Large magnetic anisotropy in highly *c*-axis-oriented $RuEu_{1.5}Ce_{0.5}Sr_2Cu_2O_{10-\delta}$ epitaxial films

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We investigated the magnetic properties in $Ru(Eu_{1.5}Ce_{0.5})Sr_2Cu_2O_{10-\delta}$ (Ru-1222) epitaxial films. Large magnetic anisotropy was observed, showing that the *c* axis is the hard axis of magnetization, while all the directions in the *ab* plane are isotropic easy axes for magnetization. A possible arrangement of the Ru moments is suggested to interpret the magnetic anisotropy as well as the complex magnetic properties of Ru-1222 including the ferromagnetic, the antiferromagnetic, and the spin-glass behaviors.

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Superconductivity (SC) and magnetic ordering are two very different cooperative phenomena, and the question regarding their coexistence is important because of their antagonistic character.[1] Recently, a high-T_c superconductor (HTS), $Ru(Eu_{1.5}Ce_{0.5})Sr_2Cu_2O_{10-\delta}$ (Ru-1222), attracted much attention due to its peculiar coexistence of SC and magnetic order. The superconducting Ru-1222 (with the critical temperature $T_c=32$ K) is also ferromagnetic with the magnetic ordering temperature $T_M=122$ K.[2] The fact that $T_M>T_c$ is contrary to what was observed in the conventional intermetallic magnetic superconductors, in which T_M is much lower than T_c.[1,3] More unusually, the coexistence of superconductivity and ferromagnetism (FM) in Ru-1222 continues from T_c down to the lowest temperature measured,[2] whereas in the intermetallic magnetic superconductors, the occurrence of magnetic ordering is usually accompanied by the destruction of SC (reentrance of resistance).[1,3]Thus the compatibility of SC and FM in Ru-1222 greatly interests researchers, and a great deal of effort had been made to study the material as well as the elucidation of the physical mechanism.

Based on the previous studies of Ru-1222, which involved every respect of its synthesis,[4,5] crystal structure,[6–8] and superconductive and magnetic behaviors,[2,9–19] it is generally considered that SC is confined to the CuO_2 planes, while FM originates from the Ru sublattice.[2] This configuration may imply that the coexistence of SC and FM is due to their isolated locations in different crystal sublattices. However, there is no detailed conclusion yet because the magnetic structure of Ru-1222 is still unclear. Felner *et al.* suggested[2] that the ferromagnetic behavior of Ru-1222 originates from the canting of the Ru spins, which is caused by the Dzyaloshinsky-Moriya (DM) antisymmetric exchange coupling[20] between neighboring Ru moments. The possibility of this scenario of magnetic ordering was later supported by powder neutron diffraction,[7] showing the rotation of the RuO_6 octahedrons, which breaks the tetragonal symmetry. However, Xue *et al.* questioned the DM interaction for a full interpretation of the ferromagnetic order in Ru-1222 in that the observed magnetic moment is unusually large for this mechanism.[13] They suggested the phase separation of ferromagnetic and antiferromagnetic species, and naturally attributed the unusual ferromagnetic and superconductive behaviors of Ru-1222 to this phase separation. A problem for the phase-separation scenario is that it had not been reconciled with the other experimental results, which suggested that the Ru-1222 samples were of single phase, without the separation of superconducting and magnetic grains.[2,21–23] More recently, Živkovic *et al.* proposed that the magnetic ordering in Ru-1222 is a variation of the *G*-type antiferromagnetism (AFM), with the Ru moments in adjacent RuO_2 planes canting from the *c* axis toward each other.[14] The ferromagnetism arises from the spin flop of the in-plane Ru moment component in applied magnetic field. However, confirmation of this scenario needs the support of direct evidences such as the magnetic anisotropy and the spin-flop behaviors, which were not observed due to the lack of identically oriented samples, i.e., single crystals or epitaxial films.

