

Correlations and Topology in Oxides

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Prior to 2020, the Functional Oxides group, a collaborative group led by Martin Jansen and including members of the Solid State Chemistry department, focused on the synthesis of novel oxides with interesting electronic and magnetic properties. Starting in 2021, the Solid State Chemistry department now includes a new research direction investigating topology of covalently bonded oxides and chalcogenides with the aim of synthesizing traditional chemical understanding of bonding with the possibilities of topology. It is likely that topology and correlations are deeply intertwined due to complex interactions of orbital parities, structural symmetries, spin texture, and electron–electron interactions. Herein we review the recent findings of the Jansen group in light of this new direction and outline the envisioned new research to come.

In correlated materials, the elements of orbital, spin, charge, and crystalline lattice are intimately and complexly interrelated, giving rise to a number of exciting phenomena. As topology engages the orbital, spin, and lattice degrees of freedom, the interplay of topology and correlations likely yields rich spin and electronic behavior, which we aim to discover.

Anionic mixed-valence sesquioxides Rb_4O_6 and K_4O_6

Alkali metal sesquioxides are an interesting case of strongly correlated electronic systems with degenerate open-shell $O\ 2p$ orbitals, and their electronic properties are remarkably similar to those of transition metal (TM) $3d$ compounds. An example is the Verwey-type charge-ordering (CO) transition in Cs_4O_6 from a high-temperature cubic variant with disordered open-shell superoxide O_2^- and closed-shell peroxide O_2^{2-} anions to a charge-ordered tetragonal variant at low temperatures. We found that this transition depends on history which reflects its martensitic character [1]. In addition, owing to its smaller volume, the tetragonal phase can also be stabilized by high pressure [2]. We have now verified a similar charge-ordering transition in Rb_4O_6 at a slightly higher T_{CO} (290 K). However, in contrast to the case for Cs_4O_6 , a second structural transition was also observed at $T_s = 90$ K. We attribute this to orbital ordering (OO) [3]. The nature of the orbital-ordered state and its coupling to the magnetic properties was studied using powder neutron diffraction analysis, nuclear magnetic resonance spectroscopy, and low- and high-field electron paramagnetic resonance spectroscopy as well as by density-functional theory (DFT) calculations. The subtle structural transition leading to OO involves a reorientation of the π^* molecular orbitals of the magnetically active O_2^- anions, which changes the space group from $\bar{I}4$ to $P\bar{4}$ near T_s . This orbital reorientation drives the formation of a quantum spin

state of weakly coupled spin dimers. The absence of long-range magnetic order at temperatures as low as at least 1.6 K was verified through muon spin rotation experiments. As in $3d$ TM compounds with orbital degeneracy, the magnetostructural properties of open-shell p -electron systems are determined by the interplay between the Jahn–Teller-like electron-lattice and Kugel–Khomskii-type exchange interactions, where the lattice degree of freedom is reflected in the tilting of the molecular O_2^- units

We succeeded in obtaining the elusive potassium analog K_4O_6 , as a metastable phase by heating a mixture of KO_2 and K_2O_2 in an Ar atmosphere to ~ 680 K and subsequently quenching it to below room temperature [4]. The formation and decomposition of K_4O_6 can be followed visually based on the change in the color from yellow to black (Fig. 1, top). Powder diffraction analysis shows that the quenched product exhibits the tetragonal $\bar{I}4$ charge-ordered structure with

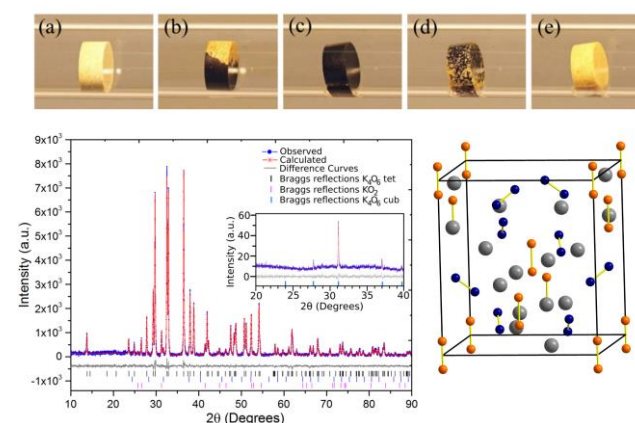


Fig. 1: Top: Formation and decomposition of K_4O_6 (black product) on heating and cooling. Bottom: X-ray diffraction pattern at ambient temperature after quenching shows that, after quenching, tetragonal CO K_4O_6 (crystal structure given on right) is obtained. In-situ XRD pattern obtained at 630 K reveals disordered cubic variant (inset). Figures were taken from Ref. [4].

