

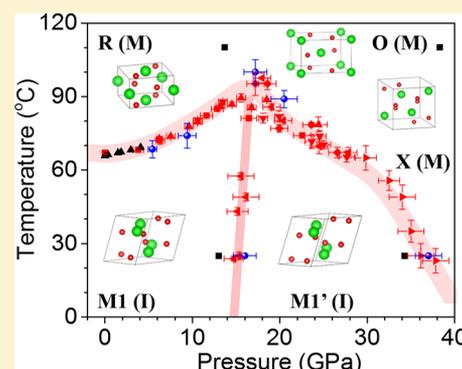
Pressure–Temperature Phase Diagram of Vanadium Dioxide

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Supporting Information

ABSTRACT: The complexity of strongly correlated electron physics in vanadium dioxide is exemplified as its rich phase diagrams of all kinds, which in turn shed light on the mechanisms behind its various phase transitions. In this work, we map out the hydrostatic pressure–temperature phase diagram of vanadium dioxide nanobeams by independently varying pressure and temperature with a diamond anvil cell. In addition to the well-known insulating M1 (monoclinic) and metallic R (tetragonal) phases, the diagram identifies the existence at high pressures of the insulating M1' (monoclinic, more conductive than M1) phase and two metallic phases of X (monoclinic) and O (orthorhombic, at high temperature only). Systematic optical and electrical measurements combined with density functional calculations allow us to delineate their phase boundaries as well as reveal some basic features of the transitions.

KEYWORDS: VO₂, phase transition, phase diagram, hydrostatic pressure, diamond anvil cell



Vanadium dioxide (VO₂), as a prototype of strongly correlated electron materials, is of great interest in condensed matter physics as well for device applications.^{1–3} The electron correlation interplaying with lattice stabilizes a very rich phase diagram of VO₂ that consists of many phases with distinct structures and electronic properties. Transitions between these phases can be driven by temperature, photo-excitation, hydrostatic pressure, uniaxial stress, or electrical gating.^{1,4–12} For example, the well-known, insulating M₁ (monoclinic, space group *P2₁/c*) phase transforms to the metallic R (tetragonal, *P4₂/mmm*) phase at 68 °C under ambient pressure.¹ This M₁–R transition can also be driven by hydrostatic pressure⁶ or uniaxial compression.⁴ The application of hydrostatic pressure is a clean and powerful way to tune the lattice and electronic degrees of freedom. Hydrostatic pressure applied via a diamond anvil cell (DAC) has also been able to drive the M₁ phase to another isostructural, more conductive M₁' phase, and finally a new metallic X (monoclinic) phase at room temperature, and to drive the metallic R phase to new metallic O and X phases at 383 K.⁹ A pressure–temperature phase diagram has been proposed for VO₂.⁸ However, this phase diagram with three regions of M₁, M_X, and R is largely schematic, and their phase boundaries, especially at high pressures, are unclear, undefined, and unsubstantiated with experimental data. In this work, we establish a clear hydrostatic

pressure–temperature (*P*–*T*) phase diagram for VO₂, quantitatively delineating the phase boundaries between the M₁, M₁', R, O, and X phases, and provide comparisons to first-principles calculations.

The phase transitions were identified within a heated DAC by various techniques, including Raman spectroscopy, optical reflectance, and electrical transport. The VO₂ nanobeams used in this work were grown using a vapor transport method.¹³ They typically have a flat surface and small (<1 μm) thickness, and exhibit a single-domain, sharp metal–insulator transition (MIT) at *T*_{MIT} = 68 °C, with a narrow hysteresis. All high-pressure experiments were performed in a four-post DAC with 300 μm culet size (see Supporting Information). The pressure-transmitting medium was a mixture of methanol–ethanol (4:1) and Daphne 7373, for Raman and electrical measurements, respectively. A quasi four-probe geometry was used for the electrical measurements using Pt foil as electrodes, and the microdevice fabrication method can be found elsewhere.¹⁴ High temperatures were realized by heating the DAC in a water bath or with heating belts. The pressure was calibrated with the standard method of ruby photoluminescence.¹⁵ The temper-

