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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 $2p$ -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 ($12 \times 6 \times 4$) 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 $5p_z$ orbitals. The calculated partial DOS for the filled $5p$ and empty $6s$ orbitals of cesium is shown in Fig. S2, together with the partial DOS of oxygen.

FIG. S2. (a) Calculated partial DOS for Cs $5p_x$, $5p_y$, $5p_z$, and $6s$ -orbitals, and O π -orbitals (vertically offset for clarity). (b) Expanded view of Cs $6s$ 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:

$$\Gamma^{\text{op}}(4/mmm) = A_{2u} + E_u$$

$$\Gamma^{\text{op}}(4mm) = A_{1g} + A_{2u} + E_g + E_u$$

Only two Raman-active modes are expected in $I4/mmm$ symmetry: $A_{1g} + E_g$. The A_{1g} component is the normal (stretching) mode, Σ_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 AO_2 [12]. The weak, broad peak observed at $\sim 205 \text{ cm}^{-1}$ (Fig. 3 of main article) is probably associated with the librational mode of 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 $\sim 75 \text{ cm}^{-1}$ 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 CsO_2 as a function of applied field

The magnetization of CsO_2 was measured as a function of applied magnetic field and is shown in Fig. S3(a) for 2.5 K, 7.5 K and 15 K. An essentially linear dependence of the magnetization on field is observed in each case, although the data collected in the 3D AFM regime deviate slightly from linearity above $\sim 28 \text{ kOe}$. This effect is more clearly seen in the derivative of the magnetization [inset of Fig. S3(a)]. A similar anomaly was observed by Zumsteg et al. [16], who regarded it as a metamagnetic transition. Any metamagnetic transition in CsO_2 would involve a rotation of the anions because the spins are perpendicular to the molecular axis. The

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.

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