Monoclinic distortion in the insulating phase of $PrNiO_3$

Takashi Saito [a,1], Masaki Azuma [a,2], Eiji Nishibori [b], Masaki Takata [b], Makoto Sakata [b],
Noriaki Nakayama [c], Takahisa Arima [d], Tsuyoshi Kimura [e], Chiharu Urano [f,3],
Mikio Takano [a]

[a] *Institute for Chemical Research, Kyoto University, Gokasho, Uji, Kyoto, Japan*
[b] *School of Engineering, Nagoya University, Furo-cho, Chigusa-ku, Nagoya, Aichi, Japan*
[c] *Faculty of Engineering, Yamaguchi University, Tokiwadai, Ube, Yamaguchi, Japan*
[d] *College of Engineering Sciences, Tsukuba University, Tennodai, Tsukuba, Ibaraki, Japan*
[e] *Department of Applied Physics, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo, Japan*
[f] *Cryogenic Center, University of Tokyo, Yayoi, Bunkyo-ku, Tokyo, Japan*

Abstract

Single crystals of $PrNiO_3$ perovskite were grown under 4.5 GPa with NaCl and KCl flux. The electron diffraction and single crystal synchrotron X-ray diffraction experiments clearly detected the presence of a monoclinic distortion (space group $P2_1/n$) below the metal-insulator transition temperature $T_{\rm MI}$, which implies the splitting of the Ni sites in the crystal in the insulating state.

Key words: metal-insulator transition; charge disproportionation; crystal structure; single crystal

---

1. Introduction

RNiO$_3$ perovskites (R= La to Lu, Y) are well known to undergo a bandwidth-controlled metal-insulator (MI) transition [1]. However, the origin and the mechanism is still mysterious, and much effort are being made to solve this issue. Except for $LaNiO_3$, which is metallic down to the lowest temperature, RNiO$_3$ perovskites exhibit temperature driven MI transition at $T_{\rm MI}$, and a further long-range antiferromagnetic (AF) ordering at $T_{\rm N}$. In $PrNiO_3$, both MI transition and AF ordering occur simultaneously at $T_{\rm MI}$ [1]. Since there is nominally one electron in the Ni e_g orbital, a Jahn-Teller distortion associated with an orbital ordering is expected in the insulating state. However, no such distortion has been observed for $PrNiO_3$ so far [2]. Another possibility is the existence of a charge disproportionation of Ni (*e.g.* $2\mathrm{Ni}^{3+} \rightarrow \mathrm{Ni}^{3+\delta} + \mathrm{Ni}^{3-\delta}$) as found in $CaFeO_3$ [3]. Indeed, orthorhombic to monoclinic distortion indicating the occurrence of a charge disproportionation was observed recently in RNiO$_3$ with Y and small lanthanides (R = Ho to Lu) [4], and more recently even in $NdNiO_3$ [5].

In this paper, single crystals of $PrNiO_3$ were grown under high pressure, and electron diffraction (ED), single crystal synchrotron X-ray diffraction (SXRD) and powder SXRD measurements were performed above and below $T_{\rm MI}$. Monoclinic distortion was found in $PrNiO_3$below $T_{\rm MI}$ for the firs time.

2. Experiments

Single crystals of $PrNiO_3$ were grown as follows. Pr_6O_{11} and NiO were sealed in a Pt capsule (ϕ 10 mm × 15 mm) with a flux mixture of KCl, NaCl, $KClO_4$ and $NaClO_4$. The last two served also as oxidizers. The sample was slowly cooled from 1400°C to 1200°C in

---

[1] E-mail:saito@msk.kuicr.kyoto-u.ac.jp

[2] also at PRESTO-JST, Kawaguchi, Saitama, Japan

[3] present address: Metrology Institute of Japan, AIST, Tsukuba, Ibaraki, Japan

Preprint submitted to LT23 Proceedings *29 June 2002*

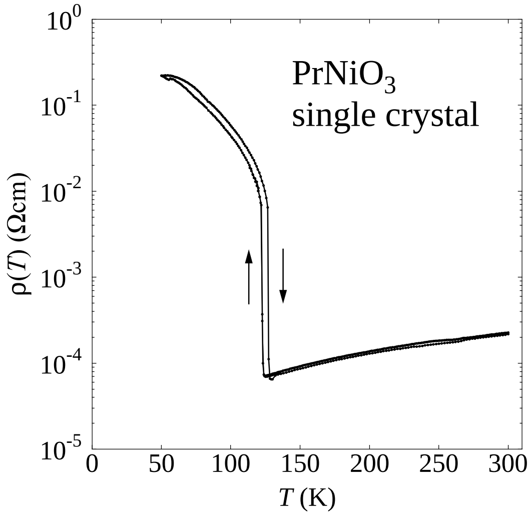

Fig. 1. The electric resistivity ity of a singe crystal of $PrNiO_3$.

