneisen's parameters of the modes having high amplitudes especially at high temperature. To check the validity of such choice, a study of the shape of the potential energy curve along two vibrational modes of lowest frequency of periclase was performed: each nucleus was shifted along its normal coordinates, and the static energy was correspondingly evaluated, in order to check if the potential energy surface calculated for the analysed modes was close to the harmonic shape.

One general problem that I encountered, having an impact on the choice of the specific computational technology to be employed, concerns the spin state of the bivalent iron in (Mg,Fe)O at the lower mantle P/T conditions. Such a phase can have two electronic configurations, the *low-spin* (LS) and the *high-spin* (HS) one, which differ for the different arrangement of the electrons in the *d* orbitals. The choice between the two configurations depends on the value of the energy gap between the *eg* and the *t2g* orbitals, compared to the energy requested for the pairing of the electrons into a single *t2g* orbital. At ambient pressure the energy gap is lower with respect to the pairing energy, consequently the *high-spin* is the favoured configuration. At higher pressure the structure shrinks and the oxygens shift closer to the iron, thus increasing the repulsive Coulomb force. This increases the energy gap between the *eg* and the *t2g* orbitals since, at a certain pressure, such gap becomes higher than the pairing energy and there is a transition from the *high-spin* to the *low-spin* configuration.

This is what happens in the Earth's interior, where, at a certain depth of the lower mantle there is the transition from the low-pressure HS configuration to the high-pressure LS one. At present, most of the studies on ferropericlase are focused on the determination of such transition (Fei *et al.*, 2007; Jacobsen *et al.*, 2002; Komabayashi *et al.*, 2010; Lin *et al.*, 2003, 2005, 2006, 2007; Speziale *et al.*, 2005; Tsuchiya *et al.*, 2006): these works confirm how the LS configuration is the predominant one in the lower mantle. Despite the recognized importance of such configuration, works aimed at the determination of its thermoelastic properties in its LS configuration are very few (Fei *et al.*, 2007; Lin *et al.*, 2005; Speziale *et al.*, 2007 among experimental works - Persson *et al.*, 2006 among computational ones). For this reason I decided to bridge this gap determining the P/T/X dependence of the properties of LS ferropericlase in all the lower mantle. I made some calculations also for the HS phase in order to further highlight the difference between the two phases.

The lack of data about the LS ferropericlase did not allow us to make a direct validation of our results. For such a reason, a preliminary study about the P/T dependence of the thermoelastic properties of periclase was necessary. I chose periclase both because it is end member of the solid solution under study and because is one of the most studied mineralogical phases, at both the experimental and computational levels (see Garai *et al.*, 2009 for an exhaustive reference list on this phase).

## RESULTS AND DISCUSSION

### *Periclase and harmonic approximation*

I calculated the static and the total energies of periclase in a pressure range that include the pressure range of the lower mantle (24, 136 GPa), then I fitted the  $E_{st}(V)$  and the  $E(V, T)$  points with a third-order Birch-Murnaghan (BM3) equation of state (EoS) in order to obtain the resulting EoS parameters ( $V_0$ ,  $V_T$ ,  $K_0$ ,  $K_T$ ,  $K'_0$ ,  $K'_T$ ). A very short summary of the obtained results is shown in Table 1.

As regards the thermodynamic and the thermoelastic parameters, the values obtained at ambient conditions (36.25 J/(mole·K), 36.67 J/(mole·K), 26.22 J/(mole·K) and  $2.79E-05$  K<sup>-1</sup> respectively for  $C_V$ ,  $C_P$ ,  $S$  and  $\alpha$ ) fully confirm the literature data (*e.g.* Dubrovinsky & Saxena, 1997; Ghose *et al.*, 2006; Karki *et al.*, 2000; Oganov *et al.*, 2003; Saxena *et al.*, 1993). The results exposed so far have demonstrated that the employed methodology is able to predict with a very good accuracy the experimental results, even at HP and HT conditions. For this reason, the analogous results obtained for ferropericlase can be considered reliable.

Table 1 - Static and ambient equilibrium parameters ( $K_0$ ,  $K'$ ,  $V_0$ ,  $a_0$ ,  $K_T$ ,  $K'_T$ ,  $V_T$ ,  $a_T$ ) of periclase obtained by the fit of the  $E_{st}(V)$  or  $E(V, T)$  data by different EoS's.  $V_0$ ,  $V_T$ ,  $a_0$  and  $a_T$  are referred to the conventional cell with eight atom.

