PHYSICAL REVIEW B **93**, 205150 (2016)

Pressure-induced crossing of the core levels in 5*d* metals

Alexey A. Tal,[1,2,*] Mikhail I. Katsnelson,[3,4] Marcus Ekholm,[1] H. Johan M. Jönsson,[1] Leonid Dubrovinsky,[5]
Natalia Dubrovinskaia,[6] and Igor A. Abrikosov[1,2]

[1]*Theory and Modeling, IFM-Material Physics, Linköping University, SE-581 83, Linköping, Sweden*
[2]*Materials Modeling and Development Laboratory, National University of Science and Technology "MISIS", Moscow 119049, Russia*
[3]*Institute for Molecules and Materials, Radboud University of Nijmegen, Heyendaalseweg 135, NL-6525 AJ Nijmegen, The Netherlands*
[4]*Department of Theoretical Physics and Applied Mathematics, Ural Federal University, Mira street, 19, Ekaterinburg 620002, Russia*
[5]*Bayerisches Geoinstitut, Universitat Bayreuth, D-95440 Bayreuth, Germany*
[6]*Material Physics and Technology at Extreme Conditions, Laboratory of Crystallography, University of Bayreuth, D-95440 Bayreuth, Germany*

(Received 12 October 2015; revised manuscript received 27 April 2016; published 26 May 2016)

A pressure-induced interaction between core electrons, the core-level crossing (CLC) transition, has been observed in hcp Os at $P \approx 400$ GPa [L. Dubrovinsky *et al.*, Nature (London) **525**, 226 (2015)]. By carrying out a systematic theoretical study for all metals of the 5*d* series (Hf, Ta, W, Re, Os, Ir, Pt, Au) we have found that the CLC transition is a general effect for this series of metals. While in Pt it occurs at ≈1500 GPa, at a pressure substantially higher than in Os, in Ir it occurs already at 80 GPa. Moreover, we predict that in Re the CLC transition may take place already at ambient pressure. We explain the effect of the CLC and analyze the shift of the transition pressure across the series within the Thomas-Fermi model. In particular, we show that the effect has many common features with the atomic collapse in rare-earth elements.

DOI: 10.1103/PhysRevB.93.205150

I. INTRODUCTION

The properties of matter are determined by the electronic structure, which is sensitive to external parameters such as pressure, temperature, and chemical composition. An ability to understand and the possibility to predict the response of a physical system upon a variation of the parameters is a core problem for modern physics. A modification of the electronic structure may lead to a phase transition and change the material properties, allowing for a synthesis of new materials. Structural and magnetic transitions upon compression have often drawn the attention of a broad research community. Moreover, the pressure can affect the electronic structure in such a way as to induce isostructural phase transitions. Insulator-to-metal transitions (IMTs) [1] and the topological changes of the Fermi surface for valence electrons, the so-called electronic topological transition (ETT) [2], represent two classic examples of electronic transitions. Investigating Os compressed to over 770 GPa, Dubrovinsky *et al.* [3] have discovered another type of electronic transition, the core-level crossing (CLC) transition at 440 GPa, associated with interactions between the core electrons induced by pressure. Though the consequences of the CLC transition are less dramatic than those of structural and magnetic transitions, they appear to be of great importance from a fundamental point of view. Indeed, the influence of fully occupied deep lying core states on thermodynamic properties of materials is an unexpected phenomenon. However, the peculiarity of the pressure dependence of the lattice parameter ratio c/a in Os at the CLC transition pressure has been reproduced in several experimental runs, and the peculiarity of the compressibility observed experimentally at the same pressure should be important for an accurate description of the equation of state of Os [3]. Besides, electronic transitions are expected to influence material properties, such as elastic moduli, thermal expansion, resistivity, and thermal conductivity [4,5].

