ISSN 1674-1056
http://cpb.iphy.ac.cn
http://iopscience.iop.org/cpb
中国物理 B
Chinese Physics
中国物理 Chinese Physics B

Equation of state of $LiCoO_2$ under 30 GPa pressure

Yong-Qing Hu(户永清), Lun Xiong(熊伦), Xing-Quan Liu(刘兴泉), Hong-Yuan Zhao(赵红远), Guang-Tao Liu(刘广涛), Li-Gang Bai(白利刚), Wei-Ran Cui(崔巍然), Yu Gong(宫宇), Xiao-Dong Li(李晓东)

Citation: Chin. Phys. B . 2019, 28(1): 016402. **doi:** 10.1088/1674-1056/28/1/016402
Journal homepage: http://cpb.iphy.ac.cn; http://iopscience.iop.org/cpb

What follows is a list of articles you may be interested in

The effect of dislocations on the thermodynamic properties of Ta single crystal under high pressure by molecular dynamics simulation

Yalin Li(李亚林), Jun Cai(蔡军), Dan Mo(莫丹), Yandong Wang(王沿东)

Chin. Phys. B . 2018, 27(8): 086401. **doi:** 10.1088/1674-1056/27/8/086401

Transport properties of mixing conduction in CaF_2 nanocrystals under high pressure

Ting-Jing Hu(胡廷静), Xiao-Yan Cui(崔晓岩), Jing-Shu Wang(王婧姝), Jun-Kai Zhang(张俊凯), Xue-Fei Li(李雪飞), Jing-Hai Yang(杨景海), Chun-Xiao Gao(高春晓)

Chin. Phys. B . 2018, 27(1): 016401. **doi:** 10.1088/1674-1056/27/1/016401

Anomalous behavior and phase transformation of α -GaOOH nanocrystals under static compression

Zhao Zhang(张钊), Hang Cui(崔航), Da-Peng Yang(杨大鹏), Jian Zhang(张剑), Shun-Xi Tang(汤顺熙), Si Wu(吴思), Qi-Liang Cui(崔啟良)

Chin. Phys. B . 2017, 26(10): 106402. **doi:** 10.1088/1674-1056/26/10/106402

Structure phase transformation and equation of state of cerium metal under pressures up to 51 GPa

Ce Ma(马策), Zuo-Yong Dou(窦作勇), Hong-Yang Zhu(祝洪洋), Guang-Yan Fu(付广艳), Xiao Tan(谈笑), Bin Bai(白彬), Peng-Cheng Zhang(张鹏程), Qi-Liang Cui(崔啟良)

Chin. Phys. B . 2016, 25(4): 046401. **doi:** 10.1088/1674-1056/25/4/046401

Structural phase transitions of tellurium nanoplates under pressure

Li Chao, Arfan Bukhtiar, Shen Xi, Kong Pan-Pan, Wang Wei-Peng, Zhao Hao-Fei, Yao Yuan, Zou Bing-Suo, Li Yan-Chun, Li Xiao-Dong, Liu Jing, Jin Chang-Qing, Yu Ri-Cheng

Chin. Phys. B . 2015, 24(3): 036401. **doi:** 10.1088/1674-1056/24/3/036401

Equation of state of $LiCoO_2$ under 30 GPa pressure*

Yong-Qing Hu(户永清)[1], Lun Xiong(熊伦)[1,2,†], Xing-Quan Liu(刘兴泉)[3], Hong-Yuan Zhao(赵红远)[4], Guang-Tao Liu(刘广涛)[5], Li-Gang Bai(白利刚)[6], Wei-Ran Cui(崔巍然)[6], Yu Gong(宫宇)[6], and Xiao-Dong Li(李晓东)[6]

[1] *School of Intelligent Manufacturing, Sichuan University of Arts and Science, Dazhou* 635000, *China*
[2] *DaZhou Industrial Technology Institute of Intelligent Manufacturing, Dazhou* 635000, *China*
[3] *School of Materials and Energy, University of Electronic Science and Technology, Chengdu* 610054, *China*
[4] *Research Branch of Advanced Materials & Green Energy, Henan Institute of Science and Technology, Xinxiang* 453003, *China*
[5] *National Key Laboratory of Shock Wave and Detonation Physics, Institute of Fluid Physics, China Academy of Engineering Physics, Mianyang* 621900, *China*
[6] *Institute of High Energy Physics, Chinese Academy of Sciences, Beijing* 100049, *China*

