High-pressure phases of calcium: Prediction of phase VI and upper-pressure phases from first principles

Takahiro Ishikawa,[1,*] Hitose Nagara,[2] Naoshi Suzuki,[3] Taku Tsuchiya,[1] and Jun Tsuchiya[4]
[1]*Geodynamics Research Center, Ehime University, 2-5 Bunkyo-cho, Matsuyama, Ehime 790-8577, Japan*
[2]*Division of Frontier Materials Science, Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan*
[3]*Department of Pure and Applied Physics, Kansai University, Suita, Osaka 564-8680, Japan*
[4]*Senior Research Fellow Center, Ehime University, 2-5 Bunkyo-cho, Matsuyama, Ehime 790-8577, Japan*
(Received 5 September 2009; revised manuscript received 29 November 2009; published 31 March 2010)

Comparing enthalpies among the crystal structures which have recently been determined by experiments or been predicted by first-principles calculations, we have reconstructed the phase diagram of calcium and found further high-pressure phases. Our phase diagram predicts that the phase V of an orthorhombic *Cmca* structure exists only in a small pressure range narrower than 10 GPa and it transforms to another phase, phase VI of an orthorhombic *Pnma* structure. In addition, we found that the phase VI prevails about 20 GPa range and transforms to still another phase, phase VII of a tetragonal $I4/mcm(00\gamma)$ structure at 135 GPa and finally takes the hexagonal-close-packed structure above 495 GPa. Calculated results of the superconducting transition temperature T_c on the basis of our phase diagram suggest that T_c of 25 K, which is the experimentally reported highest value in calcium, should have been observed in the phase VI or phase VII, rather than in phase V.

DOI: 10.1103/PhysRevB.81.092104 PACS number(s): 61.50.Ah, 62.50.−p, 74.62.Fj, 74.62.Bf

Interesting pressure-induced structural phase transitions of calcium have been reported by experimental studies. The face-centered-cubic (fcc) structure (Ca-I) at ambient pressure transforms to the body-centered-cubic (bcc) structure (Ca-II) at 20 GPa and then it transforms to the simple cubic (sc) structure (Ca-III) at 32 GPa.[1] In 2005, by further pressurization, the structural phase transitions to the high-pressure phases Ca-IV and Ca-V were found above the Ca-III phase.[2] According to the report, the Ca-III of sc structure transforms to Ca-IV at 113 GPa and then it transforms to Ca-V at 139 GPa. We recently predicted theoretically the structures of the Ca-IV and Ca-V via a metadynamics simulation[3] based on first-principles calculations.[4] The predicted structure of Ca-IV and that of Ca-V are a tetragonal $P4_12_12$ structure with fourfold helical atomic arrangements and an orthorhombic *Cmca* structure with zigzag atomic arrangements, respectively. Those structures were very recently confirmed experimentally, by Fujihisa *et al.*,[5] to be very close to the experimentally determined structures.

The superconductivity in calcium under high pressure is another interesting property which sets in with low transition temperature, T_c, above 50 GPa in Ca-III.[6,7] The transition temperature increases linearly with compression and rises drastically to above 20 K through the structural phase transition from Ca-III to Ca-IV, and it reaches the highest value of 25 K at 161 GPa, which is the champion value of T_c in all elements.[7]

Such interesting structural phase transitions and superconductivity in calcium have brought about many first-principles studies. Very recently other structures have been theoretically predicted. Yao *et al.*[8] explored the structures of Ca-IV and Ca-V by quasirandom method and genetic algorithm, and calculated the superconducting T_c in those structures. They predicted that the crystal structure of Ca-V is *Cmca* which is consistent with our result and the experimental result by Fujihisa *et al.* They guessed, however, that the structure of Ca-IV is an orthorhombic *Pnma* structure and is not $P4_12_12$. From their enthalpy curve of *Pnma*, which shows that the enthalpy of *Pnma* becomes lower than that of *Cmca* above 117 GPa [see Fig. 1(a) of Ref. 8], it seems more natural to consider *Pnma* to be a structure of a higher pressure phase above Ca-V rather than Ca-IV.

