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Soft x-ray resonant magnetic powder diffraction on PrNiO₃

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Abstract

We report on the first soft x-ray resonant powder diffraction experiments performed at the Ni L_{2,3} edges of PrNiO₃. The temperature, polarization and energy dependence of the (1/2 0 1/2) reflection indicates a magnetic origin for the signal. This experiment demonstrates that x-ray resonant magnetic powder diffraction can be relatively easily performed in the soft x-ray regime due to the very large enhancement factors at the absorption edges. Such experiments allow us to extract important information on the electronic states of the d shell. Similar results can be anticipated from orbital reflections measured in a powder.

(Some figures in this article are in colour only in the electronic version)

In recent years, resonant x-ray diffraction has become a powerful technique for studying electronic and magnetic ordering phenomena. The early work on Ho metal found large magnetic enhancement factors at the L_{2,3} absorption edges [1]. Over the years, magnetic x-ray diffraction experiments have successfully been applied to actinides [2, 3] and further extended to transition metal oxides [4, 5]. Composites containing actinides and 4f elements represent materials where resonant x-ray diffraction experiments are not prevented by low scattered intensity. Large enhancement factors of up to 10⁶ and 10² were observed for the actinide M_{4,5} and rare earth L_{2,3} absorption edges, respectively. In contrast, the magnetic resonant signals at the transition metal K edges turn out to be weak, and relatively small enhancements have been observed. Due to the lack of spin-orbit splitting in the core state, only the quenched orbital momentum contributes to the resonance. The resonance is broad in energy due to the extended width of the unoccupied 4p states and the short core hole lifetime. The 4p states also have a small induced magnetic moment. All in all, this leads to enhancement factors of the order of 10. They are comparable in strength to the quadrupole transitions at the K-edge (1s to the 3d), in particular for transition metal ions for which the 3d states are probed directly.

Resonant diffraction from even-rank multipoles (charge and orbital) further extends the experimental possibilities. In particular, resonant x-ray diffraction has been used to determine orbital and charge ordering in manganates, titanates and nickelates [6–10], including 4f electron materials [11, 12] and other complex oxides, where the origin of the scattering peak is still under discussion [13, 14]. The observed signals at transition metal K edges can be quite strong for even-rank tensors. Often they are dominated by Jahn–Teller distortions, and it is then difficult to extract direct information on orbital and charge ordering. Resonant diffraction studies have also been performed in the soft x-ray regime on multilayers [15], and recently expanded to bulk materials [16, 17] at energies in the range of 3d transition metal ion L edges and 4f M edges [18]. Here, again the d and f valence states are probed directly.

Independently of the absorption edges probed, high quality single crystals or epitaxially grown films are required, and resonant x-ray diffraction is limited to systems for which such samples are available. Therefore, neutron scattering to date is still the most powerful technique for studying magnetic ordering phenomena in detail, in particular due to the simplicity of magnetic powder diffraction experiments.

Pioneering work on magnetic powder *x-ray* diffraction was performed by Collins *et al* [19], exploiting the very large enhancement of the uranium M_4 edge in UO_2 , where with significant effort a weak magnetic diffraction peak was observed. More recently, Kim *et al* have reported on a resonant powder diffraction study in which a magnetic diffraction peak at the Gd L_2 edge in $GdNi_2Ge_2$ [20] was observed. There, the magnetic reflection was detected using a high-quality analyser crystal to suppress the fluorescence radiation and elastic scattering by suppressing the photon polarization with a state which was not rotated by the sample (charge scattering).

Here we report on the first resonant magnetic powder diffraction study performed in the soft x-ray regime. We chose the transition metal perovskite $PrNiO_3$, for which large high quality single crystals, suitable for resonant x-ray diffraction at the Ni K edge, are unavailable. Moreover, a recent study of epitaxially grown films of $NdNiO_3$ failed to detect a resonant magnetic scattering signal at the K edge [21]. In the present study we demonstrate large enhancement factors at the transition metal L edges and show that resonant x-ray diffraction can be performed relatively easily on a powder sample. Measurement of the energy dependence of the magnetic diffraction peak yields important information on the electronic states of the transition metal ions, which cannot be obtained from neutron investigations.