distinct ordered O_2^- and O_2^{2-} anions (Fig. 1, bottom). Thermodynamic investigations along with DFT calculations incorporating a Hubbard U correction for the molecular π^* orbitals demonstrate that the formation reaction is endothermic and that K_4O_6 is stabilized at elevated temperatures because of a configuration entropy attributable to polaronic disorder. The latter arises from the localized electrons in combination with the nuclear degrees of freedom; however, the polaronic disorder requires the presence of a cubic lattice. In fact, the results of in-situ XRD analysis performed at temperatures greater than 600 K reveal the presence of the charge-disordered cubic variant (inset of Fig. 1, bottom left), which transforms into the tetragonal variant upon quenching. The results of this study are of general relevance for the detection of other supposedly “non-existent” compounds, which may be stabilized by polaronic entropy and may not be found by conventional materials-screening approaches.

Structural dimensionality and magnetic ordering in novel ruthenates

We synthesized novel silver ruthenates by hydrothermal methods and studied their magnetic properties using a variety of techniques. The Ru^{6+} ($4d^2$, $S = 1$) oxide Ag_2RuO_4 [5] crystallizes in an orthorhombic structure (space group $Pnma$) where the Ru ions are in a trigonal bipyramidal coordination of oxygen and form Ru/O chains. A subtle interplay between the ferromagnetic intrachain and antiferromagnetic interchain interactions determines the overall antiferromagnetic spin structure, which displays canting of the magnetic moments. $AgRuO_3$ is a layered Ru^{5+} oxide ($4d^3$, $S=3/2$) with a honeycomb lattice, which forms a Néel-type antiferromagnetic structure below 342 K [6].

Spiral magnetism in negative charge-transfer gap insulator Sr_2FeO_4

Oxides with TM ions in high oxidation states such as Ni (III) or Fe (IV) oxides are strongly covalent and can be considered as negative charge-transfer energy (negative- Δ) materials, where the insulating and metallic states are both dominated by holes in the oxygen bands. These compounds are located near the insulator–metal borderline and exhibit peculiar correlated electronic and spin texture properties such as charge disproportionation, unconventional metallic states, and non-collinear spin structures. Recently, topological Hall effects and topological helical spin structures were reported for the metallic perovskite

$SrFeO_3$ [7], a centrosymmetric cubic system in which Dzyaloshinskii–Moriya interactions are not possible. While negative charge-transfer energy broadly determines the magnetism in Fe (IV) oxides, the details of the interplay between the double exchange, superexchange interactions, and anisotropy in these compounds remain to be elucidated. The complex Mössbauer spectra of the insulating Ruddlesden–Popper relative Sr_2FeO_4 indicate a non-collinear spin structure too. However, the actual spin arrangement remained unknown [8]. We now succeeded in determining the spin structure of Sr_2FeO_4 from powder neutron diffraction (PND) data.

Sr_2FeO_4 was synthesized from SrO and Fe_2O_3 in an autoclave at 500 °C and an oxygen pressure of 2.5 kbar in order to minimize the oxygen deficiency. The virtually complete oxidation to Fe^{4+} was confirmed through Mössbauer spectroscopy. The Mössbauer spectrum of the magnetically ordered phase at 6 K is complex (Fig. 2(c)) and was modelled by a superposition of several components that differed in terms of their hyperfine field, B_{hf} , and quadrupole splitting, but had the same isomer shift. This excludes a charge disproportionation of Fe^{4+} , which occurs in other iron (IV) oxides. The PND patterns at temperatures lower than $T_N = 56$ K clearly reveal magnetic Bragg reflections. The spin structure, determined from the pattern obtained at 1.8 K (Fig. 2 (a)), basically consists of a cycloidal elliptically shaped spiral with an incommensurate propagation vector $\mathbf{k} = (0.137, 0.137, 0)$ lying in the ab plane of the tetragonal crystal structure (space group $I4/mmm$). The elliptical

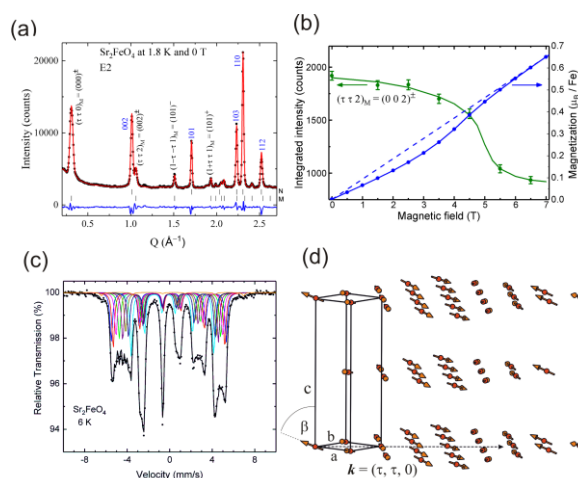


Fig. 2: Spin structure of Sr_2FeO_4 . (a) Powder neutron diffraction pattern at 1.8 K. (b) Field dependence of magnetic $(002)^\pm$ reflection and of magnetization at 2 K. (c) ^{57}Fe Mössbauer spectrum at 6 K. (d) Illustration of spiral spin structure at zero field.

