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Supporting information for article:

First spin-resolved electron distributions in crystals from combined polarized neutron and X-ray diffraction experiments

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The detailed classical treatment of the orbital contribution may be found in [Gillon & Becker, 2012], page 287.

In the independent atom model, the magnetic structure factor of scattering vector **Q** is written as a sum over the atoms i in the cell:

$$F_M\left(\vec{Q}\right) = \sum_i^{atoms} m_i f_m^i\left(\vec{Q}\right) e^{i\vec{Q}\vec{R}_i} e^{-W_i}$$

where $f_m^i\left(\vec{Q}\right)$ is the magnetic form factor of atom i which carries a magnetic moment m_i.

In the case of weak spin-orbit coupling, like for a transition metal atom i, the form factor may be written as the sum of a pure spin form factor $f_m^{iS}\left(\vec{Q}\right)$ and a form factor $f_m^{iL}\left(\vec{Q}\right)$ due to the orbital contribution. The magnetic structure factor is then the sum of a pure spin magnetic structure factor $F_M^S\left(\vec{Q}\right)$ and an orbital structure factor $F_M^L\left(\vec{Q}\right)$:

$$F_M\left(\vec{Q}\right) = F_M^S\left(\vec{Q}\right) + F_M^L\left(\vec{Q}\right)$$

The term $F_M^L\left(\vec{Q}\right)$ may be treated as a correction and is taken into account in the theoretical expression of the flipping ratio in the program MOLLYNX.

As described in reference [Squires, 1978] the usual dipole approximation consists in writing the above form factor as:

$$f_m^{iL}\left(\vec{Q}\right) = m_S^i \frac{\left(g_i - 2\right)}{g_i}\left(\left\langle j_0^i\right\rangle + \left\langle j_2^i\right\rangle\right)$$

where m^i_S is the magnetic moment of atom i associated with spin, g_i is the Landé splitting factor of atom i and $\left\langle j_\ell^i\left(Q\right)\right\rangle$ are the radial integrals for atom i:

$$\left\langle j_\ell^i\left(Q\right)\right\rangle = \int_0^\infty r^2\left(\mathcal{N} r_i^{N-1} e^{-\xi_L^i r_i}\right)^2 j_\ell^i(Qr)dr$$

where $\left(\mathcal{N} r_i^{N-1} e^{-\xi_L^i r_i}\right)$ is a Slater type radial function with exponent ξ^i_L for the unpaired electron orbital belonging to the atomic shell with quantum numbers N and L and $j_\ell^i\left(Qr\right)$ are the spherical Bessel functions of order ℓ = 0, 2 which are tabulated for the 3d elements in [Brown, 1992].

The orbital magnetic structure factors $F_M^L\left(\vec{Q}\right)$ were calculated using the magnetic form factor $\left(\left\langle j_0\right\rangle + \left\langle j_2\right\rangle\right)$ for Cu^{2+} and a coefficient:

$$m_S^{Cu}\frac{\left(g_{Cu} - 2\right)}{g_{Cu}} = 0.07\mu_B$$

with $m_S^{Cu} = 0.7\mu_B$ and $g_{Cu} = 2.175$ [Aronica, 2007]. This estimation was confirmed by refinement of the valence population associated with the orbital form factor introduced in the PND-only refinement.

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