Recently, we observed the magnetic anisotropy of Ru-1222 in the highly *c*-axis oriented thin films grown by the flux-assisted solid phase epitaxy technique.[24] Felner *et al.*[25] also observed the similar phenomenon and suggested that the Ru ions are in a pentavalent state with the $3\mu_B$ moment lying in the *ab* plane. However, this magnetic configuration cannot account for the antiferromagnetic features exhibited by Ru-1222,[2,13,14] and also the $3\mu_B$/Ru in-plane moment is too large to account for the small Ru moment ($0.83\mu_B$/Ru) observed in bulk polycrystalline Ru-1222 samples.[2] Thus further examinations of the anisotropic magnetization behaviors of Ru-1222 are warranted. In general, since magnetic anisotropy is very sensitive to the out-of-plane and in-plane crystal epitaxy of the sample, the crystallinity should be paid the greatest attention. In the case of the report in Ref. 25, there is no data about such crystallinity information as rocking curves and in-plane x-ray-diffraction patterns. In this paper, we report the magnetic anisotropy exhibited by our highly *c*-axis oriented Ru-1222 films. All samples showed qualitatively the same properties, and the representative data (measured from the same sample with the film thickness of 300 nm) are shown in this paper. We found that the magnetic anisotropy is larger, but the in-plane magnetization is significantly smaller than that reported in Ref. 25. A simplified

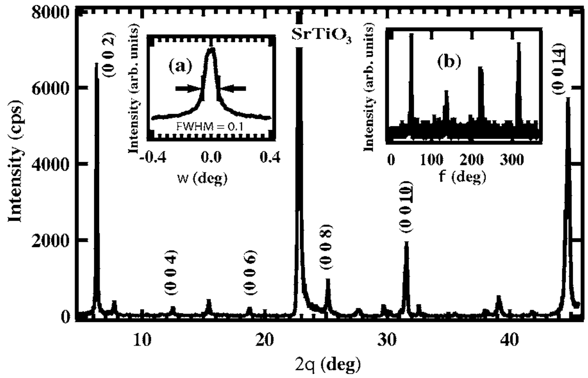

FIG. 1. XRD pattern of the highly c-axis oriented epitaxial Ru-1222 films grown on a $SrTiO_3(001)$ substrate. Inset (a): ω scan taken on the Ru-1222(002) diffraction peak, FWHM=0.1°. Inset (b): in-plane fourfold symmetry indicated by the x-ray ϕ scan taken on the 10-17 diffraction.

magnetic structure was suggested for a qualitative interpretation of the phenomena.

The highly c-axis oriented Ru-1222 epitaxial films in the present study were grown by the flux-assisted solid phase epitaxy technique.[24,26] As shown in Fig. 1, the Ru-1222 (001) peaks in the x-ray-diffraction pattern are very clear, and no randomly aligned Ru-1222 phases are detected. The full width at half maximum (FWHM) of the Ru-1222 (002) peak is 0.1° [Fig. 1, inset (a)], indicating excellent crystallinity. The x-ray ϕ scan taken on the 10-17 diffraction [Fig. 1, inset (b)] indicated a fourfold symmetry in the film plane, suggesting Ru-1222(100)‖$SrTiO_3(100)$ epitaxial growth. Temperature dependence of the resistance in the films showed the superconducting transition at T_c=25 K, but zero resistance was not obtained down to 5 K.[24,26] Since the present study focuses on the magnetic properties of the films, the transport behaviors will be discussed in detail elsewhere.