(Received 10 September 2018; revised manuscript received 28 October 2018; published online 12 December 2018)

$LiCoO_2$ is one of the most important cathode materials for high energy density lithium ion batteries. The compressed behavior of $LiCoO_2$ under high pressure has been investigated using synchrotron radiation x-ray diffraction. It is found that $LiCoO_2$ maintains hexagonal symmetry up to the maximum pressure of 30.1 GPa without phase transition. The elastic modulus at ambient pressure is 159.5(2.2) GPa and its first derivative is 3.92(0.23). In addition, the high-pressure compression behavior of $LiCoO_2$ has been studied by first principles calculations. The derived bulk modulus of $LiCoO_2$ is 141.6 GPa.

Keywords: equation of state, high pressure, $LiCoO_2$

PACS: 64.30.Jk, 64.60.–i, 07.35.+k, 61.05.cp **DOI:** 10.1088/1674-1056/28/1/016402

1. Introduction

Efficient and durable energy storage is an important factor limiting the development of renewable energy. Compared with other energy systems, chemical power has been widely studied because of its higher energy conversion efficiency, safe and convenient use, and environmental friendliness. Lithium-ion batteries, as a promising new type of chemical power supply, have a series of advantages over other batteries, including (i) high monomer voltage (generally about 3.6 V, three times as high as traditional Ni–Cd, Ni–MH and Pb-acid batteries); (ii) high energy density (up to 300 Wh/kg, 6–7 times as high as the traditional Pb-acid batteries, 3–4 times as high as the conventional Ni–Cd and Ni–MH batteries); (iii) long life cycle (up to 10000 cycles); (iv) no memory effect; and (v) environmental friendliness. Lithium ion batteries have been applied and developed more and more because of their advantages. Applications not only expand the market scope of lithium-ion batteries, but also put forward higher requirements for the performance of lithium-ion batteries. One of the popular cathode materials for lithium-ion batteries is lithium cobaltite ($LiCoO_2$).[1]

$LiCoO_2$ has a remarkable property of allowing reversible removal and reinsertion of lithium.[2] Due to its excellent electrochemical properties, $LiCoO_2$ has become one of the most widely used cathode materials in lithium-ion batteries.[3] Pressure can tune the distance of atoms in the material, and can make the atoms arrange in a more compact way. Pressure can also change the structural, physical, and chemical properties, e.g., pressure-induced phase transition, metallization, strength,[4] and texture. High-pressure science has been integrated in the fields of physics, material science, chemistry, earth science, and others. Lithium atoms in $LiCoO_2$ are intercalated between cobalt oxide layers, and are combined with the nearest six oxygen atoms to form lithium oxide octahedron. The Li–O bond is much weaker than the Co–O bond. Under certain conditions, Li^+ can be intercalated and detached from the CoO layers, making $LiCoO_2$ an ideal intercalation material for lithium ion batteries. The conductivity of lithium ion is high because of the two-dimensional movement of the lithium ion between the strong bonded CoO layers. In addition, the octahedron distribution of CoO_6 makes the interaction between Co and Co in the form of Co–O–Co, and the electronic conductivity is also high. The physical properties of $LiCoO_2$ at high pressure are closely related to its structure and electrochemical properties.[5] Thus, a deep understanding of the connection between crystal structure and electrochemical properties (such as Li^+ migration properties under high pressure) may help to improve the efficiency of layered

*Project supported by the Program of Education Department of Sichuan Province of China (Grant No. 18ZB0506), the Project of Sichuan University of Arts and Science, China (Grant No. 2017KZ001Z), and Outstanding Talent Introduction Project of Henan Institute of Science and Technology, China (Grant No. 203010617011). This work was performed at 4W2 beamline of Beijing Synchrotron Radiation Facility (BSRF), which was supported by Chinese Academy of Sciences (Grant Nos. KJCX2-SWN03 and KJCX2-SW-N20).

