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 Cs_4O_6, a compound with mixed-valence negatively charged oxygen molecules in its crystal structure. Cs_4O_6 shows a structural transition from a cubic charge disordered to tetragonal charge ordered phase with distinct superoxide O_2^- and peroxide O_2^{2-}anions, which is accompanied by a drastic change in electrical conductivity. A similar transition was found for Rb_4O_6, where spin dimerization occurs at low temperatures, possibly driven by orbital ordering. The new layered oxoruthenates(V) with low-dimensional structural features, β-Ag_3RuO_4 and $AgRuO_3$, were synthesized by hydrothermal methods. While β-Ag_3RuO_4 exhibits cluster-like magnetism in the paramagnetic regime and magnetic ordering below 80 K, $AgRuO_3$ 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 their various 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 O_2^- anions. A prototype system is the superoxide CsO_2, 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 CsO_2 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, A_4O_6 (A = Cs, Rb), which contain one diamagnetic peroxide O_2^{2-} and two paramagnetic O_2^- units per formula unit and thus constitute anionic mixed-valence systems, extend the analogy between 3*d* and 2*p* open-shell systems by adding the charge degree of freedom. Our previous study revealed the existence of a charge-ordered tetragonal variant of Rb_4O_6 [3] in addition to the known cubic structure, whereas EPR and NMR studies on Cs_4O_6 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, Fe_3O_4 (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 A_4O_6 (A = Cs, Rb)

The Verwey transition in Fe_3O_4, 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 Fe_3O_4, however, is complex and the mechanism of Verwey transition is still not clear. We have demonstrated that the open *p*-shell mixed-valence compound Cs_4O_6 shows an archetypical Verwey-type CO transition in the anionic sublattice [5]. Using powder neutron diffraction, it was established that Cs_4O_6 undergoes a phase change from a cubic structure with a single crystallographic site for the molecular O_2^{x-} building

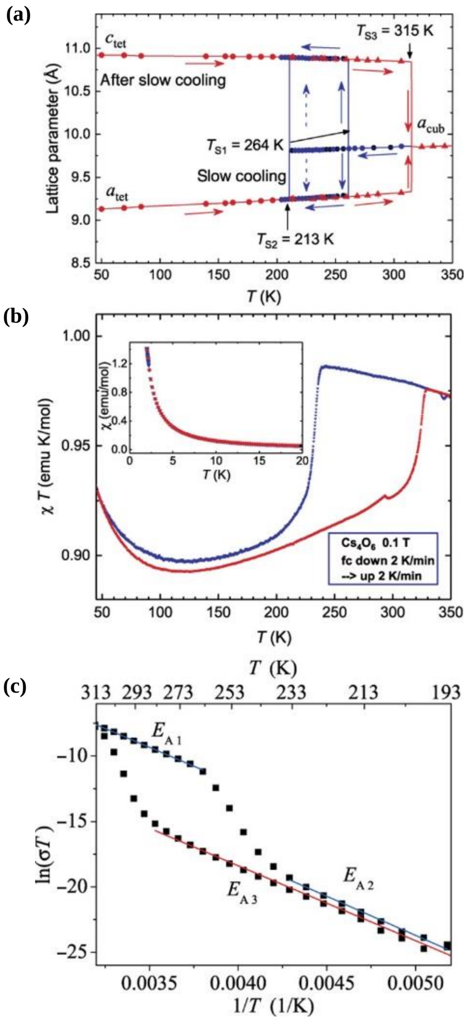

Fig.-1: (from Ref. [5]). Signatures of the Verwey-type CO transition in Cs_4O_6. (a) Temperature dependence of the lattice parameters: a_{cub} of the cubic , and a_{tet} and c_{tet} of the tetragonal phases. On cooling, the cubic to tetragonal transformation starts at T_{S1}= 264 K and is completed at T_{S2} = 213 K. Upon heating, the transformation back to the cubic phase occurs near T_{S3} = 315 K. (b) The structural transition is reflected in anomalies and a hysteresis in the magnetic susceptibilities $\chi(T)$, as apparent in the representation of χT versus T. The inset shows the low-temperature magnetic susceptibilities verifying the absence of long-range magnetic order down to 1.8 K. (c) Arrhenius plot of the conductivity of Cs_4O_6, featuring a hysteresis in the temperature range 313- 233 K. Blue and red lines are the line fits for the determination of the activation energies E_{A1} to E_{A3}.

