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Phase transition and thermodynamic properties of TiO_2 from first-principles calculations*

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The pressure induced phase transitions of TiO_2 from anatase to columbite structure and from rutile to columbite structure and the temperature induced phase transition from anatase to rutile structure and from columbite to rutile structure are investigated by *ab initio* plane-wave pseudopotential density functional theory method (DFT), together with quasi-harmonic Debye model. It is found that the zero-temperature transition pressures from anatase to columbite and from rutile to columbite are 4.55 GPa and 19.92 GPa, respectively. The zero-pressure transition temperatures from anatase to rutile and from columbite to rutile are 950 K and 1500 K, respectively. Our results are consistent with the available experimental data and other theoretical results. Moreover, the dependence of the normalized primitive cell volume V/V_0 on pressure and the dependences of thermal expansion coefficient α on temperature and pressure are also obtained successfully.

Keywords: local density approximation, transition phase, thermodynamic property, TiO_2
PACC: 7115M, 6470K, 6740K

1. Introduction

Titanium dioxide (TiO_2), a large-band gap semiconductor, has been widely studied because of its unique optical and chemical properties.[1−4] Currently, much attention is focused on the investigation of its photocatalytic properties and its applications in optoelectronic devices. Owing to its optical transparency in visible spectrum, the ultra-fine particle of TiO_2 is used in cosmetics, resin and paint, while its UV-screening properties can make it into the UV-preventing cosmetics and films. Under various chemical, temperature and pressure conditions, it can form multiple polymorphs. The understanding and the controlling of the crystalline phase and the phase transition process of TiO_2 are important but difficult. Thus much attention has been paid to its investigations experimentally and theoretically over the past decades.[5−12]

Under ambient condition, four natural polymorphs of TiO_2 are known to exist, i.e. anatase, brookite, rutile, and columbite (α-PbO2-type).[13] The brookite appears to exist only as a metastable phase, while the columbite is a quenched material.[14] At room temperature, as the applied pressure increases, both the anatase (space group $I4/amd$) and the rutile (space group $P42/mnm$) undergo phase transitions to the columbite (space group $Pbcn$). The x-ray-diffraction study by Arlt *et al* [9] showed that the single-crystal tetragonal anatase transformed to the orthorhombic columbite structure at about 4.5 GPa. The Raman scattering study revealed that the pressure range of the phase transition from the anatase to the columbite was between 4.5 and 7 GPa.[11] Shock-wave experiments on the rutile up to a peak-pressure of 20 GPa revealed a phase transformation to the columbite.[5,6] While other researches revealed that the rutile underwent a transition at about 10 GPa.[15−17] On the other hand, several research groups have theoretically investigated the pressure induced phase transitions from the anatase to the columbite and from the rutile to the columbite. Joseph *et al* [8] predicted that the anatase–columbite (A–C) transformation occurred at about 3.5 GPa, and the rutile–columbite transformation (R–C) took place at about 21 GPa.

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Dachille *et al*[18] found that the rutile phase could be transformed from other phases of TiO_2 at higher temperatures. The transition temperature of the anatase to the rutile for nanocrystalline TiO_2 is greatly reduced from that of the bulk value (between 973 and 1173 K).[10] The results of the XRD and visible Raman spectra show that TiO_2 undergoes the anatase-to-rutile phase transformation (A–R) gradually in a temperature range of 823–953 K.[19] Mitsuhashi and Kleppa[20] found the anatase structure to transform irreversibly to the rutile structure above 870 K. To our knowledge, there has been no theoretical investigation on the temperature induced phase transition of single-crystalline TiO_2 up to now. In the present work, we only focus on the pressure and temperature induced phase transitions among the rutile, anatase and columbite phases of TiO_2 by using the plane-wave pseudopotential density-functional theory (DFT) through the Cambridge Serial Total Energy Package (CASTEP) programme[21,22] together with the quasi-harmonic Debye model.[23]

