Incommensurate magnetic ordering in Sr$_2$Ru$_{1-x}$Ti$_x$O$_4$

M. Braden, 1,2 O. Friedt, 2 Y. Sidis, 2 P. Bourges, 2 M. Minakata, 3 and Y. Maeno 3,4

1 Forschungszentrum Karlsruhe, IFP, Postfach 3640, D-76021 Karlsruhe, Germany
2 Laboratoire Léon Brillouin, C.E.A./C.N.R.S., F-91191 Gif-sur-Yvette CEDEX, France
3 Department of Physics, Kyoto University, Kyoto 606-8502, Japan
4 CREST, Japan Science and Technology Corporation, Japan

(Dated: March 22, 2022, DRAFT)

In Sr$_2$RuO$_4$ the spin excitation spectrum is dominated by incommensurate fluctuations at $q_r=(0.3 \ 0.3 \ q_z)$, which arise from Fermi-surface nesting. We show that upon Ti substitution, known to suppress superconductivity, a short range magnetic order develops with a propagation vector $(0.307 \ 0.307 \ 1)$. This finding confirms that superconducting Sr$_2$RuO$_4$ is extremely close to an incommensurate spin density wave instability. In addition, the ordered moment in Sr$_2$Ru$_{0.91}$Ti$_{0.09}$O$_4$ points along the c-direction, which indicates that the incommensurate spin fluctuations exhibit the anisotropy required to explain a p-wave spin triplet pairing.

Sr$_2$RuO$_4$ the only superconducting layered perovskite isostructural with the cuprates has attracted considerable interest. Though there is some evidence that the pairing in this compound is unconventional and of triplet character, the coupling mechanism is still subject of debate. Inspired by the ferromagnetism in the 3D-perovskite SrRuO$_3$, it has been proposed that the coupling is mediated by ferromagnetic fluctuations, for which, however, no experimental evidence has been found so far. Instead, band structure calculations reveal magnetic fluctuations at incommensurate positions arising from Fermi-surface nesting in the 1D-like bands associated to the $d_{x^2-y^2}$ and $d_{y^2}$-orbitals. Inelastic neutron scattering has perfectly confirmed this nesting scenario with peaks in the dynamic magnetic susceptibility appearing at $q_r=(0.3 \ 0.3 \ q_z)$. We use the notation $Q=\tau+q_r$ with $Q$ the scattering vector, $q_r$ the propagation vector in the first Brillouin-zone and $\tau$ a reciprocal lattice vector; all vectors are given in reciprocal lattice units corresponding to $(\frac{2\pi}{a}, \frac{2\pi}{a}, \frac{2\pi}{c})$.

The pairing in Sr$_2$RuO$_4$ could be rather complicated since the Fermi surface is formed by three bands. Of the three bands only two contribute directly to the dynamical nesting. The third band, the $\gamma$-band associated to the $d_{xy}$-orbitals, is thought to be closer to ferromagnetism with a possibly stronger role for the superconducting pairing. However, recent calculations still do not give evidence for ferromagnetic fluctuations arising from the $\gamma$-band. In addition there is no evidence for a dominant role of ferromagnetic fluctuations in the transport properties, and the superconducting transition temperature decreases upon pressure increase, though ferromagnetic fluctuations should be enhanced. The question about the dominant magnetic interaction is, hence, still of strong interest.

Substitution may allow to identify the character of the magnetic interaction, when static magnetic order is induced. Complete Ca-substitution leads to an antiferromagnetic insulator. The structural properties of Ca$_2$RuO$_4$ are, however, quite distinct from those of Sr$_2$RuO$_4$; in particular the in plane RuO distances are significantly enhanced. Therefore, the antiferromagnetic order in Ca$_2$RuO$_4$ is not necessarily relevant for the Sr compound. The intermediate Ca$_{2-x}$Sr$_x$RuO$_4$-compositions present strongly enhanced magnetic susceptibility near $x=0.5$ again in a region far away from the superconducting compound; nevertheless this observation indicates some ferromagnetic instability also in the 214-system.

