Influence of static Jahn-Teller distortion on the magnetic excitation spectrum of PrO$_2$: A synchrotron x-ray and neutron inelastic scattering study

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A synchrotron x-ray diffraction study of the crystallographic structure of PrO$_2$ in the Jahn-Teller distorted phase is reported. The distortion of the oxygen sublattice, which was previously ambiguous, is shown to be a chiral structure in which neighbouring oxygen chains have opposite chiralities. A temperature dependent study of the magnetic excitation spectrum, probed by neutron inelastic scattering, is also reported. Changes in the energies and relative intensities of the crystal field transitions provide an insight into the interplay between the static and dynamic Jahn-Teller effects.

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I. INTRODUCTION

In recent years there has been strong interest in the interplay between electric and magnetic degrees of freedom in lanthanide and actinide dioxides, e.g. UO$_2$, NpO$_2$ and PrO$_2$. These compounds share many similar structural and magnetic characteristics, but also present a wealth of unusual individual behaviour. For example, the longstanding mystery over the nature of the single phase transition at 25.5 K in NpO$_2$ brought about suggestions first of octupolar ordering, then of triakontadipolar ordering. Also, a recent study of UO$_2$ by resonant x-ray magnetic scattering has revealed electric quadrupolar ordering that coincides with a Jahn-Teller distortion and magnetic scattering has revealed electric quadrupolar ordering. Below $T_D$ the Pr spins order antiferromagnetically, adopting a magnetic structure with two components: one with the same unit cell as the fluorite crystallographic structure, and the other with the same unit cell as the distorted structure below $T_D$. Below $T_N$ the populations of both structural and magnetic domains can be influenced by the application of a magnetic field.

We present a synchrotron x-ray diffraction study of the crystallographic structure, which distinguishes between two previously ambiguous possibilities for the distortion below $T_D$. Both possibilities consist of an internal distortion of the oxygen sublattice, but one involves a shear and the other a chiral deformation. We also present temperature dependent measurements of the magnetic excitation spectrum, probed by neutron inelastic scattering, which show that the dynamic Jahn-Teller effect persists over a wide range of temperature from 1.8 K to room temperature.

In this paper we focus on PrO$_2$, which exhibits strong correlations between its structure and magnetism. At room temperature it is paramagnetic and possesses the fluorite crystal structure. Below $T_D = 120$ K it undergoes a cooperative Jahn-Teller distortion which doubles the unit cell along one axis. Magnetic ordering does not accompany this transition, but below $T_D$ it is possible to influence the population of structural domains through the application of a magnetic field. Below $T_K = 13.5$ K the Pr spins order antiferromagnetically, adopting a magnetic structure with two components: one with the same unit cell as the fluorite crystallographic structure, and the other with the same unit cell as the distorted structure below $T_D$. Below $T_N$ the populations of both structural and magnetic domains can be influenced by the application of a magnetic field.

II. X-RAY DIFFRACTION EXPERIMENT

The fluorite structure (space group $Fm\overline{3}m$) exhibited by PrO$_2$ at room temperature is illustrated in Fig. 2(a). In a recent neutron diffraction study we found that a cooperative Jahn-Teller transition at $T_D = 120$ K caused an internal distortion of the oxygen sublattice which doubled the unit cell along the [100] axis. However, in that study the exact configuration of the oxygen ions remained ambiguous. Two possible structures were suggested: an or-
thorhombic structure (space group $I\overline{m}3b$), shown in Fig. 1(b), in which the cubic oxygen sublattice was sheared along a single crystallographic direction, and a tetragonal structure [space group $I4(1)/acd$], shown in Fig. 1(c), in which the oxygen ions were displaced chirally, with neighbouring chains possessing opposite chiralities.

![Diagram](image)

**FIG. 1**: (Color online). (a) PrO$_2$ possesses the fluorite crystal structure above $T_D$. The spheres are the oxygen ions. The Pr ions are not shown here, but they occupy positions at the corners and face centres of the dashed cube. (b) Sheared structure. (c) Chiral structure. (b) and (c) are alternative models for the structural distortion that occurs below $T_D$. The arrows show the directions in which the oxygen ions are displaced.