$PrNiO_3$ belongs to the $RNiO_3$ series (R = rare earth), exhibiting metal-to-insulator (MI) transitions, where the transition temperature T_{MI} depends on the ionic radii of the R ions [22]. For small R ions, T_{MI} exceeds the antiferromagnetic ordering temperature T_N . For large R ions (except La), T_{MI} and T_N coincide, and for $R = Pr$, $T_N = T_{MI} = 135$ K. $PrNiO_3$ crystallizes in the orthorhombic distorted perovskite structure with $Pbnm$ symmetry and unit cell dimensions $\sqrt{2}a_p \times \sqrt{2}a_p \times 2a_p$, where a_p is the simple perovskite lattice parameter. High-resolution powder diffraction found a charge disproportionation for heavy rare earth ions [23, 24], occurring at the metal–insulator transition. Resonant x-ray diffraction [10] and Raman spectroscopy [25] studies indicate that a disproportionation also occurs for the larger Nd ion. The magnetic ordering wavevector $(1/2\ 0\ 1/2)$ found by neutron powder diffraction supports an orbital ordering scenario of the Ni e_g orbitals [26]. Nevertheless, the proposed orbital ordering is inconsistent with a charge disproportionation. Recently, resonant soft x-ray magnetic diffraction studies [27] revealed that the magnetic structure is non-collinear, allowing a consistent interpretation of both charge disproportionation and magnetic ordering without orbital ordering. Moreover, resonant hard x-ray diffraction showed that the Ni 4p shell is already aspheric above the MI transition temperature [21], removing the possible degeneracy of the 3d states and disabling the occurrence of an orbital ordering with the $(1/2\ 0\ 1/2)$ wavevector at T_N .

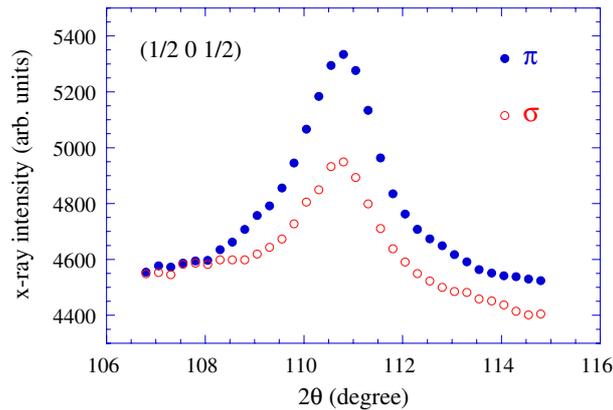


Figure 1. Magnetic $(1/2\ 0\ 1/2)$ reflection of polycrystalline PrNiO_3 recorded for σ and π polarized incident radiation at 30 K and an x-ray energy of 853 eV. No polarization analysis of the scattered beam was performed.

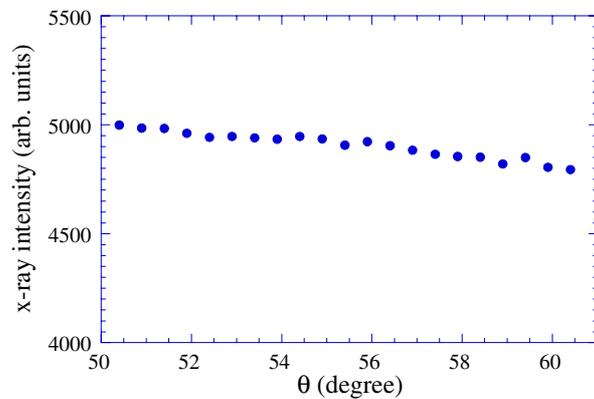


Figure 2. Rocking curve of the magnetic $(1/2\ 0\ 1/2)$ reflection collected at 30 K and 853 eV, indicating that numerous grains contribute to the scattering signal and that a good powder average is achieved.