Replacing a part of the Ru by non-magnetic four-valent Ti (configuration 3d$^0$) leads to magnetic anomalies even for very low Ti-concentration, $x>0.025$ in Sr$_2$Ru$_{1-x}$Ti$_x$O$_4$. These anomalies have been interpreted in terms of an appearance of weak magnetic moments around Ti impurities. In this work we show that these Ti-doped samples exhibit incommensurate magnetic ordering corresponding to the Fermi-surface nesting instability. Concerning the pure compound, one may conclude that it is much closer to an incommensurate spin density wave instability than to a ferromagnetic one.

Two single crystals of Sr$_2$Ru$_{1-x}$Ti$_x$O$_4$ with $x=0.025$ and 0.09 and a volume of about 100mm$^3$ each were grown with a floating zone method in an infrared image furnace. The inclusion of the Ti was verified by electron probe microanalysis. Furthermore, there is a clear reduction of the c-lattice constant and a shift of the frequency of the rotational phonon mode from 7.86 meV in the pure compound to 9.97 meV in Sr$_2$Ru$_{0.91}$Ti$_{0.09}$O$_4$. This agrees to the smaller ionic radius of Ti compared to Ru which should shift Sr$_2$Ru$_{0.91}$Ti$_{0.09}$O$_4$ further away from the rotational structural instability. Magnetic neutron scattering experiments were performed on the triple axis.
spectrometers 1T (thermal source) and 4F (cold source) at the Orphée reactor using pyrolithic graphite (PG) monochromators and analyzers. Higher order contamination was suppressed by either PG or cooled Be-filters.

The search for commensurate magnetic order did not reveal intensity neither at ferromagnetic nor at antiferromagnetic scattering vectors for Sr$_2$Ru$_{0.91}$Ti$_{0.09}$O$_4$. The dominant features in the magnetic excitation spectrum in Sr$_2$RuO$_4$, being observed at incommensurate positions, it appeared promising to look for corresponding order in Sr$_2$Ru$_{0.91}$Ti$_{0.09}$O$_4$. Indeed we found an elastic peak appearing very close to the positions of the inelastic scattering in Sr$_2$RuO$_4$. Due to the better peak to background ratio we performed an extensive study on the cold triple axis 4F using long-wavelength neutrons, ($k_i=1.48\text{Å}^{-1}$, $\lambda=4.25\text{Å}$). Figure 1 shows elastic scans across the incommensurate magnetic Bragg point for different temperatures. The elastic intensity appears below $T_N \sim 25$ K, however, it is evident that the magnetic order remains limited in its spatial extension even at low temperature. The maximum intensity was found at $Q_f=(0.693 0.307 0)$ which indicates the propagation vector $q_i=(0.307 0.307 1)$, note that $(1 0 0)$ is not a zone-center in the I4/mmm lattice.

The second crystal with a lower Ti-content of $x=0.025$ does not exhibit similar magnetic ordering. The comparison of the elastic scans between 20 and 1.6 K indicates a low-temperature intensity at $Q_i$ roughly a factor 20 less than in the $x=0.09$-sample (relative to the intensity of a fundamental reflection). This finding agrees well with the appearance of a sizeable ferromagnetic moment for concentrations higher than $x=0.03$.

FIG. 2: Dependence of the peak height of the Lorentzian profiles at the incommensurate Bragg point $(0.693 0.307 q_i)$ on the out of plane component of the scattering vector. The horizontal bar indicates the experimental resolution along this direction and the solid line is a fit with a Lorentzian.

