HIGH PRESSURE FROM FIRST PRINCIPLES

INTRODUCTION

Properties of inorganic and organic materials under high pressure are of great fundamental and applied relevance. However, the experimental determination of structures and properties under extreme conditions is often difficult and sometimes impossible due to limitations of the available experimental approaches. Fundamental scientific problems that require this information are related, e.g., establishing the nature of materials at pressure and temperature conditions corresponding to those found in planetary cores or in the interior of giant gas planets where only very limited experimental information exists. The challenge is to find the likely structures of crystals formed by small molecules such as H2, NH3, etc., and to predict the properties (mostly mechanical, such as elastic coefficients) of alloys, such as the iron-nickel alloy which is present in the Earth's core. At slightly less extreme conditions such as in the Earth's upper mantle, the problems are often related to establishing the stability and nature of compressed materials that undergo pressure-induced phase transitions. Such transitions can have a dramatic effect on properties; e.g., metal oxides containing magnetic ions such as 3d, 4f and 5f elements can undergo spin collapse that is accompanied by a sharp change in the unit cell volume and in elastic properties (especially compressibility). Insight into these pressure-induced changes is a prerequisite for the interpretation of seismic signatures, which in turn are our only means to study the structure of our planet. In addition to studies at extreme conditions, fundamental understanding of stabilities and structure-property relations and their accurate prediction is vital for evaluation of various materials and of technologies employed for underground storage of nuclear waste materials (for example).

RESEARCH IN FRANKFURT

Professor Björn Winkler, BIOVIA Ambassador, with his group at the University of Frankfurt and with his collaborators worldwide has been successful in promoting the field of Computational Crystallography and in particular of modeling applications relevant to high pressure research and nuclear storage applications. A comprehensive review of the computational methodology for high pressure research is provided in the recent review paper [1]. In its simplest form, computational high-pressure experimentation literally mimics the real laboratory work: external pressure is applied to the crystal and the structure is optimized under the external pressure constraint. Subsequently it is possible to construct the pressure-volume equation of state (EOS), fit EOS using an analytical expression and hence evaluate bulk modulus, B, and its derivative with respect to pressure, B'. It is equally straightforward to investigate pressure-induced phase transitions by comparing enthalpies of different polymorphs as a function of pressure. Finally, one can investigate effect of pressure on material properties, e.g., electronic, vibrational, etc. For example, compression normally reduces interatomic distances and increases overlap between electron densities on neighboring atoms. This results in the broadening of electronic bands, reduction and sometimes even closure of a band gap and hence can cause a metallization transition in a semiconductor or insulator. Most of these studies can be performed using empirical forcefields to describe interatomic interactions, but truly predictive and accurate investigations require quantum mechanical modeling. Density functional theory, DFT, provides a robust and well validated framework for such calculations [1].

Experimental studies that can return similar information are often too expensive and require highly specialized equipment. Professor Winkler's group is one of very few research centers that complement cutting-edge experimental facilities (diamond anvil cells, Raman and infrared spectroscopy, single crystal growth facility, single crystal and powder synchrotron X-ray diffraction, thermodynamic properties measurement) with application of quantum mechanical modeling. All computational experiments described below use BIOVIA Materials Studio® modeling and simulation software to model crystals under extreme conditions.

> "Computational studies of material properties under compression have a long and successful history. Nowadays density functional-based calculations are commonly used to complement and guide expensive and often challenging experimental studies. A set of recent papers provides a comprehensive review of the theoretical methodology and of its applications.
>
> — B. Winkler et al. (Frankfurt University), V. Milman (BIOVIA)

PRESSURE-INDUCED SPIN TRANSITIONS

Recent exciting applications of experimentation and modeling in this group address an important issue of the behaviour of magnetic ions under pressure [2-5]. A pressure-induced volume collapse driven by a high spin to low spin transition is remarkable both as a fundamental scientific effect and a potential route to developing magnetic pressure sensors and switches. The interplay between elastic energy that is stored during compression and magnetic energies of transition metal ions such as Fe and Mn stabilizes low spin state under high pressure. This effect is qualitatively explained by the fact that ions in high spin state typically have bigger ionic radii and hence they become energetically unfavorable when interatomic distances decrease. Computational studies help to understand and quantify spin collapse transitions. They are also useful in estimating spin-pairing energy for electrons that belong to 3d metal ions.

