Usage Report for Fiscal Year 2018

Project Title:

Prediction of Crystal Structure and Properties

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1. Background and purpose of the project, relationship of the project with other projects

Behavior of materials under the extreme environments, such as silicate minerals, liquid- and solid-iron in deep Earth and planets, are still unknown. Our goal is to establish the basic knowledge to understand the history of Earth from the cradle to the grave (project: Q18416) by exploring the properties of these materials with the first principles molecular dynamics simulation and cooperating with researchers of high pressure experiment and earth sciences.

2. Specific usage status of the system and calculation method

System: Hokusai bwmpc

Jobs: vnode=4, vnode-core=40, vnode-mem=60000Mi

Used: ~60% of the total allocated CPU hours.

Method: DFT Geometry optimization (Quasi-Newton method) with meta-GGA(SCAN) + van der Waals (rVV10) functional implemented in Quantum Espresso package. The number of k-points in the irreducible Brillouin zone was equal to 88 (the 5 x 5 x 7 Monkhost-Pack sampling). The kinetic energy cutoff for wavefunctions was set at 150 Ry with 10-9 Ry total energy convergence for one SCF cycle. Variable-cell optimization was carried out in order to optimize both lattice parameters and atomic coordinates. A unit cell consists of 8 oxygen atoms. The Broyden - Fletcher - Goldfarb - Shanno (BFGS) algorithm18 was used for optimization of both ion positions and unit cell vectors under pressure. The convergence threshold on forces for ionic minimization was set at 10-3 a.u.

3. Result

The optimization method was applied to solid oxygen. For the first time, DFT levels (GGA+vdW-D+U and SCAN+rVV10) can predict the epsilon-zeta transition at high pressure, e.g. 70 GPa, which is closed to the experimental value 90 GPa.

The GGA+vdW-D+U calculations were performed with the various values of the same constant U_{eff} for all pressures and all inequivalent atoms as well as the first principles U_{eff}*'s* estimated for each pressures and each inequivalent atoms using the first-principles linear response method. For non spin-polarized calculation, GGA+vdW-D+U method with the constant U_{eff} (~9.6 eV), which is close to the first principles U_{eff}, predicts the structural transition from the epsilon phase to the zeta phase at 90 GPa, which is closer to the experimentally observed transition pressure (96 GPa) than the transition pressure (70 GPa) predicted by SCAN+rVV10. However, once spin-polarization is allowed, GGA+vdW-D+U method with the first-principles U_{eff} predicts magnetic and crystal structures which have not been observed experimentally. Only when we reduce the value of U_{eff} to 2 eV, which was determined by fitting to the experimental Raman spectrum at low pressure (~10 GPa), GGA+vdW-D+U method predicts the crystal structure close to the experimental one and magnetic epsilon phase up to 20 GPa, while the epsilon-zeta transition reduces to 50 GPa. The limitation of the linear response method in considering the screening effect of the opposite spin channel of the same site may be an origin of the failure of the linear response method at low pressure (~10 GPa). Spin-polarized SCAN+rVV10 predicts crystal structures reasonably

consistent with the experiment in the whole pressure range without any hand-waving parameters and also it predicts magnetic epsilon phase up to 20 GPa.

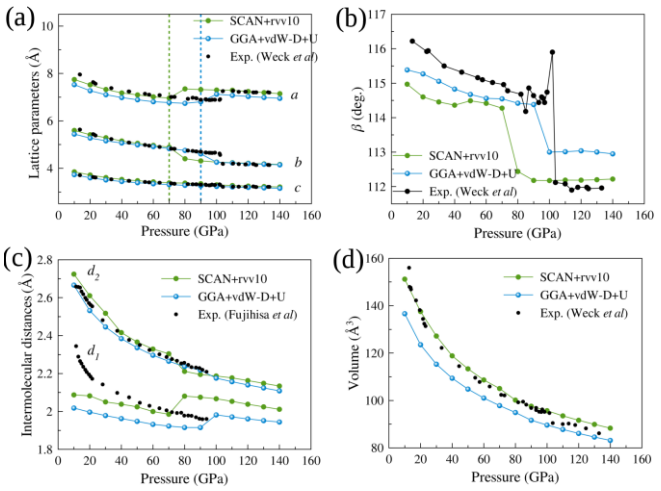

Figure 1. (a-d) Optimized *a, b, c* lattice parameters, β angle, inter-atomic distances d_1, d_2 and volume of an unit cell calculated with non spin-polarized SCAN+rVV10 and GGA+vdW-D+U in comparison with experimental data.