In this paper we perform a systematic theoretical study of the CLC effect focusing on three most important questions for the novel phenomenon: Is the core-level crossing a unique effect in Os or can it be observed in other metals? Is this effect only observed under ultrahigh pressures or is there a possibility to investigate it in less demanding experiments in comparison to those carried out in Ref. [3]? What is the fundamental reason for the core-level crossing phenomena? To answer these question, we investigate the influence of pressure on the electronic structure of all the 5*d* metals (Hf, Ta, W, Re, Os, Ir, Pt, Au).

The metals of the 5*d* group are of particular interest for high-pressure studies due to their remarkable properties. Hafnium (Hf) has attracted great scientific and technological interest due to the position of its *d* band in the middle of a broad *sp* band, which impacts its electronic and superconducting properties [6–9]. The instability of the hcp phase of Hf at high pressure was demonstrated both theoretically and experimentally [10,11]. Tantalum (Ta) is stable even at pressures of hundreds of GPa [12,13]. Even though the stability at higher pressure is still under debate [14,15], only the hcp phase was observed experimentally. Ta shows high chemical and thermodynamical stability, having a melting point at an ambient pressure of about 3950 K [16] and it is widely used in the microelectronics industry for producing integrated circuits. The strength of tungsten (W) is of considerable importance for optimizing the design and operation of high-pressure apparatuses. Pressure calibration in diamond anvil cells is largely based on equations of state derived from shock data for standard materials such as W, Mo, and Cu [17,18]. Neither theoretical calculations nor experimental observations suggest that W may suffer a structural transition under pressure. Rhenium (Re) was studied under extremely high pressures

---

[*] aleta@ifm.liu.se

up to 600 GPa and showed no structural transformations in the considered pressure range. That makes Re a good candidate for ultrahigh-pressure calibration [19–22].

The stability of fcc iridium (Ir) under pressure has been debated for years. The formation of a complex superlattice in iridium under a pressure of 59 GPa has been reported [23], however, in other experimental and theoretical studies such a structure has not been observed [24]. Platinum is also widely used as a pressure standard and is known to be stable in the fcc structure up to 600 GPa [25,26]. The uniqueness of gold and its important role in modern science is closely related to its exceptional stability to chemical reactions, extreme pressures, and temperatures [27,28]. Gold in the fcc structure becomes unstable in favor of the hcp structure only under a pressure of 240 GPa and at elevated temperatures [29]. Thus, these metals show structural stability under high pressure, they are nonmagnetic, and they may be good candidates for investigations of the electronic transitions.

II. METHODOLOGY

For our calculations we used the WIEN2K code [30] with the local density approximation (LDA) functional and a k mesh of $32 \times 32 \times 32$ k points in fcc and bcc structures and $39 \times 39 \times 21$ in hcp structures. The radius of the real-space muffin-tin sphere varied under different pressures, while the product $K_{\max} \cdot R_{\mathrm{MT}}$ was kept equal to 10. The spin-orbit interaction is included variationally.

III. RESULTS AND DISCUSSION

Calculations of the density of states (DOS) have been carried out in $5d$ metals from Hf to Au. DOS calculations at zero pressure were performed for the structures experimentally proven to be stable at ambient pressure. The results are shown in Fig. 1 (left). DOS under pressure was calculated for the structures observed at the highest pressures reported for the respective elements experimentally. In fact, only two $5d$ metals Hf and Au are unambiguously known to undergo a structural transformation under pressure. Starting with Hf, we see that the $4f$ and $5p$ levels are far from each other. However, with an increase of the atomic number (Z), the $4f$ and $5p$ levels both shift towards higher binding energies. Importantly, the $4f$ levels shift faster than the $5p$ states. Thus, the $4f$ levels “outrun” the $5p$ levels. In particular, $4f_{5/2}$ levels cross $5p_{3/2}$ already in Re, and finally in Pt both $4f_{5/2}$ and $4f_{7/2}$ electrons lie below $5p$ electrons.

