

Interplay between Spin, Charge, and Orbital Order with Molecular Orientation in Anionic p-Electron Systems

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We studied the interplay between spin, charge, orbital, and orientation degrees of freedom in mixed-valence alkali sesquioxides A_4O_6 ($A = \text{Rb}, \text{Cs}$) featuring two paramagnetic O_2^- anions and one diamagnetic O_2^{2-} anion per formula unit. Charge ordering of O_2^- and O_2^{2-} ions is clearly apparent in a new tetragonal modification of Rb_4O_6 . Detailed magnetization, EPR, NMR, and powder neutron diffraction experiments on Cs_4O_6 show that anomalies in the magnetic properties of the sesquioxides reflect structural transitions between the tetragonal and cubic variants of $A_4\text{O}_6$, which involve reorientation of the molecular anions. Recent EPR and NMR studies on CsO_2 show that the dynamics of the spin chain formed in response to orbital ordering in this prototype superoxide can be described by the Tomonaga-Luttinger liquid model.

The interplay between spin, orbital, charge, and lattice degrees of freedom has been explored widely in strongly correlated transition metal (TM) compounds with partially filled d shells. However, similar phenomena are also observed in open shell p electron systems. For instance, there is some analogy between the properties of TM compounds with Jahn-Teller $t_{2g}^6 e_g^3$ (Cu^{2+}) or $t_{2g}^3 e_g^1$ (Mn^{4+}) electron configurations and alkali metal superoxides, AO_2 , with paramagnetic O_2^- ions that have a degenerate $(\pi^*)^3$ electron configuration. Here, the π^* orbitals are antibonding molecular orbitals formed from O $2p_\pi$ atomic orbitals. A prototype system is CsO_2 , where, similar to the Cu^{2+} compound KCuF_3 , a quasi-one-dimensional magnetic ordering was observed, which is driven by orbital ordering [1]. The orbital ordering involves a reorientation of the molecular anions, which is an important degree of freedom in molecular anionic p electron systems. The main focus of our work is on alkali sesquioxides, $A_4\text{O}_6$ ($A = \text{Rb}, \text{Cs}$), which are anionic mixed valence compounds with two paramagnetic O_2^- anions and one diamagnetic O_2^{2-} anion per formula unit and thus also feature the charge degree of freedom [2]. In addition, new insights into the low-dimensional physics of CsO_2 were obtained recently.

Tetragonal Modification of Rb_4O_6

Surprisingly, the $A_4\text{O}_6$ compounds adopt a cubic crystal structure (space group $I-43d$), which furnishes only one crystallographic site for the O_2^{n-} anions present. However, inelastic neutron and Raman experiments revealed the presence of distinct O_2^- and O_2^{2-} units. Recently, we succeeded in isolating a single crystal of a tetragonal modification of Rb_4O_6 and determined its crystal structure (space group $I-4$) [3]. In the tetragonal variant, charge ordering of distinct O_2^- and O_2^{2-} anions is clearly apparent from

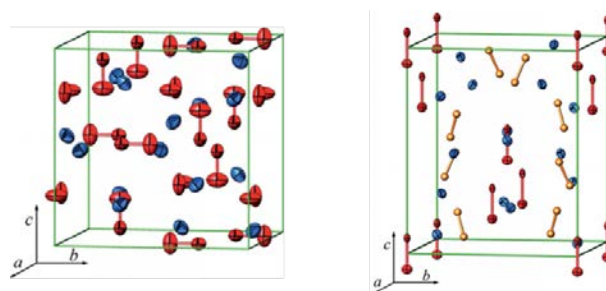


Fig. 1 (from Ref. [3]): Illustration of the crystal structures of the cubic (left) and tetragonal (right) modification of Rb_4O_6 . The blue ellipsoids correspond to Rb^+ ions. In the left picture the red dumbbells correspond to the indistinguishable O_2^- and O_2^{2-} units, whereas in the right picture the red and yellow dumbbells correspond to O_2^{2-} and O_2^- units, respectively.

the different O-O distances in the molecular anions (1.34 and 1.56 Å, respectively; see Fig. 1). Because the molecular position and orientation fix the orbital orientations and lift the orbital degeneracy, charge ordering may be associated with orbital ordering.