Static conditions	P(V) range fit [GPa]	EoS	$K_0$ [GPa]	$K'$	$a_0$ [Å]	$V_0$ [Å <sup>3</sup> ]	Methodology
Oganov & Dorogokupets (2003)	-5 – 150	BM3	181.24	3.997	4.187	73.425	GGA + PAW
Karki <i>et al.</i> (2000)	0 – 200	BM4	169	4.18	4.197	73.920	LDA + PP
Wu <i>et al.</i> (2008)	0 – 150	BM4	173.2	4.09	4.162	72.10	LDA + LAPW
Wilson & Muscat (2002)	-12 – 21.5	BM3	156.3	4.0	4.25	76.77	HF/DFT(B3LYP)
Persson <i>et al.</i> (2006)	-20 – 200	BM3	153	4.255	4.10	77.04	GGA + PAW
This work	0 – 170	BM3	163.75	4.273	4.219	75.089	HF/DFT(WC1LYP)
Ambient conditions	P(V) range fit [GPa]	EoS	$K_T$ [GPa]	$K'_T$	$a_T$ [Å]	$V_T$ [Å <sup>3</sup> ]	Methodology
Speziale <i>et al.</i> (2001)	0.8 – 52.2	BM3	170	3.59	4.208	74.53	X-ray diffraction
Jacobsen <i>et al.</i> (2008)	0 – 87	BM3	164.1	4.05	4.211	74.698	X-ray diffraction
Fei (1999)	0 – 23	BM3	160	4.15	4.213	74.792	X-ray diffraction
Karki <i>et al.</i> (2000)	0 – 150	BM4	159	4.30	4.222	75.240	LDA + PP
Wu <i>et al.</i> (2008)	0 – 150	BM4	160	4.23	4.221	75.190	LDA + PP
Matsui <i>et al.</i> (2000)	0 – 20	BM4	160.5	4.10	4.211	74.648	MD simulation
This work	0 – 170	BM3	160.14	4.234	4.236	75.999	HF/DFT(WC1LYP)
This work	0 - 124	BM3	163.02	4.283	4.219	75.125	HF/DFT(WC1LYP)

The abbreviations signify: LDA (local density approximation); GGA (generalized gradient approximation); PP (pseudopotentials); PAW (projector augmented-wave method); ECP (effective core pseudopotentials); LAPW (linearized augmented plane wave); MD (Molecular dynamics).

As regards the study of the shape of the potential energy curve along two vibrational modes of periclase, as mentioned before, I fitted the calculated energies as a function of the nuclear displacement (six times the maximum classical displacement used in the calculation of the frequencies) with a quartic polynomial function: the coefficients of the quartic term, for both the mode analyzed, were three order of magnitude smaller than the quadratic term. The same test, performed for P/T conditions different from the ones of the Earth's lower mantle (3000 K and 0.0001 MPa), gave different results: the quartic coefficients of the fitting curves were only one order of magnitude smaller than the quadratic terms. In the light of these results, the real potential energy curve of periclase and ferropericlase can be approximated to a harmonic one in all the P/T range of the lower mantle. At the same time our results confirmed the observations of Oganov & Dorogokupets (2004) on the necessity to include the anharmonic effects at high temperature.

### Ferropericlase

The static energies of ferropericlase with growing iron content, from  $(Mg_{0.97}Fe_{0.03})O$  to  $(Mg_{0.41}Fe_{0.59})O$ , were calculated for 26 configurations (for some stoichiometric compositions I calculated the static energies for more classes, which differ for the different distribution of Fe and Mg in the crystal structure). The resulting EoS static parameters (Table 2) show an increase of the equilibrium  $K_0$  with the iron content and a simultaneous decrease of the equilibrium  $V_0$ , whereas  $K'_0$  shows a non linear increase with the iron content. The trends I obtained are fully confirmed by the only computational work concerning LS ferropericlase (Persson *et al.*, 2006). In order to study the vibrational and temperature effects on the properties of ferropericlase, I calculated the vibrational frequencies for two stoichiometric compositions, the  $(Mg_{0.97}Fe_{0.03})O$  [ $Fe_{03}$  ferropericlase] and the  $(Mg_{0.54}Fe_{0.46})O$  [ $Fe_{46}$  ferropericlase]. Starting from the calculated frequencies it was possible to obtain the thermal energies  $E(V, T)$ , which provided the EoS equilibrium parameters at ambient conditions (Table 2). The only comparable datum for the LS ferropericlase is the one by Speziale *et al.* (2007) which, for a  $(Mg_{0.83}Fe_{0.17})O$  ferropericlase, observed a reduction of  $V_T$  and an increase of  $K_T$ , as in this work.