Figure 1 (right) demonstrates DOS of $5d$ metals upon compression. We provide DOS for structures which are known from experiment to be stable at high pressure. In fact, the crystal structure has very little effect on the CLC transitions, as will be discussed below. Applied pressure causes broadening of the p and s levels, so that they form rather broad bands due to an overlap of the wave functions. As shown in Ref. [3], the bulk modulus and its derivative calculated from Birch-Murnaghan fitting may theoretically give very inaccurate pressure estimates for the highly reduced volumes. Thus, for pressure estimations we used the experimental bulk moduli and their pressure derivatives for cases where there were experimental measurements, as shown in Table I. In Hf, Ta, and W, the broadening of the $5p$ levels due to pressure does not lead to an overlap of the $4f$ and $5p$ levels even at the highest pressures considered in this study. On the contrary, in Re, $4f_{5/2}$ and $5p_{3/2}$ are overlapping at zero pressure, and compression just causes a broadening of the $5p$ levels. Since hcp Hf is unstable under high pressure and transforms first to the ω phase, and then to the bcc phase, we provide DOS for hcp and bcc structures for approximately the same volume reduction. One can clearly see that the structure does not have a strong effect on the behavior of the core-level energies under pressure. We observe a CLC of $4f_{7/2}$ and $5p_{3/2}$ in fcc Os at the same pressure as in Ref. [3]. In Ir, $4f_{5/2}$ and $5p_{1/2}$ states are very close, thus relatively small compression up to 80 GPa results in a CLC. These pressures are substantially lower than in Os, which makes Ir extremely interesting for a detailed experimental study of the CLC transition. In Pt, the $4f$ level lies below $5p$ and the distance between them is rather big. Therefore, the CLC transition in Pt occurs at a pressure above 1.5 TPa. Our calculations suggest that one should not expect to see a CLC in Au at any realistic pressures for either fcc or hcp structures. Our analysis of the whole series of DOS for $5d$ metals shows that in addition to broadening, pressure causes shifts of all the core states towards higher binding energies, and the shift is more pronounced for higher values of Z. It is important to stress that the phenomenon of core-level crossing is strongly linked to the fact that the f level shifts faster towards higher binding energies than the p level with increasing atomic number. Let us explain this effect.

The early work Mayer [34] demonstrated how atomic collapse appears in rare-earth elements. She showed that the effective f-electron potential suffers drastic changes with an increase of atomic number Z. In order to understand the behavior of the f and p levels in $5d$ metals, we analyzed the atomic potential behavior with the change of Z in the Thomas-Fermi approximation for the effective potential:

$$V = -\frac{e^2}{r}[1 + (Z-1)\phi(r/\mu)] + \frac{h^2}{8\pi^2 m}\frac{l(l+1)}{r^2}. \qquad (1)$$

The approximation suggested by Tietz [35] was used for the Thomas-Fermi function $\phi(r/\mu)$,

$$\phi(x) = \frac{1}{(1+\alpha x)^2}, \qquad (2)$$

where $x = r/a$, $a = 0.885\,34 Z^{-1/3}$, and $\alpha = 0.536\,25$. This approximation is believed to reproduce the shifts properly enough to distinguish the trends [34].

Figure 2 shows how the potential V changes with the atomic number. We considered a series from $Z = 70$ to 80. It is clear that the effective potential for the f electrons is more sensitive to Z. Indeed, with the increase of Z, both the p and f potentials become deeper, but the f potential shifts faster and the f levels will at some point outrun the p levels. This behavior is clearly seen in our first-principles results in Fig. 1. Two other effects seen in Fig. 1 are the pressure-induced broadening, strongly pronounced for the p levels, and a slight pressure-induced upshift of the states in energy, which is an effect of the higher spatial localization of the corresponding potential walls upon a decrease of the interatomic distances. These two effects lead