In figure 1(a-d), we shows lattice parameters *a, b, c,* β angle, inter-molecular distance d_1, d_2, and volume of a unit cell calculated using SCAN+rVV10, GGA+vdW-D+U with updated U_{eff} obtained from linear response method in comparison with measurement[1,2]. The parameters from GGA+vdw-D+U are close to those from SCAN+rVV10 although SCAN+rVV10 shows more improvement in overall. In general, non spin-polarized GGA+vdW-D+U (U_{eff} ~ 9eV) can predict reasonable lattice parameters of epsilon-phase of solid oxygen at pressure above 40 GPa and even can predict the epsilon-zeta transitional pressure at 90 GPa which is very close to experimental value 96 GPa. Below 40 GPa, both GGA+vdW-D+U and SCAN+rVV10 underestimate d_1 significantly. It is noted that the experiment was carried out under room temperature. The inconsistency between calculations and experiment may come from the temperature effect: The calculations were done at 0K while the experimental data was obtained at 300K. The structure of epsilon phase at below 40 GPa at low temperature may be different from that at high temperature. This evidence supports to the phase diagram[3] that epsilon phase has two phases at low temperature: magnetic and non magnetic phase, but the magnetic phase disappears at high temperature.

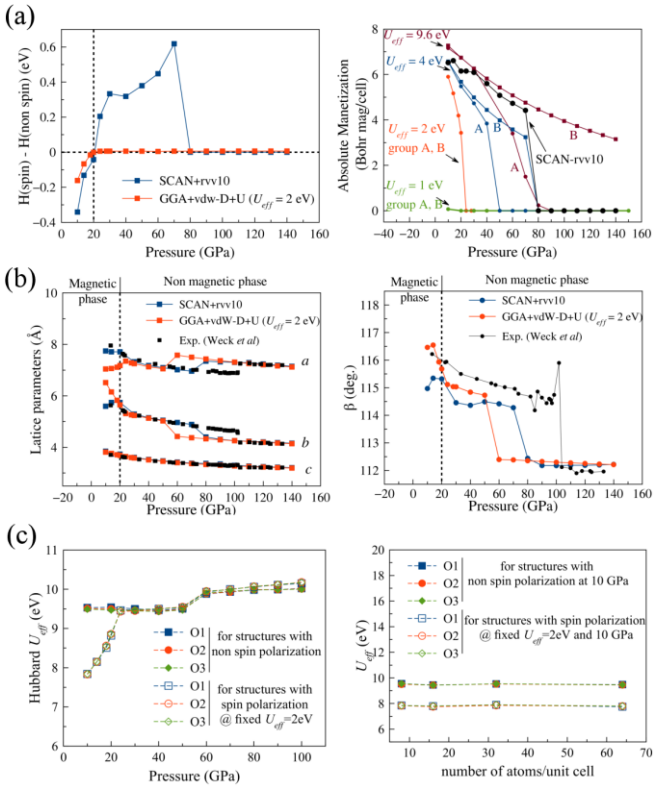

Figure 2. (a) The difference of enthalpies between spin-polarized and non spin-polarized calculations for SCAN+rVV10 and GGA+vdW-D+U (with U_{eff} = 2eV); (b) the optimized lattice parameters a, b, c and β for magnetic phase (below 20 GPa) and non magnetic phase (above 20 GPa); (c) the dependence of U_{eff} in compression (left) and the unit cell' s size (right) in non spin polarization and spin polarization calculated with GGA+vdw-D.

Figure 2(a) shows the difference of enthalpies between spin-polarized and non spin-polarized calculations for SCAN+rVV10 in comparison with GGA+vdW-D+U method with U_{eff} = 2eV. In both methods, the magnetic phase was predicted to be more stable than non magnetic phase up to ~20 GPa. Spin-polarized SCAN+rVV10 also predicted ferrimagnetic order for low-pressure epsilon phase. The magnetization collapses at 70 GPa where epsilon-zeta transition occurs. The result from