PrNiO_3 powder was prepared by a citrate technique, by dissolving Pr_6O_{11} and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in citric acid, decomposing the formed resin at 700°C in air and then oxygenating the sample at 900°C under 200 bar of O_2 pressure for 12 h. The sample, a sintered 5 mm diameter pellet, was polished to obtain a smooth surface and was mounted in a continuous helium-flow cryostat. The resonant soft x-ray scattering experiments were performed in the vicinity of the Ni $L_{2,3}$ edges in a horizontal scattering geometry using the RESOXS station at the SIM beamline of the Swiss Light Source at the Paul Scherrer Institut. The polarization of the incoming beam was horizontal (π) or vertical (σ). The beam spot size was approximately $2 \times 2\ \text{mm}^2$.

Figure 1 shows a 2θ scan of the $(1/2\ 0\ 1/2)$ reflection measured in the vicinity of the Ni L_3 edge at 853 eV with π and σ polarized incident light and an angle of incidence of 40° . To test the quality of the scattered signal, we collected a rocking curve, thereby changing the particular grains that contribute to the Bragg reflection. Figure 2 shows that the rocking curve is flat. The slope of the intensity in figure 2 originates from the fluorescence of the sample that dominates

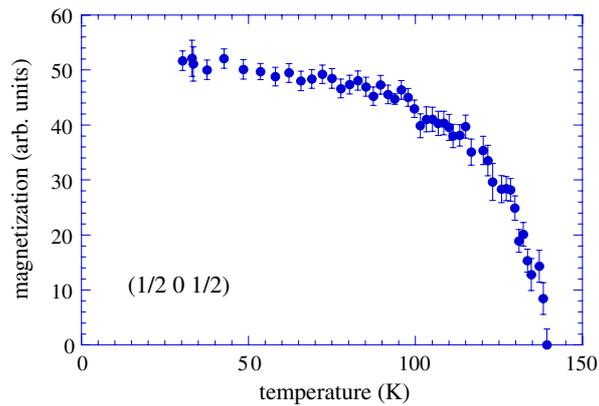


Figure 3. Temperature dependence of the square root of the intensity of the magnetic $(1/2\ 0\ 1/2)$ reflection of PrNiO_3 taken at 853 eV at the Ni L_3 edge. The form of this curve represents the temperature dependence of the Ni magnetic moments.

the background and decreases with increasing angle of incidence, corresponding to a reduced illuminated sample surface. Figure 2 indicates that there are enough grains contributing to the scattering signal to achieve a good powder average. This is significant, because the penetration depth of the incident light, which is of the order of a few hundred nanometres, restricts the sampling to a single layer of powder grains.

Figure 1 shows that the intensity for π polarized incident radiation is approximately 1.85 times larger than that for σ incident radiation. Because magnetic scattering is inherently absent in the σ - σ scattering channel, the lack of polarization analysis leads to $I_\pi \geq I_\sigma$ for magnetic scattering rather than orbital scattering. This implies a magnetic origin of the reflection. The intensity of the reflection originates from grains which fulfil the Bragg condition and are oriented with random azimuthal angles. This allows one to compare the intensity ratio between σ and π to that obtained from the epitaxial NdNiO_3 film [27], after integrating the latter over the azimuthal angle. NdNiO_3 has the same magnetic wavevector as PrNiO_3 , and the equality of the ratio of I_π/I_σ suggests that PrNiO_3 exhibits the same non-collinear spin arrangement as that found for NdNiO_3 [27].

The temperature dependence of $(1/2\ 0\ 1/2)$ is shown in figure 3. Each point corresponds to a 2θ scan recorded in approximately 1 min. The $(1/2\ 0\ 1/2)$ intensity disappears at the Néel temperature T_N . A similar temperature dependence was found by neutron powder diffraction [26], but with a steeper slope close to T_N . The difference may be caused by a larger defect concentration in our experiment, since resonant soft x-ray scattering probes the near surface region of the grains.

Often the most interesting information acquired with resonant soft x-ray scattering arises from the energy dependence of the reflections, since it contains information on the electronic states of the 3d shell. Figure 4 shows the energy dependence of the signal recorded with the detector at the Bragg position and at a position two degrees higher. In both cases, fluorescence radiation dominates the collected signal, and only at the L_3 edge could an obvious difference in the spectra be observed directly. The difference spectrum gives the resonant diffraction signal for $(1/2\ 0\ 1/2)$ and is shown in the bottom panel of figure 4, after making an absorption correction. Comparison of the fluorescence radiation at the L edges with atomic calculations allows one to extract the energy dependent absorption coefficient $\mu(E)$. Because the width of the reflection is likely to be dominated by the penetration depth and not significantly affected by the instrumental resolution, the data are corrected with $\mu(E)^2$.