units to a tetragonal structure with ordered superoxide O_2^- and peroxide O_2^{2-}entities. The O_2^- units tilt by an angle of 17° relative to the *c*-axis in the tetragonal phase, which is a signature of the partially filled molecular orbitals of the paramagnetic O_2^- units. In contrast to our previous studies, the CO transition was complete for the present samples of Cs_4O_6. This was achieved by employing a new synthesis method for the alkali sesquioxides, where the respective superoxides (here CsO_2), are thermally decomposed [6].

Due to its molecular nature, Cs_4O_6 has a much lower conductivity than Fe_3O_4. The electrical conductivity σ was studied by impedance spectroscopy. The structural CO transition is accompanied by an increase in σ 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}O NMR spectroscopy which was performed on a sample enriched with the ^{17}O isotope. Due to the large hyperfine fields associated with paramagnetic units, the ^{17}O NMR signal is observed only when diamagnetic 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 O_2^- units. The results obtained from the different experimental techniques are summarized in Fig. 2.

More recently, we could also verify that Rb_4O_6 with smaller Rb^+ ions in its crystal lattice reveals a Verwey-

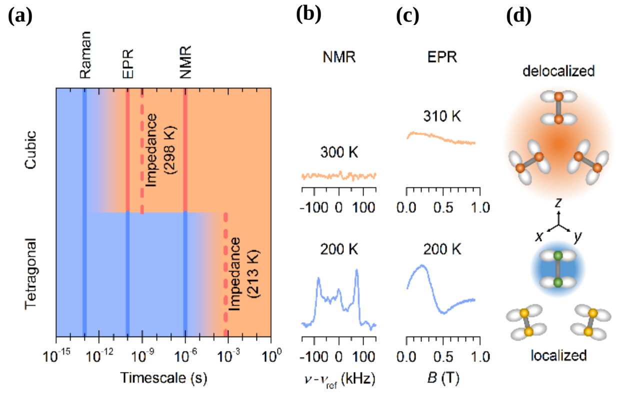

Fig.-2: (from Ref. [5]) (a) Sketch of the characteristic timescales covered by various experimental techniques applied to Cs_4O_6. (b, c) Due to rapid charge exchange ^{17}O NMR and EPR signals are not observed in the charge-disordered phase (top), whereas both, a ^{17}O NMR signal due to non-magnetic O_2^{2-}units and an EPR signal due to paramagnetic O_2^- are apparent in the CO phase (bottom). (d) Schematic illustration of charge disorder with equivalent O_2^{x-} units and CO with distinctly different O_2^{2-} (green) and O_2^- (yellow) units.

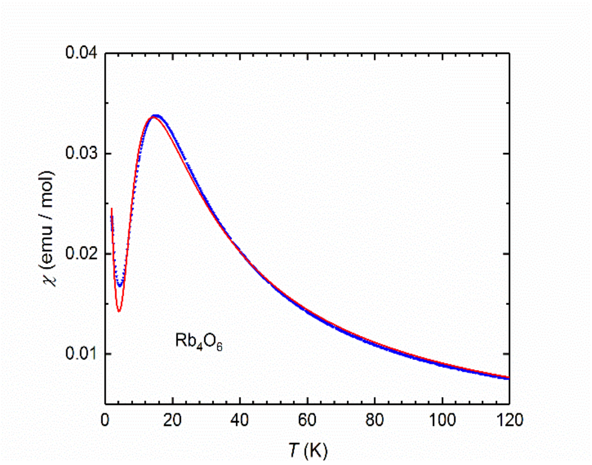

Fig.-3: Temperature dependence of the molar magnetic susceptibility, χ, of Rb_4O_6 in the low temperature region. The red solid line corresponds to a Bleaney-Bowers fit to the experimental data (blue). The spin Hamiltonian of the dimers is defined as $H = -2JS_1S_2$ and $J = -8.5\ cm^{-1}$ was obtained from the fit. A Curie-term was added to take into account the upturn in χ below 5 K.