2. Theoretical method

In our calculations, we employ the norm-conserving pseudopotentials introduced by Hammer *et al*[24] for the interactions of the electrons with the ion cores, together with the local density approximation (LDA) proposed by Vosko *et al*[25] for exchange–correlation potential. Pseudo-atom calculations are performed for O $2s^2 2p^4$ and Ti $3d^2 4s^2$. The electronic wavefunctions are expanded in a plane wave basis set with energy cut-offs of 400, 400, and 340 eV for the rutile, anatase, and columbite phases, respectively. For the Brillouin-zone sampling, we use 5×5×6, 6×6×3, 4×4×4 k-point Monkhorst–Pack meshes, respectively, where the self-consistent convergence of the total energy is 2×10^{-6} eV/atom.

To investigate the thermodynamic properties of TiO_2, we apply the quasi-harmonic Debye model [23] in which the non-equilibrium Gibbs function $G*(V;P,T)$ takes the form of

$$G*(V;P,T) = E(V) + PV + A_{\rm vib}(\Theta(V);T), \quad (1)$$

where $E(V)$ is the total energy per unit cell, PV corresponds to the constant hydrostatic pressure condition, $\Theta(V)$ is the Debye temperature, and the vibrational contribution $A_{\rm vib}$ can be written as

$$A_{\rm vib}(\Theta;T) = nkT\left[\frac{9}{8}\frac{\Theta}{T} + 3\ln(1-{\rm e}^{-\Theta/T}) - D(\Theta/T)\right], \quad (2)$$

where the $D(\Theta/T)$ represents the Debye integral, n is the number of atoms per formula unit. The Debye temperature Θ is expressed as

$$\Theta = \frac{\hbar}{K}[6\pi^2 V^{1/2} n]^{1/3} f(\delta)\sqrt{\frac{B_{\rm s}}{M}}, \quad (3)$$

where M is the molecular mass per formula unit, $B_{\rm s}$ is the adiabatic bulk modulus, δ is the Poisson ratio, and $f(\delta)$ is given by

$$f(\delta) = \left\{3\left[2\left(\frac{2}{3}\left(\frac{1+\delta}{1-2\delta}\right)\right)^{\frac{3}{2}} + \left(\frac{1}{3}\left(\frac{1+\delta}{1-\delta}\right)\right)^{\frac{3}{2}}\right]^{-1}\right\}^{\frac{1}{3}}. \quad (4)$$

By solving the following equation with respect to V

$$\left(\frac{\partial G*(V;P,T)}{\partial V}\right)_{P,T} = 0, \quad (5)$$

one could obtain the thermal expansion coefficient α

$$\alpha = \gamma C_V/(B_T V), \quad (6)$$

where B_T is the isothermal bulk modulus, C_V is the heat capacity and γ is the Grüneisen parameter. Applying this method, we have successfully investigated the thermodynamic properties of some materials.[26–30]

3. Results and discussion

For the rutile and the anatase structures, there are three independent structural parameters, i.e. the primitive cell volume V, the axial ratio c/a (a and c are the lattice constants), and the cell-internal dimensionless parameter u, which denotes the position of the second atom along the c-axis. The calculated equilibrium lattice parameters are as follows: a=0.4552 nm, c=0.2922 nm, and u=0.304 for the rutile phase; a=0.3744 nm, c=0.9461 nm, and u=0.2081 for the anatase phase. For the columbite, there are seven independent structure parameters, i.e. the three lattice constants (a, b, c) and four internal fractional coordinates (u, x, y, z). Thus the structure optimizations are carried out by the Broyden–Flecher–Goldfarb–Shanno minimization algorithm, and the obtained results are as follows: a=0.4504 nm, b=0.5462 nm, c=0.4857 nm, u=0.172,

x= 0.272, y=0.381 and z=0.418. Our results are consistent with the available experimental data and other theoretical data.[8,31–36] In comparison with the experimental data (a=0.4587 nm and c=0.2954 nm for the rutile;[31] a=0.3782 nm and c=0.9502 nm for the anatase;[31] a=0.4541 nm, b=0.5493 nm and c=0.4906 nm for the columbite.[33]), the lattice parameters obtained are underestimated slightly (by about 1% for the rutile, anatase, and columbite structures each). Obviously, that is due to the use of the local density approximation (LDA).