In another theoretical study, Arapan *et al.*[9] reported a further phase transition from Ca-V by applying commensurate analogs of the incommensurate host-guest structure, which is observed in scandium phase II, to calcium and comparing the enthalpy with those of other experimentally observed structures up to 180 GPa. The space group of Arapan's structure is a tetragonal $I4/mcm(00\gamma)$ with the parameter γ defined by $\gamma=c_{host}/c_{guest}$, where c_{host} and c_{guest} are lattice parameters along c axis for a host sublattice and a guest sublattice, respectively. They reported that the enthalpy of $I4/mcm(00\gamma)$ becomes lower than that of *Cmca* above 122 GPa and concluded that $I4/mcm(00\gamma)$ is the structure of Ca-VI.

At lower pressures, Gao *et al.*[10] and Teweldeberhan *et al.*[11] made a phonon calculation for sc of calcium and reported that the structural instability of the sc phase below 120 GPa. From eigenvectors of dynamical matrices for imaginary frequency modes, Teweldeberhan *et al.* obtained the mechanically stable structure of an orthorhombic *Cmcm* structure. They confirmed that the enthalpy of *Cmcm* is lower than that of bcc above 37.5 GPa and it continuously transforms to *Pnma* which is predicted earlier by Yao *et al.*[8] as the structure of Ca-IV, above 45.5 GPa.

Very recently Yao *et al.*[12] explored stable structures in the pressure region of Ca-III using the metadynamics and a genetic algorithm of structural search methods and found a tetragonal $I4_1/amd$ structure. They confirmed that the structure has lower enthalpy than *Cmcm* and becomes the most stable structure in the pressure range from 34 to 78 GPa.

The papers on these *Pnma*, $I4/mcm(00\gamma)$, *Cmcm*, and $I4_1/amd$ structures were published around same time. Therefore, the stability among all those structures have not been fully investigated on the equal footing. Then, in this paper,

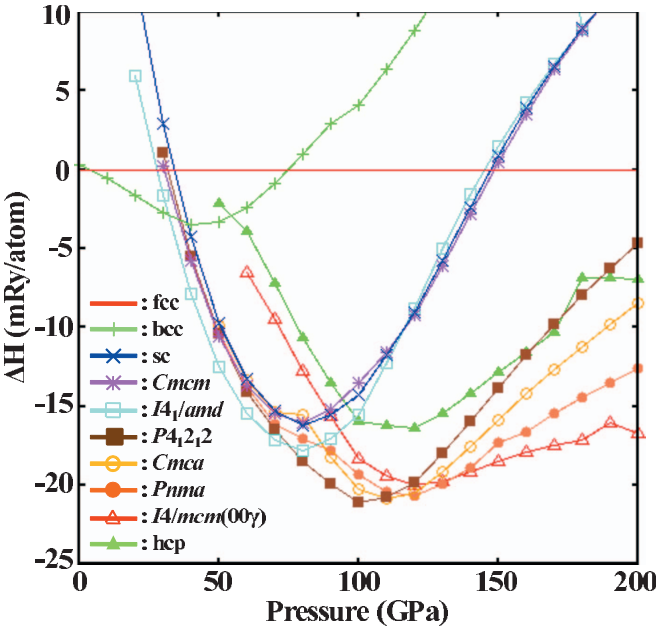

FIG. 1. (Color) Comparison of the enthalpies among all the structures studied in the present work up to 200 GPa. The enthalpy of fcc is taken as the reference. Note that this figure was obtained by adding the enthalpy of $I4_1/amd$, which has been predicted recently by Yao *et al.* (Ref. 12), to Fig. 2(a) of Ref. 13.

