The ground-state structure and physical properties of RuC: first-principles calculations*

Zhang Mei-Guang(张美光)[a)†], Yan Hai-Yan(闫海燕)[b)], Zhang Gang-Tai(张刚台)[a)], and Wang Hui(王 晖)[c)‡]

[a)] *Department of Physics and Information Technology, Baoji University of Arts and Sciences, Baoji* 721016, *China*

[b)] *Shaanxi Key Laboratory for Phytochemistry, Department of Chemistry and Chemical Engineering, Baoji University of Arts and Sciences, Baoji* 721013, *China*

[c)] *National Laboratory of Superhard Materials, Jilin University, Changchun* 130012, *China*

(Received 19 October 2011; revised manuscript received 21 March 2012)

We have extensively explored the ground-state structure of RuC using the particle swarm optimization algorithm for crystal structural prediction. A hexagonal *R*-3*m* structure has been proposed as the best candidate, which is energetically more favorable than the previously proposed zinc blend structure. The *R*-3*m*-RuC possesses alternative stacking of double hexagonal close-packed Ru atom layers and C atom layers, and it is dynamically stable evidenced by the calculation of phonon dispersion. The calculated large bulk modulus, shear modulus, and elastic constant C_{44} reveal that it is an ultra-incompressible and hard material. The evidence of strong covalent bonding of Ru–C, which plays an important role to form a hard material, is manifested by the partial densities of states analysis.

Keywords: transition metal carbides, structure prediction, ultra-incompressible material

PACS: 61.66.Fn, 61.50.Ah, 62.20.de **DOI:** 10.1088/1674-1056/21/7/076103

1. Introduction

Designing and searching for ultra-incompressible and superhard materials are always of great scientific interest due to their variety of industrial applications, such as cutting tools, abrasives, oil exploitations, and coatings. The introduction of light and covalent-bond-forming elements (B, C, N, and O) into the transition metal (TM) lattices is expected to have profound influences on their chemical, mechanical, and electronic properties.[1−5] Based on this prospect, diatomic transition metal carbides (TMCs) have been considerably investigated[6−10] for their outstanding physical properties, such as high stiffness, high hardness, high thermal conductivity, and high melting point. It is known that these excellent properties are of industrial interest, being properties of good candidates for (super)hard materials. For example, WC, SiC and CrC have been widely used for cutting and shaping hard metals and ceramics. Recently, intensive interest for platinum-metal (Ru, Rh, Pd, Os, Ir, and Pt) carbides[11−15] has re-emerged after the successful synthesis of PtC[16−17] and the discovery of its excellent mechanical properties.

It is known that crystal structures are the key for the understanding of mechanical properties of materials. Most diatomic TMCs possess the NaCl-type structure with a few exceptions (MoC and WC) that have the WC-type structure. However, the crystal structure of ruthenium monocarbide (RuC) is the subject of continuing debate. RuC was first empirically thought to have a hexagonal WC-type structure,[18,19] but later argued to adopt the NaCl-type structure.[20] Recently, Zhao *et al.*[21] suggested that the zinc blend RuC (ZB-RuC) was energetically most stable at the ground state using first-principles calculations based on the ten structures of known transition metal compounds. The work of Zhao *et al.* is extremely important, since this new polymorph for RuC will inevitably advance our understanding of the ground-state structure for other platinum-metal carbides. However, the proposed ground-state structure of RuC is based on the knowledge of known information. There is

*Project supported by the Natural Science Basic Research Plan of Shaanxi Province of China (Grant No. 2012JQ1005), the Key Research Foundation of Baoji University of Arts and Sciences, China (Grant Nos. ZK1032, ZK11060, ZK11061, and ZK11146) and the Fund from the Phytochemistry Key Laboratory of Shaanxi Province, China (Grant No. 11JS008).

