Anomalous spin density distribution on oxygen and Ru in Ca$_{1.5}$Sr$_{0.5}$RuO$_4$: A polarised neutron diffraction study

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By means of polarized neutron diffraction in a magnetic field of 7.0 T at 1.6 K an anomalously large magnetization density is observed on the in-plane oxygen in Ca$_{1.5}$Sr$_{0.5}$RuO$_4$. Field-induced moments of different ions are determined by refinement on the flipping ratios, yielding $\mu_{Ru} = 0.346(11)\ \mu_B$, $\mu_O = 0.076(6)\ \mu_B$ and $\mu_{O2} = 0.009(6)\ \mu_B$. The moment on the oxygen arises from the strong hybridization between the Ru-4d and O-2p orbitals. The maximum entropy magnetization density reconstruction reveals a strongly anisotropic density at the Ru site, consistent with the distribution of the $xy$ ($t_{2g}$ band) $d$-orbitals.

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Layered perovskite ruthenates have attracted considerable interest because of their magnetic properties and in particular because of the recent discovery of superconductivity in Sr$_2$RuO$_4$[1]. It is now widely accepted that superconductivity in this compound is unconventional and the pairing of triplet $p$-wave symmetry. Sr$_2$RuO$_4$ does not exhibit any magnetic ordering, but among the related compounds with a Ru$^{4+}$-ion various magnetic structures are observed: ferromagnetic order occurs in the metallic perovskite SrRuO$_3$[2], antiferromagnetic one in insulating Ca$_2$RuO$_4$[3] and incommensurate order in Sr$_2$RuO$_{0.91}$Ti$_{0.09}$O$_4$[4].

According to the band-structure calculations, the Fermi-surface in Sr$_2$RuO$_4$ is formed by three bands associated with the three $t_{2g}$ Ru orbitals, $x^2-y^2$ and $xz$. Since 4$d$ ions generally have more extended $d$ orbitals than the corresponding 3$d$ ions, the 4$d$-oxides exhibit larger overlap and hybridization between the transition metal and O 2$p$ orbitals. As a result magnetism becomes more itinerant in character and there is stronger interplay between structural degrees of freedom, and the magnetic and electronic properties. Another important point is that in 3$d$ transition-metal systems, the strong crystal field interaction dominates over the spin-orbit interaction and consequently the orbital moment is quenched, $\mu_L = 0$, whereas, in layered ruthenates, much stronger spin-orbit effects may be anticipated, which should manifest themselves in the radial part of the Ru form factor.

The substitution of Sr by Ca in Sr$_2$RuO$_4$ leads to a complex phase diagram [3][6]. Already small concentrations of Ca give rise to appearance of a structural distortion characterized by the rotation of RuO$_6$-octahedra around the c-axis, which is accompanied by a strong increase of the low temperature magnetic susceptibility. For Sr-concentrations higher than 0.5 in Ca$_{2-x}$Sr$_x$RuO$_4$ additional distortions are observed characterized by a tilt of the octahedra around an in-plane axis. In contrast to the rotational distortion, the increase of the tilt leads to a decrease of the low temperature magnetic susceptibility. The critical point $x=0.5$, where the tilt distortion appears, corresponds to the maximum of the low temperature susceptibility. The susceptibility at this point is about 100 times larger than that of pure Sr$_2$RuO$_4$[6]. We choose this composition for our study, since the large susceptibility is favorable for the polarized neutron measurements.

Polarized neutron diffraction (PND) is a uniquely powerful tool to study the magnetization densities in crystals, due to the fact that it provides direct information about the 3D distribution of the magnetization throughout the unit cell. In favorable cases, PND further allows to determine the symmetry of occupied orbitals. The aim of the present work is two-fold: i) to check the presence of unpaired electron density on the ligands O1 (and O2) which the theory predicts to be anomalously high, and ii) to determine the radial part of the Ru magnetic form factor and possibly to establish the symmetry of Ru 4$d$ orbitals occupied by unpaired electrons.