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ature was measured with a thermocouple placed very close to the gasket chamber. Theoretical calculations were performed within the framework of density functional theory (DFT). Electron–electron exchange and correlation effects were described by the generalized gradient approximation with the Perdew–Burke–Ernzerhof (PBE)¹⁶ functional plus Hubbard U .¹⁷ The density-functional or Kohn–Sham equations were solved with the plane-wave pseudopotential method, as implemented in Vienna ab initio Simulation Package.^{18,19} The k -mesh for sampling the Brillouin zone and plane-wave cutoff energy for expanding the electronic wave functions were chosen such that the total energies were converged within 0.65 meV/formula unit (f.u.). We chose $U = 3.4$ eV, which produces the bandgap of M1 phase (0.7 eV) correctly.²⁰

Figure 1 shows the phase transition driven by temperature under constant pressure (i.e., isobaric conditions). The pressure

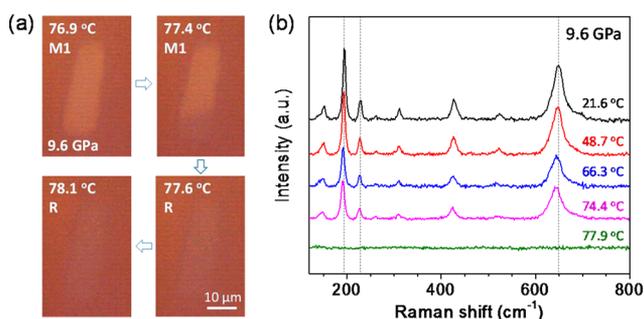


Figure 1. Phase transition of VO₂ driven by temperature under isobaric conditions. (a) Optical images of a VO₂ nanobeam across the M1–R phase transition at fixed pressure of 9.6 GPa. M1 and R phases show bright-yellow and dark-green contrast, respectively. (b) Raman spectrum evolving with temperature at the fixed pressure of 9.6 GPa.

was fixed at 9.6 GPa for experiments in Figure 1. As shown in Figure 1a, a sharp change in optical reflection is seen within a narrow temperature range ($< \sim 0.2$ °C), signifying the transition from the insulating (bright) phase to the metallic (dark) phase, consistent with previous observations on this type of specimens.^{21,22} The very narrow temperature range further confirms the nearly single-domain nature of the phase transition. This is also an indication that the specimens, which are transferred from the as-grown substrate to the diamond surface, sit loosely on the surface instead of being firmly clamped on it, and as such, any strain imposed by the diamond surface onto the specimen is negligible. The lack of strong clamping is also beneficial for the molecules of the

pressure medium to sip in underneath the sample, thus ensuring the hydrostaticity of the pressure transmitted to the sample. Raman spectra of the sample obtained at these temperatures are shown in Figure 1b. From the Raman spectrum, the low-temperature phase is clearly identified as the M1 phase. Combining isotope substitution and density functional theory calculations, it has been established that, in the M1 phase, the two low-frequency peaks of $\omega = 193.9$ and 228.5 cm⁻¹ (at 21.6 °C) correspond to V–V lattice vibration, and all other Raman peaks are related to V–O vibration modes.²³ All of these modes slightly soften with increasing temperature, until reaching the transition temperature, above which all Raman peaks disappear owing to the metallicity of the R phase. The transition temperature obtained by Raman is identical with that obtained by optical reflection. More importantly, the transition temperature of $T_{\text{MIT}} = 77.4$ °C at 9.6 GPa is higher than $T_{\text{MIT}} = 68$ °C at ambient pressure (~ 0 GPa). This is consistent with previous report of a positive slope in the M1–R phase boundary.⁶