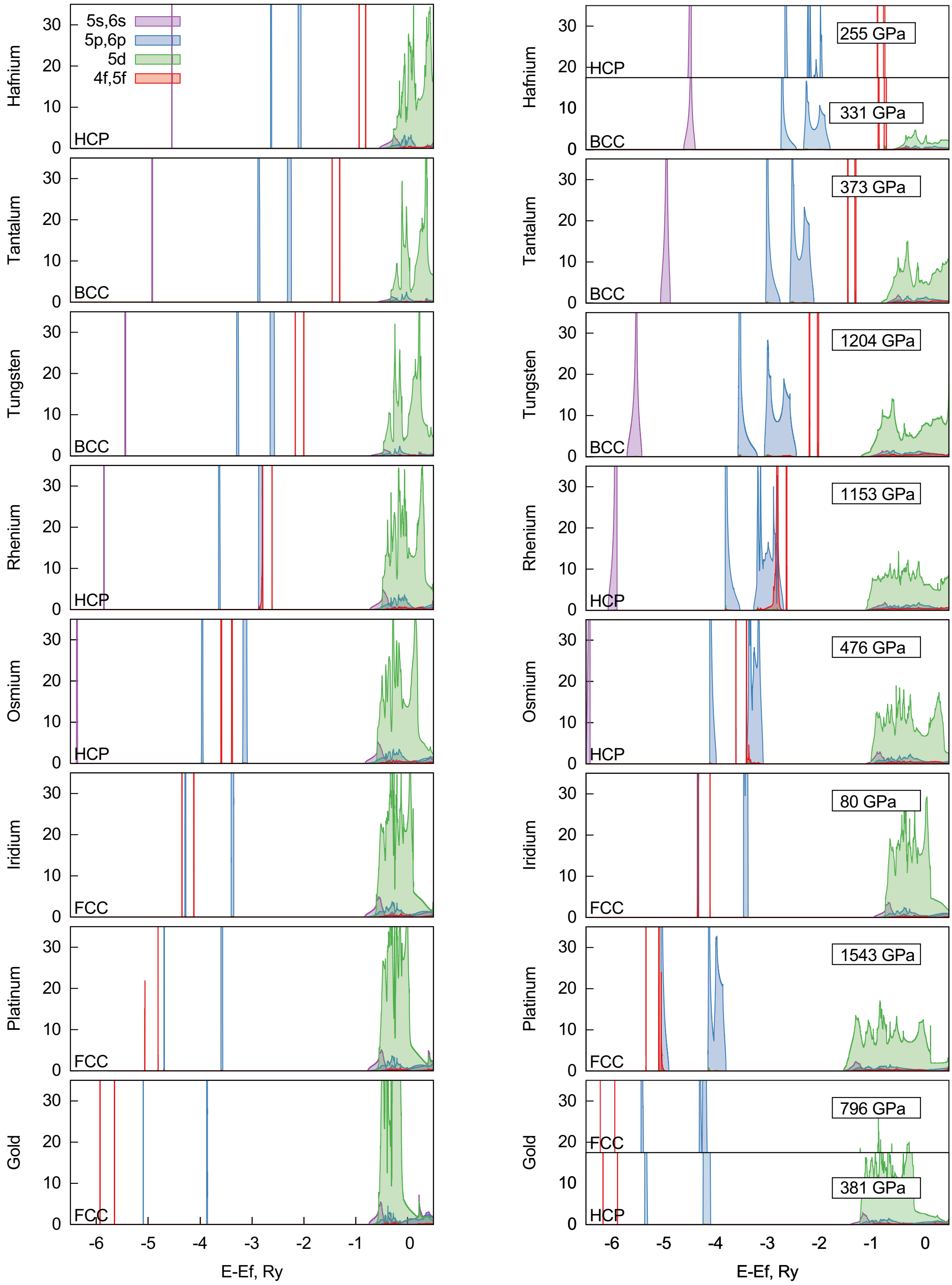

FIG. 1. Left: Electronic density of states (DOS) for $5d$ metals from Hf to Au at zero pressure. Right: DOS for $5d$ metals from Hf to Au in structures experimentally known to be stable at high pressures. For each element the pressure shown in the figure corresponds either to the pressure of the core-level crossing transition or to the highest pressure considered in this study.

to a crossing of the core levels for the elements which turn out to be sufficiently close to each other at ambient pressure.

