Localized 4f States and Dynamic Jahn-Teller Effect in PrO$_2$

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Neutron spectroscopic measurements of the magnetic excitations in PrO$_2$ reveal (1) sharp peaks characteristic of transitions between levels of the 4$f^1$ configuration of Pr$^{4+}$ split by the cubic crystal field, and (2) broad bands of scattering centred near 30 meV and 160 meV. We present a simple model based on a vibronic Hamiltonian that accounts for the main features of the data. The analysis shows that 90 ± 10% of the Pr ions have a localized 4$f^1$ configuration and provides strong evidence for a dynamic Jahn-Teller effect in the $\Gamma_8$ electronic ground state.

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Anomalous static and dynamic magnetic properties of rare earth and actinide compounds containing strongly correlated electrons are usually attributed to Kondo or valence fluctuations, or to the formation of heavy fermion states. If there are unquenched orbital degrees of freedom, however, then other mechanisms for anomalous behavior are possible. One such mechanism is the coupling of electronic charge fluctuations to phonons, and leads to magnetoelastic and Jahn-Teller phenomena. In the case of localized electrons the dynamic Jahn-Teller effect (DJTE) may quench electronic degrees of freedom, causing a reduction in the magnetic moment and forming states of mixed magnetic and phonon character.

Electron-lattice effects of this kind are of course well known but the absence of a clean reference system has undoubtedly hindered their identification among other anomalous properties, especially in Ce and U compounds. In this Letter we show that PrO$_2$ represents such a model DJTE system. We find that magnetoelastic coupling has a dramatic influence on the static and dynamic properties of PrO$_2$, and we provide the first direct measurements of the magnetovibrational spectrum in a rare earth DJTE system. We also show that the Pr ions exist almost entirely in a localized 4$f^1$ configuration, in disagreement with an intermediate valence model for PrO$_2$.

PrO$_2$ is an insulator with the fluorite structure type. It exhibits type-I antiferromagnetic ordering below $T_N = 14$ K with an anomalously low ordered moment of $\sim 0.6 \mu_B$. The electronic ground state of PrO$_2$ has, together with CeO$_2$ and TbO$_2$, been controversial for many years. Core-level photoabsorption and photoemission spectra have been interpreted by some authors in terms of an intermediate valence ground state comprised of a roughly 50:50 admixture of localized (i.e. atomic-like) 4$f^1$ and 4$f^2$ states. Others, however, believe in a localized 4$f^1$ configuration with a degree of covalent mixing such that the oxygen 2$p$ valence band contains some extended states of $f$ symmetry. Publication of an influential model describing an intermediate valence state in the anomalous cuprate PrBa$_2$Cu$_3$O$_{6+z}$ (PrBCO) similar to that proposed for the lanthanide dioxides has increased interest in PrO$_2$, making it a key reference compound in high energy spectroscopic studies of PrBCO and related materials.

The aim of the present work was to clarify the electronic ground state of PrO$_2$. Neutron spectroscopy probes electronic transitions within the ground state configuration both within and between the $^{2S+1}L_J$ terms, including splittings due to the crystalline electric field (CEF) or exchange fields. The low neutron energies ($\lesssim 1$ eV) and weak coupling to the electronic angular momentum ensure that final state effects are insignificant. The experiments were performed on the High Energy Transfer (HET) chopper spectrometer at the ISIS Facility. On HET neutrons of well-defined incident energy $E_i$ are delivered to the sample in short pulses. Spectra are recorded as a function of flight time in banks of detectors surrounding the incident beam direction. Because the spectra are recorded at constant scattering angle $\phi$ the scattering vector $Q$ varies with energy $E$ thus:

$$\hbar^2 Q^2/2m = 2E_i - E - 2\cos\phi \sqrt{E_i(E_i - E)}.$$

Polycrystalline samples of PrO$_2$ were prepared by oxidation of commercially obtained Pr$_6$O$_{11}$. The starting material was baked in air at 1000°C for several hours and then annealed either in flowing O$_2$ at 280°C for approximately 20 days or under 300–500 atm pressure of O$_2$ at 350°C for 3–5 days. The products were checked by x-ray diffraction and no trace of residual Pr$_6$O$_{11}$ could be detected. From this, and a comparison of our neutron data with that of Pr$_6$O$_{11}$, we estimate an upper limit of 1% on the amount of Pr$_6$O$_{11}$ impurity in our samples.

