

Title	新奇層状超伝導体に対する第一原理フォノン計算
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Abstract

Layered titanium-oxypnictides, ATi_2Pn_2O [$A = Na_2, Ba, (SrF)_2, (SmO)_2$; $Pn = As, Sb, Bi$], have the common undistorted structure, including Ti_2O -plane that leads to quasi two-dimensional (2D) electronic structures. Recently, Kageyama's group (Kyoto Univ. Japan) has synthesized $BaTi_2Sb_2O$ and reported its superconductivity with the transition temperature, $T_c = 1.2$ K. Guloy's group (USA) has also synthesized $Ba_{1-x}Na_xTi_2Sb_2O$ individually and reported its superconductivity with $T_c = 5.5$ K. Followed by their pioneering works, similar kinds of compounds, $BaTi_2Bi_2O$, $BaTi_2(Sb_{1-x}Bi_x)_2O$, $BaTi_2(Sb_{1-x}Sn_x)_2O$, $Ba_{1-x}K_xTi_2Sb_2O$, and $Ba_{1-x}Rb_xTi_2Sb_2O$, have been synthesized to get superconductivities, achieving the current highest T_c around 6.1 K. Although they are not high- T_c superconductors, they have been still studied because there has been a puzzle between experiments and theoretical predictions on the structural phase transition at low temperature. The layered titanium oxypnictides show anomalies attributed to charge density wave (CDW) in resistivity and magnetic susceptibility at low temperature. Subedi predicted that $\sqrt{2} \times \sqrt{2} \times 1$ superstructure is realized at low temperature by using *ab initio* phonon calculation for $BaTi_2Sb_2O$ in 2013. However, such a superstructure had not been detected for a long time even by intensive diffraction experiments. Recently, Frandsen *et al.* have reported a four-fold symmetry breaking for $BaTi_2As_2O$ and $BaTi_2Sb_2O$ by using neutron diffraction (ND). Based on the result, they argued that the structural transition in the layered pnictides oxide could be attributed to *exotic* mechanism such as intra-unitcell nematic CDW detected in cuprates and iron-arsenides superconductors, because the four-fold symmetry breaking cannot be predicted *ab initio* phonon calculation for $BaTi_2Sb_2O$. On the other hand, Davies *et al.* have detected $2 \times 2 \times 1$ superstructure for $Na_2Ti_2As_2O$ and $2 \times 2 \times 1$ one for $Na_2Ti_2Sb_2O$ by using single-crystal X-Ray diffraction (XRD) in 2016. They concluded the structural transition is caused by *conventional* electron-phonon mechanism, which is completely contradicted to the conclusion by Frandsen *et al.* Thus, the mechanism of the structural transition in layered titanium-oxypnictides is still under intensive discussion.

Unfortunately, the aforementioned experimental results have been interpreted only by the phonon calculation for $BaTi_2Sb_2O$ so far. On the other hand, the previous experimental and theoretical studies revealed that electronic properties such as band structure and Fermi surface are governed not only by $Ti-3d$ orbital but also by $Pn-p$ orbital. Therefore, the structural transition should be also discussed based on a comprehensive phonon calculation for ATi_2Pn_2O [$A = Na_2, Ba, Pn = As, Sb, Bi$]. In this thesis, I performed a comprehensive phonon calculation for $BaTi_2Pn_2O$ [$Pn = As, Sb, Bi$] and $Na_2Ti_2Pn_2O$ [$Pn = As, Sb$] to reveal the relation between a type of pnictogen and the structural transition. For $BaTi_2As_2O$, I provide a new theoretical prediction, by which the above discrepancy is resolved without any unconventional explanation. Phonon dispersions and changes of nesting vectors in Fermi surfaces are clarified to lead to orthorhombic $2 \times 2 \times 1$ superstructure for $BaTi_2As_2O$ that is completely consistent with the experimentally observed one by Frandsen. On the other hand, there is still discrepancy for $BaTi_2Sb_2O$ and $BaTi_2Bi_2O$ that the predicted tetragonal $2 \times 2 \times 1$ superstructures are inconsistent with the experimental one (Sb), or have not been detected so far (Bi). I also applied *ab initio* phonon analysis for $Na_2Ti_2Pn_2O$ ($Pn = As, Sb$), and found a clear contrast between the cases with lighter/heavier pnictogen in comparisons with experiments. The result completely explains the experimental structure at low temperature, $C2/m$ for $Pn = As$, within the conventional charge density wave, while there arise discrepancies when the pnictogen gets heavier. Our phonon calculation predicts that a *Cmce* polymorph is more stable than the experimentally observed superstructure (*Cmcm*) for $Pn = Sb$. The trend is again consistent with $BaTi_2Pn_2O$ ($Pn = As, Sb, Bi$), where the phonon calculation could explain experiments only for $Pn = As$, but not for the other heavier Pn . It might be a general tendency also applicable to the layered titanium-oxypnictides that the heavier Pn induces the discrepancy between experiments and calculations.

To reveal the origin of discrepancy, I focus on the height of Pn toward Ti_2O plane in layered titanium-oxypnictides. This is because the tendency toward electronic correlation is well captured by a trend of h , a vertical distance between Fe layer and Pn or Ch in iron arsenide superconductors that have similar electronic structures to our layered titanium-oxypnictides. Based on quantitative analysis according to the previous study, I revealed that $Ti-As$ bonding is more covalent than $Ti-Sb$ one, and the distance of $Ti-Pn$ (the height of Pn toward Ti_2O plane) governs the covalency as well as electronegativity in layered titanium-oxypnictides. Our analysis could support the correlation effect gets more enhanced for Sb than As in layered titanium-oxypnictides. I currently believe that the present discrepancy could be attributed to the electronic correlation effects that are not taken into consideration at the GGA-PBE level. If the discrepancy is attributed to the electronic correlation as I suggest, calculation using exchange-correlation functional beyond GGA such as GGA+ U and hybrid functionals is necessary to reproduce the experimentally observed superstructures of $Pn = Sb, Bi$. This is a promising future work.

Keywords, Layered titanium-oxypnictides, Superconductivity, Structural transition, DFT, Phonon calculations