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Spintronic materials based on main-group elements

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Abstract

Recently, half-metallic magnetism was predicted for rubidium sesquioxide at relatively high temperatures. Here, we present density-functional calculations on related potassium and caesium oxides as well as hypothetical continuous series. Finally, we consider ammonium sesquioxide and estimate a Curie temperature of 250 K. All these half-metals possess band gaps for the majority spin direction.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Besides the charge, spintronics also exploits the spin of the electron. This requires the generation of electrons with some degree of spin-polarization as well as their detection. A straightforward way to realize this is to use electron injection from elemental ferromagnets like iron, cobalt or nickel. These elements are widely applied in devices based on the giant magneto-resistance. In other areas within spintronics as high as possible a degree of spin-polarization is required, preferably 100%. Half-metals are considered in this area [1]. These are materials that are metals for one spin direction, while being semiconductors or insulators for the opposite spin direction. Several factors complicate the application of half-metals, however. Half-metallicity is a genuine bulk property of a material, where its application in spintronics relies on the injection of electrons with preferably 100% spin-polarization into another material (e.g. a semiconductor). This requires the crossing of an interface or a surface, whose properties can be very different from the bulk, depending on the origin of the half-metallicity. In ionic half-metals, like the colossal magneto-resistance materials and chromium dioxide, the half-metallicity is practically a property of a transition-metal ion and its valence ($\text{Mn}^{3.5+}$, Cr^{4+}). No problems are to be expected as long as this valence is maintained at the interface or surface. However, the half-metallic properties of alloys like NiMnSb also depend sensitively on the crystal structure [2]. Consequently, its surfaces are not half-metallic, and half-metallic interfaces based on them require clever engineering [3].

Since actual devices work at finite temperatures, the effects of temperature need to be considered. The thermal excitations of spin-waves (magnons) lead to a reduction of the spin-polarization of the conduction electrons until, at the Curie point, no net polarization persists. Thus, devices based on half-metals should operate well below the Curie temperature, requiring half-metals with high Curie temperatures and/or low temperatures. Several ways of influencing the magnon spectrum and thus the control temperature have been suggested [4]. Also, many-body effects like non-quasi-particle states have been suggested as a source of depolarization at finite temperatures. However, these states have not been observed experimentally and the influence on the conductivity remains unsolved. It is worth mentioning that, theoretically, the effect is expected to be different, depending on whether the bandgap occurs for the majority-spin direction or the minority-spin direction [5]. Half-metals with majority-spin bandgaps are rare. Magnetite has been considered, but its half-metallic properties are being challenged; for details, see the article ‘The case against half metallicity in Fe_3O_4 ’ elsewhere in this issue. Rb_4O_6 has been predicted [6], but its physical properties await experimental verification. The most promising candidate at this moment is the double perovskite $\text{Sr}_2\text{FeMnO}_6$ [7]. Mn_2VAI is calculated to be a half-metal with a majority gap, but only so in the generalized gradient approximation (GGA) [8]. Experimentally it has a low magneto-resistance so it is doubtful whether it is truly half-metallic [9]. All the half-metals in this paper have majority-spin bandgaps.

Another important factor is the spin-orbit coupling. It couples the spin and orbital degrees of freedom into a vector J replacing the quantum numbers l and s with j and j_z . Strictly speaking, spin is not a good quantum number anymore and spintronics ceases to exist. However, often the influence of the spin-orbit interaction is less drastic. The strength of the spin-orbit interaction is an almost atomic quantity which increases rapidly with the nuclear charge (with the fourth power actually). The spin-orbit interaction is maximally effective if electron states for the different spin directions as well as for the different components of the angular momentum are degenerate. The first condition is usually violated by the exchange splitting in the case of a magnetic system, while the second degeneracy can be strongly lifted by the chemical bonding in a solid. Consequently, the net result is very much dependent on details of the bandstructure. In NiMnSb , for example, it is minimal, since the three bands intersecting the Fermi energy are nondegenerate and show a very large dispersion (free electrons have no angular momentum). Nevertheless, spin-orbit interaction will be a limiting factor in critical applications at low temperatures (where magnon excitations play a negligible role) even in the case of NiMnSb . Therefore we consider a new class of half-metals here: anionogenic ferromagnets. The magnetic properties originate from oxygen, the anion, while the (heavier) cations are alkali metals and their dominant valence electrons do not possess angular momentum and hence no spin-orbit interactions. Moreover, the cation-derived states are quite remote from the Fermi energy anyway.