For the neutron measurements approximately 10 g of PrO$_2$ was wrapped in aluminium foil and mounted in contact with the cold head of a closed-cycle refrigerator. Data were collected with $E_i = 30, 180, 450, 750$ and 1200 meV, and the scattering from vanadium was used to normalize...
the spectra and to convert them into units of absolute scattering cross-section. The presented spectra correspond to the partial differential cross-section \(d^2\sigma/d\Omega dE_i\) multiplied by the factor \(k_i/k_l\) \[1\], where \(k_i\) and \(k_l\) are the initial and final neutron wavevectors and \(E_i\) is the final energy. Measurements were made under identical conditions on a 10 g sample of polycrystalline CeO\(_2\) in order to estimate the non-magnetic (phonon + multiple scattering) background in the PrO\(_2\) data. CeO\(_2\) is an almost ideal material for this purpose as it has the same structure as PrO\(_2\) and the scattering cross-sections of Pr and Ce differ by only 10%. The estimated transmission of the PrO\(_2\) and CeO\(_2\) samples was 93–97% (depending on \(E\) and \(E_i\)), and the spectra were corrected accordingly.

Fig. 1(a) shows spectra of PrO\(_2\) and CeO\(_2\) with \(E_i = 180\) meV averaged over the angular ranges 9–19° (⟨\(\phi\)⟩ = 14°) and 125–139° (⟨\(\phi\)⟩ = 133°). At high angles the scattering is dominated by one-phonon processes, and so the 133° data measures the phonon density of states weighted by the neutron cross-section of the atoms. The 133° data for the two compounds are similar except that some PrO\(_2\) peaks are shifted to lower energies relative to CeO\(_2\), most noticeably below 30 meV. At low angles more marked differences are observed. The PrO\(_2\) data contains a sharp peak at 131 meV and a broad peak centred on ∼30 meV extending from 10 meV to 80 meV, whereas the CeO\(_2\) spectrum shows little structure and lies below the PrO\(_2\) spectrum at all energies. The 131 meV peak has been observed previously \[2\]. Both the broad and sharp peaks in the PrO\(_2\) data decrease in intensity with increasing \(Q\) consistent with a typical 4\(f\) magnetic form factor, and so we identify these features as magnetic in origin. Conversely, the CeO\(_2\) signal systematically increases in intensity with \(Q\), and this implies that the CeO\(_2\) scattering is non-magnetic as expected for a 4\(f\) configuration with no admixture of localized 4\(f^1\) states.

Several other magnetic features were observed in the PrO\(_2\) data in addition to those already described. The runs with \(E_i = 750\) meV and 1200 meV detected two more peaks. These are shown in Figs. 1(b) and (c). The peak centred near 350 meV in the 750 meV run is significantly broader than the resolution, whereas the peak centred at 730 meV in the 1200 meV run is resolution-limited. The 450 meV run revealed a shoulder of scattering above the 131 meV peak, centred at ∼160 meV. This feature is displayed in the inset to Fig. 1(d). Finally, the \(E_i = 30\) meV run revealed a peak centred at 3 meV shown in Fig. 1(d). This peak shifted to lower energies as the temperature was raised, becoming quasielastic above ∼15 K. Given that \(T_N = 14\) K we can confidently attribute this 3 meV peak to spin wave excitations of the antiferromagnetically ordered ground state. We found no evidence in our data for an excitation at 5.4 meV reported in a previous work \[12\], and so we conclude that this feature is not intrinsic to PrO\(_2\).

Fig. 1(d) shows data from several runs after correction for the non-magnetic scattering and for the calculated (see below) magnetic form factor. The form factor correction extrapolates the data to zero \(Q\) and hence allows comparison of runs with different incident energies.

We begin our interpretation of the results by considering the effect of the CEF. The splitting of a localized 4\(f^1\) configuration in a cubic CEF is described by the spin-orbit coupling constant \(\zeta\), which sets the \(2F_{5/2} \rightarrow 2F_{7/2}\) separation, and the fourth and sixth order CEF parameters \(B_2^0\) and \(B_4^0\). Using the free ion value of \(\zeta\) for Pr\(^{4+}\) \[1\] Kern et al \[1\] have calculated the energy levels as a function of the ratio \(B_2^0/B_4^0\). They assigned the 131 meV peak to the \(\Gamma_8 \rightarrow \Gamma_7\) transition of \(2F_{5/2}\), and by estimating the ratio \(B_2^0/B_4^0\) from a point charge model they arrived at a parametrization of the CEF. Kern et al’s model predicts the levels in the CEF-split \(2F_{7/2}\) term to be \(\sim 320\) meV \((\Gamma_6')\), \(\sim 390\) meV \((\Gamma_6'')\) and \(\sim 580\) meV \((\Gamma_4'\) above the ground state in rough accord with the peaks in Figs. 1(b) and (c). We conclude, therefore, that these high energy peaks arise from the \(2F_{5/2} \rightarrow 2F_{7/2}\) intermultiplet transitions, the only proviso being that the signal in Fig. 1(b) must encompass both the \(\Gamma_6'\) and \(\Gamma_8\) levels. Assuming this to be the case we refined the CEF model with the 14 states \(|J_i,m_i,\phi\rangle\) of \(2F_{5/2}\) and \(2F_{7/2}\) as a basis. With all 3 parameters allowed to vary independently the fitting procedure converged yielding \(B_2^0 = (-776 \pm 8)\) meV, \(B_4^0 = (207 \pm 5)\) meV and \(\zeta = (100.5 \pm 1)\) meV \[3\] and gave excellent agreement with the observed energies.

