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A BADER'S TOPOLOGICAL APPROACH FOR THE CHARACTERIZATION OF PRESSURE INDUCED PHASE TRANSITIONS

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INTRODUCTION

The main purpose of the present PhD thesis is to propose a procedure for the characterization of mineralogical phases under non-ambient conditions by exploiting the potentiality of the computational methods and of the Bader's topological analysis of the electron density. Two important phase transitions which affect the geodynamics of the Earth's deep interior, namely the post-spinel and the Mg-perovskite to post-perovskite transitions, have been explored.

Two issues have been addressed: the first is the construction of the equation of state at zero temperature of the involved mineralogical phases and the determination of the stability fields; the second concerns the investigation of the evolution of the electron arrangement across the pressure induced phase transitions in terms of topology of the electron density.

THEORETICAL BACKGROUND

Bader analysis

In this section we would briefly summarize some basic concepts of the topological analysis of the electron density by pointing out the connections between the topological features of the electron density distribution, the structural stability and the breaking/formation of chemical bonds.

The topological analysis of the electron density $\rho(r)$, based upon the theory of atoms in molecules (AIM) developed by Bader (1991) analyzes the curvature of $\rho(r)$ at the so-called critical points (CPs), *i.e.* the points where the gradient field vanishes. The CPs are denoted as (ω,σ) according to their rank (ω), which is the number of nonzero eigenvalues (or curvatures), and their signature (σ), which is the algebraic sum of the signs of the eigenvalues. With relatively few exceptions, the rank of CPs in an equilibrium geometry is equal to 3, since the CP with $\omega < 3$ (degenerate critical points) are unstable and indicate an incipient change in the topology of the electron density. There are four types of stable CPs depending of the signature values: (3,-3), (3,-1), (3,+1) (3,+3). A (3,-3) critical point is a maximum in $\rho(r)$ and, for all atoms but hydrogen, it can coincide with the position of a nucleus. As for the (3,-1) critical point, $\rho(r)$ is a maximum in the plane and a minimum along a third axis, perpendicular to this plane. This point is located between two neighbouring atoms defining a bond between them, and it is therefore called bond critical point (BCP). As for the (3,+1) critical point, $\rho(r)$ is a minimum in the plane and a maximum along a third axis, perpendicular to this plane. This point has to be found in the middle of several bonds forming a ring, and it is also called a ring critical point (RCP). A (3,+3) critical point is a minimum and it is found when several rings form a cage and it is therefore called a "cage" critical point (CCP). At this point it is important to point out that the mechanism of making and breaking of chemical bonds is closely related with changes in the morphology of a molecular charge distribution. In particular, according with the Palis-Smale's theorem, (Palis & Smale 1970) two different mechanism of structural instability, both illustrated in terms of the behavior of the molecular charge distribution, exists. The first mechanism consists in the formation of a degenerate critical point, or singularity, in the electronic charge distribution and is called bifurcation catastrophe, while the second corresponds to the creation of an unstable intersection of the stable and unstable submanifolds of two neighboring critical points, and is called conflict catastrophe. It should be recalled that, the stable and the unstable manifolds of the CP at r_c are defined to be the manifolds generated by the eigenvectors of the Hessian matrix of r at r_c associated with the negative and positive eigenvalues respectively.

AIMS AND OBJECTIVES OF THE STUDY

Mg_2SiO_4 ringwoodite (γ-spinel phase) is thought to be the most abundant mineral in the lower part of the mantle transition zone (Ita & Stixrude, 1992), which implies that its structural, elastic and thermodynamic properties should affect those of the mantle at this depth.

According to the most reliable geophysical models, its dissociation into MgO periclase and $MgSiO_3$ perovskite, the post-spinel transformation, is believed to be responsible for the 660-km discontinuity that defines the boundary between transition zone and lower mantle (Zhao & Anderson, 1994), and would seem to have significant implications for mantle convection processes (Ringwood, 1994; Tackley *et al*., 1993). In this context, the total lack of direct observations of the interior of the earth greatly hampers the understanding of the mechanisms influencing the deep geodynamics. Only in the last years, the development of sophisticated experimental techniques rendered feasible the experimental approach to the problem (Chopelas *et al*., 1994; Meng *et al*., 1994; Zerr *et al*., 1993).

