Electronic structure of some organic, inorganic and hybrid materials
Shokaryev, Igor

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

Publication date:
2009

Link to publication in University of Groningen/UMCG research database

Citation for published version (APA):

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Chapter 6

Metamagnetism in Unfrustrated Linear Chain Cobaltvanadate (CoV$_2$O$_6$)

6.1. Introduction

Ternary transition-metal oxides show a large variety of interesting physical properties. One example that received attention recently is the class of linear chain ternary cobalt oxides. Best studied is the case of Ca$_3$Co$_2$O$_6$ [1–6]. The crystal structure shows linear Co-O chains on a hexagonal lattice. A chain consists of cobalt atoms six-fold coordinated by oxygens in an alternating trigonal prismatic and octahedral symmetry [1]. The chains couple antiferromagnetically, which at low temperature leads to a magnetization that increases step-wise as function of an applied magnetic field. This is interpreted as resulting from the frustration of the hexagonal lattice [2]. A number of electronic structure calculations have been reported on this compound. Wangbo et. al. [3] obtain a halfmetallic ground state with a magnetic moment mainly localized on the trigonal prismatically coordinated cobalt ion. The octahedrally coordinated cobalt shows a magnetic moment an order of magnitude smaller than the trigonal prismatic one, in agreement with experiment [4,5]. Eyert et. al. [6] confirm these results and stress the differences between trigonal prismatic and octahedral coordination. Vidya et. al. [7] obtain a ferrimagnetic metallic groundstate with two chains magnetically parallel and one antiparallel. The moments are mainly carried by the cobalt in the trigonal prismatic coordination, the moments at the octahedral sites being one order of magnitude smaller. A paramagnetic solution shows a small bandgap, this solution presumably has no local moments. The calculations by Hua et. al. [8] emphasize the importance of the special case of D$_{3h}$ symmetry. The crystal field splitting is by the magnetic quantum numbers into a singlet ($m_l = 0$) and two doublets: ($m_l = \pm 1$) and ($m_l = \pm 2$). Consequently, this point group does not show orbital quenching. Unusual large effects
of the spin-orbit interaction are to be expected, comparable with those in isolated ions. In the LDA+U calculation both spin and orbital moments for the octahedrally coordinated Co are vanishingly small, whereas the trigonal prismatic cobalt has a spin-moment of $3\mu_b$ and an orbital moment of $1.57\mu_b$ and oxygen has a sizable moment of $0.13\mu_b$.

Another interesting material is CoNb$_2$O$_6$ ([9] and references therein). It has a crystal structure that consists of chains with a kinked structure that order in an orthorhombic unit cell. The magnetic behavior is very complex: it orders antiferromagnetically and the magnetization as function of applied field shows a multitude of steps with marked anisotropy. Many different magnetic structures have been determined and even the field-dependence of the specific heat is anisotropic. The iso-electronic vanadium CoV$_2$O$_6$ occurs in two crystal structures, the triclinic low temperature form [10] and the high temperature Brannerit structure [11]. In the latter structure cobalt is octahedrally coordinated. The octahedra form one-dimensional chains sharing edges along the crystallographic direction [010] as it is shown in Fig. 6.1. Recently, the magnetic properties of CoV$_2$O$_6$ in the high temperature structure were reported [12]. The magnetic properties of CoV$_2$O$_6$ are remarkable. They are summarized in $M(H)$ dependence and the corresponding phase diagram which are both shown in Fig. 6.2. It is an antiferromagnetic insulator with a magnetic moment of $3\mu_b$ per cobalt (high spin) and a Néel temperature of 7 K. Between 5 and 7 K the application of a magnetic field of 4 KOe induces a metamagnetic transition to a ferromagnetic phase with identical local moments. Below 5K the system first moves through an intermediate plateau, before reaching saturation. This occurs at almost exactly 1/3 of the saturation magnetization. This plateau is similar as in Ca$_3$Co$_2$O$_6$ and CoNb$_2$O$_6$. An increase in applied magnetic field to 6 KOe leads to a transition to a ferromagnetic state with the full moment. This behaviour is quite unexpected: the crystal structure of CoV$_2$O$_6$ does not show any ingredient for frustration, neither in the packing of chains, or in the structure of the chains themselves. We calculated the electronic structure of CoV$_2$O$_6$ in the antiferromagnetic groundstate, the ferromagnetic state and the ferromagnetic state with reduced moment corresponding to the 1/3 plateau state. It will be shown that for all the three phases the density of states at the Fermi energy vanishes for both spin directions. Both the ferromagnetic and antiferromagnetic state are characterized by a Co$^{3+}$ in a high spin-state, $(d^7; t_{2g}^5 e_{g}^3)$ while the plateau state has a low spin-state $(d^7; t_{2g}^6 e_{g}^1)$ configuration.
6.1 Introduction