Let us finally consider two elements, Ir and Re, where our calculations predict a CLC transition at a relatively low pressure, and analyze the experimental information available in the literature. In fcc metals, such as Ir, the CLC transition cannot be searched from the changes in the c/a ratio, in contrast to hcp Os [3]. However, electronic transitions may lead to changes of compressibility (such a possibility has been discussed for Os [3]). X-ray diffraction experiments

TABLE I. Data used for pressure estimations. Values with the superscripts are taken from the corresponding experimental studies. The rest are calculated in this study by fitting the equation of state with the Vinet equation. * Bulk modulus and its derivative were calculated. Volume per one atom is in $\mathrm{\AA}^3$; bulk modulus is in GPa.

	Hf		Ta	W	Re	Os	Ir	Pt	Au	
	bcc*	hcp	bcc	bcc	hcp	hcp	fcc	fcc	fcc	hcp*
V_0	20.0	22.5	18.0	15.8	14.5	14.0	14.2	15.1	17.1	18.1
V_P	9.5	10.6	9.2	7.5	7.5	8.8	12.1	7.2	7.1	9.2
B_0	114	113[a]	195[b]	312[c]	353[d]	399[e]	306[f]	273[g]	167[h]	172
B_0'	3.7	3.3[a]	3.4[b]	4.3[c]	4.6[d]	4.0[e]	6.8[f]	5.2[g]	5.9[g]	3.7

[a] Reference [10].
[b] Reference [13].
[c] Reference [31].
[d] Reference [19].
[e] Reference [3].
[f] Reference [23].
[g] Reference [32].
[h] Reference [33].

performed by Cerenius and Dubrovinsky [23] on fcc iridium showed a distortion of the structure by the appearance of additional diffraction peaks at pressures exceeding 59 GPa, which was attempted to be explained by the formation of a superlattice. However, the superstructures were not observed in other experiments or in theoretical calculations.

Moreover, a possible change in compressibility as a function of pressure was observed in recent experiments on Ir-rich Ir-Os alloys [36]. All this points to a possible electronic transition in these systems. In Fig. 3 we show the band structure of Ir at $P = 0$ GPa and at $P = 80$ GPa, covering the pressure range of interest for this element. One can see that the presented band structure does not point to any Fermi-surface topology change and therefore the behavior cannot be explained by an ETT. On the other hand, in our calculations the CLC has been clearly shown at a pressure of 80 GPa, and it may give an explanation for the observed peculiarity. In fact, this situation is remarkably similar to the one seen in Os at 400 GPa [3]. Of course, new experimental studies should be carried out for Ir. On the other hand, the possibility of a structural transition in this metal can complicate the task. For that reason, CLC could be verified experimentally in alloy systems, for example, in an Ir-Os alloy.

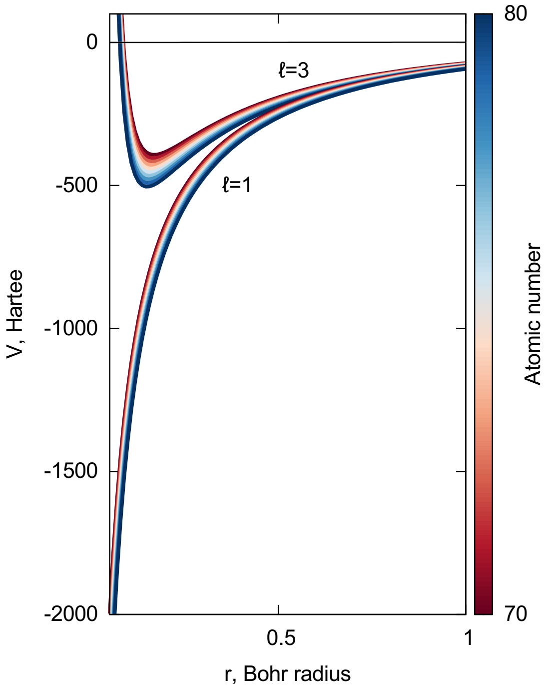

FIG. 2. Thomas-Fermi potentials for orbital numbers $l = 1$ (p electrons) and $l = 3$ (f electrons). Potentials are plotted for the series of Z from 70 to 80. The color of the line corresponds to Z, as shown in the right palette.

