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Ab initio study on phase transition and magnetism of $BiFeO_3$ under pressure

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In this paper the first-principles calculations within local spin density approximation (LSDA)+U show that $BiFeO_3$ experiences a mixed phase state with P4mm structure being the intermediate phase before the pressure of phase transition is reached. The critical pressure for the insulator–metal transition (IMT) is found to be about 50 GPa. A pressure induced crossover of high-spin states and low-spin states is observed close to the IMT pressure in R3c structure. The LSDA+U calculations account well for the mechanism of the IMT and crossover of spin states predicted in recent experiment (Ref.[1]).

Keywords: density functional theory, phase transition, $BiFeO_3$
PACC: 7115, 7510, 7780

1. Introduction

Multiferroic materials have attracted much attentions owing to its ferroelectric order controlled by external magnetic field, and *vice versa*. $BiFeO_3$, as a potential multiferroic, has been extensively investigated both experimentally and theoretically.[1−6] It takes the rhombohedral structure in R3c space group where Bi, Fe, and O displace relatively to each other along [1 1 1] crystalline direction, producing the high spontaneous polarization partly due to the lone-pair activity of Bi. Although different values of polarization have been reported experimentally in different literatures, this might be explained theoretically by the complicated switching paths in which the transforming of centrosymmetric structure into the two enantiomorphs have non-zero polarization.[7] The neighbouring antiferromagnetic (AFM) magnetic moments of Fe are arranged alternatively along [1 1 1] direction, also known as the G-type AFM up to 643 K, which makes the magnetization significantly reduced.[8,9] The neighbouring magnetic moments tend to be canted to produce a net magnetic moment away from the original direction in (1 1 1) plane due to the D-M interaction.[10] In our previous work, we show that this small net magnetic moment about $0.1\,\mu_B$, is coupled with the antiferrodistortive rotation of the neighbouring oxygen octahedra[11] and nearly eliminated by the cycloidal magnetic ordering in the periodic crystal with a wavelength of period of 640 Å (1 Å=0.1 nm),[8,9] while magnetization can be improved by partly substituting Fe ions epitaxially by Ti in our preceding literature.[12] However, the magnetoelectric property and the coupling effect between ferroelectric order and magnetic order still remains ambiguous and becomes the controversial topic.[13] Theories, especially under external field or pressure, are required to unambiguously explain the mechanism of magnetoelectric property in multiferroics such as $BiFeO_3$. Investigation on the phase transition under extremely experimental condition, such as high pressure, becomes interesting and crucial for understanding the coupling between ferroelectricity and magnetism in $BiFeO_3$. First principles calculations based on density functional theory (DFT) have been well developed and widely used in studying the ground state electronic and magnetic properties,[14,15] as well as the ferroelectric property of perovskite materials under applied electric field by treating the external field as perturbation.[16] Few experimental works have been done on the phase transition of $BiFeO_3$.[1] To our knowledge, there is no theoretical investigation done on the phase transition of $BiFeO_3$ under pressure by using first-principles calculations up to now. In this paper we constructed 5 space groups: R3c, P4mm, Pnma, Cm, and $Pm\bar{3}m$ to investigate the possible phase transformations, elec-

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tronic properties and the magnetic moments under the hydrostatic pressure. All lattice parameters and atomic coordinates were taken from Ref.[2]. For all space groups, we considered non-spin and ferromagnetic (FM) spin configurations to investigate the phase transition. In addition, we took into account the G-type AFM spin configuration, which is found to be the room temperature structure of $BiFeO_3$, in R3c space group.

