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Published in:
Journal of the American Chemical Society

DOI:
10.1021/ja0550834

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

Publication date:
2005

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):
Attema, JJ., de Wijs, GA., Blake, GR., de Groot, RA., & Wijs, G. A. D. (2005). Anionogenic ferromagnets. *Journal of the American Chemical Society*, *127*(46), 16325-16328. https://doi.org/10.1021/ja0550834

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Published on Web 10/28/2005

Anionogenic Ferromagnets

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Contribution from the Electronic Structure of Materials, IMM, Radboud University Nijmegen, Toernooiveld 1, 6525 ED Nijmegen, The Netherlands, and the Solid State Chemistry Laboratory, MSC, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands

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Abstract: Magnetism in molecules and solids is understood to originate from atoms in that part of the periodic table where a particular value of the angular momentum appears first (i.e., the 2p, 3d, and 4f series). In contrast to the many magnetic compounds containing transition metal or lanthanide atoms, *ferro*magnetism based on atoms from the 2p series is very rare. We report density functional calculations that show the existing compound rubidium sesquioxide is a ferromagnet with an estimated Curie temperature of 300 K, unprecedented in p-electron magnetism. The magnetic moment is carried by the anion. Rubidium sesquioxide is a conductor, but only for the minority spin electrons (a so-called "half-metal"). Half-metals play an important role in spintronics, that is, electronics that exploits the electron spin. Since the magnetic moment resides on a light element (oxygen), spin−orbit interactions are considerably reduced compared to other half-metals. Consequently spin relaxation is expected to be suppressed by up to 2 orders of magnitude in comparison with materials presently used in spintronics.

Introduction

The recent emergence of a technology known as spintronics, where information is carried by the spin of electrons, has led to the requirement for materials with unpaired, mobile electrons whose spins can be aligned in parallel fashion. Suitable materials for practical spintronic applications need to have highly spin-polarized carriers that can be transported with low decoherence.[1,2] However, the vast majority of currently available magnetic materials, which generally contain unpaired d- or f-electrons associated with transition metal or rare-earth atoms, fall short of these demanding requirements. We present electronic band structure calculations showing that the existing compound Rb_4O_6 is an intrinsic ferromagnet in which the magnetic moment is carried exclusively by the p-electrons of the oxygen anions. The calculated magnetic ordering temperature is 302 K, unprecedented in p-electron magnetism. Furthermore, this compound displays metallic conductivity for one spin direction only and is thus in line with the requirements of an ideal spin injector for spintronic devices. Several more existing materials that are plausible candidates for anionogenic ferromagnetism and spintronic applications are discussed.

Although magnetic materials have fascinated mankind since ancient times, unexpected magnetic compounds are still being frequently discovered. Magnetism requires a degree of electron localization and magnetic moments are thus most likely to be found in series of the periodic table where a particular value of angular momentum first arises (that is, the 2p, 3d, and 4f series). Materials containing magnetic 3d and 4f cations have been widely studied and are generally well understood. However, a further evolution in the study of magnetism is currently taking place, and it is emerging that 2p-electron and even closed-shell systems can display remarkable magnetic properties. For example, ferromagnetism with the surprisingly high Curie temperature (T_C) of 600 K has been reported in La-doped CaB_6 (ref 3) and in HfO_{2-x} films where the T_C is 500 K.[4] The origin of the spontaneous moments in these closed-shell materials is still unexplained. Ferromagnetism has also been demonstrated in organic charge-transfer salts,[5] stabilized free radicals,[6] rhombohedral C_{60},[7] and nanostructured carbon foam.[8] Systems that have been considered theoretically include CaO with a small number of calcium vacancies,[9] B-, C-, or N-doped[10] CaO, calcium pnictides with the zinc blende structure,[11] and H-, B-, and P-doped diamond.[12] It is not clear whether these systems can be realized in practice. Magnetic systems based on 2p-electrons are expected to display novel properties not found in

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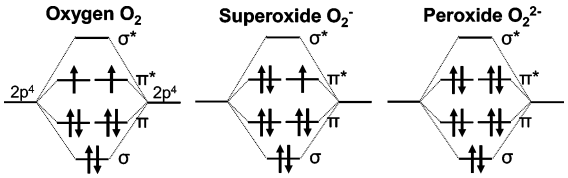

Figure 1. Electronic structure of the oxygen molecule (O_2), the superoxide ion (O_2^-), and the peroxide ion (O_2^{2-}).

3d- or 4f-electron systems for the following reasons. First, valence electrons in p-orbitals are more delocalized than those in d- and f-orbitals. Second, spin−orbit coupling is small or negligible for atoms containing 2p valence electrons since it scales with the fourth power of the atomic number. Properties such as extremely high magnetic ordering temperatures, spin-polarization with low decoherence and stable quantum states can thus be expected, with possible applications in devices such as spin valves and spin transistors, and also in quantum computing. Despite these considerations, the scientific and technological potential of materials that contain unpaired p-electrons has thus far been surprisingly little explored.