†Corresponding author. E-mail: zhmgbj@126.com

‡Corresponding author. E-mail: huiwang@jlu.edu.cn

© 2012 Chinese Physical Society and IOP Publishing Ltd

a possibility that hitherto unknown structures are more stable instead. Here, we extensively explore the ground-state structure of RuC using a specifically developed particle swarm optimization (PSO) algorithm for crystal structure prediction.[22] This methodology has been successful in correctly predicting crystal structures for various systems including elements and compounds,[23−27] unbiased by any known information. In the present work, a hexagonal R-3m structure is uncovered to be the best ground-state candidate for RuC, which possesses excellent mechanical properties.

2. Computational detail

Our PSO methodology on crystal structural prediction has been implemented in the CALYPSO (crystal structure analysis by particle swarm optimization) code[28] at 0 GPa with 1–4 formula units (f.u.) per simulation cell. The underlying *ab initio* calculations were carried out using the density functional theory within the generalized gradient approximation, as implemented in the Vienna *ab initio* simulation package (VASP).[29−31] The electron and core interactions were included by using the frozen-core all-electron projector augmented wave method,[32] with C: $2s^2p^2$ and Ru: $4p^64d^75s^1$ treated as the valence electrons. To reduce the errors, the cut-off energy for the expansion of the wave function into plane waves was set to be 500 eV in all calculations, and the Monkhorst–Pack grid[33] had a maximum spacing of 0.03 Å^{-1}. In the geometrical optimization calculations, all forces were converged to less than 0.001 eV/Å. The total stress tensor was reduced to within 0.01 GPa. The phonon frequency was calculated using the direct approach, which was based on first-principles calculations of Hellman–Feynman forces and the dynamical matrix implemented in the VASP and PHONOPY code.[34] The elastic constants were calculated by evaluating the stress tensor to generate a small strain. The bulk modulus, the shear modulus, Young's modulus and Poisson's ratio were thus derived from the Voigt–Reuss–Hill approximation.[35]

3. Results and discussion

At ambient pressure, the structural simulations predict a low-energy hexagonal R-3m structure, as shown in Fig. 1. The R-3m structure contains six f.u. per cell with C occupying the Wyckoff 6c (0, 0, 0.963) sites and Ru sitting at 6c (0, 0, 0.771) sites. The R-3m-RuC consists of the double hexagonal close-packed (hcp) like Ru atom layers and the double hexagonal close-packed C atom layers stacking alternatively along the [001] crystal direction, revealing an intriguing C–Ru–C sandwiches stacking order. The C–C distance of the adjacent C atom layers is ∼1.40 Å, which is smaller than the C–C bond length in diamond (1.54 Å) but close to the N–N single bond observed in WN_2, OsN_2, and PtN_2. The Ru–C bond length in R-3m-RuC is 2.049 Å and is close to those (TM–C) in ZB-RuC (1.968 Å), PtC (2.254 Å), TiC (2.159 Å), VC (2.085 Å), and TaC (2.177 Å).[21]

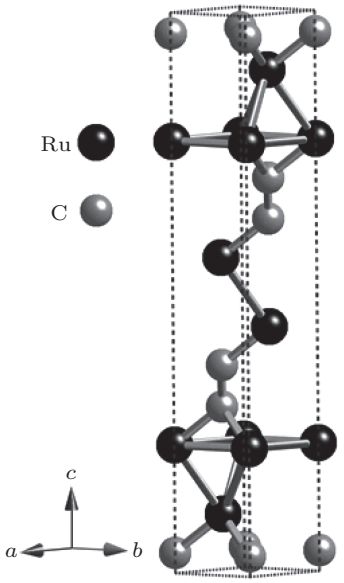


Fig. 1. Crystal structure of R-3m-RuC.

