

Calculation of Atomic Charge- Moment- and Current densities using McPhase, a versatile modelling suite for Magnetic Neutron Scattering

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2011 J. Phys.: Conf. Ser. 325 012005

(<http://iopscience.iop.org/1742-6596/325/1/012005>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 156.35.192.3

This content was downloaded on 17/03/2015 at 08:42

Please note that [terms and conditions apply](#).

Calculation of Atomic Charge- Moment- and Current densities using McPhase, a versatile modelling suite for Magnetic Neutron Scattering

M. Rotter^{1,2}, M. D. Le³, H. Lewtas¹, A. T. Boothroyd¹, J.A. Blanco⁴, R. Hammerling⁵

¹University of Oxford, Dep. of Physics, Clarendon Lab., Parks Road, Oxford OX1 3PU, U.K

²Max Planck Institute for Chemical Physics of Solids, Nöthnitzer Str. 40, D-01187, Dresden, Germany

³HZB für Materialien und Energie, Hahn-Meitner-Platz 1, D-14109, Berlin, Germany

⁴Departamento de Física, Universidad de Oviedo, Calvo Sotelo s/n, 33007 Oviedo, Spain

⁵Vienna University of Technology, CCMS, Gusshausstr. 25-25a, A-1040 Wien, Austria

E-mail: martin.rotter@cpfs.mpg.de

Abstract. Information on the anisotropy of the atomic magnetic moment density can be obtained from neutron scattering. Within the dipole approximation the effect of the anisotropy is usually neglected. We show how the anisotropy of the charge-, spin-, orbital moment and current densities of an unfilled shell can be calculated. The theoretical formulae have been implemented in the McPhase software suite. We illustrate the theory for some representative examples of different magnetic ions in an idealized crystal field. Moreover, we also evaluate the various densities for some real systems.

1. Introduction

Neutron scattering techniques are mainstays of many aspects of the science of materials. In contrast to the information provided by bulk measurements such as specific heat, magnetisation, magnetic susceptibility,..., neutron scattering is able to probe directly both the electronic wave functions and energy levels of the systems. In this way, the interplay of long-range interactions and anisotropy has been at the focal point of research in magnetism for decades. Complex magnetic properties are frequently observed and studied in experiment and theory. Numerical computations have become an important tool in order to interpret data and evaluate models. In the past decade joint efforts led to the development of a new modelling software suite: McPhase [1] is a program package designed to calculate properties of a magnetic system with localized magnetic moments given the crystal field and/or the two-ion interaction constants. In particular, calculations can be efficiently performed within the standard model of rare earth magnetism [2]. Alternatively, a more complex Hamiltonian can be used which includes all terms in intermediate coupling - this is important for transition metal and actinide ions. Anisotropic and high-order (such as biquadratic or orbital) two-ion interactions may be included in the mean field analysis. Excitations can be calculated by evaluating the dynamical susceptibility within the random phase approximation, a special DMD (dynamical matrix diagonalisation) technique [3] has been developed to do such calculations with high speed. McPhase is designed to output various

physical observables, such as magnetisation, magnetic contribution to the specific heat, thermal expansion and magnetostriction, among other. Apart from that, magnetic phase diagrams may also be generated and magnetic structures can be visualized; resonant magnetic X-ray scattering intensities may be computed. Moreover, the package allows the user to evaluate quantitatively the elastic and the inelastic magnetic neutron scattering cross section that may then be compared to experimental diffraction patterns and spectra. Model parameters can be fitted simultaneously to the different types of experimental data.

The magnetic neutron scattering cross section depends in a fundamental way on the magnetisation density. In this article we will describe in detail the calculation of the charge- and spin density of the unfilled shell. Moreover, the gauge problem of the orbital moment density will be discussed and an expression for the orbital current density is given. The calculation of these quantities is illustrated for some rare earth and transition metal ions.