type CO transition, which is shifted by about 50 K towards higher temperature. In contrast to Cs_4O_6, a hump is seen around 20 K in the low-temperature magnetic susceptibility data (Fig. 3) that can be roughly fitted to the Bleaney-Bowers equation, indicating dimerization of the S = ½ spins of the O_2^- units. The deviations between the experimental and calculated curves suggest that intermolecular interactions play a role as well. Most remarkably, powder neutron diffraction patterns of Rb_4O_6 reveal the emergence of new peaks below 90 K, indicating an orbital ordering transition driving the dimerization of O_2^- units. Attempts to solve the low-temperature crystal structure, as well as EPR and NMR studies, are in progress in order to understand the relation between orbital ordering and spin arrangements in Rb_4O_6.

The simple CO pattern of molecular O_2^{2-} and O_2^- units, as well as the lack of long-range magnetic order down to 2 K, suggest the A_4O_6 sesquioxides as model systems for disentangling the complex interplay of charge, lattice, orbital, and spin degrees of freedom in Verwey-type CO processes.

Silver oxoruthenates(V) with low-dimensional structural motifs

Layered transition metal oxides frequently display special electronic instabilities and reveal unexpected magnetic exchange couplings. Here, the two new oxoruthenates(V), Ag_3RuO_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_3RuO_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_3RuO_4 separate into layers, as can be expressed by the formula $Ag(Ag_{1/2}Ru_{1/2})O_2 \equiv Ag_2[AgRuO_4]$. 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 $[Ru_4O_{16}]^{12-}$ are the most prominent local structural constituent. The crystal structure of $AgRuO_3$ can be essentially described as a stacking of honeycomb-type $(RuO_3)^-$ polyoxoanions along the *c*-axis with silver ions located within the van der Waals gap.

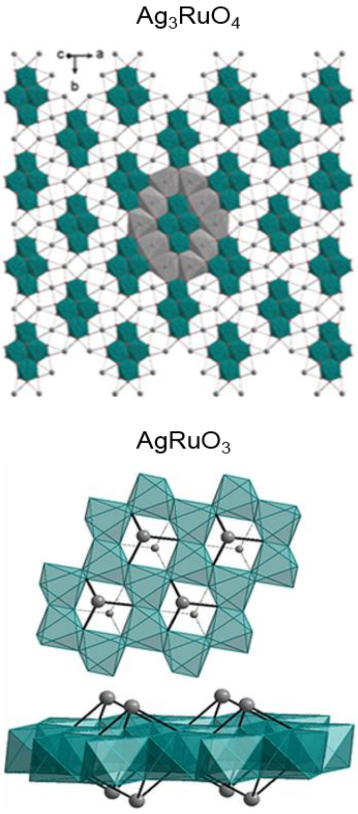

Fig.-4: Illustration of the crystal structures of β- Ag_3RuO_3 and $AgRuO_3$. The crystal structure of Ag_3RuO_4 features $[Ru_4O_{16}]^{12-}$ tetramers (green) which are separated by silver ions (grey polyhedra). For $AgRuO_3$ a single $(RuO_3)^-$ slab is shown which builds up the crystal structure [5]. The silver atoms occupy the voids of the structure. The illustrations are adapted from Refs. [7] and [8], respectively.

