Ruthenocuprates: Intrinsic magnetic multilayers

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We report ac susceptibility measurements on polycrystalline samples of SrRuO₃ and three ruthenocuprates: superconducting Ru₃Sr₂Eu₂−xCexCu₂O₈ (Ru-1212), superconducting Ru₃Sr₂Eu₂−xCexCu₂O₈ (Ru-1222, x=0.5) and nonsuperconducting, insulating Ru₃Sr₂Eu₂−xCexCu₂O₈ (Ru-1222, x=1.0). Ac susceptibility of both Ru-1222 compositions exhibit logarithmic time relaxation and ‘inverted’ hysteresis loops. Ru-1212 samples exhibit none of these behaviors. We interpret the magnetic behavior of Ru-1222 in the framework of weakly coupled magnetic multilayers and argue that superconductivity coexists with qualitatively different magnetic behaviors.

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The coexistence of superconductivity and long-range magnetic order, and the types of magnetic order compatible with superconductivity, have long been of interest. For ruthenocuprate samples, the precise type of the long-range magnetic order coexisting with superconductivity remains controversial and intriguing. In this report we find that superconductivity coexists with qualitatively different magnetic behavior within the ruthenocuprate family. The main result of this report is that the Ru-1222 ruthenocuprates exhibit unexpected magnetic properties: By studying ac susceptibility in step-like and continuously sweeping low magnetic fields we report a pronounced susceptibility switching, logarithmic time relaxations (magnetic aftereffect) and hysteretic, inverted-in-sense, susceptibility butterfly loops. Most of these properties have been individually reported previously in other, nonsuperconducting, magnetic systems, but the Ru-1222 ruthenocuprates exhibits all of these properties. In marked contrast, superconducting Ru-1212 samples exhibit none of these properties. We argue that Ru-1222 samples are intrinsic magnetic multilayers, and provide a model for the magnetic coupling.

Polycrystalline samples were fabricated as published elsewhere. We fabricated SrRuO₃ polycrystalline samples to serve as a three dimensional itinerant ferromagnet reference material. Ac susceptibility measurements were performed using a CryoBIND system. An ac frequency of 230 Hz and an ac magnetic field amplitude of 0.15 Oe were typically used. A dc magnetic field amplitude up to 100 Oe was also used. Fig.1 shows, from ac susceptibility data, that there are significant differences in magnetic ordering of Ru-1212 and Ru-1222 sample families. While Ru-1212 is characterized by a single maximum at $T_N = 133K$, ac susceptibility of Ru-1222 samples exhibit a peak at $T_M (=85K$ or $117K$, for $x=0.5$ and $x=1.0$ samples) and a less pronounced feature in the temperature range 120-140K (detailed shape depends on $x$), followed by anomalous susceptibility behavior extending up to 180K. Neutron diffraction studies of Ru-1212 indicate that the sharp ac susceptibility maximum at $T_N$ corresponds to the onset of antiferromagnetic long range order of the Ru moments. Magnetization studies establish that there is also a ferromagnetic component of magnetic order, usually attributed to weak ferromagnetism of canted Ru moments. Assigning a precise interpretation to each particular anomaly is not straightforward and will be, as well as obviously important role of Ce in magnetic ordering (Fig.1), a subject of separate publication. In this Letter we focus primarily the temperature range of susceptibility maxima of the Ru-1222 family

![Graph showing ac susceptibility measurements of Ru-1222 samples](image-url)

FIG. 1: Ac susceptibility measurements of Ru-1222 ($x=0.5$ and $x=1.0$) and Ru-1212 samples. Note different scales for the two sample types. Vertical arrow indicates superconductivity transition.
Next, we report the observation of inverted hysteresis phenomena. In measuring the magnetization hysteresis one ramps the applied magnetic field (H) from positive to negative and back and continuously measures the magnetization M(H). In a similar, ‘butterfly’ hysteresis technique, the ac susceptibility \( \chi_{ac}(H) \), instead of magnetization, is measured. In general, these two hysteresis loops yield similar information. For example, the characteristic maxima in butterfly hysteresis (Fig.3a and inset) correspond to the points in magnetization hysteresis satisfying \( M(H) = 0 \). Therefore, the positions of butterfly maxima define the coercive field \( H_{dc} \). Fig.3a shows typical butterfly hysteresis data taken for Ru-1222 and Ru-1212 samples. The data immediately establish that the two types of ruthenocuprates exhibit qualitatively different responses. Comparing the Ru-1222 data to the results characterizing the itinerant bulk ferromagnet \( SrRuO_3 \) (Inset to Fig.3a), there are also pronounced differences. The most striking difference is the inverted sense of loop circulation for Ru-1222: the susceptibility \( \Delta \chi_{ac} \) becomes positive (for turning the field on) or it can be both negative and positive (for turning the field off). The field-induced metastable state is characterized by an ac susceptibility that relaxes in time, a phenomenon variously attributed to disaccommodation or, in wider context of relaxing magnetization, to magnetic aftereffect. By contrast, there is no indication of time relaxation in Ru-1212 samples (Fig.2b, inset):