†Corresponding author. E-mail: 1094129778@qq.com

© 2019 Chinese Physical Society and IOP Publishing Ltd

$LiCoO_2$ cathode materials for lithium-ion batteries. For example, Fell *et al.*[6] found that the structural modification of $LiNi_xCo_yMn_zO_2$ induced by the high pressure and high temperature treatment is retained in the quenched samples, which results in electrode characteristics different from those of pristine materials. Although $LiCoO_2$ is one of the important cathode materials for lithium-ion batteries, there are few reports on its structures and compressed properties. Wolverton and Zunger[7] reported a phase transition of $LiCoO_2$ from the layered phase to a cubic phase at ~ 3 GPa by *ab initio* calculations. Wang *et al.*[8] performed high-pressure x-ray diffraction (XRD) of $LiCoO_2$ up to 26 GPa using nitrogen as the pressure transmitting medium. The authors found no phase transition and derived the zero-pressure bulk modulus and its first pressure derivate as 149(2) GPa and 4.1(0.3), respectively. Wu *et al.*[9] calculated the mechanical properties of $LiCoO_2$ under high pressure by first principles, and the authors obtained the bulk modulus of 166.74 GPa. Xu *et al.*[5] investigated the high-pressure structure of $LiCoO_2$ up to 20.3 GPa with silicone oil as the pressure transmitting medium. The authors found no structural phase transition and gave the derived bulk modulus as 118.5 GPa.

Despite several experimental and theoretically calculated results for $LiCoO_2$, the obtained bulk moduli are strongly different from each other (118.5–166.74 GPa),[5,8,9] and the differences call for a further study. Thus, in the present work, the phase transition and equation of state of $LiCoO_2$ up to 30.1 GPa are investigated using angle dispersive XRD technique in a diamond anvil cell (DAC) with silicone oil as the pressure transmitting medium.

2. Experimental details

The $LiCoO_2$ (99.5%) sample was purchased from Alfa Aesar company. At ambient pressure, $LiCoO_2$ has a hexagonal crystal structure (α-$NaFeO_2$ prototype), with space group of *R*-3*m* (see Fig. 1). In the high-pressure XRD experiments, a modified Mao–Bell DAC with 400 μm diameter culet was used. A T301 gasket was pre-indented to ~ 35 μm, and a sample hole with a diameter of 140 μm was made using laser. Silicone oil can maintain a good quasi-hydraulic pressure environment below 20 GPa, and is superior to the 4:1 alcohol mixture beyond 20 GPa.[10] Thus, silicone oil was used as a pressure transmitting medium. A ruby with a diameter of 10 μm was used as the pressure sensor,[11] and placed on the top of the sample center.

In situ synchrotron radiation high-pressure XRD experiments were performed at 4W2 beam line of Beijing Synchrotron Radiation Facility (BSRF), Chinese Academy of Sciences. The incident monochromatic x-ray beam with a wavelength of 0.6199 Å was focused by a pair of Kirkpatrick–Baez mirrors, and the full width at half maximum (FWHM) of the spot was 30 μm (vertical) ×10 μm (horizontal). The diffraction patterns were collected by a Pilatus detector. The distance between sample and detector and the orientation of the detector were calibrated using CeO_2 standard. The exposure time of each XRD pattern was 10–12 min. The accumulated images were processed and analyzed by the Fit2D software.[12]

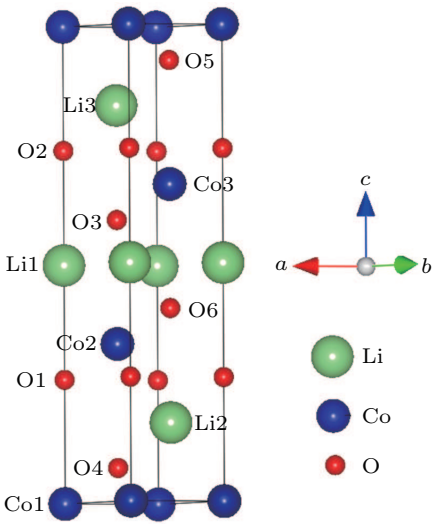


Fig. 1. Crystal structure of the investigated $LiCoO_2$ at ambient pressure.

3. Theoretical calculation details

Density functional theory (DFT) calculations, including structural optimizations and enthalpies, were performed using the Vienna *ab-initio* simulation package (VASP)[13] code which employs the Perdew–Burke–Ernzerhof[14] exchange-correlation functional. The $2s^1$, $3d^74s^2$, and $2s^22p^4$ electrons were treated as the valence electrons for Li, Co, and O, respectively. The cutoff energy was 600 eV and the Monkhorst–Pack grid was $2\pi\times$ 0.06 $Å^{-1}$ in reciprocal space to ensure that all enthalpy calculations were well converged to about 1 meV/atom. The $LiCoO_2$ has a hexagonal structure (space group *R*-3*m*) with lattice parameters $a = 2.8166$ Å, $c = 14.0520$ Å, $\alpha = \beta = 90°$, and $\gamma = 120°$ at ambient pressure. There are three inequivalent crystallographic sites per cell, labeled as Li1, Co1, and O1, occupying the 3*b* (0, 0, 1/2), 3*a* (0, 0, 0), and 6*c* (0, 0, *x*) ($x = 0.260$) positions, respectively. The bulk modulus (K_0) and its first derivative (K_0') were derived from fitting the calculated volume–pressure data by the third-order Birch–Murnaghan equation of state (EOS).

