Magnetic order from molecular oxygen anions
Riyadi, Syarif

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version
Publisher's PDF, also known as Version of record

Publication date:
2012

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

Copyright
Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

Take-down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): http://www.rug.nl/research/portal. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.
Chapter 4

Ferromagnetic Order from p-Electrons in Rubidium Oxide

4.1 Introduction

The scientific and technological potential of materials whose magnetism arises from main-group elements with unpaired p-electrons has been little explored, largely due to a strong tendency towards electron delocalization and the formation of covalent bonds. Nevertheless, a number of "d⁰ magnets" have been reported in recent years, some of which are ferromagnets with high ordering temperatures [1–3]. In most cases the origin of the magnetism is rather unclear, arising from either defects or low-level chemical doping that apparently induces local moments. Crucially, the magnetic properties of such systems are difficult to control and reproduce. An intuitive approach towards the realization of more concentrated magnetic systems with strong exchange interactions is instead to focus on crystalline solids in which the magnetic entities are spatially ordered and in close proximity.

The best known example of a crystalline p-electron magnet is molecular oxygen, which has two unpaired electrons in a doubly degenerate antibonding π_g level. The dioxygen molecule adopts a linear dumbbell shape, the orientation of which in the crystalline state provides an additional degree of freedom when considering the magnetic exchange interactions that are possible. Oxygen possesses an exceedingly rich temperature-pressure phase diagram that includes metallic and superconducting phases as well as a range of antiferromagnetic (AFM) structures [4]. At ambient pressure, solid O₂ exhibits three-dimensional AFM ordering in the α-phase below 24 K [5]. The high-pressure δ-phase adopts three different AFM

Part of this chapter have been previously published as S. Riyadi, S. Giriyapura, R.A. de Groot, A. Caretta, P.H.M. van Loosdrecht, T.T.M. Palstra, and G.R. Blake, Chemistry of Materials 23, 1578 (2011).
configurations and magnetic ordering probably exists up to room temperature [6]. The AFM exchange interactions in solid O$_2$ are attributed to the ubiquitous parallel arrangement of the molecules. However, theory indicates that ferromagnetic (FM) exchange should be realized when adjacent oxygen molecules are orthogonal [7] or "crossed" with respect to each other [8]. Attempts have been made to stabilize this geometry by confining oxygen molecules within nanotubes [9] and organometallic host-guest structures [10, 11].

An alternative route towards manipulating the magnetic exchange interactions of oxygen is to study ionic salts based on dioxygen anions. Molecular oxygen readily accepts one or two electrons from alkali or alkaline earth metals to form the magnetic superoxide and non-magnetic peroxide anions, with three and four electrons in the $\pi_g$ level, respectively [12]. The alkali metal superoxides AO$_2$ all undergo multiple structural phase transitions that involve cooperative tilts and/or shifts of the anions [13]. These transitions are thought to lift the orbital degeneracy of the $\pi_g$ level that is present at room temperature [14, 15], resulting in probable spatial ordering of the fully occupied and half occupied $\pi_x$ and $\pi_y$ orbitals. This is similar to the Jahn-Teller effect in transition metal oxides in which orbital order (OO) is induced by shifts of the ligands that surround the orbitally degenerate cation. The magnetic exchange interactions in AO$_2$ are expected to depend on the resulting interplay between spin, orbital and lattice (orientational) degrees of freedom [16–20]. Although the AO$_2$ materials adopt a range of different crystal structures, the long-range magnetic ordering that sets in below $\sim 15$ K is always AFM in nature [13, 21].

Here I study the effect of oxygen deficiency on the properties of AO$_2$, a parameter that in principle allows control of the $\pi_g$ level filling via the formation of mixed-valent anion states intermediate to superoxide and peroxide. Although the tuning of mixed valency in transition metal oxides often allows dramatic variation of the physical properties, typified by the doped manganite perovskites [22], the effect on the properties of the alkali metal oxides has been little explored. I focus on the RbO$_{2-\delta}$ phase diagram ($\delta < 1$) in which three phases are currently known: the end members rubidium peroxide (RbO) and superoxide (RbO$_2$), and the intermediate rubidium sesquioxide (RbO$_{1.5}$). The latter material is mixed-valent and is an insulator that exhibits magnetic frustration below $\sim 8$ K [23, 24]. Here I demonstrate that a fourth compound exists in this region of the phase diagram, with composition RbO$_{1.66}$. This material has vacancies on the anion sublattice and exhibits short-range FM ordering below $\sim 50$ K. A FM cluster-glass state forms below $\sim 20$ K, embedded in an AFM matrix that orders at $\sim 5$ K. This inhomogeneous magnetism results either from structural domains with different types of anion ordering or from clusters in which double exchange takes place between the mixed-valent anions.
4.2 Experiment

Polycrystalline rubidium superoxide (RbO\textsubscript{2}) was used as a precursor and was prepared by the oxidation of Rb metal dissolved in liquid ammonia at -60°C. The synthesis procedure is described in Chapter 2. The RbO\textsubscript{2} precursor was then transferred to a crucible boat and put inside a horizontal tube furnace. Heating in vacuum was performed at temperatures up to 300°C to induce oxygen vacancies. Details of the other experimental procedures (x-ray diffraction, DSC/TGA, magnetic measurement, and Raman spectroscopy) are given in Chapter 2.