The intensity profiles measured for Sr$_2$Ru$_{0.91}$Ti$_{0.09}$O$_4$ were fitted to Lorentzians folded with the experimental resolution. The resulting peak heights and resolution corrected half widths at half maximum, $\kappa$, are shown in figure 1 as a function of temperature. The peak height and the intensity at the peak maximum indicate a sluggish phase transition near 25 K. In a weakly antiferromagnetic metal the squared ordered moment measured by the intensity of the superstructure Bragg peak should be proportional to $(T_{N}^{1.5} - T^{1.5})$, while the temperature dependence in a nesting-model may be more complex. The fit by this power law is not very satisfactory, since the transition is definitely not sharp. This behavior suggests a crossover from damped inelastic fluctuations to elastic or quasi-elastic order at low temperature, somehow reminiscent of a continuous slowing down observed in spin glass systems. Furthermore, the spin-spin correlation length in the RuO$_2$-planes remains finite and changes only gradually below the transition. It saturates at $\sim 50\text{Å}$ at 1.6 K. At this temperature, we do not find any evidence for a finite energy-width of the signal, the intrinsic width may be estimated to be lower than 0.06 meV.

The magnetic correlation is isotropic within the planes, but there is only little modulation of the signal along c. Figure 2 shows the peak height of scans across $(0.693 0.307 q_i)$ on the out of plane component of the scattering vector with the Lorentzian fit.
0.307 \( q_z \) as a function of \( q_z \). The \( q_z \)-dependence has been described by a Lorentzian yielding a half width at half maximum of 0.7 reduced lattice units or 0.35\( \AA^{-1} \). Such broad signals may not be interpreted in terms of a correlation length; nevertheless, the broadening indicates that the inter-plane coupling is restricted to the nearest neighbors. The weak inter-plane coupling reflects the character of the incommensurate fluctuations [10], which was reported to be essentially two-dimensional [16]. The intensity at the incommensurate peak maximum is rather weak compared to that in a fundamental nuclear reflection, a few \( 10^{-5} \) for \( x=0.09 \); however, due to the enormous broadening of the magnetic peaks the ratio of the integrated intensities is much larger, close to \( 10^{-3} \).

In order to determine the incommensurate magnetic structure, we have measured several Bragg intensities using the \((100)/(010)\) and \((110)/(001)\) orientations. The observations were corrected for the broadening in order to obtain integrated intensities. The last column in Table 1 gives the seven examined intensities relative to the strongest one, \((0.307 \ 0.307 \ 1)\). Since the propagation vector is determined, only a few simple models may be applied. As the propagation vector is not along the tetragonal axis, sine-wave modulations with longitudinal and transverse character are likely, whereas, a helimagnetic structure would imply some accidental degeneracy. We have considered different models: with the magnetic moment along \( c \), M1, with an in-plane moment perpendicular to the modulation, M2, with in-plane moment parallel to \([110]\), M3, and the less likely helimagnetic structure, M4 [17]. The calculated intensities are given in Table 1 relative to that of \((0.307 \ 0.307 \ 1)\). The intensity ratios are determined with good accuracy since the severe corrections for broadening and extinction almost cancel out. The best description is obtained with M1, the sine-wave with the moments parallel \( c \); models M2 and M3 are ruled out. Also the helimagnetic model yields a description worse than M1, but a minor in-plane contribution of the ordered moment may not be excluded. Nevertheless, this analysis shows that the main part of the ordered moment (possibly all of it) is pointing along \( c \).

The estimation of the amplitude of the modulation is less straightforward, since the corrections for the broadening and for extinction enter. From the integrated intensity of the magnetic \((0.307 \ 0.307 \ 1)\) Bragg-peak relative to that of \((1 \ 1 \ 0)\) we obtain the ordered moment to 0.3(1)\( \mu_B \); the error takes account of the reliability of the corrections. We emphasize that the ordered moment may not be below 0.1\( \mu_B \), since this would imply intensities a factor of 10 smaller.