Polarized neutron measurements were performed on the two-axis lifting-counter diffractometer 5C1 at the ORPHEE reactor, LLB CEA/Saclay, using a wavelength $\lambda = 0.845$ Å (Heusler alloy monochromator, polarization of the incident neutron beam $P_i = 0.91$). Higher-order contamination was suppressed to less than 0.01% by means of erbium filters. The flipping ratio (ratio between neutron spin-up and spin-down intensity) measurements provided the experimental data used in the subsequent magnetic moment refinement and in the magnetization reconstruction. The programs MAGLSQ and SORgam of the Cambridge Crystallography Subroutine Library[8] were used for least squares refinement on the flipping ratios and for the calculation of magnetic amplitudes, respectively.

A single crystal of Ca$_{1.5}$Sr$_{0.5}$RuO$_4$ was obtained by
Ca$_{1.5}$Sr$_{0.5}$RuO$_4$ crystalizes in the tetragonal $I4_1/acd$ structure, for which the oxygen octahedra are rotated around the $c$ axis with an opposite phase of rotation for the planes separated by 12.5 Å. The structural parameters of the Ca$_{1.5}$Sr$_{0.5}$RuO$_4$ crystal used in our experiment can be summarized as follows: $a=b=5.3$ Å, $c=25.0$ Å, Ru 8$a$ position, Ca(Sr) $16d$ $z=0.549$, O1 $16f$ $x=0.193$, O2 $16d$ $z=0.457$ (see [7] for details).

The temperature dependence of the magnetic susceptibility $\chi$ of our Ca$_{1.5}$Sr$_{0.5}$RuO$_4$ crystal was measured directly by means of PND in magnetic external fields of 1 T, 4 T and 7 T. For this purpose, the spin-up ($I^+$) and spin-down ($I^-$) intensities of the (004) reflection were collected as a function of temperature, and the difference $I^+ - I^-$ plotted versus temperature (see Fig. 1). This difference, $I^+ - I^- = 2P_0\chi HF_N$, where $F_N$ is the nuclear structure factor for the same reflection and $P_0$ the polarization of the incoming beam, is proportional to the Fourier component (004) of the wave-vector dependent susceptibility of the crystal. As seen from Fig. 1 and magnetization data, the susceptibility of Ca$_{1.5}$Sr$_{0.5}$RuO$_4$ increases strongly at low temperatures but the crystal remains paramagnetic down to 1.6 K; at 7 T the magnetization is near saturation.

Overall, two sets of polarized neutron flipping ratios were measured at 1.6 K. Regarding the first, a vertical magnetic field of 7 Tesla was applied parallel to the [110]-axis of the crystal and a total of 94 flipping ratios with $\sin \theta/\lambda < 0.6$ Å$^{-1}$. This yielded 53 independent reflections of which only a subset of 13 reflections has a pure oxygen contribution. (Note that oxygen atoms contribute to all the reflections since they occupy low symmetry $16f$ and $16e$ positions.) The second set consisted of 97 (34 independent and among them 13 pure oxygen reflections) flipping ratios also measured at 1.6 K, but with the magnetic field along the [001] direction.

The magnetic amplitudes of all measured reflections were obtained using the SORGAM [8] program, except for those containing a pure oxygen contribution. They are shown in Fig. 2 together with the theoretical magnetic form factor of Ru. (For convenience, the amplitudes were normalized by the geometrical structure factor of the Ru.) As seen from Fig. 2, the majority of measured magnetic amplitudes lie reasonably close to the theoretical curve. There are, however, a large number of reflections, especially those at low $Q$, for which the disagreement between experimental and theoretical values is very significant. A simple analysis shows that these are the reflections with a strong contribution of the O1 sub-lattice. Those amplitudes of 16 reflections containing a pure oxygen contribution ($h+k=2n+1$) were normalized by the geometrical structure factor of O1. The amplitudes calculated in such a way should be proportional to the oxygen form factor, if one neglects the aspherical part of Ru magnetic density. The comparison of experimental results (see inset in Fig. 2) with the solid line representing the theoretical form factor of oxygen shows that an additional moment of the order of 0.075 $\mu_B$ is present at the O1 site.