Figure 6.1: Perspective view of the crystal structure of CoV$_2$O$_6$. Cobalt is octahedrally coordinated by oxygen atoms. Vanadium is at the center of the basal plane of the square pyramid with oxygen atoms at the corners. The Co-octahedra have the edge sharing with each other along b-axis and corner sharing with V-pyramids. The cobalt octahedra form one-dimensional (1D) arrays along the b-crystallographic direction.

Figure 6.2: 1/3 Plateau (taken from the ref. [12]). a) Magnetic susceptibility M(H) of CoV$_2$O$_6$ as a function of applied magnetic field at different temperatures. The 1/3 plateaus are clearly seen. The lower the temperature the more pronounced is the plateau state. b) Field/temperature phase diagram of CoV$_2$O$_6$. Shaded area is an extent of hysteresis at 1/3 plateau.
6.2. Method of Calculation

The first-principles electronic structure calculations were performed using density-functional theory (DFT) [13] implemented in the Vienna ab initio Simulation Package (VASP) [15–20] where projected augmented wave (PAW) method [19–21] was invoked. We use the PW91 [14] generalized gradient approximation (GGA) to the exchange correlation potential. The atomic positions and the volume of the unit cell were relaxed using a conjugate gradient algorithm with a tolerance of 10 meV/Å on interatomic forces. For Brillouin zone integration we used a Monkhorst-Pack k-point mesh [22] with $4 \times 8 \times 6$ points. An energy cutoff of 500 eV for the plane-wave basis set was used in all calculations. The crystal structure used in the calculations can be found in the Appendix C.

6.3. Electronic Structure of CoV$_2$O$_6$

The first calculations of the ground state of CoV$_2$O$_6$ using the experimentally determined crystal structure (see Appendix C for details) showed the importance of optimizing both the atomic positions and the volume of the unit cell. We optimized both the unit cell axes and the atomic positions in order to reduce the residual external pressure and forces on the atoms. The optimization of the volume only leads to its increase by 2.6% with respect to the experimental value. The corresponding DFT band gap for the relaxed structure is 3 times smaller than for the unrelaxed one. This is a somewhat unexpected result since the opposite is usually observed. For the optimized crystal structure we found that the ferromagnetic ground state ($T = 0$ K) is 0.019 eV lower than the antiferromagnetic state. This is, surprisingly, opposite to the experimental result [12]. The local spin moment at the Co$^{2+}$-site is $3 \mu_b$ which is in agreement with the expected high spin state at the Co-site. The partial densities of states for antiferromagnetic and ferromagnetic ground states are given in Fig. 6.3 and Fig. 6.4. From the total DOS (both FM and AFM) we can conclude that CoV$_2$O$_6$ is a small band gap magnetic semiconductor at zero temperature. Close examination of the DOS for ferromagnetic structure, shown in Fig. 6.4, concludes that the top of the valence band is 100% spin polarized. The band gap for minority-spin is two orders of magnitude smaller than that for majority-spin states. The top of the valence band and the bottom of the conduction band for majority-spin states have a different character in contrast to the antiferromagnetic ground state shown in Fig. 6.3.

The irreducible part of the Brillouin zone (IBZ) for the monoclinic unit cell of CoV$_2$O$_6$ is shown in Fig. 6.5. It was generated by the LSW-code [23]. The eight edges of the obtained IBZ are labeled by numbers (1-8). From that we can chose a path for the band structure. We calculated the band structure for AFM, FM and FM with the spin orbit (SO) coupling. The band structure for the AFM structure is shown in Fig. 6.6. It shows that CoV$_2$O$_6$ has an indirect band-gap since the
top of the valence band is at the middle of 1-4 and the bottom of the conduction band is between 2-1. The valence band dispersion in panel 7-3 indicates the biggest interaction specifically in the \( k_y \) direction corresponding to the direction along the \( b \)-axis. This is a very important observation for the following discussion of the 1/3 magnetization plateau. The band structure for the FM structure is shown in Fig. 6.7 for both majority-spin and minority-spin channels. It also shows clearly the dominant interaction along the \( b \) crystallographic direction. The difference in the band gap for majority-spin and minority-spin channels is evident.