However, in the laboratory experiments some results are extremely difficult to obtain either because of the extreme P-T condition or for the very slow reaction kinetics. The experimental research can be conveniently integrated by computational methods which allow, not only to explore the extreme conditions that cannot be realized in a laboratory, but also to rule out the experimental problems relating to the slow kinetics.

In the light of all these considerations, we decided to undertake the present computational study aimed at obtaining a comprehensive picture of the post-spinel phase transition and an internally consistent set of references to compare with the various experiments.

Moreover, the evolution of the electron arrangement in the ringwoodite crystal-structure across the pressure induced phase transition has been investigated in terms of topology of the electron density and a topological approach based on the Catastrophe Theory in the framework of the Bader's theory has been proposed for the first time.

In a second step, in order to test the reliability of the proposed procedure in the characterization of the structural stability of mineralogical phases, the Bader's topological analysis has been performed on the Mg-perovskite structure. The interest in the structural stability of this phase comes from the consideration that the Mg-perovskite is assumed to be the dominant component of the Earth's lower mantle (Oganov & Price, 2005) and the transition to the so-called post-perovskite phase can explain the discontinuity in seismic velocities observed above the core-mantle boundary (the D" discontinuity).

Although quite a large amount of data on the perovskite so far exists, its behavior at the extreme conditions of the Earth mantle is still lacking information. This is mainly due to the technical difficulties related to the experimental setup. As already stated, at extreme conditions, where the experiments lose its accuracy, computational approach can be very helpful in complementing these studies.

COMPUTATIONAL DETAILS

The calculations have been performed by means of the *ab-initio* CRYSTAL09 program (Dovesi *et al.,* 2009) at the HF/DFT level, using Hamiltonians based on the Becke-LYP and the WC1LYP schemes,

For all structures, the adopted choices yielded equilibrium geometry close to the experimental one measured at room temperature.

To address the compression mechanism, calculations have been performed at different unit cell volumes and the energies obtained as function of the volumes have been fitted by means of the Birch-Murnaghan equation.

At each cell volume, the topological analysis of the calculated electron density (Bader, 1994) has been performed by means of the TOPOND 98 program (Gatti, 1999) and TOPOND09 (Gatti, private communication).

RESULTS AND DISCUSSION

Equation of state

The compression process has been simulated by performing calculations at different unit cell volumes. The E(V) data obtained for each of the three structures have been fitted by means of different equations of state. The obtained values of V_0 (volume at minimum energy), K_0 (zero-pressure bulk modulus) and K' (pressure derivative of K at $P = 0$) are in good accordance with those obtained from previous computational and experimental studies.

The pressure values corresponding to each volume have been determined by introducing the fitting parameters in the corresponding P(V) equations.

The construction of the equations of state allowed us not only to identify the pressure value where the CPs is observed to change, but also to determine the most stable structure on the basis of the computed enthalpies (H).

Fig. 1 shows the theoretical enthalpies of the ringwoodite phase and that of the sum of MgO and Mg-perovskite plotted against pressure.

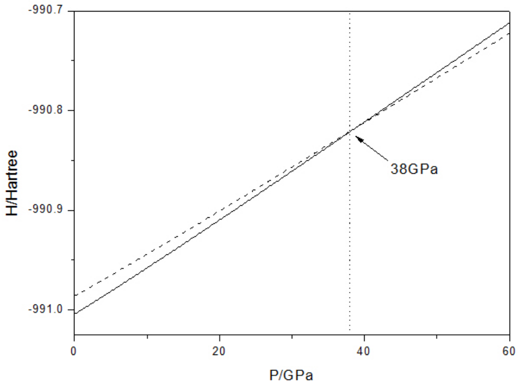

Fig. 1 - Calculated enthalpies per formula unit of ringwoodite (solid line) and of the assembly $MgO + MgSiO_3$ (dashed line) *versus* pressure.

