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Synergy Between First-Principles Computation and Experiment in Study of Earth Science

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1. Introduction

Atomic-scale modeling of materials based on first-principles quantum mechanics is playing an important role in a broad range of sciences, such as chemistry, biology, and geophysics. Part of our aim in this article is to introduce the usefulness of atomic-scale modeling of materials to the geoscience field. The structure, dynamics, and evolution of the Earth and other planets depend on processes that take place deep in their interiors. However, these interiors are inaccessible to direct observation due to extremely high pressures and temperatures. Laboratory experiments at high pressures and temperatures can provide important information on the physical properties of materials that constitute the Earth's and planets' interiors. However, recently, a new tool for materials modeling based on first-principles quantum mechanics has come into use for probing the properties of planetary interiors. This method has advanced to the point where it can provide reliable data for conditions of extreme high pressure and high temperature that experiments cannot achieve. High-pressure experimental and materials modeling studies regarding the physical properties of materials were generally presented in separate papers and often with a publication gap of a couple of years. A recent approach using both high-pressure experimental data and first-principles materials modeling was successful in discovering new minerals and predicting the physical properties of many materials at high pressures and temperatures.

This article provides examples of the synergy between first-principles computation and high-pressure experiments. First, the argument for the determination of equations of state for materials used as pressure calibrants in high-pressure experiments is discussed. In this discussion, the advantages and disadvantages of first-principles materials modeling or high-pressure experiments are described. It is hoped that the reader can understand the reliability of both the first-principles materials modeling and the high-pressure experiment. Second, some approaches to the discovery of new materials and the exploration of their physical properties at extremely high pressures and temperatures are described.

2. Pressure scale

It is particularly important to know precisely the temperature and pressure conditions of a system in all scientific fields. However, it is often difficult to determine the temperature and pressure when they are extremely higher than ambient conditions. The uncertainty of the

pressure scale at extremely high temperatures has recently become an open question in earth science. Although "Pressure" is an important index in all science fields, the problem of the uncertainty of a standard scale for pressure is debated in the small earth science community. Extreme pressures and temperatures cause various problems for the earth science discipline. It is known that the Earth's deep interior reaches high temperatures and high pressures. Therefore, when we want to know the behavior of materials that constitute the Earth's interior, it is necessary to investigate materials at temperatures of up to ~6000 K and pressures of up to ~400 GPa. This is greatly different from other scientific fields. For instance, studies at low temperatures are performed quite often in the field of physics, because generally it is easy to observe the essence of the physical phenomenon. Furthermore, the Earth's interior is probed by observing seismic wave velocities, and a detailed 3D map can be used to investigate it. This is a similar to obtaining a X-ray computed tomography (CT) scan of the human body. This approach obtains the change in the elastic properties of the Earth's interior as a 3D map. Thus, we can determine the elastic properties of the Earth's interior as a function of depth (equal to pressure). Our next aim is to know what type of material corresponds to the elastic property determined by the mapping of seismic wave velocities. However, earth scientists face a problem at this step. It is thought that some vast changes in seismic velocities have taken place in the Earth's interior because of phase transitions of materials that constitute the Earth. Therefore, the hypothesized phase transitions have been investigated to determine the pressure at which they occur (equal to depths) in the laboratory, and this hypothesis has been verified. This attempt led to the conclusion that the accuracy of the pressure standards used by earth scientists was not satisfactory. This indicates that the accuracy of the observed mapping of elastic properties of the Earth's interior probed by seismic wave velocities is much better than that of the pressure determined in laboratory experiments. In the past 10 years, this "Pressure" problem has been debated by not only earth scientists, but also by physicists.

Here, the attempt to research a reliable pressure scale is performed by both an experimental and theoretical approach. The combination of both approaches leads to an understanding of the uncertainty of each method, and establishes a new pressure scale that is more reliable than previous scales. We use a molecular dynamics method based on first-principles quantum mechanics for the theoretical approach, and use a method of combining a high-pressure diamond anvil cell apparatus with synchrotron X-ray powder diffraction for the experimental approach. In particular, the first-principles computation approach has developed rapidly in recent years and can reliably predict the interesting physical properties of materials that cannot be investigated by high-pressure experiments. This chapter introduces the reliability of first-principles computation and a new pressure scale obtained by combining computational and experimental methods. Moreover, the essential problem of previous pressure scales is discussed and has been clarified by using the data from our first-principles computations.

2.1 Overview of first-principles techniques

To begin, a brief introduction of the first-principles quantum mechanics calculation is described. The first-principles method can predict various physical properties of materials, which is independent of experimental observations. Although it is best if the Schrödinger equation can be strictly solved based on quantum mechanics, this approach is impossible because most materials have many atoms that contain many electrons. Therefore, simplifications and approximations are needed to solve the interaction with many electrons

in atoms. Examples based on density functional theory (DFT) are shown. DFT is assumed to calculate the physical properties of materials using calculated density of electrons. The reader who wants to achieve a detailed understanding of DFT can turn to several comprehensive papers (Parr & Yang, 1994; Martin, 2004; Kohanoff, 2006). The reliability of DFT calculations depends on the approximation used. A pseudopotential method has been used in classical DFT calculations. The computational speed of this technique is very fast, although the first-principles calculations need huge computer power. In the case of the pseudopotential method, it is assumed that the core electrons play little or no role in the energetics of the material, which depends almost entirely on the valence electrons. The core electrons are not handled directly, and these are replaced by the potential function of the valence electrons. Good results have been obtained in predicting physical properties, because the influence of core electrons is small. However, there is a significant problem in estimating physical properties under extremely high-pressure conditions. The material is compressed at high pressures, and the distance between atoms is shortened. In a word, the overlap of the adjacent electrons is nonnegligible. It is expected that the influence of not only valence electrons, but also the core electrons, cannot be disregarded when this overlap increases. Therefore, it is expected that the pseudopotential method is unsuitable for high-pressure studies. Recently, the all-electron method has been used to estimate the physical properties of materials under high pressures instead of pseudopotential methods. Generally, the all-electron method needs huge computing time, and it is difficult to handle materials with many atoms and/or complicated chemical composition. We use the Projector Augmented Wave (PAW) method, because this is a comparatively fast calculation method in the all-electron approach. In most studies of first-principles calculation, the physical properties of materials have been estimated in the ground state (at 0 K). However, earth scientists want to know the behavior of materials at not only high pressures, but also high temperatures, such as those in the interior of the Earth and other planets. Although it is possible to extrapolate the physical properties at high temperatures from the ground state, this approach has a significant error. Therefore, it is necessary to combine a molecular dynamics method that actually deals with the thermal vibration of atoms to estimate physical properties at high temperatures. We use a calculation code (Vienna *Ab initio* Simulation Package) that combines the first-principles calculation of the all-electron approach with a molecular dynamics method (Kresse & Hafner, 1993; Kresse & Furthmuller, 1996). It is possible to estimate precisely the physical properties of a material under high temperatures and pressures using this method. However, there is a problem in that the maximum number of atoms that can be considered is about several hundred, which is much smaller than Avogadro's constant, because this first-principles molecular dynamics method needs huge computer resources. Moreover, it is almost impossible to calculate the duration of a second in real time; however, the duration of tens of picoseconds can be treated. Therefore, it is necessary to estimate thermodynamic parameters under high temperatures and pressures carefully.