Considering Re, the CLC transition is predicted to occur already at ambient pressure. In this respect, it is interesting to point out that the results of investigations of the equation of state of Re are not totally consistent: While the reported bulk moduli [3,19,37] are basically the same within the uncertainty of the measurements, the reported pressure derivatives of the bulk moduli are substantially different. Therefore, Re is another interesting candidate for studies of the CLC transition. Moreover, because we predict it to occur at ambient pressure, spectroscopic methods can be employed as well.

IV. CONCLUSIONS

In summary, it is well known that chemical bonding in solids is mainly due to valence electrons, while core electrons are often considered "frozen": They should not influence the macroscopic properties of materials. However, strong rearrangements of the $5p$ and $4f$ states at the recently discovered core-level crossing transition [3] may affect the valence electrons due to the nonlocal nature of the electron interactions, and to influence structural, thermal, and transport properties of the metals. In this paper we have analyzed the effect of the CLC in $5d$ metals under pressure. We predict that this is a general effect. Besides Os, it appears in Re, Ir, and Pt. We identify mechanisms that lead to CLC transitions in the $5d$ metals, which have many features in common with the atomic

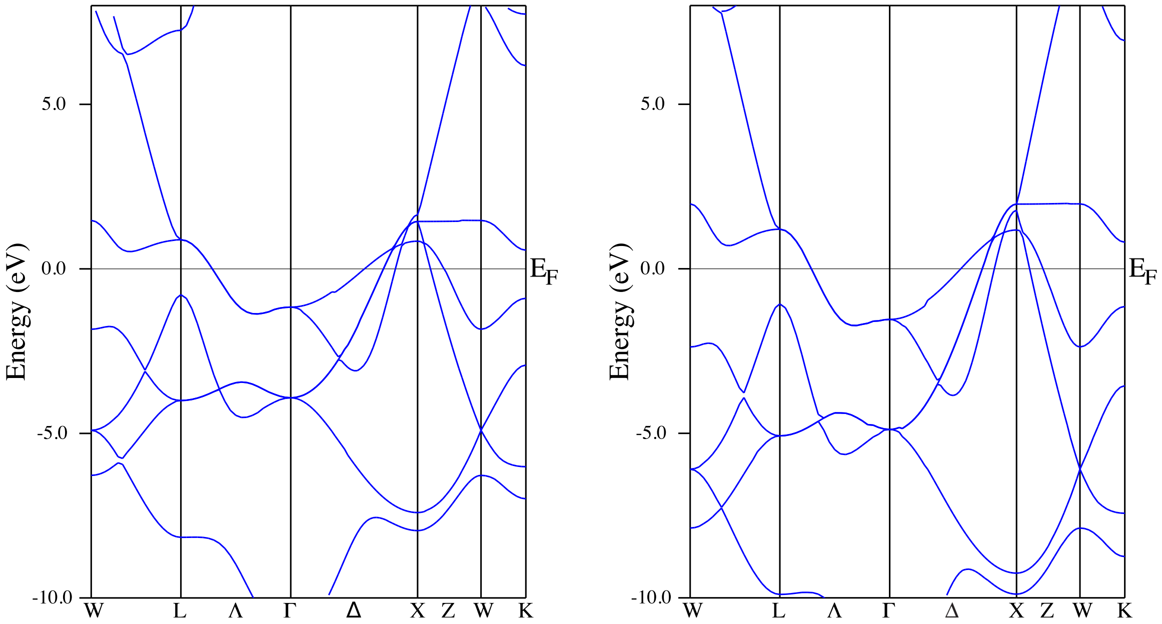

FIG. 3. Left: Band structure of iridium at ambient pressure. Right: Band structure of iridium under a pressure of 80 GPa.

collapse in rare-earth elements. The understanding of the CLC obtained in the present work allows us to expect to find this phenomenon in a variety of different systems. The fact that the CLC is predicted for metals used as pressure standards indicates that further investigations of this phenomenon are important.

