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Research into magnetic materials has begun to extend beyond $d$ and $f$-block electron systems to those in which magnetism arises from unpaired spins in $p$ orbitals [1]. Such compounds are relatively scarce because the more extended $p$ orbitals result in a tendency toward electron pairing in covalent bonds. Perhaps the most suitable model systems for the study of $p$-electron magnetism are the alkali metal superoxides (AO$_2$), which form ionic crystals adopting structures related to rocksalt [2]. The valence electrons in AO$_2$ reside in states that are almost purely of oxygen character. In the superoxide anion (O$_2^-$), three electrons occupy a pair of degenerate antibonding $\pi^*$ molecular orbitals; thus, there is one unpaired spin ($S = 1/2$). Accordingly, these compounds are susceptible to structural distortions that split the $\pi^*$ energy levels and lift the orbital degeneracy [3], similar to the Jahn-Teller effect for degenerate $d$ orbitals. Orbital ordering (OO) similar to that found in transition-metal systems [4] may then be expected. The linear O$_2^-$ anion has an additional orientational degree of freedom compared to JT-active transition-metal species and the orbital degeneracy in AO$_2$ compounds is lifted by cooperative tilting and displacement of the anions [2,5].

It is becoming increasingly clear that AO$_2$, as well as the A$_2$O$_3$ sesquioxides [6,7] and the O$_2$MF$_6$ ($M =$ Sb, Pt) dioxygenyl compounds [8], can be considered within the framework of correlated electron systems. In AO$_2$, direct antiferromagnetic (AFM) exchange can occur when the axes of nearest-neighbor O$_2^-$ anions are parallel and the lobes of their half-occupied $\pi^*$ orbitals point toward each other [9]. It is also probable that superexchange via either the empty $s$ orbitals or filled $p$ orbitals of the A$^+$ cations can occur, which probably determines the ground-state magnetic structures of KO$_2$, RbO$_2$, and CsO$_2$, reported to be AFM below 7.1 K, 14.7 K, and 9.6 K, respectively [10,11]. Only the magnetic structure of KO$_2$ has been studied by neutron diffraction. Here, spins in the pseudotetragonal $ab$ plane are aligned in ferromagnetic (FM) fashion, while planes are AFM coupled along the $c$ axis [12]. Electron paramagnetic resonance (EPR) studies have suggested that the same magnetic structure is present in RbO$_2$ and CsO$_2$, and that the magnetic easy axis is orthogonal to the anion axis in all AO$_2$ [11]. These experimental observations, made more than three decades ago, have recently inspired further theoretical work on KO$_2$ and RbO$_2$ [13–15] focused on the possible ground-state OO configurations and their influence on spin ordering. Although no consistent picture has yet emerged, it is becoming clear that the coupling in AO$_2$ between spin, orbital, and lattice degrees of freedom (the latter including the tilting of the anions) is as relevant as for strongly correlated transition-metal systems. Here, we reinvestigate the magnetic properties of CsO$_2$ and show that OO drives the formation of a 1D AFM spin chain, the clearest demonstration thus far of correlated electron physics in an inorganic $p$-electron spin system.

Polycrystalline CsO$_2$ was prepared by passing dry oxygen gas through a solution of Cs metal in liquid ammonia at $-65$ °C for 2 h. The solution was then warmed to remove ammonia, leaving yellow CsO$_2$ powder. Magnetic measurements were performed on samples sealed in vacuum inside glass tubes using a Quantum Design MPMS-XL 7 magnetometer. X-ray powder diffraction (XRPD) was performed using a Huber G670 diffractometer operating with Cu Kα$_1$ radiation. The sample was sandwiched between two Mylar films to avoid exposure to air. The XRPD data were analyzed using the General Structure Analysis System (GSAS) software [16]. Raman spectroscopy was performed in a backscattering configuration using a liquid nitrogen-cooled charge coupled device (CCD) connected to a three-grating micro-Raman spectrometer (T64000 Jobin Yvon). Samples were contained on a copper plate in thermal contact with a cold finger inside a cryocooled,
evacuated chamber. A laser power density of 0.05 mW/μm² was used. Density functional theory (DFT) calculations were carried out from first principles using the generalized gradient approximation (GGA) + U method with $U = 4.0$ eV, as implemented in the Vienna $ab$ intio simulation package (VASP) [17]. More details are given in the Supplemental Material [18].