2.2 Reliability of the first-principles calculation

The first-principles calculation is used in various fields, such as physics, chemistry, and material science, and huge efforts to increase the accuracy of the calculation have been attempted. Therefore, developments concerning the first-principles technique are very rapid. However, it is important to determine whether its reliability satisfies our purpose to estimate precisely the physical properties of materials at high temperatures and pressures.

For example, it is generally known that the values of the lattice parameters of most crystals estimated by first-principles calculations have about 1–2% errors compared with experimental values at ambient conditions. Next, we will consider the reliability of first-principles calculations under high pressures, which is our subject of interest.

In Figure 1, the relationship between the volume and the pressure of a high-pressure phase of B2-type sodium chloride (NaCl) is shown. In the case of a crystal that is stable at ambient conditions, it is better to obtain physical properties by an experimental method compared with estimations by first-principles calculations. However, there is an advantage of first-principles calculations to estimate the physical properties of materials that cannot be recovered at ambient conditions by high-pressure experiments. As the high-pressure phase of NaCl cannot be quenched at ambient pressures, a complicated method and/or much time is necessary to obtain good experimental data. In such a case, first-principles calculations have a significant advantage in estimating the physical properties of materials compared with experiments. In this chapter, the reliability of first-principles calculations is considered using the example of the high-pressure phase of NaCl.
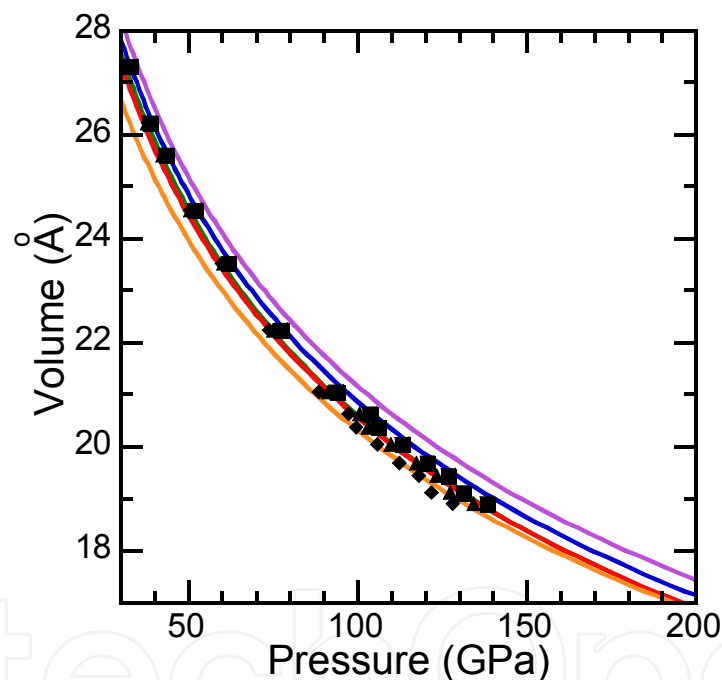

Fig. 1. Comparison of pressure–volume data of B2-type NaCl between high-pressure experiments and first-principles calculations. Symbols represent the experimental data calculated by different gold pressure scales. Diamonds, Jamieson et al. (1982); triangles, Anderson (1989); squares, Takemura (2007) corrected by the ruby scale of Dorogokupets and Oganov (2007). Lines represent the calculated data by different approximations: orange, Local Density Approximation (LDA); purple, PW91 (Wang & Perdew, 1991); blue, HSE06 (Paier et al., 2006); green, AM05 (Armiento & Mattsson, 2005); red, PBEsol (Perdew et al., 2008).

The volume data for the high-pressure phase of NaCl observed by high-pressure experiments at pressures higher than 30 GPa are shown in Figure 1. A high-pressure diamond anvil cell apparatus and a synchrotron X-ray diffraction technique were used to measure volume data at each pressure increment. NaCl powder was mixed with gold powder where the latter was

used as the pressure standard (Ono et al., 2006a). The sample was compressed into a thin pellet, and was sandwiched in the pressure-transmitting medium of magnesium oxide (MgO). This composite sample was placed into the sample chamber of the high-pressure apparatus. It is known that the high-pressure diamond anvil cell-type apparatus has the disadvantage that a significant differential stress is accumulated in the sample chamber during the compression of the sample. Even if a rare gas is used as the pressure-transmitting medium, the influence of differential stress is nonnegligible at pressures higher than ~50 GPa (Takemura, 2007). An alternative approach is annealing the sample using an infrared laser to reduce the differential stress in the sample chamber at each pressure increment. In Figure 1, three experimental data sets are plotted at each volume, because the experimental pressure is calculated using the three proposed pressure scales based on the equation of state for gold (Jamieson et al., 1982; Anderson, 1989; Takemura, 2007). The colored lines are the volume–pressure curves calculated by the first-principles approach. Some types of approximation for the exchange–correlation functional have been proposed. It is necessary to know the exchange–correlation energy between electrons in the materials when the physical properties of the materials are calculated based on the DFT method. As it is difficult to strictly determine the exchange–correlation energy, an approximation must be used. The improvement of the exchange–correlation functional is important for the reliability of the DFT method. Therefore, the results from the different approximations for the exchange–correlation functional are shown in Figure 1. One of the classical approximations is the Local Density Approximation (LDA), where the result is shown as the orange line. Historically, the LDA was partially successful in predicting the physical properties of materials. However, a small difference between the LDA results and the experimental data for the volume–pressure curve of B2-type NaCl is confirmed. For instance, it is known that the volumes of most crystals calculated by the LDA are slightly smaller than those measured experimentally. As the estimations for other physical properties have nonnegligible uncertainties in the LDA method, other approximations were proposed to improve the exchange–correlation functional. One of the other classical approximations is the generalized gradient approximation established by Wang & Perdew (1991) (PW91). The results from the PW91 approximation are also shown as the purple line in Figure 1. In the case of the PW91 approximation, the calculated volumes are larger than are those from experiments. The experimental values of B2-type NaCl are plotted in the intermediate region between the LDA and PW91 calculations. According to previous studies, we understand that the physical properties of materials can be predicted qualitatively using classical approximations. However, it should be noted that further improvements are needed to achieve quantitative predictions. For the last decade, several new approximations have been suggested to improve the accuracy of the DFT calculation. The volume–pressure data calculated by several new approximations are also shown in Figure 1. The results from the new approximations of HSE06 (Paier et al., 2006), AM05 (Armiento & Mattsson, 2005), and PBEsol (Perdew et al., 2008) are in excellent agreement with experimental values, especially at low pressures. This indicates that the computations using the new approximations are likely to produce predictions that are more reliable for the various physical properties of materials.

2.3 Reliability of high-pressure experiments

Next, we will discuss the reliability of data obtained by high-pressure experiments. The three experimental data sets using different pressure standards are plotted in Figure 1. The discrepancy between the different pressure standards increases as the pressure increases.

