Structural aspects of metamagnetism in Ca$_{2-x}$Sr$_x$RuO$_4$ ($0.2 < x < 0.5$): field tuning of orbital occupation

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The crystal structure of Ca$_{2-x}$Sr$_x$RuO$_4$ with $0.2 < x < 1.0$ has been studied by diffraction techniques and by high resolution capacitance dilatometry as a function of temperature and magnetic field. Upon cooling in zero magnetic field below about 25 K the structure shrinks along the c-direction and elongates in the a, b planes ($0.2 < x < 1.0$), whereas the opposite occurs upon cooling at high-field ($x = 0.2$ and 0.5). These findings indicate an orbital rearrangement driven by temperature and magnetic field, which accompanies the metamagnetic transition in these compounds.

The phase diagram of Ca$_{2-x}$Sr$_x$RuO$_4$ possesses quite different end members with the spin-triplet superconductor Sr$_2$RuO$_4$ on the one side and the antiferromagnetically ordered Mott insulator Ca$_2$RuO$_4$ on the other side. Since Sr and Ca are both divalent, one has to attribute the different physical behavior entirely to the difference in the ionic radii. For small Ca content the octahedra present a c axis rotation and for higher Ca content ($x < 0.5$) a tilt of the octahedra around an in-plane axis occurs. These distortions, through reduction of the hybridization, imply smaller band widths, which together with a constant Hubbard type interaction, enhance the correlation effects. For Sr content lower than 0.2, finally Mott localization occurs in a material which exhibits a strong rotation and a strong tilt deformation.

Outstanding physical properties are found in compounds in the metallic regime but close to localization, $0.2 < x < 0.5$. At $T \sim 2$ K samples with $x \sim 0.5$ exhibit a magnetic susceptibility a factor of 200 higher than that of pure Sr$_2$RuO$_4$. In addition, the linear coefficient in the specific heat is exceptionally high, of the order of $C/T \sim 250$ mJ mol$^{-1}$ K$^{-2}$, well in the range of typical heavy fermion compounds. Inelastic neutron scattering has revealed strongly enhanced magnetic fluctuations of incommensurate character, very different from those in pure Sr$_2$RuO$_4$.

For Sr concentrations lower than 0.5, but still in the metallic phase, the tilt distortion occurs and strongly modifies the physical properties. The magnetic susceptibility at 2 K, measured in a low field, decreases with decreasing Sr content and increasing tilt; for $0.2 < x < 0.5$ there is a maximum in the temperature dependence of the susceptibility. In this concentration range the low-temperature low-field magnetization is, hence, small compared with the extrapolation both from high temperatures and from high Sr concentration. A metamagnetic transition occurs in these compounds at low temperature yielding a high-field magnetization for $x = 0.2$ which actually exceeds that for $x = 0.5$. A similar metamagnetic transition has been reported for Sr$_3$Ru$_2$O$_7$, where the related quantum critical end point has been proposed to cause outstanding transport properties.

Single crystals of Ca$_{2-x}$Sr$_x$RuO$_4$ were grown by a floating zone technique in image furnaces at Kyoto University ($x = 0.2, 0.62$ and 1.0) and at Université Paris Sud ($x = 0.5$); a powder sample of Ca$_{1.8}$Sr$_{0.2}$RuO$_4$ was prepared by the standard solid state reaction at Universität zu Köln. Single crystal neutron diffraction experiments were performed on the lifting counter diffractometer 6T.2 at the Orphée reactor in magnetic fields up to 7 T. Using the GEM time of flight diffractometer at the ISIS facility, powder diffraction patterns were recorded in fields up to 10 T. Thermal expansion and magnetostriction were studied in magnetic fields up to 14 T.

The thermal expansion was determined on the single crystals of compositions, $x = 0.2, 0.5, 0.62$, and 1.0, along the c axis and along an in-plane direction. The results are presented in Fig. 1 together with the relative length changes obtained by integration. In all samples we find qualitatively identical anomalies occurring near $T \sim 25$ K; these are strongest in Ca$_{1.8}$Sr$_{0.2}$RuO$_4$. There is a shrinking of the c axis and an elongation of the RuO$_2$ plane at low temperature. In contrast to these low-temperature anomalies, the thermal expansion at higher temperatures is qualitatively different within the series. Samples with $x > 0.5$ show a normal positive thermal expansion along the planes but a negative thermal expansion...
hence, a transfer of electrons from the one-dimensional direction perpendicular to them qualitatively resembles expansion of the lattice along the planes and the tilt distortion suggests a pronounced coupling. The overall features are strongest in the sample with strongest lattice. Nevertheless, the fact that the low-temperature anomalies are thus not directly related to the tilt distortion. Where all high-temperature effects may be explained by the structural arguments, the thermal expansion anomalies at low temperature must have an electronic origin. The expansion coefficients exhibit extrema below 10 K excluding an explanation by anomalous phonon Grüneisen parameters, since there are no optical or zone-boundary modes in the energy range of 1 meV and below. Instead, the electronic Grüneisen parameter at low temperature appears to be extraordinarily large.

