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Magnetic order from molecular oxygen anions

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Summary

Despite the delicate and sophisticated processes that are required for handling and synthesis, alkali metal oxides are interesting materials to study in terms of their magnetic properties. The unpaired electron located in the antibonding π^* molecular orbital of the superoxide anion is responsible for the magnetic moment in this class of materials. Similar to the physics of transition metal oxides with strongly correlated electrons, I show in this thesis that alkali metal oxides exhibit close interplay between their spin, orbital, and lattice degrees of freedom. I focus mainly on the physical properties of rubidium (Rb) and cesium (Cs) oxides. Different magnetic properties emerge as the oxygen composition and the alkali cations are varied.

A general overview of magnetic alkali oxides is presented in chapter 1, with an emphasis on what is already known from the literature. A discussion of magnetic interactions and magnetic ordering in the general field of solid state materials is also provided and it is explained how these concepts apply to the magnetic exchange interactions in alkali metal oxides. In chapter 2 the experimental methods (sample handling, synthesis, and measurement techniques) used in this thesis are introduced.

In chapter 3 I provide a discussion of the various rubidium oxide phases (RbO_x) that can be synthesized by varying the oxygen content, ranging from $x = 1.5$ (sesquioxide) to $x = 2$ (superoxide). The first part of the chapter discusses the crystallographic properties of polycrystalline RbO_2 (tetragonal, $I4/mmm$ at room temperature). It appears that due to the presence of different grain sizes and the possibility of accommodating oxygen vacancies, polycrystalline RbO_2 behaves differently from single crystal RbO_2 . The crystallographic phase transitions previously reported for single crystal RbO_2 are less sharp in my polycrystalline sample. The monoclinic distortion previously reported to occur at 70 K is barely visible. On heating above room temperature, a range of phase coexistence (tetragonal + cubic) is entered before the entire sample becomes cubic. I also discuss the possible magnetic exchange interactions that might give rise to the long-range antiferromagnetic ordering below 15 K. I propose that in-plane (ab -plane) direct ferromagnetic exchange and out-of-plane antiferromagnetic superexchange are responsible.

It is demonstrated that rubidium superoxide can accommodate up to $\sim 17\%$ oxygen vacancies. Heating tetragonal RbO_2 in vacuum progressively removes oxy-

gen and allows a cubic compound $\text{RbO}_{2-\delta}$ (space group: $Fm\bar{3}m$) to be stabilized. Before transformation to single phase cubic $\text{RbO}_{2-\delta}$ is complete, a range of phase coexistence (tetragonal + cubic) is crossed. The oxygen content can be probed by thermogravimetric analysis and by the lattice parameters determined using X-ray diffraction. On further removal of oxygen, the previously reported phase Rb_4O_6 is stabilized. A general overview of the phase diagram of RbO_x ($1.5 \leq x \leq 2$) is given at the end of the chapter.

In chapter 4, a cubic oxygen-deficient form of rubidium superoxide (space group $Fm\bar{3}m$) with composition $\text{RbO}_{1.66}$ is studied in detail. As the temperature is decreased, the orientationally disordered dioxygen anions in the cubic structure become ordered in the bc -plane at 230 K. As a consequence, an orthorhombic crystal structure (space group $Fmmm$) is obtained. This transition lifts the orbital degeneracy of the cubic phase and is analogous to a Jahn-Teller distortion in transition metal compounds. Below 50 K, magnetic behavior typical of a ferromagnetic cluster glass is observed using time-dependent magnetization measurements. It is proposed how orbital ordering might induce ferromagnetic exchange. Chapters 3 and 4 both contain discussions on how the crystallographic behavior of rubidium oxides as a function of temperature depends on the cooling rate. Such behavior is less pronounced in fully stoichiometric tetragonal RbO_2 , but has a strong influence on how the phase transition proceeds in $\text{RbO}_{2-\delta}$. It appears that slow cooling allows the diffusion of oxygen vacancies, leading to the formation of chemically inhomogeneous nanodomains. Faster cooling gives a more homogeneous crystallographic state, shown by sharper x-ray diffraction peaks.

To the best of my knowledge, the first example of low-dimensional magnetism in an inorganic magnetic p-electron system is discussed in chapter 5. Despite its structural resemblance with RbO_2 and KO_2 , cesium superoxide (CsO_2) exhibits an $S = 1/2$ antiferromagnetic spin-chain around 28 K. The spin chain is formed by orbital ordering, which allows superexchange interactions mediated by Cs cations along only one crystallographic direction. The experimental observation of this feature is supported by density functional theory (DFT) calculations, which are used to determine the lowest energy structure and orbital ordering configuration.

One may expect that applying pressure to rubidium oxides will compress the structure and enhance the magnetic exchange interactions. Chemical pressure (incorporating smaller cations) and introducing epitaxial strain by thin film deposition are two methods for exploring this idea. Moreover, thin film deposition is promising for allowing the oxygen stoichiometry to be controlled more closely. In chapter 6 I describe the deposition of thin films of rubidium oxides on a MgO substrate. Similar to bulk synthesis, different types of oxygen species (O^{2-} , O_2^{2-} , O_2^-) are formed, suggesting that different rubidium oxide phases are deposited. With increasing deposition temperature the ratio of superoxide to peroxide gradually increases, indicating that the oxygen content can be precisely controlled. Attempts to explore the KO_x and CsO_x phase diagrams by bulk synthesis methods are also described in chapter 6.

In general, the magnetic alkali metal oxides show many similarities with tran-

sition metal and rare-earth oxides. Physical properties typical of strongly correlated electron systems (coupling between structural, orbital, and spin degrees of freedom) are observed. In particular, I propose that the mechanisms of magnetic exchange interactions in alkali metal oxides, particularly in $\text{RbO}_{1.66}$, RbO_2 and CsO_2 , are driven by orbital ordering. Nevertheless, more experimental and theoretical work is necessary to obtain a better understanding. I also expect that better control of the oxygen stoichiometry in alkali oxides will reveal novel phases with different magnetic properties.

