学位論文の要約

題目　Atomic Vibration Effects on Core-Excited Spectra
（内殻電子励起スペクトルにおける原子熱振動効果）

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Chapter 1 General Introduction

Core electron energy-loss spectroscopy (EELS) combined with scanning transmission electron microscopy (STEM) enables electronic structure investigation with atomic resolution. However, its interpretation remains underexplored, particularly regarding the effects of atomic vibration. Despite the significant influence of atomic vibrations on material properties, these effects on the $L_{2,3}$-edge of transition metals are often oversimplified as broadening factors. Therefore, this thesis aims to fill this gap by offering a quantitative analysis of the atomic vibration effect on the Ti $L_{2,3}$-edge of perovskite oxide. Vibrational effects in core-excited spectra were explored through both experimental and simulated spectra, along with the development of a method for extracting Debye-Waller factors and its application.

Chapter 2 Theory & Instrumentation

This chapter gives an overview of the theory of STEM-EELS method, especially on EELS measurements, monochromator, and electron energy loss near-edge structure (ELNES). Furthermore, we explained the crystal-field multiplet effect, which provides the physical basis of $L_{2,3}$-edge ELNES. Finally, we explained the theories related to atomic vibration, including Debye-Waller factor, frozen phonon approximation, and the Einstein model.

Chapter 3 Methodology

The focus materials are perovskite $SrTiO_3$ and $PbTiO_3$. Experimentally, temperature-dependent Ti $L_{2,3}$-edges were obtained with monochromated STEM at 200 kV with energy resolution around 0.1 eV. Simulated Ti $L_{2,3}$-edge spectra were conducted by the cluster-based crystal field multiplet calculation program *MultiX*, combined with our self-developed *Python* program to include atomic vibration effects. Atomic vibrations were incorporated with displaced atomic positions based on the Einstein model and frozen phonon approximation. In addition, theoretical thermal vibration factors of $SrTiO_3$ were simulated by *ALAMODE*, and calculations for the density of states (DOS) and charge density map were performed with the DFT program *WIEN2K*.

Chapter 4 Investigation of thermal vibration effects in Ti $L_{2,3}$-edge spectrum

Firstly, we developed a method to analyze the effects of atomic vibrations on core-loss spectra based on crystal field multiplet calculation. We further investigated how the thermal vibrations of individual elements affect the Ti $L_{2,3}$-edge spectra of $SrTiO_3$, specifically focusing on the connection with multiplet terms and the spectral changing. The results reveal that only the atomic vibration of O mainly affects the spectral shape with sensitivity while the effects of Ti and Sr are negligible.

Chapter 5 Extract Thermal Vibration Factors of Oxygen from ELNES in $SrTiO_3$

Based on the findings in the previous chapter, we demonstrated a method to extract the anisotropic thermal vibration factors for oxygen in $SrTiO_3$ using experimental Ti $L_{2,3}$-edge EELS spectra fitting with calculated one. As a result, temperature-dependent anisotropic atomic vibration factors for oxygen in $SrTiO_3$ can be obtained and show good agreement with previously reported experiments and theoretical values.

Chapter 6 Isotropic Oxygen Vibration Behavior in $PrTiO_3$

We applied our methodology to explore the thermal vibration of oxygen in cubic perovskites $PbTiO_3$ at 873 K, and compared it with that of $SrTiO_3$ at 1850K, which share an identical crystal structure and lattice constant but exhibit different low-temperature phase transitions. The results revealed relatively isotropic vibration behavior in $PbTiO_3$, in contrast to strong anisotropic vibration in $SrTiO_3$. The larger oxygen vibration in the A-O plane of $SrTiO_3$ is consistent with its rotational phase transitions due to R_{25} mode softening. In contrast, smaller oxygen vibration in the A-O plane of $PbTiO_3$ suggests a zone-center displacement-type phase transition induced by a softened Γ_{15} mode. DFT calculation also showed a broader valence electron distribution for Pb^{2+} compared to Sr^{2+}, with greater electron repulsion between Pb and O, potentially contributing to smaller oxygen vibration in the Pb-O plane of $PbTiO_3$.

Chapter 7 Summary

We established an approach to study the thermal vibration effects on the Ti $L_{2,3}$-edge spectra of $SrTiO_3$ and $PbTiO_3$. Using vibration-included crystal field multiplet calculations, we observed that only oxygen vibrations, particularly along the Ti-O direction, significantly influence the spectral shape. We also developed a method to successfully extract Debye-Waller factors for oxygen, applicable to local measurements such as small single crystals, interfaces, and surfaces, providing a complementary approach to X-ray and neutron diffraction methods. Furthermore, the different vibration behavior found in $SrTiO_3$ and $PbTiO_3$ demonstrates their relationship with phase transition mechanisms and offer predictive insights into phase transition types for perovskites in the high-temperature cubic phase.