ACKNOWLEDGMENTS

The work was financially supported by the Knut and Alice Wallenberg Foundation through Grants No. 2012.0083 and No. 2014-2019 and the Swedish Government Strategic Research Area Grant Swedish e-Science Research Centre (SeRC). A.A.T. gratefully acknowledges the financial support of the Ministry of Education and Science of the Russian Federation in the framework of Increase Competitiveness Program of MISiS. I.A.A. is grateful for the support provided by the Swedish Foundation for Strategic Research (SSF) program SRL Grant No. 10-0026, the Swedish Research Council (VR) Grant No. 2015-04391, and the Swedish Government Strategic Research Area in Materials Science on Functional Materials at Linköping University (Faculty Grant SFO-Mat-LiU No 2009 00971). Support by the grant from the Ministry of Education and Science of the Russian Federation (Grant No. 14.Y26.31.0005) is gratefully acknowledged. The calculations were performed on resources provided by the Swedish National Infrastructure for Computing (SNIC) at the National Supercomputer Centre (NSC). L.D. and N.D. acknowledge financial support from the German Research Foundation (DFG) and the Federal Ministry of Education and Research (BMBF), Germany. N.D. thanks the DFG for funding through the Heisenberg Program and the DFG project No. DU 954-8/1, and the BMBF for Grant No. 5K13WC3 (Verbundprojekt O5K2013, Teilprojekt 2, PT-DESY). The work of MIK was supported by Act 211 Government of the Russian Federation, Contract No. 02.A03.21.0006.

---

[1] I. G. Austin and N. F. Mott, Science **168**, 71 (1970).
[2] I. M. Lifshitz, Sov. Phys. JETP **11**, 1130 (1960).
[3] L. Dubrovinsky, N. Dubrovinskaia, E. Bykova, M. Bykov, V. Prakapenka, C. Prescher, K. Glazyrin, H. P. Liermann, M. Hanfland, M. Ekholm *et al.*, Nature (London) **525**, 226 (2015).
[4] K. Glazyrin, L. V. Pourovskii, L. Dubrovinsky, O. Narygina, C. McCammon, B. Hewener, V. Schünemann, J. Wolny, K. Muffler, A. I. Chumakov *et al.*, Phys. Rev. Lett. **110**, 117206 (2013).
[5] A. A. Varlamov, V. S. Egorov, and A. V. Pantsulaya, Adv. Phys. **38**, 469 (1989).
[6] J. C. Duthie and D. G. Pettifor, Phys. Rev. Lett. **38**, 564 (1977).
[7] H. L. Skriver, Phys. Rev. B **31**, 1909 (1985).
[8] J. S. Gyanchandani, S. C. Gupta, S. K. Sikka, and R. Chidambaram, J. Phys.: Condens. Matter **2**, 6457 (1999).
[9] Y. K. Vohra and P. T. Spencer, Phys. Rev. Lett. **86**, 3068 (2001).
[10] R. Hrubiak, V. Drozd, A. Karbasi, and S. K. Saxena, J. Appl. Phys. **111**, 112612 (2012).
[11] Y. Hao, J. Zhu, L. Zhang, H. Ren, and J. Qu, Philos. Mag. Lett. **91**, 61 (2011).
[12] J. A. Moriarty, J. F. Belak, R. E. Rudd, P. Söderlind, F. H. Streitz, and L. H. Yang, J. Phys.: Condens. Matter **14**, 2825 (2002).
[13] H. Cynn and C.-S. Yoo, Phys. Rev. B **59**, 8526 (1999).
[14] Y. Yao and D. D. Klug, Phys. Rev. B **88**, 054102 (2013).
[15] L. Burakovsky, S. P. Chen, D. L. Preston, A. B. Belonoshko, A. Rosengren, A. S. Mikhaylushkin, S. I. Simak, and J. A. Moriarty, Phys. Rev. Lett. **104**, 255702 (2010).