To calculate the equilibrium lattice constants and bulk modulus, the total energy is calculated by varying the volume for R-3m-RuC. The calculated E–V data is fitted to the third-order Birch–Murnaghan equation of state,[36] and the obtained equilibrium structure parameters, bulk modulus, and its pressure derivatives are tabulated in Table 1 together with the theoretical results of ZB-RuC for comparison. Figure 2 presents the dependences of the total energy on the f.u. volume for R-3m-RuC and ZB-RuC. It can be seen clearly that R-3m-RuC is energetically far more stable than ZB-RuC, and this further confirms our structural prediction. At zero temperature, a stable crystalline structure requires all phonon frequencies to be positive. Therefore, we perform the phonon dispersion calculation for R-3m-RuC at 0 GPa, the results are shown in Fig. 3. No imaginary phonon frequency is found in the whole Brillouin zone, supporting its dynamical stability. In order to explore

the thermodynamic stability for experimental synthesis, the formation enthalpy of R-3m-RuC with respect to the separate phases is quantified by the reaction route $\Delta H_{\rm f} = H_{\rm (RuC)} - H_{\rm (Ru)} - H_{\rm (C)}$. The $\Delta H_{\rm f}$ is the formation enthalpy, the hexagonal Ru (space group: $P6_3/mmc$) and the graphite C are chosen as the reference phases. The calculated $\Delta H_{\rm f}$ per atom of R-3m-RuC is positive (0.361 eV) at zero pressure, as expected, since the external pressure and temperature are necessary conditions in the synthesis of transition metal carbides.[16,17,37] Therefore, high pressure and high temperature are needed to synthesize it in actual experiments.

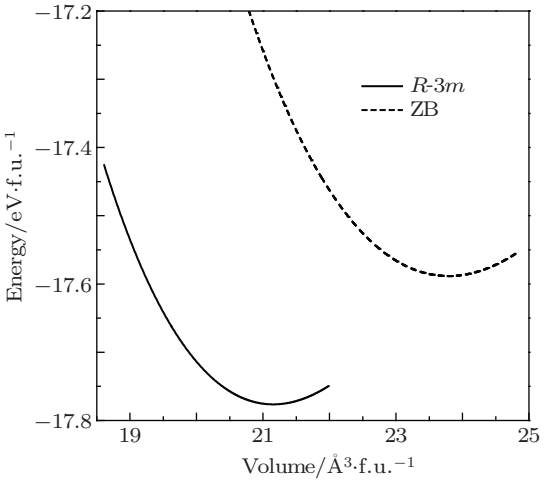


Fig. 2. The total energy versus f.u. volume for R-3m-RuC and ZB-RuC.

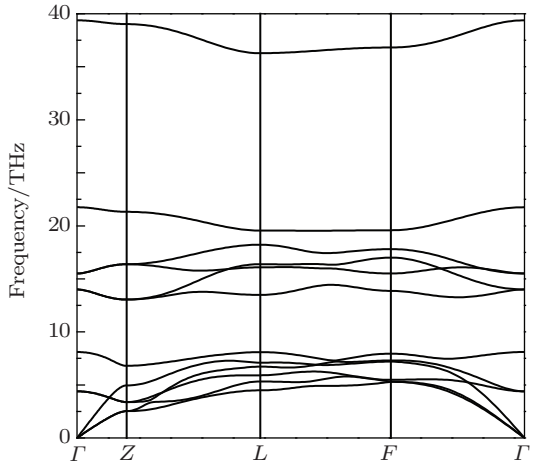


Fig. 3. Phonon dispersion curves of R-3m-RuC at 0 GPa.

Table 1. Calculated equilibrium lattice constants a_0, c_0, equilibrium volume V_0, bulk modulus B_0, and its pressure derivative B_0' for R-3m-RuC and ZB-RuC.