Perusal of the figure clearly indicates that the energy differences involved in the reaction are quite small and that, at zero-temperature, ringwoodite phase transforms in Mg-perovskite and MgO at ~ 38 GPa. The phase boundary pressure between ringwoodite and perovskite was found to be ~ 21-24 GPa at 1550-2100 K (Chudinovskikh & Boehler, 2001; Katsura *et al.*, 2003; Shim *et al.*, 2001). The higher value of pressure transition obtained from our calculation can be explained in the light of a negative Clapeyron slope (Deuss *et al.*, 2006; Fei *et al.*, 2004). Moreover it has to be noted that the PT point obtained from the present study refers to the completely anhydrous and totally ordered pure γ-Mg_2SiO_4, Mg-perovskite and periclase, whereas the experimentally determined PT points at higher temperature refers to samples where water, impurities or structural disorder also contribute to the localization of the phase boundary by promoting the phase transitions and decreasing the transition pressure (Katsura *et al.*, 2003).

Topological analysis of the ringwoodite electron density

The Bader topological analysis applied to the electron density of the ringwoodite, for pressure values ranging from 0 to ~ 33 GPa, revealed the presence of 8 different critical points, while, at higher pressure values, the appearance of two more critical points, namely a bond and a ring critical point, has been observed (Fig. 2).

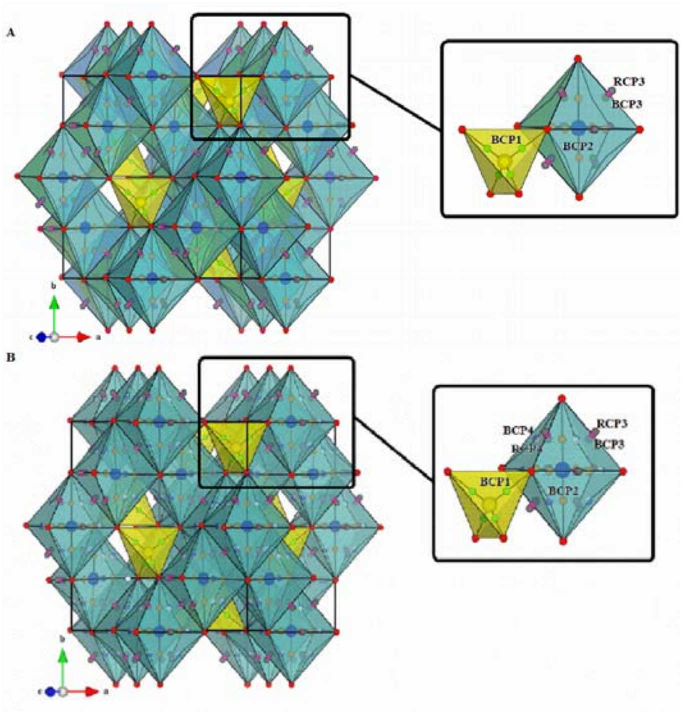

Fig. 2 - Projection onto the (201) plane of the structure of ringwoodite at (A) P = 7.3 GPa and (B) 45.7 GPa with the related bond and ring critical points. The inset is the enlargement of the selected rectangle.

In order to obtain more information about the chemical bonds, some topological properties related to the BCPs, namely the electron density, $\rho(r)$, the Laplacian of the electron density, $\nabla^2\rho(r)$, the eigenvalues λ_i's and the ellipticity ε have been investigated.

The trends of the topological variables as a function of the pressure are consistent with those observed by Prencipe & Nestola (2007) in the case of the beryl.