Further analysis of the measured flipping ratios was performed by refinement. The refinement of the first data set using the tetragonal group $I4_1/acd$ demonstrated clearly that there is a very large moment induced both on Ru and on O1. The moments induced by the field of 7 T were obtained as $\mu_{Ru} = 0.350(15)$ $\mu_B$, $\mu_{O1} = 0.076(8)$ $\mu_B$ and $\mu_{O2} = 0.014(8)$ $\mu_B$, with $\chi^2 = 1.87$ for 94 reflections. For comparison a model in which the oxygen moment is neglected gives $\mu_{Ru} = 0.33(15)$ $\mu_B$ and $\chi^2 = 10.2$. The refinement performed using only 13 pure oxygen reflections yields $\mu_{O1} = 0.072(12)$. The refinement of the second data set with the applied magnetic field parallel to the [001] direction gives a very similar
result $\mu_{Ru} = 0.342(15)\ \mu_B$, $\mu_{O1} = 0.076(8)\ \mu_B$ and $\mu_{O2} = 0.009(6)\ \mu_B$ with $\chi^2 = 1.98$ for 97 reflections.

These refinements show unambiguously that apart from the relatively large magnetic density induced at the Ru position a huge amount of density exists at the O1 site. This moment exists and should be taken into account. The decomposition of the Ru form factor into the radial functions of the Ru is shown in Fig. 2. The validity of this approach for $4d$ compounds also characterized by a strong hybridization. For actinides, it has been found that the radial part of the wave functions does not change appreciably through the actinide series and for different ionic states. On the contrary the mixing coefficient $C2 = \frac{\mu_L}{\mu_S + \mu_L}$ depends strongly on the hybridization. The value of coefficient $C2$ will strongly depend on the ionic state and hybridization of Ru, and as in actinides, it can be obtained from refinement against the flipping ratios. In our instance, the orbital component of the Ru moment was included and was found to be $\mu_L = 0.140(15)\ \mu_B$. Neglect of the orbital part of the Ru form factor deteriorated the quality of the fit considerably, from $\chi^2 = 2.88$, thereby indicating that the orbital part of the moment exists and should be taken into account. The decomposition of the Ru form factor into the radial functions $\langle j_0(Q) \rangle$ and $\langle j_2(Q) \rangle$ is shown in Fig. 3.

The results of our refinements show a significant spin density at the O1 site and it is useful to check to what extent this can be substantiated by a model-free analysis of our data, obtained for instance by reconstructing the 3D magnetization distribution using the maximum entropy method (MEM). This method has been shown to give much more reliable results than conventional Fourier syntheses, by considerably reducing both noise and truncation effects. In order to carry out the MEM reconstructions, the magnetic structure factors of both data sets, related to two different orientations of the sample, were merged into 70 independent flipping ratios. The magnetization density distribution was discretized into $48 \times 48 \times 240$ sections along a, b and c respectively. Then it was reconstructed using a conventional unform (flat) density prior $\left[\mu\right]$. Such a procedure is biased against the creation of any magnetic density in the unit cell. In spite of the negative bias of the MEM procedure the ensuing reconstruction revealed the presence of strong peaks at the positions of Ru and weaker but well pronounced ones at the O1 positions. Numerical integrations of the magnetization density over the Ru and the O1 positions yield $\mu_{Ru} = 0.307\ \mu_B$, $\mu_{O1} = 0.030\ \mu_B$. Because of the negative bias mentioned above, the MEM values are slightly smaller than those from the refinement. Moreover, sections through the Ru site revealed a strongly anisotropic magnetization density, while sections through the Sr and the O2 sites did not detect any magnetic density above the $3 \times 10^{-3}\ \mu_B$ level. To check the robustness of the density reconstruction against possible spurious features, the MEM procedure was repeated using a non-uniform (adverse) density prior $\left[\mu\right]$ such as in all the magnetisation in the crystal is spherically concentrated around the Ru sites. This non-uniform prior was calculated analytically using the spherical magnetic density of Ru ions at the 8a position via the moment and radial integrals values obtained from the least-squares refinement mentioned previously. Such a procedure considerably enhances the bias against both the creation of magnetic density at either oxygen sites and the asphericity of Ru density, as compared to the uniform prior strategy. Nevertheless, both features of interest, the oxygen density and the asphericity of the Ru distribution, survive the acid test of an unfavorable non-uniform prior. The final results using the non-uniform prior on the basis of all measured flipping ratios are shown in Fig. 4.