This type of pressure-induced transition has been studied in detail for the Fe-containing garnet andradite [2] and for Mn-containing hydrogarnet henritermierite [3].

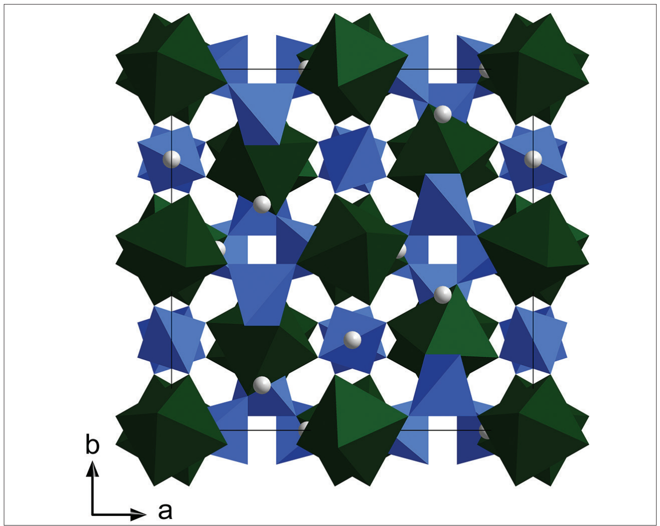

Figure 1: Andradite structure in polyhedral representation (Reproduced with permission from [2] © 2014 American Physical Society)

The cell volume drop at the transition pressure is related to the volume occupied by the metal-centered octahedra in the overall structure. In andradite the cell volume changes by 2.5% while the individual FeO6 octahedra shrink by more than 10%. There is a roughly linear correlation between the fraction of the overall volume occupied by FeO6 octahedra in iron containing o¬xides and the amount of volume change at the spin collapse pressure, Fig.2.

Computational experiment using the CASTEP module of BIOVIA Materials Studio® software provides detailed knowledge of crystal structure as a function of pressure, which helps to relate modifications of internal structure to the experimentally observed changes of the cell volume. For example, the critical Fe-O distance that can still support high-spin state is quantified to be about 1.9 Å, and FeO6 octahedra are shown to become less distorted as a result of the transition. The latter effect is even more pronounced in Mn-containing henritermierite [3], where spin collapse removes Jahn-Teller distortion completely and results in nearly perfect MnO6 octahedra. It is also possible to use computational results to rule out previously suggested speculative theories: i.e., the high spin – low spin transition is not accompanied by the insulator-metal transition, nor is there a hydrogen bond symmetrization in the case of hydrogarnet.

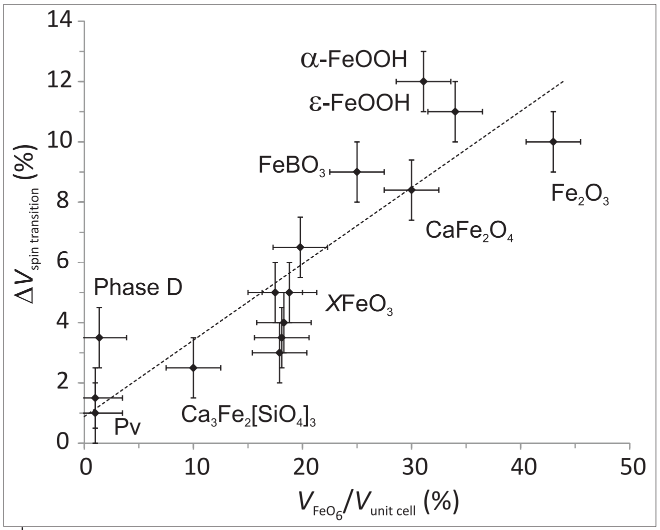

Figure 2: Dependence of the volume collapse at the spin transition on the volume proportion of FeO6 octahedra within the unit cell for Fe3+-bearing oxides. Results are shown for the series XFeO3, X = La, Pr, Nd, Bi, Eu, Lu from bottom to top. A linear regression to the data is plotted as a dashed line. (Reproduced with permission from [2] © 2014 American Physical Society)

These isosymmetric phase transitions in magnetic garnets represent a very delicate example of pressure-induced structural changes where a variety of experimental and theoretical tools is needed to understand fully the nature of a transition.