b) Relaxation is precisely logarithmic in time for both field on and off (Fig.2c), following the usual form \( \chi(t) = \chi_0[1-\alpha n(t-t_0)] \). The parameters, \( \chi_0 \) and the relaxation rate \( \alpha \), depend on temperature, \( H_{dc} \), and on the magnetic history (i.e., on whether the field has been turned on or turned off):

c) For \( |H_{dc}| \) above a threshold value of \( \approx 40 \text{ Oe} \), when \( H_{dc} \) is turned off there is a pronounced ‘overshoot’ phenomenon, i.e., a sizeable positive (\( \Delta \chi \)) (Fig.2b);

d) Applying a rectangular field pulse results in a magnetic state with, surprisingly, increased ac susceptibility (Fig.2b). This state is logarithmically metastable in time. The slow relaxation rate indicates the existence of the field-induced excited ac susceptibility for many time decades.

and report on important new aspects characterizing the complex magnetic order. The Ru-1222 samples of both compositions (x=0.5, superconductor, and x=1.0, insulator) exhibit qualitatively similar behavior. Quantitatively, the effects are more pronounced in x=1.0 sample and Figs.2-4 show the results for this sample only. We first report on time relaxation measurements shown in Fig.2. In these experiments we monitor ac susceptibility of the zero-field-cooled (ZFC) sample in its response to the step-like changes (\( H_{dc} \)) of the dc magnetic field (Fig.2a, inset). Fig.2 shows the time dependence of ac susceptibility for two values of \( H_{dc} \). The data indicate:

a) A step-like change of magnetic field causes i) ac susceptibility switch to a new value, and ii) a sudden transformation of the equilibrium (ZFC) to a metastable magnetic state. The magnitude of the switch (\( \Delta \chi \)) (Fig.2a, 2b) depends on \( H_{dc} \) and then, while its sign can be positive (for turning the field on) or it can be both negative and positive (for turning the field off). The field-induced metastable state is characterized by an ac susceptibility that relaxes in time, a phenomenon variously attributed to disaccommodation or, in wider context of relaxing magnetization, to magnetic aftereffect. By contrast, there is no indication of time relaxation in Ru-1212 samples (Fig.2b, inset):

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magnetometer measurements of the same samples, both SrRuO₃ and Ru-1222, (data not shown) show the dc magnetization hysteresis loop in the normal sense of circulation. Therefore, the inverted hysteresis phenomenon represents a unique feature of the Ru-1222 system, which arises from field-induced metastable states observed in magnetic aftereffect. Other noteworthy features of the Ru-1222 butterfly hysteresis are i) the presence of a maximum even in the initial ZFC (virgin curve), ii) pronounced dependence on the observing time used to obtain the data, and iii) the presence of the two (instead of only one) maxima per field-ascending or -descending branch.

As shown in Fig.3a the virgin branch is characterized by a maximum formed at the characteristic field \( H_{sf} \). In ferromagnets the virgin curve typically does not exhibit a maximum because the remanence, and thus coercive field [11], builds up only after the first field swing, as seen in the SrRuO₃ results (Inset to Fig.3a). The quantitative size of the butterfly hysteresis loop depends on the observation time, another indication that the metastable magnetic states are involved. Qualitatively, however, over the range of sweep times we studied—several minutes to one day—the inverted butterfly loops exhibit the same features. It is further noteworthy that the field \( H_{sf} \) approximately coincides with the minimum field needed to apply in order to get closed butterfly loops: if the range of sweeping field was narrower than \((-H_{sf}+H_{dc})\) no closed loops would be observed whatsoever.