The dominant feature in the magnetic susceptibility of polycrystalline CsO$_2$ is a broad maximum centered at $\sim 28$ K [Fig. 1(a)]. A similar feature was previously observed by Zumsteg et al. [10], who remarked only that considerable magnetic order remained above $T_N = 9.6$ K.

Such a maximum is a typical indication of low-dimensional magnetic ordering [19]. The spins in AO$_2$ can rotate in the plane perpendicular to the molecular axis, but EPR shows only moderate anisotropy of the $g$ tensor [11,20]; thus, we can treat CsO$_2$ as an isotropic (Heisenberg) spin system. The susceptibility maximum was fitted using the $S = 1/2$ square-lattice Heisenberg model formulated by Keith et al. [21]. There are three variable parameters in this model: the exchange constant for a particular crystal direction $J/k_B$, the ratio $\alpha$ between two orthogonal exchange constants on a square lattice ($J' = \alpha J$), and the Curie constant. For 2D AFM ordering, $J = J'$ and $\alpha = 1$; for an AFM spin chain, $\alpha = 0$. This model can also be applied to 2D systems incorporating mixed AFM and FM interactions, for which $-1 \leq \alpha < 0$. The best fit to our data is shown in Fig. 1(a), which yielded $J/k_B = 20.27$ K, $\alpha = 0$, and $C = 0.325$. The zero value of $\alpha$ implies that CsO$_2$ is essentially an AFM spin chain. Fits performed with fixed nonzero positive or negative values of $\alpha$ were visibly worse. We also fitted the susceptibility maximum using an alternative expression reported by Feyerherm et al. [22], based on the original formulation for a $S = 1/2$ Heisenberg AFM chain by Bonner and Fisher [19]. We obtained $J/k_B = 20.0$ K, in good agreement with the model of Keith et al. [21]. Both models fitted the data equally well between 15 K and 70 K, at which a small anomaly associated with a structural transition (see below) is apparent. The spin chain appears to persist in applied fields up to at least 40 kOe [18]. A Curie-Weiss fit to the inverse susceptibility above 150 K [Fig. 1(b)] yielded an effective moment of 2.03 $\mu_B$. This is significantly higher than the expected spin-only value for $S = 1/2$ and is consistent with previous reports on CsO$_2$ and other AO$_2$ [10,20], suggesting unquenched orbital momentum. The fitted Weiss constant of $\theta = -40.3$ K, which corresponds to $\sim 47$ K, is more evidence for the quantum AFM nature of CsO$_2$.

Long-range 3D AFM ordering in CsO$_2$ was previously reported below $T_N = 9.6$ K on the basis of specific heat, magnetic susceptibility, and EPR measurements [11,10]. We observe a magnetic susceptibility anomaly at $\sim 9.5$ K [Fig. 1(b)] and the spin chain models no longer fit the data below $\sim 15$ K, supporting a transition to 3D ordering. The low-temperature susceptibility tail below 7 K is likely due to residual spins; a fit to the Curie law yielded a concentration of $\sim 8\%$ $S = 1/2$ disordered spins.