In Fig.1, we show the curves for total energy with respect to volume for the anatase, the columbite and the rutile structures of TiO_2. There have been a number of attempts to determine the relative stability of the rutile and the anatase structures by using calorimetric methods.[37–41] Mackrodt[42] showed that there was a relative stability that is generally believed to be from rutile to anatase to columbite. However, Joseph *et al* [8] predicted that the anatase was more stable than the rutile at 0 K and the difference in energy between the two phases was small (between 2 KJ/mol and 10 KJ/mol). Our results are in agreement with Joseph *et al*'s (the difference in energy between the two phases is 2.95 KJ/mol). Thus, the further experiment is required to ascertain which structure is more stable at low temperatures between the anatase and the rutile structures.

The transition pressures from anatase ($I4$/amd) to columbite ($Pbcn$) and from the rutile ($P42$/mnm) to the columbite ($Pbcn$) can be obtained by calculating Gibbs free energy between two phases. The Gibbs free energy is defined as $G^* = U + PV - TS$, where U is the internal energy, PV is volume work, and TS represents the energy from vibrational contribution. When the temperature is zero, the Gibbs free energy equals the enthalpy ($H = U + PV$). The variations of the calculated enthalpies $H_{\mathrm{C-R}}$ and $H_{\mathrm{C-A}}$ with pressure P at 0 K are shown in Fig.2. It is found that the transition pressure from anatase to columbite (A–C) is 4.55 GPa, and the transition pressure from rutile to columbite (R–C) is 19.92 GPa. In Table 1, we list the transition pressures from the available experimental data and other calculations. There appears a slight discrepancy between our results and the available experimental data, which maybe results from two important respects: one is that they adopted the experimental properties of TiO_2 at room temperature, but we used the experimental properties of TiO_2 at zero temperature in our calculation, and the other may be due to the LDA used in our calculation. However, our results correctly predict that the anatase phase will undergo a phase transition at lower pressures than rutile phase. Joseph *et al* [8] obtained the transition pressures 3.5 GPa and 21 GPa from the anatase to the columbite and from the rutile to the columbite, respectively. Our results are well consistent with theirs.

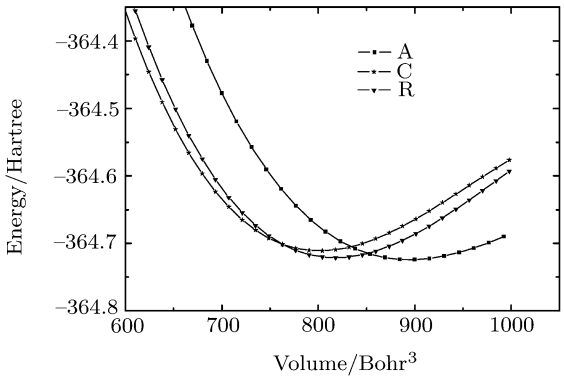


Fig.1. Curves for total energy versus volume for the anatase, columbite and rutile.

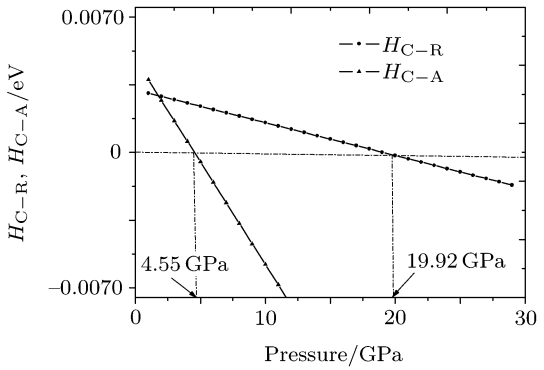


Fig.2. Variation of enthalpy with pressure for TiO_2.