4.3 Results

4.3.1 Chemical Composition

Attempts to synthesize rubidium oxides of lower oxygen content were carried out by the vacuum thermal decomposition of tetragonal RbO\textsubscript{2} at different temperatures. Heating at 220°C yielded a sample containing a thus far unreported cubic compound RbO\textsubscript{2}−δ. Heating at 300°C for 16 hours was necessary to obtain a pure sample of the cubic phase. A DSC/TGA experiment was carried out in a reducing atmosphere (Ar) in order to probe the transformations that take place during thermal decomposition (see Figure 4.1). The first phase transition signified by a peak in the DSC curve around 140°C corresponds to the disordering of the superoxide anion orientations in RbO\textsubscript{2}, where a phase transition from tetragonal to cubic symmetry occurs [13]. A weight decrease also begins above this temperature, indicating the loss of oxygen during decomposition. At 190°C another peak in the DSC curve is seen and the weight decrease becomes much less rapid, signifying the formation of the cubic RbO\textsubscript{2}−δ phase.

The composition/stoichiometry of the compounds obtained by thermal decomposition (reduction) could be determined by TGA/DSC measurements in an oxygen atmosphere at 50°C (see Figure 4.2). The increase in weight, as shown in Figures 4.2(b) and (d), corresponds to the uptake of oxygen (oxidation). After a certain amount of time an inflection in the weight increase curve is observed, corresponding to the point at which the fully stoichiometric superoxide RbO\textsubscript{2} is obtained. A much less rapid weight increase after this point is most likely due to the absorption of residual water in the sample chamber. By extrapolating the curve above the inflection point in weight gain back to zero time, the oxygen composition of a sample can be determined. Two samples of the cubic RbO\textsubscript{2}−δ phase were synthesized under identical conditions (the RbO\textsubscript{2} precursor was heated at the same temperature and for the same time). Nevertheless, the oxygen content of the precursor can vary slightly (see Chapter 3), and this resulted in samples with compositions of RbO\textsubscript{1.78} and RbO\textsubscript{1.66}. The difference in composition was also reflected in the lattice parameters: \(a = 4.218(2)\) Å for RbO\textsubscript{1.78} and \(a = 4.1994(1)\) Å for RbO\textsubscript{1.66}. It can thus be inferred that cubic RbO\textsubscript{2}−δ is not a line phase but can incorporate a
4.3. Results

Figure 4.1. DSC/TGA curve for thermal decomposition of RbO$_2$ carried out in Ar atmosphere.

Figure 4.2. TGA/DSC curves for the oxidation of two cubic RbO$_{2-\delta}$ samples carried out in O$_2$ atmosphere under isothermal conditions (50°C). The compositions of the compounds are determined to be RbO$_{1.78}$ and RbO$_{1.66}$. 


range of oxygen contents. The step seen in the DSC signal that coincides with the weight inflection point (Figures 4.2(a) and (c)) can be regarded as a change in the heat capacity because of the change in crystal structure [25].

![Image of Raman spectra](image)

Figure 4.3. Room temperature Raman spectra of cubic RbO$_{1.66}$ (top) and tetragonal RbO$_2$ (bottom). The inset shows an expanded view of the 1138 cm$^{-1}$ peaks with the values of full-width-at-half-maximum indicated.

The oxygen species present in the RbO$_{1.66}$ sample were investigated using Raman spectroscopy. As shown in Figure 4.3, a peak centered at 1137.6 cm$^{-1}$ is observed for both RbO$_{1.66}$ and the RbO$_2$ precursor, close to the previously reported O-O stretching mode of the superoxide anion in RbO$_2$ (1141 cm$^{-1}$) [13]. A weak peak is also present for RbO$_{1.66}$ at 800.6 cm$^{-1}$, close to the 782 cm$^{-1}$ stretching mode reported for the peroxide anion in RbO [26]. The integrated intensity is 2.5% that of the 1137.6 cm$^{-1}$ peak, consistent with a filling of the $\pi^*$ level close to that found in the superoxide anion. It is noted that strong peaks close to both of these positions were observed for RbO$_{1.5}$, which nominally contains two superoxide anions to one peroxide anion [23]. In RbO$_{1.66}$, assuming that the strongly electropositive Rb atom transfers a full electron to the dioxygen molecules, charge balance requires that the $\pi_g$ orbitals contain 0.80 holes per anion, a mixed-valent situation. The pale yellow color of the current sample suggests insulating behavior and hence that the $\pi_g$ electrons are largely localized, as discussed further in Section 4.4. The inset to Figure 4.3 shows fits to the 1137.6 cm$^{-1}$ peak for both the RbO$_2$ precursor and RbO$_{1.66}$ using pseudo-Voigt functions; the RbO$_{1.66}$ peak is slightly broader, which probably reflects a greater degree of disorder in the local environment of the dioxygen anions. In stoichiometric RbO$_2$, opposite tilts and shifts of the anions give rise to domains, the coherency of which is broken by stacking faults [13]. In RbO$_{1.66}$, the orientation of the anions is disordered in
essentially spherical fashion, as discussed in Section 4.3.2.