Figs. 3, 4 illustrate two interesting phenomena—magnetic logarithmic relaxation (Fig.2) and inverted hysteric behavior (Fig.3). Figure 4 shows that these two phenomena are related in the Ru-1222 system. Fig. 4a illustrates the temperature dependence of \( H_{sf} \) (Fig.3) and of \( \alpha \), the logarithmic relaxation rate (Fig.2). It is noteworthy that the temperature dependence of these two parameters is virtually identical, indicating that they have a common origin. Another indication that the two phenomena are interrelated is shown in the inset of Fig.4a. Note that \( \alpha \) changes rapidly at low fields, but saturates at a \( H_{dc} \) field value slightly above \( H_{sf} \). Another quantity that qualitatively changes for fields close to \( H_{sf} \) is \( \Delta \chi \), shown in Inset to Fig.2c. Above \( H_{sf} \), \( \Delta \chi \) becomes positive and just monotonously increases with \( H_{dc} \). Again, these qualitative changes in relaxation parameters are connected to the inverse hysteretic behavior.

Now we interpret our results. Based on the feature of inverted hysteresis loops and on the presence and the properties of the field \( H_{sf} \), we propose that the magnetism of weakly antiferromagnetically (AF) coupled magnetic multilayers [14] underlies the ordering in Ru-1222 for the temperature range around \( T_M \). Further, based on the time relaxations, we argue that the weak AF coupling relies primarily on the long range dipole-dipole interaction: as it is well-known [14] this interaction may be responsible for slow, in particular logarithmic, relaxation without any additional assumptions. Our model stems from previous reports of inverted hysteresis loops, limited exclusively to magnetic multilayers [14] and nanoscale magnetic films [17]. Ref. [16] argued for ad-

FIG. 3: a) Left axis: ‘Butterfly’ hysteresis for Ru-1222, \( x=1.0 \) at 80K. Right axis: Analogous data for Ru-1212, just below magnetic ordering temperature. Note just monotonous ac susceptibility decrease and no hysteresis. Inset: Butterfly hysteresis for SrRuO₃ at 160K (\( T_c = 165K \)). Note the response for increasing and decreasing \( H_{dc} \) are opposite to that of Ru-1222. b) Numerical integral \( NIS (\equiv \int_0^H \chi(h) dh ) \) of butterfly susceptibility shown in a) versus \( H_{dc} \) for Ru-1222. Note the inverse hysteresis loop. Inset: \( NIS \) for SrRuO₃ at 160K. Note that this hysteresis corresponds, by all means, to the standard ferromagnetic one.

FIG. 4: Left axis: \( \alpha_{sf} \), the relaxation rate constant defined in text, when \( H_{dc} \) is switched off, versus temperature. Right axis: The field attributed to spin flop, \( H_{sf} \) (Fig.3a), versus temperature. Note that both quantities are zero at temperatures above the susceptibility peak. Inset: \( \alpha_{sf} \), at 80K, versus \( H_{dc} \).
adjacent layers having co-existing magnetic moments, with AF-like coupling between adjacent layers. Ref. [16] also demonstrated that the inverted hysteresis loop behavior disappears if the AF coupling between adjacent layers is changed to ferromagnetic coupling. We argue that the observed hysteretic behaviors actually originate from spin flop or spin flip processes by which the net magnetization \( M \) of adjacent, weakly antiferromagnetically coupled, RuO\(_2\) layers increases. Compared to bulk antiferromagnets, however, the ruthenocuprate magnetic multilayer spin flop fields are weaker by several orders of magnitude (which is generally true for atomic-scale multilayers \([15]\)). Our assignment is further supported by the fact that the dynamical hysteresis loops close only for applied fields higher than \( H_{sf} \). Previous reports \([2]\) indicate that the RuO\(_2\) planes are the main source of magnetic moment for Ru-1222. Consistent with weak magnetic interactions of our model we argue that only a small interlayer component of canted Ru moments participates in ferromagnetic intralayer and AF interlayer coupling.

Logarithmic relaxations, considered independently from other observations, could perhaps be interpreted in framework of domain-wall stabilization (disaccommodation) involving a broad range of activation energies, as has recently been applied to observations in a perovskite manganite \([8]\). However, one of us (IF) and colleagues have performed temperature-dependent x-ray diffraction studies of Ru-1222; these indicate no structural change- necessary for disaccommodation- with temperature \([21]\). Therefore, this model favors the active role of dipole-dipole interaction due to its consistency with both the inferred weak AF coupling \([18]\) and the observed logarithmic relaxations \([15]\).

In summary, we have reported data indicating that Ru-1222 exhibits qualitatively new magnetic behavior, including magnetic logarithmic relaxation, inverted hysteresis loops, and metastable magnetic states. However, superconductivity in the ruthenocuprates is consistent both with the presence of these metastable magnetic states in Ru-1222 and with the qualitatively different magnetic behavior of Ru-1212.

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