Although magnetism based on d or f electrons is more common, several cases of magnetism based on p electrons are known. The best example, of course, is elemental oxygen. It possesses two unpaired electrons as a molecule. Solid oxygen orders antiferromagnetically with a Néel temperature of 24 K [10]. Other well established examples are organic charge transfer salts [11], as well as stabilized organic radicals [12]. Of more speculative nature is the magnetism in lanthanum-doped calcium hexaboride [13], oxygen-deficient hafnium oxide [14] and rhombohedral C_{60} [15, 16]. Computational studies include calcium-deficient or doped calcium oxide [17, 18], calcium monopnictides in the zinc-blende structure [19], cation vacancies in nickel and manganese oxide [20] and diamond with various dopants [21, 22]. It is not clear, however, whether these systems can be synthesized in practise.

In this paper, we extend our previous work on rubidium sesquioxide to caesium sesquioxide. This is an existing compound, isostructural with Rb_4O_6 . Also, the continuous

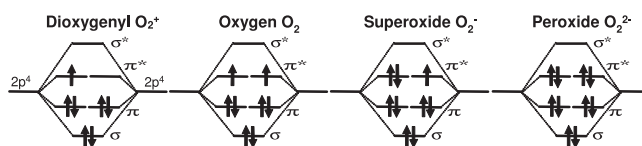


Figure 1. The electronic structure of several di-oxygen species.

series $(\text{Rb}_{1-x}\text{Cs}_x)_4\text{O}_6$ is considered as well as the hypothetical system $(\text{Rb}_{1-x}\text{K}_x)_4\text{O}_6$. Also, the variation in the rubidium/oxygen ratio in sesquioxides will be considered. Next, we will consider the feasibility of realizing ammonium sesquioxide $(\text{NH}_4)_4\text{O}_6$, computed to be a half-metallic ferromagnet with a Curie temperature of 250 K and containing elements from the first row of the periodic table exclusively. Finally, we give an update of a phase diagram of half-metals, including the recent developments.

2. The origin of ferromagnetism in alkali sesquioxides

Two aspects of the ferromagnetism in the sesquioxides are somewhat unexpected: oxygen as the carrier of the magnetic moment and the ferromagnetic coupling of the moments leading to a predicted rather high Curie temperature. Concerning the first aspect: the magnetic moment in rubidium sesquioxide is carried by molecular ions rather than isolated ions. Four O_2 species are known (see figure 1). The neutral O_2 molecule contains two unpaired electrons in the π^* antibonding level. Solid oxygen orders antiferromagnetically at a Néel temperature of 24 K.

The superoxide ion, sometimes referred to as a hyperoxide ion, has one more electron in the π^* level and, consequently, the magnetic moment of the ion is reduced to $1 \mu_B$. The heavier alkali metals form superoxides. They are transparent insulators: apparently, the half-filled π^* band leads to a Mott insulating state. Consistent with this is the magnetic ordering: alkali hyperoxides are antiferromagnets with Néel temperatures up to 15 K [23].

The O_2^{2-} ion occurs in peroxides. Peroxides of alkali metals, including hydrogen, and alkaline earth metals are well known, their stability increases markedly with the mass of the cation. As expected, they are non-magnetic, insulating transparent solids.

The fourth O_2 species is the *positive* dioxygenyl ion O_2^+ . As expected, it has a magnetic moment of $1 \mu_B$. It forms solids like O_2MF_6 with $M = \text{As}, \text{Sb}, \text{Pt}$ as well as $\text{O}_2\text{Sb}_2\text{F}_{11}$ [24, 25]. These compounds are paramagnets with asymptotic Curie temperatures close to 0 K, indicating a very small magnetic coupling [26]. In O_2PtF_6 , the platinum also possesses a magnetic moment, resulting in a ferrimagnetic coupling with a dioxygenyl moment at 4.2 K.