The thermal-expansion anomalies have been confirmed by diffraction techniques, which may analyze both orthorhombic in-plane directions independently, see Fig. 2. The low-temperature expansion upon cooling is observed along both in-plane directions, whereas the $a$ and $b$ directions show a different thermal expansion at higher temperature due to the tilt-induced orthorhombic distortion. The low-temperature anomalies are thus not directly related to the tilt distortion. Nevertheless, the fact that all features are strongest in the sample with strongest tilt distortion suggests a pronounced coupling. The observed expansion of the lattice along the planes and the compression perpendicular to them qualitatively resembles the effect observed at the metal-insulator transition in $\text{Ca}_2\text{RuO}_4$. However, in $\text{Ca}_2\text{RuO}_4$, the changes of the lattice constants are about a factor 30–50 larger, and the electric resistivity strongly increases below the structural change, whereas $\text{Ca}_{1.8}\text{Sr}_{0.2}\text{RuO}_4$ stays metallic to the lowest temperatures. Nevertheless, the structural anomalies in $\text{Ca}_{1.8}\text{Sr}_{0.2}\text{RuO}_4$ are associated with the same electronic effect: a down shift of the $d_{xy}$ orbital energy compared to those of the $d_{xz}$ and $d_{yz}$ orbitals and, hence, a transfer of electrons from the one-dimensional bands into the planar $\gamma$-band (for notation see). For $\text{Ca}_{1.8}\text{Sr}_{0.2}\text{RuO}_4$, there is clear evidence that the anomalous structural behavior at low temperature is accompanied by anomalies in the magnetic and electronic properties detected earlier. In Fig. 3a)–c) the change in the lattice constants is compared to the temperature dependencies of the low-field magnetization and of the in-plane electric resistivity. The latter shows a down-turn just around the temperature range where the thermal expansion anomaly is observed. The magnetic susceptibility deviates from Curie-Weiss behaviour in this temperature range, presenting a maximum at about 10 K.

The response to the metamagnetic transition in $\text{Ca}_{1.8}\text{Sr}_{0.2}\text{RuO}_4$ was studied by neutron diffraction, see Fig. 2, by the measurement of the magnetostriction with a high-resolution capacitance dilatometer, Fig. 3d) and 3g), and by heat capacity studies, Fig. 3h). In the magnetostriction experiment, see Fig. 3d) and 3g), the field was oriented along the $c$ direction and the length change was recorded parallel to the field. The metamagnetic transition is clearly seen at 7 T leading to an enhancement of the $c$ axis by $\varepsilon_c = \frac{\Delta L_c(B)}{L_c} \sim 6 \times 10^{-4}$. In close resemblance with their temperature dependen-
In the diffraction experiment the metamagnetic transition is smeared out due to the random orientation of the grains with respect to the field $\mathbf{B}$. However, the overall magnetostriction remains clearly visible, see Fig. 2. Crossing the transition into the high-field phase we find a shrinking along both in-plane directions and an enhancement along the c direction. The absolute value of the magnetostriction along c agrees well with the dilatometer result. These observations indicate that the structural distortion occurring upon cooling in zero-field may be suppressed and even be inverted by applying a high field at low temperature. From the neutron powder diffraction data obtained on GEM at ISIS we may deduce that the crystal structure remains essentially unchanged with the field. In particular, there is no evidence for superstructure reflections which would appear or disappear with magnetic field. By measuring the tilt superstructure reflection on a single crystal with the lifting counter diffractometer 6T.2 at the Orphée reactor, we can precisely determine the tilt angle reduction to only 3% (under a field of 7 T) in agreement with the powder diffraction study on GEM (ISIS). Since the tilt distortion is coupled with a shrinking of the c axis and with an increase of the averaged in-plane parameters, the observed tilt reduction agrees well with the effect in the lattice constants.