At constant temperature (i.e., isothermal condition), the hydrostatic pressure also drives VO₂ from the M1 phase to new phases. Shown in Figure 2a is the Raman spectra taken at fixed temperature of 50 °C with increasing pressure. The Raman peaks of the M1 structure gradually shift to higher wavenumbers with pressure, until very high pressure (~ 33 GPa) where they all disappear, indicating a metallic phase at and beyond that pressure. We mark this metallic phase as the X phase following previous work.⁹ Plotting the pressure dependence of the three most prominent Raman peaks reveals new information, as shown in Figure 2b. It can be seen that the V–O mode at $\omega = 617.5$ cm⁻¹ (2.5 GPa) blue shifts linearly with an initial rate of $d\omega/dP = 4.1$ cm⁻¹/GPa, but then the rate changes to a much shallower, 2.4 cm⁻¹/GPa when the pressure is higher than 16.5 GPa. The two V–V modes, on the other hand, show no obvious change in the slope ($d\omega/dP$). However, we note that, at lower temperatures such as room temperature (Supporting Information, Figure S2), these two V–V modes also show slight slope change at the same pressure where the V–O mode shows the slope change. This is consistent with previous, room-temperature pressure studies.^{7,23} Therefore, before reaching the metallic phase, all of the M1 Raman modes remain, but some (or all, depending on temperature) of them show a change in the pressure rate at ~ 16.5 GPa. This effect points to a continuous phase transition from M1 to a new, insulating M1' phase at this pressure, as suggested also by our previous room-temperature micro-X-ray diffraction (XRD)

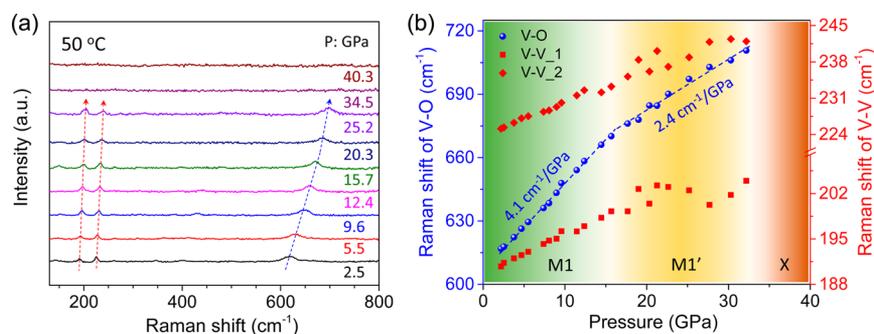


Figure 2. Phase transition of VO₂ driven by pressure under isothermal conditions. (a) Raman spectrum evolving from M1 to M1' and then X phase at fixed temperature of 50 °C. (b) Peak positions of different Raman modes as a function of pressure extracted from panel a.

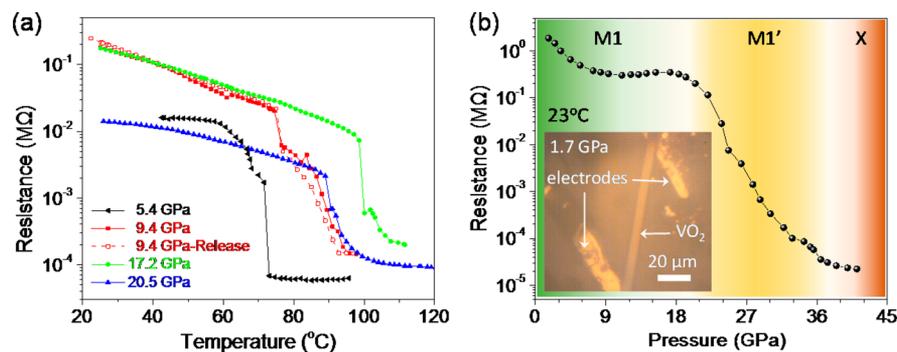


Figure 3. Electrical resistance of VO₂ across the phase transitions driven by temperature or pressure. (a) Temperature dependence of resistance of VO₂ under isobaric conditions. (b) Pressure dependence of resistance of VO₂ at room temperature. The inset is optical image of a quasi-four probe device for electrical measurements.

experiments.⁹ The M1' phase is isostructural to M1, yet with very different electrical resistances as discussed below.