4. Results and discussion

4.1. General

The accumulated diffraction patterns were analyzed by Fit2D software.[12] The maximum experimental pressure is 30.1 GPa; and the pressure is derived from the ruby marker.[11] The selected 2θ–intensity diffraction patterns of $LiCoO_2$ under different pressures are shown in Fig. 2. Six diffraction

peaks of $LiCoO_2$ which are indexed to (003), (101), (006), (104), (015), and (009) can be observed in all diffraction patterns. There are neither new diffraction peaks appearing nor old diffraction peaks disappearing, indicating no crystal phase transition of $LiCoO_2$ in the experimental pressure range.

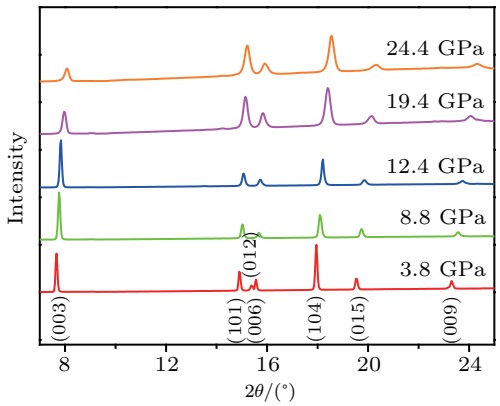


Fig. 2. Representative diffraction patterns of $LiCoO_2$ under different pressures.

4.2. Hydrostatic EOS

The compressibilities of the a and c axes of $LiCoO_2$ with pressure are shown in Fig. 3. It can be seen that parameters a and c decrease continuously with the increasing pressure, indicating that the $LiCoO_2$ sample maintains the hexagonal structure in the entire pressure range. Although the experimental values are in good agreement with the theoretically calculated ones of the present work, there are minor differences. As DFT transforms the actual multi-electron problem into a single-electron problem, and gives a method for calculating the effective potential of a single electron. The total energy of an electron gas is only a function of the electron density. The minimum value of energy functional is the ground state energy of the system, and the density corresponding to it is the ground state density of a single particle. The widely used approximation is the generalized-gradient approximation (GGA). The exchange correlation energy in the GGA approximation is not only related to the density, but also related to the density gradient. On the other hand, the temperature of electronics calculated by DFT is absolute zero, but the temperature of electronics in real materials at ambient conditions is not absolute zero. In addition, the compression ratio of $LiCoO_2$ along the c axis is about 2.6 times of the compression rate along the a axis in this work, much less than the value (4.5) obtained by Xu *et al.*[5] The compression ratio of the a axis in the present work is close to the value of Xu *et al.*[5]

The variation of c/a with pressure is shown in Fig. 4. It can be seen that, the results below 15 GPa of the present work are inconsistent with the results obtained by Wang *et al.*,[8] but less than those of Wang *et al.*[8] over 15 GPa. On the other hand, the results of this work are slightly smaller than those of Xu *et al.*[5] below 6 GPa, while significantly larger than the values derived by Xu *et al.*[5] above 6 GPa.

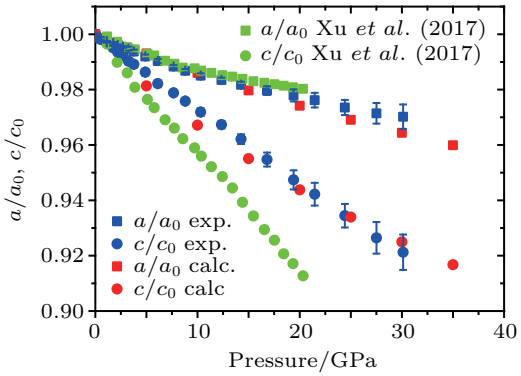


Fig. 3. Compressibility of the normalized lattice parameters of $LiCoO_2$ compared with the data obtained by Xu *et al.* (Ref. [5]).