Thus, the uncertainty of experimental pressures is significant at extremely high pressures. The experimental pressure standards using the equations of state for materials have been determined by a dynamic compression experiment (shock-wave compression experiment) or a static compression experiment (e.g., diamond anvil cell experiment). Shock-wave experimental data have frequently been used to establish and verify a pressure standard. It is useful that the three independent parameters (length, density, and time) can be obtained from each shock-wave experiment and these parameters can be converted to volume, temperature, and pressure, which constitute the equation of state of materials. However, there are a couple of problems in the construction of the equation of state used as the pressure standard by the shock-wave compression data. One of the problems is that the error of the experimental data is great, compared with that of static compression experiments. When the equation of state of a solid is determined and used as the pressure standard, the data from the shock-wave experiments are used sometimes to analyze small changes in thermoelastic parameters, whose changes are smaller than the error in the experimental data. This is quite misleading. Another problem is that there is a significant problem in that an uncertain parameter, such as the Grüneisen constant, is used to estimate the experimental pressure. The dependence of the Grüneisen constant on temperature and pressure has to be assumed with great uncertainty.

On the other hand, static compression experiments also provide invaluable data to investigate a pressure standard. Here, we consider the problem of the pressure standards proposed from previous studies by using the data of the high-pressure phase of NaCl shown in Figure 1. The experimental data in Figure 1 are plotted by using the pressure standards that have been frequently used in previous experimental studies. The difference in pressure data among the different pressure standards indicates the rough size of error for the pressure standard. A comparison of the first-principles calculation and the high-pressure experiment data leads to a valuable discussion. It has already been pointed out that the difference in pressure values obtained by the different approximations used in the first-principles calculation indicates the rough size of the error of the calculations. At low pressures, it is clear that the error in the numerical results is remarkably large compared with the error associated with the experimental data. However, this relationship changes at high pressures. The magnitude of the error in the experimental data increases as the pressure increases, and at pressures higher than ~100 GPa, it becomes almost the same size as the error in the calculation. In addition, this relation is reversed at extremely high pressures. It is known that the difficulty in obtaining reliable measurements increases as the pressure increases, and the error in experimental data becomes significant at high pressures. In the case of the first-principles calculation, the error does not increase as highly when compared with experiments conducted at extremely high pressures. Although significant uncertainties at ambient conditions of the first-principles calculations compared with those of experiments are recognized, the first-principles calculations can provide invaluable data in high-pressure science, where there is great difficulty with experimental approaches.

There is another interesting relationship between the calculated and experimental data. At low pressures, the experimental data are located in the middle of the calculated data. As the pressure increases, the experimental data based on two pressure standards (Jamieson et al., 1982; Anderson, 1989) shift to the low-volume side compared with the calculated values. This indicates that these pressure standards give pressures lower than those from another standard (Takemura, 2007) corrected by the new ruby scale of Dorogokupets & Oganov (2007). The pressures from Takemura's standard are in good agreement with those from the

first-principles calculations using modern approximations. It is believed that the compression data for gold reported recently by Takemura (2007) are among the most reliable. The correction of Takemura's pressure standard is done by one of the reliable ruby standards (Dorogokupets & Oganov, 2007). On the other hand, the experimental data that significantly deviated from the first-principles calculations are based on the old ruby pressure standards (e.g., Mao et al., 1978; Mao et al., 1986). Their pressure standards based on the pressure shift in the fluorescence line of the ruby crystal has been used frequently in many high-pressure studies, especially at ambient and low temperatures. According to the comparison between our numerical results and experimental data, these old ruby standards may underestimate the experimental pressure. Recently, the ruby pressure standard has been revised using experimental data or numerical results by other research groups (Holzapfel, 2003; Kunc et al, 2003; Dewaele et al., 2004; Chijioke et al., 2005; Dorogokupets & Oganov, 2007). These studies reported that the old ruby standards have a significant uncertainty, which is consistent with our study. The underestimation of the old ruby standards seems to be of the order of 5–10%. Finally, we can confirm that the volume–pressure data of B2-type NaCl based on the modern pressure standard are in excellent agreement with those of the first-principles calculations using modern approximations.

2.4 The problem with the Grüneisen constant

Some formulas can be used to describe the equation of state for crystals. For instance, the Mie–Grüneisen–Debye formula has been frequently used because it is simple and easy to apply to various types of systems. Is not there a problem in using this formula? In the Mie–Grüneisen–Debye formula, a thermal pressure (the increase in pressure by heating a solid at constant volume) is expressed as

$$P_{th} = \frac{\gamma}{V} \Delta E_{th} \tag{1}$$

where ΔE_{th}, V, and γ are the internal energy, the volume, and the Grüneisen constant, respectively. The internal energy is given by the Debye's model, and the Grüneisen constant is expressed as a function of the volume.

$$\gamma = \gamma_0 \left(\frac{V}{V_0} \right)^q \tag{2}$$

This expression is the Mie–Grüneisen–Debye equation of state. The Grüneisen constant used in the Mie–Grüneisen–Debye equation of state has a significant problem. This equation indicates that the pressure value might have a large error if the Grüneisen constant has a significant uncertainty. In the case of the Mie–Grüneisen–Debye equation of state, the temperature dependence of the Grüneisen constant is assumed to be negligible. If the temperature dependence of the Grüneisen constant is nonnegligible, the Mie–Grüneisen–Debye equation of state gives misleading values of pressure in the study of solid crystals. Therefore, we verified the dependence of the temperature and the pressure on the Grüneisen constant using the first-principles molecular dynamics method (Ono et al., 2008).
The first-principles molecular dynamics method can directly calculate the internal energy, the volume, and the thermal pressure defined in equation (1), and the dependence of the temperature and the pressure on the Grüneisen constant can also be calculated by using these values. The pressure dependence of the Grüneisen constant included in the Mie–

Grüneisen–Debye equation of state was confirmed and is demonstrated in Figure 2. On the other hand, the temperature dependence neglected in the Mie–Grüneisen–Debye equation
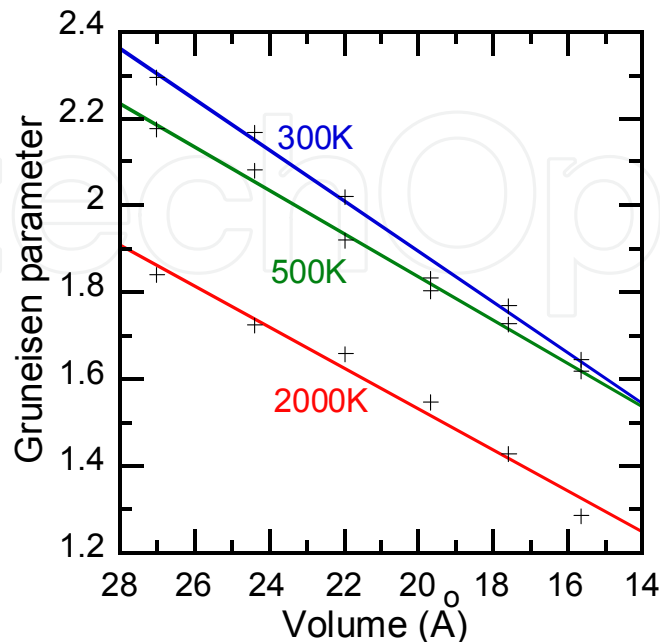