2. Computational details

Our calculations were performed within the local spin density approximation (LSDA) to DFT using the ABINIT package.[17,18] The ion-electron interaction was modelled by the projector augmented wave (PAW) potentials[19,20] with a uniform energy cutoff of 500 eV. The Bi $5d$, $6s$, and $6p$ electrons, Fe $3s$, $3p$, $3d$, and $4s$ electrons, and O $2s$ and $2p$ electrons were considered as valence states. Two partial waves per l quantum number were used. The cutoff radii for the partial waves for Bi, Fe, and O were 2.5, 2.3, 1.1 a.u., respectively. The $10 \times 10 \times 10$ Monkhorst–Pack sampling of the Brillouin zone was used for all calculations. We also calculated the electronic properties within the LSDA+U method where the strong Coulomb repulsion between localized d states has been considered by adding a Hubbard-like term to the effective potential.[21−23] The effective Hubbard parameter, the difference between the Hubbard parameter U and the exchange interaction J, was varied between 0 and 6 eV for the Fe d states. An appropriate value of 4 eV was adopted in comparison with the previous work and experimental result.[7] The forces on the atoms were calculated by using the Hellmann–Feynman theorem and they were used to perform a conjugate gradient relaxation. Structural optimizations were performed until the forces on atoms converge to 0.1 meV/Å.

3. Results and discussion

Figure 1 shows the volume-pressure (V-P) relation for $BiFeO_3$ obtained by our present calculation. There is no significant difference between the FM and AFM spin configuration in R3c structure, indicating that the magnetism takes smaller effect on the lattice structure under pressure. A volume collapse for P4mm structure occurs in the lower pressure range at about 20 GPa. Apparently, the phase transition between the P4mm and the $Pm\bar{3}m$ structure would occur at about 35 GPa. Moreover, the increase of pressure, about 50 GPa, is very close to the experimental value of the IMT pressure (Ref.[1]), we found a series of transitions between P4mm, Cm, Pnma, and specifically the R3c structure. These indicate that $BiFeO_3$ may exist in a mixed phase at lower pressure range, and P4mm group serves as an intermediate structure among the other phases.

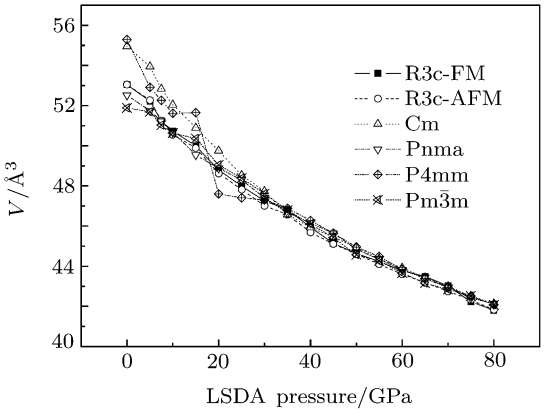


Fig.1. The calculated volume-pressure curves for different phases of $BiFeO_3$.

In order to investigate the phase transition under pressure clearly, we have analysed the enthalpy as a function of pressure. For zero temperature phase transition, the enthalpy $H = E_0 + PV$ should be taken into account. A common tangent in the enthalpy-pressure (H-P) curves gives the critical transition pressure. In the lower pressure stage at about 35 GPa shown in Fig.2(a), a phase transition between P4mm and $Pm\bar{3}m$ space group takes place. It can be explained as the much smaller energy barrier needed to change the tetragonal c/a ratio, which agrees well with the V-P graph in the segment of lower pressure. One can see, in Fig.2(b), the P4mm-Cm transition occurs at about 50 GPa which is close to the IMT pressure (Ref.[1]). Moreover, figures 2(c) and 2(d) show that P4mm space group transformed into Pnma and R3c structures at about 75 GPa and 80 GPa, respectively. It is suggested that the pressure of transition between P4mm, Pnma and R3c group is significantly enhanced by our LSDA+U calculation, partly due to the large energy barrier between these structures. However, in experiment, phase transition is relatively complicated, and the transition pressure tend to be decreased closely to the IMT pressure through easy switching paths between the different space groups. Meanwhile, R3c structure, which is determined to be the room

temperature structure in experiments, is energetically favourable when pressure approaches to about 50 GPa, which indicates that the P4mm space group serves as an intermediate phase to be transformed into R3c phase under IMT pressure.

