

Spin reorientation of Fe³⁺ induced by peculiar Pb charge ordering in PbFeO₃

The cross interplays and correlations among lattices, charges, spins, and orbital degrees of freedom in transition metal perovskite oxides give rise to various fascinating electronic and magnetic properties, such as high-temperature superconductivity, colossal magnetoresistance, metal-insulator transition, multiferroicity, electrocatalysis, and negative thermal expansion. Such functions generally originate from transition metal ions, but Pb also has a charge degree of freedom stemming from the possibility of having either the 6s² (Pb²⁺) or 6s⁰ (Pb⁴⁺) electronic configuration. Perovskite oxide PbMO₃ (*M*: 3d transition metal) shows systematic charge distribution changes depending on the depth of the 3d level of *M* [1]. PbVO₃ is Pb²⁺V⁴⁺O₃, similar to Pb²⁺Ti⁴⁺O₃ [2], but PbCrO₃ has been found to be Pb²⁺_{0.5}Pb⁴⁺_{0.5}Cr³⁺O₃ with charge disproportionated Pb²⁺ and Pb⁴⁺ [3]. PbCoO₃ has been found to be Pb²⁺Pb⁴⁺₃Co²⁺₂Co³⁺₂O₁₂ [4]. PbNiO₃ has a valence distribution of Pb⁴⁺Ni²⁺O₃ [5]. That is, PbMO₃ changes from Pb²⁺M⁴⁺O₃ to Pb²⁺_{0.5}Pb⁴⁺_{0.5}Cr³⁺O₃ (average valence state of Pb³⁺M³⁺O₃) to Pb²⁺_{0.25}Pb⁴⁺_{0.75}Co²⁺_{0.5}Co³⁺_{0.5}O₃ (Pb^{3.5+}Co^{2.5+}O₃) and finally to Pb⁴⁺M²⁺O₃ following the order of *M* in the periodic table corresponding to the depth of the *M* *d* level. However, the charge distribution of PbFeO₃ remains a mystery.

Our hard X-ray photoemission spectroscopy (HAXPES) measurement performed at SPring-8

BL09XU revealed the Pb²⁺_{0.5}Pb⁴⁺_{0.5}Fe³⁺O₃ charge distribution [6]. **Figure 1** shows the HAXPES results for PbFeO₃ and other PbMO₃ compounds with *M*=Ti, Cr, Co, and Ni used as standard references. Two components appeared in both the Pb 4f_{7/2} and Pb 4f_{5/2} peaks for PbCrO₃ (Pb²⁺_{0.5}Pb⁴⁺_{0.5}CrO₃), PbCoO₃ (Pb²⁺_{0.25}Pb⁴⁺_{0.75}CoO₃), and PbFeO₃. Each peak can be deconvoluted into two Gaussians, as reported previously. The 6s⁰ electronic configuration in Pb resulted in a binding energy lower than that of 6s² because of a strong screening effect; hence, the components at lower binding energies are attributable to Pb⁴⁺ ions. The peak energies of PbFeO₃ were close to those of Pb²⁺_{0.5}Pb⁴⁺_{0.5}Cr³⁺O₃, indicating the coexistence of Pb²⁺ and Pb⁴⁺ ions. We estimated the fractions of Pb²⁺ and Pb⁴⁺ from their area ratios using PbCrO₃ data as the standard for Pb²⁺_{0.5}Pb⁴⁺_{0.5} and concluded that PbFeO₃ also had the Pb²⁺_{0.5}Pb⁴⁺_{0.5}Fe³⁺O₃ charge distribution.

On the bases of the above-estimated valence distribution, the crystal structure was determined by comprehensive scanning transmission electron microscopy, synchrotron X-ray powder diffraction (SPring-8 **BL02B2**) and neutron powder diffraction analyses. PbFeO₃ crystallized into a unique charge-ordered state in which a layer of Pb²⁺ ions was interleaved by two layers each made up of a mixture of Pb²⁺ and Pb⁴⁺ ions in a 1:3 ratio, along