The evolution of the electron density across the phase transition has been further characterized by evaluating the "radial atomic expectation" value, GR(0), over the ionic basins (Ω) of Mg, Si and O atoms of the ringwoodite structure, as follows:

$$GR(0) = \int \mathbf{r}_\omega \bullet \nabla\rho(\mathbf{r})\, d\tau$$

where $\mathbf{r}_\omega$ is the radial distance of the electron from the nucleus.

The quantity GR(0) reflects the distortion of the $\nabla\rho(\mathbf{r})$ field of the charge density that is caused by the formation of chemical bond. It is worth to highlight (Bader, 1994) that in the case of a free atom where the vector $\nabla\rho(\mathbf{r})$ and the radial vector $\mathbf{r}$ are parallel and oppositely directed the integral reaches its negative maximum value $-3N(\Omega)$, where $3N(\Omega)$ is the basin electron population. In Fig. 3 the ratio SPHD = GR(0)/[-3N], is reported as a function of the pressure for the three atoms. Perusal of the figure indicates that, both Mg and Si atoms have their gradient vector fields $\nabla\rho(\mathbf{r})$ appreciably distorted from those of isolated atom, as indicated by the departure of SPHD from the value of unity, in the whole pressure range. On the contrary, for the O atom, at P = 32.9 GPa, which is very close to the transition pressure, the SPHD value attain the value of unity, which is indicative of an extremely loosely bound atom, and therefore to a certain tendency of the atom to break the bonds with the neighboring atoms.

This result is an important topological evidence of the approaching of the phase transition and can also be taken as an indication of the central role played form the oxygen atoms in the pressure induced phase transition.

At this point it is challenging to interpret the topological results in the light of the catastrophe theory.

The topological analysis performed across the pressure transition reveals the occurrence of a *fold catastrophe*, *i.e.* the appearance of two coalescent CPs (BCP4 and RCP4) corresponding to the formation of new

O-O bond. At the same time a *conflict-type catastrophe* occurs since the stable and the unstable manifolds of a couple of two neighboring critical points (BCP3 and BCP4) do not intersect transversally.

In particular a non-transversal interaction between the bond path (unstable manifolds) of a (3,-1) critical point, namely the BCP4, with the interatomic surface (stable manifolds) of a second (3,-1) critical point, namely the BCP3, has been recognized. According to the Palis-Smale's theorem (Palis & Smale, 1970) this arrangement is unstable and corresponds to a *conflict* structure.

Since the fold catastrophe simply corresponds to the formation of a bond, while the conflict catastrophe give rise to the formation of an instable structure, the catastrophe mechanism to be invoked in the investigated phase transition is the conflict-type.

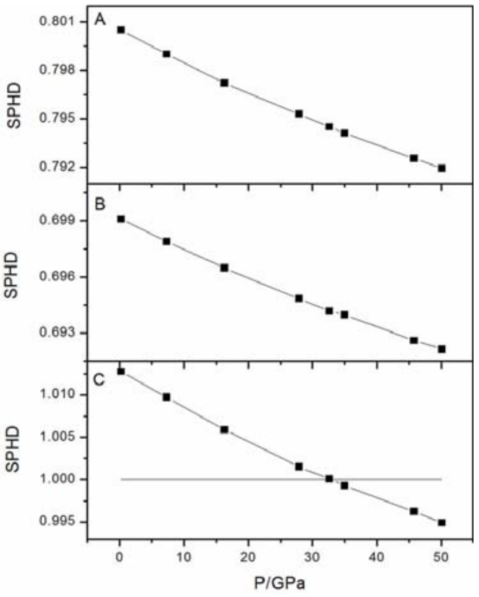

Fig. 3 - SPHD ratio as a function of the pressure for the Mg (A), Si, (B) and O (C) atoms.

Topological analysis of the Mg-perovskite electron density

In order to verify the reliability of this approach we performed the topological analysis of the Mg-perovskite.

First of all, the investigation of the quantity GR(0) revealed that no destabilization of this phase could be detected by this parameter.