2. Formalism

The contribution to the charge density of the electrons in an unfilled shell may be calculated as a multipole expansion of the wavefunction¹, giving,

$$\langle \hat{\rho}(\mathbf{r}) \rangle = -|e||R(r)|^2 \sum_{k,q} Z_{kq}(\Omega) \langle \sum_{i=1}^n Z_{kq}(\Omega_i) \rangle \quad (1)$$

Here e is the elementary charge and $R(r)$ is the radial wavefunction of the l -electrons ($l = s, p, d, f$) in the l^n configuration. The radial wavefunction may be determined for example by Dirac-Fock calculations. The Z_{kq} are the tesseral harmonic functions which are Hermitian combinations of spherical harmonics Y_{kq} .

$$Z_{k0} = Y_{k0}, \quad Z_{k,\pm|q|} = \frac{\pm 1}{\sqrt{\pm 2}} \left[Y_{k,-|q|} \pm (-1)^{|q|} Y_{k,|q|} \right] \quad (2)$$

One can use the tensor operator methods of Racah [4] (and references therein) to determine the matrix elements of operators which act in the same way as the spherical harmonic (or tesseral harmonic) functions. Defining the operator \hat{T}_{kq} to be equivalent to the tesseral harmonics Z_{kq} , we have,

$$\langle \hat{\rho}(\mathbf{r}) \rangle = -|e||R(r)|^2 \sum_{k,q} Z_{kq}(\Omega) \sqrt{\frac{2k+1}{4\pi}} \langle \hat{T}_{kq} \rangle \quad (3)$$

where the normalisation factor $\sqrt{\frac{2k+1}{4\pi}}$ is needed because of the definitions of \hat{T}_{kq} ,

$$\hat{T}_{k0} = \hat{C}_{k0}, \quad \hat{T}_{k,\pm|q|} = \frac{\pm 1}{\sqrt{\pm 2}} \left[\hat{C}_{k,-|q|} \pm (-1)^{|q|} \hat{C}_{k,|q|} \right] \quad (4)$$

where \hat{C}_{kq} are operators which transform in the same way as the functions $\sqrt{\frac{4\pi}{2k+1}} Y_{kq}(\theta, \phi)$. Using $3j$ and $6j$ symbols and fractional parentage coefficients the matrix elements of \hat{C}_{kq} can be written as [5].

$$\begin{aligned} \langle \Theta J m_J | \hat{C}_{kq} | \Theta' J' m'_J \rangle &= (-1)^{J-m_J} \begin{pmatrix} J' & k & J \\ -m_J & q & m'_J \end{pmatrix} \langle l | \hat{c}_k | l \rangle n \sum_{\bar{\Theta}} (\Theta | \bar{\Theta}) (\Theta' | \bar{\Theta}) \\ &\times (-1)^{\bar{L}+L+k+l} ([L][L'])^{\frac{1}{2}} \begin{Bmatrix} L' & k & L \\ l & \bar{L} & l \end{Bmatrix} (-1)^{S+L+k+J} ([J][J'])^{\frac{1}{2}} \begin{Bmatrix} J' & k & J \\ L & S & L' \end{Bmatrix} \end{aligned} \quad (5)$$

¹ see also www.mcphase.de, manual

The single electron matrix element is,

$$\langle l|\hat{c}_k|l\rangle = (-1)^l(2l+1) \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix} \quad (6)$$

Using the equations above the thermal expectation values of the physical quantities (scalar, vectors or, more general tensor operators) can be evaluated for any eigenstate of the Hamiltonian and for example the charge density can be computed using equation (3).

A similar procedure can be adopted for the spin and orbital magnetisation densities, which we write as [6]

$$\hat{M}_S(\mathbf{r}) = \sum_{kq} \hat{s}_{kq} |R(r)|^2 Z_{kq}(\Omega) \quad (7)$$

$$\hat{M}_L(\mathbf{r}) = \sum_{kq} \hat{a}_{kq} F(r) Z_{kq}(\Omega) \quad \text{with} \quad F(r) = \frac{1}{r} \int_r^\infty |R(\xi)|^2 d\xi \quad (8)$$

The vectors \hat{s}_{kq} and \hat{a}_{kq} are given by

$$\hat{s}_{k0} = \hat{\sigma}_{k0}, \quad \hat{s}_{k,\pm|q|} = \frac{1}{\sqrt{\pm 2}} \left[\hat{\sigma}_{k,-|q|} \pm (-1)^{|q|} \hat{\sigma}_{k,|q|} \right] \quad (9)$$

$$\hat{a}_{k0} = \hat{\alpha}_{k0}, \quad \hat{a}_{k,\pm|q|} = \frac{1}{\sqrt{\pm 2}} \left[\hat{\alpha}_{k,-|q|} \pm (-1)^{|q|} \hat{\alpha}_{k,|q|} \right] \quad (10)$$