PRESSURE-INDUCED STRUCTURAL PHASE TRANSITIONS

A more typical example would be a first order phase transition where the symmetry of the structure changes discontinuously at the transition pressure. An investigation of uranium-containing oxide coffinite, USiO4, showed that, with a judicious choice of the theoretical model, one can obtain an accurate description of experimental behaviour and explain the underlying mechanism of the phase transition [4].

The key to successful description of uranium-containing compounds that are extremely relevant in the context of nuclear waste management is the correct representation of highly correlated f-electrons. The DFT+U formulation treats localized d and f electrons using a Hubbard model by adding to the Hamiltonian an explicit term describing strong Coulomb on-site interaction between localized states.

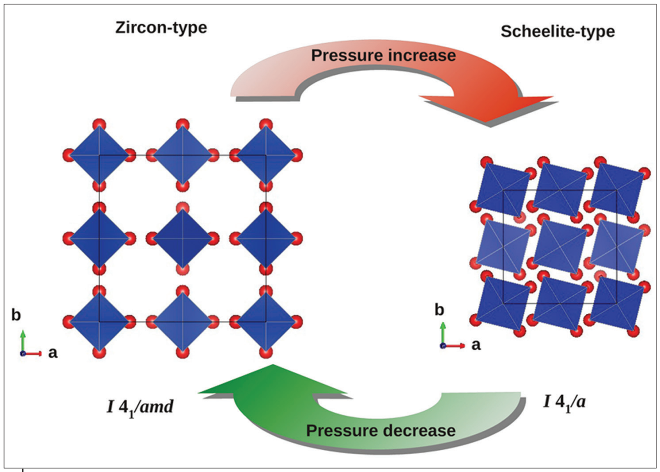

Figure 3: Structural relationship between two structures of USiO4 (Reproduced with permission from [4] © 2014 American Chemical Society)

DFT+U calculated compressibility agrees with experiment to within 5%, which is the standard level of accuracy for elastic coefficients from quantum mechanical calculations. Importantly, it allows us to investigate other properties such as vibrational frequencies and their dependence on pressure. Such analysis helps to interpret experimental spectra by assigning positions of Raman spectra peaks to specific symmetry modes; more importantly, it provides insight into the nature of lattice instability that causes phase transition.

In the case of coffinite, it was shown [4] that there is a pressure-induced decrease of the frequency of the silent mode with B2u symmetry which becomes imaginary at the transition point. The presence of a soft mode at Γ point implies that the lattice becomes energetically unstable with respect to the atomic displacements along the mode in question. It is particularly relevant in this case that the soft mode is silent, i.e., it cannot be measured with Raman or in infrared spectroscopy. In this case computational experimentation provides unique insight into the mechanism of phase transition.

A family of compounds that exhibits an unusually wide range of possible anionic and cationic substitutions is A2B2O7 pyrochlores. This ability to accept numerous additional ions makes them valuable matrix materials for nuclear waste disposal. High pressure behaviour is important in this context, as it expands our knowledge of the interatomic interactions in the crystal structure. See the recent study of Sm2B2O7 pyrochlore combined single crystal synchrotron X-ray diffraction in diamond anvil cell with CASTEP modeling [5].

Computed structural characteristics describe experimental findings very well (see Fig. 4), and the combination of theory and experiments allowed the authors to dispel earlier speculations regarding amorphization or order-disorder transition in this material under pressure. This careful study underlines the importance of using appropriate pressure- transmitting medium when investigating materials that are sensitive to nonhydrostatic conditions.

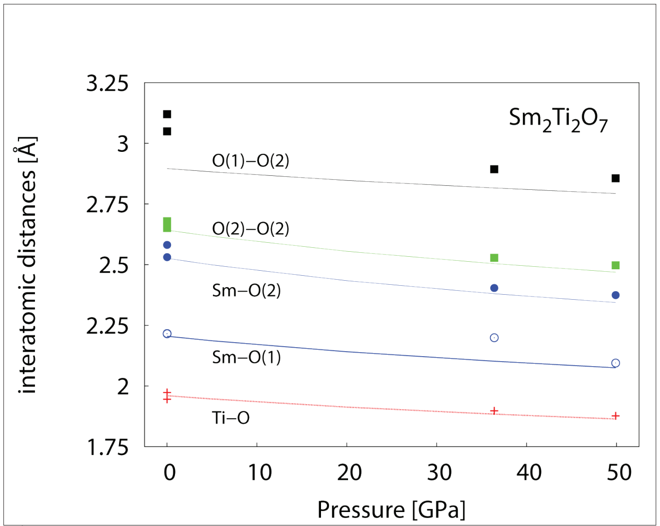

Figure 4: Experimental and theoretical bond lengths in $Sm_2Ti_2O_7$ pyrochlore up to 50 GPa [5] © 2014 Springer