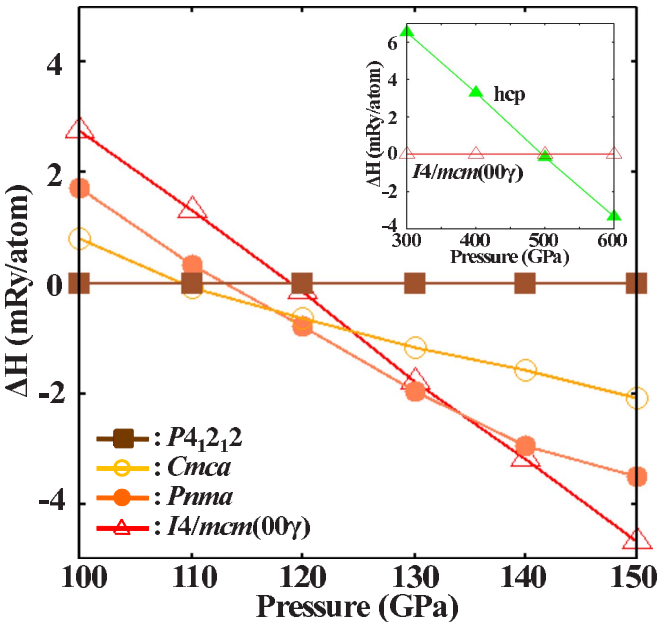

FIG. 2. (Color online) Comparison of the enthalpies among $P4_12_12$, *Cmca*, *Pnma*, and $I4/mcm(00\gamma)$ in the pressure region from 100 to 150 GPa. For $I4/mcm(00\gamma)$, we used the structure of the commensurate analog with $\gamma=4/3$. The inset shows the comparison of the enthalpies between $I4/mcm(00\gamma)$ and hcp from 300 to 600 GPa.

we theoretically study all of these different structures and experimentally observed structures, reconstruct the phase diagram of calcium and propose phases above the Ca-V phase based on the new phase diagram. We also calculate T_c and discuss the superconductivity comparing the behavior of T_c between theoretical and experimental results.

In this work, we employed density-functional theory in a generalized gradient approximation (GGA). For the exchange-correlation energy functional in GGA, we employed the expression by Perdew and Wang[14] and used an ultrasoft pseudopotential (USPP). For constructing USPP of calcium, we regarded ten electrons in the $3s$, $3p$, and $4s$ states as the valence electrons. We set the energy cutoff (E_c) of the plane-wave basis at 40 Ry. We checked the accuracy of our calculation by comparing the enthalpy differences between the results using E_c=40 Ry and those using E_c =80 Ry, and also by comparing the equation of states with all electron results.[15]

All the crystal structures investigated in this study are the following, with the number of the calcium atoms in the unit cell, N_a, and the number of the $\boldsymbol{k}$-point sampling in the Brillouin zone, N_k: fcc (N_a=1, N_k=16×16×16), bcc (N_a=1, N_k=16×16×16), sc (N_a=1, N_k=16×16×16), hcp (N_a=2, N_k=16×16 ×16), *Cmca* (N_a=4, N_k=8×8×8), *Cmcm* (N_a=4, N_k =8×8×8), *Pnma* (N_a=4, N_k=8×8×8), $I4_1/amd$ (N_a =4, N_k=8×8×8), $P4_12_12$ (N_a=8, N_k=8×8×8), and $I4/mcm(00\gamma)$ (N_a=32, N_k=4×4×4). For the incommensurate $I4/mcm(00\gamma)$ structure, we used the commensurate analog by setting the value of γ at 4/3, which is the most stable γ according to Arapan *et al.*[9] For all the structures, we ran the structural optimization at each pressure using the QUANTUM ESPRESSO code[16] and compared the enthalpies up to 200 GPa. We also investigated the hcp structure, which has not been experimentally observed but can be considered as the candidate structure of the high-pressure phase.

Figure 1 shows the enthalpies of all the structures relative to fcc up to 200 GPa. Note that this figure was obtained by adding the enthalpy curve of $I4_1/amd$, which has been predicted very recently by Yao *et al.*, to the enthalpy curves of all the structures examined in our very recent work.[13] In this figure, we confirmed that there is no region of stable sc phase at 0 K which has been experimentally reported. Instead $I4_1/amd$ appears from 32 to 74 GPa, which is consistent with the results by Yao *et al.*[12]

This discrepancy between the theories and the experiments has been reported by many other studies. In 2008 Gao *et al.*[10] calculated the phonon dispersion for sc by the use of supercell method and the linear-response method. As the results, they reported large imaginary phonon frequencies along *X*-*M*-*R* and *T*-*M* directions in the Brillouin zone in the pressure range from 40 to 110 GPa. They proposed that either the experimental reinvestigation of the sc phase or the consideration of the anharmonic effect on the phonon frequencies in sc of calcium is needed in order to reconcile the discrepancies between theory and experiment. After the report by Gao *et al.*, Gu *et al.*[17] experimentally reinvestigated the structural phase transitions of calcium and reconfirmed the transition from bcc to sc at 33 GPa, which is consistent with the previous experimental results. They confirmed that sc remains stable above the transition pressure.