Table 1. Phase transition pressures (GPa) and phase transition temperatures (K) of TiO_2.

	present work.	experimental data	other calculations
transition pressure (A–C)	4.55 GPa at 0 K	4.5 GPa,[9] 4.5–7 GPa,[11] 5.4 GPa[15]	3.5 GPa at 0 K[8]
transition pressure (R–C)	19.92 GPa at 0 K	20 GPa,[5,6] above 10 GPa[15–17]	21 GPa at 0 K[8]
transition temperature (A–R)	950 K at 0 GPa	820–950 K,[19] above 870 K[20]	
transition temperature (C–R)	1500 K at 0 GPa		

Similarly, the transition temperatures between the rutile, the anatase and the columbite structures can be obtained by calculating the Gibbs free energy changes between two phases. When the pressure is zero, the Gibbs free energy G^* equals the Helmholtz free energy F ($F = E + A_{\rm vib}$). In Fig.3, we show the variations of the calculated Helmholtz free energies $F_{\rm R-A}$ and $F_{\rm R-C}$ with temperature T at 0 GPa. It is found that the transition temperature from anatase to rutile (A–R) is about 950 K, at which the anatase will automatically revert to the rutile structure. And this transition temperature is slightly larger than the transition temperature 870 K calculated by Mitsuhashi and Kleppa,[37] and the transition temperature from columbite to rutile (C–R) is about 1500 K. To our knowledge, it is the first time that the transition temperature from columbite to rutile phase of TiO_2 has been obtained theoretically. No experimental and other theoretical data are available for our comparison.

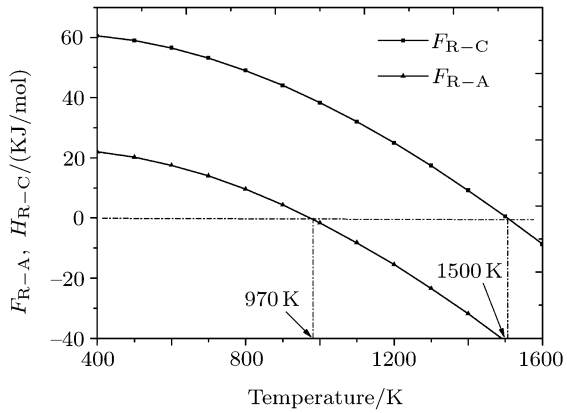


Fig.3. Variation of Helmholtz free energy with temperature for TiO_2.

In Fig.4, we present the dependences of calculated normalized volume V/V_0 (V_0 is the zero pressure equilibrium primitive cell volume) on pressure P at a given temperature for the rutile, anatase and columbite structures. It is seen that as pressure P increases, the relative volume V/V_0 decreases at a given temperature, and the values of relative volume V/V_0 at higher temperatures are smaller than those at lower temperatures at the same pressure. When the applied pressure equals 5 GPa, the cell volume becomes 2% of the zero pressure equilibrium cell volume. It seems that the variations in volume with pressure are trivial for the three polymorphs, because of their toughness and high melting point, and we believe that they can be used as a kind of coating material for supersonic aircrafts. Our results are well consistent with the single-crystal x-ray-diffraction experimental data given by Arlt *et al* [9] and by Glassford and Chelikowsky.[43]