It is also interesting to look at the influence of spin-orbit (SO) coupling. The total energy difference between FM and AFM states calculated with SO does not differ from the result without SO coupling. The band structure of CoV\(_2\)O\(_6\) calculated with SO is shown in Fig. 6.8. It coincides with the band structure calculated without SO coupling. The inclusion of SO coupling doesn’t remove the degeneracy at the high symmetry point labeled by 3. This is the direct consequence of the symmetry of the crystal structure.

The analysis of the complex density of states curves is facilitated by a schematic level diagram showing the influence of the various interactions: the crystal-field splitting and the exchange splitting. Since we are primarily interested in the states several eV around the Fermi energy the states of interest are primarily the cobalt \( d \)-states. These states are split by the octahedral crystal field \( \Delta_{oct} \), the exchange splitting \( \Delta_x \) and the linear chain interactions \( \Delta_{ci} \). The schematic indication for both the high-spin and the low-spin configuration is given in Fig 6.9. The dominant splitting for the high-spin configuration is the exchange splitting, leading to a completely filled majority spin-channel. It is split into a low lying triplet (\( t_{2g} \)) and a doublet (\( e_g \)). The Fermi level is lying in the minority triplet manifold. The one-dimensional chain interaction is responsible for the splitting within this manifold and responsible for the vanishing density of states at the Fermi energy. The top of the valence-band and bottom of the conduction-band are formed from minority spin \( t_{2g} \) states. Figure 6.4 shows the density of states for CoV\(_2\)O\(_6\) in the ferromagnetic state. The overall structure is similar as the one for the antiferromagnetic one (see Fig. 6.3). Overall the bandwidths are larger in the ferromagnetic case as compared to the antiferromagnetic one, reflecting the dominant role of the exchange splitting in the high-spin configuration. Consequently bandgaps are reduced, although a (DFT) bandgap of 0.012 eV remains at the Fermi energy. The one-dimensional spectral character of the peak at -0.5 eV is (partially) destroyed, since nearest chain-chain interactions are no longer in competition with the exchange splitting.
Figure 6.3: Density of states (DOS) per atomic species for antiferromagnetic (AFM) CoV$_2$O$_6$. The DFT band gap is 0.066 eV.

Figure 6.4: Density of states (DOS) per atomic species for ferromagnetic (FM) CoV$_2$O$_6$. The upper part of the plot shows DOS for minority-spin and the lower for majority-spin states. The DFT band gap for minority-spin and majority-spin states are 0.012 and 1.237 eV correspondingly.
6.3 Electronic Structure of CoV$_2$O$_6$

Figure 6.5: IBZ and high symmetry points of CoV$_2$O$_6$ with the space group C2/m. The direction of the 7-3 edge corresponds to the 1D chain direction.

Figure 6.6: Band structure for antiferromagnetic (AF) ground state of CoV$_2$O$_6$. Fermi energy is chosen at the top of the valence band (at 0 eV).
Figure 6.7: Band structure of ferromagnetic CoV$_2$O$_6$. Fermi energy is chosen at the top of the valence band (at 0 eV). The top panels represent band structure for minority-spin and bottom for majority-spin states.
Figure 6.8: Band structure of CoV$_2$O$_6$ with the spin orbit (SO) coupling. Fermi energy is chosen at the top of the valence band (at 0 eV).

Figure 6.9: Schematic diagram of the d-orbital energies for the High Spin State and Low Spin State at the Co-atom. It agrees with the pictures of DOS shown in Fig. 6.4, 6.3 and Fig. 6.10 correspondingly. The splitting between $t_{2g}$ and $e_g$ ($\Delta_{\text{oct}}$) are caused by the ligand field. The exchange splitting ($\Delta_e$) corresponds to the splitting within $t_{2g}$ and $e_g$ manifolds of the opposite spin direction. The chain interaction causes splitting ($\Delta_{ci}$) within the $t_{2g}$ and $e_g$ manifolds. The applied magnetic field changes the relative values of $\Delta_{\text{oct}}, \Delta_e$ and $\Delta_{ci}$. Two different cases are expressed in the High Spin and the Low Spin States.
6.4. The Nature of the 1/3 Plateau

One of the most interesting results on magnetic studies of \( \text{CoV}_2\text{O}_6 \) is the observation of the horizontal plateau in the magnetization \( M(H) \) which is shown in Fig. 6.2 and discussed in detail in ref. [12]. The plateau is observed at 1/3 of the saturation magnetization. The origin of this plateau was not explained, however, and only the analogy with \( \text{CoNb}_2\text{O}_6 \) has been anticipated [12]. It is very tempting since the Niobium (Nb) has the same valence electron configuration as vanadium (V). Here we will show that it is not the case and the 1/3 plateau in \( \text{CoV}_2\text{O}_6 \) has a different origin.