about 4 hours under pressure of 4.5 GPa. The flux was washed away with water, to obtain glossy and dark brown single crystals. The typical size of the crystals were about 0.5 × 0.5 × 0.5 mm^3.

The electric resistivity of a piece of single crystal was measured with 4-probe method, and the magnetic susceptibility of above grown crystals was measured under magnetic field of 1000 Oe.

The ED measurements were done at the room temperature (RT) and at about 20 K. The SXRD measurements of $PrNiO_3$ were performed on a piece of single crystal at Photon Factory, and on a powder sample at SPring-8, both at RT and 90 K. The wave length of the X-ray used for the measurements on single crystal and powder sample were 0.690 Åand 0.55129 Å, respectively. All the SXRD data were collected on imaging plates. The crystal structure at both temperatures were refined by the Rietveld analysis of the powder SXRD data.

3. Results and Discussion

The electric resistivity of the single crystal clearly showed the existence of the MI transition around 128 K, which is shown in Fig. 1. The AF ordering of the Ni moment was also seen in the magnetic susceptibility at 128.5 K. These are in good agreement with T_{MI} reported previously for powder samples [2].

The ED and single crystal SXRD pattern at RT showed that the sample was twinned. This is possibly because $PrNiO_3$ crystallizes in rhombohedral $R\bar{3}c$ symmetry at high temperatures. On cooling the sample to 90K, however, $0kl$ (k =odd) reflection peaks, forbidden in $Pbnm$ symmetry, appeared in both measurements, indicating the lowering of the symmetry from orthorhombic $Pbnm$ to monoclinic $P2_1/n$. This means that the unique Ni site in orthorhombic metallic phase is split into two inequivalent sites in the insulating phase. It appears to mean that the charge disproportionation found in other $R$$NiO_3$ perovskites (Nd, Y, Ho to Lu) occurs in $PrNiO_3$ as well.

The crystal structure refinements were performed based on $Pbnm$ and $P2_1/n$ symmetries for the data taken at RT and 90 K, respectively. The crystal structure at room temperature was in good agreement with the previous study [2]. But at 90 K, the mean Ni-O bond distances for the two Ni site differed, which may be a sign of charge disproportionation of Ni. However, the difference in the two mean Ni-O bond distances was very small compared to that in $YNiO_3$ (about an order of 2). The MI transition in $PrNiO_3$ might be caused not by charge disproportionation alone, but also by orbital ordering as well. Further charge density distribution analysis by Maximum Entropy Method (MEM) is under way to confirm whether charge disproportionation and orbital ordering coexist below T_{MI}.

4. conclusion

The single crystals of $PrNiO_3$ were grown by flux method under high pressure. The crystal structure of $PrNiO_3$ above and below T_{MI} was closely examined by SXRD and ED measurements, and monoclinic distortion with $P2_1/n$ symmetry was clearly found below T_{MI} for the firs time. Structure refinement and charge density study by MEM/Rietveld analysis are under way to find out whether orbital ordering and charge disproportionation coexist in the insulating phase below T_{MI}.

Acknowledgements

The SXRD experiments at SPring-8 were done with the approval of the Japan Synchrotron Radiation Research Institute (Proposal No.2001B0594). The SXRD experiments at Photon Factory were done with the approval of the High Energy Accelerator Research Organization (Proposal No. 2001S2-002).

References

[1] M. L. Medarde *et al.*, J. Phys. Cond. Matt. **9** (1997) 1679.
[2] J. L. García-Muñoz *et al.*, Phys. Rev. B **46** (1992) 4414.
[3] T. Takeda *et al.*, Solid State Sciences **2** (2000) 673.
[4] J. A. Alonzo *et al.*, Phys. Rev. B **64** (2001) 094102.
[5] U. Staub *et al.*, Phys. Rev. Lett. **88** (2002) 126402.