POLYMERS AND MOLECULAR CRYSTALS

High pressure studies are not limited to crystalline inorganic materials; the same combination of DFT tools with X-ray diffraction and Raman spectroscopy has been applied recently to investigate local atomic structures of liquid and polymerized CO and its decomposition products up to 30 GPa in diamond anvil cells [6].

The initial object for investigation was liquid CO. Pair distribution function analysis and comparison with CASTEP results for crystalline phases of CO showed a pronounced short-range order in the liquid phase. The pressure-induced polymerization of molecular CO with the creation of random polymer network is illustrated in Fig. 5.

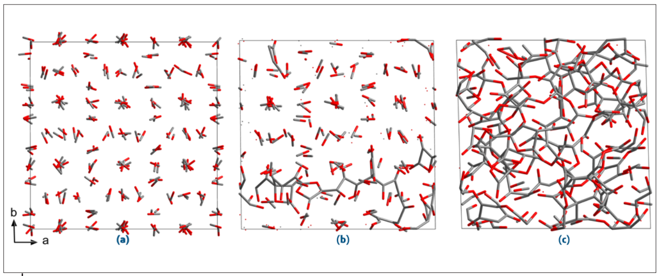

Figure 5: Structures of 432 atom model of δ-CO optimized at 3 GPa (a), 7 GPa (b) and 18 GPa (c) [6] © 2014 Wiley-VCH

Further analysis showed that the likely models consist of a random network of 4-, 5-, and 6-membered cyclic ethers and lactones and carbonyl groups decorating the rings as well as long bent carbon chains with carbonyl groups and bridging atoms. The ring structures were a minor feature in the models. Laser heating of polymerized CO at high pressure resulted in the formation of CO2 and probably graphitic carbon. The laser-induced decomposition of a quenched sample at ambient conditions yielded disordered amorphous graphite.

This study adds useful information to the general research topic – which compositions in the C-H-N-O system can provide quenchable polymerization under pressure.

A common question relevant to such studies of molecular crystals under pressure is the accuracy of DFT description of weakly bonded van der Waals systems. This issue has been discussed in detail by Schatschneider et al. [7] using olygoacenes as an example. The main conclusion is that the use of dispersion correction in the DFT-D formalism [8] provides an accurate and efficient technology to study weakly bonded molecular assemblies. It is reasonable to expect that the accuracy of the method improves in high pressure studies where intermolecular distances become smaller and the role of dispersion interactions decreases.

Another recent application of the DFT-D formalism is a study of pressure-induced structural changes in sulfur hexafluoride SF6, a widely used insulator material in the electrical industry [9]. A combination of X-ray diffraction, Raman spectroscopy and CASTEP DFT-D calculations was used to establish the high-pressure phase diagram of this compound. Dispersion correction is important in applying DFT methodology to a crystal like SF6 that consists of weekly bonded molecules. Even with this correction and with extremely accurate computational settings, the lattice parameters are ≈2.5% too large compared with the experimental data for the ordered phase. However, the computed effect of pressure on the structure and properties is in excellent agreement with the results of measurements – e.g., both the bulk modulus and its pressure derivative agree with the experimental result within the measurement error. Interestingly, DFT results confirm the experimental finding of an unusually high value of the pressure derivative of the bulk modulus, B'. The value in excess of 7 is in agreement with earlier measurements for other molecular solids. It transpires that the second order Birch-Murnaghan equation of state, which is usually quite accurate for inorganic substances, is inapplicable for molecular solids.

SUMMARY

Accurate DFT calculations with the settings appropriate for the systems studied (DFT+U for compounds of d- and f-elements, DFT-D for molecular crystals) reproduce the material response to external pressure well. Combining theoretical studies with experimental data – structural, spectroscopic and thermodynamic – provides valuable insights into the nature of changes in crystallographic and electronic structure caused by external pressure.

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