SCAN+rVV10 is consistent with the GGA+vdW-D+U with U_{eff}= 2eV where the ferrimagnetic phase also was predicted up to 24 GPa. This suggest that U_{eff}= 2 eV is suitable value for epsilon oxygen at low pressures (below 20 GPa). Moreover, when we compared the absolute magnetization M between SCAN+rVV10 and GGA+vdW-D+U as shown in Figure 8(a), we found that U_{eff}=4 eV gave similar value of M to the SCAN+rVV10's estimation in 10-20 GPa pressure range, U_{eff}=2eV gave a bit smaller M while U_{eff} =9.6 eV results higher value of M. Figure 8(b) show the comparison between SCAN+rVV10, GGA+vdW-D+U and experiment. The lattice parameters *a, b, c* predicted from SCAN+rVV10 are better than those from GGA+vdW-D+U but the β is worse especially at pressure below 20 GPa. Overall, at low pressure (10 ~ 20 GPa), our calculations suggest the existence of magnetic epsilon phase at 0K. Our results also suggest that the value of Hubbard U at low pressure should be about 2 eV, which is much smaller than 9.6 eV predicted by the first-principles linear response method. Figure 8(c) shows the dependence of U_{eff} calculated from the linear response method for non magnetic and magnetic structures with respect to the compression (left) and with respect to the unit cell's size at 10 GPa (right) calculated with GGA+vdw-D. In the left figure, we used structures from non spin-polarized optimization to calculate U_{eff} with non spin-polarization and used structures from spin-polarized optimization with fixed U_{eff} = 2eV to calculate again U_{eff} with spin-polarization. We want to see the difference of the first-principles U_{eff} in non magnetic and in magnetic structures. The values of U_{eff} for magnetic structures are still high (~ 8 eV) but smaller than those for non magnetic structures (~ 9.6-10 eV) at pressure below 24 GPa. The difference becomes very small at pressure above 24 GPa where the enthalpy comparison shows that the structures are non magnetic at pressure above 24 GPa. We checked the size dependence of U_{eff} at 10 GPa as shown in the right figure. The values of U_{eff} virtually do not depend on the size of the unit cell in both non spin polarization and spin polarization. These results encourages the argument that the epsilon phase at low pressure (≤20 GPa) is magnetic phase. The limitation of the linear response method in accounting screening effect of the opposite spin channel of the same site was demonstrated in recent paper[4]. This fact explain to our result that the U_{eff} values (~8 eV) for magnetic phase are still high.

4. Conclusion

The SCAN+rVV10 was considered as the most accurate DFT method to treat molecular crystalline structures. We reported the DFT calculations in predicting structural, electronic and magnetic properties of epsilon phase of solid oxygen using GGA+vdW-D+U and meta-GGA (SCAN)+vdW functionals (rVV10) methods. The GGA+vdW-D+U calculations were performed with the various values of the same constant U_{eff} for all pressures and all inequivalent atoms as well as the first principles U_{eff}'s estimated for each pressures and each inequivalent atoms using the first-principles linear response method. For non spin-polarized calculation, GGA+vdW-D+U method with the constant U_{eff} (~9.6 eV), which is close to the first principles U_{eff}, predicts the structural transition from the epsilon phase to the zeta phase at 90 GPa, which is closer to the experimentally observed transition pressure (96 GPa) than the transition pressure (70 GPa) predicted by SCAN+rVV10. However, once spin-polarization is allowed, GGA+vdW-D+U method with the first-principles U_{eff} predicts magnetic and crystal structures which have not been observed experimentally. Only when we reduce the value of U_{eff} to 2 eV, which was determined by fitting to the experimental Raman spectrum at low pressure (~10 GPa), GGA+vdW-D+U method predicts the crystal structure close to the experimental one and magnetic epsilon phase up to 20 GPa, while the epsilon-zeta transition reduces to 50 GPa. The limitation of the linear response method in considering the screening effect of the opposite spin channel of the same site

may be an origin of the failure of the linear response method at low pressure (~10 GPa). Spin-polarized SCAN+rVV10 predicts crystal structures reasonably consistent with the experiment in the whole pressure range without any hand-waving parameters and also it predicts magnetic epsilon phase up to 20 GPa.

References:

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2.Y. Crespo, M. Fabrizio et al., Collective spin 1 singlet phase in high-pressure oxygen, PNAS 111 (29), 10427-10432, (2014).

3.H. Fujihisa, Y. Akahama, et al., O8 Cluster structure of the epsilon phase of solid oxygen, Phys. Rev. Lett., 97, 085503, (2006).

4.Edward B. Linscott, Daniel J. Cole, Michael C. Payne, and David D. O'Regan, Role of spin in the calculation of Hubbard U and Hund's J parameters from first principles, Phys. Rev. B 98, 235157, (2018).

５． Schedule and prospect for the future

The results is submitting to Scientific Reports journal. The experiment about X-ray Raman Scattering which enables us to clarify fine structures of solid oxygen under low temperature may be carried out in the future to double-check the predictions from SCAN+rVV10 calculations. We want to continue using this system in the future.

Usage Report for Fiscal Year 2018

Fiscal Year 2018 List of Publications Resulting from the Use of the supercomputer

[Oral presentation]

1.Le The Anh, Masahiro Wada, Hiroshi Fukui, and Toshiaki Iitaka, "The first-principles calculation of K-edge X-ray Raman spectrum (XRS) of epsilon phase of solid oxygen", The 58th High Pressure Conference of Japan, Nagoya, Japan 2017.

2.第 2 回ポスト「京」萌芽的課題「基礎科学の挑戦」・「極限マテリアル」合同公開シンポジウム, 3rd July 2018, Sendai, Japan.

3.The 59th High Pressure Conference of Japan, 25th - 28th November 2018, Okayama, Japan.