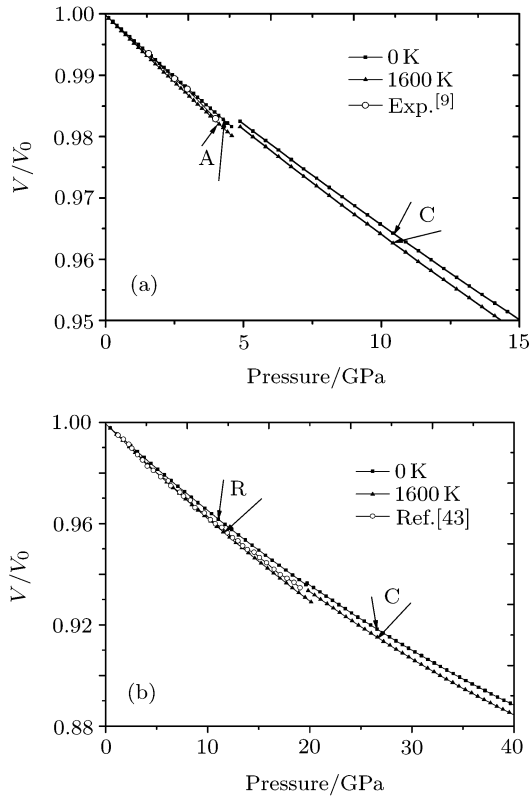


Fig.4. Variations of normalized primitive cell volume V/V_0 with pressure P for anatase and columbite (a) and for columbite and rutile (b) at 0 K and 1600 K separately.

The temperature and the pressure dependences of the thermal expansion coefficient α of rutile, anatase and columbite are indicated in Fig.5. Obviously, as pressure increases, thermal expansion coefficient α decreases rapidly, and almost exponentially. It is noted that the curves for 300, 500, 800 and 1500 K seem parallel to each others. However, the thermal expansion coefficient increases with T^3 at low temperatures and gradually turns into almost a linear increase at high temperatures, besides, the increasing trend becomes subdued. The effects of pressure on the thermal expansion coefficient α are very small at low temperatures, but as temperature increases the effects become prominent. It is found that the rutile structure is the most sensitive to temperature, and the anatase and columbite structures are relatively sluggish.

