# Experimental Magnetic Form Factors in $Co_3V_2O_8$: A Combined Study of *Ab Initio* Calculations, Polarized Neutron Diffraction and Magnetic Compton Scattering

A detailed study combining first principles calculations, magnetic Compton scattering (MCS) and polarized neutron diffraction (PND) has been carried out leading to new insights into the magnetic properties of the kagome staircase structure $Co_3V_2O_8$. *Ab initio* wave functions obtained by cluster calculations yield a theoretical model for analyzing the real space magnetization and momentum space spin density simultaneously. The two crystallographically inequivalent Co ions on the cross-tie ($Co_c$) and spine sites ($Co_s$) reveal significantly different magnetic moments in the zero-field ferromagnetic structure, which do not saturate by applying an external magnetic field along the easy axis *a*. The increased bulk magnetization has been found on the V and O sites leading to a clarification of the superexchange and super-superexchange pathways in this system. From the Co3*d* orbital occupation a covalent character could be deduced for the cross-tie site giving a reasonable explanation for its relatively weak magnetic moment.

$Co_3V_2O_8$ represents the 3*d* transition metal ortho-oxo-vanadates labeled as kagome staircase structures and crystallizes in the orthorhombic space group Cmca [1]. Its crystallographic structure is characterized by edge-sharing $CoO_6$ octahedra forming buckled layers of corner-sharing triangles, the kagome staircases, which are separated along the *b* axis by $VO_4$ tetrahedra. The magnetic exchange is mainly effectuated by a 90° Co-O-Co intralayer pathway. The ferromagnetic structure reveals two strongly different magnetic moments for the $Co_c$ and $Co_s$ of 1.54 $\mu_B$ and 2.73 $\mu_B$ respectively [2], despite the fact that both $Co^{2+}$ ions apparently present high-spin configurations as macroscopic measurements exhibit saturation of the cross-tie moments [3]. In the kagome staircase structure several nearest and next-nearest neighbor exchange interaction pathways are possible. Investigating the magnetization density, which is reflected by the respective magnetic form factors of the ions, may reveal preferred exchange pathways with the presence of magnetization on the involved O sites. Eventual induced magnetization on the empty *d*-shell of V sites would allow interlayer coupling by super-superexchange. Therefore, MCS and PND experiments have been carried out leading to the spin density in momentum space and the magnetization density in real space, respectively.

However, detailed and precise analysis of these quantities are required in order to determine the exact contribution of the atomic species involved in the studied system. In this context, density functional (DFT) based electronic structure calculations are carried out in order to get better understanding and newer insights into the observed phenomena.

*Ab initio* wave functions have been derived by hybrid DFT-based quantum chemical cluster calculations for the two different $CoO_6$ clusters. These were used to build up a theoretical model able to be refined to the real and momentum space quantities at the same time. Such a correlated refinement is possible as the unpaired electron density must be reflected in a similar way in real space as well as in momentum space. The fact that the MCS technique probes only the spin part of the magnetic moment has been handled by refining the size of the magnetic moment only on the PND data; the magnetic Compton profiles (MCP), which are depicted in Fig. 1, have been normalized and analyzed concerning their line shape. In doing so the occupation of the molecular orbitals relevant to the Co3*d* and the magnetic moments of all involved species could be derived. The sum of the obtained magnetic moments within

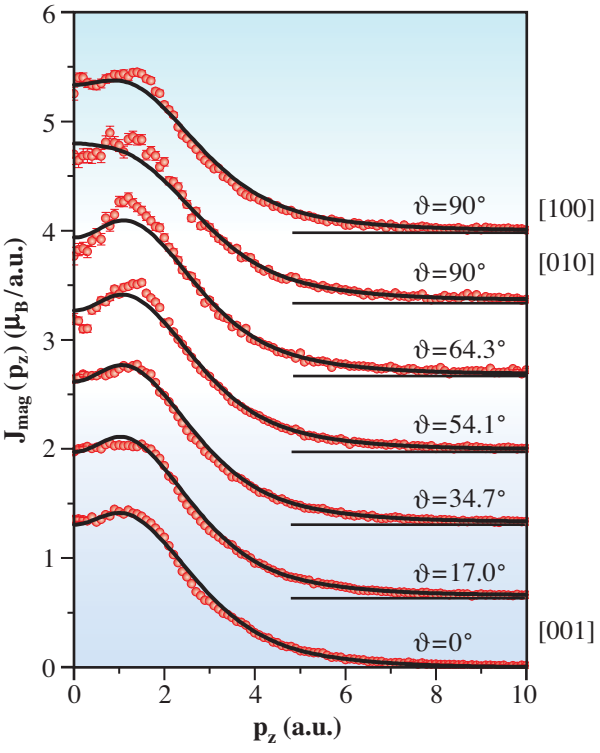


Fig. 1. Observed (dots) and calculated (solid lines) MCPs yielding the projection of the momentum spin density onto different scattering vectors.