Fig. 2. Calculated Grüneisen parameter. The crosses represent the calculated Grüneisen parameters at 300, 500 and 2000 K using first-principles molecular dynamics calculations. The solid lines denote the linear fit using the least-squares method.

of state is small at temperatures of up to several hundred degrees. However, the difference in the dependence between low and high temperatures could not be neglected especially at temperatures higher than 1000 K. According to this behavior, the Mie–Grüneisen–Debye equation of state can be applied at several hundred degrees at the highest, when it is constructed using experimental data obtained at low temperatures. In other words, the Mie–Grüneisen–Debye equation of state is not suitable for constructing the equation of state of solids applied to a wide range of temperatures, and the pressure standard based on the Mie–Grüneisen–Debye equation of state may involve significant uncertainty. According to Maxwell's relations in thermodynamics, the temperature dependence of the Grüneisen constant at constant volume is given by

$$\left(\frac{\partial \gamma}{\partial T}\right)_V = \frac{1}{T}\left(\frac{\partial \ln C_V}{\partial \ln V}\right)_S \tag{3}$$

When the temperature is much higher than the Debye temperature, the Dulong–Petit law suggests that the specific heat (C_V) is almost constant in solids. That is, the temperature dependence of the Grüneisen constant is extremely small at extremely high temperatures. As the temperature dependence is not small at middle temperatures, it is possible that an obvious difference in the temperature dependence of the Grüneisen constant between low and high temperatures can be confirmed. It can explain the change in the Grüneisen constant calculated by the first-principles molecular dynamic method. Here, the high-pressure phase of NaCl, which is a typical crystal constituted by an ionic bond, has been investigated. It is thought that similar studies for other materials with different bond types,

such as metals or oxides, should be carried out to understand a general rule for the temperature dependence of the Grüneisen constant of solids at high pressures. It is extremely dangerous to use the Grüneisen constant without understanding its behavior at high temperatures, because it is one of the most important parameters to establish the equations of state of solids for not only static compression, but also shock-wave compression experiments. Indeed, most studies on constructing pressure standards have not considered this influence of the Grüneisen constant.

2.5 New pressure standard obtained by first-principles calculations combined with high-pressure experimental data

It is difficult to construct a new pressure standard that is more reliable than those proposed by previous studies using experimental data at high pressures by the first-principles method, because it is clear that the errors are not negligible in the current first-principles computations. On the other hand, we have understood that there are serious problems in determining experimental pressure standards under high pressure because of the uncertainties of the ruby pressure standard or the Grüneisen constant.

Recent approaches to establish a reliable pressure standard employed much previously reported experimental data obtained with static and the shock-wave compression methods to determine the parameters of the equation of state. However, a serious problem is associated with this approach. The previous static compression data used to construct the equation of state are affected directly or indirectly by the old ruby pressure standard. As described above, a significant error is confirmed in the old ruby pressure standards (Mao et al., 1978; Mao et al., 1986), which have been widely used in previous studies. Thus, it is thought that most static compression experimental data used in the construction of the equation of state for the pressure standard have nonnegligible errors. Therefore, it should only be used as fundamental data to construct the equation of state after the problem of the old ruby pressure standard is solved. In Figure 1, one of the experimental data of B2-type NaCl is plotted using the new gold pressure values corrected by the new ruby pressure standard. This is one of the approaches that can be used to avoid the uncertainty of the old ruby pressure standard. Moreover, it is also clear that the problem with the Grüneisen constant must be solved before previous shock-wave compression experimental data are used to establish the equation of state for a reliable pressure standard.

Recently, an attempt to understand an internal consistency among some pressure standards using high-pressure experiments has been reported (Fei et al., 2007), as it is not easy to construct a reliable pressure standard. This approach in constructing a reliable pressure standard also has a major problem. Each experimental data set has a different uncertainty that is dependent on the experimental conditions, such as skill and/or the method. When these experimental data are combined to analyze the pressure standard, the uncertainties of each data are accumulated. The most reliable gold pressure standard used in Figure 1 is established using the compression data of gold reported by Takemura (2007). This compressibility of gold was obtained using the correction of the nonhydrostatic pressure conditions for the experimental data of Takemura (2001) and Dewaele et al. (2004). Both research groups have published many papers concerning the equations of state for solids, and their experimental data have been cited repeatedly. Although the reliability of their experimental skills is recognized in the community of high-pressure science, it is necessary to correct their raw data when we establish a precise pressure standard. This indicates that it is quite difficult to compare the experimental data reported by different research groups that

have different levels of experimental skills and use different methods. In other words, the study of consistency between different pressure standards is difficult without considering experimental errors, such as the nonhydrostatic condition. Indeed, investigation into the consistency of pressure standards while considering the error of each experiment is rare.

In order to overcome the difficulties mentioned above, we have performed an alternative approach of combining high-pressure experimental data and first-principles calculations to make up for each disadvantage. According to our study, the volume–pressure relation of B2-type NaCl estimated by first-principles calculations may have nonnegligible errors. The reliability of high-pressure experimental data obtained at ambient temperatures is better than that of first-principles calculations if an appropriate correction for the experimental pressures is done. Therefore, the reliability of the numerical results is improved considerably if the pressure–volume–temperature data estimated by the first-principles molecular dynamics calculations are corrected based on the experimental data.

On the other hand, it is known that there is significant uncertainty of the temperature in the study of the equation of state of solids reported by previous high-pressure experiments. It is difficult experimentally to determine precisely the thermal pressure and the coefficient of thermal expansion at high temperatures. In the case of the static compression experiments using a large volume press apparatus, a thermocouple is used to measure the sample temperature. The thermocouple indicates the sample temperature using a voltage (EMF) proportional to the temperature difference between two different metal conductors. Although the method has been established at ambient pressures, it is thought that a significant uncertainty is introduced at high pressures. The influence of pressure on the EMF has to be considered in high-pressure experiments. Indeed, most experimental studies have not taken into account this pressure effect on EMF. At higher pressures performed using large volume press experiments, laser-heated diamond anvil cell experiments have often been performed. In this experimental method, the temperature of the sample is estimated using the radiation from the sample during heating. It is known that this temperature measurement has an extremely large error. In addition to the large fluctuation of temperature (~several hundred K) on heating, the conversion from the spectrum of the radiation from the sample to sample temperature has a significant uncertainty that concerns thermal emission. If the sample is an ideal black body, it is simple in that the emissivity is 1. However, the sample is not a black body. Therefore, it is necessary to know the dependence of the emissivity on the temperature, pressure, and wavelength of each material to estimate an accurate temperature from the radiation of the sample. These dependencies under high pressures and temperatures are uncertain. In the case of the shock-wave compression experiments, the experimental data might contain large errors because of the problem concerning the Grüneisen constant mentioned above. Thus, there is a significant advantage in the use of data calculated by first-principles molecular dynamics to know the dependence of the temperature concerning the equations of state for materials.