The study of the evolution of the topological critical points across the whole pressure range revealed very interesting features. The setting of critical points present in the structures from 0 to 140 GPa are reported in Figs. 4-6, where two different planes of the crystallographic cell are presented for each pressure values.

Note that, for brevity reasons, all the figures refer to the topological analysis performed on the electron density constructed by means of the WC1LYP Hamiltonian.

At low pressure values (Fig. 4), 28 different critical points can be recognized. In particular, Fig. 4A shows a region of the crystallographic cell where, at low pressure regime, no critical points are present (this figure will be compared in the following paragraph with Fig. 5A) while in Fig. 4B the presence of a couple of coalescent critical points, namely a BCP along the bond path joining two oxygen atoms and a RCP (indicated as BCP1 and

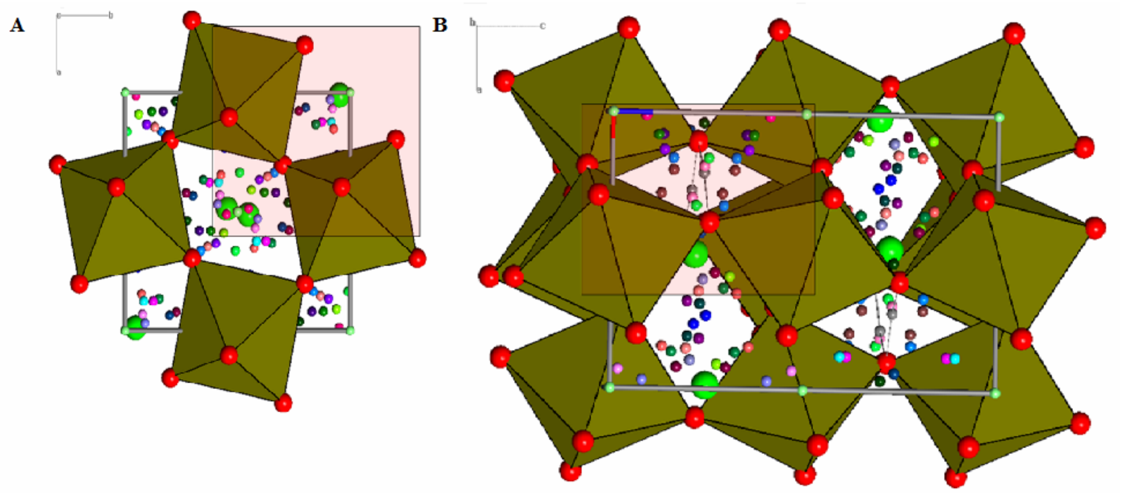

Fig. 4 - Projection onto the (A) (001) plane and (B) $(0\bar{1}0)$ plane of the structure of Mg-perovskite at P = 0.0001 GPa with the related bond, ring and cage critical points. ● = BCP1, ● = RCP1, ● = CCP2, ● = RCP2.

RCP1) and, surrounding them, two couples of critical points very close to each other, namely a cage and a ring critical points (indicated as CCP2 and RCP2) are marked.

The analysis of the critical points at higher pressures (Fig. 5) revealed the appearance of a third couple of coalescent critical points, namely a cage, CCP3, and a ring, RCP3 and the simultaneous decrease of the distance CCP2-RCP2, while the distance BCP1-RCP1 is not affected from the pressure increase.