At room temperature, the XRPD pattern of CsO$_2$ is consistent with the previously reported tetragonal average structure (space group $I4/mmm$) [23]. However, Raman spectroscopy (see below) demonstrates that the true symmetry is lower. An impurity phase (CsOH$_2$H$_2$O, $\sim 20\%$ by weight) was also present but does not contribute to the magnetic response. Splitting of the CsO$_2$ XRPD peaks with $h \neq k$ was observed below 70 K (see Fig. 2), consistent with a transition to orthorhombic symmetry. However, Rietveld refinements were rather insensitive to the oxygen positions and we were unable to determine details of the low-temperature structure. An earlier XRD study on CsO$_2$ single crystals reported a tetragonal-to-orthorhombic transition at the higher temperature of 190 K [23], below which incommensurate satellite reflections also appeared. No such peaks were apparent in our data. It was previously reported that different solution-grown CsO$_2$ single crystals from the same batch did not always exhibit a

![FIG. 1 (color online).](image1.png) (a) Magnetic susceptibility versus temperature for polycrystalline CsO$_2$, measured on warming in a field of 10 kOe after cooling in the same field. Fits to the models of Keith et al. [21] (green solid line) and Feyerherm et al. [22] (red dashed line) are shown. The arrow indicates an anomaly at 70 K. (b) Low-temperature magnetic susceptibility showing $T_N$ and a fit of the low-temperature susceptibility tail to the Curie law. A Curie-Weiss fit to the inverse susceptibility above 150 K is shown in the inset.

![FIG. 2 (color online).](image2.png) (a),(b) 200 and 103 XRPD peaks in the tetragonal and orthorhombic regimes. (c) Evolution of lattice parameters and (d) selected microstrain peak-broadening parameters with temperature.
tetragonal-orthorhombic transition [24], which suggests a sensitive dependence of the structure on oxygen stoichiometry. The evolution of the lattice parameters with temperature of our sample is shown in Fig. 2(c). Apart from the phase transition at ~70 K, the other noteworthy feature is a decrease of the c parameter above 200 K. This might be due to increasing librational freedom of the anions in the a and b directions on heating. The c axis also shortens on cooling below ~100 K, suggestive of coherent anion tilting away from the axis. The refinement of anisotropic microstrain peak-broadening parameters, using the Stephens formulation [25], was necessary at all temperatures to fit the peak profiles. The $S_{a00}$ and $S_{000}$ parameters were much larger than $S_{004}$ [Fig. 2(d)], indicating either a degree of disorder or smaller coherently diffracting domain size in the pseudotetragonal basal plane.

Raman spectroscopy provided greater insight into the crystal structure. For the tetragonal average structure, three Raman active modes are apparent [Fig. 3(a)]. The stretching mode of $\text{O}_2^-$ is observed at 1134 cm$^{-1}$, which agrees well with the previously reported 1137 cm$^{-1}$ [26]. The broad peaks at 75 cm$^{-1}$ and 205 cm$^{-1}$ are probably a phonon mode involving the Cs cations and a $\text{O}_2^-$ librational mode, respectively (see below). The presence of the 75 cm$^{-1}$ mode is incompatible with $I4/mmm$ symmetry [18] and is evidence that the local symmetry is lower, as previously inferred from single-crystal XRD measurements [23].

Figure 3(b) shows the Raman spectrum at 4.5 K. Four peaks are apparent at low wave numbers, the origin of which was investigated by optimizing the orthorhombic structure of Cs$_2$O using DFT calculations without symmetry constraints. By using a supercell doubled along all three axes and the lattice parameters determined by XRPD at 20 K, we obtained two degenerate solutions. In the first structural solution, the anions are tilted by ~5° from c toward the basal plane diagonal, as shown in Fig. 4(b). The tilt directions are staggered along b and uniform along a, corresponding to a doubled b axis. The tilting of anions in the $z = 1/2$ layer of the supercell (which is the same as that in the $z = 1/4$ layer) is opposite to the tilting of anions in the $z = 0$ layer (the same as that in the $z = 3/4$ layer). Thus, a staggered pattern is formed when viewed along c and the c axis is also doubled. Within the ab plane there are staggered shifts of the Cs cations in the a direction, such that along b the cations form a zigzag arrangement. This is likely a consequence of the staggered anion tilts. In the second structural model the $z = 0$ and $z = 1/2$ layers are identical to those in the first structure, but the patterns of Cs shifts and anion tilts in these two layers are rotated by 90° in the $z = 1/4$ and $z = 3/4$ layers, respectively, such that the tilts become staggered along a rather than along b and the a axis is also doubled. This unit cell would be metrically tetragonal because overall there is no structural anisotropy in the ab plane. However, we observe a metrically orthorhombic cell (Fig. 2); thus, we favor the first model. Calculations of the Raman modes were carried out in VASP using the $a \times 2b \times 2c$ supercell [18]. Four Raman modes at low wave numbers were obtained: 66 cm$^{-1}$, 67 cm$^{-1}$, 75 cm$^{-1}$, and 200 cm$^{-1}$, which agree well with the experimental spectrum. The first three modes are associated with interlayer motions of the Cs cations along the c direction [18], and the broad feature observed at 209 cm$^{-1}$ is the librational mode ("swing-like" motion) of $\text{O}_2^-$. Finally, the calculated $\text{O}_2^-$ stretching mode at 1120 cm$^{-1}$ agrees well with the observed mode at 1135 cm$^{-1}$.