Structure	a_0/Å	c_0/Å	V_0/Å^3	B_0/GPa	B_0'
R-3m	2.785	18.886	21.137	285	4.987
ZB	4.564	4.564	23.767	262	4.078

The mechanical properties (elastic constants, elastic moduli, and elastic anisotropy, etc.) of materials are important for the potential technological and industrial applications. They define the behaviors of the solids that undergo stress, deforms, and then recover and return to their original shapes after the stress ceases. We have computed the zero-pressure elastic constants C_{ij} of R-3m-RuC and ZB-RuC (Table 2) by using the strain-stress method.[38−40] Based on the obtained elastic constants, bulk modulus B and shear modulus G are evaluated by using the Voigt–Reuss–Hill approximation, as shown in Table 2. Young's modulus E and Poisson's ratio v are derived from the equations of $E = 9BG/(3B + G)$ and $v = (3B - 2G)/(6B + 2G)$, respectively. The key criterion for mechanical stability of a crystal is that the strain energy must be positive. This means in a hexagonal crystal that the elastic constants should satisfy the following inequalities:[41] $C_{33} > 0$, $C_{44} > 0$, $C_{12} > 0$, $C_{11} > |C_{12}|$, $(C_{11} + 2C_{12})C_{33} > 2C_{13}^2$. From Table 2, we can see that R-3m-RuC is mechanically stable. Compared to ZB-RuC, R-3m-RuC has larger values of C_{11} and C_{33}, manifesting that its a-axis and c-axis directions are extremely stiff. Moreover, R-3m-RuC exhibits a very high bulk modulus of 296 GPa, indicating its ultra-incompressible structural nature. It should be noted that the calculated bulk moduli of these two structures agree well with those obtained directly from the fitting of the third-order Birch–Murnaghan equation of state, and this further demonstrates the reliability of our elastic calculations. For the partially covalent transition metal based hard materials, the shear modulus is considered a very important parameter governing the indentation hardness. Remarkably, the calculated shear modulus is very large, 186 GPa for R-3m-RuC. Thus, R-3m-RuC is expected to withstand shear strain to a large extent as many known hard materials. One of the most interesting findings is that the elastic constant C_{44}, which relates to the lattice resistance against an applied $[11\bar{2}0]$ shear deformation, is 176 GPa. Jhi *et al.*[42] have proved that the magnitude of the shear modulus C_{44}, rather than the bulk modulus and the shear modulus, is a better predictor for transition metal carbonitrides. Here, the estimated theoretical Vickers hardness for R-3m-RuC is obtained using the empirical G-H_v and E-H_v relationships proposed by Jiang *et al.*[43] is 27.4–28.0 GPa, which is comparable to the known hard materials of α-SiO_2 (30.6 GPa) and β-Si_3N_4 (30.3 GPa).[44] All of these excellent mechanical properties have powerfully suggested that R-

3m-RuC is an ultra-incompressible and hard material. Therefore, further experimental studies on the structural and the mechanical properties are strongly recommended.

Table 2. Calculated elastic constants C_{ij} (in the units of GPa), bulk modulus B, shear modulus G, Young's modulus E, Poisson's ratio v, and G/B.

Structure	Source	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}	B/GPa	G/GPa	E/GPa	G/B	v
R-3m	this work	539	152	178	581	176	194	296	186	462	0.628	0.241
ZB	this work	351	217			82		262	76	208	0.290	0.368
	theory[21]	345	216			66		259	66		0.255	

The elastic anisotropy of crystals can exert great influences on the properties of physical mechanisms, such as anisotropic plastic deformation, crack behavior, and elastic instability. The shear anisotropic factors provide a measure of the degree of anisotropy in the bonding between atoms in different planes. For R-3m-RuC, the shear anisotropic factors are $A_1 = A_2 = 4C_{44}/(C_{11} + C_{33} - 2C_{13}) = 0.921$ and $A_3 = 4C_{44}/(C_{11}+C_{22}-2C_{12}) = 0.910$, which are all smaller than 1. This indicates that the elastic anisotropy for the $\{001\}$ shear planes between $\langle 110\rangle$ and $\langle 010\rangle$ directions is slightly larger than those for the $\{100\}$ shear planes between $\langle 011\rangle$ and $\langle 010\rangle$ directions and for the $\{010\}$ shear planes between $\langle 101\rangle$ and $\langle 001\rangle$ directions. In addition, the knowledge of elastic coefficient also provides a method to estimate the anisotropy of linear bulk modulus. The anisotropies of the bulk modulus along the a and the b axes with respect to the c axis are $A_{B_a} = B_a/B_c = 0.832$ and $A_{B_b} = B_b/B_c = 0.832$ for R-3m-RuC, where B_a (839 GPa), B_b (839 GPa), and B_c (1009 GPa) are the bulk moduli along different crystal axes defined as $B_i = i\mathrm{d}P/\mathrm{d}i$, $i = a, b$, and c. Note that a value of 1.0 indicates elastic isotropy, and any deviation from 1.0 represents elastic anisotropy. It is interesting to note that the directional bulk modulus along the c axis is larger than those along the a and the b axes, which is consistent with the predicted elastic constants (see Table 2).