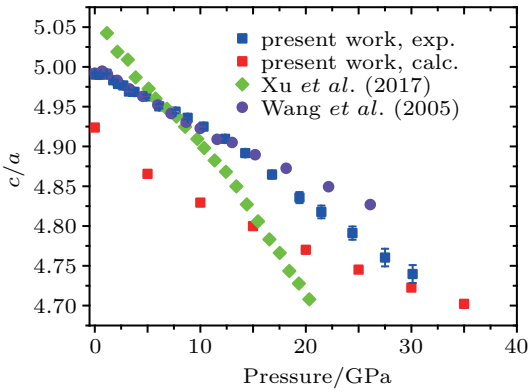


Fig. 4. The c/a ratio of $LiCoO_2$ versus pressure compared with the data obtained by Wang *et al.* (Ref. [8]) and Xu *et al.* (Ref. [5]).

The unit cell volumes as a function of pressure are shown in Fig. 5. For comparison, the results obtained in earlier XRD under quasi-hydrostatic compressions are also presented.[5,8] It is evident from Fig. 5 that the fit to the present experimental data is very good.

The unit cell volume as a function of pressure was fitted using the third-order Birch–Murnaghan EOS to obtain the bulk modulus (K_0) and its first derivative (K_0'). The third-order Birch–Murnaghan EOS is expressed as follows:[15]

$$P = 1.5K_0\left[\left(\frac{V_0}{V}\right)^{7/3} - \left(\frac{V_0}{V}\right)^{5/3}\right] \times\left\{1+\frac{3}{4}(K_0'-4)\left[\left(\frac{V_0}{V}\right)^{2/3}-1\right]\right\}, \quad (1)$$

where K_0, K_0', and V_0 are the bulk modulus, its first derivate, and the unit-cell volume at ambient conditions, respectively.

The comparison between the present results and the previously reported[5,8,9] bulk modulus and its pressure derivative of $LiCoO_2$ is shown in Table 1. The first derivative of the bulk modulus is close to 4 in the present results, indicating that the data has a good accuracy. The experimental bulk modulus of this work is inconsistent with the experimental result obtained

by Wang *et al.*,[8] the GGA calculation result derived by Wu *et al.*,[9] and the LDA calculation result obtained by Xu *et al.*,[5] but much larger than the experimental result of Xu *et al.*[5] On the other hand, the result of GGA calculation of the present work is inconsistent with the experimental result obtained by Wang *et al.*[8] and the result of GGA calculation by Xu *et al.*[5]

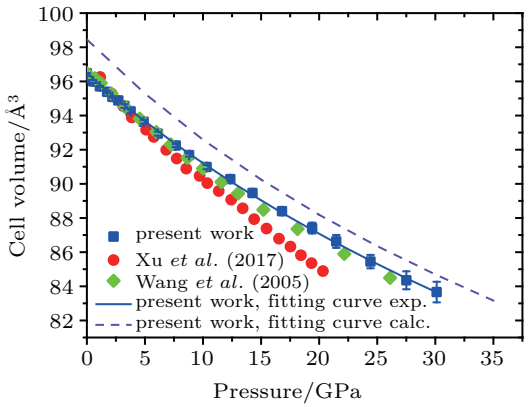


Fig. 5. Compression curves of $LiCoO_2$. The line is a Birch–Murnaghan equation fitted to the present experimental data. The dotted line is a Birch–Murnaghan equation fitted to the theoretical calculation data. The solid diamonds are the static compression data from Ref. [8]. The solid circles are the static compression data obtained by Xu *et al.*[5]

Table 1. Summary of the bulk modulus (K_0) and its pressure derivative (K_0') of $LiCoO_2$ obtained with various methods.

K_0/GPa	K_0'	Method	PTM	Ref.
159.5(2.2)	3.92(0.23)	x-ray	Si oil	present work
141.6	4.52	GGA	–	
118.5	4(fixed)	x-ray	Si oil	Xu *et al.*[5]
168.5	4.67	LDA	–	
142.9	4.51	GGA	–	
149(2)	4.1(0.3)	x-ray	nitrogen	Wang *et al.*[8]
166.74	–	GGA	–	Wu *et al.*[9]

Note: PTM: pressure transition medium; Si oil: silicone oil; GGA: the generalized gradient approximation.