As it was pointed out in the introduction there are many cases for the 1/3 plateau observed previously in a number of other quasi one-dimensional materials, however, the reason for the observation of such a plateau in \( \text{CoV}_2\text{O}_6 \) is different. The case of \( \text{CoV}_2\text{O}_6 \) compound is very special. Its crystal structure significantly differs from that of \( \text{Ca}_3\text{Co}_2\text{O}_6 \) [8] and \( \text{CoNb}_2\text{O}_6 \) [9] although it is quasi one-dimensional as well. Since the crystal structure of \( \text{CoV}_2\text{O}_6 \) lacks the ingredients for frustrated spin-structures we investigated the possibility of a configuration based on a low-spin cobalt ion. For this purpose we calculated the electronic structure in the ferromagnetic state constrained to 1 \( \mu_B \) per formula unit. We performed the electronic structure calculations specifically for the magnetic state corresponding to the 1/3 plateau state. First the relaxation of the atomic positions with the constraint for the total magnetic moment at Co-site to be 1 \( \mu_B \) has been allowed. The important observation is that in this case the unit cell tends to contract. This follows from the sign of the calculated external pressure (the opposite was concluded for the FM case with 3 \( \mu_B \) per Co). The structure optimization lead to a shortening of the Co-O distances, indicating an increasing of strength of the Co-O bond. This would imply a strong magneto-elastic coupling.

The calculated density of states for the majority-spin is shown in Fig.6.10. The corresponding energy band gap between occupied and unoccupied states in the spin-majority DOS is 0.33 eV. This is considerably larger than that for the AFM spin state (Fig. 6.3) and FM spin state (Fig. 6.4). For the low spin configuration the situation is different from that of the high spin state discussed earlier (see Fig. 6.9). Here both majority and minority \( t_{2g} \) states are occupied and the Fermi level is in the majority \( e_g \) state also split by the chain interaction. This scheme is already reflected in the actual calculated density of states for the antiferromagnetic ground state (Fig. 6.3): The \( t_{2g} \) manifolds for the two majority spin directions are found around -2 eV in the density of states curve. The depression at -1.8 eV signals the chain-interaction and the third \( t_{2g} \) state is positioned around -1.6 eV. Just above this state the first \( e_g \) state appears, the second \( e_g \) state is separated by a 0.5 eV gap. This splitting is a direct measure of the intra-chain interaction, which as expected is larger for the \( e_g \) states. Overlapping with this state is the lowest \( t_{2g} \) minority-state. It shows a structure which is prototypical for a one dimensional chain, representing direct \( d-d \) overlap. The two remaining
6.5 Conclusions

The results of this chapter show the exotic magnetic properties of the cobaltvanadate compound CoV$_2$O$_6$. It has been shown how the nature of the 1/3 plateau can be completely different from that of the other 1D compounds. Since the crystal crystal structure of CoV$_2$O$_6$ does not suggest a frustrated spin-structure we investigated the possibility of a configuration based on a low-spin state cobalt ion. The electronic structure of CoV$_2$O$_6$ was calculated in the ferromagnetic configuration with a magnetic moment of 1$\mu_b$ per Cobalt ion. The ligand field causes the lifting of all $t_{2g}$ and $e_g$ degeneracies. Depending on the value of the applied magnetic field this leads to the 1/3 plateau low spin state (1$\mu_b$) per Co-atom and the high spin state (3$\mu_b$) per Co-atom which is observed in the experiment. The different configurations of the Co$^{2+}$, $t_{2g}^6$ $e_g^1$ and $t_{2g}^5$ $e_g^2$ respectively, imply a strong magneto-elastic effect.

Acknowledgment. This work work was supported by the NWO breedte strategie program MSC$^{plus}$ and is part of the research programme of the Stichting voor Fundamenteel Onderzoek der
Materie (FOM) with financial support from the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO). We would also wish to thank Dr. A. Nugroho who initiated the studies of CoV$_2$O$_6$ for numerous discussions. We would like to acknowledge A. Meetsma for determination of the crystal structure of CoV$_2$O$_6$ compound.
Bibliography