The matrix elements of the spherical components $\hat{\sigma}_{kq}^Q$ and $\hat{\alpha}_{kq}^Q$ ($Q = -1, 0, +1$)² of the vector operators $\hat{\sigma}_{kq}$ and $\hat{\alpha}_{kq}$ are given by [6]

$$\begin{aligned} \langle \Theta J m_J | \hat{\sigma}_{kq}^Q | \Theta' J' m'_J \rangle &= -\frac{2\mu_B}{\sqrt{4\pi}} \sum_{k'q'} (-1)^{\frac{1}{2}+m_J+Q-J'+L'+S'} \sqrt{\frac{3}{2}} [l][k']([k][S][S'][L][L'][J][J'])^{\frac{1}{2}} \\ &\times \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} 1 & k & k' \\ S' & L' & J' \\ S & L & J \end{matrix} \right\} n \Sigma_{\bar{\Theta}}(\Theta\{|\bar{\Theta}\})(\Theta'\{|\bar{\Theta}\})(-1)^{\bar{S}+\bar{L}} \\ &\times \left\{ \begin{matrix} S & 1 & S' \\ \frac{1}{2} & S & \frac{1}{2} \end{matrix} \right\} \left\{ \begin{matrix} L & k & L' \\ l & L & l \end{matrix} \right\} \begin{pmatrix} J & k' & J' \\ -m_J & q' & m'_J \end{pmatrix} \begin{pmatrix} k & k' & 1 \\ q & q' & -Q \end{pmatrix} \end{aligned} \quad (11)$$

and

$$\begin{aligned} \langle \Theta J m_J | \hat{\alpha}_{kq}^Q | \Theta' J' m'_J \rangle &= -\frac{2\mu_B}{\sqrt{4\pi}} \sum_{k'q'} (-1)^{Q+m_J+L'+L'+S} \delta_{SS'} [l]^{\frac{3}{2}} ([J][J'][L][L'][k])^{\frac{1}{2}} [k'] [l(l+1)]^{\frac{1}{2}} \\ &\times \begin{pmatrix} l & k & l \\ 0 & 0 & 0 \end{pmatrix} \left\{ \begin{matrix} l & k' & l \\ k & l & 1 \end{matrix} \right\} \left\{ \begin{matrix} k' & L' & L \\ S & J & J' \end{matrix} \right\} n \Sigma_{\bar{\Theta}}(\Theta\{|\bar{\Theta}\})(\Theta'\{|\bar{\Theta}\})(-1)^{\bar{L}} \\ &\times \left\{ \begin{matrix} k' & l & l \\ \bar{L} & L & L' \end{matrix} \right\} \begin{pmatrix} J & k' & J' \\ -m_J & q' & m'_J \end{pmatrix} \begin{pmatrix} k & k' & 1 \\ q & q' & -Q \end{pmatrix} \end{aligned} \quad (12)$$

² cartesian components can be calculated e.g. $\sigma^{x,y} = \frac{\pm 1}{\sqrt{\pm 2}}(\sigma^{-1} \mp \sigma^{+1}), \sigma^z = \sigma^0$.

Note that the orbital magnetisation density $\mathbf{M}_L(\mathbf{r})$ is not unique, expression (8) corresponds to the Trammel gauge [6, 7]. This gauge has the advantage of leading to a very localised magnetisation density. However, the singularity at $r = 0$ is inconvenient and misleading. A unique quantity describing the orbital magnetism is the orbital current density. Using the expression (8) and applying $\hat{\mathbf{j}}(\mathbf{r}) = \nabla \times \hat{\mathbf{M}}_L(\mathbf{r})$ we find the following expression for the orbital current density operator $\hat{\mathbf{j}}(\mathbf{r})$:

$$\hat{\mathbf{j}}(\mathbf{r}) = \frac{1}{r} \sum_{kq} [\hat{\mathbf{b}}_{kq}(\Omega) R^2(r) + \hat{\mathbf{d}}_{kq}(\Omega) F(r)] Z_{kq}(\Omega) \quad (13)$$

$$\hat{\mathbf{b}}_{kq}(\Omega) = \hat{\mathbf{a}}_{kq} \times \mathbf{J}^r \quad (14)$$

