Structural Aspects of Metamagnetism in Ca_{2-x}Sr_xRuO₄: **Evidence for Field Tuning of Orbital Occupation**

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The crystal structure of $Ca_{2-x}Sr_xRuO_4$ with $0.2 \le x \le 1.0$ 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, the crystal structure and the octahedra shrink along the c direction and elongate in the a and b planes, whereas the opposite occurs upon cooling at high field (x = 0.2 and 0.5). These findings yield evidence for an orbital rearrangement driven by temperature and magnetic field, which accompanies the metamagnetic transition at low temperature. The temperature and magnetic-field dependencies are found to be governed by the same energy scale.

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The phase diagram of $Ca_{2-x}Sr_xRuO_4$ possesses quite different end members with the superconductor Sr_2RuO_4 [1] and the antiferromagnetic Mott insulator Ca_2RuO_4 [2– 5]. For small Ca content the RuO_6 octahedrons exhibit a *c*-axis rotation (space group $I4_1/acd$), and for higher Ca content (x < 0.5) an additional octahedron tilt around an in-plane axis occurs (space group Pbca) [6]. These distortions, through reduction of the hybridization, imply smaller band widths, which enhance the correlation effects [7]; in addition, there may be a change in the Madelung potentials. For Sr content lower than 0.2, Mott localization finally occurs.

Remarkable 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 Sr₂RuO₄ [8]. In addition, the linear coefficient in the specific heat is exceptionally high, of the order of $C/T \sim$ 250 mJ/mole K^2 [8,9], well in the range of typical heavy fermion compounds. For Sr concentrations lower than x =0.5, the magnetic susceptibility at 2 K, measured in a low field, decreases with decreasing Sr content and concomitant increasing tilt [5]. In this concentration range the lowtemperature low-field magnetization is small compared with the extrapolation from both high temperature and high Sr concentration. However, 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 [8]. A similar metamagnetic transition has been reported for $Sr_3Ru_2O_7$ [10], where the related quantum critical end point has been proposed to cause remarkable transport properties.

The role of the orbital degrees of freedom is well documented for the metal-insulator transition and the insulating phases in the Ca-rich 214 ruthenates [3,11], but much less is known about the impact of the orbital occupation in the metallic part of the $Ca_{2-x}Sr_{x}RuO_{4}$ -phase diagram. By detailed structural analyzes we show that the variety of physical phenomena in metallic Ca_{2-r}Sr_rRuO₄—in particular, the metamagnetic transition-is associated with a tunable orbital occupation of the t_{2g} levels.

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) following the technique described in [12]; a powder sample of Ca_{1.8}Sr_{0.2}RuO₄ was prepared at Universität zu Köln [13]. 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 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 [14].

The thermal expansion was determined on the single crystals of compositions, x = 0.2, 0.5, 0.62, and 1.0; see Fig. 1. In all samples, we find qualitatively identical anomalies occurring at low temperature; however, these are by far the strongest in Ca_{1.8}Sr_{0.2}RuO₄. There is a shrinking of the c axis and an elongation of the RuO_2 plane at low temperature. In contrast to these lowtemperature anomalies, the thermal expansion at higher temperature is qualitatively different within the series. Whereas all high-temperature effects may be explained by structural arguments [15], the thermal-expansion



FIG. 1 (color online). Temperature dependence of the integrated relative length changes (a),(b) and the thermal-expansion coefficients (c),(d) for different Sr concentrations: (a),(c) and (b),(d) refer to the in-plane and c directions, respectively.

anomalies at low temperature must have an electronic origin. The expansion coefficients exhibit extrema below 10 K, defying an explanation by anomalous phonon Grüneisen parameters, since there are no optical or zoneboundary 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 for $Ca_{1.8}Sr_{0.2}RuO_4$ analyzing 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 and temperaturedependent 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.