Based on the band-structure calculations a strong hybridization between Ru-4d and the O-2p orbitals was postulated for the ruthenates in general $\left[14\right]$. In consequence a significant oxygen contribution was introduced into the Stoner interaction parameter for Sr$_3$RuO$_4$. Since the oxygen may not be polarized in an antiferromagnetic fluctuation, the Stoner interaction is then $q$-dependent. Taking this Stoner-interaction into account the magnetic excitation spectrum for Sr$_2$RuO$_4$ has been calculated and used as an input for many theories to explain superconductivity in this compound $\left[2, 4, 14, 15\right]$. Our finding of a large spin-density on the oxygen-site validates the basis of these procedures. So far, there are no calculations of the spin-density induced by an external field available, but the magnetization in two rather distinct ferromagnetically ordered ruthenates was calculated $\left[15\right]$, SrRuO$_3$ and Sr$_2$RuYO$_6$. In both compounds one third of the total spin density was found on the oxygen sites, in perfect agreement with the value we observe for the paramagnetic compound. A comparable amount of transferred magnetization has so far not been observed in any oxide, which underlines this outstanding property of the ruthenates compared to the better studied 3d-compounds. For
FIG. 3: Maximum entropy reconstruction of the magnetization distribution in Ca$_{1.5}$Sr$_{0.5}$RuO$_4$ at 1.6 K and 7 T. The maps A and B show the sections passing through the RuO$_2$-plane at $z=\frac{1}{8}$ and map C shows the section perpendicular to the plane through the Ru-position. The edge lengths of the maps correspond to the tetragonal lattice constant of $a=5.34\AA$ for maps A and B and to $a$ and a quarter of $c$ for map C respectively. Note that in space-group I4$_1$/acd a Ru is situated at $(\frac{1}{2},\frac{1}{2},\frac{1}{8})$ and an O1-site lies at $(0.19,0.44,\frac{1}{8})$. The section in A) relates to the adverse 3D non-uniform prior density used to compute B) and C), which biases the MEM reconstruction against any magnetization at the O sites as well as against an aspherical magnetization at the Ru site. The contour step is 0.03$\mu_B$Å$^{-3}$.

Example, PND found an induced moment of only a few percent in an Fe-garnet [17] as well as in two manganates [18].

The anisotropic density distribution at the Ru is extended along the diagonals of the original planar perovskite lattice (i.e. in the direction 45 degrees to the bonds) and it is flattened along the $c$-direction, see Fig. 3. This anisotropy suggests that the main part of the spin-density arises from the two-dimensional $\gamma$-band related to the planar $xy$-orbitals. In general the $\gamma$-band is considered as being the driving element for a ferromagnetic instability in the 214-ruthenates, since there is a van Hove singularity slightly above the Fermi-level [4]. Fang and Terakura have analyzed the phase diagram of Ca$_{2-x}$Sr$_x$RuO$_4$ by ab-initio calculations based on the local density approximation [19]. They observe that the rotation of the octahedra flattens and slightly lowers the $\gamma$-band which enhances the influence of the van Hove singularity as well as the instability towards ferromagnetism. The anisotropy observed for Ca$_{1.5}$Sr$_{0.5}$RuO$_4$, a sample very close to ferromagnetic order, is fully consistent with this explanation. However, it does not agree with the result of the LDA plus U calculation by Anisimov et al. for that particular concentration [20].

In conclusion, we have unambiguously evidenced a significant induced spin density at the positions of Ru $\mu_{Ru} = 0.350(15)$ and anomalously high spin density at the in-plane oxygen O1 $\mu_{O1} = 0.076(8)$ $\mu_B$ in Ca$_{1.5}$Sr$_{0.5}$RuO$_4$. In contrast, neither the least-squares refinement nor the model-free MEM procedure show a significant magnetic moment at the sites of Sr and apical oxygen O2. The large magnitude of the moment transferred to O1 is consistent with theoretical predictions [4].

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