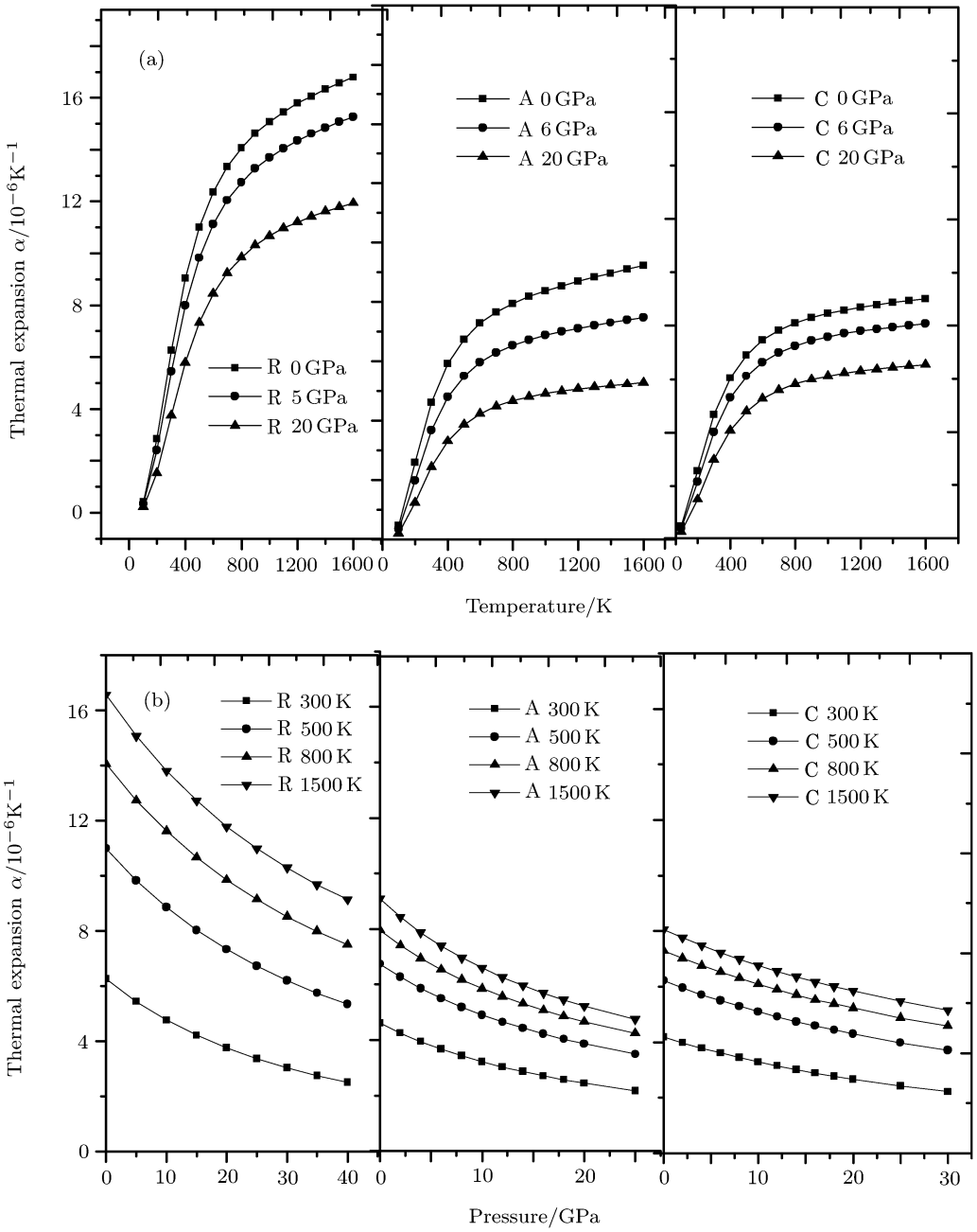


Fig.5. Variations in thermal expansion coefficient with temperature (a) and pressure (b) for rutile, anatase, and columbite.

4. Summary

In summary, we have investigated the pressure and temperature induced phase transitions of TiO_2 among the anatase, the rutile, and the columbite structures by *ab initio* plane-wave pseudopotential density functional theory method through the Cambridge Serial Total Energy Package (CASTEP) program, together with quasi-harmonic Debye model. It is found that the zero-temperature transition pressures from anatase to columbite and from rutile to columbite are 4.55 GPa and 19.92 GPa, respectively. The zero-pressure transition temperatures from anatase to rutile and from columbite to rutile are 950 and 1500 K, respectively. Our results are well consistent with the available experimental data and other theoretical results. Moreover, the dependence of the normalized primitive cell volume V/V_0 on pressure and the dependences of thermal expansion coefficient α on temperature and pressure are also obtained successfully.