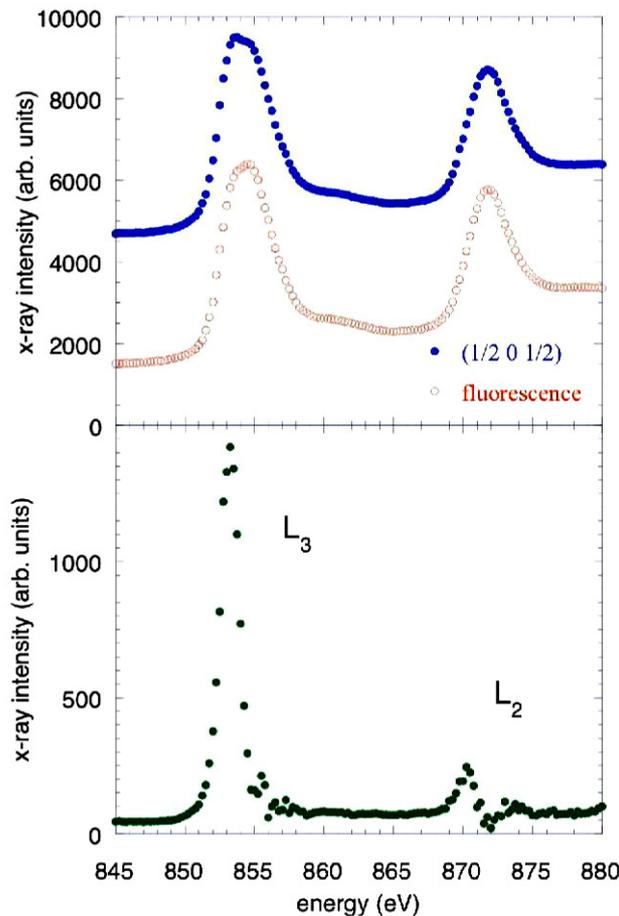


Figure 4. Top: energy dependence of the $(1/2\ 0\ 1/2)$ reflection of PrNiO_3 at 30 K in the vicinity of the Ni $L_{2,3}$ edges recorded at the Bragg position (closed circles) and at two degrees above (open circles). Bottom: energy dependence of the resonant $(1/2\ 0\ 1/2)$ reflection obtained from the difference between the curves of the top panel, corrected for absorption as explained in the text.

The energy dependence of the $(1/2\ 0\ 1/2)$ reflection in PrNiO_3 looks different from that obtained from the NdNiO_3 epitaxial film [27]. This may indicate that the electronic Ni states in PrNiO_3 are different from those from NdNiO_3 . Note that T_{MI} of PrNiO_3 is significantly lower than that of NdNiO_3 . Correspondingly, the band gap is also expected to be smaller, which probably affects the degree of charge disproportionation. We note that no significant change in the Ni–O bond lengths has been found [24] in the charge disproportionated RNiO_3 as a function of rare earth ionic radii for the small R ions, and data for the larger Pr and Nd ions are absent. It is unclear if such an extrapolation is valid for T_{MI} below room temperature. Further resonant x-ray diffraction experiments on RNiO_3 powders are needed to clarify the significance of the energy dependence of the $(1/2\ 0\ 1/2)$ reflection.

In conclusion, we have performed for the first time resonant soft x-ray powder diffraction. The $(1/2\ 0\ 1/2)$ reflection of PrNiO_3 has been characterized at the Ni $L_{2,3}$ edges. The dependence of the $(1/2\ 0\ 1/2)$ intensity on temperature and the polarization of the incident radiation indicates a magnetic origin for the reflection. This relatively simple experiment

demonstrates that, as a new technique, resonant soft x-ray magnetic diffraction permits the extraction of electronic and magnetic information on transition metal oxides without the need for high quality single crystals. We are led to believe that orbital reflections can be easily observed for powders in the soft x-ray regime, allowing the investigation of materials for which the ordering wavevector (either magnetic or orbital) is unknown.

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