In another line of theoretical study, Errea *et al.*[18] showed the importance of the anharmonicity for the stability of the sc phase by solving Schrödinger equation associated with the

imaginary phonon mode at the M point. Yao *et al.*[12] also studied the stability of the sc phase treating only 4*s* electrons as the valence, which is not highly accurate calculation, and obtained sc as the stable structure at 300 K using the metadynamics at high pressures and finite temperature. These studies suggest the importance of the anharmonicity, although more complete treatments may be necessary to confirm the anharmonic effects on the stability of the sc phase at low temperature.

The enthalpy of $P4_12_12$ becomes lower than that of $I4_1/amd$ above 74 GPa. Figure 2 is the closeup of Fig. 1 with respect to the enthalpy of $P4_12_12$ from 100 to 150 GPa. In Fig. 2, $P4_12_12$ is a very stable structure up to 109 GPa and then it makes the structural phase transition to *Cmca*. The *Cmca* structure is stable in a very small pressure range narrower than 10 GPa and it transforms to *Pnma* at 117 GPa. Above 135 GPa, the enthalpy of $I4/mcm(00\gamma)$ becomes lower than that of *Pnma*. The *Cmcm* structure, which has been predicted by Teweldeberhan *et al.*, does not appear in this entire pressure region.

Furthermore, we investigated how much pressure is required for $I4/mcm(00\gamma)$ to transform to another different structure. We compared the enthalpies between $I4/mcm(00\gamma)$ and hcp in the pressure region from 300 to 600 GPa (Ref. 19) (the inset in Fig. 2), where we fixed the value of γ at 4/3. As the result, the enthalpy of hcp becomes lower than that of $I4/mcm(00\gamma)$ above 495 GPa. In addition to $\gamma=4/3$, we investigated the enthalpies for $\gamma=6/5$ and $\gamma=7/5$ at 400 GPa and found that the enthalpy for $\gamma=4/3$ is the lowest of the three. The structure with $\gamma=7/5$ has the second lowest enthalpy and its enthalpy difference between the results for $\gamma=4/3$ and $\gamma=7/5$ is about 0.6 mRy/atom. The enthalpy for $\gamma=6/5$ is much higher by about 6.0 mRy/atom than that for $\gamma=4/3$. Although we have not investigated so many γ's, the structure with $\gamma=4/3$ seems to be the most stable in very wide pressure range. We do not, however, exclude the possibility that some other intermediate phases appear between $I4/mcm(00\gamma)$ and hcp.

In the present calculation, we obtained the following sequence of the structural phase transitions:[20]

$$\begin{aligned}\mathrm{fcc}(0-3.5\ \mathrm{GPa}) &\rightarrow \mathrm{bcc}(3.5-32\ \mathrm{GPa})\\ &\rightarrow I4_1/amd(32-74\ \mathrm{GPa})\\ &\rightarrow P4_12_12(74-109\ \mathrm{GPa})\\ &\rightarrow Cmca(109-117\ \mathrm{GPa})\\ &\rightarrow Pnma(117-135\ \mathrm{GPa})\\ &\rightarrow I4/mcm(00\gamma)(135-495\ \mathrm{GPa})\\ &\rightarrow \mathrm{hcp}(495\ \mathrm{GPa}).\end{aligned}$$

The $P4_12_12$ structure, which corresponds to Ca-IV, transforms to *Cmca*, which corresponds to Ca-V, at 109 GPa and the pressure region of $P4_12_12$ is shifted to a lower pressure region compared with the experimental one. However, we think that the sequence of the phase transitions by the present calculations is consistent with the experimental one except for the sc phase. Actually the structures of Ca-IV and Ca-V were obtained by our previous work using the first-principles calculation prior to the experimental determination.[4]

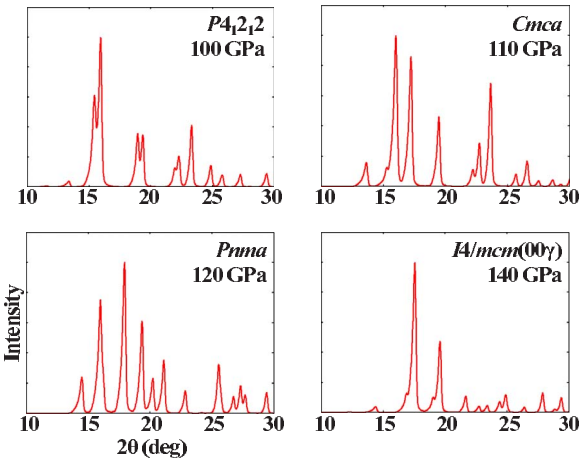

FIG. 3. (Color online) Simulated x-ray diffraction patterns of $P4_12_12$ at 100 GPa, *Cmca* at 110 GPa, *Pnma* at 120 GPa, and $I4/mcm(00\gamma)$ at 140 GPa. The wavelength is set at 0.6198 Å.