Rubidium sesquioxide has a composition in-between the superoxide and peroxide. It is rather stable thermally, releasing oxygen slowly at temperatures of 1000 K [27, 28]. However, it is hygroscopic and reacts with carbon dioxide in air. The black colour suggests that the electronic structure is very different from that of the superoxides or peroxides. The crystal structure has been studied with neutron diffraction at a temperature of 5 K [29]. It is cubic, all the oxygen atoms are equivalent and form di-oxygen species with an oxygen–oxygen distance in-between those characteristic for peroxide and hyperoxide. Large athermal (5 K) atomic displacement factors perpendicular to the O–O axis were observed. This indicates that the single oxygen–oxygen distance observed is a time-average, with a dynamic occupation of the hyperoxide hole over all oxygen pairs. The neutron diffraction did not show any extra lines due to antiferromagnetic ordering at 5 K (only a limited part of the spectrum was displayed, however).

The Curie temperature was calculated to be 300 K [6]. The phonon modes consistent with the observed low-temperature displacement factors were calculated. These modes show a

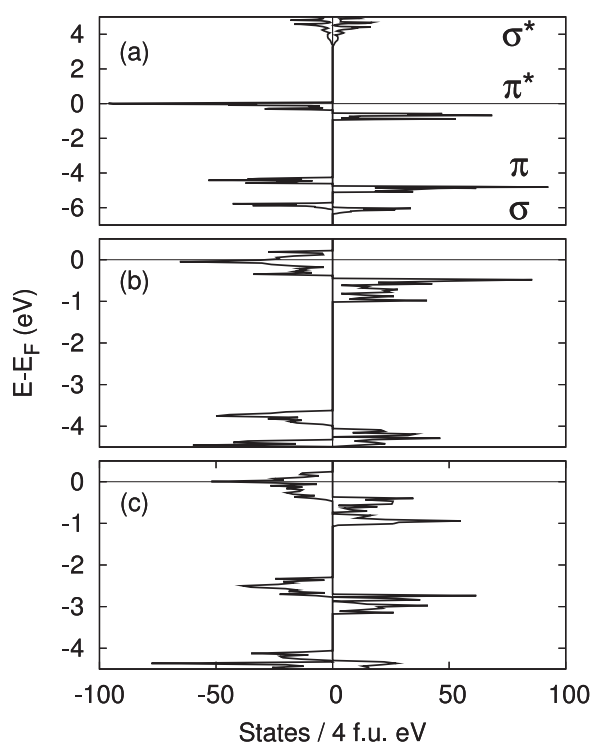


Figure 2. The calculated density of states of rubidium sesquioxide near the Fermi level (E_F) for the majority (left side) and minority (right side) spins. (a) The ground state with the states labelled as in figure 1. (b) The influence on the π and π^* bands of a phonon mode with a displacement of 1 rms as observed at 5 K. (c) The same phonon mode with a displacement of 2 rms. For details, see [6].

very large electron–phonon coupling (see figure 2). Thus the physics of rubidium sesquioxide may be richer than ‘just’ a half-metallic ferromagnet! This paper discusses the electronic structure of the isostructural compound Cs_4O_6 . Its electronic structure is quite comparable to that of its rubidium analogue. Since usually more can be learned from (experimental) studies on a continuous series of compounds, the electronic structure of the series $(\text{Rb}_{1-x}\text{Cs}_x)_2\text{O}_3$ is considered as well as the mixed series between Rb_2O_3 and the hypothetical K_2O_3 . Also, the series $\text{Rb}_{4-x}\text{O}_6$ will be considered. The electronic structure of $(\text{NH}_4)_4\text{O}_6$ is calculated and its Curie temperature determined.

3. Calculations

The calculations in this report were carried out using *ab initio* density functional theory (DFT), within the generalized gradient approximation (GGA) [30]. The implementation used is the Vienna *ab initio* simulation package (VASP) [31–34]. The projector augmented wave (PAW) method was employed [35, 36]. For all calculations, the plane-wave kinetic energy cut-off was 875 eV. The Brillouin zone was sampled using a $10 \times 10 \times 10$ Monkhorst–Pack grid, leading to at least 44 k -points in the irreducible part.