The magnetic properties of the films were measured by using a Quantum Design superconducting quantum interference device (SQUID) magnetometer. By rotating the films in a constant magnetic field, we found that the hard axis of magnetization was along the c axis, while the directions in the ab plane are all easy for magnetization without anisotropy. Figure 2 shows the temperature dependence of the in-plane magnetization ($M_{\parallel}$) and out-of-plane magnetization ($M_{\perp}$) under a 40 Oe magnetic field. $M_{\perp}$ is replotted in the inset, in a proper scale, to show the detailed feature. The behaviors of $M_{\parallel}$ and $M_{\perp}$ are qualitatively the same and in agreement with that of the bulk polycrystalline Ru-1222 samples reported,[2] and no anomaly was observed. This means that the origin of the ferromagnetic ordering should be the same in our films as in the bulk polycrystalline samples, in spite of the fact that our films are not bulk superconducting. On decreasing temperature the abrupt decrease of $M_{\perp}$ on both zero-field-cooled (ZFC) and field-cooled (FC) branches at 25 K were caused by the superconducting transition. In contrast, no sudden decrease at 25 K was observed on $M_{\parallel}$, probably due to the large in-plane magnetic moment, which masked the diamagnetic contribution of the superconducting phase, as suggested by Felner *et al.*[12]

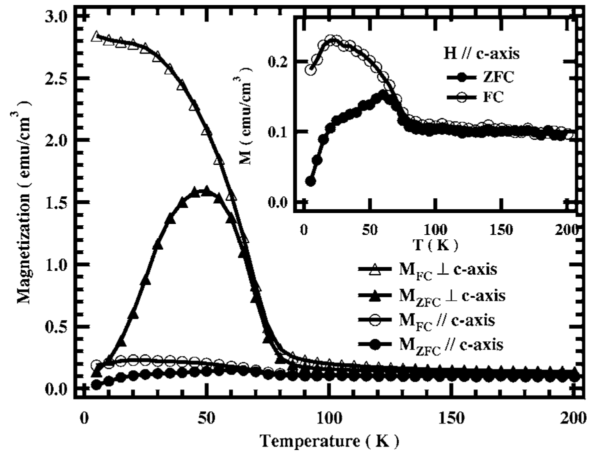

FIG. 2. Temperature dependence of in-plane and out-of-plane magnetizations. Inset: temperature dependence of the out-of-plane magnetization in a proper scale to show the detailed features.

Figure 3 shows the in-plane and out-of-plane $M(H)$ curves at 30 K after subtracting the linear diamagnetic contribution of the $SrTiO_3$ substrate. The in-plane hysteresis loop represents the results obtained along various in-plane directions—all these measurements gave exactly the same result, suggesting isotropic in-plane magnetization. The features of the hysteresis curves are in agreement with those of polycrystalline samples in the previous reports[2]—they are composed of a ferromagnetic and a paramagnetic component due to the Ru and the rare earth ions, respectively. It can be seen in both Fig. 2 and Fig. 3 that the magnetic anisotropy between the in-plane and out-of-plane directions is very large. The ratio of the saturated value of $M_{\parallel}$ to $M_{\perp}$ in Fig. 3 is 12, larger than the reported value of 7.5.[25] The in-plane magnetization saturates at about 5000 Oe at 5 K [Fig. 3, inset (a)]. By extrapolating the linearly increased high-field part of the curve to 0 Oe, the saturated Ru moment is evalu-

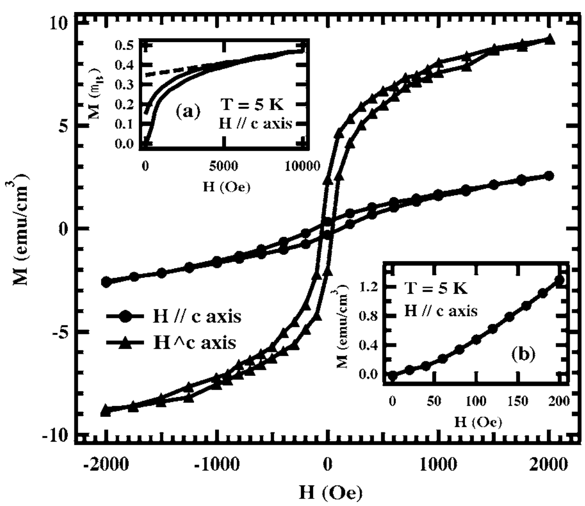

FIG. 3. In-plane and out-of-plane magnetizations changing with the magnetic field at 30 K. Inset (a): saturated in-plane Ru moment component indicated by extrapolating the linearly increased part of the $M(H)$ curve. Inset (b): low-field part of the initial in-plane magnetization, showing no abrupt change.

ated to be 0.34 μ_B per Ru ion, which is much smaller than the 1.1μ_B/Ru observed in$SrRuO_3$.[27]. The small Ru moment and the irreversible behavior (Fig. 2) suggest weak ferromagnetism (WFM) arising from canting of the Ru moments.