As a fundamental parameter, the Debye temperature is closely related to many physical properties of solids, such as specific heat, dynamic properties, and melting temperature.[45] At low temperatures, it can be derived from the elastic constants using the average sound velocity ν_m as

$$\Theta_\mathrm{D} = \frac{h}{k}\left[\frac{3n}{4\pi}\left(\frac{\rho N_\mathrm{A}}{M}\right)\right]^{1/3}\nu_\mathrm{m}, \qquad (1)$$

where h is the Planck constant, k is the Boltzmann constant, N_A is the Avogadro number, n is the number of atoms per f.u., M is the molecular mass per f.u., and ρ is the density. The average sound velocity ν_m is given by

$$\nu_\mathrm{m} = \left[\frac{1}{3}\left(\frac{2}{\nu_\mathrm{t}^3} + \frac{1}{\nu_\mathrm{l}^3}\right)\right]^{-1/3}, \qquad (2)$$

where ν_t and ν_l are the transverse and the longitudinal elastic wave velocities of the polycrystalline materials and are given by Navier's equation.[46] The results have indicated that the Debye temperature of R-3m-RuC (688 K) is higher than that of ZB-RuC (459 K), which may be attributed to the lower shear modulus of ZB-RuC.[11]

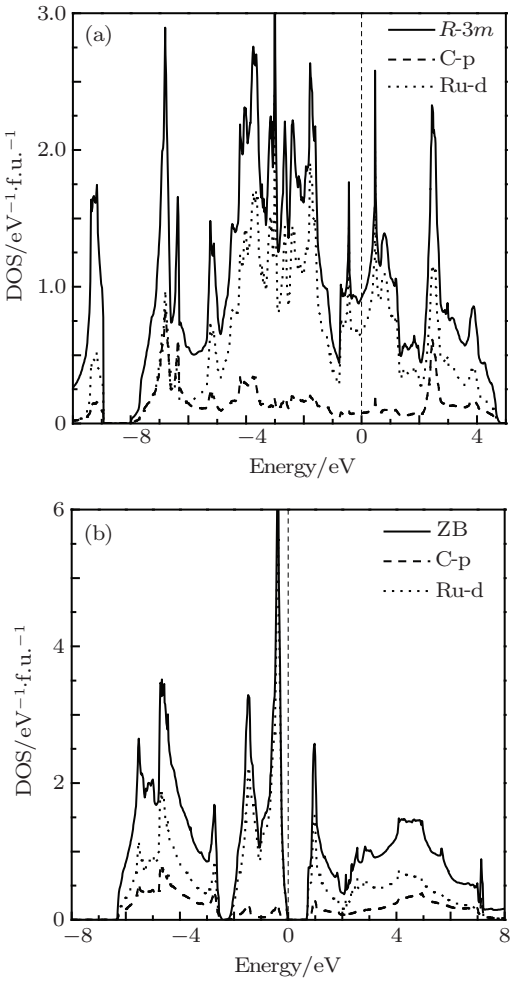


Fig. 4. Total and partial DOS of (a) R-3m-RuC and (b) ZB-RuC at 0 GPa. Vertical dashed line is the Fermi energy.