4.3.2 Crystal Structure

![XRD profiles](image)

**Figure 4.4.** The observed, calculated and difference XRD profiles of RbO$_{1.66}$ at (a) 300 K and (b) 20 K.

The refined XRD profiles of RbO$_{1.66}$ at room temperature and 20 K are shown in Figure 4.4. At room temperature all reflections could be indexed in the cubic $Fm\overline{3}m$ space group. Rietveld refinements were carried out using a fixed oxygen site occupancy of 83% to reflect the chemical composition determined by TGA. It is noted that refinement of the site occupancy using the low temperature datasets consistently gave values of 88(1)%; although the site occupancy is strongly correlated with the isotropic displacement factor in the refinements, this value is within experimental uncertainty of the oxygen content determined by TGA. The best fit to the room-temperature data ($wR_p = 0.0173$, see Figure 4.3(a)) was obtained using a model with Rb atoms at the origin and dioxygen anions aligned along the four equivalent [111] directions, similar to the room temperature "disordered pyrite" structure of NaO$_2$ [27]. Alternative models in which the anions are aligned along the three equivalent crystal axes ($wR_p = 0.0182$) and in which they are approximated by a spherical distribution of electron density ($wR_p = 0.0191$) gave slightly worse fits. It is concluded that the anion axes are essentially spherically disordered at room temperature but with a slight statistical preference for alignment along [111]. Shortcomings in this spatially and time-averaged model were evident from an inability to refine physically meaningful isotropic displacement factors on either the Rb or O sites.

On cooling, a phase transition was observed at $\sim$230 K. The cubic 111 (Figures 4.5(a) and (c)) and 222 (not shown) peaks remain single and sharp, whereas the cubic 200 and 220 (Figures 4.5(a)-(d)) peaks split, indicating elongation of two of the cubic crystal axes and shortening of the other. Taking $c$ as the short axis, peaks with $hkl, h \neq k$ are broader than those with $h = k$ below the transition (see...
Table 4.1. Refined crystallographic parameters for RbO$_{1.66}$ at 20 K in space group $Fmmm$ with $a = 6.3028(3)$ Å, $b = 6.2558(2)$ Å, $c = 5.8180(1)$ Å.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Position</th>
<th>$x$</th>
<th>$y$</th>
<th>$z$</th>
<th>Occupancy</th>
<th>$U_{iso}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rb</td>
<td>16o</td>
<td>0.0547(7)</td>
<td>0.0518(5)</td>
<td>0</td>
<td>0.25</td>
<td>0.0117(7)</td>
</tr>
<tr>
<td>O</td>
<td>16o</td>
<td>0.399(1)</td>
<td>0.529(3)</td>
<td>0.5</td>
<td>0.415</td>
<td>0.0193(12)</td>
</tr>
</tbody>
</table>

for example Figure 4.5(d)), suggesting that $a \neq b$. All peaks could be indexed in the orthorhombic space group $Fmmm$.

The evolution of the lattice parameters and unit cell volume with temperature is shown in Figure 4.5(e); the sample was cooled to 20 K over $\sim$1.5 h (hereafter referred to as "fast cooled") before diffraction patterns were collected for 1 h each at intervals of 10 K on warming. Between 220 K and 240 K the cubic 200 peak coexists with the orthorhombic 002 peak. This, together with the sudden change in lattice parameters between the high and low temperature phases, indirectly suggests that the transition is first-order in nature. However, in the vicinity of the transition all peaks except 111 and 222 are significantly broadened (Figure 4.5(f)), preventing the determination of precise lattice parameters for either phase. The phase transition involves orientational ordering of the anions, which become confined to the pseudo-tetragonal $ab$ plane below $\sim$230 K. In structural refinements of the low-temperature phase it was necessary to introduce a soft constraint to keep the O-O bond length within a realistic range; it was constrained to lie within $\sim$0.02 Å of the expected value of $\sim$1.33 Å for the superoxide anion [28]. The refinements were made more difficult by complex anisotropic peak broadening. Peaks with dominant $h$ and $k$ Miller indices such as 220 were broader than those with dominant $l$ indices such as 002 (Figure 4.5(f)). However, the width of the 111 peak remained close to the instrumental resolution at all temperatures. The peak profiles could be modeled reasonably well using the microstrain broadening formalism of Stephens [29]. The refinements suggested that the anions lie with their axes at an angle of $\pm$20 degrees to $a$ (disordered in the $Fmmm$ space group), which is consistent with the larger $a$ lattice parameter; the oxygen $x$ and $y$ coordinates are rather strongly correlated with the microstrain broadening parameters in the refinement so this tilt angle has an uncertainty of a few degrees. Difference Fourier plots revealed the presence of electron density around the unit cell origin where the Rb atoms were initially placed. Consequently, the Rb atoms were moved from the 4$a$ site at the origin to the split 16o site at $(x, y, 0)$ with fractional occupancy 1/4. A significant improvement in the fit was obtained on freely refining the $x$ and $y$ coordinates of this four-fold split site. The resulting structural model is, in effect, one where Rb lies at the origin of the orthorhombic unit cell and the centers of the anions are shifted by $(\pm xa \pm yb)$ from their original positions. Combined with the disordered positive and negative tilts, 8 anion orientations are possible as shown schematically in Figure 4.6. The refined crystallographic parameters for RbO$_{1.66}$ at 20 K in $Fmmm$ symmetry are given in Table 4.1.
4.3. Results

