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Ferroelectric-like structural transition in metallic LiOsO₃

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It is assumed that ferroelectric behaviour only appears in the materials with an energy gap. However, a ferroelectric-like structural transition has been experimentally explored in metallic LiOsO₃ [*Nature Materials* **12**, 1024 (2013)]. In this paper, we investigate the possible origin of a ferroelectric-like transition and its effect on the electronic structure through theoretical simulations. By performing first-principles calculations, we found that the topologically compact structures formed by strong Os–O bonds forces Li ions to be displaced, which is responsible for the ferroelectric-like structural transition. Our calculations also indicate that the chemical valence should be Li^{*n*+}[OsO₃]^{*n*-}, where *n* < 1. Furthermore, the intrinsic electric dipoles induced by the ion displacement are spontaneously screened by the remanent electrons of Li ions. Thus, the explored mechanism of the ferroelectric-like transition in metallic LiOsO₃ may help develop other ferroelectric materials.

Introduction

As a classical example of collective physical interactions, ferroelectricity has been well explored in many materials.^{1–3} The switchable character of electric polarization endows ferroelectrics with abundant applications in modern electric devices, such as memory devices, sensors,^{4–7} *etc.* For typical hightemperature ferroelectrics (for example, perovskites ABO₃ materials), it is assumed that the 2nd Jahn–Teller distortion of metal atoms and the surrounding ligands displaces the metal atoms, and forms the spontaneous electric polarizations.^{8–11} Consequently, to keep the robust nature of the static internal electric polarization, ferroelectrics should have a large energy gap to avoid the leakage currents or charge screening.

Recently, Kazunari Yamaura *etc.* reported that they successfully synthesize LiOsO₃ materials through solid-state reaction under high pressure.¹² Using power X-ray diffraction (XRD) method, the structure of LiOsO₃ is refined as $R\bar{3}c$ space group under room temperature. The measurement of the electrical resistivity indicates such material is metallic. Surprisedly, LiOsO₃ shows a ferroelectric-like structural transition from $R\bar{3}c$ to R3c at a temperature of 140 K, and keeps the metallic character.¹² But the intrinsic mechanism of phase transition is still not clear. Besides, from the centrosymmetric $R\bar{3}c$ to noncentrosymmetric R3c structure, the loss of inversion symmetry may lead to the ferroelectric behaviors, namely, LiOsO₃ may be a unique material which has ferroelectric and metallic characters.¹³

Until now, the origin of this amazing ferroelectric-like phase transition remains untouched, which may help develop new functional ferroelectrics. Moreover, it is also interesting to explore how the ferroelectric-like character coexists with the metallic property in LiOsO₃. Therefore, a comprehensively theoretical study is highly desired to clarify such issues. In this work, we perform first-principles calculations to explore the origin of such ferroelectric-like structural transition and how the ferroelectric-like phase transition affects the electronic structure of metallic LiOsO₃.

Experimental method

Our first-principles calculations were based on spin-polarized density functional theory (DFT) using the generalized gradient approximation (GGA) known as PW91,¹⁴ implemented in the *Vienna ab initio simulation package* (VASP) code. The projected augmented wave (PAW) method,^{15,16} with a plane-wave basis set was used. We set the energy cutoff and convergence criteria for energy and force to be 400 eV, 10^{-5} eV, and 0.01 eV Å⁻¹, respectively. During the optimization, $9 \times 9 \times 5$ *K*-point is adopted, while $11 \times 11 \times 7$ is used for total energy calculations.

Results and discussion

To explore the origin of ferroelectric-like structural transition, it is necessary to understand how the atoms displace under the

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phase transition. It has been well explored that centrosymmetric $R\bar{3}c$ structure loses the inversion symmetry at 140 K when the temperature lows down from 300 K to 2 K for LiOsO₃. As shown in Fig. 1, accompanied by the phase transition, Li ions move towards the nearest-neighbour [OsO₆] along *c* direction, while oxygen ions move outwards Os ions (note: the displaced distance of oxygen ions is about 0.04 Å, while the one of Li ions is about 0.4 Å). Moreover, we found that Os ions keep their positions without any displacements. Consequently, the structure at low temperature shows a ferroelectric-like phase, as explored in LiNbO₃.^{17,18}

