Strongly Enhanced Magnetic Fluctuations in a Heavy-mass Layered Ruthenate

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We have studied the magnetic excitations in $\text{Ca}_2\text{Sr}_x\text{RuO}_4$, $x=0.52$ and 0.62, which exhibit an anomalous high susceptibility and heavy mass Fermi liquid behavior. Our inelastic neutron scattering experiments reveal strongly enhanced magnetic fluctuations around an incommensurate wave vector (0.22,0,0) pointing to a magnetic instability. The magnetic fluctuations show no correlation in c-direction and also along the RuO$_2$-planes the signal is extremely broad, $\Delta q = 0.45\,\text{Å}^{-1}$. These fluctuations can quantitatively account for the high specific heat coefficient and relate to the high macroscopic susceptibility. The magnetic scattering is attributed to the $\gamma$-band, the active band for spin triplet superconductivity in Sr$_2$RuO$_4$.

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The interest in ruthenates initiated by the discovery of the unconventional superconductivity in Sr$_2$RuO$_4$ has revealed a rich variety of physical phenomena. Inelastic neutron scattering (INS) finds dominating incommensurate (almost antiferromagnetic) fluctuations arising from strong nesting in the one-dimensional bands of $d_{xy}$- and $d_{xy}$-character. However, there is evidence, that superconductivity in Sr$_2$RuO$_4$ is originating mainly in the two-dimensional band of $d_{xy}$-character. This band exhibits a van-Hove singularity only 50 meV above the Fermi-level, which may be related to the tendency of the perovskite ruthenates towards ferromagnetism.

The substitution of Sr by Ca yields a very complex Ca$_2$Sr$_x$RuO$_4$-phase diagram. Due to the smaller ionic radius of Ca compared to that of Sr, the structure first exhibits a rotation around the c-axis, $1.5>x>0.5$ followed by a tilt distortion for $0.5>x>0.2$. For the highest Ca-concentration, $x<0.2$, Mott localization sets in ending in the antiferromagnetic insulator Ca$_2$RuO$_4$. The different structural distortions are reflected in the magnetic properties which could semi-quantitatively be explained through LDA band structure calculations.

Particularly interesting behavior is found in the concentration range next to localization but still in the metallic phases, $0.5>x>0.2$, where partial localization has been proposed. Ca$_{1.5}$Sr$_{0.5}$RuO$_4$ exhibits the largest macroscopic magnetic susceptibility, $\chi_{\text{mac}}$, at low temperature, a factor of 200 higher than the one of pure Sr$_2$RuO$_4$. Furthermore, Nakatsuji et al. observed magnetic hysteresis and an exceptionally large linear coefficient of the specific heat of 255 mJ/mol-RuK. This puts Ca$_{1.5}$Sr$_{0.5}$RuO$_4$ well in the range of typical heavy fermion compounds and there is only one other transition metal oxide known with a comparable specific heat coefficient.

When searching for the so far undetected ferromagnetic fluctuations, Ca$_{1.5}$Sr$_{0.5}$RuO$_4$ seems to be favorable due to its large magnetic susceptibility. We have studied this material by INS and find indeed strongly enhanced magnetic fluctuations around the two-dimensional zone center, which furthermore may account for the high specific heat ratio.

Several single crystals were obtained with a floating zone technique. We have studied two compositions, $x=0.52$ and 0.62, with volumes of 140 and 350 mm$^3$, respectively. INS experiments were performed on the thermal triple axis spectrometer 1T at the Orphée reactor using double focusing monochromator and analyzer crystals (pyrolitic graphite (002)). Since the scattered intensity was rather low and since it turned out that the magnetic scattering is little modulated in q-space, we relaxed the diaphragms defining the scattered beam. INS measures the imaginary part of the dynamical susceptibility as function of energy and q:

$$\frac{d^2\sigma}{d\Omega dq} = \frac{k_f}{k_i} \frac{2F^2(Q)}{\pi g^2\mu_B^2} \frac{\chi''(Q,\hbar\omega)}{1 - \exp(-\hbar\omega/k_BT)}$$

where $r_0^2 = 0.292$ barn, $g \approx 2$ is the Landé factor, $k_i$ and $k_f$ are the incident and final neutron wave vectors, and $F(Q)$ is the magnetic form factor.