The reliability of my fittings at static and ambient conditions was tested by the  $F$ - $f$  plot, which confirmed that ferropericlasite is correctly described by the BM3.

Table 2 - EoS Equilibrium parameters at static and ambient conditions for the low-spin (LS) ferropericlasite sorted according to the percentage of iron. The iron percentage is referred to the stoichiometric formula  $(\text{Fe}_{\delta/100}\text{Mg}_{1-(\delta/100)})\text{O}$ .

Static conditions	P(V) fitting interval [GPa]	% Fe $[\delta]$	EoS	$K_0$ [GPa]	$K'$	$V_0$ [ $\text{\AA}^3$ ]	Methodology
This work	-5 – 177	3	BM3	172.17	4.10	74.190	HF/DFT (WC1LYP)
This work	-5 – 177	9	BM3	179.62	4.054	73.535	HF/DFT (WC1LYP)
This work	-5 – 177	15	BM3	186.29	4.053	73.010	HF/DFT (WC1LYP)
This work	-5 – 166	25	BM3	188.90	4.210	72.783	HF/DFT (WC1LYP)
Persson <i>et al.</i> (2006)	-20 – 200	25	BM3	170	4.1	74.96	DFT (GGA)
This work	-5 – 166	37	BM3	200.73	4.287	72.058	HF/DFT (WC1LYP)
This work	-5 – 166	46	BM3	210.75	4.283	71.423	HF/DFT (WC1LYP)
Persson <i>et al.</i> (2006)	-20 – 200	50	BM3	186	4.2	73.52	DFT (GGA)
This work	-5 – 166	56	BM3	220.49	4.256	71.030	HF/DFT (WC1LYP)
This work	-5 – 166	59	BM3	224.92	4.204	70.809	HF/DFT (WC1LYP)
Persson <i>et al.</i> (2006)	-20 – 200	75	BM3	203	4.2	72.52	DFT (GGA)
Ambient conditions	P(V) fitting interval [GPa]	% Fe $[\delta]$	EoS	$K_T$ [GPa]	$K'_T$	$V_T$ [ $\text{\AA}^3$ ]	Methodology
This work	0 – 170	3	BM3	167.42	4.09	75.145	HF/DFT (WC1LYP)
Lin <i>et al.</i> (2005)	55 – 135	17	BM2	250	4 (fixed)	/	X-ray diffraction
Speziale <i>et al.</i> (2007)	40 – 134	17	BM3	186	4.60	71.390	X-ray diffraction
Fei <i>et al.</i> (2007)	40 – 95	20	BM2	170	4 (fixed)	74.200	X-ray diffraction
Mao <i>et al.</i> (2011)	0 – 140	25	BM2	166	4 (fixed)	74.4	X-ray diffraction
Fei <i>et al.</i> (2007)	60 – 148	39	BM2	170	4 (fixed)	73.600	X-ray diffraction
This work	0 – 158.62	46	BM3	205.57	4.242	72.216	HF/DFT (WC1LYP)
This work	0 – 128.73	46	BM3	204.13	4.279	72.244	HF/DFT (WC1LYP)

The symbol / means that the datum is not reported.

The lack of data for the LS phase, compared with the amount of data for the HS phase, inspired me to calculate the static energy also for the HS ferropericlasite, in order to further emphasize the difference that there is between these two spin configurations.

I chose to study only the stoichiometric composition  $(\text{Mg}_{0.97}\text{Fe}_{0.03})\text{O}$ . For such phase it was necessary to use a Hamiltonian with a larger Hartree-Fock contribution to the total electronic exchange, which had the side effects to reduce the cell volume and to increase the bulk modulus at the equilibrium, thereby confirming a behaviour already observed in other studies (Prencipe & Nestola, 2005).