It is quite interesting to explore how the phase transition affects the electronic structure of LiOsO₃, which may provide the important clues to uncover the origin of phase transition. As shown in Fig. 2(a), the band dispersion of centrosymmetric $R\bar{3}c$ structure is very similar with that of non-centrosymmetric R3c structure. Only along M-L line, the energy levels have relative energy shifts, indicating that the difference is not caused by the chemical interactions/bonding. The projected density of states (PDOS) clearly shows two important characters: (1) Li ions have lots of electrons and do not show the electronic behavior of nominal Li¹⁺ cations; (2) different with LiNbO₃, where the width of Nb 4d and O 2p states has significantly modified by the phase transition,¹⁸ there are no observable differences in width of Li, Os, and O states going through phase transition. Consequently, the mechanism response for the ferroelectric-like phase transition in LiOsO₃ is different with that of LiNbO₃. From the calculated band dispersion and PDOS, we get a conclusion that the ferroelectric-like phase transition in LiOsO₃ is not driven by any chemical/orbital interactions, as in normal perovskites ferroelectrics.

Generally, ferroelectric phase transition is accompanied by phonon softening, as explored in all other ferroelectrics, such as $LiNbO_3$.^{17,18} However, even for $LiNbO_3$, the intrinsic mechanics response for the phase transition is still not clear. To find a clue to the ferroelectric-like phase transition in $LiOsO_3$, we look back the geometric structures of $R\bar{3}c$ phase. As shown in Fig. 3(a), crystal structure of $LiOsO_3$ is closely connected by the



Fig. 2 The calculated band structure and density of states (DOS) of LiOsO₃. (a) The calculated band dispersions for $R\overline{3}c$ (red lines) and R3c (black lines) phases. The bands with the largest energy shift are indicated by the blue circle. (b) The plotted DOS for $R\overline{3}c$ (red lines) and R3c (black lines) phases.

topological motif of $[OsO_6]$ cluster. Each Li ion is located inside the cubic lattice formed by the 8 Os and 12 O ions, and is closely contacted by three oxygen ions. It is clear that the nearestneighbour Li–O distances are dominated by the bond length of Os–O. Since Li ions have no direct bonding with O ions, and Li ions are surrounded by the Os and O ions, as shown in Fig. 3(a), consequently, the nearest-neighbor Li–O distance is modified only when the length of Os–O bonds is changed. Due to the strong chemical bonding of Os and O ions, the bond length of Os–O is only about 1.94 Å. Consequently, the nearest-neighbour Li–O distances are only 1.866 Å in $R\bar{3}c$ structure, which are much smaller than the sum of the Li and O ionic radii (2.0 Å). Therefore, it is energetically favorable to increase the nearestneighbour Li–O distances to reduce the coulomb interactions between Li and O ions.

Moreover, the band dispersion along M-L line (Fig. 2(a)) shows energy shift between $R\bar{3}c$ and R3c phases, indicating the existence of electron coulomb interactions. As shown in Fig. 3(b), considerable charges are distributed between Li and O ions, as explored



Fig. 1 Ferroelectric-like structural transition of metallic LiOsO₃. The left one is the centrosymmetric $R\bar{3}c$ structure, and the right one is noncentrosymmetric $R\bar{3}c$ structure. The middle one shows the atomic displacements from $R\bar{3}c$ to $R\bar{3}c$ one, the arrows indicate the directions of displacements (The displaced distance of oxygen ions is enhanced by 10 times.). Red, green, and pink balls are oxygen, osmium, and lithium ions, respectively.