Most experiments were done with the Ca$_{1.35}$Sr$_{0.65}$RuO$_4$-crystal due to its larger volume. Near the q-position $q_{\text{ce}-\text{af}}=(0.3,0.3,q_y)$, where strong incommensurate scattering is observed in pure Sr$_2$RuO$_4$, we find only weak scattering, but there is strong scattering around $Q=(1,0,0)$, which is not a zone-center in the three-dimensional space with the body-centered stacking of the planes. However, due to the weak inter-layer electronic coupling, magnetism should have little dependence on the $q_y$-component and we may consider $(1,0,0)$ as the two-dimensional zone center. Fig. 4 shows a map of the scattering observed around $(1,0,0)$ at the energy of 4.1 meV. In contrast to
pure Sr$_2$RuO$_4$, the magnetic fluctuations exhibit a broad plateau around the position expected for ferromagnetism. However, they are still not peaking at the zone center but remain incommensurate with a very broad maximum at the finite q-value of $q_{ic-fm}=(0.22,0,0)$.

We have verified the magnetic nature of the $q_{ic-fm}$-scattering by similar studies around the (3,0,0) and (2,1,0) lattice points (near (1,1,0) or (2,0,0) phonon scattering is too strong). At the first positions no similar signal could be detected in agreement with the expected decrease of a magnetic signal due to the form-factor. In contrast any phononic signal should get enhanced at these larger Q-positions. We know, that around (1,0,0) the transfer of 4.1 meV ((a) is a simulation and (b) the measured data). Due to the enhanced background contribution at lower scattering angles the scans were restricted to Q-values larger than 1.66 Å$^{-1}$. For clarity the background has been subtracted and the data has been corrected for the magnetic form factor of Ru$^+$. The schematic representation in (a) assumes four peaks at (1 ± 0.22, 0, 0) and at (1, ±0.22, 0) with Gaussian profiles and the experimentally determined parameters, see text.

The magnetic scattering in Ca$_{1.38}$Sr$_{0.62}$RuO$_4$ is not well defined in Q-space leading to sizeable overlap of the four symmetrically equivalent contributions from (±0.22,0,0) and (0,±0.22,0). The map as, well as all the scans presented below, can be described by the superposition of four Gaussians isotropic in q-space:

$$I(Q,\omega) = BG + \sum_{i=1,...,4} I_i e^{-\frac{i\pi}{2}(Q-S_i|^2)}$$ \quad (2)

This description allows to analyze the scattering quantitatively, even though it might be more complex. In the related compound Sr$_3$Ru$_2$O$_7$, for example, a multiple peak structure was observed which we may not rule out in our case. Figure 2 shows the results of constant energy scans across G=(1,0,0) passing through the two maxima at (1,±0.22,0) with fits according to Eq. (2). We may follow the incommensurate scattering corresponding to $q_{ic-fm}$ up to 8 meV, at higher energy the contamination with phonon scattering is too strong. The position of the scattering is independent of the energy transfer, as expected for a Fermi-surface feature in the paramagnetic phase.

For the energy of 4.1 meV at 12 K we obtain a q-width (full width at half maximum) isotropic in the x,y-plane of 0.45 Å$^{-1}$, which is more than three times larger than the width of the incommensurate fluctuations in Sr$_2$RuO$_4$. Thus, even at this low temperature the fluctuations in Ca$_{1.38}$Sr$_{0.62}$RuO$_4$ exhibit a very short correlation length of only about 5 Å, but we may not exclude that the broadening arises from a multiple peak structure. We have also studied the $q_l$-dependence of this scattering and did not find any dependency besides the decrease in intensity with increasing $q_l$ due to the magnetic Ru$^+$ form factor. The magnetic fluctuations around $q_{ic-fm}$ are thus not correlated in the $c$-direction similar to the incommensurate scattering in Sr$_2$RuO$_4$. We find only a weak increase in the in-plane peak width for decreasing energies at 1.6 K, but at higher temperatures, there is significant additional energy dependent broadening. Astonishingly, the low energy fluctuations get broadened approximatively when $k_BT$ exceeds their energy.