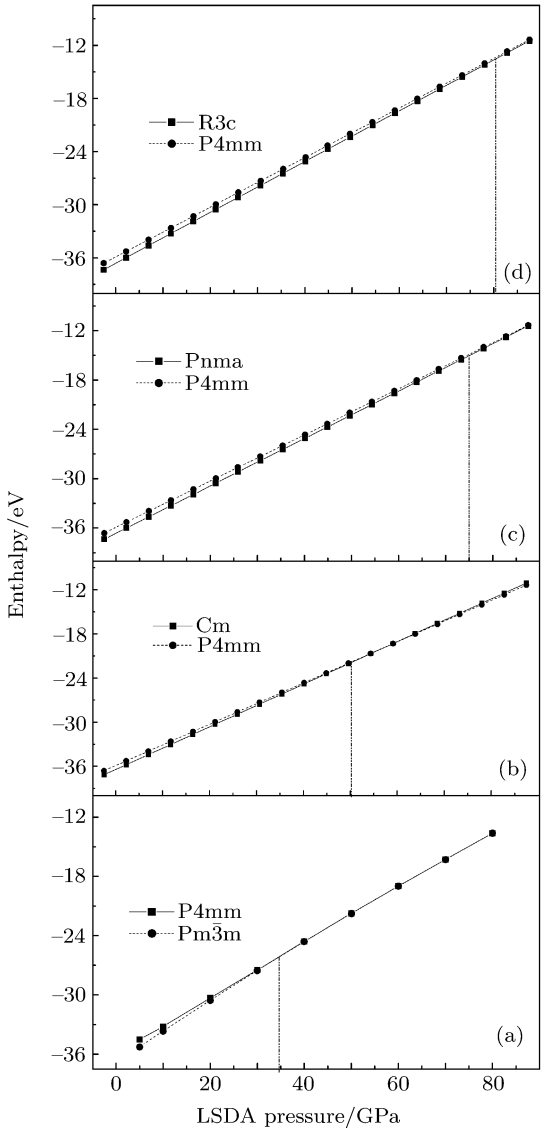


Fig.2. Calculated enthalpy against pressure for different phases of $BiFeO_3$. Transitions from P4mm to (a) $Pm\bar{3}m$; (b) Cm; (c) Pnma; (d) R3c are shown.

The relationship between magnetic moment and pressure is shown in Fig.3. Space groups, including P4mm, Pnma, Cm, and $Pm\bar{3}m$, experience a spin transition between the high-spin and low-spin states at about 50 GPa in the vicinity of the IMT pressure. However, the R3c group which undergoes an anomaly with a lower-spin state as in Pnma at about 50 GPa, also close to the IMT pressure, remains the high-spin state after passing through the critical pressure, and comes back to the low-spin state in the higher pressure range. From the discussion in the previous section, we suggest that all space groups are transformed into R3c group through the intermediate structure P4mm under the IMT pressure. From our LSDA+U calculation, it is worth mentioning that the IMT takes place at about 50 GPa, accompanying with the fluctuation of magnetization. The fluctuation of magnetization

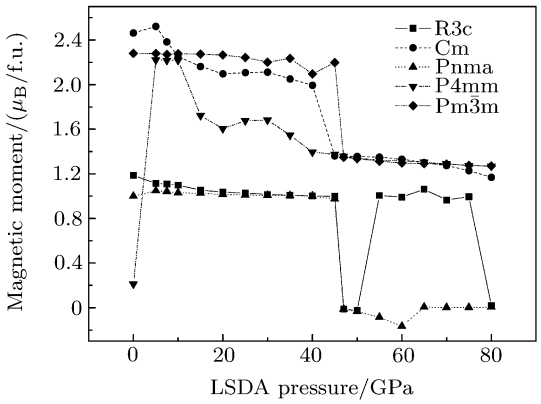


Fig.3. Calculated magnetic moment as a function of pressure for different phases in the FM spin configuration.

