Oxides with peculiar electronic and magnetic properties
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The Functional Oxides group explores oxides with unusual electronic and magnetic properties that are a manifestation of the delicate balance between charge, spin, orbital, and lattice degrees of freedom. An important result was the discovery of a Verwey-type charge ordering transition in Cs₆O₆, a compound with mixed-valence negatively charged oxygen molecules in its crystal structure. Cs₆O₆ shows a structural transition from a cubic charge disordered to tetragonal charge ordered phase with distinct superoxide O₂⁻ and peroxide O₂²⁻ anions, which is accompanied by a drastic change in electrical conductivity. A similar transition was found for Rb₄O₆, where spin dimerization occurs at low temperatures, possibly driven by orbital ordering. The new layered oxoruthenates(V) with low-dimensional structural features, β-Ag₃RuO₄ and AgRuO₃, were synthesized by hydrothermal methods. While β-Ag₃RuO₄ exhibits cluster-like magnetism in the paramagnetic regime and magnetic ordering below 80 K, AgRuO₃ apparently lacks any long-range magnetic order despite strong antiferromagnetic exchange interactions.

Oxides with open-shell electronic systems attract a lot of research interest due to their unusual physical properties, which are a consequence of competing interactions with comparable energy scales. The particular balance between kinetic energy gain accompanying electron delocalization, electron correlation, electron-lattice interactions, magnetic exchange interactions, and spin-orbit coupling gives rise to phenomena like charge and orbital ordering, insulator-to-metal transitions, spin-orbit assisted Mott-insulating states, frustrated magnetism, colossal magnetoresistance, multiferroicity, and high-temperature superconductivity. In this report, we summarize our work on two peculiar oxide systems: (i) oxides with anionic molecular units featuring an open-shell p electron configuration, and (ii) new ruthenates with layered crystal structures.

Recently, commonalities have been pointed out between strongly correlated transition metal compounds and molecular solids with open-shell O₂⁻ anions. A prototype system is the superoxide Cs₂O₂, where low-dimensional magnetic order driven by orbital order was established. Our nuclear magnetic resonance (NMR) [1] and electron paramagnetic resonance (EPR) [2] spectroscopy studies revealed Cs₂O₂ to be a versatile model system for one-dimensional quantum antiferromagnetism; here, the low-temperature ground state could be considered as a spin Tomonaga-Luttinger liquid, while at higher temperatures, phonon-modulated magnetic interactions occur between spins on a square lattice. The alkali sesquioxides, A₃O₆ (A = Cs, Rb), which contain one diamagnetic peroxide O₂²⁻ and two paramagnetic O₂⁻ units per formula unit and thus constitute anionic mixed-valence systems, extend the analogy between 3d and 2p open-shell systems by adding the charge degree of freedom. Our previous study revealed the existence of a charge-ordered tetragonal variant of Rb₃O₆ [3] in addition to the known cubic structure, whereas EPR and NMR studies on Cs₆O₆ indicated a structural transition from the high-temperature cubic to a lower-symmetry phase [4]. We now could resolve the detailed nature of the phase transitions in alkali sesquioxides by a unique combination of experimental techniques. It was demonstrated that the sesquioxides feature a Verwey-type charge ordering (CO) transition that can be compared with that of the canonical example, Fe₃O₄ (magnetite) [5].

Low-dimensional magnetism in layered crystal structures provides basic insights into the nature of exchange interactions and often gives rise to peculiar magnetic properties due to spin frustration and quantum spin fluctuations. Herein we report the synthesis and magnetic properties of two new layered ruthenates with low-dimensional structural and magnetic features.

**Verwey-type charge ordering transition in alkali sesquioxides A₃O₆ (A = Cs, Rb)**

The Verwey transition in Fe₃O₄, a structural phase transition concomitant with a jump in electrical conductivity by two orders of magnitude, has been a benchmark for CO phenomena in mixed-valence transition metal materials. The CO pattern in Fe₃O₄, however, is complex and the mechanism of Verwey transition is still not clear. We have demonstrated that the open p-shell mixed-valence compound Cs₆O₆ shows an archetypical Verwey-type CO transition in the anionic sublattice [5]. Using powder neutron diffraction, it was established that Cs₆O₆ undergoes a phase change from a cubic structure with a single crystallographic site for the molecular O₂⁻ building
units to a tetragonal structure with ordered superoxide $\text{O}_2^-$ and peroxide $\text{O}_2^{2-}$ entities. The $\text{O}_2^-$ units tilt by an angle of $17^\circ$ relative to the $c$-axis in the tetragonal phase, which is a signature of the partially filled molecular orbitals of the paramagnetic $\text{O}_2^-$ units. In contrast to our previous studies, the CO transition was complete for the present samples of $\text{Cs}_4\text{O}_6$. This was achieved by employing a new synthesis method for the alkali sesquioxides, where the respective superoxides (here $\text{CsO}_2$), are thermally decomposed [6].

Due to its molecular nature, $\text{Cs}_4\text{O}_6$ has a much lower conductivity than $\text{Fe}_3\text{O}_4$. The electrical conductivity $\sigma$ was studied by impedance spectroscopy. The structural CO transition is accompanied by an increase in $\sigma$ of two orders of magnitude, which verifies that a Verwey-type transition occurs. The transition is characterized by a broad hysteresis which is also reflected as an anomaly in the magnetic susceptibility. The various signatures of the Verwey-type transition are represented in Fig. 1. The charge dynamics was investigated on a molecular level by using spectroscopic probes. Particularly useful was $^{17}\text{O}$ NMR spectroscopy which was performed on a sample enriched with the $^{17}\text{O}$ isotope. Due to the large hyperfine fields associated with paramagnetic units, the $^{17}\text{O}$ NMR signal is observed only when diamagnetic $\text{O}_2^{2-}$ ions, which are localized on the NMR time scale, are present. Similarly, an EPR signal is observed only in the presence of localized paramagnetic $\text{O}_2^-$ units. The results obtained from the different experimental techniques are summarized in Fig. 2.