For Ca_{1.8}Sr_{0.2}RuO₄, there is clear evidence that the anomalous structural behavior at low temperature is accompanied by anomalies in the magnetic and electronic properties. First, the flattening of the octahedrons at low temperature is accompanied by a strong reduction of the in-plane electric resistivity. Second, the magnetic susceptibility deviates from Curie-Weiss behavior in this temperature range, presenting a maximum at about 8 K [4,5]. Third, the specific heat ratio C_p/T also exhibits a maximum at about 5 K, very close to those in thermal expansion [8,16]. One has to conclude that the structural anomaly in Ca_{1.8}Sr_{0.2}RuO₄ is associated with an electronic crossover



FIG. 2 (color online). Lattice parameters as a function of temperature and magnetic field. Left column: temperature dependence of the orthorhombic lattice parameters in $Ca_{1.8}Sr_{0.2}RuO_4$ determined with a laboratory x-ray diffractometer and the GEM diffractometer at ISIS. Middle column: magnetic-field dependence of the lattice parameters obtained by neutron diffraction on GEM at 0.35 K. Right column: magnetic-field dependence of the RuO-bond lengths; the octahedron gets clearly elongated in the magnetic field (T = 0.35 K).

governed by a characteristic temperature of the order of $T^* \sim 6$ K. In Ca_{1.5}Sr_{0.5}RuO₄, there is a similar though much weaker effect in the in-plane resistivity [4] and a comparable increase in C_p/T upon cooling to about 1 K [8,16]; the related reduction of the low-temperature magnetic susceptibility seems to be hidden by its normal low-temperature increase. It appears that the characteristic temperature T^* of the electronic crossover clearly seen in Ca_{1.8}Sr_{0.2}RuO₄ shifts to much lower values in Ca_{1.5}Sr_{0.5}RuO₄. We may conclude that the anomalous temperature dependencies of transport and magnetic properties are associated with the flattening of the lattice occurring upon cooling.

The response to the metamagnetic transition in Ca_{1.8}Sr_{0.2}RuO₄ was studied by neutron diffraction (see Fig. 2), by the measurement of the magnetostriction [14] [Figs. 3(a) and 3(d)], and by heat capacity studies [Fig. 3(e)] [16]. In the magnetostriction experiment [see Figs. 3(a) and 3(d)], 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 $\varepsilon_c = \frac{\Delta L(B)}{L} \sim 6 \times 10^{-4}$. The structural change at the metamagnetic transition is coupled to changes in magnetization and electrical resistivity. On one side, as shown in Figs. 3(a)–3(c), magnetization, length change, and *c*-axis magnetoresistivity scale with each other. On the other side, the field derivative of the elongation corresponding to the magnetostriction



FIG. 3 (color online). Comparison of the magnetic-field dependencies in Ca_{1.8}Sr_{0.2}RuO₄: (a) the longitudinal magnetostriction $\varepsilon_c = \Delta L/L$ for a field along the [001] direction, (b) the magnetization for fields along [110] and [001] directions (note that the metamagnetic transition depends on the orientation of the field), (c) the magnetoresistivity along the [001] direction, (d) the field derivative of the magnetization and the linear coefficient of the specific heat $\frac{C_p}{T}$ at T = 0.4 K [16], and (f) the inplane longitudinal magnetoresistivity. Resistivity, magnetoresistivity, and magnetization data were taken from Refs. [4,5,8].

and that of magnetization $\frac{dM}{dB}$ show a similar field dependence as the in-plane magnetoresistivity. Also the specific heat over the *T* ratio at low temperature, $\frac{C_P}{T}$ [16], increases around the critical field but much less than $\frac{dM}{dB}$. All these observations indicate that Ca_{1.8}Sr_{0.2}RuO₄ transits between two different magnetic instabilities or ground states. The entities of the left side of Fig. 3, *c*-axis elongation, magnetization, and *c*-axis resistivity, reflect the change in the ground state, whereas specific heat and the in-plane resistivity reflect the enhanced fluctuations at the metamagnetic transition. Indeed, inelastic neutron scattering has recently revealed strongly enhanced magnetic fluctuations of incommensurate character in Ca_{2-x}Sr_xRuO₄ for $x \sim 0.5$ [17], which are different from those in pure Sr₂RuO₄ [18].

