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 $\mathbf{Q}$ is written as a sum over the atoms $i$ in the cell:

$$F_M(\mathbf{Q}) = \sum_{\text{atoms}} m_i f_m^i(\mathbf{Q}) e^{i\mathbf{Q} \cdot \mathbf{R}_i} e^{-W_i}$$

where $f_m^i(\mathbf{Q})$ 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 $f_m^{iS}(\mathbf{Q})$ and a form factor $f_m^{iL}(\mathbf{Q})$ due to the orbital contribution. The magnetic structure factor is then the sum of a pure spin magnetic structure factor $F_M^{iS}(\mathbf{Q})$ and an orbital structure factor $F_M^{iL}(\mathbf{Q})$:

$$F_M(\mathbf{Q}) = F_M^{iS}(\mathbf{Q}) + F_M^{iL}(\mathbf{Q})$$

The term $F_M^{iL}(\mathbf{Q})$ 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:

$$f_m^{iL}(\mathbf{Q}) = m_s(I_s - 2) g_i \left(\langle j^1_0 \rangle + \langle j^1_2 \rangle\right)$$

where $m_s(I_s)$ is the magnetic moment of atom $i$ associated with spin, $g_i$ is the Landé splitting factor of atom $i$ and $\langle j^\ell_0 \rangle$ and $\langle j^\ell_2 \rangle$ are the radial integrals for atom $i$:

$$\langle j^\ell_0 \rangle = \int_0^{\infty} r^2 \left(\mathcal{N}_i^{N_L} e^{-\xi_L r} \right)^2 j^\ell_0(Qr) dr$$

where $\left(\mathcal{N}_i^{N_L} e^{-\xi_L r}\right)$ is a Slater type radial function with exponent $\xi_L$ for the unpaired electron orbital belonging to the atomic shell with quantum numbers $N$ and $L$ and $j^\ell_0(Qr)$ are the spherical Bessel functions of order $\ell = 0, 2$ which are tabulated for the 3d elements in [Brown, 1992].

The orbital magnetic structure factors $F_M^{iL}(\mathbf{Q})$ were calculated using the magnetic form factor $\left(\langle j^1_0 \rangle + \langle j^1_2 \rangle\right)$ for Cu\(^{2+}\) and a coefficient:

$$m_s Cu \left(\frac{g_{Cu} - 2}{g_{Cu}}\right) = 0.07 \mu_B$$
with $m^*_S = 0.7 \mu_B$ 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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