It is noted that the demagnetization effect[28] is not a significant reason for the magnetic anisotropy because the demagnetization field is estimated to be at most 122 Oe at an out-of-plane field of 2000 Oe, which apparently cannot account for the large difference between $M_\parallel$ and $M_\perp$ in Fig. 3. In fact, the magnetic anisotropy was largely moderated in the case of Ru-1222 films containing randomly aligned phases.[29] In these films, the $M_\perp$ is larger while the $M_\parallel$ is smaller than that shown in Fig. 2 and Fig. 3 due to an average of the anisotropic magnetism. These facts indicate that the large magnetic anisotropy exhibited by our films is an intrinsic property of Ru-1222.

The observed magnetic anisotropy provides evidence for the study of the magnetic structure of Ru-1222. At first sight the phenomenon that $M_\parallel \gg M_\perp$ may suggest an in-plane alignment of Ru moments, with the FM order arising from the DM interaction. However, under such a scenario the ferromagnetic components should have specified orientations corresponding to the well-defined rotation of the RuO_6 octahedron around the *c* axis.[7,20] Thus anisotropy should also be observed in the *ab* plane, while this is inconsistent with our experimental observations. Alternatively, Živkovic *et al.* had suggested an out-of-plane alignment of Ru moments,[14] in which the Ru moments are arranged as a variation of the *G*-type antiferromagnetism, with the Ru moments canting a little from the *c* axis and turn toward their interlayer neighbors. The canting is caused by the dipole-dipole interaction between the nonvertically aligned interlayer Ru neighbors and this contributes a nonzero component in the *ab* plane. It was suggested in Ref. 14 that, since the dipole-dipole interaction is very weak, a small in-plane magnetic field (about several tens of Oersted[14]) can easily transform the antiferromagnetically aligned in-plane Ru moment components, via a spin-flop mechanism, into a ferromagnetic orientation, while the spin-flop of the out-of-plane Ru moment components needs to overcome the strong interaction between the intraplane Ru ions and thus is much more difficult. To support such a scenario of magnetic ordering, not only the anisotropic behavior, i.e., $M_\parallel \gg M_\perp$, but also the spin-flop of the in-plane Ru moment components, which appears as an abrupt increase of the in-plane magnetization, should be observed. However, although in our experiments it is manifestly demonstrated that $M_\parallel \gg M_\perp$, the predicted spin-flop behavior[14] was not observed: the initial in-plane magnetization increased smoothly with the field, as shown in the inset (b) in Fig. 3. Thus it needs further considerations on this magnetic structure to interpret the observed phenomena.

Considering the positions of the Ru ions in the crystal structure of Ru-1222, one may find that for each Ru ion, there are eight interlayer neighbors residing in equal crystal sites relative to it, as shown in Fig. 4. Therefore, as far as the dipole-dipole interaction between interlayer Ru neighbors being considered as the reason for canting of the Ru moments, there is no reason for the Ru moment canting toward a specified neighbor without any limitations, and consequently, it is less likely for a long-range antiferromagnetic