Fig. 3 (a) The local geometric structures of Li ion, which is confined by 8 Os ions and 12 O ions. And there are three nearest-neighbour O ions around Li ion (indicated by the lines). (b) The plotted charge density around the Li ions and three nearest-neighbour O ions. (c) The plotted band dispersions of $R\overline{3}c$ (red lines) and $R\overline{3}c$ (black lines) phases under different biaxial strain, where defined as $\varepsilon = (a - a_0)/a_0$, where a_0 is experimental parameters at 300 K, *a* is the new parameters under strain.

in the plotted charge density of bands which have the largest energy shift (indicated by the circle in Fig. 2(a)). To confirm the existence of electron coulomb interactions, we have performed band calculations with biaxial strain in *xy* plane, and strain is defined as $\varepsilon = (a - a_0)/a_0$, where a_0 is experimental parameters at 300 K, *a* is the new parameters under strain.¹⁹ Since the lattice parameters of both phases are very close, the cell parameters of *R3c* structure are used for both *R3c* and *R3c* phases. As shown in Fig. 3(c), the energy splitting between *R3c* and *R3c* structures is enlarged by reducing the cell parameters. On the other hand, by increasing the cell parameters, we found that the energy splitting is gradually reduced, and the bands of *R3c* are almost identical with that of *R3c* at $\varepsilon = 2.5\%$.

Since both ions and electrons form strong coulomb interactions between Li and O ions, it is energetically favorable for LiOsO₃ to go through from $R\bar{3}c$ to R3c phase. Interestingly, accompanied with the ferroelectric-like structural transition, we did not see significant modification of electronic structures from the calculated band dispersion. Thus, it is quite confusing how the metallic material is stabilized without inverse symmetry. Keeping atomic charge of Li ions may be one of the possible ways, namely, $\text{Li}^0[\text{OsO}_3]^0$. However, as shown in Fig. 4, the plotted charge difference density clearly shows that Li ions have transferred some charges into $[\text{OsO}_6]$ cluster. Thus, the valence state should be $\text{Li}^{n+}[\text{OsO}_3]^{n-}$, where n < 1. Consequently, in the ferroelectric-like R3c structure, there should be a net electric dipole between Li^{n+} ions and $[\text{OsO}_6]^{n-}$.

As explored in metallic films, if an external electric filed is applied, the net electric dipole will be removed by the charges transfer from one side to the other side, as shown in Fig. 5(a). However, in the bulk structure of $LiOsO_3$, we did not see any



Fig. 4 The plotted charge difference density for *R3c* structure, which is defined as $\rho = \rho_{\text{LiOsO}_3} - (\rho_{\text{Li}} + \rho_{\text{OsO}_3})$, where ρ_{LiOsO_3} is the charge density of *R3c* LiOsO₃, ρ Li (ρ_{OsO_3}) is the charge density of pure Li (OsO₃) atoms in the same geometric structure of *R3c* LiOsO₃. (a and b) Separately show the charge positive and negative parts of ρ at isovalue of 0.014 e Å⁻³, and the red circle indicates the electrons of Li ions. (c) The plotted density of states for OsO₃ in *R3c* LiOsO₃ (green lines) and *R3c* OsO₃ with the same atomic positions (blue lines).



Fig. 5 (a) The schematic diagram of metal films under external electric field. The electrons move toward the bottom of the film to screen the polar field. Two-dimensional (2D) plot of the charge density of R3c LiOsO₃ for (b) *ab* plane and (c) *ac* plane.

clues about the charge transfer. Thus, it is quiet important to explore how the net electric dipole is screened. As shown in Fig. 5(b), for the polar structure of R3c phase, we found the charge density around Li ions is uniformly distributed in *ab* plane. However, in the *ac* and *bc* plane, and charge is not uniformly distributed around Li ions. Therefore, the noncentrosymmetric charge density screens the intrinsic polar field formed by ions displacement. Such picture is also confirmed by the uniform charge of $[OsO_6]$ clusters.

Conclusions

In conclusion, we have performed comprehensive first-principles calculations to explore the possible origin of ferroelectriclike transition and its effect on the electronic structure through theoretical simulations. Our results show that the topologically compact structures formed by strong Os–O bonds forces Li ions to be displaced, which is response for the ferroelectric-like structural transition observed in experiments. Besides, our calculations also indicate that the intrinsic electric dipoles induced by the ions displacement are spontaneously screened by the remanent electrons of Li ions. Thus, the explored mechanism of ferroelectric-like transition in metallic LiOsO₃ may help develop other ferroelectric materials.

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