To understand the mechanical properties of these two structures on a fundamental level, the total and the partial densities of states (DOS) are calculated and plotted in Fig. 4, where the vertical line is the Fermi level. Compared to the semiconducting ZB-RuC, R-3m-RuC exhibits a clear metallic behavior, as shown by the finite electronic DOS at the Fermi level. This is similar to many other TM monocarbides. The typical feature of the total DOS is the presence of so-called pseudogap, which is considered as the borderline between the bonding and the antibonding states. It can be seen that the calculated Fermi energy is located above the pseudogap for R-3m-RuC, which indicates that its bonding states are fully occupied and its antibonding states are partially occupied. The partial DOS shown in Fig. 4(a) reveals that the Ru-4d orbital has a significant hybridization with the C-2p orbital, indicating the strong Ru–C covalent bonding nature within the layers. The contribution to the Fermi level is mainly due to the 4d electrons of Ru, which is the principal cause for the metallicity. It is not surprising that R-3m-RuC reveals a metallic behavior, as it contains Ru atom chains along the [010] crystal direction with a Ru–Ru distance of 2.852 Å compared to the value of 2.650 Å in hcp-Ru.

4. Conclusion

In summary, we have predicted that RuC energetically favors the hexagonal R-3m structure at the ground state by using the developed PSO algorithm for crystal structural predictions. The structural, mechanical, and electronic properties have been investigated using first-principles calculations in comparison with ZB-RuC. The total energy calculations reveal that R-3m-RuC is more energetically stable than ZB-RuC. R-3m-RuC is an ultra-incompressible and hard material with very high bulk modulus of 296 GPa and hardness of 27.4–28.0 GPa, and has been demonstrated to be dynamically stable in phonon calculations. Meanwhile, R-3m-RuC shows a certain degree of elastic anisotropy. The density of states analysis has unraveled the covalent bonding between Ru and C atoms as the driving force of the high bulk modulus and the high shear modulus as well as the small Poission's ratio. We expect that our calculations will stimulate extensive experimental works on synthesizing this technologically important material.