The close relation between the metamagnetic transition and the temperature driven crossover in Ca_{1.8}Sr_{0.2}RuO₄ can further be seen in their characteristic energy scales: the characteristic temperature $T^* \sim 6 \text{ K} \sim 0.5 \text{ meV}$ and the critical field $B_c \sim 7 \text{ T} \sim 0.4 \text{ meV}$ are of the same order. Close to x = 0.5 the characteristic energy scale appears to be much smaller; therefore, the electronic crossover is less pronounced and the metamagnetic transition is shifted towards lower fields. The critical field indeed decreases when enhancing the Sr content from x = 0.2 to 0.4 [8].

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 pro-



FIG. 4 (color online). Thermal expansion (top row) and integrated length changes (bottom row) determined at different magnetic fields. The left and right parts present data for $Ca_{1.8}Sr_{0.2}RuO_4$ and $Ca_{1.5}Sr_{0.5}RuO_4$, respectively. Data were taken parallel to the field applied along the *c* direction (left and middle columns) and along the RuO₂ planes (right column).

nounced 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 at high fields. These measurements illustrate once more how closely the temperature-dependent crossover and the metamagnetic transition are related.

In the diffraction experiment the metamagnetic transition is smeared out due to the random orientation of the grains with respect to the field [8]. 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. 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, 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. The powder diffraction experiments, however, show that the structural change at the metamagnetic transition is directly related to the elongation of the RuO₆ octahedron; see Fig. 2. The relative

increase of the Ru-O2 bond, $\frac{ARu-O2}{Ru-O2} \sim 14 \times 10^{-4}$ is larger than that of the *c*-axis parameter, $\sim 6 \times 10^{-4}$. Note that the error bars in Fig. 2 refer to the absolute precision of the bond length; the relative precision is much higher.

The flattening of the RuO₆ octahedrons upon cooling and the elongation under magnetic field resemble the effects observed across the metal-insulator transition in Ca_2RuO_4 [6]. However, in Ca_2RuO_4 , the changes are about a factor 40 larger than the temperature effect and still a factor 15 larger than the magnetic-field effects in Ca_{1.8}Sr_{0.2}RuO₄. Nevertheless, the structural anomalies in Ca_{1.8}Sr_{0.2}RuO₄ are associated with the same electronic effect; in all cases the effects in the Ru-O-bond lengths are stronger than those in the lattice parameters. At zero field, the d_{xy} orbital energy is lowered upon cooling compared to those of the d_{xz} and d_{yz} orbitals. Consequently, a transfer of electrons from the one-dimensional bands of d_{xz} and d_{yz} character into the planar γ band of d_{xy} character occurs similar to observations in pure Ca₂RuO₄ [11] (for notation, see [19]). Upon increasing magnetic field, the opposite effect occurs—electrons move into the d_{xz} and d_{yz} orbitals. In Ca_{1.8}Sr_{0.2}RuO₄ and related materials, the orbital occupation is hence tuned by temperature as well as by magnetic field.

One may ask why the essential change of the physical properties in $Ca_{1.8}Sr_{0.2}RuO_4$ is related with structural effects so much smaller than those occurring in other ruthenates such as Ca_2RuO_4 [6] or $La_4Ru_2O_{10}$ [20]. This strong sensitivity can be related to the presence of two almost degenerate magnetic instabilities, which, however, remain dynamic and do not yield static ordering [17].

Metamagnetism in Ca_{1.8}Sr_{0.2}RuO₄ and in Sr₃Ru₂O₇ was discussed on the basis of itinerant and of localized electron models [10,21]. For the $Ca_{2-x}Sr_xRuO_4$ compounds, a full localization of only one of the t_{2g} orbitals was assumed, but this scenario is debated [21,22]. A localized or nearly localized band explains the extraordinary large electronic Grüneisen parameter due to the resulting high density of states (DOS) near the Fermi level. The orbital rearrangement in this picture corresponds to a rearrangement between nearly localized and metallic bands. The physical properties of the $Ca_{2-x}Sr_xRuO_4$ ruthenates strongly resemble those of LiV_2O_4 [23,24] or those of typical heavy fermion compounds. In particular, there is a striking similarity with CeRu₂Si₂, which also exhibits a comparable electronic specific heat coefficient, a metamagnetic transition, and two competing magnetic instabilities [25]. But in CeRu₂Si₂, the states with local character arise from the Ce-4f states, whereas both local and itinerant states are associated with the 4d orbitals in $Ca_{2-x}Sr_xO_4$. The van Hove singularity (vHs) in the γ band formed by the d_{xy} orbitals and the related DOS peak [19] might be another key element for metamagnetism in Ca_{1.8}Sr_{0.2}RuO₄, since it appears to be very sensitive to the Sr content [7,26]. The orbital rearrangement in $Ca_{2-x}Sr_xRuO_4$ described above will change the position of the vHs in respect to the Fermi level and thereby its relevance for ferromagnetism.