[16] A. Dewaele, M. Mezouar, N. Guignot, and P. Loubeyre, Phys. Rev. Lett. **104**, 255701 (2010).

[17] A. Dewaele, P. Loubeyre, and M. Mezouar, Phys. Rev. B **70**, 094112 (2004).

[18] A. D. Chijioke, W. J. Nellis, and I. F. Silvera, J. Appl. Phys. **98**, 073526 (2005).

[19] S. Anzellini, A. Dewaele, F. Occelli, P. Loubeyre, and M. Mezouar, J. Appl. Phys. **115**, 043511 (2014).

[20] C. S. Zha, W. a. Bassett, and S. H. Shim, Rev. Sci. Instrum. **75**, 2409 (2004).

[21] L. Dubrovinsky, N. Dubrovinskaia, V. B. Prakapenka, and A. M. Abakumov, Nat. Commun. **3**, 1163 (2012).

[22] A. K. Verma, P. Ravindran, R. S. Rao, B. K. Godwal, and R. Jeanloz, Bull. Mater. Sci. **26**, 183 (2003).

[23] Y. Cerenius and L. Dubrovinsky, J. Alloys Compd. **306**, 26 (2000).

[24] S. Grussendorff, N. Chetty, and H. Dreysse, J. Phys.: Condens. Matter **15**, 4127 (2003).

[25] S. Ono, J. P. Brodholt, and G. David Price, J. Phys. Chem. Solids **72**, 169 (2011).

[26] A. B. Belonoshko and A. Rosengren, Phys. Rev. B **85**, 174104 (2012).

[27] B. Hammer and J. K. Norskov, Nature (London) **376**, 238 (1995).

[28] D. Batani, A. Balducci, D. Beretta, A. Bernardinello, T. Löwer, M. Koenig, A. Benuzzi, B. Faral, and T. Hall, Phys. Rev. B **61**, 9287 (2000).

[29] L. Dubrovinsky, N. Dubrovinskaia, W. A. Crichton, A. S. Mikhaylushkin, S. I. Simak, I. A. Abrikosov, J. S. de Almeida, R. Ahuja, W. Luo, and B. Johansson, Phys. Rev. Lett. **98**, 045503 (2007).

[30] P. Blaha *et al.*, *WIEN2K: An Augmented Plane Wave Plus Local Orbitals Program for Calculating Crystal Properties* (Technical University, Vienna, 2001).

[31] D. He and T. Duffy, Phys. Rev. B **73**, 134106 (2006).

[32] M. Matsui, E. Ito, T. Katsura, D. Yamazaki, T. Yoshino, A. Yokoyama, and K. I. Funakoshi, J. Appl. Phys. **105**, 013505 (2009).

[33] C. Bercegeay and S. Bernard, Phys. Rev. B **72**, 214101 (2005).

[34] M. G. Mayer, Phys. Rev. **60**, 184 (1941).

[35] T. Tietz, J. Chem. Phys. **25**, 789 (1956).

[36] K. V. Yusenko, E. Bykova, M. Bykov, S. A. Gromilov, A. V. Kurnosov, C. Prescher, V. B. Prakapenka, M. Hanfland, S. van Smaalen, S. Margadonna *et al.*, J. Alloys Compd. **622**, 155 (2015).

[37] R. Jeanloz, B. K. Godwal, and C. Meade, Nature (London) **349**, 687 (1991).