4. Alkali sesquioxides

The question arises whether the half-metallic properties of alkali sesquioxides are confined to the case of rubidium only. The stability of superoxides and peroxides increases with the

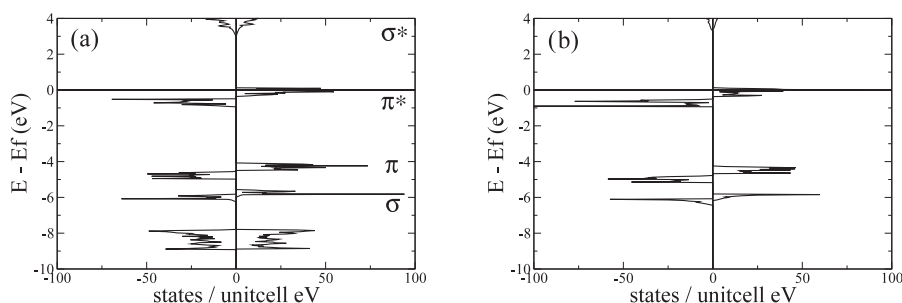


Figure 3. (a) The density of states for Cs_4O_6 for the majority (left panel) and minority (right panel) spins, with the levels labelled as in figure 1. (b) The density of states for K_4O_6 .

polarizability of the cation. Thus lithium peroxide is unstable and even explosive, while sodium burns to its peroxide in air. The potassium superoxide is stable; it is even applied in closed-circuit breathing apparatus, where it reacts with exhaled carbon dioxide and water, releasing oxygen. Other alkali metals that are most likely to form sesquioxides are thus potassium and caesium (we will not consider francium for obvious reasons). Caesium sesquioxide indeed exists; it has the same crystal structure as its rubidium analogue, but has a slightly larger lattice constant of 9.86 \AA [37]. The positions of the oxygen atoms were not refined, but the centre of the oxygen pairs was given. We determined the crystal structure of the sesquioxide by relaxing the atomic positions, keeping the lattice parameter fixed. The resulting structure is that caesium occupies the 16c positions with positional parameter $x = 0.0508$, while oxygen occupies 24d with $x = 0.4458$. This leads to an oxygen–oxygen distance of 1.40 \AA , the same as in the rubidium sesquioxide. The density of states is displayed in figure 3(a). It is rather similar to rubidium sesquioxide (figure 2). The Curie temperature was determined by total energy calculations of the ferromagnetic ground state and two antiferromagnetic states. From these energies the nearest- and next-nearest-neighbour coupling constants were calculated. A standard statistical mechanical analysis (for a description, see [40]) then gives an estimated Curie temperature of 350 K. We tested this method for the half-metal NiMnSb, and obtained a calculated Curie temperature of 830 K, whereas the experimental value is 730 K.

Attempts to synthesize potassium sesquioxide failed [37]. However, we are interested in the series $(\text{Rb}_{1-x}\text{K}_x)_2\text{O}_3$ (see next paragraph). There is much hope that this series exists, at least for values of x that are not too big. Therefore we calculate the electronic structure as well as the lattice parameter of potassium sesquioxide in the structure of rubidium sesquioxide. The resulting calculated density of states is shown in figure 3(b). The equilibrium lattice parameter is 9.0 \AA . The potassium atoms are in the 16c positions with $x = 0.0518$, and the oxygen atoms in 24d with $x = 0.4528$. The Curie temperature was calculated to be 323 K.

Comparing figures 3(a) and (b) and figure 2 it is clear that there is very little difference between K_2O_3 , Rb_2O_3 and Cs_2O_3 . The π^* level for the majority-spin states is filled and an energy gap for the majority-spin direction exists between π^* and σ^* . For the minority-spin direction, the Fermi level intersects the π^* band. The reason the calculated densities of states are so similar is that there are no metal derived states at all in a broad range of more than 15 eV around the Fermi level. Below the Fermi energy, metal derived states occur at -9 , -10 and -13 eV for the caesium, rubidium and potassium sesquioxides, respectively. The σ and π bonding and antibonding levels originate from oxygen 2p functions. Above them, states of oxygen 3s character are found and, only at much higher energy, metal derived states occur. This situation is similar to the alkali halides where, contrary to textbooks, the band gap is between

halogen p states (valence band) and a halogen s derived conduction band [41, 42]. The main influence of the cation is on the lattice parameters of the sesquioxides, and through this on the Curie temperatures.

The absence of metal states in a rather wide energy range around the Fermi level explains (partially) why the Curie temperatures of the sesquioxides are so much higher than the Néel temperatures of the superoxides. Three contributions to the exchange coupling can be distinguished in sesquioxides: direct exchange, double exchange and superexchange. The first two are positive here (ferromagnetic). Superexchange is an indirect coupling of magnetic moments on cations through anions. It can be either positive or negative. However, here the magnetic moments are localized on anions. Consequently, superexchange in anionogenic magnets requires the coupling through cations, but since the alkali metals have no states in the vicinity of the Fermi level, superexchange is very weak (of the order of the Néel temperature of an alkali superoxide). Its competition with the ferromagnetic direct and double exchange is therefore negligible.