Figure 4.5. (a), (b) Partial XRD patterns of RbO$_{1.66}$ showing the evolution of selected peaks as a function of temperature (color scale shows intensity in arbitrary units). (c), (d) Partial XRD patterns collected at 300 K (black) and at 20 K after fast cooling (red) and slow cooling (blue). (e) Evolution of lattice parameters and unit cell volume with temperature for fast cooled sample. (f) Peak broadening (instrumental peak width has been subtracted) of 111, 002 and 220 peaks as a function of temperature for fast cooled sample.
Figure 4.6. (a) Average crystal structure of RbO$_{1.66}$ at 20 K. (b) Schematic view of $ab$ plane showing anion geometry. The anion tilts are disordered in $Fmmm$ symmetry. Four pairs of shifted anions labeled 1-4 are shown, giving 8 possible configurations for every site.

The diffraction patterns collected on the low-temperature phase depend strongly on the rate at which the sample is cooled through the phase transition. After the first set of diffraction data (fast cooled) had been collected on warming from 20 K to room temperature, a second set of scans was immediately collected for 1h each at intervals of 10 K on cooling back to 20 K (hereafter referred to as ”slow cooled”). The cubic-to-orthorhombic phase transition gave rise to anisotropic broadening that was much more extreme than for the fast-cooled data; although the 111 and 222 peaks remained as sharp as previously, peaks with $hkl$, $h \neq k$ and $hkl$, $l = 0$ can best be described as diffuse (Figures 4.5(c) and (d)). The presence at low temperature of some cubic phase cannot be ruled out from the diffraction patterns. The extreme broadening persisted down to the lowest measured temperature of 20 K and prevented meaningful structural refinements from being performed. The peak maxima remain in approximately the same positions as in the fast-cooled data, indicating that the anion axes are largely confined to the $ab$ plane below the transition.

The anisotropic peak broadening most likely arises from the presence of microdomains in which the anion shifts and tilts adopt different configurations. The diffraction peaks will be broadened if these domains are small. This picture has previously been used to account for diffuse scattering in single crystal XRD data collected on KO$_2$ [27]. If the anion tilts and shifts are ordered on short length scales then the true symmetry of RbO$_{1.66}$ on a local level would be non-centrosymmetric and monoclinic at highest; this cannot be probed further using the current powder diffraction data. It is noted that the relative sharpness of the 111 and 222 peaks suggests a well-defined long-range periodicity in the [111] direction, which implies that the structural domains are strongly elongated. It appears that slow cooling rather surprisingly results in smaller structural domains in the $ab$ plane. Sub-
sequent XRD measurements revealed that the domain density is only influenced by the rate at which the sample is cooled through the phase transition; for example, the rate of cooling between 200 K and 20 K is unimportant. Furthermore, an XRD pattern collected after holding a slow-cooled sample at 20 K for a further 12 h was unchanged, implying that the domain structure below the transition is “locked-in”. It is possible that slow cooling can induce a diffusion of oxygen vacancies (defects) so that domains with different chemical compositions are formed. In this case, oxygen-rich domains would tend to exhibit a cooperative Jahn-Teller effect more than oxygen-poor domains which might remain cubic, but neither type of domain would be easily distinguished if they are small. With fast cooling, the sharper diffraction peaks indicate a clear Jahn-Teller distorted phase and there is unlikely to be significant diffusion of oxygen to give domains with different chemical composition. This phenomenon might be similar to what is observed in ZnMn$_x$Ga$_{2-x}$O$_4$ spinels [30, 31]. There a slow cooling rate allows a redistribution of the Mn and Ga ions into small Mn-rich (Jahn-Teller distorted) and Mn-poor (non-distorted) domains, which form ordered patterns stabilized by strain and give similarly broad diffraction peaks. Fast cooling prevents this diffusion from taking place and the Mn and Ga ions remain randomly distributed in a homogeneous structure. A similar scenario might also be relevant in other RbO$_x$ compounds, as discussed in Chapter 3.

![Figure 4.7](image)

Figure 4.7. Differential scanning calorimetry (DSC) curve of RbO$_{1.66}$. A noticeable step at 230 K in the heating mode is characteristic of a phase transition between an ordered state and a glassy (disordered) state.