In the paper published simultaneously with this one, Jensen describes a theoretical model which shows that the chiral structure is the more stable of the two. Although both structures exhibit identical structure factors for the Bragg reflections measured previously by neutron diffraction, a separate set of reflections exists, which distinguishes the two. This set is present for the chiral structure and absent for the sheared structure. However, the structure factors are extremely weak compared to those of the parent fluorite structure. As large single crystals are not available, we decided to exploit the high dynamic range achievable with synchrotron x-ray diffraction to study these weak reflections.

We present the results of an experiment performed at the European Synchrotron Radiation Facility, Grenoble, France on the instrument ID20. The sample used for the experiment was a single crystal of mass ~ 1 mg (the same sample as used for previous neutron diffraction studies), possessing a single flat face. The sample was enclosed in a closed-cycle refrigerator, with a base temperature of 12 K, which was mounted within a five-circle diffractometer with a vertical scattering plane. An incident energy of 10 keV was used, corresponding to a wavelength of 1.24 Å.

We studied three sets of Bragg reflections, two of which were previously studied by neutron diffraction. The first set, corresponding to the fluorite structure, obeys the selection rule $h, k, l$ all even or all odd. We label this set $F$. These reflections contain scattering intensity from both the Pr and O atoms, but the cross section for x-rays is dominated by the contribution from Pr due to its much larger atomic number. Since the Jahn-Teller (JT) distortion is predominantly an internal distortion of the oxygen atoms, the fluorite reflections remain strong below $T_D$. The second set, corresponding to the distorted structure below $T_D$, and arising purely from oxygen scattering, obeys the selection rule $h = (2n + 1)/2, k = odd, l = even, l \neq 0$ (or permutations thereof). We label this set $JT(I)$. This set is common to both the sheared and chiral structures, so it cannot help us distinguish between the two. The third set, which also arises purely from oxygen scattering, was not previously studied by neutron diffraction. This set obeys the selection rule $h = odd, k = 2n, l = 4n$ (or permutations thereof), and is present for the chiral structure only. We label it $JT(II)$.

First, we selected three Bragg reflections typical of each of the sets described above, and measured the temperature dependence of these using $\theta$-scans over a range of temperatures between 20 K and 150 K. A Ge (111) analyzer crystal was used for these scans in order to optimize the resolution and dynamic range. The integrated intensity and the full width at half maximum (FWHM), obtained by fitting a Lorentzian profile to each $\theta$-scan, are plotted as a function of temperature for the three peaks in Fig. 2. Above $T_D$ only the fluorite peak (422) is present. Below $T_D$, the oxygen peaks (432) and (630) appear. The presence of the $JT(II)$ peak (630) immediately rules out the sheared structure and provides strong evidence in favour of the chiral structure.

Next, we measured all the accessible peaks in each set using $\theta$-scans at 20 K to determine the crystallographic structure factors. These scans were done without the Ge (111) analyzer crystal in order to improve the counting statistics. The integrated intensities were obtained by fitting Lorentzian profiles and were subsequently corrected for the geometric Lorentz factor and the absorption factor. The peaks in set $F$ were also corrected for attenuation occurring from an aluminium plate of 1 mm thickness that was placed in the beam to prevent detector saturation. Finally, the intensities were multiplied by a universal scaling factor to allow direct a comparison with the squared structure factors $|F(Q)|^2$ calculated for the chiral structure. The scaling factor was chosen such that the intensity of the (630) reflection matched its squared structure factor exactly.

Table I compares the corrected scaled intensities of the observed peaks with the calculated squared structure factors $|F(Q)|^2$ for the chiral structure, assuming each oxygen ion is displaced by 0.0726 Å in the direction shown in Fig. 1(c). The observed intensities agree with the calculated $|F(Q)|^2$ to within a factor of 4 for sets $JT(I)$ and $JT(II)$, and to within an order of magnitude for set $F$. Better agreement cannot be expected due to the difficulty in estimating the absorption factor away from the specu-
lar condition. There is also an additional uncertainty on the measured intensity of the peaks in set $F$ due to the possible nonuniformity of the thickness of the aluminium attenuator. In addition to the measurements shown in Table I we checked several reflections whose indices did not satisfy the selection rules for sets $F$ and $JT(II)$. All of these were absent, as expected.