With the eigenfunctions from the CEF refinement we can now evaluate the cross-sections for the observed transitions as a function of \(Q\). The formulae \[10\] contain radial moments of the \(4f\) wavefunction, and values for Pr\(^{4+}\) were taken from Ref. \[1\]. The curve in Fig. 1(b) represents the calculated cross-sections for the \(\Gamma_8 \rightarrow \Gamma_6\) and \(\Gamma_8 \rightarrow \Gamma_6''\) transitions, and the curve on Fig. 1(c) is likewise for the \(\Gamma_6' \rightarrow \Gamma_4'\) transition. Considering that no additional parameters are needed to obtain the calculated cross-sections the level of agreement with the data is very good. The same cannot be said, however, when the cross-sections for the \(\Gamma_8 \rightarrow \Gamma_8\) and \(\Gamma_8 \rightarrow \Gamma_7\) transitions are calculated. At zero \(Q\) these are 182 and 99 mb sr\(^{-1}\)Pr\(^{-1}\) respectively \[1\], considerably greater than the integrated spectral weights 47 and 48 mb sr\(^{-1}\)Pr\(^{-1}\) in the 3 meV and 131 meV peaks shown in Fig. 1(d) \[7\].

We will now describe a model that both accounts for the puzzling intensities just mentioned and explains the origin of the 10–80 meV broad peak and the 160 meV shoulder. Our hypothesis is that these effects derive from a strong coupling between \(4f^1\) electronic states and local dynamic lattice distortions. This coupling mixes electronic and phonon degrees of freedom and causes a dynamic Jahn-Teller effect in the \(\Gamma_8\) ground state.

The existence of a DJTE in PrO\(_2\) was in fact suggested some time ago to explain the factor ∼2 reduction in ordered moment relative to a pure \(\Gamma_8\) ground state \[2\]. An analogous moment reduction in UO\(_2\) had already
been attributed to a DJTE [18], and so its occurrence in PrO$_2$ would not be a surprise. Moreover, the neutron data in Fig. 1(a) showing substantial phonon shifts in PrO$_2$ relative to CeO$_2$ provide direct evidence for a significant magnetoelastic interaction. To find out how this interaction influences the magnetic excitation spectrum we describe a simple model for the coupling of a set of CEF levels with phonons. Group theory shows that the $\Gamma_8$ CEF ground state couples in first order to local distortions of either $\Gamma_3$ or $\Gamma_5$ symmetry, and point charge calculations indicate that the coupling strengths are comparable [15]. For the sake of simplicity, however, we will restrict our model to three degenerate local distortions of $\Gamma_5$ symmetry with vibrational frequency $\omega_{ph}$. We describe the magnetoelastic coupling with the Hamiltonian

$$H_{ME} = g \sum_i (a_i + a_i^\dagger) O_i,$$

where $g$ is the coupling constant, $a_i$ and $a_i^\dagger$ are phonon annihilation and creation operators, and $O_i$ are the $\Gamma_5$ symmetry quadrupolar operators: $O_1 = (J_y J_z + J_z J_y)/2$, $O_2 = (J_x J_z + J_z J_x)/2$, and $O_3 = (J_x J_y + J_y J_x)/2$. To investigate the ordered magnetic moment we also included a molecular exchange field interaction $H_{EX} = \mathbf{H} \cdot \mathbf{J}$. The magnitude of $\mathbf{H}$ was chosen so as to reproduce the observed 3 meV splitting of the ground state.

We take as a basis the 24 states $|\phi_n\rangle$, $n = 1, \ldots, 24$, represented by $|\Gamma_8;0\rangle$, $|\Gamma_7;0\rangle$, $|\Gamma_8;1^{(i)}\rangle$, and $|\Gamma_7;1^{(i)}\rangle$. These are products of the CEF eigenstates and the three $\Gamma_5$ phonon modes ($i = 1, 2, 3$) containing either 0 or 1 quanta $\hbar \omega_{ph}$. The energy separation $\Delta$ of $|\Gamma_8;0\rangle$ and $|\Gamma_7;0\rangle$ is chosen so as to reproduce the observed peak at 131 meV. The vibronic states are obtained by diagonalisation of the matrix $\langle \phi_{n'} | H_{ME} + H_{EX} | \phi_n \rangle$, and the magnetic part of the neutron cross-section is calculated from the matrix elements of $\mathbf{J}$.