Magneto-Structural Properties of Cs_4O_6

The formation of a tetragonal modification of $A_4\text{O}_6$ is also the clue to understanding anomalies in the magnetic properties of the sesquioxides, which were established in depth for Cs_4O_6 . Combining magnetization measurements with EPR and ^{133}Cs NMR measurements showed that the magnetic properties and structural phases present depend on the chosen temperature protocol [4]. Both the NMR and EPR spectra show evidence of the existence of two competing phases of Cs_4O_6 , which differ in the orientation of the molecular O_2^{n-} units. While slow cooling leads to a lower-symmetry modification of Cs_4O_6 , rapid cooling leads to quenching of the high-temperature cubic phase. Powder neutron diffraction

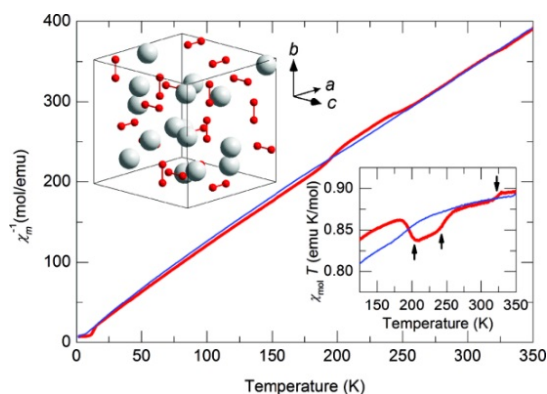


Fig. 2 (from Ref. [4]): Inverse molar magnetic susceptibility, χ_m^{-1} , of Cs_4O_6 as a function of temperature. Anomalies in data obtained on heating (red) are most evident in the product $\chi_m^{-1}T$ and reflect the structural transformations occurring in samples that were rapidly cooled from room temperature.

studies performed under different temperature protocols show that the lower-symmetry phase corresponds to a tetragonal charge-ordered modification of Cs_4O_6 , similar to that of tetragonal Rb_4O_6 . The cubic-to-tetragonal transition appears to be kinetically hindered and is not complete. The structural transformations are reflected in magnetic anomalies seen in the magnetic susceptibility data upon heating after rapid cooling (Fig. 2). The anomaly near 180 K reflects the transformation of the frozen cubic to the tetragonal phase, the anomaly near 250 K the transformation back to the high-temperature cubic phase. A more detailed understanding of the molecular reorientation processes may arise from ^{17}O NMR studies. A sample of Cs_4O_6 was prepared for such experiments, which was enriched by about 50% with ^{17}O , as confirmed by Raman spectroscopy.

High-Pressure Properties of A_4O_6 Sesquioxides

Our work on alkali sesquioxides was part of the collaborative EU-Japan project LEMSUPER (Light Element Molecular Superconductivity, 2011 – 2015) [5]. Compared to C_{60} superconductors, the insulating oxygen anion-based solids are electronically more localized ($U \gg W$, where U is the correlation energy and W the bandwidth). Application of high pressure could be a strategy to metallize these solids. However, resistance measurements on Rb_4O_6 and Cs_4O_6 indicated that the compounds remain insulating up to pressures of 80 GPa and 180 GPa, respectively [2].

We investigated the high-pressure structural properties of Cs_4O_6 and Rb_4O_6 by synchrotron powder x-ray diffraction experiments. Even at pressures of a few GPa, Cs_4O_6 transforms completely and Rb_4O_6 partially to the tetragonal charge ordered phase. Further increase of pressure above 15 GPa leads to strong broadening of the XRD pattern, which indicates pressure-induced amorphization. Structural changes under pressure may prevent metallization, which has been predicted by electronic structure calculations [6].

Low-Dimensional Physics of CsO_2

Deeper insights into the low-dimensional physics of the prototype superoxide CsO_2 emerge from the analysis of recent ^{133}Cs NMR [7] and EPR [8] spectra. The one-dimensional magnetic order driven by orbital ordering is confirmed, and the analysis of both the EPR and NMR data suggests that the dynamics of the spin chain in CsO_2 follows the predictions of the Tomonaga-Luttinger liquid model. At higher temperatures, the dimensionality of the system changes and an unusual variation of the exchange interactions with temperature is found.

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