More recently, we could also verify that $\text{Rb}_4\text{O}_6$ with smaller $\text{Rb}^+$ ions in its crystal lattice reveals a Verwey-
Fig. 3: Temperature dependence of the molar magnetic susceptibility, $\chi$, of Rb$_2$O$_6$ in the low temperature region. The red solid line corresponds to a Bleaney-Bowers fit to the experimental data (blue). The spin Hamiltonian of the dimers is defined as $H = -2J S_1 S_2$ and $J = -8.5$ cm$^{-1}$ was obtained from the fit. A Curie-term was added to take into account the upturn in $\chi$ below 5 K.

Layered transition metal oxides frequently display special electronic instabilities and reveal unexpected magnetic exchange couplings. Here, the two new oxoruthenates(V), Ag$_3$RuO$_4$ and AgRuO$_3$, with low-dimensional structural motifs were synthesized by applying hydrothermal methods [7,8]. Their crystal structures (Fig. 4) were determined by single-crystal X-ray diffraction. The crystal structure of β-Ag$_3$RuO$_4$ can be regarded as a ternary, cation-ordered variant of the NiAs type of structure; oxygen replaces As, which consequently adopts a hexagonal close packing (hcp) motif wherein Ag and Ru occupy the octahedral voids in a fully ordered fashion. The cations in β-Ag$_3$RuO$_4$ separate into layers, as can be expressed by the formula $\text{Ag(}Ag_{12}\text{Ru}_{12})O_2 \equiv \text{Ag}_2[\text{AgRuO}_4]$. In this manner, the frustration of the antiferromagnetic exchange coupling on the trigonal sublattice hosting Ru(V) has been lifted. The ruthenium(V) ions segregate into clusters of (Ru$_4$) diamonds that are separated by diamagnetic silver ions. The resulting tetrameric polyoxoanions [Ru$_4$O$_{16}$]$^{12-}$ are the most prominent local structural constituent. The crystal structure of AgRuO$_3$ can be essentially described as a stacking of honeycomb-type (Ru$_3$O$_6$)$_2$ polyoxoanions along the c-axis with silver ions located within the van der Waals gap.

Silver oxoruthenates(V) with low-dimensional structural motifs

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Fig. 4: Illustration of the crystal structures of β-Ag$_3$RuO$_4$ and AgRuO$_3$. The crystal structure of Ag$_3$RuO$_4$ features [Ru$_4$O$_{16}$]$^{12-}$ tetramers (green) which are separated by silver ions (grey polyhedra). For AgRuO$_3$, a single (Ru$_3$O$_6$)$_2$ slab is shown which builds up the crystal structure [5]. The silver atoms occupy the voids of the structure. The illustrations are adapted from Refs. [7] and [8], respectively.
The magnetic properties of $\beta$-Ag$_3$RuO$_4$, $\chi$ and $\chi T$, as a function of temperature (Fig. 5), reflect its cluster nature. Above 80 K, within the regime of paramagnetic response, $\chi$ is reversible and independent of the applied magnetic field. The approximately linear part of $1/\chi(T)$ between 200 and 300 K follows the Curie-Weiss equation with $\mu_{\text{eff}} = 4.01 \ \mu_B$ per Ru atom and $\theta = -390 \ \text{K}$. This corresponds fairly well to Ru$^{3+}$ ions with $S = 3/2$ ($\mu_{\text{eff}} = 3.87 \ \mu_B$). It is noteworthy that the large $\theta$ indicates that strong intra-cluster antiferromagnetic exchange interactions prevail. Around ~65 K, a pronounced cusp in the susceptibility suggests a magnetic phase transition. The susceptibility in the range 90–300 K was analyzed using a Heisenberg model with four equal exchange integrals, $J$, along each side of the rhomb, and different $J_2$ and $J_3$ along the short and long diagonals, respectively (see Fig. 5). The ground state of such a tetramer is a spin singlet with two spins pointing down at the long diagonal and two spins pointing up at the short one [7]. Upon cooling below 80 K, after a sharp increase, $\chi(T)$ exhibits a maximum at about 62–64 K. In AC susceptibility measurements there is no distinct sign of a magnetization relaxation behaviour characteristic of a transition to the spin-glass state. Therefore, it is likely that a transition to a particular magnetically ordered state occurs below 80 K. The field dependence of the magnetization below the transition temperature shows a hysteresis and the coercive field, $H_c$, approaches 10 kOe at 1.8 K. The small remanent magnetization, $M_r$, which reaches its maximum value of 0.015 $\mu_B$ at 62 K, suggests a canted antiferromagnetic spin structure. The spin canting can be ascribed to anti-symmetric exchange interactions which are a consequence of spin-orbit coupling. The magnetization curves feature a small exchange bias effect, if they are recorded after cooling in a magnetic field. The strong magnetic anisotropy of the [Ru$_6$O$_{16}$]$^{12-}$ anion implies that it may reveal the properties of a single-molecule magnet if well-diluted in a diamagnetic matrix.

AgRuO$_3$ is a semiconductor and, in spite of strong magnetic exchange coupling up to its decomposition temperature of 673 K, neutron diffraction patterns do not show unambiguous evidence of long-range magnetic order. Density functional theory calculations (GGA+U) confirm the 2D character of AgRuO$_3$ with large intra-layer exchange coupling, $J_{\text{ab}}$, and much weaker inter-layer coupling, $J_z$.

**External Cooperation Partners**

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**References**