The effect of cooling rate on the structure is implicitly seen in differential scanning calorimetry (DSC) measurements (see Figure 4.7). During cooling down
Ferromagnetic Order from p-Electrons in Rubidium Oxide

(2 K/min), no anomalies are visible in the downwards curve, thus no clear phase transition is observed. This is consistent with the extreme broadening of the 200 and 020 peaks in the XRD data, suggesting that a poorly defined phase transition governed by oxygen diffusion occurs on slow cooling. On the other hand, a step observed in the DSC curve during heating at the same rate shows that a sharp, well-defined ordered (orthorhombic) to disordered (cubic) transition occurs. The step unambiguously resembles a glass transition (order-disorder) and its small size might indicate that the phase transition occurs partially, not across all structural domains. Moreover, the heating was carried out continuously, the rate of 2 K/min being much faster than 10 K/hour in the x-ray diffraction experiments. This could result in an apparent broadening of the transition due to temperature lag in the sample. During cooling down, the diffusion of oxygen vacancies is involved in the process which prevents the phase transition from being observed. The effect is different from heating-up, where thermal activation can easily induce fluctuations/disorder in the dumbbell orientations.

4.3.3 Magnetic Properties

All magnetic data discussed below were collected after fast cooling RbO\textsubscript{1.66} from room temperature to the starting temperature of each given measurement (the \(~\sim\)50 K phase transition region was always crossed in less than 10 minutes). The sample was always warmed back to room temperature between successive measurements. Figure 4.8(a) shows the magnetization of RbO\textsubscript{1.66} as a function of temperature, measured on warming in a field of 1 T. The field-cooled (FC) and zero-field-cooled (ZFC) curves exhibit splitting below an irreversibility temperature of \(~\sim\)50 K; the splitting becomes more pronounced below 20 K. Larger applied fields of up to 5 T gave essentially identical susceptibility curves. Peaks are apparent at \(~\sim\)20 K in the ZFC curve and at \(~\sim\)5 K in the FC curve. The ZFC-FC irreversibility is typical of magnetically frustrated or disordered systems and can indicate a spin-glass in which individual spins interact strongly, a superparamagnet consisting of isolated clusters of FM-coupled spins, or the intermediate situation of a cluster glass with weak to moderate interactions between the FM clusters [32–34]. In the latter case, the ZFC peak at 20 K would correspond to the so-called blocking temperature $T_f$, below which the net moments in different clusters are frozen into a random configuration. This scenario is supported by further magnetic measurements described below. A Curie-Weiss fit to the temperature dependence of the inverse magnetic susceptibility ($\chi^{-1}$) in the paramagnetic region (not shown) yielded an effective moment of 1.64 \(\mu_B\). The inclusion of a temperature-independent $\chi^{-1}$ term was necessary in order to obtain linear temperature dependence. Considering that 83% of the anion sites are occupied, this value corresponds to an effective moment of 1.80 \(\mu_B\) per anion, which is somewhat higher than the spin-only value expected for a $S = 1/2$ system (1.73 \(\mu_B\)) considering that there are nominally only 0.80 spins on each anion. It is noted that spin-orbit coupling is significant for the superoxide anion and considerable unquenched orbital moments are thought to be present in
4.3. Results

The paramagnetic phases of stoichiometric AO$_2$ [16, 18], often manifested by high values of $\mu_{\text{eff}}$ [27, 35]. A Weiss constant ($\theta_{cw}$) of -3.4 K was obtained from the Curie-Weiss fit, which is small compared to the magnetic irreversibility temperature of 50 K and suggests that AFM and FM interactions compete. The presence of FM interactions is evidenced by measurements of magnetization as a function of applied magnetic field (see Figure 4.8(b)). At 2.5 K, a narrow, pinched hysteresis loop opens at applied fields of above $\sim$1 T, indicating a FM response. However, there is no remanence and saturation was not achieved up to 6 T, where a magnetization of $\sim$0.25 $\mu_B$/f.u. is reached. This corresponds to 35% of the nominal saturation of a FM magnetization. Holding the sample overnight in 6 T did not result in any further increase in magnetization. The shape of the 2.5 K M-H curve is consistent with either an additional AFM component or with spins that remain disordered to low temperature. The peak in the FC magnetization at 5 K and the low value of $\theta_{cw}$ suggest that the remaining spins order in AFM fashion. It is noted that at low fields, the virgin M-H curve lies outside the hysteresis loop measured on subsequent cycling (see inset to Figure 4.8(b)), a feature previously observed for the cluster glass superconductor Ru1222 [36] and magnetic Fe$_2$O$_3$ nanoparticles that act as a cluster glass [37]. At 6 K the field-induced ferromagnetism is weaker; the hysteresis loop is narrower and opens only above $\sim$1.5 T. A linear M-H dependence with no hysteresis is apparent at 25 K.

The splitting of ZFC and FC magnetization data versus temperature shown in Figure 4.8(a) indicates glassy behavior. In other words, short-range magnetic order takes place. A neutron diffraction pattern of RbO$_{1.66}$ was collected on the GEM diffractometer at ISIS at 2 K. The data were extremely noisy due to the small sample size of $\sim$0.1g, but the diffraction pattern was consistent with the

Figure 4.8. (a) ZFC and FC magnetization as a function of temperature. The inset shows an expanded view of the curves below 80 K. (b) Magnetization versus applied magnetic field at different temperatures. The inset shows an expanded view of the virgin curve at low field.
orthorhombic structure determined by XRD and did not show the presence of any additional peaks that could be assigned to long-range magnetic order. This is consistent with the short-range magnetic order suggested by the magnetic measurements.