III. NEUTRON SCATTERING EXPERIMENT

In a previous experiment we probed the low temperature excitation spectrum of PrO$_2$ using neutron inelastic scattering on a powder sample. The spectrum showed two main features: sharp peaks characteristic of crystal field transitions at energies above 100 meV, and a broad band of scattering in the range 10–100 meV which we interpreted as magnetic scattering from vibronic excitations associated with the dynamic Jahn-Teller effect. We developed a simple model of the magnetoelastic coupling between a single phonon mode and a crystal field excitation, which yielded a qualitative agreement with our results. However, at the time we were unaware of the existence of a static Jahn-Teller distortion, and therefore chose a phonon mode consistent with cubic symmetry for our model. Other researchers have also used cubic symmetry as the basis for more complex multiphonon models. In the light of our present knowledge, that the tetragonal distortion involves only an internal displacement of the oxygen atoms, leaving the cubic Pr lattice undisturbed, the choice of cubic symmetry is not unreasonable. However, the distortion lowers the crystal field symmetry at the Pr site and the large magnitude of the oxygen displacements is expected to cause a significant splitting of the cubic $\Gamma_8$ ground state, as well as an altering of the positions and intensities of the higher energy crystal field transitions. An examination of the temperature dependence of the excitation spectrum is therefore in order.

We report the results of a neutron inelastic scattering experiment performed at the ISIS spallation source,

| Set | Reflection | $|F(Q)|^2$ (fm$^2$) | Intensity (fm$^2$) |
|-----|------------|--------------------|-------------------|
| $F$ | (311)      | $2.6 \times 10^4$  | $2.0 \times 10^4$ |
|     | (222)      | $1.7 \times 10^4$  | $1.5 \times 10^5$ |
|     | (333)      | $1.7 \times 10^4$  | $1.6 \times 10^5$ |
|     | (422)      | $2.4 \times 10^4$  | $1.3 \times 10^5$ |
|     | (402)      | $1.4 \times 10^4$  | $5.3 \times 10^4$ |
|     | (531)      | $1.4 \times 10^4$  | $4.1 \times 10^4$ |
| $JT(I)$ | (2$\frac{1}{2}$) | 4.9 | 2.5 |
|      | (4$\frac{1}{2}$) | 5.5 | 2.8 |
|      | (63$\frac{2}{3}$) | 4.3 | 13.6 |
|      | (43$\frac{1}{2}$) | 3.3 | 5.9 |
|      | (6$\frac{1}{2}$) | 5.3 | 15.0 |
| $JT(II)$ | (621) | 0.3 | 0.3 |
|        | (401) | 0.2 | 0.2 |
|        | (201) | 0.04 | 0.03 |
|        | (432) | 0.05 | 0.19 |

TABLE I: Comparison between the squared structure factors $|F(Q)|^2$ predicted for the chiral structure [Fig. 1(c)] and the integrated intensities of the observed x-ray reflections at $T = 20$ K. $F$ denotes fluorite reflections, $JT(I)$ denotes reflections from the oxygen displacements that are common to both the sheared and chiral structures, and $JT(II)$ denotes reflections arising solely from the chiral structure. Uncertainties are not given for the integrated intensities, as these are dominated by the uncertainty in the absorption factor, which is difficult to quantify.
Didcot, UK on the high energy transfer (HET) time-of-flight chopper spectrometer. A powder sample of PrO$_2$ was prepared from a starting material of Pr$_6$O$_{11}$, which was baked at 1000 °C for several hours, then annealed in flowing oxygen at 280 °C for ~ 5 days. The products were checked by x-ray diffraction and no trace of residual Pr$_6$O$_{11}$ could be found. A sample of mass 25.83 g was sealed in an aluminium foil packet and mounted inside a temperature-controlled top-loading closed-cycle refrigerator. The spectrum was measured at 7 K, 50 K, 80 K, 100 K, 110 K, 120 K, 130 K, 165 K and 200 K, using two different incident energies at each temperature: $E_i = 80$ meV (chopper frequency 350 Hz) and $E_i = 250$ meV (chopper frequency 500 Hz). An identical set of measurements (although at a reduced set of temperatures: 7 K, 80 K, 120 K and 165 K) was made on a sample of CeO$_2$ of mass 25.98 g, sealed in a similar foil packet, to estimate the non-magnetic background due to phonons and multiple scattering in PrO$_2$. Vanadium spectra were used to calibrate the detectors and convert the scattering intensity into absolute units of cross-section, i.e. mb sr$^{-1}$ meV$^{-1}$ (Pr ion)$^{-1}$.