spiral exhibits pronounced eccentricity with a minor moment of $\sim 2 \mu_B$ along the [1,1,0] diagonal and a major moment of $\sim 3.5 \mu_B$ along [1,-1,0]. The variations in the moment of the elliptical spiral give rise to a B_{hf} distribution, which is the origin of the complex Mössbauer spectra. Most remarkably, the spin structure undergoes a spin-flop (SF) transition near 5 T, as evidenced by the non-linearity in the magnetization curve and the field dependence of the magnetic (002) $^\pm$ reflection [Fig. 2(b)]. In the SF phase, the size and shape of the spin spiral essentially remain unchanged. The tuning of non-collinear spin structures by magnetic fields is important for the stabilization of topological spin textures in ferrates as well as for multiferroic materials.

Oxygen deficiency in the $\text{Sr}_2\text{FeO}_{4-y}$ system was explored using an electrochemical method (solid state electrolyte coulometry) that allows the oxygen content to be adjusted and analyzed. In this manner, samples with y up to about 0.2, which correspond to Fe^{3+} fractions of up to 40%, could be obtained. Magnetization, Mössbauer, and PND studies performed on a sample with $y \approx 0.15$ indicate a coexisting spiral spin order and cluster-glass-like magnetism.

Future Direction: Correlations + Topology

Topological materials and their protected surface states have arguably been the biggest research thrust in quantum materials over the past decade, as they provide a playground for exciting new theories such as novel states of matter as well as potentially revolutionizing applications such as quantum computing. Research on these fascinating materials will likely only continue to grow as more discoveries are made and applications are developed. Initially, topology research focused on heavy-element materials, as strong spin-orbit coupling served as the critical factor for gapping out the band inversion(s) around the Fermi level. The advent of topological crystalline insulators, in which the surface states are protected by crystalline symmetry rather than time-reversal, highlighted the importance of structure with respect to topology. However, the field's focus continued to remain on predominantly intermetallic heavy-element materials.

The Felser group now aims to prove the existence of topological oxides. We argue that covalent bonding, with its high degree of directional orbital overlap and its dependence on orbital parity and local symmetry, offers a powerful force for both generating a band

inversion and affecting the structural symmetries at play in topological materials.

Topological oxides and the role of covalent bonding as a driving force have thus far not been explored due to (1) the weakness of computational methods in accurately predicting oxides' band structure due to electronic correlations and (2) the dearth of traditionally trained chemists involved in the study of topological materials. We in the Felser group address these points respectively:

- 1) Electronic correlations, prevalent in oxides, are poorly captured in most computational methods. Calculations are a critical guide to discovering topological materials because experimental verification of non-trivial topology via ARPES poses a bottleneck. Thus, poor calculations of oxides directly result in fewer topological oxide candidates being proposed and indirectly in fewer securing synchrotron beamtime, as their proposals lack the standard theoretical justification for this limited, highly sought-after resource. The work of new group leader theorist Maia Garcia Vergniory improves calculational methods to more accurately capture correlations, leading to the proposal of more candidate topological oxides [9-11].
- 2) The interfacial Solid State Chemistry department synthesizes the knowledge and research approaches of solid-state chemists and condensed matter physicists. Moreover, the Felser group has recent publications which increase the universal awareness of the importance of chemical bonding in topological materials [9; https://www1.cpsf.mpg.de:2443/SSC_08] and promote topological materials and the theory thereof to chemists in their own language [12].

For these reasons, topology in oxides has been much overlooked over the initial decade of topology and the Felser group is uniquely situated to advance its study.