5. Possible continuous series

In materials science it is often advantageous to investigate the properties of a continuous series of compounds as a function of composition rather than the study of a single, individual compound. Scientifically, it enables the study of the functional dependence of physical and chemical properties and this often leads to more understanding than the investigation of the properties for a single compound only. It also enables the optimization of a desired property, or the suppression of an undesirable aspect. One possibility for realizing a continuous series is the application of more than one alkali metal. The existence of both rubidium sesquioxide as well as caesium sesquioxide in an identical crystal structure and with similar lattice parameters makes the existence of a continuous series $(\text{Rb}_{1-x}\text{Cs}_x)_4\text{O}_6$ very probable. The half-metallic ferromagnetic properties of K_2O_3 , as calculated, make it worthwhile considering mixed potassium/rubidium sesquioxides. The failure to synthesize potassium sesquioxide itself may very well imply that the compound does not exist, but the rubidium-rich part of the series could be stable. On the other hand, the influence of the alkali metal on the bandstructure and calculated Curie temperatures is small, so other series should be investigated as well.

An interesting question in this respect is how wide (in composition) the stability region of the rubidium sesquioxide itself is; in other words, for what range of rubidium–oxygen ratios is the sesquioxide structure stable? Very early work gives hope that the stability region is not very narrow, even at low oxygen pressures [38]. The variation of the stoichiometry influences the number of charge carriers directly. So a large influence on the physical properties is expected.

Nothing is known about the crystal structure of rubidium sesquioxide with stoichiometries deviating from the ideal stoichiometry. Experimentally, quite some effort has been devoted to a (partial) substitution of an alkali metal by an alkaline earth metal [39]. This could similarly influence the physical properties through the concentration of charge carriers but, unfortunately, no structures have been determined here either. In order to get an impression of the influence of the concentration of charge carriers, we calculated rubidium sesquioxide in its existing crystal structure as a function of the electron concentration. Charge neutrality was ensured by compensating with a uniform background charge. Figure 4 shows the calculated Curie temperature as a function of the electron concentration expressed as a ratio of peroxide and hyperoxide species in the material. The curve peaks near the sesquioxide composition 0.5. It should be stressed that the system will certainly transform to other crystal structures, especially away from the sesquioxide composition. For example, the point 0 corresponds to the hyperoxide, which is actually antiferromagnetic in a very different crystal structure.

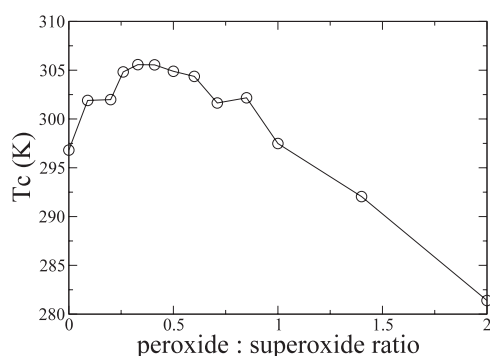


Figure 4. The calculated T_C for hole- or electron-doped rubidium sesquioxide. Rubidium sesquioxide is at $O_2^{2-}:O_2^- = 0.5$.

6. Ammonium-sesquioxide

In this section we will discuss the possibility of realizing ammonium sesquioxide and predict its physical properties. The ammonium group NH_4 has a crystal chemistry which is very much like that of alkali ions. It resembles potassium and is similar in size to rubidium (compare $RbCl$ $a = 6.57 \text{ \AA}$ with NH_4Cl , $a = 6.533 \text{ \AA}$). If ammonium sesquioxide could be synthesized and if it were to have similar physical properties to its rubidium analogue, it would be a ferromagnet with a reasonably high Curie temperature containing only elements with a nuclear charge of 8 or less. Since the spin-orbit coupling strength scales with the fourth power of the nuclear charge, it could form a half-metal with an unprecedented pure spin state.