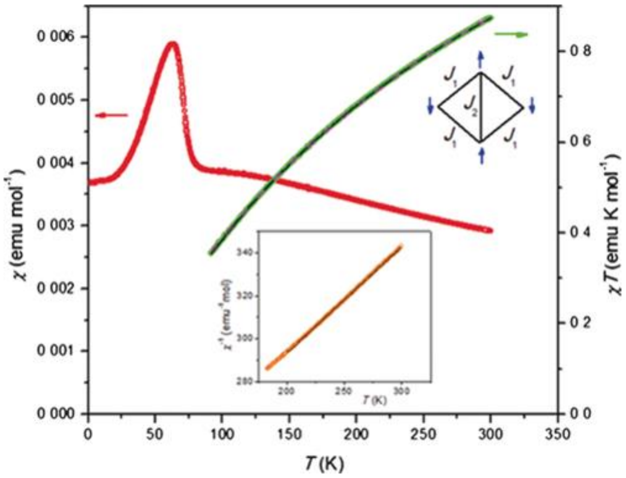

Fig.-5: (from Ref. [7]) Temperature dependence of magnetic susceptibility χ (red), reciprocal susceptibility χ^{-1} (inset, orange), and product χT (green) of β-Ag_3RuO_4 under a field of 50 kOe. Fits of χT with the constraint $J_2=J_1$ (dashed magenta line), and without constraints (black line). Inset, top right: rhomb of ruthenium tetramer, the spin orientation for the ground state is shown.

The magnetic properties of β-Ag_3RuO_4, χ and χT, as a function of temperature (Fig. 5), reflect its cluster nature. Above 80 K, within the regime of paramagnetic response, χ 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 μ_{eff} = 4.01 μ_B per Ru atom and θ = -390 K. This corresponds fairly well to Ru^{5+} ions with $S = 3/2$ (μ_{eff} = 3.87 μ_B). It is noteworthy that the large θ 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_1, 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 μ_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 $[Ru_4O_{16}]^{12-}$ 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_{ab}, and much weaker inter-layer coupling, J_c.

External Cooperation Partners

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References

[1]* *Phonon-modulated magnetic interactions and spin Tomonaga-Luttinger liquid in the p-orbital antiferromagnet CsO_2, M. Klanjšek, D. Arčon, A. Sans, P. Adler, M. Jansen and C. Felser, Phys. Rev. Lett.* ***115*** *(2015) 057205.*

[2]* *One-dimensional quantum antiferromagnetism in the p-orbital CsO_2 compound revealed by electron paramagnetic resonance, T. Knaflič, M. Klanjšek, A. Sans, P. Adler, M. Jansen, C. Felser and D. Arčon, Phys. Rev. B* ***91*** *(2015) 174419.*

[3]* *Structural implications of spin, charge, and orbital ordering in rubidium sesquioxide, Rb_4O_6. A. Sans, J. Nuss, G. H. Fecher, C. Mühle, C. Felser and M. Jansen, Z. Anorg. Allg. Chem.* ***640*** *(2014) 1239.*

[4]* *Influence of O_2 molecular orientation on p-orbital ordering and exchange pathways in Cs_4O_6, D. Arčon, K. Anderle, M. Klanjšek, A. Sans, C. Mühle, P.Adler, W. Schnelle, M. Jansen and C. Felser, Phys. Rev. B* ***88*** *(2013) 224409.*

[5]* *Verwey-type charge ordering transition in an open-shell p-electron compound, P. Adler, P. Jeglič, M. Reehuis, M. Geiß, P. Merz, T. Knaflič, M. Komelj, A. Hoser, A. Sans, J. Janek, D. Arčon, M. Jansen and C. Felser, Sci. Adv.* ***4*** *(2018) eaap7581.*

[6]* *Thermo-analytical investigations on the superoxides AO_2 (A = K, Rb, Cs), revealing facile access to sesquioxides A_4O_6,P. Merz, M. Schmidt, C. Felser and M. Jansen, Z. Anorg. Allg. Chem.* ***643*** *(2017)544.*

[7]* *β-Ag_3RuO_4, a ruthenate(V) featuring spin tetramers on a two-dimensional trigonal lattice, B. E. Prasad, P. Kazin, A. C. Komarek, C. Felser, M. Jansen, Angew. Chem. Int. Ed.* ***55*** *(2016) 4467.*

[8]* *$AgRuO_3$, a strongly exchange-coupled honeycomb compound lacking long-range magnetic order, B. E. Prasad, S. Kanungo, M. Jansen, A. C. Komarek, B. Yan, P. Manuel and C. Felser, Chem. Eur. J.* ***23*** *(2017) 4680.*

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