The left part of Fig. 1 gives the energy dependence of the $q_{ic-fm}$-scattering at 1.6 K which may be described...
with a single relaxor fit:

$$\chi''(q_{ic-fm}, \omega) = \chi'(q_{ic-fm}, 0) \frac{\Gamma \omega}{\Gamma^2 + \omega^2}$$  \hspace{1cm} (3)

relating the imaginary part $\chi''(q_{ic-fm}, \omega)$ of the generalized dynamical susceptibility with the corresponding real part $\chi'(q_{ic-fm}, 0)$ at $\omega = 0$. For the characteristic damping energy we find $\Gamma = 2.5 \pm 0.2$ meV at $T = 1.6$ K, which is much less than the value of 7.5 meV reported for the incommensurate spin fluctuations in Sr$_2$RuO$_4$. We conclude that Ca$_{1.38}$Sr$_{0.62}$RuO$_4$ is close to a magnetic instability, in spite of the rather broad Q-width of the peaks. For the amplitude we obtain $\chi'(q_{ic-fm}, 0) = 454 \mu_B^2 V^{-1}$, which is much higher than that of the incommensurate scattering in Sr$_2$RuO$_4$, which is indicated in the simulated map in Fig. 3. Upon heating the amplitude of the spectrum at $q_{ic-fm}$ decreases and the characteristic energy shifts to higher values, see Fig. 3 b-d). All these observations support the interpretation that Ca$_{1.38}$Sr$_{0.62}$RuO$_4$ approaches a magnetic instability at low temperature.

In Fig. 3 we compare the scattering near $q_{ic-fm}$ for pure Sr$_2$RuO$_4$, Ca$_{1.38}$Sr$_{0.62}$RuO$_4$ and Ca$_{1.48}$Sr$_{0.52}$RuO$_4$. The quasi-ferromagnetic signal is absent in the pure compound but is even stronger in Ca$_{1.48}$Sr$_{0.52}$RuO$_4$, following the behavior of $\chi_{mac}$. The strength of the scattering observed here implies its relevance for the anomalous physical properties reported for compositions around Ca$_{1.5}$Sr$_{0.5}$RuO$_4$. The high macroscopic susceptibility relates to the scattering around $q_{ic-fm}$, since its strong broadening implies a significant overlap to the ferromagnetic position $q = (000)$. However the temperature dependence of $\chi_{mac}$ and $\chi''(q_{ic-fm}, \omega)$ or $\chi'(q_{ic-fm}, \omega = 0)$ are only qualitatively similar, see Fig. 3. $\chi_{mac}$ exhibits a steeper increase at low temperature where it exceeds $\chi''(q_{ic-fm}, \omega)$ by more than a factor five. We conclude that the anomalously high macroscopic susceptibility evolves from the little correlated magnetic fluctuations observed here, but the details of the crossover require further studies at low temperature and energy. Ca$_{1.5}$Sr$_{0.5}$RuO$_4$ further exhibits an extremely high linear coefficient in the specific heat, but it differs from typical heavy fermion compounds by the strong temperature dependence of both specific heat coefficient and magnetic susceptibility, and by the large Wilson ratio of about 40 in the ruthenate LiV$_2$O$_4$, where a magnetic instability and anomalous low temperature properties were reported. There are similarities with the only other known transition metal compound with comparable C/T-ratio, LiV$_2$O$_4$, where a magnetic instability and anomalous low temperature properties were reported. The strongly enhanced fluctuations in Ca$_{1.38}$Sr$_{0.62}$RuO$_4$ can quantitatively account for the specific heat ratio. Following reference, one may relate the specific heat coefficient with the inverse of the characteristic energy averaged over the Brillouin-zone: $\gamma = \frac{\pi k_B}{\hbar} \frac{1}{\Gamma(BZ)}$. For Ca$_{1.38}$Sr$_{0.62}$RuO$_4$, the resulting specific heat coefficient is large due to the low characteristic energy of 2.5 meV and due to the broad q-range of the fluctuations. Taking $\Gamma$ to be constant within a cylinder of radius 0.225 Å$^{-1}$ and neglecting any other contribution we obtain $\gamma = 250$ mJ/mol-RuK$^2$ in agreement with the direct measurement. The heavy mass behavior seems thus to arise from the over-damped magnetic excitations. It is in-
teresting to perform the same analysis for $\text{Sr}_2\text{RuO}_4$: the incommensurate scattering can account only for about a quarter of the observed $\gamma$-coefficient suggesting an additional source of excitations as it has also been deduced from the comparison with NMR results [2, 3]. It is tempting to assume that parts of the magnetic fluctuations dominating in $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{RuO}_4$, still play a role for the superconductivity of $\text{Sr}_2\text{RuO}_4$, where the $\gamma$-band is considered to drive the unconventional superconductivity [3].

