Antiferromagnetic $S=1/2$ Spin Chain Driven by p-Orbital Ordering in CsO$_2$

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Supplemental Material

DFT calculations: procedure
Density functional theory (DFT) calculations were carried out from first principles using the PW91 generalized gradient approximation (GGA) [1]. The projector augmented plane wave method was employed [2,3], as implemented in the Vienna Ab Initio Simulation Package (VASP) [4-7]. A value of $U = 4.0$ eV was chosen for the oxygen 2$p$-orbitals (with a Wigner-Seitz radius of 0.741 atomic units) in the GGA+$U$ [8] method. The kinetic energy cut-off was set to 700 eV, the positional parameters were relaxed until the forces were smaller than 2 meV/Å, and the convergence criterion for energy in static calculations was 0.001 meV. The Brillouin-zone integration used a gamma-centered $k$-mesh (12×6×4) with 148 irreducible $k$ points.

DFT calculations: predicted Raman-active modes
Calculations of the Raman modes associated with the structure below 70 K were carried out in VASP using a supercell with all three axes doubled. After relaxation of the atomic positions, each atom was displaced in all three independent directions by 0.01 Å and 0.02 Å and the corresponding forces were calculated via the Hellmann-Feynman theorem. The force constants were obtained from the calculated forces and displacements [9]. Finally, the phonon frequencies resulted from the diagonalization of the dynamical matrix. As described in the main article, two degenerate structural models with unit cell dimensions corresponding to $(a \times 2b \times 2c)$ and $(2a \times 2b \times 2c)$ were obtained, the former being consistent with the metrically orthorhombic unit cell that we observed by X-ray diffraction. Four Raman modes at low wavenumbers were obtained using this optimized structure, which is shown in Fig. 4(b) of the main article. Calculated modes at 66 cm$^{-1}$, 67 cm$^{-1}$, and 75 cm$^{-1}$, which were observed between 70 cm$^{-1}$ and 85 cm$^{-1}$ (see Fig. 3(c) of the main article), are attributed to three different interlayer motions of the Cs$^+$ cations along...
the \( c \)-direction (Fig. S1). The fourth mode at 200 cm\(^{-1} \) is attributed to the librational mode ("swing-like" motion) of the superoxide anions.

**FIG. S1.** View of CsO\(_2\) along the \( b \)-axis showing interlayer motions of Cs\(^+\) cations (blue spheres) giving rise to three Raman-active modes below 70 K. The calculated frequency of each mode is shown. Oxygen atoms are shown in red.

**DFT calculations: partial DOS for Cs**

As discussed in the main article, we propose that the spin chain in CsO\(_2\) is formed by superexchange via the Cs 5\( p_z \) orbitals. The calculated partial DOS for the filled 5\( p \) and empty 6\( s \) orbitals of cesium is shown in Fig. S2, together with the partial DOS of oxygen.

**FIG. S2.** (a) Calculated partial DOS for Cs 5\( p_x \), 5\( p_y \), 5\( p_z \), and 6\( s \)-orbitals, and O \( \pi \)-orbitals (vertically offset for clarity). (b) Expanded view of Cs 6\( s \) DOS.
Raman spectroscopy: group theoretical considerations

Group theoretical analysis was used to analyze the optical modes [10,11] that occur in the high-
temperature tetragonal structure (I4/mmm) as determined by X-ray powder diffraction (XRPD).
Here Cs is found at the Wyckoff position 2a with site symmetry 4/mmm. Oxygen is found at the Wyckoff position 4e with site symmetry 4mm. The optical modes expected to emerge are given by:

\[ \Gamma^{op}(4/mmm) = A_{2u} + E_u \]
\[ \Gamma^{op}(4mm) = A_{1g} + A_{2u} + E_g + E_u \]

Only two Raman-active modes are expected in I4/mmm symmetry: \( A_{1g} + E_g \). The \( A_{1g} \) component is the normal (stretching) mode, \( \Sigma^+_g \), of the superoxide anion, which appears between 1130 cm\(^{-1}\) and 1145 cm\(^{-1}\) depending on the chemical environment [12-15]. We performed a DFT calculation using the 300 K I4/mmm structure determined by XRPD and obtained a frequency of 1119 cm\(^{-1}\) for this mode (observed at 1134 cm\(^{-1}\)). The same calculation gave a frequency of 119 cm\(^{-1}\) for the \( E_g \) mode, which was absent in both our experimental spectra and those of a previous study on \( \text{AO}_2 \) [12]. The weak, broad peak observed at \( \sim 205 \) cm\(^{-1}\) (Fig. 3 of main article) is probably associated with the librational mode of \( \text{O}_2^- \) that is allowed in the low-temperature structure, suggesting that the symmetry above 70 K is locally lower than I4/mmm or that a degree of structural disorder is present. We also note from the considerations above that I4/mmm symmetry does not allow any Raman-active mode originating from Cs. However, the broad peak observed at \( \sim 75 \) cm\(^{-1}\) is almost certainly a phonon mode or a set of modes involving Cs (see Fig. 3 of main article and Fig. S1), providing more evidence that the symmetry is lower than I4/mmm.

Magnetic properties of \( \text{CsO}_2 \) as a function of applied field

The magnetization of \( \text{CsO}_2 \) was measured as a function of applied magnetic field and is shown in Fig. 3 of main article) is probably associated with the librational mode of \( \text{O}_2^- \) that is allowed in the low-temperature structure, suggesting that the symmetry above 70 K is locally lower than I4/mmm or that a degree of structural disorder is present. We also note from the considerations above that I4/mmm symmetry does not allow any Raman-active mode originating from Cs. However, the broad peak observed at \( \sim 75 \) cm\(^{-1}\) is almost certainly a phonon mode or a set of modes involving Cs (see Fig. 3 of main article and Fig. S1), providing more evidence that the symmetry is lower than I4/mmm.
magnetization is essentially linear with respect to field up to 60 kOe in the spin-chain regime. We note that the peaks in the derivative curves at ~9 kOe are artifacts due to relaxation effects because the measuring interval with respect to field was changed here.

We also measured the zero-field-cooled magnetic susceptibility in different applied fields. As shown in Fig. S3(b), the broad maximum persists up to at least 40 kOe, suggesting that the spin chain stays intact. The anomaly corresponding to the 3D AFM ordering transition becomes less distinct with field and disappears above ~20 kOe, suggesting that the 3D ordering is gradually suppressed. A second, weaker anomaly of unknown origin is present at ~12 K in all fields.

**FIG. S3.** (a) Magnetization as a function of applied field at 2.5 K, 7.5 K, and 15 K. The inset shows the derivatives of the curves. (b) Zero-field-cooled magnetic susceptibility versus temperature, measured on warming in different magnetic fields.
Supplemental references