From the viewpoint mentioned above, an attempt to establish a reliable equation of state for a material to construct a new pressure standard has been performed by combining the data from high-pressure experiments at room temperature with the data from first-principles molecular dynamics calculations at high temperatures. We have already discussed the synergy between the high-pressure experiments and the first-principles computations concerning the equation of state for the high-pressure phase of B2-type NaCl. Recently, a study on a pressure standard of B2-type NaCl combining both experiments and computations has been reported (Ono, 2010a). A study on Ta metal has also been reported

(Ono, 2009). The equations of state of B2-type NaCl and Ta have been revised considerably by these studies. In contrast, a certain amount of error in the parameters of the equation of state concerning the temperature was confirmed in the first-principles molecular dynamics calculations. The error in the calculations is thought to be related to the estimation of the interaction factor between the electrons. As the first-principles computations clarified the interesting features of the ruby pressure standard and the Grüneisen constant, which are important factors to determine the precise equation of state for materials, synergy between first-principles computations and high-pressure experiments is necessary to establish more reliable pressure standards in future studies.

3. Implications for earth science

It is believed that the Earth's and terrestrial planets' interiors consist of oxides and iron compounds. The physical properties of these minerals are important keys to understand their structure, composition, and evolution. Recently, the approach of combining high-pressure experiments with first-principles computations was successful in discovering new minerals and predicting physical properties of minerals at high pressures and temperatures. In this section, some interesting topics are introduced.

3.1 High-pressure phase of iron

The stable structure of iron under ambient conditions is body-centered cubic (bcc) Fe (α-Fe). The phase transition from bcc to the face-centered cubic (fcc) structure (γ-Fe) has been confirmed to occur at a temperature of 1185 K. Under high pressure, the bcc-Fe transforms into the hexagonal close-packed (hcp) structure (ϵ-Fe) (Takahashi and Bassett, 1964), and this structure seems to be stable over a wide range of pressures and temperatures approaching those existing in the Earth's core. It is known that the magnetic and spin states of iron have a major influence on the physical properties of iron. Although the magnetic structure of hcp-Fe has been investigated for over four decades, there is an inconsistency between experimental and theoretical studies. Mössbauer experiments have been interpreted to show the absence of magnetism in hcp-Fe (Williamson et al., 1972; Nasu et al., 2002). In contrast, the theoretical study based on DFT has shown that the antiferromagnetic state is stable at pressures below 50 GPa (Steinle-Neumann et al., 1999). However, it has not been clearly explained why it is difficult to identify the antiferromagnetic state experimentally. A first possibility is that the significant hysteresis of the bcc–hcp transition may disturb the magnetic ordering in hcp-Fe; this is because most previous experiments were performed at low temperatures where the accumulated differential stress in the sample could not be released. Second, the experimental errors of the Mössbauer technique used in previous studies were not negligible, because the antiferromagnetic moment predicted by first-principles calculations is small. Third, the quantum spin fluctuation in hcp-Fe (Mazin et al., 2002) is too fast for the time scale of the Mössbauer measurement, thereby inhibiting detection of a hyperfine field.

We investigated the magnetic properties of hcp-Fe using first-principles calculations to determine the change in the cell parameters. The antiferromagnetic type II structure (space group = *Pmma*) was used in our calculations. The antiferromagnetic type II structure has two different Fe sites, and their magnetic moments are opposed to each other. Figure 3 shows the change in the ratio of the cell parameters of hcp-Fe as a function of pressure. In the case of the antiferromagnetic type II structure, the calculated c/a ratio decreases up to
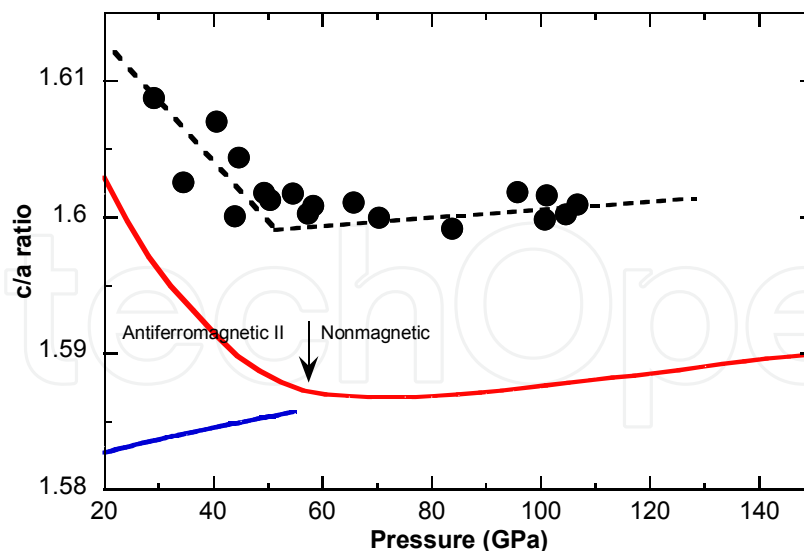
Fig. 3. Changes in the ratio of the cell parameters of hcp-Fe. Black circles represent the c/a ratio from experimental data at room temperature. The red line represents the change in c/a ratio calculated by the first-principles computations including the spin effect at 0 K. The blue line represents the calculated ratio without the spin configuration.

approximately 55 GPa, and then increases slightly with increasing pressure. In contrast, the nonmagnetic type structure without the spin effect shows that the calculated c/a ratio increases simply with increasing pressure. Experimental data (Ono et al., 2010b) are also shown in Figure 3. Although the ratio of the cell parameters from our first-principles calculations is approximately 1% greater than that observed in our experiments, the change in the ratio from the calculations for the antiferromagnetic type II structure is in good agreement with the experimental data. The change in the ratio of the metastable nonmagnetic state calculated without the spin effect is apparently inconsistent with that observed in experiments. The magnetic moment of the antiferromagnetic state decreased gradually, with increasing pressure, and reached zero at approximately 55 GPa (Ono et al., 2010b). The disappearance of the magnetic moment indicates that a magnetic transition occurred from the antiferromagnetic to the nonmagnetic state. As the spin directions of the antiferromagnetic state are oriented perpendicular to the c axis in the hexagonal symmetry cell, and the a axis is less compressible than the c axis, it is therefore clear that a magnetic transition would induce a change in the rate at which the c/a ratio responds to compression. Finally, the disagreement between previous experiments and computations was reconciled by our approach using both first-principles calculations and high-pressure experimental data. This study indicates that the low-spin hcp-Fe is the most stable phase in the Earth's core at pressures of ~350 GPa.

3.2 High-pressure phases of $MgSiO_3$

Seismic measurements infer that the Earth's interior has two layers, the mantle and the core. The core is much denser than the mantle, and consists of iron-rich materials. The chemistry of the mantle can be estimated from information obtained from meteorites and cosmochemistry. This indicates that the composition of the mantle is close to that of the universe as a whole, but with a strong depletion of volatile elements, such as hydrogen,

carbon, and rare gases. According to mineralogy studies, the upper mantle must be dominated by Mg_2SiO_4 compounds (Ono, 2008). In contrast, the lower mantle may consist of $MgSiO_3$ and MgO. High-pressure experiments and first-principles calculations show that $MgSiO_3$ in the lower mantle has a perovskite structure. The nature of the D″ layer at the base of the lower mantle is unique. It has quite a variable thickness and a significant seismic anisotropy. The most plausible explanation is that $MgSiO_3$ transforms from a perovskite to a $CaIrO_3$-type (post-perovskite) structure in this region (Oganov & Ono, 2004). First-principles computations contributed to the discovery of this new mineral.