Perhaps the best known example of a magnetic 2p-compound is molecular oxygen, which orders in antiferromagnetic (AFM) fashion at 24 K.[13] Other dioxygen species exist, two of which are shown in Figure 1. The superoxide (also known as hyperoxide) anion (O_2^-) is also magnetic since it contains one unpaired electron in the π^* antibonding level, while the filled π^* level in the peroxide anion (O_2^{2-}) renders it nonmagnetic. Peroxide and superoxide ions resemble dumbbells in shape, with oxygen−oxygen distances of 1.50 and 1.28 Å, respectively.[14] They can be stabilized by alkali metal cations to form ionic salts; this type of material is more likely to possess strong magnetic exchange interactions and exhibit long-range ordering phenomena than molecule-based systems due to the close proximity of magnetic species in the ionic lattice. Indeed, long-range AFM ordering has been observed for the alkali metal superoxides at temperatures up to 15 K.[15] Superoxides are intrinsically stable compounds that release oxygen under heating and on contact with water and carbon dioxide. They are insulators and appear transparent orange or yellow in color. The peroxide anion is stable in combination with a wider range of cations, including all of the alkali and alkaline-earth metals, and these compounds are all nonmagnetic insulators. However, very few examples of mixed superoxide−peroxides have been reported. In the literature, compounds with stoichiometries between CsO_2 and Cs_2O_2, presumably containing both superoxide and peroxide anions, have been synthesized[16] but their structures and physical properties are unknown. Detailed information is available only for rubidium sesquioxide, Rb_4O_6, which has been studied by elastic and inelastic neutron diffraction.[17,18] It contains two superoxide anions to one peroxide anion in a cubic lattice; the chemical formula can be written as $(Rb^+)_4(O_2^-)_2(O_2^{2-})$. Interestingly, the black color of Rb_4O_6 indicates a very different electronic structure than that of rubidium superoxide (yellow) and rubidium peroxide (white). Furthermore, this compound may be thought of as being mixed-valent with respect to oxygen, the π^* level containing $^2/_3$ of an electron per O_2 unit. An analogy may thus be drawn between the alkali metal superoxide−peroxides ($A_{1+x}O_2$) and transition metal oxides that possess a partially filled e_g level such as the well-known doped rare-earth manganite series $La_{1-x}AE_xMnO_3$. These perovskites contain mixed-valent Mn^{3+} and Mn^{4+}, the relative proportions of which change as trivalent La^{3+} is replaced by a divalent alkaline-earth cation AE^{2+}. The nature of the magnetic ordering and the electrical conductivity vary widely across the doping series; the end members are both AFM insulators, but ferromagnetic insulating and ferromagnetic metallic phases are found in between.[19] The changes in magnetic and electronic properties arise from the different electronic configurations of Mn^{3+} and Mn^{4+}: Mn^{3+} has one electron in a doubly degenerate e_g level, whereas Mn^{4+} has an empty e_g level and a half-filled t_{2g} level, a closed-shell-type configuration. The superoxide ion is similar to Mn^{3+} in that it possesses orbital degeneracy (in the π^* level). In fashion similar to the manganites, this degeneracy is known to have a major effect on the crystal structure, giving rise to a rich variety of orbital ordering phenomena.[20] Furthermore, AFM ordering is observed for the $x = 0$ members of both the $La_{1-x}AE_xMnO_3$ series and the hypothetical $A_{1+x}O_2$ series. The nonmagnetic peroxide ion is analogous to Mn^{4+} due to its closed-shell electronic configuration, with no orbital degeneracy. These observations raise the question of whether the mixed-valent character of the superoxide−peroxides could give rise to metallicity and ferromagnetism, as happens in a broad region of the $La_{1-x}A_xMnO_3$ series. Such a possibility prompted us to investigate the existing compound Rb_4O_6 by electronic structure calculations.

Method

The calculations in this report were carried out by use of an ab initio technique based on density functional theory (DFT), in the generalized gradient approximation. This method is implemented in the Vienna Ab initio Simulation Package (VASP)[21−27] (see references for more details). The crystal structure determined at 5 K by Jansen, Hagenmayer, and Korber[18] from neutron diffraction data was used for the calculations (space group *I*-43*d*, $a = 9.227\,40$ Å at 5 K; Rb at 16c, $x = 0.053\,95$; O at 24d, $x = 0.4488$; see Figure 2).