$$\hat{\mathbf{d}}_{kq}(\Omega) = \hat{\mathbf{b}}_{kq}(\Omega) - q \hat{\mathbf{a}}_{k,-q} \times (r\mathbf{J}^\phi) - |q| \cot \theta \hat{\mathbf{a}}_{kq} \times (r\mathbf{J}^\theta) + \hat{\mathbf{f}}_{kq}(\Omega) \quad (15)$$

$$(16)$$

Here $\mathbf{J}^r, \mathbf{J}^\theta, \mathbf{J}^\phi$ are the three vectors of the Jacobi Matrix for spherical coordinates

$$(\mathbf{J}^r, \mathbf{J}^\theta, \mathbf{J}^\phi) = \begin{pmatrix} \sin \theta \cos \varphi & \cos \theta \cos \varphi / r & -\sin \varphi / r \sin \theta \\ \sin \theta \sin \varphi & \cos \theta \sin \varphi / r & \cos \varphi / r \sin \theta \\ \cos \theta & -\sin \theta / r & 0 \end{pmatrix} \quad (17)$$

The vectors $\hat{\mathbf{f}}_{kq}(\Omega)$ are

$$\begin{aligned} \hat{\mathbf{f}}_{kq}(\Omega) &= & (18) \\ q < -1 : &= \sqrt{l(l+1) - m(m+1)} [\cos \varphi \hat{\mathbf{a}}_{k,q+1} + \sin \varphi \hat{\mathbf{a}}_{k,-q-1}] \times (r\mathbf{J}^\theta) \\ q = -1 : &= \sqrt{\frac{l(l+1)}{2}} \sin \varphi \hat{\mathbf{a}}_{k,0} \times (r\mathbf{J}^\theta) \\ q = 0 : &= 0 \\ q = +1 : &= \sqrt{\frac{l(l+1)}{2}} \cos \varphi \hat{\mathbf{a}}_{k,0} \times (r\mathbf{J}^\theta) \\ q > +1 : &= \sqrt{l(l+1) - m(m-1)} [\cos \varphi \hat{\mathbf{a}}_{k,q-1} - \sin \varphi \hat{\mathbf{a}}_{k,-q+1}] \times (r\mathbf{J}^\theta) \end{aligned}$$

In figure 1 we show the Charge-, Spin-, Orbital Moment- and Current densities for some tripositive Rare Earth ions. All ions are subjected to the same octahedral crystal field. Most anisotropy in the charge density is seen for the light rare earth, filling the shell makes the charge density more spherical. The spin density is most spherical for a half filled shell and gets more anisotropic for nearly empty and filled $4f$ shell. This effect can be understood by noting that the orbital moment is zero for a half filled shell and that for more than half filled shell the spin density can be interpreted as the spin density of holes in the $4f$ shell. Therefore the form of the spin density surface shown in figure 1 for the heavy rare earths resembles that of a positive charge being attracted by the negative point charges, which generate the crystal field. Similar properties are also exhibited by the the orbital magnetic moment density calculated in the Trammel gauge. In the following we show calculations for real systems.

3. PrNi₂Si₂

For many materials, amplitude-modulated (AM) structures are stable only just below the corresponding magnetic transition temperature, T_N , with the low- T phase having equal-moment