Despite its theoretical challenges, oxide topology has the potential to prove a rich field – not only can bonding in oxides provide chemical control of band structures, orbital/band parity, and structural symmetries at play in topology, but also oxides frequently host fascinating collective electronic behavior due to correlations. It is likely that topology and correlations in oxides are deeply intertwined: correlations are the complex interrelations of the orbital, lattice, spin, and electronic charge degrees of freedom, and topology directly involves at least the first three of these (Fig. 3). Even if the origins of topology and correlations are entirely distinct, the

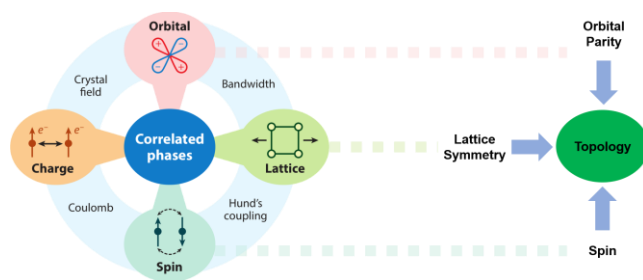


Fig. 3: Correlations (left, from [13]) and topology (right) affect the same basic degrees of freedom. Either the two are intrinsically related or are independent, competing phenomena: either case warrants research into materials systems simultaneously hosting the interaction of the two.

competing interactions of their shared elements of orbital parity, structural/lattice symmetries, and spin texture may potentially yield an array of new properties, greater control of transport behavior applications, and increased understanding of the fundamental phenomena involved.

We will use the self-developed “Topological Quantum Chemistry” (TQC) formalism to identify topological phases (https://www1.cpfs.mpg.de/2443/SSC_08). TQC has been proven to be the fastest method to identify the topology of materials [10], allowing us to perform a high-throughput search of correlated oxides. It is well known that ab-initio codes deal very poorly with correlations, underestimating the energy gap. To tackle this technical problem, we will use experimental-based hybrid pseudopotentials to better reproduce the correct gap and then apply our TQC machinery. Specifically, we plan to search for non-trivial topology among superconducting, magnetic, and chiral materials.

The interaction of magnetism with topology, which imposes spin-momentum locking, may produce novel spin behavior. However, in topological insulators, the total electronic behavior consists of both spin currents mirrored: pathways to isolate single-spin topological current include Fermi arcs, which are under widespread study, and the yet-unstudied possibility of topology in half-metals (materials in which one spin polarization is metallic and the other insulating). Our calculations have isolated a number of potential topological half-metals, including a number of Fe- and Mn-containing double perovskites (see Fig. 4), the syntheses of which are underway. Previous collaborative work at the Institute on double perovskites provides a supportive knowledge base for the present investigation.

The magnetic (containing Fe, Mn, Cr, and/or W) trirutiles present a complement to these double perovskites, as they share the same local MO_6 geometry but connected in a different long-range crystal structure; comparisons may shed light on the local versus crystal symmetries. This family offers wide variability in terms of magnetic, electronic, and topological tuning: from antiferromagnetic to ferrimagnetic to ferromagnetic, from metallic to semiconducting to insulating, and from trivial to enforced semimetal to non-trivial (predicted by [11]).

We also aim to pursue chiral correlated oxides. Chiral structure, spin-momentum-locked topological surface states, helical magnetic spin texture, and circularly polarized light all break parity symmetry. If the parity-breaking parameters of these physical concepts, were able to be effectively and systematically coupled, the multifarious combinations would open a world of potential phenomena in which incident light and magnetic field could lead to highly controllable, robust, anisotropic, and spin-specific electronic behavior. The link between circularly polarized light and chiral structure is well known, and recently the work of Ron Naaman has suggested that chiral-induced spin selection (CISS) can couple structural chirality to an involved electron’s spin state [14]. The correlations present in oxides, especially those involving spin and charge, and the range of light-accessible band gap semiconductors suggest that chiral oxides may be a productive area in which to further investigate coupling of parity-breaking. A previously published comprehensive review [15] provides a starting list of non-centrosymmetric and chiral oxides, which we have mined for magnetic and electronic behavior in order to isolate potential chiral oxide candidates that may host topology and correlated electronic behavior. Once

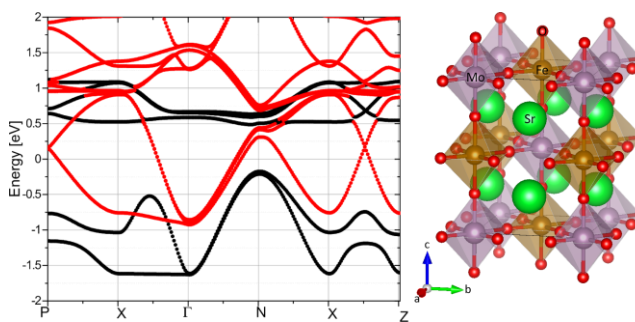


Fig. 4: Spin-resolved band structure (left) and structure (right) of half-metallic double perovskite Sr_2FeMoO_6 . Spin-down bands (red) are metallic with band crossings, while spin-up bands (black) are insulating.

synthesized, their use as topological catalysts (https://www1.cpfs.mpg.de:2443/SSC_01) and the study of their interactions with light (https://www1.cpfs.mpg.de:2443/SSC_13) may offer new insight into the interactions of multiple breakings of parity symmetry.

External Cooperation Partners

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