Figure 4.9 shows the ZFC and FC magnetization of RbO$_{1.66}$ measured on warming in different applied fields. For a canonical spin glass, mean-field theory predicts that the peak in the ZFC curve, which would correspond to the so-called spin freezing temperature, should vary with $H^{2/3}$ [38]. This is clearly not the case for the current sample (see inset to Figure 4.9), where $T_f$ initially increases rapidly at low fields and then exhibits a gradual decrease above 3000 Oe. However, this type of behavior has previously been observed in, for example, FM Fe$_2$O$_3$ and FePt nanoparticles and is instead consistent with the formation of spin clusters with a distribution of sizes [39, 40]. The temperature required to ”unblock” large clusters is higher than that required for small clusters; the maximum in the ZFC curve then has no particular physical meaning, being a superposition of contributions from larger blocked clusters and smaller deblocked clusters that behave in superparamagnetic fashion. The unusual dependence of $T_f$ on field was explained for the above nanoparticle systems by considering how the distribution of magnetic anisotropy energy barriers and the magnetic relaxation above the blocking temperature vary with respect to particle size and field [39, 40].

AC susceptibility measurements, shown in Figure 4.10, provide more evidence against the presence of a canonical spin-glass state in RbO$_{1.66}$. The sample was cooled to 2 K in zero field before applying an AC field of 3.8 Oe in the absence of
Figure 4.10. AC magnetic susceptibility as a function of temperature: (a) in-phase component, (b) out-of-phase component.
a DC field and measuring the susceptibility on warming. A peak in the in-phase susceptibility ($\chi'$) is observed at $\sim$5 K; this is consistent with the field dependence of the DC ZFC magnetization peak (see Figure 4.9, inset). The peak in $\chi'$ shifts towards lower temperature with increasing frequency, opposite to the expected trend for a spin glass. Such behavior has previously been reported for the cluster glass system NaNiO$_2$ [41] and signals the presence of multiple relaxation rates due to a distribution of cluster sizes. For canonical spin glasses, the strong interactions between spins would also result in spin lag (dissipation) manifested as a peak in the out-of-phase susceptibility ($\chi''$), the maximum slope of which should coincide with the peak in $\chi'$ [33]. The absence of a measurable change in $\chi''$ in the current data is somewhat surprising, but the signal is close to the sensitivity limit of the magnetometer and a suppression of the $\chi''$ peak is expected for spin clusters with a broad distribution of sizes and thus relaxation times [34].

Further evidence for the formation of FM clusters was obtained from measurements of magnetization versus time in low fields. The sample was cooled from room temperature to 6 K at a rate of 5 K/min in zero field, where it was left for a certain "waiting time", $t_w$. A field of 100 Oe was then applied and the magnetization was measured as a function of time, as shown in Figure 4.11 for $t_w = 1800$ s and 3600 s. It is clear that the spin dynamics are slow; the magnetization increases with time and reaches a plateau after 1-2 h. Application of a magnetic field likely rotates the anions within the FM clusters such that their associated magnetic moments become aligned closer to the field (the easy axis of magnetization is perpendicular to the anion axis in AO$_2$ [21]). The cooperative rotation of superoxide anions in AO$_2$ is known to be a hindered process with a high energy barrier, similar to that in other molecular crystals such as the non-magnetic alkali metal cyanides [42]. Therefore, the net moments of the clusters are only partially rotated in the fields accessed in the current study and a metastable state is reached corresponding to the magnetization plateau in Figure 4.9. The evolution of magnetization was fitted using the following function:

$$M = m_o(t^{-\alpha}) + m_1(1 - exp(-t/\tau))^{\beta}. \quad (4.1)$$

The fitted parameters are shown in Table 4.2. For $t_w = 3600$ s the curve could be fitted well by the sum of exponential and power law terms in Eq. 4.1. In contrast, it was necessary to split the $t_w = 1800$ s curve into two parts ($t < 1000$ s and $t > 1000$ s), each of which could be fitted well using only the exponential term of Eq. 4.1. This implies that for $t_w = 1800$ s, two groups of clusters can be distinguished that respond to the field on two distinct timescales. When the sample is held for longer before applying a field, the net moments of the FM clusters are already aligned in a more FM fashion, as indicated by the higher initial magnetization for the $t_w = 3600$ s curve. This might be the result of a small residual field in the magnet.

An exponential-type magnetic response (measured as here after applying a field) or decay (measured after switching off an applied field) has previously been
4.3. Results

Figure 4.11. Magnetization as a function of time measured at 6 K in a field of 100 Oe after waiting for 1800 s and 3600 s in zero field.

Table 4.2. Fit parameters for time dependence of magnetization at 6K, shown in Figure 4.11.