In order to probe the electronic nature of these phases, electrical transport measurements were also performed as a function of pressure or temperature. Figure 3a shows the resistance (R)–temperature (T) dependence at fixed pressures. Similar to typical transport measurements at ambient pressure, at low temperatures VO₂ behaves as a doped semiconductor, with a decreasing resistance with temperature. At a certain temperature (T_{MIT}), the resistance abruptly drops down by several orders of magnitude. The process is reversible, as cooling at the same pressure shows a very similar R – T dependence with a small hysteresis as seen in Figure 3a. There are some small features on the R – T curves, possibly attributed to inhomogeneous pressure in the DAC. The resistance was also measured as a function of pressure at room temperature, as shown in Figure 3b. A drastic change in the pressure dependence is seen in the range of 15–20 GPa, which is about the same pressure where the Raman peaks change slope in Figure 2b. Therefore, the much more rapidly decreasing resistance in Figure 3b is associated with the M1' phase. Such a new phase at high pressures has been considered as the onset of metallization process occurring in the monoclinic structure.^{7,24} Our observation of the M1-like Raman peaks together with rapidly decreasing, yet nonmetallic, resistance in the M1' phase shows that it is still a monoclinic-structured insulating phase, but with a narrow bandgap rapidly closing from that of M1 phase ($E_g \approx 0.7$ eV).²⁰ As pressure further increases beyond ~ 38 GPa, VO₂ transforms into the metallic X phase showing very low resistance.

The optical reflectance, Raman, and electrical transport data obtained in isothermal and/or isobaric conditions allow us to construct a pressure–temperature phase diagram of VO₂, including M1 (I), M1' (I), R (M), O (M), and X (M) phases as shown in Figure 4. Four phase transition points (black squares) obtained with micro-XRD at room temperature as well as 110 °C are also added for comparison.⁹ It can be seen from Figure 4 that, although these data points were taken with different techniques (Raman, electrical, reflectance or XRD), along different axes of variables (isobaric or isothermal), and on different samples, they clearly define a consistent P – T phase diagram over a wide pressure and temperature range. This phase diagram share some similarities to the largely schematic diagram of phases reported in ref 8: the P – T phase boundary has a positive slope at low pressures, and evidence of new metallic phases at high pressures. However, the most striking features of this diagram are (1) the dome-like, nonmonotonic

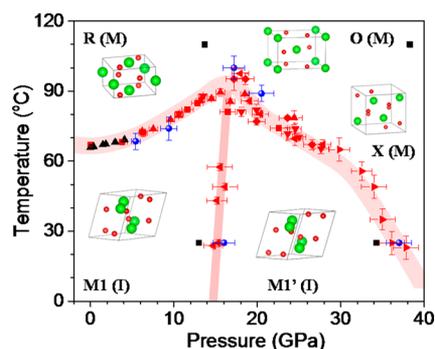


Figure 4. Phase diagram of VO₂ over a broad P – T range, including M1 (I), M1' (I), R (M), O (M), and X (M). I and M represent insulating and metallic phases, respectively. Insets are the simulated atomic structures of each phases of VO₂ (V: green atoms, O: red atoms). The red and blue data points on the phase boundaries are obtained from Raman and electrical measurements, respectively, and different shapes of symbols represent different samples. The black square data points are determined by XRD extracted from ref 9. The black triangle data points are from ref 6. The error bars include the temperature and pressure uncertainties. The broad lines defining the phase boundaries are a guide to the eye.

phase boundary between the low-temperature, I phases and high-temperature, M phases (i.e., the MIT boundary), and (2) the gradual evolution along the pressure axis from the insulating M1 to the less insulating M1' and finally the metallic X phases, while the M1–M1' boundary incidentally extrapolates to the vertex of the MIT dome. In the following we analyze these features.