At first, the $CaIrO_3$-type structure at high pressures was reported by an experimental study of iron oxide (Fe_2O_3) (Ono et al., 2004; Ono & Ohishi, 2005). It is known that one of the high-pressure phases of $MgSiO_3$ has an ilmenite-type structure. The ilmenite-type structure is the same as that of hematite, which is the stable structure of Fe_2O_3 at ambient conditions. Thus, $MgSiO_3$ may have a transition sequence similar to Fe_2O_3, and the $CaIrO_3$-type structure observed in Fe_2O_3 may appear in $MgSiO_3$ at high pressures. This assumption has been confirmed by first-principles computations. Finally, a new mineral of $MgSiO_3$ has been confirmed by both first-principles calculations and high-pressure experiments (Oganov & Ono, 2004). The structure of $CaIrO_3$-type $MgSiO_3$ determined experimentally is shown in Figure 4.

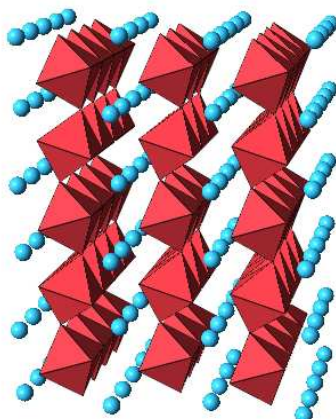Fig. 4. Crystal structure of $CaIrO_3$-type (post-perovskite) $MgSiO_3$ (JCPDS-0580689). Blue spheres are Mg atoms. Polyhedra indicate SiO_6 octahedra. The precise structure was determined by Rietveld refinement (Ono et al., 2006b).

The existence of $CaIrO_3$-type $MgSiO_3$ can explain the unique features at the base of the Earth's lower mantle (Ono & Oganov, 2005). Although at present the $CaIrO_3$-type $MgSiO_3$ phase exists in the Earth's deep interior, the condition of the Earth in the past was quite different from that of present Earth. The Earth's temperature just after its formation was much higher than it is presently. At higher temperatures, the $CaIrO_3$-type $MgSiO_3$ phase in the D″ layer did not exist at the base of the lower mantle, because perovskite-type $MgSiO_3$ is stable deep in the Earth's mantle (Figure 5). Then, the $CaIrO_3$-type $MgSiO_3$ phase appeared during the cooling of the Earth (Ono & Oganov, 2005). The solid inner core, which consists of iron compounds, also appeared during the cooling stage of the Earth.

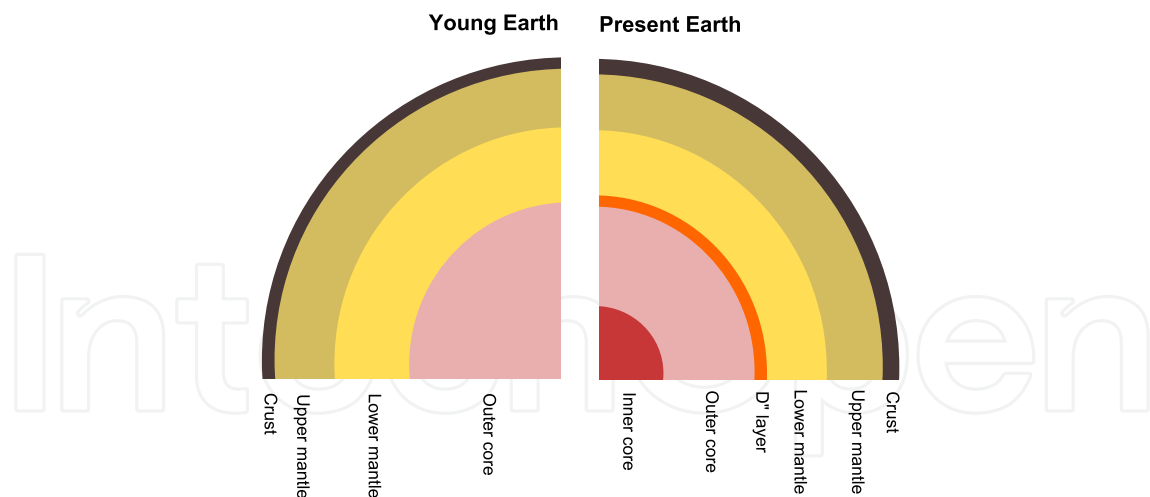**Young Earth**   **Present Earth**

Fig. 5. Structure of the Earth's interior. The temperature of the young Earth was higher than that of the present Earth (Ono & Oganov, 2005).

3.3 High-pressure phases of carbonates

High-pressure polymorphs of carbon-bearing minerals are important to understand the circulation of carbon in the Earth's interior. Therefore, phase transitions and physical properties of high-pressure phases related to carbon have been the object of intense experimental investigation. High-pressure phases of carbonates are likely to be one of the host minerals for carbon that are present deep in the mantle. However, significant discrepancies in the crystal structures of high-pressure carbonates have been reported by previous high-pressure studies because of experimental difficulties. Recent first-principles computations solved some of these experimental discrepancies and contributed to the discovery of several new high-pressure structures.
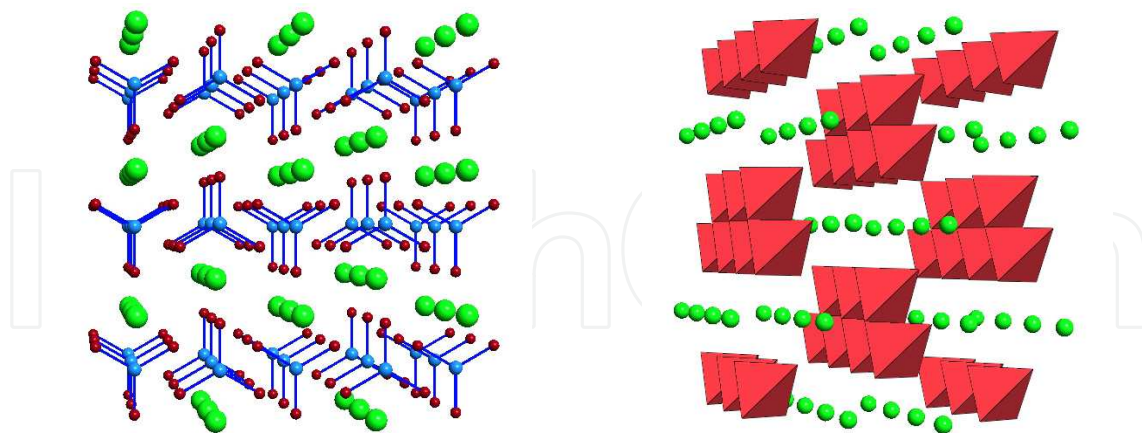
Fig. 6. Crystal structures of high-pressure polymorphs of $CaCO_3$. Left, post-aragonite $CaCO_3$; right, pyroxene-like phase. Green, blue, and red spheres are Ca, C, and O atoms, respectively. Blue bonds indicate triangular CO_3. Red polyhedra indicate CO_4 tetrahedra. The structure was predicted by first-principles calculations (Oganov et al., 2006).