Figure 3(c) shows the temperature dependence of the three low wave-number Cs modes, which merge to become a single broad peak.

**FIG. 3 (color online).** Raman spectra of Cs$_2$O at (a) 110 K and (b) 4.5 K. (c) Raman modes associated with the interlayer motion of Cs and (d) librational mode of $\text{O}_2^-$ as a function of temperature.

**FIG. 4 (color online).** (a) Partial oxygen DOS for anions A and B along the b axis in the $z = 0$ layer below 70 K. Because of the AFM configuration, the spin-up and spin-down DOS for anions in the $z = 1/4$ layer is reversed compared to the DOS shown here. (b) ab-plane view of the optimized structure of Cs$_2$O below 70 K showing anion tilting and ordering of the half-occupied $\pi^*_y$ and $\pi^*_x$ orbitals.
above the 70 K structural phase transition. The $O_2^-$ libra-
tional mode broadens and weakens between 65 K and
110 K but does not disappear completely [Fig. 3(d)].

The phase transition at $\sim 70$ K results in OO, which is
apparent from the site-projected partial oxygen DOS
shown in Fig. 4(a) for two adjacent anions $A$ and $B$ along
the $b$ axis of the optimized structure in Fig. 4(b). The four
peaks in the DOS for each anion correspond to the spin-up
and spin-down states of the two $\pi^*$ orbitals, three of which
are fully occupied and one of which, above the Fermi level
($E_F$), is empty. The states in the energy range $-1$ to 0 eV
correspond to a filled $\pi^*_z$ orbital for dimer $A$ and a filled $\pi^*_z$
orbital for dimer $B$. Here, $x$ and $y$ refer to the coordinate
system indicated by axes $x'$ and $y'$ in Fig. 4(b), which are at
$\sim 45^\circ$ to the unit cell axes $a$ and $b$. For any given dimer, the
$\pi^*_z$ orbital is fully occupied on two nearest-neighbor
dimers within the pseudotetragonal plane and the $\pi^*_x$
orbital is fully occupied on the other two. This corresponds to a
zigzag configuration of alternating half-filled $\pi^*_x$ and $\pi^*_z$
orbitals along the $b$ axis, as shown in Fig. 4(b) (the anion
axes tilt by $\sim 5^\circ$ from the $c$ axis and are almost perpen-
dercular to the plane of the picture.)

The lobes of the magnetic orbitals do not point toward
each other; thus, direct exchange will be weak and possible
superexchange pathways via Cs must be examined. The
occupied Cs $p_z$ orbitals have the correct orientation to
mediate coupling along the pathways marked by red arrows
in Fig. 4(b), whereas no obvious superexchange pathway is
available in the perpendicular direction. The Cs $p_z$
orbitals lie at energies between $-8.5$ eV and $-5$ eV with respect to
$E_F$ [18]. The sign of the superexchange along $b$ is AFM
according to the Kugel-Khomskii picture [27]. The unit cell
is doubled in the $c$ direction: when site $A$ at $z = 0$ in
Fig. 4(b) has a half-occupied $\pi^*_z$ orbital, the corresponding
site at $z = 1/2$ has a half-occupied $\pi^*_x$ orbital. Linear super-
exchange pathways along $c$ of the type $O_2^\cdash\cdash Cs\ p_z\ O_2^\cdash\cdash\pi^*_z$
are thus prevented. The result is an AFM spin chain in the $b$
direction.