The ordered moment is much larger than the ferromagnetic moment induced by a field of 1T at low temperature, 0.005\( \mu_B \) per Ru, and it is still larger than the induced moment at higher temperature, which was obtained by a Curie-Weiss fit to the susceptibility [13].

| (hkl)-indices | M1 | M2 | M3 | M4 | observed |
|---------------|----|----|----|----|----------|
| (0.307 0.307 1) | 1  | 1  | 1  | 1  | 1        |
| (0.307 0.693 0) | 0.61| 0.05| 1.00| 0.28| 0.51(4)  |
| (0.307 0.307 3) | 0.05| 0.19| 0.46| 0.13| 0.08(3)  |
| (0.693 0.693 1) | 0.23| 0.17| 0.05| 0.20| 0.27(5)  |
| (0.693 0.693 3) | 0.06| 0.07| 0.10| 0.07| 0.01(1)  |
| (1.307 0.307 0) | 0.11| 0.05| 0.06| 0.07| 0.17(5)  |
| (1.307 0.693 1) | 0.07| 0.01| 0.14| 0.06| 0.07(2)  |
| (0.307 0.307 5) | 0.00| 0.04| 0.12| 0.03| 0.00(4)  |

Table I: Comparison of the measured integrated Bragg intensities (last column) to those calculated with the models M1-M4, see text. All intensities are given relative to that of \((0.307 \ 0.307 \ 1)\) \((\lambda=4.25\AA)\) taking into account the form-factor of Ru\(^{1+}\). The calculation assumes perfect averaging of domains and was performed using the FULLPROF-program [18].

Therefore, one has to interpret the incommensurate order as arising directly from the intrinsic Fermi-surface nesting [16,18]. In the RPA treatment of itinerant magnetism the Stoner enhancement of the bare magnetic susceptibility, \( \chi_0 \), through the interaction, \( I \), is described by:

\[
\chi(q) = \frac{\chi_0(q)}{1 - I \cdot \chi_0(q)} \quad (1).
\]

In the pure compound we have found that the product \( \alpha = I \cdot \chi_0(q) \) amounts to 0.97 [8], yielding a susceptibility enhancement at the nesting vector by a factor of 33. Ti-substitution appears to shift \( \alpha \) towards the critical value of one, which implies the divergence of the susceptibility and the magnetic transition.

The magnetic excitation spectrum in Sr\(_{2}\)Ru\(_{0.91}\)Ti\(_{0.09}\)O\(_4\) has been studied by inelastic neutron scattering using the same crystal. The constant energy scans across \( Q_3 \) at energies above 3meV yield peaks at the nesting vector very similar to the observations in pure Sr\(_{2}\)RuO\(_4\), see figure 3 [8]. These scans appear to sense an excitation continuum similar to the paramagnetic phase, in particular there is no sizeable dependence of the peak width on the energy [8].

The correlation length of the excitations is comparable to that found in the pure compound, \( \sim 15\AA \), but it is much shorter than the correlation of the elastic order. Magnetic order due to Fermi-surface nesting should open a partial gap separating the high energy continuum from low energy spin-waves. One of the very few well studied examples for such behavior is found in \( V_{2-x}\)O\(_3\) [20,21]. A partial gap in Sr\(_{2}\)Ru\(_{0.91}\)Ti\(_{0.09}\)O\(_4\) agrees also with the increase in the resistivity [8]. The scans at 2.1 meV indicate that the signal becomes broadened and reduced in amplitude in the incommensurate ordered phase in qualitative agreement with a gap and the spin-wave picture expected for low energies. These observations further support the interpretation, that the magnetic

\[
\mu_B \chi(q)
\]
ordering results directly from the Fermi-surface nesting. A more quantitative analysis of the excitation spectrum, however, will require larger crystals.

The spin-glass-like behavior at low temperature observed in ref. \([13]\) may result from the disorder between Ru and non-magnetic Ti. On the one hand Ti substitution drives the system towards magnetic ordering, and on the other hand, Ti impurity acts as disorder centers, giving rise to finite correlations lengths. The average Ti-distance being of the order of the correlation length, these vacancy moments may be aligned under an applied field which may explain the observed weak ferromagnetic moments \([13]\). Furthermore, the rearrangement of the ordered clusters will imply some relaxation processes.

In the context of the stripe scenario incommensurate magnetic order has gained interest also in the cuprates \([22]\). There also, the transition from quasi-elastic to elastic order is sluggish. Furthermore, the rearrangement of the ordered clusters will imply some relaxation processes.