Based on the phase diagram thus obtained, we predict that Ca-V exists in the narrow pressure range from 109 to 117 GPa and then it makes the structural phase transition to Ca-VI of *Pnma*. In addition, *Pnma* transforms to $I4/mcm(00\gamma)$ at 135 GPa and we predict that $I4/mcm(00\gamma)$ corresponds to the structure of Ca-VII although the structures of the high-pressure phases above the Ca-V phase have not been experimentally reported yet. Figure 3 shows the simulated x-ray diffraction patterns of $P4_12_12$ at 100 GPa, *Cmca* at 110 GPa, *Pnma* at 120 GPa, and $I4/mcm(00\gamma)$ at 140 GPa. We set the wavelength, λ, at 0.6198 Å. In the diffraction pattern of *Pnma*, strong peaks are widely distributed up to $2\theta=22°$. On the other hand, the number of the peaks decreases through the structural phase transition to $I4/mcm(00\gamma)$.

The transition to the phase Ca-VI is inferred also through the behavior of the superconducting T_c above Ca-IV. We estimated T_c by the use of the Allen-Dynes formula.[21] In calculations of phonon frequency, we employed the linear-response theory in which the first-order corrections are calculated by means of the density-functional perturbation theory.[22,23] The **k**-space integrations for the calculation of the dynamical matrix at each **q** were performed over the $8\times8\times4$ grid and the $8\times8\times8$ grid for the Ca-IV phase and the Ca-V and Ca-VI phases, respectively. The electron-phonon matrix element was calculated using the $32\times32\times32$ **k**-point grid for three structures. This grid ensures the convergence of the **k**-point sampling with Gaussians of width 30 mRy, which approximates the zero-width limits with respect to double-delta functions of phonon line width. For the calculations of the electron-phonon coupling constant λ and the logarithmic-average phonon frequency $\omega_{\log}$, we used the $4\times4\times4$ **q**-point grid. We assumed the screened Coulomb interaction constant μ^* to be 0.1.

In our calculation of T_c in Ca-IV, we obtained T_c of 22 K (Ref. 24) in $P4_12_12$ at 100 GPa which is near the phase boundary between Ca-IV and Ca-V in the present phase diagram. This value is very close to the experimental one.[7] On the other hand, in Ca-V, we obtained $T_c=19$ K at 110 GPa

and it does not match the experimentally observed T_c in Ca-V.[7] In Ca-VI, T_c is higher than that of Ca-V, which is consistent with very recent results by Yin *et al.*,[25] and reaches to 21 K at 120 GPa. By extrapolating T_c of Ca-V and that of Ca-VI calculated above, we can theoretically obtain T_c=25 K around the phase boundary between Ca-VI and Ca-VII in our phase diagram. From this observation, we infer that the highest T_c of 25 K was observed not in Ca-V but in the further phase, Ca-VI or Ca-VII, in the experiment.

In summary, we reinvestigated the phase diagram of calcium at high pressures, taking all theoretically predicted and experimentally reported structures into account. We propose phases Ca-VI and Ca-VII. We also propose that Ca-V is realized in the narrow pressure region of less than 10 GPa and the highest superconducting T_c of 25 K experimentally reported is realized in the Ca-VI or Ca-VII phase.

ACKNOWLEDGMENTS

This work was partially supported by the Ehime Univ. G-COE program "Deep Earth Mineralogy," special coordination funds for promoting science and technology (Supporting Young Researchers with Fixed-term Appointments) and a Grant-in-Aid for Scientific Research from the Japan Society for the Promotion of Science under Grants No. 21740380, No. 20103005, No. 20001005, and No. 21740379.