Results and Discussion

The calculated density of states (DOS) as a function of energy is shown in Figure 3a, where the bands are labeled in the same way as Figure 1. It shows a half-metallic[28,29] ground state with a magnetic moment of 1 μ_B per Rb_2O_3 unit, that is, $^2/_3$ μ_B per oxygen pair. Important questions to be answered are whether

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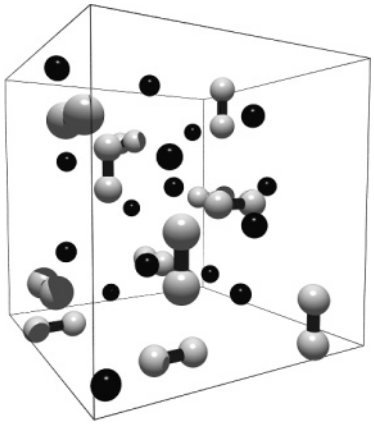

Figure 2. Conventional unit cell of rubidium sesquioxide. The oxygen and rubidium atoms are white and black, respectively.

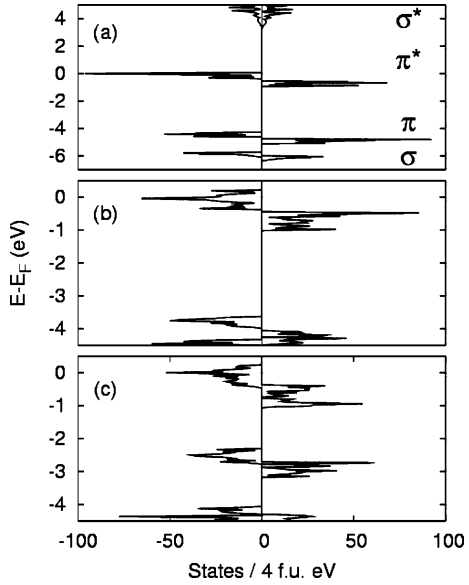

Figure 3. Calculated electronic density of states of rubidium sesquioxide (Rb_4O_6) near the Fermi level (E_F) for the majority (left side) and minority (right side) spins: (a) ground state with the bands labeled as in Figure 1; (b) influence on the π and π^* bands of a phonon mode with a displacement of 1 RMS as observed at 5 K; (c) same phonon mode with a displacement of 2 RMS. Note that the occurrence of a band gap in the majority spin channel of a half-metal is unusual.

this state is stable with respect to AFM ordering and what Curie temperature is expected. Several possible AFM-ordered structures were investigated, but the ferromagnetically ordered state was found to be most stable. The nearest and next-nearest neighbor exchange couplings between the oxygen dumbbells were calculated as $J_1 = 4.194$ meV and $J_2 = 0.398$ meV, respectively. By use of a simple Ising model,[30] a Curie temperature of 302 K was obtained. Although this is not the most accurate strategy for calculating a Curie temperature, it indicates an ordering temperature that greatly exceeds the Néel temperatures of the superoxides and is unprecedented in p-orbital magnetism. These results also suggest that the analogy drawn between the $A_{1+x}O_2$ and $La_{1-x}AE_xMnO_3$ series is a valid one (Figure 4).

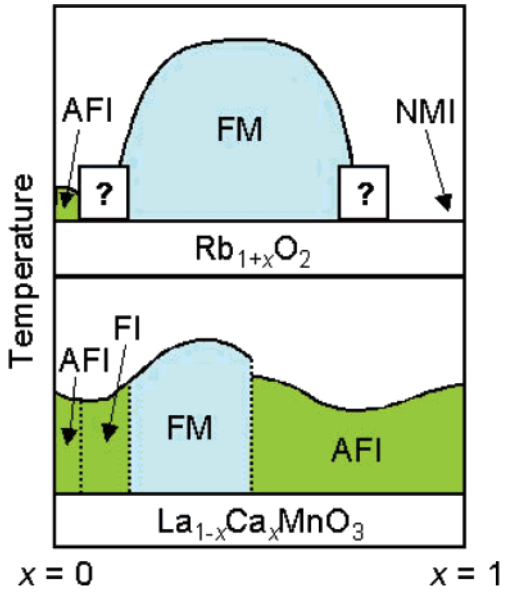

Figure 4. Schematic comparison of phase diagrams of $La_{1-x}AE_xMnO_3$ (AE = alkaline-earth; phase diagram based on that in ref 19) and the mixed superoxide−peroxide $Rb_{1+x}O_2$. Rb_4O_6 is at $x = 1/3$ in the series. Abbreviations are as follows: AFI = antiferromagnetic insulator; FI = ferromagnetic insulator; FM = ferromagnetic metal; NMI = nonmagnetic insulator. Electrically insulating and conducting regions are shaded green and blue, respectively.