At temperatures below 1 K a ferromagnetic ordering has been reported [14], but the ordered moment per Ru appears to be rather small, of the order of 0.01 $\mu_B$, in view of the sizeable magnetic fluctuations seen in our experiment. It is unclear whether the weak ferromagnetic order reflects the main magnetic contribution, or whether it arises from some disorder. We have searched for magnetic ordering in $\text{Ca}_{1.48}\text{Sr}_{0.52}\text{RuO}_4$ down to 0.3 K. There is no magnetic ordering corresponding to $\mathbf{q}_{\text{ic-fm}}$, $\mathbf{q}_{\text{ic-af}}$ or to antiferromagnetism with an ordered moment higher than 0.03 $\mu_B$.

In the right part of Fig. 4 we show the cylindrical $\gamma$-band as the bulk in the samples studied here, rotation angle of $8.5^\circ$ compared to the value of $12^\circ$ found in the bulk of $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{RuO}_4$ [2]. The structural surface reconstruction induces an electronic surface state which one may relate to a shift of the van-Hove singularity below the Fermi-level [23]. Since the rotation distortion is even stronger in $\text{Sr}_2\text{RuO}_4$ a similar effect may occur changing the $\gamma$-band from electron-like into hole-like. Hall effect measurements support this interpretation [24]. Using the tight binding parameters of reference [6] but with a down shift of the $\gamma$-band by 100 meV taken from the LDA calculation in Ref. [11] one obtains the Fermi-surface presented in the inset of Fig. 4 and indeed one may find a nesting-like vector near $(0, 0, 0)$ connecting the two ends of hole-like pockets across the $M$-point. More detailed calculations are required to confirm such interpretation; in particular the role of band folding induced by the rotational distortion should be explored. A Dzyaloshinski-Moriya interaction might also cause a shift of magnetic fluctuations from the ferromagnetic to an incommensurate position; however, a rather strong interaction would be needed to explain the observed $\mathbf{q}_{\text{ic-fm}}$.

In summary we have observed strongly enhanced magnetic excitations in the heavy mass material $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$, $x=0.52$ and 0.62. In contrast to pure $\text{Sr}_2\text{RuO}_4$, dominant scattering is found around the zone-center, indicating a quasi-ferromagnetic instability, though the wave-vector is still finite, $\mathbf{q}_{\text{ic-fm}}=(0.22, 0, 0)$. A description with four symmetrically equivalent broad peaks at $(\pm 0.22, 0, 0)$ and $(0, \pm 0.22, 0)$ yields overlap with strong weight at the center corresponding to the ferromagnetic instability. The enhanced low temperature magnetic susceptibility in $\text{Ca}_{1.5}\text{Sr}_{0.5}\text{RuO}_4$ is thus related with this magnetic instability. Quantitatively, the strongly enhanced fluctuations account for the exceptionally high specific heat C/T-ratio. These results shed further light on the possible role of the $\gamma$-band in ferromagnetism and in the pairing mechanism of $\text{Sr}_2\text{RuO}_4$.

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[16] We use reduced lattice units referring to the undistorted cell in $\text{Sr}_2\text{RuO}_4$, $2\pi/a = 1.68 \AA^{-1}$ and $2\pi/c = 0.50 \AA^{-1}$, but note that the crystal structure in $\text{Ca}_{1.38}\text{Sr}_{0.62}\text{RuO}_4$ is heavily distorted, space group $I_4/1/acd$ [2].
[17] O. Friedt, to be published.