<table>
<thead>
<tr>
<th>$t_w$ (s)</th>
<th>$m_o$ (emu)</th>
<th>$m_1$ (emu)</th>
<th>$\tau_o$ (s)</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1800 ($t &lt; 1000$ s)</td>
<td>$3.9(1) \times 10^{-4}$</td>
<td>$9.0(1) \times 10^{-5}$</td>
<td>1120(20)</td>
<td>0</td>
</tr>
<tr>
<td>1800 ($t &gt; 1000$ s)</td>
<td>$3.8(1) \times 10^{-4}$</td>
<td>$8.0(1) \times 10^{-5}$</td>
<td>634(2)</td>
<td>0</td>
</tr>
<tr>
<td>3600</td>
<td>$4.6(1) \times 10^{-4}$</td>
<td>$7.0(1) \times 10^{-6}$</td>
<td>511(6)</td>
<td>$-6.0(2) \times 10^{-4}$</td>
</tr>
</tbody>
</table>
observed in both cluster glass and ferromagnetic nanoparticle systems [36, 43–45], as well as magnetically frustrated RbO$_{1.5}$ and CsO$_{1.5}$ [23]. Monte Carlo simulations have suggested that the functional form of the slow response or decay below the blocking temperature depends on the concentration of magnetic clusters and on the strength of the interactions between them [46]. An exponential response is predicted for low cluster densities and hence weak interactions, whereas power-law behavior is predicted for higher densities where the interactions between clusters are strong, as well as for canonical spin glasses [47]. The current data suggest that an intermediate scenario is applicable to RbO$_{1.66}$, where moderately strong inter-cluster interactions are present. Above the blocking temperature RbO$_{1.66}$ acts more like a superparamagnet until the short-range FM order is lost at $\sim$50 K, followed by normal paramagnetic behavior at higher temperature. The FM clusters probably exist in a matrix of short-range AFM order with a Neel temperature of $\sim$5 K.

### 4.4 Discussion

It has been shown that RbO$_{1.66}$, unlike all other alkali metal oxides studied thus far, exhibits three-dimensional FM ordering (within clusters). Furthermore, the temperature at which the FM clusters begin to form ($\sim$50 K) is significantly higher than the AFM ordering temperatures of AO$_2$ and AO$_{1.5}$ (A = Rb, Cs) [23, 48]. The three-dimensional FM exchange in RbO$_{1.66}$ must be a consequence of the oxygen non-stoichiometry, which leads to a situation in which the $\pi_g$ orbitals nominally contain a non-integral number of electrons. Two scenarios are then possible. First, a true mixed-valent situation may arise in which the $\pi_g$ electrons are itinerant, hopping between adjacent anions. Second, the $\pi_g$ electrons may be localized, in which case there will be a tendency to remove the orbital degeneracy and split the energies of the $\pi_x$ and $\pi_y$ orbitals by means of a structural distortion. Both types of systems are well known in transition metal oxides that possess partially filled $e_g$ orbitals, typified by the doped rare-earth manganite perovskites $R_{1-x}AE_xMnO_3$ (R = rare earth, AE = alkaline earth), which are famous for their colossal magnetoresistance properties [22]. At low doping levels insulating phases are always found, and a Jahn-Teller distortion takes place at which spatial ordering of the occupied $e_g$ orbitals sets in. In most cases this OO gives rise to AFM superexchange, although OO, FM insulating phases are sometimes found, for example at 0.1 < $x$ < 0.2 in La$_{1-x}$Ca$_x$MnO$_3$ [49]. As the trivalent R$^{3+}$ is progressively replaced by divalent AE$^{2+}$, Mn$^{3+}$ is nominally replaced by Mn$^{4+}$. The Jahn-Teller distortion associated with the orbitally degenerate Mn$^{3+}$ cation is suppressed above a critical doping level [49, 50]. Electrons can then hop dynamically between the $e_g$ levels of adjacent Mn$^{3+}$ and Mn$^{4+}$ cations, a process known as double exchange, which gives rise to FM metallic behavior. Although no metallic AO$_{2-x}$ compound has yet been discovered, double exchange is a possible explanation for the FM clusters that was observed in RbO$_{1.66}$. This scenario
would likely involve droplets of non-OO anions embedded in an AFM/OO matrix, which is a type of inhomogeneity widely observed in the doped manganites [22, 51]. Alternatively, it is also possible that FM exchange might arise within an OO phase, as discussed below.

The structural properties of RbO$_{1.66}$ are now discussed in the context of possible OO configurations and their relationship with magnetic exchange interactions. In the cubic symmetry of the room-temperature phase, the $\pi_g$ orbitals are twofold degenerate [48]. On cooling through the transition at 230 K, the anions become orientationally ordered in the $ab$ plane, accompanied by small shifts of their centers of mass along the two [110] directions and a consequent reduction of the crystal symmetry. The probable driving force behind this anion ordering transition is to split the $\pi_g$ orbitals in energy and thus lift the degeneracy, as occurs in stoichiometric AO$_2$ [14, 16, 48]. This is similar to the Jahn-Teller effect in transition metal oxides, which involves displacement of the ligands surrounding the orbitally degenerate cation, but with the difference that the rotational degrees of freedom of the dioxygen anion provide an extra degree of flexibility as to how such a symmetry lowering transition can take place. It is thus expected that orbital ordering (OO) is present below 230 K in RbO$_{1.66}$, although the powder XRD data do not allow its nature to be determined due to the small size of the structural domains.