References

[1] Kaner R B, Gilman J J and Tolbert S H 2005 *Science* **308** 1268
[2] Chung H Y, Weinberger M B, Levine J B, Kavner A, Yang J M, Tolbert S H and Kaner R B 2007 *Science* **316** 436
[3] Holleck H and Vac J 1986 *Sci. Technol.* A **4** 2661
[4] Yang T X, Cheng Q, Xu H B and Wang Y X 2010 *Acta Phys. Sin.* **59** 4919 (in Chinese)
[5] Li D H, Zhu X L, Su W J and Cheng X L 2010 *Acta Phys. Sin.* **59** 2004 (in Chinese)
[6] Toth L E 1974 *Transition Metal Carbides and Nitrides* (New York: Academic) p. 8
[7] Oyama S T 1996 *The Chemistry of Transition Metal Carbides and Nitrides* (London: Black Academic and Professional) p. 28
[8] Sinha S K and Harmon B N 1975 *Phys. Rev. Lett.* **35** 1515
[9] Dubrovinskaya N A, Dubrovinsky L S, Saxena S K, Ahuja R and Johansson B 1999 *J. Alloys Compd.* **289** 24
[10] Nartowski A M, Parkin I P, MacKenzie M, Craven A J and MacLeod I 1999 *J. Mater. Chem.* **9** 1275
[11] Du X P and Wang Y X 2010 *J. Appl. Phys.* **107** 053506
[12] Meloni G, Thomson L M and Gingerich K A 2011 *J. Chem. Phys.* **115** 4496
[13] Li X, Du X P and Wang Y X 2011 *J. Phys. Chem.* C **115** 6948
[14] Grossman J C, Mizel A, Cote M, Cohen M I and Louie S G 1999 *Phys. Rev.* B **60** 6343
[15] Abidri B, Rabah M, Rached D, Baltache H, Rached H, Merzoug I and Djili S 2010 *J. Phys. Chem. Solids* **71** 1870
[16] Ono S, Kikegawa T and Ohishi Y 2005 *Solid State Commun.* **133** 55
[17] Chen Z W, Gu M X, Sun C Q, Zhang X Y and Liu R P 2007 *Appl. Phys. Lett.* **91** 1077
[18] Kempter C P and Nadler M R 1960 *J. Chem. Phys.* **33** 1580
[19] Kempter C P 1964 *J. Chem. Phys.* **41** 1515
[20] Sanjay Kumar N R, Chandra Shekar N V, Subramanian N, Sekar M and Sahu P C 2008 *Proceedings of the 53rd DAE Solid State Physics Symposium*, December 16–20, 2008 Mumbai, India
[21] Zhao Z S, Wang M, Cui L, He J L, Yu D L and Tian Y J 2010 *J. Phys. Chem.* C **114** 9961
[22] Wang Y C, Lv J, Zhu L and Ma Y M 2010 *Phys. Rev.* B **82** 094116
[23] Lv J, Wang Y C, Zhu L and Ma Y M 2011 *Phys. Rev. Lett.* **106** 015503
[24] Zhu L, Wang H, Wang Y C, Lv J, Ma Y M, Cui Q L, Ma Y M and Zou G T 2011 *Phys. Rev. Lett.* **106** 145501
[25] Wang Y C, Liu H Y, Lv J, Zhu L, Wang H and Ma Y Y 2011 *Nature Commun.* **2** 563
[26] Zhu L, Wang Z W, Wang Y C, Zou G T, Mao H K and Ma Y Y 2012 *Proc. Natl. Acad. Sci. USA* **109** 751
[27] Gao G Y, Wang H, Bergara A, Li Y W, Liu G T and Ma Y Y 2011 *Phys. Rev.* B **84** 064118
[28] Ma Y M, Wang Y C, Lv J and Zhu L http://nlshm-lab.jlu.edu.cn/∼calypso.html
[29] Kohn W and Sham L J 1965 *Phys. Rev.* A **140** 1133
[30] Perdew J P, Burke K and Ernzerhof M 1996 *Phys. Rev. Lett.* **77** 3865
[31] Kresse G and Joubert D 1999 *Phys. Rev.* B **59** 1758
[32] Blöchl P E 1994 *Phys. Rev.* B **50** 17953

[33] Pack J D and Monkhorst H J 1977 *Phys. Rev.* B **16** 1748

[34] Togo A, Oba F and Tanaka I 2008 *Phys. Rev.* B **78** 134106

[35] Hill R 1952 *Proc. Phys. Soc. London Sect.* A **65** 350

[36] Birch F1947 *Phys. Rev.* **71** 809

[37] Zhao Z S, Cui L, Wang L M, Xu B, Liu Z Y, Yu D L, He J L, Zhou X F, Wang H T and Tian Y J 2010 *Cryst. Growth Des.* **10** 5024

[38] Xu X W, Hu L, Yu X, Lu Z M, Fan Y, Li Y X and Tang C C 2011 *Chin. Phys.* B **20** 126201

[39] Fan K M, Yang L, Peng S M, Long X G, Wu Z C and Zu X T 2011 *Acta Phys. Sin.* **60** 076201 (in Chinese)

[40] Li X F, Liu Z L, Peng W M and Zhao A K 2011 *Acta Phys. Sin.* **60** 076501 (in Chinese)

[41] Born M 1940 *Proc. Cambridge Philos. Soc.* **36** 160

[42] Jhi S H, Ihm J, Louie S G and Cohen M L 1999 *Nature* **399** 123

[43] Jiang X, Zhao J J and Jiang X 2011 *Comp. Mater. Sci.* **50** 2287

[44] Gao F M, He J L, Wu E D, Liu S M, Yu D L, Li D C, Zhang S Y and Tian Y J 2003 *Phys. Rev. Lett.* **91** 015502

[45] Ravindran P, Fast L, Korzhavyi P A, Johansson B, Wills J and Eriksson O 1998 *J. Appl. Phys.* **84** 4891

[46] Anderson O L 1963 *J. Phys. Chem. Solids* **24** 909