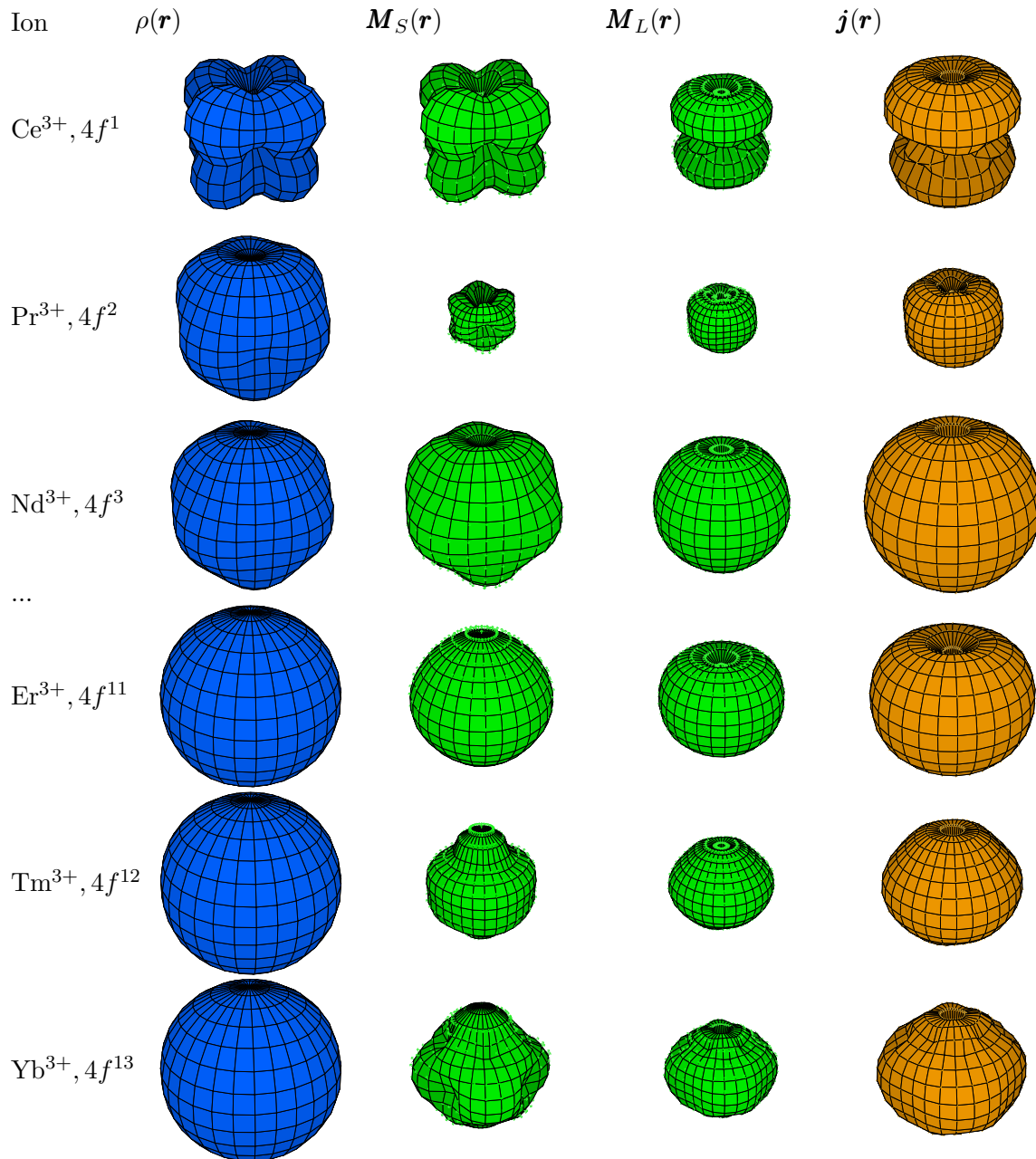


Figure 1. (from left to right) Surfaces of constant Charge-, Spin-, Orbital Moment- and Current densities for some tripositive Rare Earth ions in the same octahedral crystal field produced by point charges of $-2|e|$ in a distance of 0.2 nm. Spin-, Orbital Moment- and Current densities are calculated for a magnetic field of 10 Tesla along the z axis.

amplitudes. In contrast, the body-centered tetragonal rare-earth intermetallic compound PrNi₂Si₂ has attracted interest in this context, as it represents one of the few examples in nature where the AM magnetic structure is stable down to zero temperature, as was recently shown by single-crystal neutron diffraction [8]. The existence of a singlet crystal-field ground state in PrNi₂Si₂ that is coupled to the excited levels is responsible for the AM ordered magnetic moment, which is confined to be along the *c*-axis due to single-ion anisotropy. For these reasons, the amplitude modulated spin structure and dynamics in PrNi₂Si₂ has been subject of intensive

investigations [8]. Fig. 2 shows the spin-, orbital moment- and total magnetic moment densities. Both the spin density (spin moment= $-1.3 \mu_B$) and the orbital moment density (orbital moment= $4.0 \mu_B$) alone do not show a large deviation from spherical symmetry. There is a partial compensation of orbital and spin density leading to a more anisotropic total moment density. The Fourier Transform $\mathbf{M}_d(Q)$ of this total moment density enters the magnetic structure factor F_M , which is used to model neutron diffraction pattern [9]:

$$F_M = \sum_d \mathbf{Q} \times \{ \mathbf{M}_d(\mathbf{Q}) \times \mathbf{Q} \} / Q^2 \exp(i\mathbf{Q} \cdot \mathbf{R}_d) \exp(-W_d) \quad (19)$$