The anion tilting and OO configuration in Fig. 4(b) is
analogous to that calculated for KO$_2$, by Nandy $et\ al.$ [15].
Although the interatomic distances along the $b$ direction
in KO$_2$ are shorter, the magnetic susceptibility does not sug-
gest low-dimensional ordering [10]. It is possible that the
superexchange pathway along $b$ is disrupted by the much
greater anion tilting in KO$_2$. Similarly, no spin chain seems
to form in RbO$_2$, despite the crystal structure being very
similar to CsO$_2$ [2]. This may be due to a different ground
state OO configuration, calculated to be staggered along
both basal plane axes with orbital lobes pointing between
the Rb$^+$ cations [14]. We also note that the relevant
$p$-levels of Rb and K lie significantly deeper than for Cs
[28]. The marcasite phase of NaO$_2$ below 196 K might
exhibit a spin chain along the $c$ axis due to strong AFM
direct exchange between anions [9]. A coupling constant of
$J = -370$ K was calculated for the situation where the
lobes of half-occupied orbitals on nearest neighbors point
toward each other [29]. The magnetic susceptibility should
thus rise with temperature without reaching the typical
broad maximum associated with a spin chain; this result has
been experimentally observed [10,29], but the data
were not fitted to any model and OO has not been
confirmed.

Although several examples of AFM $p$-electron spin
chains are known in organic charge-transfer salts, these
are a consequence of low structural dimensionality [30].
The closest analogy to CsO$_2$ is found in the $d$-electron
spin chain KCuF$_3$ [31]. In this tetragonal perovskite, the
distances between Cu$^{2+}$ cations are similar along the
three principal crystallographic axes (4.14, 4.14, and
3.93 Å). A Jahn-Teller distortion removes the Cu$^{2+}$ orbi-
tal degeneracy, breaking the octahedral symmetry and
favoring an alternating occupation of half-occupied
d$_{z^2\cdash r^2}$ and $d_{x^2\cdash r^2}$ orbitals in the $ab$ plane. The lobes of
the half-occupied orbitals on neighboring cations are
orthogonal to each other in the $ab$ plane; thus, super-
exchange between nearest neighbors is extremely weak.
In contrast, the lobes of both orbitals overlap with the
fluorine $p_z$ orbitals in the $c$ direction, allowing super-
exchange along a linear pathway. An AFM spin chain
is formed with $J_s/J_a = -100$ [32]. At $\sim 40$ K, the spin
chain gives way to 3D $A$-type AFM order [33]. An
explanation for this has recently been proposed by Lee
$et\ al.$ [34], who calculated that the half-occupied orbitals
can more accurately be described as hybrids of $d_{z^2\cdash r^2}$ and $d_{x^2\cdash r^2}$, two distinct and almost degenerate
states of which exist in the spin-chain regime. One hybrid
state favors AFM order in-plane and the other FM order
in-plane, and rapid fluctuations between the two states
occur. A structural distortion involving short-range-
ordered rotations of the octahedra takes place at $\sim 40$ K,
stabilizing the AFM hybrid state. In CsO$_2$, the 3D AFM
ordering that sets in below 9.6 K requires the availability
of superexchange pathways along both $a$ and $c$. Our
Raman data (Fig. 3) reveal no obvious structural
change down to 4.5 K; thus, the OO configuration and
alternative superexchange pathways should be studied in
more detail.

In conclusion, our observation of a $S = 1/2$ AFM spin
chain in CsO$_2$ that is driven by OO is the clearest demon-
stration yet of correlated electron physics at play in an
inorganic, open $p$-shell system. Our study shows that the
concepts of orbital physics developed for transition metals
are also valid for main-group systems with orbital
degeneracy.

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