In conclusion, we find strong anomalies in the temperature and the field dependence of the crystal structure in $Ca_{2-x}Sr_xRuO_4$ (0.2 < x < 0.5), demonstrating the role of the orbital degrees of freedom in the metallic part of the $Ca_{2-x}Sr_xRuO_4$ -phase diagram. The t_{2g} orbital occupation appears to be tuned by Sr concentration, temperature, and external magnetic field.

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- [1] Y. Maeno *et al.*, Nature (London) **372**, 532 (1994).
- [2] S. Nakatsuji et al., J. Phys. Soc. Jpn. 66, 1868 (1997).
- [3] M. Braden et al., Phys. Rev. B 58, 847 (1998).
- [4] S. Nakatsuji et al., Phys. Rev. B 62, 6458 (2000).
- [5] S. Nakatsuji et al., Phys. Rev. Lett. 84, 2666 (2000).
- [6] O. Friedt et al., Phys. Rev. B 63, 174432 (2001).
- [7] Z. Fang *et al.*, Phys. Rev. B 64, 020509 (2001); 69, 045116 (2004).
- [8] S. Nakatsuji *et al.*, Phys. Rev. Lett. **90**, 137202 (2003);
 J. Low Temp. Phys. **117**, 1593 (1999).
- [9] R. Jin et al., cond-mat/0112405.
- [10] S. A. Grigera *et al.*, Science **294**, 329 (2001); R. S. Perry *et al.*, Phys. Rev. Lett. **86**, 2661 (2001).
- [11] T. Mizokawa et al., Phys. Rev. Lett. 87, 077202 (2001).
- [12] S. Nakatsuji and Y. Maeno, J. Solid State Chem. 156, 26 (2001).
- [13] Samples were from the same batches as those studied in Refs. [4,5,8] or characterized by x-ray diffraction and susceptibility to posses identical properties.
- [14] R. Pott and R. Schefzyk, J. Phys. E 16, 444 (1983);
 T. Lorenz *et al.*, Phys. Rev. B 55, 5914 (1997).
- [15] The increase of the static tilt deformation reduces the c parameter. Since uniaxial pressure along c stabilizes the tilt, the tilt mode has a negative Grüneisen parameter in the nontilted phase.
- [16] T. Zabel, Ph.D. thesis, Universität zu Köln, 2004.
- [17] O. Friedt et al., Phys. Rev. Lett. 93, 147404 (2004).
- [18] Y. Sidis et al., Phys. Rev. Lett. 83, 3320 (1999).
- [19] D.J. Singh, Phys. Rev. B 52, 1358 (1995).
- [20] P. Khalifah et al., Science 297, 2237 (2002).
- [21] V.I. Anisimov et al., Eur. Phys. J. B 25, 191 (2002).
- [22] A. Liebsch, Phys. Rev. Lett. 91, 226401 (2003); A. Koga et al., Phys. Rev. Lett. 92, 216402 (2004).
- [23] S. Kondo et al., Phys. Rev. Lett. 78, 3729 (1997).
- [24] O. Chmaissem et al., Phys. Rev. Lett. 79, 4866 (1997).
- [25] A. Lacerda *et al.*, Phys. Rev. B **40**, 11429 (1989);
 K. Ishida *et al.*, Phys. Rev. B **57**, R11054 (1998), and references therein.
- [26] S.-C. Wang et al., Phys. Rev. Lett. 93, 177007 (2004).