Figure 3(a) shows PrO$_2$ spectra measured in the low angle detector banks with an incident energy of $E_i = 250$ meV, corrected for absorption and self-shielding. The single peak is due to a crystal field transition from the ground state to the $\Gamma_7$ excited state. Above $T_D$ the peak is centred at 121 meV, but as the sample is cooled through the Jahn-Teller transition the width of the peak decreases sharply and its centre moves rapidly to higher energies, reaching 132 meV at 7 K. The data are fitted using a Lorentzian profile on a background estimated from the CeO$_2$ data. The fit parameters are used to plot the temperature dependence of the peak centre, FWHM and integrated intensity in Fig. 3(b).

The change in energy of the peak below $T_D$ can be understood qualitatively by constructing a simple model of the crystalline electric field, ignoring the spatial extent of the electron wavefunctions and treating the Pr$^{4+}$ and O$^{2-}$ ions as point charges. This type of model underestimates the separation of the crystal field levels because it disregards the overlap between the electron orbitals. However, it gives a reasonable idea of the relative energy separation of the levels and also their relative spectral weights. If the separation of a pair of levels is known experimentally, the point-charge model can be scaled to match, thus enabling us to predict the approximate positions of other levels.

Figure 4(a) shows a point-charge simulation of the excitation spectrum for the fluorite phase of PrO$_2$ above $T_D$. The simulation takes into account the resolution function of the HET spectrometer at an incident energy of 250 meV and assumes a sample temperature of $T = 0$ K, but the intensity is not normalized to absolute units of cross section. In the fluorite phase, the ground state is a $\Gamma_8$ quartet and the excited state is a $\Gamma_7$ doublet. The separation of these has been scaled to match the observed transition energy of 121 meV. Figure 4(b) shows the simulated spectrum from a point charge model of the chiral phase below $T_D$, using the same scaling factor as for the fluorite phase. It is immediately obvious that the $\Gamma_7$ level has moved to a higher energy, in agreement with our experimental observations (although the magnitude of the observed shift on cooling through $T_D$ is rather less than the point-charge prediction). The model also shows
that the spectral weight of the $\Gamma_7$ level decreases in the chiral phase, which accounts for the discrepancy between model and experiment in our previous study. Lastly, the $\Gamma_8$ ground state is predicted to split into two doublets, separated by $\sim 21$ meV.

The results of the point-charge model lead us to examine the low energy spectrum of PrO$_2$, to see if we can detect the splitting of the $\Gamma_8$ ground state below $T_D$. Figure 5 shows the difference between the PrO$_2$ and CeO$_2$ spectra measured in the low angle detector banks with an incident energy of $E_i = 80$ meV. CeO$_2$ data for temperatures intermediate between actual measurements were estimated by interpolation. The broad band of scattering above 10 meV is clearly present both below and above $T_D$. We observe that the scattering above 35 meV is relatively independent of temperature. However, the region below 35 meV is strongly temperature dependent with a maximum that shifts from $\sim 28$ meV at 7 K to $\sim 20$ meV at 100 K, before becoming quasielastic close to $T_D$. The energy of the maximum at 7 K is in good agreement with the prediction of the point-charge model for the chiral phase and also with other predictions for the splitting of the $\Gamma_8$ ground state in the distorted phase below $T_D$. This provides strong evidence that the broad band of scattering contains a component arising from a crystal field transition between the split doublets of the $\Gamma_8$ ground state.