There are no reports on the existence of ammonium sesquioxide in the literature. No conclusions can be drawn on this fact concerning the stability of the compound, since the literature on sesquioxide is very sparse anyway. But stability is an important issue. The ammonium group can be considered to be the first member of a series $NAlk_4$ with $Alk = \text{hydrogen (H), methyl (CH}_3\text{), ethyl (CH}_2\text{CH}_3\text{), etc.}$ Several of these oxides have been synthesized and we discuss them in order to obtain some insight into the stability of ammonium sesquioxide. The stability of oxygen-rich alkali oxides increases with the weight of the alkali metal. The ammonium oxides follow this trend: the tetra-methyl ammonium compounds are more stable than the simple ammonium compounds, the tetra-ethyl ones more stable than the methyl ones. Usually, the most unstable oxides are the ones with the highest oxygen content: the so-called ozonides containing the O_3^- group. The stability of the ammonium oxides compares favourably with that of the alkali-metal oxides. Ammonium ozonide exists and is stable below -126°C [43]. Tetra-methyl ozonide is more stable than the most stable alkali ozonide, caesium ozonide, which decomposes at 75°C versus 55°C for the caesium compound. Several ammonium superoxides have been synthesized. So there is good reason to assume that the stability of ammonium sesquioxide is a manageable problem.

The similarity in crystal structures between ammonium and rubidium compounds in general justifies the use of the experimentally determined structure of the rubidium sesquioxide for the starting point of the computational study of ammonium sesquioxide. The nitrogen atoms were placed at the Wyckoff position 16c. The tetrahedral symmetry is broken: a threefold rotation axis remains. Consequently, there are two inequivalent hydrogen positions: 16c and 48e.

Relaxation of the lattice parameter and the positional parameters of the atoms lead to the following result: space group 220 of international tables ($I43d$); lattice parameter $a = 9.46 \text{ \AA}$;

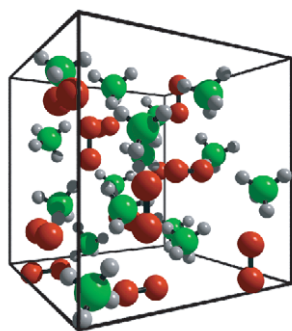


Figure 5. The conventional unit cell of ammonium sesquioxide, containing 16 ammonium ions and 12 O_2 ions. The oxygen, nitrogen and hydrogen atoms are red, green and white, respectively.

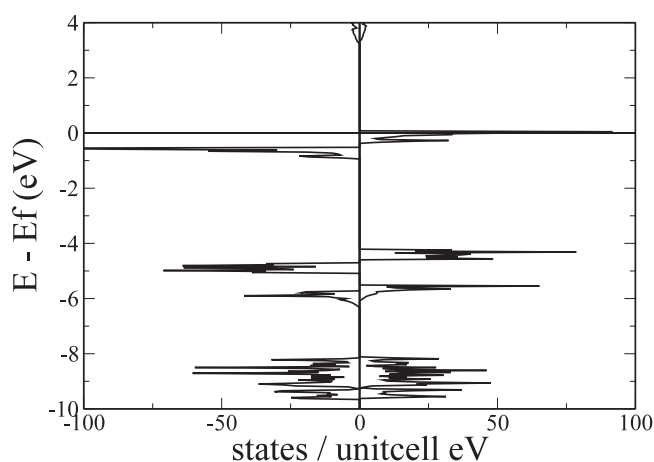


Figure 6. The density of states of ammonium sesquioxide.

nitrogen at 16c with $x = 0.0839$, hydrogens at 16c with $x = 0.0212$ and 48e with $x = 0.1734$, $y = 0.0304$ and $z = 0.4480$, and finally oxygen at 24d with $x = 0.4480$. This structure is shown in figure 5. The oxygen–oxygen distance is 1.38 Å, which is slightly smaller than the 1.40 Å in Rb_4O_6 . The tetrahedral ammonium group is slightly flattened, with one N–H distance 0.02 Å closer to the nitrogen (1.03 Å).