For the transition from the well-known M1 (I) to R (M), the slope of the phase boundary dT/dP is determined to be 1.4 °C/GPa when averaged over a wide range of P from 0 to 16 GPa. This is higher than the reported $dT/dP = 0.8$ °C/GPa measured over $P < 4$ GPa.⁶ It can be seen from Figure 4 that the M1–R phase boundary takes a convex line shape, showing a higher slope at higher pressures. The M1–R transition is a first-order phase transition, with a discontinuous change in volume of $\Delta V/V = 0.044\%$ at ambient pressure.²⁵ These quantities are related through the Clausius–Clapeyron equation $dT/dP = T\Delta V/L$, where $\Delta V = V_R - V_{M1}$ is the molar volume change and L is the molar enthalpy change (latent heat) going from M1 to R. The positive slope (dT/dP) is an indication of volume expansion going from M1 to R, consistent with reports.^{8,25} Using the average $dT/dP = 1.4$ °C/GPa and the ambient $\Delta V/V = 0.044\%$, an average L is calculated to be ~ 1.9 kJ/mol,

compared to averaged value of $L = 3.1\text{--}4.3$ kJ/mol in literature.²⁵

By considering the P dependencies of dT/dP and ΔV , it is possible to go beyond these averaged values and obtain values of L under pressure. The molar volume, V , has been experimentally measured as a function of P at 25 °C (M1 phase) and 110 °C (R phase) in ref 9, as well as a function of T (both M1 and R phases) at ambient pressure in ref 25, and these dependencies all appear linear within the range of pressure and temperature variations. Assuming that both V_{M1} and V_R depend on P and T following the linear functional form of $\alpha P + \beta T + \delta$, by fitting to the experimental data in refs 9 and 25, one can obtain α_{M1} , β_{M1} , δ_{M1} and α_R , β_R , δ_R . Consequently, the volume change $\Delta V = V_R - V_{M1}$ is obtained as a function of T and P , and its values along the M1-R phase boundary is determined. Combining the values of ΔV with the slope dT/dP of the measured phase boundary shown in Figure 4, the variation of L is obtained along the phase boundary. As shown in Figure S3c, L increases as a function of pressure, varying from 1.3 kJ/mol at ambient pressure to 12.2 kJ/mol at ~ 16 GPa. Budai et al.²⁶ showed that the R structure is much more anharmonic than the M1 phase and that the total entropy change ($0.43 k_B/\text{atom}$) across the MIT at ambient pressure is mostly attributed to softer anharmonic phonons in the R phase, rather than electronic contribution. Our discovery of increasing L points to even stronger lattice anharmonicity in the R structure at higher pressures.

We performed DFT calculations to investigate the M1'(I)–X(M) transition. The calculations for these phases covered pressures from 10 to 90 GPa as shown in Figure S4. By full optimization of the structure, the enthalpy and lattice parameters of the two phases were obtained. The volume is calculated to decrease by $\sim 5\%$ from that of the M1' to X phase, which is much higher than that of the M1–R transition. As the slope dT/dP of the M1'–X phase boundary is negative with an averaged value on the same order of magnitude with that of the M1–R boundary, the average latent heat L is estimated to be positive going from M1' to X and much higher than $L(\text{M1–R})$, reaching ~ 155 kJ/mol, suggesting a much higher entropy in the metallic X phase than in the metallic R phase.

For the M1 to M1' transition, the phase boundary is nearly vertical. We calculated the pressure-driven change in phonon frequencies using the finite difference method (see Figure S5). At $P > 15$ GPa, some phonon modes start to deviate substantially in pressure dependency from those of the M1 phase. We evaluated the room-temperature Grüneisen parameters of the Raman modes, $\gamma = -\partial \ln(\omega)/\partial \ln(V) = -(V/\omega)(d\omega/dP)/(dV/dP)$. As shown in Figure S2, for the V–V Raman mode at 222.1 cm^{-1} (0 GPa), $d\omega/dP$ increases from 0.2 for M1 to $0.8 \text{ cm}^{-1}/\text{GPa}$ for the M1' phase, while for the V–O mode at 608.2 cm^{-1} (0 GPa), it decreases from 4.2 for M1 to $1.7 \text{ cm}^{-1}/\text{GPa}$ for M1'. Using previous results of experimentally measured dV/dP ,⁹ the obtained γ values exhibit an abrupt change at the M1–M1' transition pressure, with a sharp increase in $\gamma(\text{V–V})$ and decrease in $\gamma(\text{V–O})$.