the unit cell is in good agreement with macroscopic measurements [3]. Astonishingly the Co magnetic moments do not saturate, but remarkable induced magnetization can be found on the V and O sites which can be seen in Fig. 2 ($\mu(Co_c)$=1.54 $\mu_B$, $\mu(Co_s)$=2.87 $\mu_B$, $\mu$(V)=0.41 $\mu_B$, $\mu$(O1)= 0.05 $\mu_B$, $\mu$(O2)=0.35 $\mu_B$, $\mu$(O3)=0.36 $\mu_B$). The unpaired electron density has been found to be equally distributed between the $t_g$ and $e_{2g}$ levels for $Co_s$, but in the case of $Co_c$ only 30% of the magnetic signal stems from the $e_{2g}$ orbitals. Therefore the conclusion can be drawn that covalence, as a consequence of the spin transfer from the surrounding O2 and O3 ions, is the reason for the reduced magnetic moment of the cross-tie Co ions. Furthermore, from the individual orbital occupations it could be deduced that the preferred superexchange interaction pathways are $Co_s$-O2-$Co_s$ and $Co_c$-O3-$Co_s$ [4].

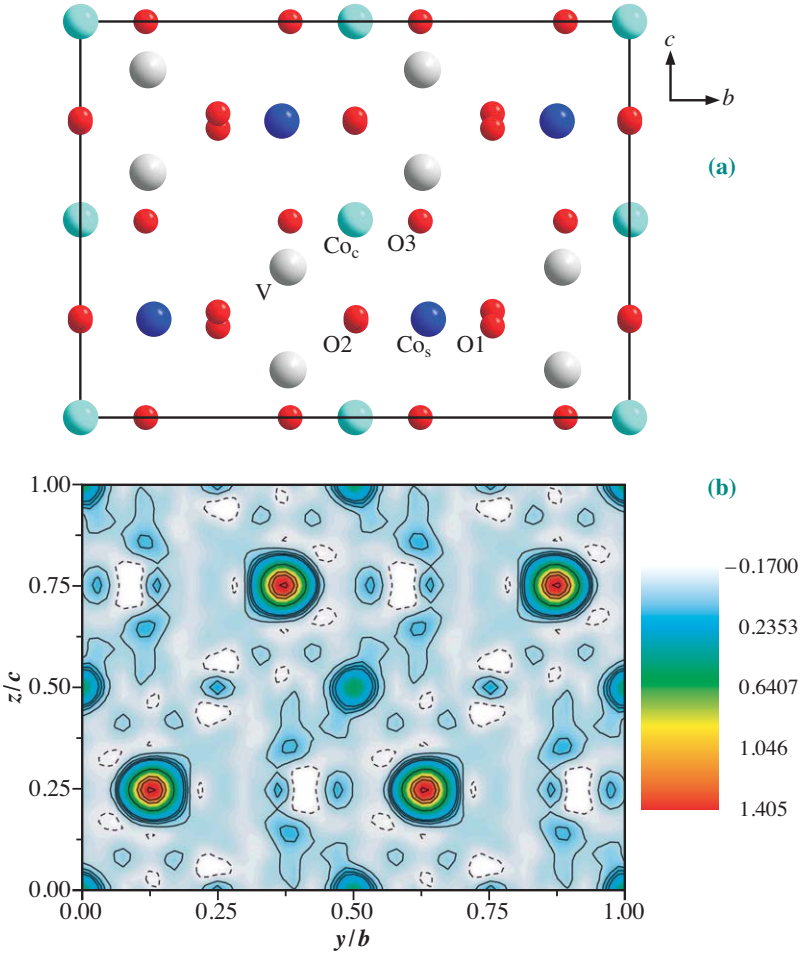


Fig. 2. Crystal structure (upper panel **(a)**) and calculated magnetization density (lower panel **(b)**) as a projection onto the *b*-*c* plane.

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**References**

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