We evaluated the model for a range of parameters. Small values of $\hbar \omega_{ph}$ are effective at mixing $|\Gamma_8;0\rangle$ and $|\Gamma_8;1^{(i)}\rangle$ states creating a DJTE. The consequences are a transfer of intensity from the ground state into the phonon-like states and a reduction in the ordered moment. A large $\hbar \omega_{ph}$ tends to create vibronic states involving the $\Gamma_7$ CEF excitation. To illustrate these effects we plot on Fig. 2 the zero-$Q$ energy spectrum for two parameter sets, one (I) with small and the other (II) large $\hbar \omega_{ph}$. In both cases new peaks appear between the 3 meV and 131 meV levels. With set I there is a factor 0.86 reduction in the ordered moment (independent of the direction of $\mathbf{H}$) and a similar decrease in the intensity of the 3 meV peak. Set II produces a smaller effect on the ordered moment and 3 meV peak, but a new feature is the signal above the 131 meV peak.

These results give us confidence that magnetoelastic coupling is responsible for the unusual energy spectrum and reduced moment of PrO$_2$. Because of its simplicity we cannot expect a single-frequency model to match the data perfectly. In reality there will be coupling to local dynamic distortions with $\Gamma_3$ as well as $\Gamma_5$ symmetry, and these distortions will exist over a range of frequencies due to dispersion. The extent of the observed broad scattering is indicative that many frequencies are actually involved. A realistic model would also need to include states with $>1$ phonons. Nevertheless, the qualitative agreement achieved with the present model is satisfying.

Before concluding we will address the nature of the $f$ states. Our analysis has assumed a localized $4f^1$ configuration. We can check this assumption two ways. Firstly, we can look for the signature of localized $4f^2$ states in the range 200–300 meV where the $^3H_4 \rightarrow ^3H_5$ transition occurs [19]. No peaks are observed. Second, we can directly determine the number of $4f^1$ states per Pr from the neutron cross-section via the sum rule for transitions within a $J$ multiplet [10]. The measured zero-$Q$ cross-section integrated up to 220 meV, including the elastic scattering [17], is 240 mb sr$^{-1}$Pr$^{-1}$. This compares with the calculated value of $182 + 99 = 281$ mb sr$^{-1}$Pr$^{-1}$ for the $J = \frac{5}{2}$ multiplet [10]. Thus, by including the broad scattering in the integral we recover almost all the missing intensity. Allowing a 10% uncertainty in the absolute calibration we conclude that $90\pm10\%$ of the Pr ions have a localized $4f^1$ configuration. The intermultiplet transitions shown in Figs. 1(b) and (c) provide further support for this conclusion since the calculated cross-sections for $4f^1$ are in good agreement with the measured intensities.

In summary, our findings support a tetravalent model for PrO$_2$ with an almost fully occupied atomic $4f$ orbital. The neutron data allow the possibility of $\sim10\%$ under-occupancy relative to a pure $4f^1$ configuration, and this may indicate a degree of covalency. Any other occupied states of $f$ symmetry must then be extended states in the O 2$p$ valence band. These results rule out the strongly intermediate valence model for PrO$_2$, and we anticipate that a similar picture will apply to CeO$_2$ and TbO$_2$. We find compelling evidence that magnetoelastic coupling in PrO$_2$ creates a ground state with mixed electronic and vibrational degrees of freedom by means of a DJTE. Being an insulator with a simple structure, localized $f$ electrons and a large CEF splitting, PrO$_2$ would seem an ideal model system for further studies of the DJTE.

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FIG. 1. Neutron inelastic scattering from PrO2 and CeO2 measured at a temperature of 10 K. In (a) the incident neutron energy Ei was 180 meV, and spectra recorded at low and high scattering angles are shown. (b) and (c) show 2F5/2 → 2F7/2 intermultiplet transitions measured with Ei = 750 meV and 1200 meV respectively. The solid lines are cross-sections calculated from the CEF model described in the text with widths corresponding to the instrumental resolution. (d) shows data corrected for the non-magnetic background and the Q dependence of the magnetic cross-section as described in the text. Main frame: Ei = 30 and 180 meV. Inset: Ei = 450 meV showing the shoulder to the 131 meV peak.

FIG. 2. Zero-Q cross-section of PrO2 calculated from the magnetoelastic model described in the text with parameter sets I (hωph = 12.5 meV, g = 8 meV and Δ = 109 meV) and II (hωph = 42 meV, g = 9 meV and Δ = 101 meV). In both cases H was 0.5 meV || (1, 1, 1). The peak widths correspond roughly with the experimental resolution in Fig. 1(d).