Another important impact of the magnetic ordering in Sr$_2$Ru$_{1-x}$Ti$_x$O$_4$ concerns the orientation of the spins along c. Several groups have analyzed the problem whether the incommensurate magnetic fluctuations may imply spin-triplet superconductivity \([8, 24, 25]\) which seems to be established in Sr$_2$RuO$_4$ \([9]\). Two groups conclude that this would require some anisotropy of the incommensurate fluctuations. The required dominance of the out of plane component may be deduced from the NMR studies \([24]\) which are, however, not restricted to the incommensurate wave-vector. The observation of the incommensurate ordering with the spins along c in Sr$_2$Ru$_{0.91}$Ti$_{0.09}$O$_4$ clearly indicates that the incommensurate fluctuations exhibit the required anisotropy at least qualitatively.

In conclusion, elastic neutron scattering on Sr$_2$Ru$_{0.91}$Ti$_{0.09}$O$_4$ reveals incommensurate magnetic ordering. The large ordered moment and the spin excitation spectrum indicate that magnetic order is directly induced by the intrinsic Fermi-surface nesting instability. The pure compound, Sr$_2$RuO$_4$, is, hence, close to a quantum critical point similar to cuprate or heavy fermion superconductors \([27]\).

We gratefully acknowledge discussions with P. Pfenty.

[1] Y. Maeno et al., Nature (London) 372, 532 (1994).
[2] K. Ishida et al., Nature (London) 396, 658 (1998).
[3] S.R. Julian et al., Physica B 259–261, 928 (1999).
[4] M. Sigrist et al., Physica C 317, 134 (1999).
[5] M.E. Zhitomirsky and T.M. Rice, condmat/0102390.
[6] T. M. Rice and M. Sigrist, J. Phys. Cond. Matt. 7, L643 (1995).
[7] I. I. Mazin and D.J. Singh, Phys. Rev. Lett 79, 733 (1997).
[8] Y. Sidis et al., Phys. Rev. Lett. 83, 3320 (1999).
[9] K.-K. Ng and M. Sigrist, J. Phys. Soc. Jpn 69, 3764 (2000).
[10] N. Shirakawa et al., Phys. Rev. B 56, 7890 (1997).
[11] M. Braden et al., Phys. Rev. B 58, 847 (1998).
[12] S. Nakatsuji and Y. Maeno, Phys. Rev. B 62, 6458 (2000); Phys. Rev. Lett. 84, 2666 (2000).
[13] M. Minakata and Y. Maeno, Phys. Rev. B 63, 180504(R) (2001).
[14] M. Braden et al., Phys. Rev. B 57, 1236 (1998).
[15] H. Hasegawa and T. Moriya, J. Phys. Soc. Jpn 36, 1542 (1974); H. Hasegawa, J. of Low Temp. Physics 31, 475 (1978); K. Nakayama and T. Moriya, J. Phys. Soc. Jpn 56, 2918 (1987).
[16] F. Servant et al., Solid State Comm. 116, 489 (2000).
[17] Models M1 and M3 may be coupled by symmetry.
[18] J. Rodriguez-Carvalho et al., J. Phys.: Condens. Matter 3, 3215 (1991).
[19] O. Friedt, Y. Sidis and M. Braden, to be published.
[20] W. Bao et al., Phys. Rev. B 58, 12727 (1998).
[21] W. Bao et al., Phys. Rev. Lett. 71, 766 (1993).
[22] J. Tranquada et al., nature 375, 561 (1995).
[23] H. Kimura et al., Phys. Rev. B 59, 6517 (1999).
[24] M. Sato and M. Kohmoto, J. Phys. Soc. Jpn. 69, 3505 (2000).
[25] T. Kuwabara and M. Ogata, Phys. Rev. Lett. 85, 4586 (2001).
[26] H. Mukuda et al., J. Phys. Soc. Jpn. 67, 3945 (1998).
[27] N.D. Mathur et al., nature 394, 39 (1998).