Finally, for the transition from the metallic R to the metallic O phase, calculations predict an onset of the transition in the range of 12–14 GPa (see Figure S6). As expected, the O phase comes with a gradually reduced volume (by 0.3% at 14 GPa and 2.2% at 30 GPa) as compared to the R-phase unit cell. Meanwhile, the a - and b -lattice parameters split into two values above the pressure for the tetragonal structure. Note that the absolute shifts of the atoms are even more pronounced, since

the oxygen parameters are given relative to the cell parameters and thus have to be multiplied by these in order to obtain the real distance between atoms. This R–O phase transition is also signaled by the difference of the enthalpies of the R and O phases as displayed in Figure S6a. The enthalpy calculated for the O structure starts to lower at about 13 GPa and then experiences a drastic drop between 15 and 30 GPa, thus stabilizing the O structure. We tried other functionals (PBE and PBEsol²⁷) and found the same energy and structural relations between R and O phases.

In conclusion, we have experimentally mapped the phase diagram of VO₂ by independently varying pressure and temperature in a diamond anvil cell, which is also analyzed and supported by first-principles calculations. The diagram establishes phase boundaries not only between the well-known, insulating M1 phase and the metallic R phase, but also between the M1 phase and a more conductive M1' phase at intermediate pressures, as well as between the M1' phase and a metallic X phase at very high pressures. At high temperatures, the existence of another metallic O phase is also discussed. Our established phase diagram may serve as an instructive benchmark for ultimate elucidation of the phase transition physics of VO₂, as well as its potential applications.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.nanolett.7b00233.

