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Author(s)	中野, 晃佑
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氏 名	中野 晃佑
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論 文 審 査 委 員	主査 前園涼 北陸先端科学技術大学院大学 教授
	下田達也 同 教授
	本郷研太 同 准教授
	稲田幹 九州大学中央分析センター 准教授
	小口多美夫 大阪大学産業科学研究所 教授

論文の内容の要旨

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 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 $\text{BaTi}_2\text{Sb}_2\text{O}$ 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 $\text{ATi}_2\text{Pn}_2\text{O}$ [$A = \text{Na}_2, \text{Ba}, Pn = \text{As, Sb, Bi}$]. In this thesis, I performed a comprehensive phonon calculation for $\text{BaTi}_2\text{Pn}_2\text{O}$ [$Pn = \text{As, Sb, Bi}$] and $\text{Na}_2\text{Ti}_2\text{Pn}_2\text{O}$ [$Pn = \text{As, Sb}$] to reveal the relation between a type of pnictogen and the structural transition. For $\text{BaTi}_2\text{As}_2\text{O}$, 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 $\text{BaTi}_2\text{As}_2\text{O}$ that is completely consistent with the experimentally observed one by Frandsen. On the other hand, there is still discrepancy for $\text{BaTi}_2\text{Sb}_2\text{O}$ and $\text{BaTi}_2\text{Bi}_2\text{O}$ 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 $\text{Na}_2\text{Ti}_2\text{Pn}_2\text{O}$ ($Pn = \text{As, Sb}$), 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 $Pn = \text{As}$, 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 $Pn = \text{Sb}$. The trend is again consistent with $\text{BaTi}_2\text{Pn}_2\text{O}$ ($Pn = \text{As, Sb, Bi}$), where the phonon calculation could explain experiments only for $Pn = \text{As}$, 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 $Pn = \text{Sb, Bi}$. This is a promising future work.

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

論文審査の結果の要旨

層状チタンニクタイト酸化物においては、低温で出現する超格子構造が、本研究開始時点までに知られていた理論予見と合致しない事を発端に、その齟齬を説明するための特異な物性機構可能性が議論されていた。本研究では、大規模並列シミュレーション技術を駆使した注意深い理論計算により、特に特異な物性機構を持ち出す必要もなく、実験結果は齟齬なく説明できる事を明らかにした。類似系列物質に亘る系統的变化に着目し、格子振動の不安定性出現(虚周波数)と、その起源となるフェルミ面形状の変化を注意深く調べ、ニクトゲンサイトを占める元素種が重元素から軽元素に向かうにつれて、特定点におけるフェルミ面の先端形状が平坦化し、電荷密度波の空間変調を支配する新しいネスティングベクトルが出現する事を見出した。本研究は、当該物質系で問題となっていた理論/実験の齟齬を問題なく解消する明快な結論を与え、原著査読プロセス時点での最新の実験報告も含めて、タイムリーに実験結果を説明した。複雑怪奇な特異機構のこじつけではなく、極めてシンプルで明快な理論計算を提示している。当該物質系の電荷密度波や超伝導を支配する機構については、精力的論争が繰り広げられているが、その流れに大きく影響を与える理論的知見を提供した研究である。本論文に関わる研究成果の一部は既に、申請者を主著者とする 2 報の査読付原著論文成果[N. Nakano, K. Hongo, and R. Maezono, *Sci. Rep.* **6**, 29661 (2016/IF = 5.228), N. Nakano, K. Hongo, and R. Maezono, *Inorg. Chem.* (2017/accepted/IF = 4.857)]に発表されており、当該コミュニティにおいて一定の評価を獲得している。

以上、本論文は、層状遷移金属酸化物で出現する重要な物性機構を明確に洗い出した。最先端の大規模シミュレーションを駆使した系統的な研究調査により、高温超伝導をはじめとした次世代技術革新への可能性が期待される当該物質系に新たな知見を提供した業績として学術的に貢献するところを認め、よって博士(情報科学)の学位論文として十分価値あるものと判断した。