References

[1] Fujishima A and Honda K 1972 *Nature* **238** 37
[2] Gratzel M 1992 *Nature* **353** 737
[3] Liu Y and Claus R O 1997 *J. Am. Chem. Soc.* **119** 5273
[4] Coulter L E and Sault A G 1995 *J. Catal.* **154** 56
[5] McQueen R G, Jamieson J C and March S T 1967 *Science* **155** 1401
[6] Linde R K and DeCarli P S 1969 *J. Chem. Phys.* **50** 319
[7] Natalia A D, Leonid S D, Rajeev A,Vitaly B P, Dmitriev V, Weber H P, Osorio-Guillen J M and Johansson B 2001 *Phys. Rev. Lett.* **87** 275501
[8] Joseph M, Varghese S and Nicholas M H 2002 *Phys. Rev.* B **65** 224112
[9] Arlt T, Bermejo M, Blanco M A, Gerward L, Jiang J Z, Staun Olsen J and Recio J M 2000 *Phys. Rev.* B **61** 14414
[10] Zhang Y H, Weidenkaffa A and Reller A 2002 *Mater. Lett.* **54** 375
[11] Lagarec K and Desgreniers S 1995 *Solid State Commun.* **94** 519
[12] Wang Y J, Chang J, Tan L N and Chen X R 2007 *Chin. Phys. Lett.* **24** 2646
[13] Luo W, Yang S F, Wang Y, Ahuja R, Johansson B, Liu J and Zou G T 2005 *Solid State Commun.* **133** 49
[14] Pathan H M, Kim W Y, Jung K D and Joo O S 2005 *Appl. Surf. Sci.* **246** 72
[15] Liu L G and Mernagh T P 1992 *Eur. J. Mineral* **4** 45
[16] Mammone J F, Sharma S K and Nicol M 1980 *Solid State Commun.* **34** 799
[17] Arashi H 1992 *J. Phys. Chem. Solids* **53** 355
[18] Dachille F, Simons P Y and Roy R l968 *Am. Miner.* **53** 1929
[19] Zhang J, Li M J, Feng Z C, Chen J and Li C 2006 *J. Phys. Chem.* B **110** 927
[20] Mitsuhashi T and Kleppa O J 1979 *J. Am. Chem. Soc.* **62** 356
[21] Payne M C, Teter M P, Allen D C, Arias T A and Joannopoulos J D 1992 *Rev. Mod. Phys.* **64** 1045
[22] Milman V, Winkler B, White J A, Packard C J, Payne M C, Akhmatskaya E V and Nobes R H 2000 *Int. J. Quantum. Chem.* **77** 895
[23] Blanco M A, Francisco E and Luana V 2004 *Comput. Phys. Commun.* **158** 57
[24] Hammer B, Hansen. L B and Norskov J K 1999 *Phys. Rev.* B **59** 7413
[25] Vosko S H, Wilk L and Nusair M 1980 *Can. J. Phys.* **58** 1200
[26] Lu L Y, Chen X R, Yu B R and Gou Q Q 2006 *Chin. Phys.* **15** 802
[27] Zhou X L, Liu K, Chen X R and Zhu J 2006 *Chin. Phys.* **15** 3014
[28] Li X F, Chen X R, Meng C M and Ji G F 2006 *Solid State Commun.* **139** 197
[29] Chen X R, Hu C E, Zeng Z Y and Cai L C 2008 *Chin. Phys. Lett.* **25** 1064
[30] Cheng Y, Lu L Y, Jia O H and Chen X R 2008 *Chin. Phys.* B **17** 1355
[31] Burdett J K, Hughbanks T, Miller G J, Richardson J W and Smith J V 1987 *J. Am. Chem. Soc.* **109** 3639
[32] Mikami M, Nakamura S, Kitao O, Arakawa H and Gonze X 2000 *Jpn. J. Appl. Phys.* **39** 847
[33] Gerward L and Olsen J S 1997 *J. Appl. Crystallogr.* **30** 259
[34] Kuo M Y, Chen C J, Hua C Y, Yang H C and Shen P 2005 *J. Phys. Chem.* B **109** 8693
[35] Milman V 1997 *Properties of Complex Inorganic Solids* (New York: Plenum)
[36] Montanari B and Harrison N M 2002 *Chem. Phys. Lett.* **364** 528
[37] Mitsuhashi T and Kleppa O J 1979 *J. Am. Chem. Soc.* **62** 356
[38] Margrave J L and Kybett B D 1965 *Tech. Rept. AFMO-TR* p65
[39] Navrotsky A and Kleppa O J 1967 *J. Am. Ceram. Soc.* **50** 626
[40] Rao C N R 1961 *Can J. Chem.* **39** 498
[41] Robie R A and Waldbaum D R 1966 *U.S. Geol. Surv. Bull.* **1259** 146
[42] Mackrodt W C 1999 *J. Solid State Chem.* **142** 428
[43] Glassford K M and Chelikowsky J R 1992 *Phys. Rev.* B **46** 1284