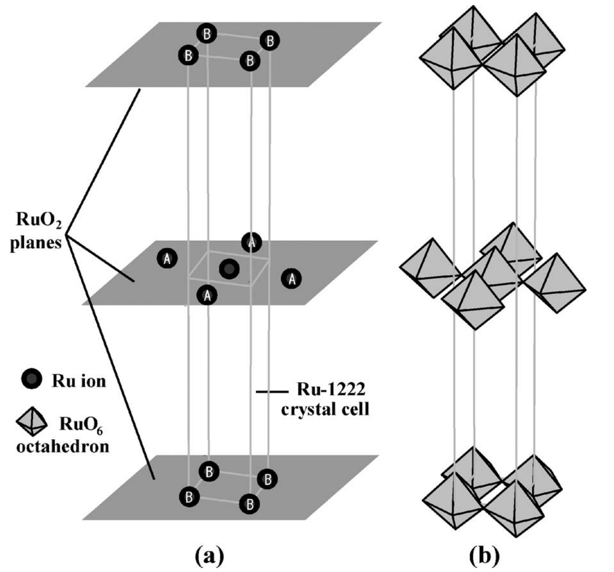

FIG. 4. Ru-1222 crystal cell with (a) Ru ions and (b) RuO_6 octahedrons selected, showing the intralayer and interlayer neighbors [labeled with "A" and "B" in (a), respectively] of the Ru ion at the center.

arrangement of the in-plane Ru moment component to be established. Alternatively, it should be more reasonable that the Ru moments cant randomly toward one of their interlayer neighbors, having their in-plane components randomly oriented to [110], $[\bar{1}10]$, $[1\bar{1}0]$, and $[\bar{1}\bar{1}0]$ directions [see Fig. 5(a)]. This randomness explains the nonobservation of the in-plane spin-flop in our results. In fact, the essence of the suggestion in Ref. 14 is the weak dipole-dipole interaction between the interlayer Ru ions and the canting of the Ru moment induced by it. It does not necessarily lead to an in-plane antiferromagnetic ordering.

It should be noted that our proposed assumption of the Ru moment arrangement of Ru-1222 is reasonably evolved, based on our experimental results, from the variation of the *G*-type antiferromagnetic model suggested by Živković *et al.*[14] The assumption of the random orientation of the in-plane Ru moment components may be more meaningful in that some other unusual magnetic behaviors of Ru-1222 reported, such as the spin-glass behavior[19] and the phase separation of FM and AFM species,[13] may also be interpreted. The spin-glass behavior should be a natural result for this

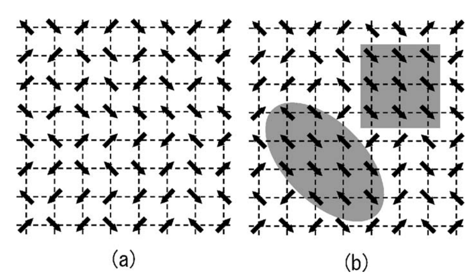

FIG. 5. Schematic illustration of the in-plane Ru moment components (a) aligned randomly, and (b) aligned ferromagnetically (rectangularly shaded) and antiferromagnetically (elliptically shaded) in small regions.

randomness of the in-plane moment components. On the other hand, note that the in-plane Ru moment components are not completely free, but affected by the weak dipole-dipole interaction from the neighboring interlayer Ru ions, thus in small regions both parallel and anitiparallel alignments, which correspond to FM and AFM ordering, respectively, are possible [Fig. 5(b)]. We highly expect neutron-diffraction experiments to give evidence on these assumptions.

In conclusion, large magnetic anisotropy was observed in the highly *c*-axis oriented epitaxial Ru-1222 films, showing that the *c* axis is the hard axis of magnetization, while all the directions in the *ab* plane are isotropic easy axes for magnetization. The phenomena were interpreted by a possible arrangement of the Ru moments in which the Ru moments cant a little from the *c* axis, with the component in the *c* axis arranged antiferromagnetically, while the component in the *ab* plane randomly points toward the [110], $[\bar{1}10]$, $[1\bar{1}0]$, and $[\bar{1}\bar{1}0]$ directions. Under this configuration of Ru moments the complex magnetic properties of Ru-1222, including the ferromagnetic, the antiferromagnetic, and the spin-glass behaviors, may also be interpreted.

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