The summation is over the ions indexed by d in the magnetic unit cell, with displacements \mathbf{R}_d from the origin. The scattering vector is denoted by \mathbf{Q} , with $Q = |\mathbf{Q}|$ and $\exp(-W_d)$ is the Debye-Waller factor.

In the dipole approximation, $\mathbf{M}_d(Q)$ may be separated into a product of a magnetic form factor $f_{\text{dip}}(Q)$, which is a scalar function of Q , and the thermal expectation value of the magnetic moment \mathbf{m}_d of the ion:

$$\mathbf{M}_d(Q \rightarrow 0) \sim f_{\text{dip}}(Q) \mathbf{m}_d \quad (20)$$

In fig. 3 the neutron intensity calculated in dipole approximation is compared to the full calculation. Corrections are significant for larger Q .

4. The high Tc superconductor NdBa₂Cu₃O₇

In this material neglecting the anisotropy of the moment density has led to a misinterpretation of the neutron diffraction intensity [9]. Fig. 2 shows the spin-, orbital moment- and total magnetic moment densities. Both the spin density (spin moment= $-0.46 \mu_B$) and the orbital moment density (orbital moment= $1.17 \mu_B$) alone do not show a large deviation from spherical symmetry. However, also in this material there is a partial compensation of orbital and spin density leading to a more anisotropic total moment density. This anisotropy is huge and has to be considered in the calculation of the elastic neutron scattering cross section in order to obtain a reliable fit of the magnetic structure [9] (compare fig. 3).

5. Crystal Field effects in multiferroic LuMnO₃

In this hexagonal system the Mn³⁺ occupy the 6c positions in the space group $P6_3cm$ (Nr. 185). The local point group symmetry is $m(C_S)$: this implies that all crystal field parameters L_k^q with odd q are zero (provided that the local z -axis is chosen normal to the mirror plane). The crystal field parameters have been calculated by applying the point charge model (with $-2|e|$ at every oxygen neighbour). Fig. 4 shows the oxygen neighbours and the charge density of the Mn³⁺ ($3d^4$) and, furthermore, the spin-, orbital moment-, current- and total magnetic moment densities. As expected for a nearly half filled shell, these quantities are not very anisotropic. The orbital moment ($-0.2 \mu_B$) is nearly quenched by the crystal field and thus much smaller than the spin moment ($4.0 \mu_B$).

6. Final remarks

All this information can be easily checked using neutron scattering with polarization analysis, because this technique is a versatile tool for identifying spin-dependent scattering processes in magnetic materials. In fact, polarized neutron scattering is a useful application for the separation of the nuclear (phonons) and magnetic Bragg (magnons) scattering. The spin density as well as the composition of the electronic wave functions can be obtained from the analysis of the elastic and inelastic neutron cross-section.

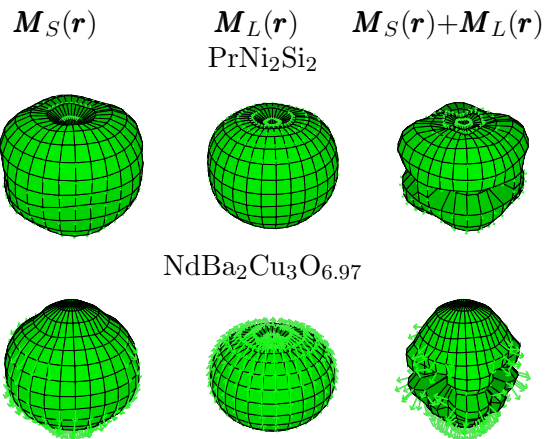


Figure 2. (from left to right) Surfaces of constant Spin-, Orbital Moment- and Total Magnetic Moment densities for PrNi_2Si_2 (top) $\text{NdBa}_2\text{Cu}_3\text{O}_7$ (bottom) at $T=2$ K.