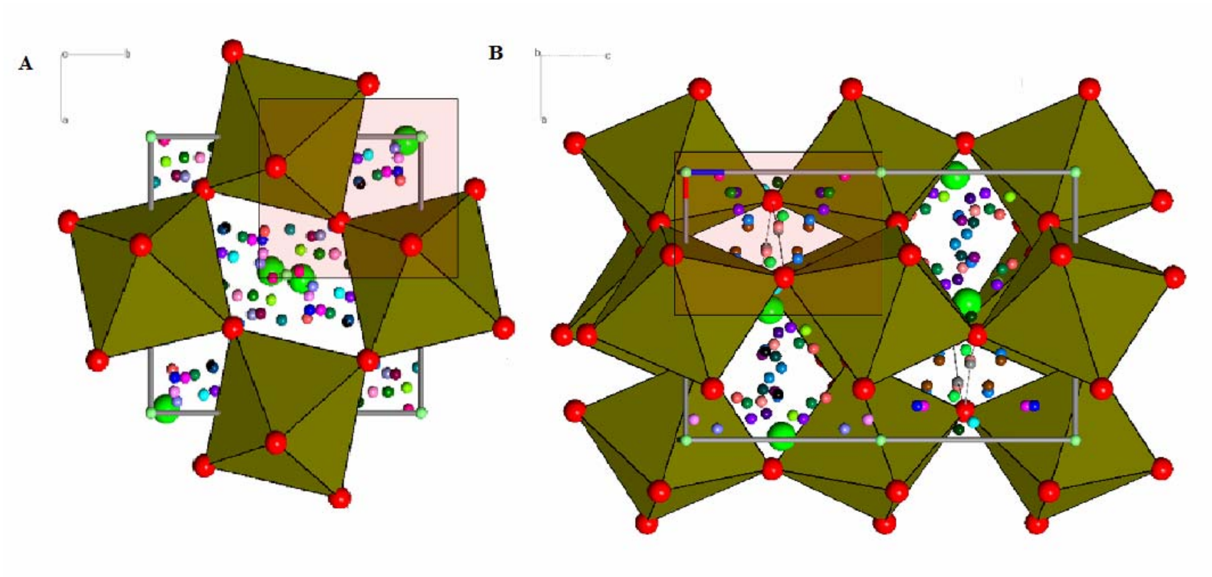

Fig. 5 - Projection onto the (A) (001) plane and (B) $(0\bar{1}0)$ plane of the structure of Mg-perovskite at P = 40 GPa with the related bond, ring and cage critical points. ● = CCP3, ● = RCP3.

It is worth to note that the emergence of the CCP3-RCP3 couples corresponds to the pressure value where the post-spinel transition occurs. Therefore it seems to indicate the passage between the stability field of the ringwoodite phase to that of the perovskite phase.

Finally, in the following pictures the topological features corresponding to very high pressure values are reported. Intriguingly, it has been observed the disappearance of the CCP2-RCP2 couple. At the same time, it has been observed that the BCP1-RCP1 distance start to slight decrease.