Calcium carbonate ($CaCO_3$) is believed to be a major mineral containing carbon that exists in the deep interior of the Earth. It is generally known that calcite, which is the stable structure of $CaCO_3$ at ambient conditions, transforms to aragonite, which often occurs in

metamorphic rocks, formed at high pressures and temperatures that correspond to the Earth's crust and the uppermost upper mantle. It was unknown whether aragonite transforms to a new high-pressure phase deep in the mantle. Recently, experimental observations indicated that aragonite $CaCO_3$ transformed into a new structure (post-aragonite phase) (Ono et al., 2005). The estimation of the crystal structure of this new $CaCO_3$ had significant uncertainty because of the poor quality of the experimental data. In contrast, the recent approach to determine the unknown crystal structure based on first-principles computation can provide a powerful tool for high-pressure mineralogy. One of the successful codes used in this approach is "USPEX" developed by Oganov & Glass (2008). The computations using the USPEX code solved the unknown structure of the high-pressure phase of $CaCO_3$ (Oganov et al., 2006). This new phase (post-aragonite $CaCO_3$) has an orthorhombic symmetry with space group *Pmmn*, as shown in Figure 6. This study also predicted the existence of another unknown structure with *C222₁* symmetry, which had not been observed in previous experimental studies. One of the interesting features of this new structure is that a change in the coordination number of the carbon atom is predicted. All $CaCO_3$ polymorphs reported in previous studies are composed of triangular CO_3 units. In contrast, the new structure has CO_4 tetrahedron units (Figure 6). After this prediction, high-pressure experiments confirmed the existence of the *C222₁* structure (pyroxene-like phase) (Ono et al., 2007). The transition pressure predicted by first-principles calculations (Oganov et al., 2006) is in excellent agreement with that observed experimentally (Ono et al., 2007). This indicates that the prediction based on first-principles computations is a powerful tool to investigate the behavior of high-pressure phases.

4. Conclusion

In conclusion, we considered uncertainties in the computations based on first-principles quantum mechanics and high-pressure experiments, and introduced a new attempt to construct a pressure standard based on the equations of state of materials using the synergy between the first-principles computations and high-pressure experiments. In the present situation of first-principles calculations, it is difficult for the computation approach to establish the equation of state for materials that are more reliable than that established by experimental data. However, the speed of the development in the field of first-principles calculation is extremely rapid because of the very high demand from many fields, such as physics, chemistry, life science, medicine, and engineering. Therefore, computations based on first-principles quantum mechanics will make an important contribution to the problem of establishing a pressure standard in the near future. Thus, the importance of the combination of experimental and theoretical approaches increases further, and the possibility of a significant breakthrough using this synergy can be expected. Indeed, our approach combining first-principles computations and high-pressure experiments led to a new insight into the interesting behavior of the high-pressure phase of iron. Furthermore, the discovery of a new type of iron oxide (Fe_2O_3) inspired the discovery of a new phase of $MgSiO_3$, which contributes to understanding the properties of the bottom of the Earth's mantle. In the case of carbonate, first-principles computations predicted the structure of new phases that had not previously been identified experimentally, and helped to identify new phases in later experiments. Our investigations into carbonates also contributed to understanding the carbon cycle in the Earth's interior.

5. References

Anderson, O.L., Isaak, D.G. & Yamamoto, S. (1989) Anharmonicity and the equation of state for gold, *Journal of Applied Physics*, (February 1989), Vol.65, No.4, pp.1534-1543, ISSN 0021-8979.

Armiento, R. &Mattsson, A. E. (2005) Functional designed to include surface effects in self-consistent density functional theory, *Physical Review B*, (August 2005), Vol.72, No.8, pp.085108, ISSN 0163-1829.

Chijioke, A.D., Nellis, W.J., Soldatov, A. & Silvera, I.F. (2005) The ruby pressure standard to 150 GPa, *Journal of Applied Physics*, (December 2005), Vol.98, No.11, pp.073526 ISSN 0021-8979.

Dewaele, A., Loubeyre, P. & Mezouar, M. (2004) Equations of state of six metals above 94 GPa, *Physical Review B*, (September 2004),Vol.70, No.9, pp.094112, ISSN 0163-1829.

Dorogokupets, P.I. & Oganov, A.R. (2007) Ruby, metals, and MgO as alternative pressure scales: A semiempirical description of shock-wave, ultrasonic, x-ray, and thermochemical data at high temperatures and pressures, *Physical Review B*, (January 2007),Vol.75, No.2, pp.024115, ISSN 1098-0121.

Fei, Y., Ricolleau, A., Frank, M., Mibe, K., Shen, G. & Prakapenka, V. (2007) Toward an internally consistent pressure scale, *Proc. Natl. Acad. Sci. U. S. A.*, (May 2007), Vol.104, No.22, pp.9182-9186, ISSN 0027-8424.

Holzapfel, W.B. (2003) Refinement of the ruby luminescence pressure scale, *Journal of Applied Physics*, (February 2003), Vol.93, No.3, pp.1813-1818, ISSN 0021-8979.

Jamieson, J.C., Fritz, J.N. & Manghnani, M.H. (1982). Pressure measurement at high temperature in x-ray diffraction studies: gold as a primary standard, In: *High-Pressure Research in Geophysics*, S. Akimoto & M.H. Manghnani, (Ed.), 27-48, Center for Academic Publishing, ISBN 978-902-7714-39-8, Tokyo, Japan

Kohanoff, J. (2006), *Electoinic Structure Calculations for Solids and Molecules : Theory and Computaional Method*, Cambridge University Press, ISBN 978-052-1815-91-8, Cambridge, UK

Kresse, G. & Hafner, J. (1993) *Ab initio* molecular-dynamics for liquid-metals, *Physical Review B*, Vol.47, No.1 (January 1993), pp. 558-561, ISSN 0163-1829.

Kresse, G. & Furthmuller, J. (1996) Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set, *Physical Review B*, Vol.54, No.16, (October 1996), pp. 11169-11186, ISSN 0163-1829.

Kunc, K., Loa, I. & Syassen, K. (2004) Diamond under pressure: Ab-initio calculations of the equation of state and optical phonon frequency revisited, *High Pressure Research*, Vol.24, No.1, pp.101-110, ISSN 0895-7959.

Mao, H-K., Bell, P.M., Shaner, J.W. & Steinberg, D.J. (1978) Specific volume measurements of Cu, Mo, Pd, and Ag and calibration of ruby R1 fluorescence pressure gauge from 0.06 to 1 mbar, *Journal of Applied Physics*, (June 1978) Vol.49, No.6, pp.3276-3283, ISSN 0021-8979.

Mao, H-K., Xu, J.P. & Bell, P. J. (1986) Calibration of the ruby pressure gauge to 800-kbar under quasi-hydrostatic conditions, *Journal of Geophysical Research-Solid Earth and Planets*, (April 1986) Vol.91, No.B5, pp. 4673-4676, ISSN 0148-0227.

Mazin, I.I., Papaconstantopoulos, D.A., & Mehl, M.J. (2002) Superconductivity in compressed iron: role of spin fluctuations. *Physical Review B*, (March 2002), Vol.65, No.10, pp.100511, ISSN 1098-0121.