4.3. Bond length

The relationship between the Li–O and Co–O bond lengths in $LiCoO_2$ under high pressure by first-principles calculation is shown in Fig. 6. It can be seen that, the bond lengths of Li–O and Co–O decrease with increasing pressure. At ambient pressure, the bond length of Co–O is longer than that of Li–O. In addition, the bond energy of Co–O is smaller than that of Li–O. Thus, the Co–O bond length is vastly more compressible than the Li–O length. The reduction of the Li–O bond length makes the activation energy required for the Li-ion transition greater. In addition, the decrease of the Co–O bond length will increase the rejection between Co-ion and Li-ion. Therefore, the decrease of Li–O and Co–O bond lengths at high pressure makes the transition of Li-ion in $LiCoO_2$ difficult.[5,16]

There are only two s^1 electrons in a Li ion, and the Li ion is relatively smaller than the Co ion. Thus, the bond length of Li–O is shorter than that of Co–O. In the other hand, the only two inner electrons of Li ions are stronger and not easy to be compressed than the Co ions. As a result, the *c* axis is much easier to compress compared to the *a* axis, and O atoms will gradually move in the direction of Co at elevated pressure. The compressive behavior of O1 *x* under high pressure is shown in the inset of Fig. 6.

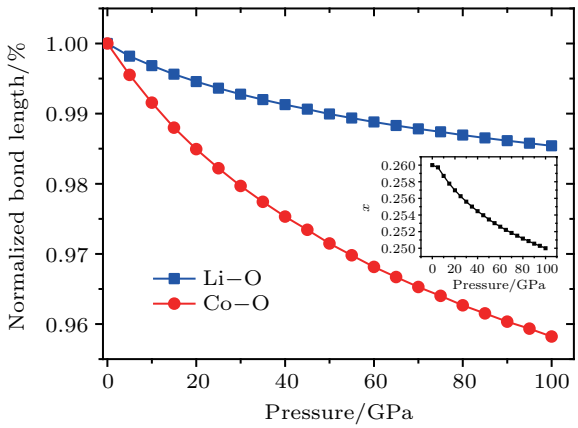


Fig. 6. The Li–O and Co–O bond lengths of $LiCoO_2$ as a function of pressure obtained by first-principles calculation. Inset is the *x* of O1 as a function of pressure.

5. Conclusion

In summary, we have investigated the phase transition and equation of state of $LiCoO_2$ up to 30.1 GPa. The result was obtained in a modified Mao–Bell DAC under quasi-hydrostatic compression using axial XRD technique at ambient temperature and showed no phase transition. The obtained bulk modulus and its first derivative are 159.5(2.2) GPa and 3.92(0.23), respectively. The experimental bulk modulus of the present work is slightly higher than the reported experimental results. The bond lengths of Li–O and Co–O decrease at elevated pressure, which makes the transition of Li-ion in $LiCoO_2$ very difficult.

References

[1] Mizushima K, Jones P C, Wiseman P J and Goodenough J B 1980 *Mater. Res. Bull.* **15** 783
[2] Reimers J N and Dahn J R 1992 *J. Electrochem. Soc.* **139** 2091
[3] Huang B, Jang Y I, Chiang Y M and Sadoway D R 1998 *J. Appl. Electrochem.* **28** 1365
[4] Xiong L and Liu J 2018 *Chin. Phys. B* **27** 036101
[5] Xu C, Sun F and Yang W G 2017 *Chin. J. High Press. Phys.* **31** 529
[6] Fell C R, Lee D H, Meng Y S, Gallardoamores J M and Dompablo M E 2012 *Energy Environ. Sci.* **5** 6214
[7] Wolverton C and Zunger A 1998 *J. Electrochem. Soc.* **145** 2424
[8] Wang X, Loa I, Kunc K, Syassen K and Amboage M 2005 *Phys. Rev. B* **72** 224102
[9] Wu L M and Zhang J 2015 *J. Appl. Phys.* **118** 225101
[10] Klotz S, Chervin J C, Munsch P, March and G L 2009 *J. Phys. D: Appl. Phys.* **42** 075413
[11] Mao H K, Xu J and Bell P M 1986 *J. Geophys. Res.* **91** 4673
[12] Hammersley A P, Svensson S O, Hanfl, M, Fitch A N and Hausermann D 1996 *High Press. Res.* **14** 235
[13] Kresse G and Furthmüller J 1996 *Phys. Rev. B* **54** 11169
[14] Perdew E M and Burke K 1996 *Phys. Rev. Lett.* **77** 3865
[15] Birch F 1978 *J. Geophys. Res.* **83** 1257
[16] Kang K and Ceder G 2006 *Phys. Rev. B* **74** 094105