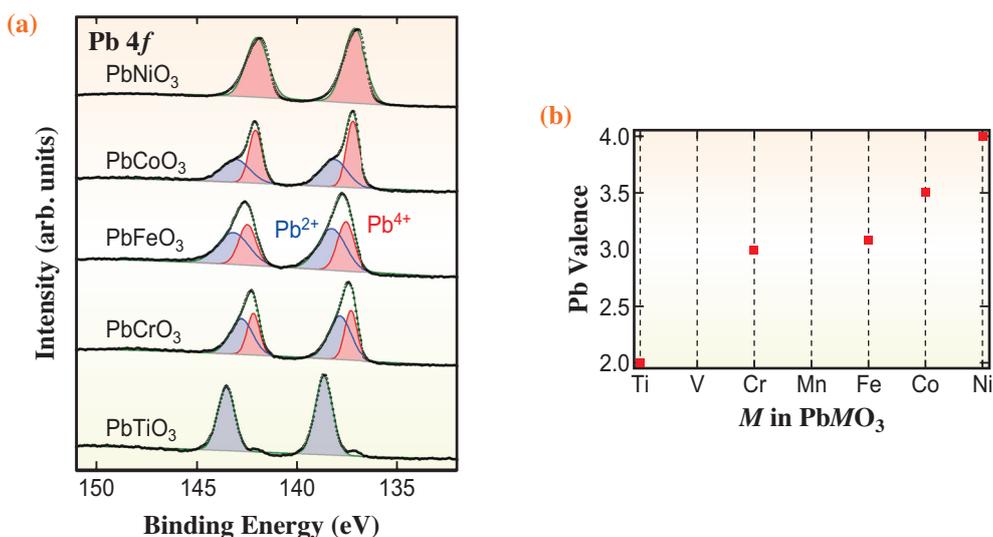


Fig. 1. Determination of the charge distribution of PbFeO₃ by HAXPES. **(a)** Pb-4f HAXPES results for PbTiO₃, PbCrO₃, PbFeO₃, PbCoO₃, and PbNiO₃ at RT. Predominant Pb⁴⁺ and Pb²⁺ are evident in the spectrum for PbFeO₃. **(b)** Average Pb valence state calculated from area ratios of Pb²⁺ and Pb⁴⁺ components. PbTiO₃, PbCrO₃, and PbNiO₃ are standards for Pb²⁺, Pb³⁺ (Pb²⁺_{0.5}Pb⁴⁺_{0.5}) and Pb⁴⁺, respectively.

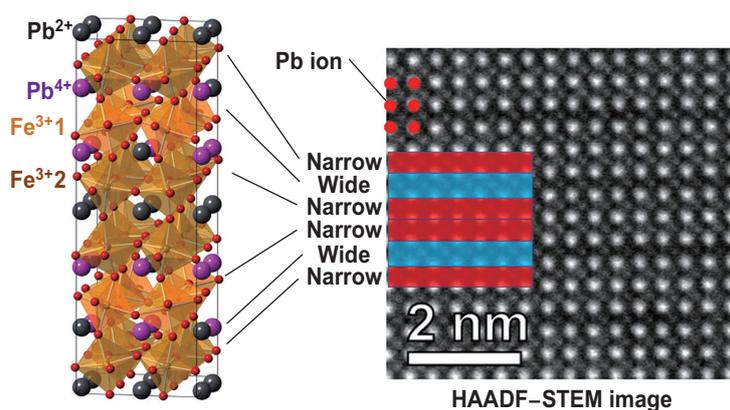


Fig. 2. Crystal structure of PbFeO_3 . Left part: illustration of structure revealing the $\text{Pb}^{2+}/\text{Pb}^{4+}$ ordering and presence of two Fe^{3+} sites. Right part: HAADF image of PbFeO_3 . Distances for the bright spots, which are the locations of Pb, indicate a modulation with a narrow–wide–narrow pattern.

the direction of layer stacking (Fig. 2). Two distinct Fe sites with different types of Pb coordination are therefore generated. Upon cooling the sample from high temperature, two distinct magnetic phase transitions were observed, as shown in Fig. 3: a weak ferromagnetic transition occurring at 600 K owing to canted antiferromagnetic spin ordering and a continuous spin reorientation (SR) transition at 418 K despite the absence of magnetic rare-earth ions that are believed to be necessary for the appearance of

spin reorientation in RFeO_3 (R: rare-earth element). Our DFT calculations revealed that the unique charge ordering in PbFeO_3 led to the formation of two Fe^{3+} sublattices with competing energies that, in turn, caused the peculiar SR transition [6]. This finding provides a new avenue for studying the charge ordering phase and distinctive SR transition with potential applications in spintronic devices because of the high transition temperature and possibility of tuning.

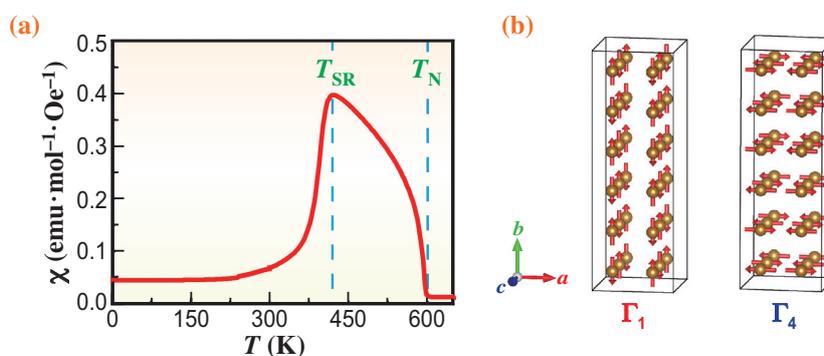


Fig. 3. Spin reorientation observed in PbFeO_3 . (a) Temperature dependence of magnetic susceptibility of PbFeO_3 measured at 0.01 T. (b) Magnetic structures of PbFeO_3 between T_{SR} and T_{N} (Γ_4) as well as below 300 K (Γ_1) determined by neutron diffraction studies.

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