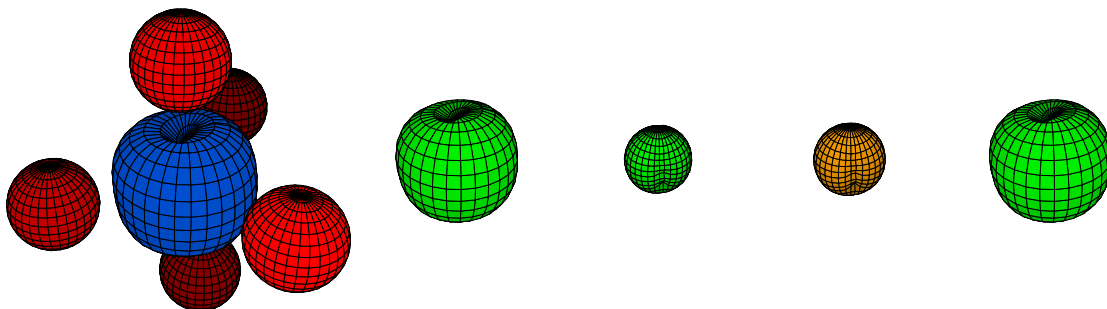


Figure 4. (from left to right) Surfaces of constant 3d Charge-, Spin-, Orbital Moment-, Current- and Total Magnetic Moment densities for LuMnO_3 at $T = 2$ K.

Acknowledgments

The authors thank the Royal Society and the EPSRC. We are grateful to P. Fabi, T. Hoffmann and S. Rotter for their contributions to McPhase. We thank the authors of Cfield, Powls, FullProf, Spectre and Amos, output of these programs has been used to test McPhase. Without the enthusiastic support of the neutron scattering community this program would not have come into existence. In particular we are thankful to B. Fak, E. Ressouche and to S. Lovesey for the inspiring discussions. JAB thanks FEDER and Spanish MICINN for financial support under project MAT2008-06542-C04-03. RH acknowledges funding by the City of Vienna Science and Technology Fund (WWTF) via the project *Mathematik und 2007*.

References

- [1] Rotter M 2004 *J. Magn. Mag. Mat.* **272-276** e481–e482
- [2] Jensen J and Mackintosh A R 1991 *Rare Earth Magnetism* (Clarendon Press Oxford)
- [3] Rotter M 2006 *Comp. Mat. Sci.* **38** 400–404
- [4] Racah G 1949 *Phys. Rev.* **76** 1352–1365

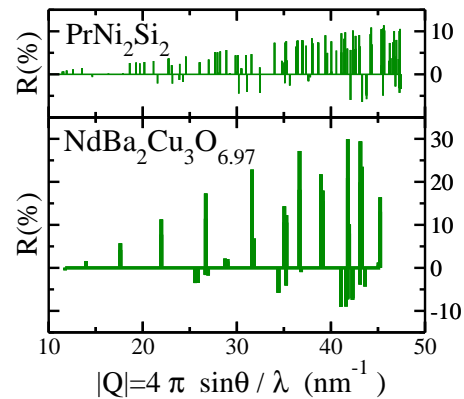


Figure 3. Magnetic Bragg peak intensities for PrNi_2Si_2 and $\text{NdBa}_2\text{Cu}_3\text{O}_{6.97}$ calculated (i) using the Fourier transform of the magnetisation density (19) in comparison to (ii) the dipole approximation (20). The figure shows deviations between the exact calculation and dipole approximation expressed as $R = 100(|F_M^{\text{exact}}|^2 - |F_M^{\text{dip}}|^2)/|F_M^{\text{dip}}|^2$

- [5] Elliot J P, Judd B R and Runciman W A 1957 *Proc. R. Soc. Lon. A* **240** 509–523
- [6] Balcar E 1975 *J.Phys. C: Solid State Phys.* **8** 1581
- [7] Trammel G T 1953 *Phys. Rev. B* **92** 1387
- [8] Blanco J A, Fak B, Ressouce E, Grenier B, Rotter M, Schmitt D, Rodriguez-Velamazán J A, Campo J and Lejay P 2010 *Phys. Rev. B* **82** 54414
- [9] Rotter M and Boothroyd A T 2009 *Phys. Rev. B* **79** 140405(R)