The main reason for the low Néel temperatures in the AO_2 superoxides (the highest ordering temperature reported is 15 K for RbO_2)[15] is the weakness of the superexchange primarily responsible for AFM interactions. Superexchange between adjacent O_2^- dumbbells is possible only via the alkali metal cations, which contain no energetically available states close to the Fermi energy, unlike the anions that mediate superexchange in "conventional" cation-based magnets.[31] Although no data on the magnetic properties of Rb_4O_6 have been reported, the neutron diffraction pattern collected at 5 K did not contain any superstructure reflections,[18] implying that no AFM ordering was detected.

Experimental data on mixed superoxide−peroxide materials are scarce. However, the pioneering work carried out by Jansen et al.[17,18] provides various clues about the electronic properties of Rb_4O_6. The black color of this material is consistent with the metallic character predicted by the calculations. More importantly, the neutron diffraction study of Rb_4O_6 was unable to distinguish between the peroxide and superoxide anions, although a pronounced anomaly in the atomic displacement factors perpendicular to the O−O bond was observed, indicating a dynamical occupation of the spin-polarized superoxide hole over all oxygen pairs and down to at least 5 K.[18] This is consistent with the occurrence of hole conduction with a polaronic dressing. Although the conduction bandwidth is rather small, the dynamic behavior down to 5 K indicates that no Mott insulating state occurs. Concerning the lattice dynamics, inelastic neutron scattering data revealed two peaks at 750 and 1130 cm^{-1},[18] corresponding well to the characteristic stretching frequencies of peroxides (780 cm^{-1}) and superoxides (1140 cm^{-1}). However, the detection of genuine peroxide and superoxide vibrational modes implies that the electron mobility is

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slower than the ionic motion, an unlikely scenario. To clarify this issue, the vibrational modes at the γ point of the Brillouin zone were calculated for the measured average structure by the method of ref 32. Three modes with frequencies of 840, 866, and 1024 cm^{-1} were obtained. Although the agreement with the observed spectra is poorer than is usually obtained by this method, these values are still consistent with the experimental measurements for the following reasons. First, the calculations were based on the harmonic approximation, but a potential landscape with at least three minima is necessarily strongly anharmonic. Moreover, the two experimental peaks show widths (fwhm) of 39 and 54 cm^{-1}. This implies that not only the extremes of a charge fluctuation but also the intermediate stages are consistent with the measurements, making the assumptions of slow electron motion with respect to ionic motion unnecessary. However, a more fundamental study with more emphasis on anharmonicity is required to fully explain the experimental observations.

As previously mentioned, the elastic neutron diffraction data showed an averaged structure in which the superoxide and peroxide oxygen pairs could not be distinguished, but with large atomic displacement factors even at 5 K,[18] implying that a strong electron−phonon interaction may be present. To test this possibility, we calculated the electronic density of states (DOS) for several phonon modes consistent with the experimentally observed broadening. Figure 3b shows the calculated DOS for a typical phonon mode with a root-mean-square (RMS) displacement as observed at 5 K, while Figure 3c shows the DOS calculated for a displacement twice as large. A large increase in bandwidths is noted, while the π band splits; the higher energy π band is shifted toward the Fermi energy by up to 2 eV in the case of Figure 3c. This signifies a very large electron−phonon interaction indeed.

Outlook

Finally, we address the question of whether anionogenic magnetism in superoxide−peroxide systems is confined to Rb_4O_6. The first issue that should be clarified is the width of the stability region of the sesquioxide phase in the $Rb_{1+x}O_2$ phase diagram. If the superoxide-to-peroxide ratio can be varied across the series, then the analogy with the doped manganite series $La_{1-x}A_xMnO_3$ represented in Figure 4 is likely to be valid, and half-metallic ferromagnetism with even higher Curie temperatures might exist in this system. Similar properties might also be found for other $A_{1+x}O_2$ materials. Cs_2O_3 is also known to be dark in color[16] and may have a similar electronic structure and properties to Rb_4O_6; furthermore, the system $(Rb_{1-x}Cs_x)_2O_3$ can be envisaged, where the half-metallic ferromagnetism could be tuned by varying the ratios of both the cations and anions. It is uncertain whether pure K_2O_3 can be isolated, but the series $(K_{1-x}Rb_x)_2O_3$ might be worth investigating. The substitution of a portion of the alkali metal atoms in A_2O_3 by alkaline-earth elements such as Ba has also been reported,[33] but the crystal structures and physical properties of the resulting materials are unknown. This modification could open up a route to half-metallic ferromagnetism in the absence of nuclear magnetic moments, further decreasing the effects of decoherence on the polarized electron spins. The realization of such novel systems will require much effort in terms of chemical synthesis, but anionogenic ferromagnets based on dioxygen species could constitute a new family of magnetic materials of both scientific and technological importance, with enhanced properties not found in currently known magnetic systems.

Acknowledgment. This work is part of the research program of the Stichting voor Fundamenteel Onderzoek der Materie (FOM), and financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) is gratefully acknowledged, in addition to that of the Technology Foundation (STW).

JA0550834

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