The  $E_{st}(V)$  and  $E(V, T)$  fitting results, compared with some literature data, are shown in Table 3. Starting from such data was possible to observe that, differently from the LS phase, in the HS one the  $K_0$  and  $K_T$  are almost unmodified by the increase of the iron content, whereas the  $V_0$  and  $V_T$  rises with the iron, thus showing an opposite behaviour with respect the LS phase.

Table 3 - EoS equilibrium parameters at static and ambient conditions for the HS ferropericlase sorted according to the percentage of iron. The iron percentage is referred to the stoichiometric formula  $(\text{Fe}_{\delta/100}\text{Mg}_{1-(\delta/100)})\text{O}$ .

Static conditions	P(V) fitting interval [GPa]	% Fe [ $\delta$ ]	EoS	$K_0$ [GPa]	$K'$	$V_0$ [ $\text{\AA}^3$ ]	Methodology
This work	0 – 180	3	BM3	175.87	4.243	73.789	HF/DFT (HF 35%)
This work	0 – 23	3	BM3	180.82	4.183	73.208	HF/DFT (HF 35%)
Persson <i>et al.</i> (2006)	-20 – 200	25	BM3	153	4.100	79.120	GGA + PAW
Persson <i>et al.</i> (2006)	-20 – 200	50	BM3	163	4.0	80.600	GGA + PAW
Persson <i>et al.</i> (2006)	-20 – 200	75	BM3	148	4.4	82.800	GGA + PAW
Ambient conditions	P(V) fitting interval [GPa]	% Fe [ $\delta$ ]	EoS	$K_T$ [GPa]	$K'_T$	$V_T$ [ $\text{\AA}^3$ ]	Methodology
Reichmann <i>et al.</i> (2008)	0 – 9	1.3	#	161.1	4.2	/	Brillouin spectroscopy
Jackson <i>et al.</i> (2006)	0 – 20	6	#	163	3.90	/	Brillouin spectroscopy
Lin <i>et al.</i> (2005)	0 – 55	17	BM3	160.7	3.280	/	X-ray diffraction
Speziale <i>et al.</i> (2007)	0 – 40	17	BM3	157.5	3.92	76.10	X-ray diffraction
Speziale <i>et al.</i> (2007)	0 – 40	20	BM3	158	4.4	76.030	X-ray diffraction
Matsui <i>et al.</i> (2012)	0 – 55	25	BM3	160 (fixed)	4.22	76.372	X-ray diffraction
Jacobsen <i>et al.</i> (2002)	0 – 9.3	27	BM3	158.4	5.49	76.336	X-ray diffraction
van Westrenen <i>et al.</i> (2005)	0 – 26.7	36	BM3	154	4	77.438	X-ray diffraction
Jacobsen <i>et al.</i> (2002)	/	37	/	164	/	76.836	X-ray diffraction
Jacobsen <i>et al.</i> (2002)	/	53	/	161	/	77.937	X-ray diffraction
Jacobsen <i>et al.</i> (2002)	0 – 8.9	56	BM3	155.8	5.53	77.453	X-ray diffraction

The symbol / means that the datum is not reported. # Finite-strain equation of state taken from Davies & Dziewonski (1975).

As regards  $\alpha$ ,  $C_V$ ,  $C_p$ ,  $S$  of LS ferropericlase the only parameter that showed to be modified by the presence of iron with respect to periclase is the thermal expansion, which decreases from  $2.25 \cdot 10^{-5} \text{ K}^{-1}$  for periclase, to  $1.97 \cdot 10^{-5} \text{ K}^{-1}$  for  $\text{Fe}_{46}$  ferropericlase, but such a decrease is not linear.

I have repeatedly stressed the importance to calculate the properties at conditions that are the ones of the lower mantle and the fact that through this methodology we are able to do it. For such reasons, for periclase,  $\text{Fe}_{46}$  and  $\text{Fe}_{03}$  ferropericlase I calculated some properties as a function of the depth, that is according to the P/T conditions of the geobar (Bina, 1998) and of the geotherm curve (Brown & Shankland, 1981) respectively. The trend for  $K_T$  and  $V_T$  are shown respectively in Fig. 1 and Fig. 2.

