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Challenging the Prediction of Anionogenic Ferromagnetism for Rb_4O_6

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For a long time, rubidium sesquioxide Rb_4O_6 has been of particular interest because its black color indicates an electronic structure that strongly differs from related systems such as regular alkali hyperoxides or peroxides. According to previous investigations, this compound exhibits a mixed valency type of behavior that is caused by differently charged dioxygen molecules, indicating that the structure may be written as $Rb_4(O_2^-)_2(O_2^{2-})$.[1] The structure type Pu_2C_3 and the space group $I\bar{4}3d$, proposed by Helms and Klemm,[2] as well as the presence of both peroxide and hyperoxide anions, have been verified by elastic and inelastic neutron scattering studies.[3] Attema et al.[4] performed density functional calculations within the local spin density approximation (LSDA), which suggest that Rb_4O_6 should be a half-metallic ferromagnet with the magnetic moment carried by the hyperoxide anions.

In the present work, magnetic measurements were performed to investigate this prediction of half-metallic ferromagnetism in Rb_4O_6. For the present experimental study, Rb_4O_6 samples were synthesized by the solid-state reaction of RbO_2 and Rb_2O in a stoichiometric ratio.[1,5] Purity and identity of the samples was confirmed by X-ray powder diffraction.

The magnetic properties of Rb_4O_6 were measured using a superconducting quantum interference device (SQUID, Quantum Design MPMS-XL5). Samples of approximately 100 mg, fused in Suprasil tubes under a helium atmosphere, were used for the analysis. Figure 1panels a and b display the magnetization data in the temperature range from 1.8 to 15 K. The sample was first cooled to a temperature of 1.8 K without applying a magnetic field. After applying an induction field μ_0H, the magnetization was then measured as the sample was heated from 1.8 to 15 K (zero-field-cooled (ZFC) modus). Directly afterward, the measurements were performed in the same field as the temperature was again lowered down to 1.8 K (field-cooled (FC) measurements). The magnetic phase transition was also examined using different strengths of the induction field μ_0H that ranged from 2 mT to 5 T. The high temperature behavior of Rb_4O_6 (ZFC) was recorded as the temperature was varied between 100 and 300 K (Figure 1c).

From Figure 1, it is clear that the magnetization versus temperature curves exhibit hysteresis. This implies that the measurements are not reversible if they are started from a zero-field-cooled state. Such irreversibility between the FC and the ZFC measurements is typical for magnetically frustrated systems, for example, this effect is well-known to occur in spin glasses. From the high-temperature data, an effective magnetic moment of $m = 1.83\ \mu_B$ per hyperoxide unit can be deduced, applying the Curie−Weiss law, on the basis of molecular field theory (MFT). This value is in fair agreement with 1.73 μ_B, which is expected from MFT using the spin-only approximation. An analysis of the high-temperature data yields a negative paramagnetic transition temperature $\Theta_p = -6.9$ K, which is a characteristic signature of an antiferromagnetic type of interaction.

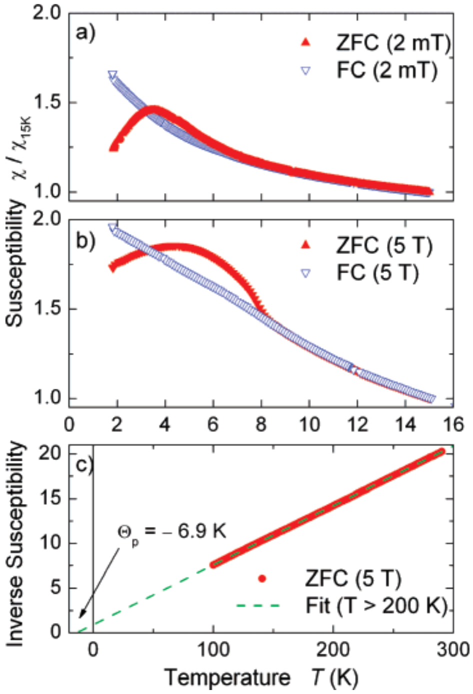

Figure 1. Magnetization data for rubidium sesquioxide. The low-temperature behavior of the magnetic susceptibility is shown in panels a and b for induction fields of 2 mT and 5 T, respectively. The high-temperature behavior of the inverse susceptibility for an expanded temperature scale is shown in panel c. (All values are normalized by the value of the susceptibility at 15 K.)

No direct indication of a pure ferromagnetic behavior of the compound was found from the measured data. The relation of Θ_p to the magnetic transition temperature of (3.4 ± 0.3) K, as measured in an induction field of 2 mT, supports the assumption of spin-glass behavior.[6] In comparison to the low-field measurement (2 mT), the measurement in an induction field of 5 T shows a distinct broadening of the magnetic phase transition. This confirms that Rb_4O_6 is a magnetically frustrated system.

In contrast to recent suggestions,[4] the present measurements of the magnetic properties do not confirm that Rb_4O_6 is a half-metallic ferromagnet. Instead, our data indicate that Rb_4O_6 may belong to the class of materials exhibiting thermally acquirable magnetically bistable states.[7] In any case, our measurements provide strong evidence that rubidium sesquioxide Rb_4O_6 is a magnetically frustrated system that exhibits spin-glass-like behavior, in a

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magnetic field. This peculiar behavior may be caused by a random charge ordering of the three charged dioxygen molecules in each formula unit.

The incompatibility between the magnetization data presented here and the predicted half-metallic ferromagnetism seems to be due to an inadequate treatment of the molecular states in the local spin density approximation, which was used in the calculations by Attema et al.[4] Moreover, the LSDA is inappropriate for addressing these particular types of charged dioxygen molecules and their magnetic ordering. It is worthwhile to note that LSDA calculations on rubidium hyperoxide RbO_2 predict this compound to be a half-metallic ferromagnet as well.[8] RbO_2 (a pale yellow powder[9]), however, is known from experiments to be an insulating antiferromagnet with a Néel temperature of approximately 15 K.[10] This again indicates that the LSDA calculations underestimate the localized bonds between the oxygen atoms as well as their magnetic states. The failure of LSDA in describing the electronic structure correctly cannot be overcome by using on-site electron−electron correlations in the form of LDA $+ U$. Calculations with varying U up to 13.6 eV are able to explain an antiferromagnetic but still metallic, and not an insulating, state for RbO_2. Other compounds with open p-shells and molecular like valence states may have similar properties, so that performing LSDA calculations on these compounds may also result in the prediction of unrealistic magnetic ground states.

Although Rb_4O_6 does not exhibit half-metallic ferromagnetism, the fact that this alkali sesquioxide shows a complicated magnetic ordering, compared to other alkali oxides, is an exceptional phenomenon that is deserving further investigation. Follow-up experimental as well as more detailed theoretical studies must be performed to fully explain and understand the magnetic state of the charged oxygen molecules in Rb_4O_6 and in the related isoelectronic, isostructural sesquioxide Cs_4O_6.

During submission of this work, Attema et al.[11] reported about half-metallicity in other sesquioxides. The authors proposed for Cs_4O_6, among others, a half-metallic state with a Curie temperature of 350 K. However, preliminary magnetic measurements on that compound did not confirm the predicted magnetic state.[8] Therefore, it can be concluded that the mixed oxides as proposed in ref 11 will also not show the predicted half-metallicity.

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