Microscopic Derivation of Magnetic Coupling in Ca$_3$Co$_2$O$_6$

C. Laschinger$^1$, T. Kopp$^1$, V. Eyert$^1$, and R. Frésard$^2$ *

$^1$ Institut für Physik, Universität Augsburg, 86135 Augsburg, Germany
$^2$ Laboratoire Crismat-ENSICAEN, 6, Bld. du Marchal Juin, 14050 Caen, France

Abstract

For cobalt atoms placed along chain structures in Ca$_3$Co$_2$O$_6$, we investigate the spin exchange coupling between atoms in high spin states. Consistent with experimental findings, the coupling is weakly ferromagnetic.

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Quasi one-dimensional structures have long been acknowledged to exhibit intriguing transport and magnetic properties. New members in this family are Ca$_3$Co$_2$O$_6$ [1] and a series of related isostructural compounds, which crystallize in the R3c structure [2]. In this structure, two inequivalent cobalt atoms exist, one in an octahedral environment (labeled Co1), and the other one in a trigonal-prismatic environment (labeled Co2). Both atoms are in a 3+ configuration, but in different spin states. Cobalt atoms form covalent bonds along chains while the interchain coupling is far weaker. One therefore expects that this rather unique situation is going to give rise to a peculiar magnetic response.

Along the chains the cobalt spins tend to order ferromagnetically whereas the interchain coupling is antiferromagnetic. However, the antiferromagnetic order is affected by the frustration inherent in the crystal structure. At low temperature, this system appears to be in a partially disordered antiferromagnetic state. On top, the magnetization versus field curves display several plateaus [1].

An appealing starting point to the understanding of the magnetic structure of a particular compound is provided by the Kanamori-Goodenough-Anderson rules [3]. Given the electronic configuration of the ions one can estimate their magnetic couplings and, at mean-field level, the magnetic ground state. In Ca$_3$Co$_2$O$_6$, the problem is more involved, in particular since each second Co$^{3+}$ is non-magnetic, as indicated by neutron scattering data [2]. One therefore needs to determine the next-nearest neighbor magnetic coupling. This is the purpose of the paper.

To that aim one needs i) to determine the electronic configuration of the ions, and ii) the matrix elements of the hopping operator. Both are described by a set of parameters obtained from density functional theory calculations using the augmented spherical wave method (ASW) [5]. In particular, it turns out that both Co ions are in a 3d$^6$ configuration. The parameters entering the local

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* Corresponding author. Tel.: +33 231 45 26 34; fax: +33 231 95 16 00; email address: Raymond.Fresard@ismra.fr
part of the standard multi-band Hubbard Hamiltonian, upon integrating out the oxygen degrees of freedom, are the Hubbard $U$, the Hund’s rule coupling $J_H$, and the crystal field splitting $10D_q$. For Co$_2$, the splitting of the “three-fold degenerate” lowest level turns out to be small [6], and is neglected. In contrast to $10D_q$ both $U$ and $J_H$ are weakly affected by the difference between the prismatic and octahedral environments. The six electrons can be in three spin configurations: a low spin one (LS) ($S = 0$) with energy $E_{LS} = (30U - \sqrt{(3J_H + 20D_q)^2 + 24J_H^2 - 57J_H - 28D_q})/2$, an intermediate spin one (IS) ($S = 1$) with energy $E_{IS} = (30U - \sqrt{(J_H + 20D_q)^2 + 8J_H^2 - 65J_H - 8D_q})/2$, or a high spin one (HS) ($S = 2$) with energy $E_{HS} = 15U - 38J_H - 4D_q$. As a result the LS configuration is stable for $J_H < 2.68D_q$, and the HS one otherwise. Stabilizing the IS configuration requires different physical input, such as an additional splitting of the $e_g$ level or a lowering of the symmetry [4].

We are now in the position to estimate the intra-chain magnetic couplings. For Co$_1$ we choose the coordinate axes to point towards the oxygens, while for Co$_2$ we choose the $z$-axis to point along the $c$-direction of the $R3c$ group. Therefore when determining the matrix elements of the hopping term one needs to carefully distinguish the relevant contributions. It turns out that the $3z^2 - r^2$ orbital on Co$_2$ identically couples to the $x'y'$, $x'z'$, and $y'z'$ orbitals on Co$_1$, with amplitude $t$, while other matrix elements are negligible. At this stage one can determine the magnetic ground state performing a hopping expansion. It is obvious that the magnetic structure does not enter the result to order $t^2$. To order $t^4$ the exchange paths between two Co$_2$ sites are sensitive to the magnetic structure and the respective Hund’s rule coupling on Co$_1$. A typical exchange path is sketched in Fig. 1 for a ferromagnetic configuration. Any $t_{2g}$ down spin on Co$_1$ can hop onto the $3z^2 - r^2$ orbital on one neighboring Co$_2$, and any remaining $t_{2g}$ down spin on Co$_1$ can hop onto the $3z^2 - r^2$ orbital onto the second neighboring Co$_2$, (this leaves Co$_1$ on a spin state where $J_H$ is important), and then both electrons return to Co$_1$. There are 48 such contributions. For an antiferromagnetic configuration, we find that: i) there are only 42 such paths, and ii) it leaves Co$_1$ on an intermediate low spin state, which has a higher energy. As a result the ferromagnetic configuration has a lower energy. Using the numerical values resulting from the ASW calculation [6] and $U = 5.5$ eV, we finally obtain

$$E_F - E_{AF} \simeq -10^{-3}t^4/eV^3.$$  

Using $t \simeq 0.8$ eV, the energy gain is around 40 K, in good agreement with the onset temperature of the ferromagnetic ordering along the chains.

In summary, we have identified a mechanism leading to a ferromagnetic coupling between magnetic ions through a non-magnetic one. The driving forces are i) the Hund’s rule coupling on the non-magnetic ion, and ii) the large number of contributions to the magnetic energy due to the $R3c$ structure. The magnetic coupling is found to be in good agreement with experiment.

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