The comparison of the thermal expansion coefficients measured with and without magnetic field is shown in Fig. 4 for Ca$_{1.8}$Sr$_{0.2}$RuO$_4$ and Ca$_{1.5}$Sr$_{0.5}$RuO$_4$. The pronounced shrinking along the c direction in zero field is successively suppressed by the field and turns into a low-temperature elongation at fields larger than 6 T. In contrast, the effect observed along the RuO$_2$ planes in Ca$_{1.5}$Sr$_{0.5}$RuO$_4$ changes from a low-temperature elongation into a low-temperature compression. All our observations indicate that there is an electronic rearrangement occurring at low temperature which may be tuned by the magnetic field. At zero field, electrons shift from $d_{xz}$ and $d_{yz}$ orbitals into the $d_{xy}$ orbitals upon cooling, whereas they do the opposite at high field. This thermal effect is largely enhanced by the octahedron tilt. The structural anomalies indicate a competition between different electronic ground states similar to typical heavy fermion compounds $^{10}$ or LiV$_2$O$_4$ $^{20, 21}$. The low-magnetization state is most likely related to the magnetic instability evidenced in the strongly enhanced magnetic fluctuations in Ca$_{1.5}$Sr$_{0.5}$RuO$_4$ $^{10}$.

The observed anomalies in the temperature dependence of the lattice parameters clearly indicate a change in the orbital occupation which may be tuned by the external field. We propose an interpretation based on the van Hove singularity, vHs, in the $\gamma$-band formed by the $d_{xy}$ orbitals $^{18}$. The vHs is unoccupied in pure Sr$_2$RuO$_4$, but the electronic structure is significantly changed by the rotational distortion which reduces the width of the $\gamma$-band. LDA calculations and recent ARPES measurements indicate that the vHs in

![Figure 3: Comparison of the temperature dependencies of a) thermal expansion, b) magnetization, and c) in-plane resistivity for Ca$_{1.8}$Sr$_{0.2}$RuO$_4$. d) – i) Comparison of the magnetic-field dependencies in Ca$_{1.8}$Sr$_{0.2}$RuO$_4$: d) the longitudinal magnetostriction $\varepsilon_c = \Delta L/L$ for a field along the c direction, e) the magnetization for fields along [110] and [001] directions (note that the metamagnetic transition depends on the orientation of the field), f) the magneto-resistivity along c direction, g) the field derivative of the magnetostriction, h) the field derivative of the magnetization and the linear coefficient of the specific heat $C_p$ $^{22}$, and i) the in-plane longitudinal magneto-resistivity. Resistivity, magneto-resistivity and magnetization data were taken from references $^{4, 38}$.](image-url)
Ca$_{1.5}$Sr$_{0.5}$RuO$_4$ is occupied and that the $\gamma$-band is hole-like [7, 24], as it was also deduced from the inelastic magnetic scattering [10]. The zero-field thermal expansion anomalies are associated with a transfer of electrons from the one-dimensional $d_{xz}$ and $d_{yz}$ bands into the $\gamma$-band. This corresponds to a shift of the DOS peak related to the vHs away from the Fermi level as the vHs singularity is below the Fermi-level in Ca$_{1.5}$Sr$_{0.5}$RuO$_4$ [24]. Since the high DOS is intrinsically related to ferromagnetism, the shift may explain the reduction of magnetic susceptibility as a function of both temperature and Sr content. In the tilted phase the structural anomalies are strengthened due to some direct coupling between the tilt and orbital occupation. The tilting reduces the band width in the one-dimensional bands [7], thereby increasing the local character of these particles, and induces a further deformation of the RuO$_6$ octahedra, i.e. an elongation perpendicular to the tilt axis [4, 6]. Upon increase of the magnetic field, the high DOS arrangement is stabilized, thereby the structural distortions are reversed and electrons are shifted from the $\gamma$-band to the one-dimensional bands. The almost localized character of the electrons in this concentration range rather close to the metal-insulator transition must be very important, since the relatively small structural changes are able to cause qualitatively different physical behavior. Also, the occurrence of the zero-field thermal expansion anomalies at low temperature may be understood in such a picture only if the Fermi surface and Fermi liquid effects are restricted to low temperature. In an usual metal the interplay between the crystal structure and the electron system should be determined at much higher temperature due to the high electronic energy scale involved.

In conclusion, we find strong anomalies in the temperature and field dependence of the crystal structure in Ca$_{2-x}$Sr$_x$RuO$_4$ ($0.2 < x < 0.5$) which indicate that the $t_{2g}$ orbital occupation is tuned by Sr concentration, temperature and external magnetic field.

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