The calculated density of states is shown in figure 6. The compound is ferromagnetic with a magnetic moment of $2 \mu_B$, corresponding to $\frac{2}{3} \mu_B$ per oxygen pair. It is a half-metal with a band gap for the majority-spin electrons. The total energy of the ferromagnetic configuration was compared with several antiferromagnetic configurations. The ferromagnetic state was more stable than the antiferromagnetic configurations considered here (100, 111). The energy differences between the various configurations were used in a simple Ising model in order to estimate the strengths of the couplings and the Curie temperature. The nearest-neighbour coupling constant J_1 was 2.596 meV; the next-nearest-neighbour constant was $J_2 = 1.983$ meV. This leads to a Curie temperature of 250 K. These results are quite similar compared with rubidium sesquioxide. Differences that are to be expected are in the vanishingly small spin–orbit interactions compared with heavier alkali metals. Also, the phonon amplitudes and electron–phonon interactions might be stronger compared with the rubidium compound.

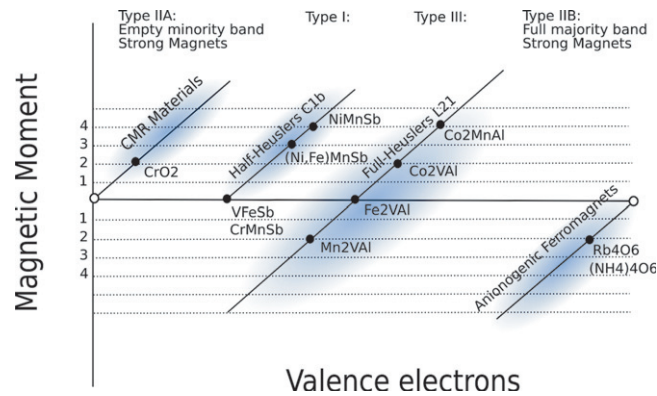


Figure 7. Slater–Pauling curves for a selection of half-metals from the different classes of [49]. The first class contains half-metals with a covalent band gap. The second class contains half-metals with a band gap caused by charge transfer, and two sub-cases can be distinguished. For IIA, the minority band is empty and for IIB the majority band is full. The third class contains half-metals with a d–band gap.

7. Discussion

In this section, the relation of the anionogenic ferromagnets to other half-metals is discussed. The discovery of half-metallic magnetism originates from computational studies on half-Heusler alloys in order to elucidate the mechanism of the magneto-optical Kerr effect [44]. Computational studies have continued to contribute to the field, mainly because there is only one smoking gun experiment to prove half-metallicity. The best experiment to prove half-metallicity is (at this moment) spin-resolved positron annihilation. This requires specialized, dedicated equipment, which is relatively expensive and consequently has (up to now) only been applied to the archetype of half-metallicity: NiMnSb [45, 46]. Thus NiMnSb is the only experimentally proven half-metal. This does not necessarily imply that it is a useful half-metal. In spintronics, half-metals can be applied as a source of spin-polarized electrons. This requires spin injection through an interface that may not be half-metallic, while the situation is also complicated by the effects of conductivity mismatches, etc [47]. The importance of these complications has been realized only recently. Thus, the only proven half-metal has performed poorly as a spin injector until now, mainly because none of its surfaces are half-metallic and spin injection requires very specific interfaces [3], which have not yet been realized experimentally [48]. Besides the Heusler $C1_b$ half-metals, half-metals based on the $L2_1$ structure are actively studied with applications in spintronics in mind. Where the origin of the half-metallicity in the Heusler $C1_b$ is directly related to the similarity of these systems to III–V semiconductors (category I), the $L2_1$ compounds have reduced bandwidths and smaller band gaps (category III) of the classification scheme of [49]. All these half-metals are weak ferromagnets. Strong half-metals are found in oxidic materials; the best known examples are the colossal magneto-resistance materials and CrO₂ (category II).

Another distinction is the sign of the polarization of the half-metal; in other words, does it conduct for majority- or minority-spin electrons. Practically all half-metals conduct for the majority-spin direction, with very few exceptions. The anionogenic ferromagnets, which are the subject of this paper, conduct for the minority-spin electrons. Another example is in the double perovskites.

The properties of half-metals and some of their systematics can be visualized by plotting the magnetic moments as function of number of valence electrons. These Slater–Pauling curves

are plotted in figure 7 for a selection of half-metals. The criterion for selection is to show the wide variety of half-metals; the half-metallic properties for some of them are subject to discussion. The ordinate separates the half-metals with minority-spin gap from those with majority-spin gap. The ordinate itself shows half-metallic antiferromagnets, systems with 100% polarization, but no net magnetization. This unique state competes in stability with non-magnetic semiconductors.

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