Martin, R.M. (2004). *Electoinic Structure,* Cambridge University Press, ISBN 978-052-1534-40-6, Cambridge, UK

Nasu, S., Sasaki, T., Kawakami, T., Tsutsui, T., & Endo, S. (2002) Mossbauer study of epsilon-Fe under an external magnetic field, *Journal of Physics Condensed Matter*, (November 2002), Vol.14, No.44, pp.11167-11171, ISSN 0953-8984.

Oganov, A.R. & Ono, S. (2004) Theoretical and experimental evidence for a post-perovskite phase of MgSiO3 in Earth's D″ layer, *Nature,* (July 2004), Vol.430, No.6998, pp.445-448, ISSN 0028-0836.

Oganov, A.R., Glass, C.W. & Ono, S. (2006) High-pressure phases of $CaCO_3$: crystal structure prediction and experiment, *Earth and Planetary Science Letters*, (January 2006) Vol.241, No.1-2, pp.95-103, ISSN 0012-821X.

Oganov, A.R. & Glass, C.W. (2008) Evolutionary crystal structure prediction as a tool in materials design, *Journal of Physics Condensed Matter*, (February 2008) Vol.20, No.6, pp.064210, ISSN0953-8984.

Ono, S., Kikegawa, T. & Ohishi, Y. (2004) High-pressure phase transition of hematite, Fe_2O_3, *Journal of Physics and Chemistry of Solids*, (August-September 2004) Vol.65, No.8-9, pp. 1527-1530, ISSN 0022-3697.

Ono, S. & Ohishi, Y. (2005) In situ X-ray observation of phase transformation in Fe_2O_3 at high pressures and high temperatures, *Journal of Physics and Chemistry of Solids*, (October 2005) Vol.66, No.10, pp.1714-1720, ISSN 0022-3697.

Ono, S. & Oganov, A.R. (2005) In situ observations of phase transition between perovskite and $CaIrO_3$-type phase in $MgSiO_3$ and pyrolitic mantle composition, *Earth and Planetary Science Letters*, (august 2005), Vol.236, No.3-4, pp.914-932, ISSN 0012-821X.

Ono, S., Kikegawa, T., Ohishi, Y. & Tsuchiya, J. (2005) Post-aragonite phase transformation in $CaCO_3$ at 40 GPa, Am. Mineral., *American Mineralogist*, (April 2005), Vol.90, No.4, pp.667-671, ISSN 0003-004X.

Ono, S., Kikegawa, T. & Ohishi, Y. (2006b) Structural properties of $CaIrO_3$-type $MgSiO_3$ up to 144 GPa, *American Mineralogist*, (February-March 2006)Vol.91, No.2-3, pp.475-478, ISSN 0003-004X.

Ono, S., Kikegawa, T. & Ohishi, Y. (2006a) Structural property of CsCl-type sodium chloride under pressure, *Solid State Communications*, Vol.137, No.10, (March 2006), pp. 517-521, ISSN 0038-1098.

Ono, S., Kikegawa, T. & Ohishi, Y. (2007) High-Pressure Transition of $CaCO_3$, *American Mineralogist*, (July 2007), Vol.92, No.7, pp.1246-1249, ISSN 0003-004X.

Ono, S. (2008) Experimental constraints on the temperature profile in the lower mantle, *Physics of the Earth and Planetary Interiors*, (November 2008), Vol.170, No.3-4, pp.267-273, ISSN 0031-9201.

Ono, S., Brodholt, J.P., Alfè, D., Alfredsson, M. & Price, G.D. (2008) Ab initio molecular dynamics simulations for thermal equation of state of B2-type NaCl, *Journal of Applied Physics*, (January 2008), Vol.103, No.2, pp.023510, ISSN 0021-8979.

Ono, S. (2009) First-principles molecular dynamics calculations of the equation of state for tantalum, *International Journal of Molecular Sciences*, (October 2009), Vol.10, No.10, pp.4342-4351, ISSN 1422-0067.

Ono, S. (2010a) The equation of state of B2-type NaCl, *Journal of Physics: Conference Series*, Vol.215, (March 2010), pp. 012196, ISSN 1742-6588.

Ono, S., Kikegawa, T., Hirao, N. & Mibe, K. (2010b) High-pressure magnetic transition in hcp-Fe, *American Mineralogist*, (May-June 2010), Vol.95, No.5-6, pp.880-883, ISSN 0003-004X.

Paier, J., Hirschl, R., Marsman, M. & Kresse, G. (2005) The Perdew-Burke-Ernzerhof exchange-correlation functional applied to the G2-1 test set using a plane-wave basis set, *Journal of Chemical Physics*, (June 2005), Vol.122, No.23, pp.234102, ISSN 0021-9606.

Parr, R.G. & Yang, W. (1994). *Density-Functional Theory of Atoms and Molecules*, Oxford University Press, ISBN 978-019-5092-76-9, Oxford, UK

Perdew, J.P., Ruzsinszky, A., Csonka, G.I., Vydrov, O.A., Scuseria, G.E., Constantin, L.A., Zhou, X. & Burke, K. (2008) Restoring the density-gradient expansion for exchange in solids and surfaces, *Physical Review Letters*, (April 2008), Vol.100, No.13, pp.136406 ISSN 0031-9007.

Steinle-Neumann, G., Stixrude, L. & Cohen, R.E. (1999) First-principles elastic constants for the hcp transition metals Fe, Co, and Re at high pressure. *Physical Review B*, (July 1999), Vol.60, No.2, pp.791-799, ISSN 0163-1829.

Takahashi, T. & Bassett, W.A. (1964) High-pressure polymorph of iron, *Science*, (July 1964), Vol.145, No.3631, pp.483-486, ISSN 0036-8075.

Takemura, K. (2001) Evaluation of the hydrostaticity of a helium-pressure medium with powder x-ray diffraction techniques, *Journal of Applied Physics*, (Juanuary 2001), Vol.89, No.1, pp.662-668, ISSN 0021-8979.

Takemura, K. (2007) Pressure scales and hydrostaticity, *High Pressure Research*, (December 2007), Vol.27, No.4, pp.465-472, ISSN 0895-7959.

Wang, Y. & Perdew, J.P. (1991) Correlation hole of the spin-polarized electron gas, with exact small-wave-vector and high-density scaling, *Physical Review B*, (December 1991), Vol.44, No.24, pp.13298-13307, ISSN 0163-1829.

Williamson, D.J., Bukshpan, S. & Ingalls, R. (1972) Search for magnetic ordering in hcp iron. *Physical Review B*, (December 1972), Vol.6, No.11, pp.4194-4206, ISSN 0163-1829.
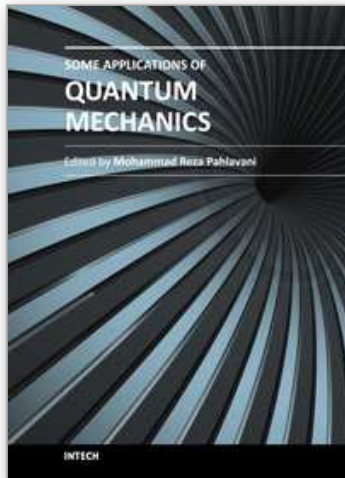
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Edited by Prof. Mohammad Reza Pahlavani

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