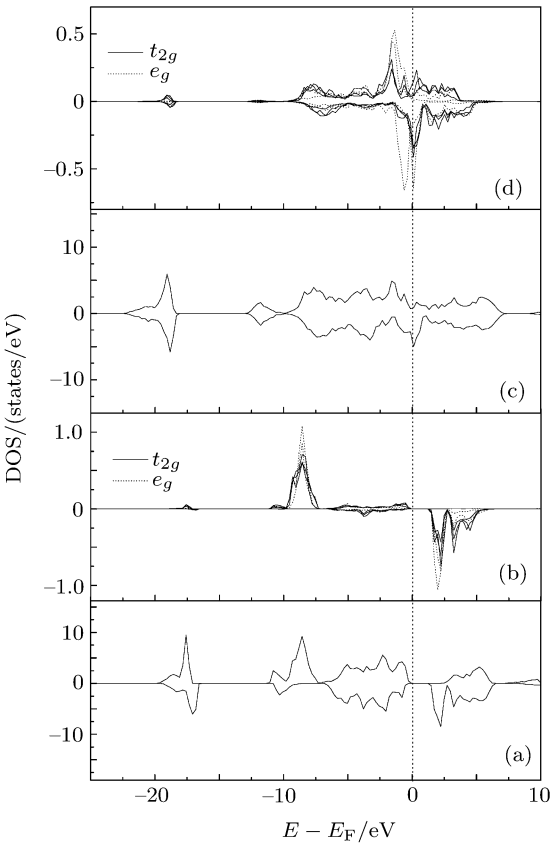


Fig.4. Total DOS and orbital-resolved DOS for Fe in FM R3c $BiFeO_3$ under ambient condition and IMT pressure from our LSDA+U calculation. (a), (b), (c), and (d) show total DOS, orbital-resolved DOS of Fe under ambient condition, and those under IMT pressure, respectively.

for R3c group around the IMT pressure can reflect the fact that there is a crossover of high-spin and low-spin states under the critical pressure, which agrees well with the recent experimental result (Ref.[1]). And the crossover of high-spin and low-spin states is not due to spin flip fluctuations of the spin wave, but the fluctuations of different spin values. Moreover, we believe that the R3c structure is in the FM ordering where there is really a band collapse and an IMT under the critical pressure, while the band gap in the AFM G-type configuration still remains in the high pressure range, which should be the feature of a band insulator under the high pressure where the Mott insulating condition breaks down. The total density of states (DOS) and the projected DOS of Fe for FM R3c structure under ambient condition and IMT pressure are shown in Figs.4(a), 4(b), 4(c), and 4(d), respectively. The manifold near the Fermi level is mainly attributed to the localized d states in Fe. One can see that, in our LSDA+U calculation, the triply degenerate t_{2g} states in down-spin channel and the doubly degenerate e_g states in up-spin channel are pushed away from the Fermi level under the ambient condition to open a band gap of 1.4 eV. It is apparent that $BiFeO_3$ becomes metallic under the IMT pressure, with Fermi level cutting through the narrow bands composed of up-spin e_g states and down-spin t_{2g} states. Moreover, the e_g states are further split into d_{z^2} and $d_{x^2-y^2}$ orbitals under the IMT pressure, while the t_{2g} states are split into d_{xy}, d_{yz}, and d_{xz} orbitals due to the external pressure. The bandwidth broadening behaviour in FM spin configuration under IMT pressure coincides with the characteristic of the Mott insulator, while the G-type structure takes the band insulator behaviour. We suggest that the crossover of high-spin states and low-spin states under IMT pressure is caused by the fluctuation of suppression of magnetic moments in FM spin arrangement.

4. Conclusion

In summary, we have performed first-principles calculations of the pressure induced phase transformation and magnetism, and found that the IMT occurs at about 50 GPa accompanying with the crossover of high-spin and low-spin states in FM R3c structure, which accounts well for the previous experiment.

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