Details of VO₂ growth and device fabrication in the DAC; Raman of a VO₂ nanobeam under isobaric heating; Raman during M1 to M1' transition driven by isothermal compression at room temperature; volume change and latent heat of M1–R transition; calculated M1' to X transition; calculated phonon frequencies as a function of pressure for the M1–M1' transition; calculated R–O transition; comparison of calculated enthalpy among M1, M1', R, O, and X phases at different pressures (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Morin, F. J. *Phys. Rev. Lett.* **1959**, *3* (1), 34–36.
- (2) Eyert, V. *Ann. Phys. (Berlin, Ger.)* **2002**, *11* (9), 650–702.
- (3) Yang, Z.; Ko, C. Y.; Ramanathan, S. *Annu. Rev. Mater. Res.* **2011**, *41*, 337–367.
- (4) Cao, J.; Ertekin, E.; Srinivasan, V.; Fan, W.; Huang, S.; Zheng, H.; Yim, J. W. L.; Khanal, D. R.; Ogletree, D. F.; Grossman, J. C.; Wu, J. *Nat. Nanotechnol.* **2009**, *4* (11), 732–737.
- (5) Neuman, C.; Lawson, A.; Brown, R. J. *Chem. Phys.* **1964**, *41* (6), 1591–1595.
- (6) Berglund, C. N.; Jayaraman, A. *Phys. Rev.* **1969**, *185* (3), 1034–1039.
- (7) Arcangeletti, E.; Baldassarre, L.; Di Castro, D.; Lupi, S.; Malavasi, L.; Marini, C.; Perucchi, A.; Postorino, P. *Phys. Rev. Lett.* **2007**, *98* (19), 196406–196409.
- (8) Marini, C.; Baldassarre, L.; Baldini, M.; Perucchi, A.; Di Castro, D.; Malavasi, L.; Lupi, S.; Postorino, P. *High Pressure Res.* **2010**, *30* (1), 55–59.
- (9) Bai, L. G.; Li, Q.; Corr, S. A.; Meng, Y.; Park, C.; Sinogeikin, S. V.; Ko, C.; Wu, J. Q.; Shen, G. Y. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2015**, *91* (10), 104110.
- (10) Yajima, T.; Nishimura, T.; Toriumi, A. *Nat. Commun.* **2015**, *6*, 10104.
- (11) Hsieh, W. P.; Trigo, M.; Reis, D. A.; Artioli, G. A.; Malavasi, L.; Mao, W. L. *Appl. Phys. Lett.* **2014**, *104* (2), 021917–021921.
- (12) Zhang, X.; Zhang, J. K.; Ke, F.; Li, G. H.; Ma, Y. M.; Liu, X. Z.; Liu, C. L.; Han, Y. H.; Ma, Y. Z.; Gao, C. X. *RSC Adv.* **2015**, *5* (68), 54843–54847.
- (13) Guiton, B. S.; Gu, Q.; Prieto, A. L.; Gudixsen, M. S.; Park, H. J. *Am. Chem. Soc.* **2005**, *127* (2), 498–499.
- (14) Chen, Y.; Ke, F.; Ci, P.; Ko, C.; Park, T.; Saremi, S.; Liu, H.; Lee, Y.; Suh, J.; Martin, L. W.; Ager, J. W.; Chen, B.; Wu, J. *Nano Lett.* **2017**, *17*, 194.
- (15) Rekhii, S.; Dubrovinsky, L. S.; Saxena, S. K. *High Temp. - High Pressures* **1999**, *31* (3), 299–305.
- (16) Perdew, J. P.; Burke, K.; Ernzerhof, M. *Phys. Rev. Lett.* **1996**, *77* (18), 3865–3868.
- (17) Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y.; Humphreys, C. J.; Sutton, A. P. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1998**, *57* (3), 1505–1509.
- (18) Kresse, G.; Furthmüller, J. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *54* (16), 11169–11186.
- (19) Blöchl, P. E. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, *50* (24), 17953–17979.
- (20) Fu, D. Y.; Liu, K.; Tao, T.; Lo, K.; Cheng, C.; Liu, B.; Zhang, R.; Bechtel, H. A.; Wu, J. Q. *J. Appl. Phys.* **2013**, *113* (4), 043707.
- (21) Wu, J. Q.; Gu, Q.; Guiton, B. S.; de Leon, N. P.; Ouyang, L.; Park, H. *Nano Lett.* **2006**, *6* (10), 2313–2317.
- (22) Liu, W. T.; Cao, J.; Fan, W.; Hao, Z.; Martin, M. C.; Shen, Y. R.; Wu, J.; Wang, F. *Nano Lett.* **2011**, *11* (2), 466–470.
- (23) Marini, C.; Arcangeletti, E.; Di Castro, D.; Baldassarre, L.; Perucchi, A.; Lupi, S.; Malavasi, L.; Boeri, L.; Pomjakushina, E.; Conder, K.; Postorino, P. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2008**, *77* (23), 235111.
- (24) Marini, C.; Bendele, M.; Joseph, B.; Kantor, I.; Mitrano, M.; Mathon, O.; Baldini, M.; Malavasi, L.; Pascarelli, S.; Postorino, P. *Epl-Europhys. Lett.* **2014**, *108* (3), 36003.
- (25) Kucharczyk, D.; Niklewski, T. *J. Appl. Crystallogr.* **1979**, *12* (4), 370–373.
- (26) Budai, J. D.; Hong, J. W.; Manley, M. E.; Specht, E. D.; Li, C. W.; Tischler, J. Z.; Abernathy, D. L.; Said, A. H.; Leu, B. M.; Boatner, L. A.; McQueeney, R. J.; Delaire, O. *Nature* **2014**, *515* (7528), 535–539.
- (27) Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Vydrov, O. A.; Scuseria, G. E.; Constantin, L. A.; Zhou, X. L.; Burke, K. *Phys. Rev. Lett.* **2008**, *100* (13), 136406.