*ishikawa@sci.ehime-u.ac.jp

[1] H. Olijnyk and W. B. Holzapfel, Phys. Lett. A **100**, 191 (1984).
[2] T. Yabuuchi, Y. Nakamoto, K. Shimizu, and T. Kikegawa, J. Phys. Soc. Jpn. **74**, 2391 (2005).
[3] R. Martoňák, A. Laio, and M. Parrinello, Phys. Rev. Lett. **90**, 075503 (2003).
[4] T. Ishikawa, A. Ichikawa, H. Nagara, M. Geshi, K. Kusakabe, and N. Suzuki, Phys. Rev. B **77**, 020101(R) (2008); see also **78**, 029901(E) (2008).
[5] H. Fujihisa, Y. Nakamoto, K. Shimizu, T. Yabuuchi, and Y. Gotoh, Phys. Rev. Lett. **101**, 095503 (2008).
[6] S. Okada, K. Shimizu, T. C. Kobayashi, K. Amaya, and S. Endo, J. Phys. Soc. Jpn. **65**, 1924 (1996).
[7] T. Yabuuchi, T. Matsuoka, Y. Nakamoto, and K. Shimizu, J. Phys. Soc. Jpn. **75**, 083703 (2006).
[8] Y. Yao, J. S. Tse, Z. Song, D. D. Klug, J. Sun, and Y. Le Page, Phys. Rev. B **78**, 054506 (2008).
[9] S. Arapan, H. K. Mao, and R. Ahuja, Proc. Natl. Acad. Sci. U.S.A. **105**, 20627 (2008).
[10] G. Gao, Y. Xie, T. Cui, Y. Ma, L. Zhang, and G. Zou, Solid State Commun. **146**, 181 (2008).
[11] A. M. Teweldeberhan and S. A. Bonev, Phys. Rev. B **78**, 140101(R) (2008).
[12] Y. Yao, D. D. Klug, J. Sun, and R. Martoňák, Phys. Rev. Lett. **103**, 055503 (2009).
[13] T. Ishikawa, H. Nagara, N. Suzuki, J. Tsuchiya, and T. Tsuchiya, J. Phys.: Conf. Ser. (to be published).
[14] J. P. Perdew, in *Electronic Structure of Solids '91*, edited by P. Ziesche and H. Eschrig (Akademie Verlag, Berlin, 1991), p. 11.
[15] The convergence with respect to the cutoff energy, E_c, has been checked by comparing the enthalpy difference between *Cmca* and *Pnma* ($\Delta H=H_{Pnma}-H_{Cmca}$) with that of increased E_c. At 120 GPa, ΔH's are −0.147 mRy/atom and −0.149 mRy/atom for E_c=40 Ry and 80 Ry, respectively, which shows sufficient convergence. The enthalpy differences have also been checked by comparing our results with those of all electron calculation by the WIEN2K code (Ref. 26). Around 80 GPa, the enthalpy differences between fcc and sc coincide with each other in about 1 mRy.
[16] S. Baroni, A. D. Corso, S. de Gironcoli, and P. Giannozzi, the QUANTUM ESPRESSO code is available through http://www.pwscf.org/
[17] Q. F. Gu, G. Krauss, Y. Grin, and W. Steurer, Phys. Rev. B **79**, 134121 (2009).
[18] I. Errea, M. Martinez-Canales, A. R. Oganov, and A. Bergara, High Press. Res. **28**, 443 (2008).
[19] Around 400 GPa, the relative enthalpies of hcp to fcc obtained in the present calculation coincide within about 1 mRy with that obtained by the all electron calculation.
[20] Note that our pressures of the phase boundaries shown in this paper are absolute values obtained by the calculations and are shifted a little from the experimental values or the other theoretical values because of the numerical errors and some unknown reasons. See the similar discussion in Ref. 4. When the equation of states is plotted as a function of the relative volume, it is satisfactory as is shown in the supplementary material of Ref. 8.
[21] P. B. Allen and R. C. Dynes, Phys. Rev. B **12**, 905 (1975).
[22] S. Y. Savrasov, Phys. Rev. B **54**, 16470 (1996).
[23] S. Baroni, S. de Gironcoli, A. D. Corso, and P. Giannozzi, Rev. Mod. Phys. **73**, 515 (2001).
[24] T. Ishikawa, H. Nagara, K. Kusakabe, and N. Suzuki, High Press. Res. **29**, 204 (2009).
[25] Z. P. Yin, F. Gygi, and W. E. Pickett, Phys. Rev. B **80**, 184515 (2009).
[26] P. Blaha, K. Schwarz, G. K. H. Madsen, D. Kvasnicka, and J. Luitz, *WIEN2k, An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties*, edited by K. Schwarz (Technische Universität Wien, Austria, 2001).