A series of recent theoretical studies on stoichiometric AO$_2$ suggest that the spin, orbital and lattice degrees of freedom in dioxygen anion systems are intimately connected [16–20], as is commonly the case in transition metal oxides. The best studied member of the series is KO$_2$, which adopts a magnetic structure thought to consist of FM planes that are coupled in AFM fashion [52]. Calculations have suggested that at low temperature the lobes of half-filled $\pi$ orbitals on adjacent anions point toward each other in the $ab$ plane, a "ferro" OO state [16, 18]. Although this geometry promotes AFM direct exchange [48, 53], it has been proposed that superexchange via the cations is also significant in KO$_2$; this has been calculated to tip the balance in favor of FM interactions within the plane [18].

It is likely that the vacancies on the dioxygen sublattice in RbO$_{1.66}$ lower the energy barrier to anion rotation with respect to that in stoichiometric RbO$_2$, allowing lifting of the orbital degeneracy by the adoption of a different crystal structure. Looking at the $ab$ plane of low-temperature RbO$_{1.66}$, two local structural configurations can be envisaged; nearest-neighbor (NN) anions can be rotated in the same or opposite directions to give parallel or staggered patterns. In domains adopting the former configuration, assuming the simplest case of "ferro" OO in which the lobes of the half-occupied antibonding $\pi$-orbitals also lie in the $ab$ plane, a degree of direct orbital overlap is possible, giving small AFM coupling constants $J_1$ and $J_2$ (Figure 4.12(a)). The anion tilt angle of $\sim 20$ degrees prevents strong orbital overlap in any configuration and is consistent with the low ordering temperature of $\sim 5$ K of the AFM component of the sample (Figure 4.8(a)). In the staggered anion arrangement in Figure 4.12(b) no significant orbital over-
Ferromagnetic Order from p-Electrons in Rubidium Oxide

Figure 4.12. Possible "ferro" ordering of half-filled antibonding $\pi$-orbitals in the $ab$-plane for domains in which anions are rotated in the same (a) and opposite (b) directions. The Rb$^+$ cations are represented by the larger circles.

Weak AFM direct exchange

FM superexchange via Rb
(AFM direct exchange negligible)

lap between NN anions will occur and no significant in-plane AFM exchange is possible. No appreciable interplane NN orbital overlap would occur for either anion configuration. However, if the unoccupied 4d-states of Rb are accessible in terms of energy, three-dimensional FM superexchange via Rb might dominate for the staggered configuration ($J_3$ in Figure 4.12(b) indicates a NN superexchange pathway within the $ab$ plane). The FM clusters observed experimentally might be comprised of domains with the staggered anion arrangement, an alternative to the double-exchange scenario described above. It is noted that the coexistence of domains with different OO configurations is known in polycrystalline samples of transition metal oxides, as demonstrated for RVO$_3$ perovskites [54, 55].

Finally, preliminary measurements of magnetization versus temperature and field on a sample of RbO$_{1.66}$ that was slow-cooled through the phase transition indicated AFM ordering below $\sim 5$ K, with none of the signals of FM ordering or cluster glass behavior observed for fast cooling (see Figure 4.13). It thus appears that slow cooling suppresses formation of the FM domains (whether orbitally ordered or not) that are formed on fast cooling; these might be associated with a metastable structural state. It is evident that the local structure of RbO$_{1.66}$ should be examined as a function of cooling rate in order to gain more insight into the anion configurations that exist within domains, and calculations are necessary in order to confirm whether FM superexchange is feasible or whether double exchange is more likely. Furthermore, one cannot neglect the influence on the magnetic properties of domain boundaries between structurally coherent regions (the density of which also depends on the cooling rate), and of grain boundaries in the polycrystalline sample.
4.5 Conclusions

I have studied the effect of oxygen deficiency on the properties of AFM RbO$_2$. A novel phase with composition RbO$_{1.66}$ can be stabilized by heating RbO$_2$ in vacuum. Below $\sim$230 K the orientationally disordered anions become ordered in a plane and the orbital degeneracy of the superoxide anion is lifted. The low-temperature structure is comprised of orbitally ordered nanodomains, the density of which depends on the cooling rate through the transition. Short-range FM ordering sets in at $\sim$50 K in the form of clusters; a FM cluster-glass state is formed below a blocking temperature of $\sim$20 K, embedded in an AFM matrix that orders at $\sim$5 K. The non-spherical nature of the dioxygen anions in AO$_{2-x}$ plays an important role in the interplay between the spin, orbital and lattice degrees of freedom. I have studied the effect of another parameter, non-stoichiometry, and have shown that it can generate strong FM interactions, in contrast to the AFM interactions conventionally present in stoichiometric AO$_2$. I have thus demonstrated a new mechanism to induce ferromagnetism in p-electron systems.

Figure 4.13. Zero-field-cooled magnetic susceptibility of a second sample of RbO$_{1.66}$ as a function of temperature, measured on warming in a field of 1000 Oe. One set of data was collected after fast-cooling through the phase transition region from 230-170 K over $\sim$5 min and another set after slow-cooling through the transition region over 5 h.
Bibliography