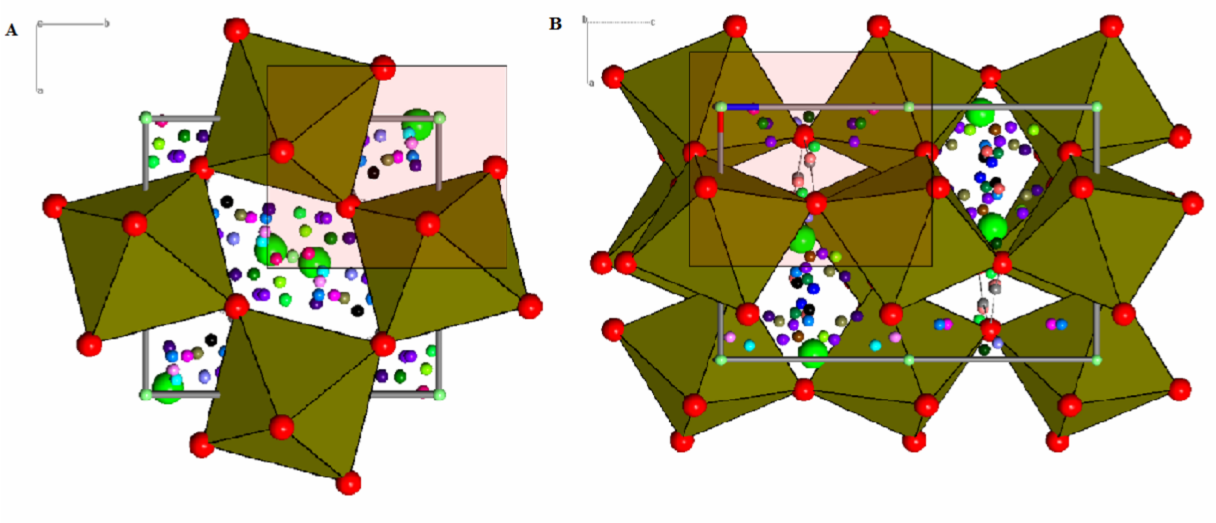

Fig. 6 - Projection onto the (A) (001) plane and (B) $(0\bar{1}0)$ plane of the structure of Mg-perovskite at P = 135 GPa with the related bond, ring and cage critical points.

It is interesting to underline that the pressure where the disappearance of the RCP2-RCP3 couple occurs is ~ 130 GPa which corresponds to the pressure where the perovskite to post-perovskite phase transition takes place.

The most important topological results are summarized in Fig. 7, where the distances between the three critical points couples are reported.

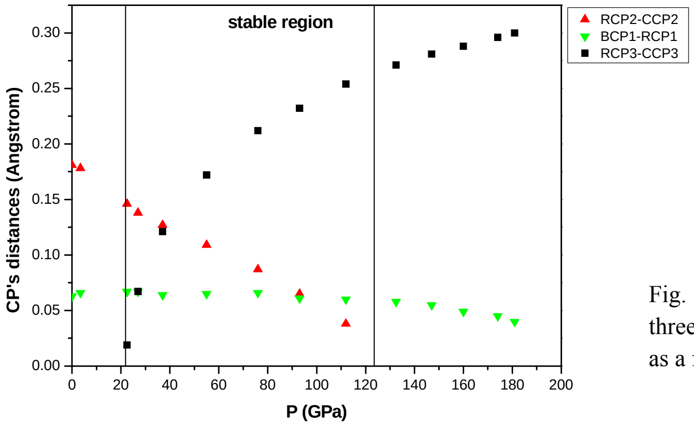

Fig. 7 - Plot of the distances between the three couples of coalescent critical points as a function of the pressure.

Perusal of Fig. 7 illustrates how the Bader's topological analysis provides an effective tool for the delineation of the stability field of the mineralogical phases. The first topological anomaly, *i.e.* the emergence of the CCP3-RCP3 couple at ~ 20 GPa, is a clear indication of the stabilization of the perovskite phase, while the inverse process observed at ~ 130 GPa, *i.e.* the vanishing of the CCP2-RCP2, indicates the destabilization of this phase.

Since the two observed phase transitions involve the coalescence of two critical points, they can be interpreted in the light of the catastrophe theory as fold catastrophes.

It is worth to underline the important geophysical implication of these results. In particular, the second observed fold catastrophe occurs at a pressure value that correspond at ~ 2900 Km depth, exactly to the "*D"-layer*" a 100-300 km thick layer lying just above the core-mantle boundary, under a pressure of ~ 100 to 135 GPa. In this region, seismic observations provide evidence of heterogeneities in wave propagation and sound velocities. In various works the perovskite to post-perovskite phase transition, that occurs at this pressures, is invoked as the reason for this heterogeneities.

CONCLUSIONS AND OUTLOOK

An approach based of the Bader's topologycal analysis of the *ab-initio* computed electron density has been successfully applied to the characterization of two mineralogical phases, namely the ringwoodite and the Mg-perovskite, under high pressure conditions.

The proposed approach proved to be a useful method for the investigation and the prediction of phase changes or phase breakdowns occurring under conditions at which laboratory experiments are extremely difficult, such as those of the lower mantle phases.

The present analysis, characterizing the electron arrangement in the polymorphs, allowed us to determine the real coordination environments as a function of pressure and therefore its relationship with the high-pressure transition. Moreover the proposed approach proved to be a useful method for the investigation and the prediction of phase changes which occurs under conditions at which laboratory experiments are extremely difficult.

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