I have to recall that the LS configuration, for the  $\text{Fe}_{46}$  ferropericlase, becomes the most

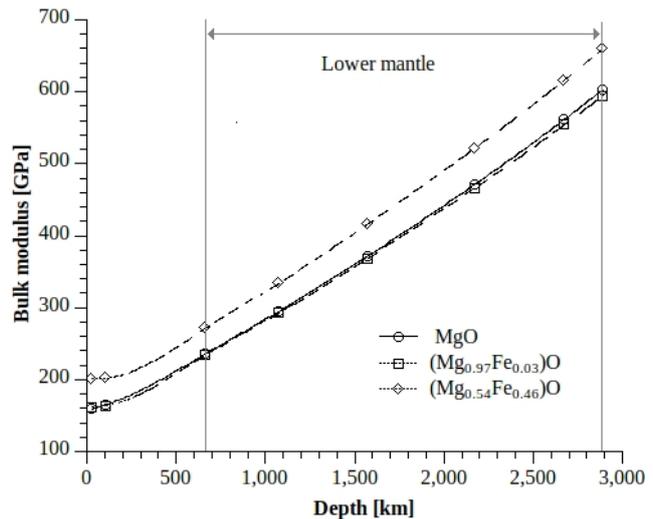


Fig. 1 - Bulk modulus  $K_T$  as a function of depth. The P/T conditions reflect the ones of the Earth's interior according the values of the geotherm and the geobar curves. At the points indicated in the figure correspond the following P/T conditions: 25 km (0.6 GPa / 773 K); 100 km (3.3 GPa / 1475 K); 660 km (23.5 GPa / 1866 K); 1071 km (41.5 GPa / 2004 K); 1571 km (65.1 GPa / 2147 K); 2171 km (95.3 GPa 2296 K); 2671 km (122.4 GPa / 2405 K); 2885 km (134.8 GPa / 2449 K).

stable one at about 60 GPa, corresponding to about 1500 km of depth, whereas the  $\text{Fe}_{0.3}$  ferropericlasite should become at about 55 GPa / 1250 km. It does not mean that the results for lower depth are meaningless or wrong, the curves describe the correct behaviour of the LS phases for those P/T conditions, but not necessarily their spin configuration is the most stable one. Considering that the expected LS FeO content of ferropericlasite in the lower mantle ranges from 15 to 20 mole%, the graphs proposed can be used as thresholds within which lie the values that the thermodynamic and the thermoelastic parameters of ferropericlasite really have into the lower mantle.

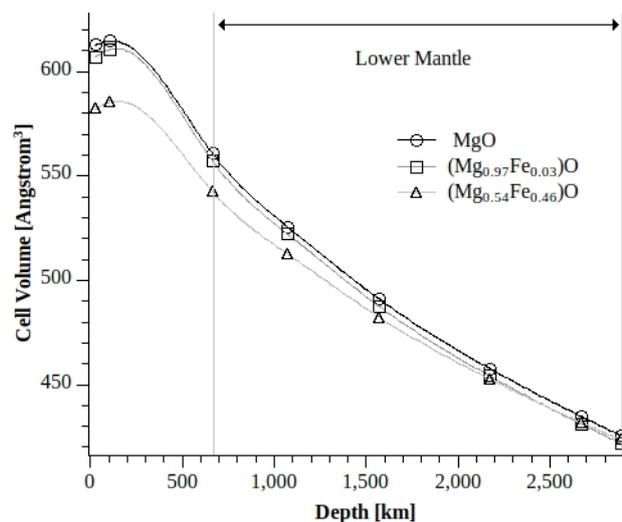


Fig. 2 - Cell volume  $V_T$  as a function depth. The P/T conditions reflect the ones of the Earth's interior according the values of the geotherm and the geobar curves. For the P/T conditions associated at the points in the picture see Fig. 1.

## CONCLUSION

The work here shown it is proposed to be the first complete retrospective about the LS ferropericlasite as it is the first work to treat it in such a detail, showing, moreover, how the two different spin-configurations give rise to two different phases that can not be considered equivalent.

The whole thesis is a further confirmation of the huge potentiality of such methodology in the prediction of the elastic and thermodynamic properties, even at P/T conditions that are hardly reachable experimentally as in this thesis it was proved that the QHA is reliable at the P/T conditions of the lower mantle.

Finally the data concerning the bulk modulus and its P/T/X dependence can have a geophysical impact as they can be entered in the geodynamic models, integrated with other data from another source (density, shear modulus, etc.), to obtain the change in the seismic speeds.

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