In order to extract the temperature dependence of the splitting in an unbiased way, we constructed a lineshape to fit the broad band of scattering from three symmetrized Gaussians and a symmetrized Lorentzian, as shown in Fig. 6. Peak A represents quasielastic scattering from the ground state, peak B represents the transition between the two doublets of the split $\Gamma_8$ ground state, and peak C represents a broad continuum of vibronic scattering. Peak L (the symmetrized Lorentzian) was added to improve the quality of the fit at low energies. Each peak was weighted by a detailed balance factor to take into account the thermal population of the levels. In order to determine the width and amplitude of peak B, the lineshape was initially fitted to the spectrum at 7 K. We then fitted the lineshape simultaneously to all the spectra for temperatures between 7 K and 130 K, keeping the width and amplitude of peak B fixed. The other peak widths, centres and amplitudes were free pa-
rameters, but were not allowed to vary with temperature. The only parameters allowed to vary with temperature were the centre of peak B and the amplitude of peak L.

![Graph](https://via.placeholder.com/150)

**FIG. 6:** (Color online). Temperature dependence of the ground state splitting in the chiral phase. The circles are the results of the fit to all spectra between 7 K and 130 K, where the centre of peak B was allowed to vary with temperature. The dashed line is a guide to the eye. The inset shows the functions used to construct the lineshape which was fitted to the data. A, B and C are symmetrized Gaussians, whereas L is a symmetrized Lorentzian. All are weighted by a detailed balance factor.

The solid black lines in Fig. 5 show the fitted lineshape, which agrees well with the data. Figure 6 shows the temperature dependence of peak B. The peak clearly moves to lower energies as the temperature rises, becoming quasielastic near \( T_D \).

**IV. SUMMARY AND CONCLUSIONS**

We have presented the results of two experiments on \( \text{PrO}_2 \): a synchrotron x-ray diffraction experiment which confirms that the displacement of the oxygen atoms in the Jahn-Teller distorted phase is chiral and a neutron inelastic scattering experiment which probes the crystal field transitions above and below the Jahn-Teller transition temperature \( T_D \). The cubic \( \Gamma_4 \) ground state is found to split into two doublets in the distorted phase, and the splitting is found to be \( \sim 20–30 \text{ meV} \), in good agreement with a simple point charge model of the crystal field.

Our results indicate that existing models of the dynamic Jahn-Teller effect should be revised to include the effect of the static distortion. The accompanying paper by Jensen presents such a model, which exhibits an improved agreement between the calculated and measured intensities of the crystal field transitions. Our neutron scattering data show that vibronic excitations due to the dynamic Jahn-Teller effect are largely independent of temperature, despite the presence of a static Jahn-Teller transition. It is likely that this is because the magnetoelastic energy is comparable to the crystal field splitting of the ground state in the distorted phase. Hence, the static Jahn-Teller effect does not quench the dynamic Jahn-Teller fluctuations.

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17 The flat face of the crystal was close to the (111) plane, but
18 did not coincide directly with a plane of high symmetry. Therefore, a Laue image was used to align the crystal with
19 respect to the instrument.
20 A θ-scan in a five-circle vertical diffractometer is the equiv-
21 alent of an ω-scan in a four-circle horizontal diffractometer.
22 CeO$_2$ possesses the fluorite structure and has a similar
23 lattice parameter to PrO$_2$. The neutron scattering lengths
24 of Ce and Pr differ by no more than 10%, but the Ce$^{4+}$ ion
25 has no 4f-electrons, making it non-magnetic. Hence, CeO$_2$
26 provides a good estimate of the non-magnetic scattering
27 from PrO$_2$. This type of scan involves the rotation of the crystal about
28 an axis normal to the scattering plane, while keeping the
29 scattering angle 2θ fixed.