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Magnetic properties of the $RuSr_2Ln_{1.5}Ce_{0.5}Cu_2O_{10-\delta}$ (Ln = Y, Ho and Dy) and $RuSr_2YCu_2O_{8-\delta}$ rutheno-cuprate families: a comparative study

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Abstract

The magnetic behavior of polycrystalline samples of the magneto-superconductors $RuSr_2Ln_{1.5}Ce_{0.5}Cu_2O_{10-\delta}$ (LnRu-1222, Ln = Y, Ho and Dy) and $RuSr_2YCu_2O_{8-\delta}$ (YRu-1212) is analyzed and compared. Clear evidences for the occurrence of a spin glass phase on all LnRu-1222 samples are provided by ac susceptibility (χ_{ac}) and dc magnetization measurements. A frequency-dependent peak in χ_{ac} vs. T measurements, at low magnetic field, is observed. The strong suppression of this peak in the presence of magnetic fields as low as 500 Oe, as well as the results of thermoremanent magnetization (TRM) and isothermal remanent magnetization (IRM) measurements, suggest a spin glass behavior. Interestingly, the same measurements on the YRu-1212 sample show no indication of glassy behavior, contrasting with the results for LnRu-1222. We suggest that frustration of the Ru magnetic moments due to the presence of oxygen vacancies would be favored only in the LnRu-1222 compounds, thus causing the glassy behavior. This idea is supported by the observation of large oxygen deficiency that affects the RuO_2 planes in Ru-1222, but does not occur in Ru-1212.

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1. Introduction

A large number of reports have recently appeared focusing on the magnetic and superconducting properties of the rutheno-cuprates $RuSr_2Ln_{2-x}Ce_xCu_2O_{10-\delta}$ (LnRu-1222) [1] and $RuSr_2LnCu_2O_{8-\delta}$ (LnRu-1212) [2] families. However, despite the intensive research on these

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materials, some unanswered questions still remain. For instance, the oxygen non-stoichiometry, carrier concentration and valence state of Ru are not well understood yet [3,4]. One of the most controversial questions is the exact type of magnetic ordering in the LnRu-1222 family. In contrast to the LnRu-1212 family, for which a consensus has been reached on the canted antiferromagnetic ordering for the Ru sublattice [5,6], the detailed magnetic ordering of the LnRu-1222 family is still lacking. Although the magnetic behavior of LnRu-1222 has been considered to be analogous to the magnetic response for LnRu-1212 samples, some recent results point towards various differences between them [7,8]. In particular, strong evidences of spin glass behavior was found in GdRu-1222 [8].

In order to test the generality of the spin glass phase in LnRu-1222 and to understand the mechanism behind its appearance, in the present work we extend our previous study [8] to other LnRu-1222 compositions (Ln = Y, Dy, Ho). The verification of the spin glass behavior for these new samples and the differences between these results with those obtained for an YRu-1212 sample lead us to conclude that the spin-glass phase is characteristic of the LnRu-1222 phase. We propose here that the presence of oxygen vacancies in the RuO_6 octahedra for LnRu-1222 may cause the frustration of the magnetic ordering of the Ru ions, leading to a glassy behavior in these compounds, which does not usually occur for LnRu-1212 samples. Studies comparing the oxygen non-stoichiometry for both families support our interpretation [4].

2. Experimental

Samples of composition $RuSr_2Ln_{1.5}Ce_{0.5}Cu_2O_{10-\delta}$ (LnRu-1222) with Ln = Y, Ho, and Dy were synthesized through a high-pressure high-temperature (HPHT) solid-state reaction route, described elsewhere [9]. All LnRu-1222 samples present a tetragonal structure within the I4/mmm space group as confirmed by X-ray powder diffraction (XRD) patterns obtained at room temperature (Philips-PW1800; CuK_α radiation). The lattice parameters are $a = b = 3.824(1)$, $3.819(1)$, and $3.813(1)$ Å and $c = 28.445(1)$, $28.439(1)$, and $28.419(1)$ Å for Ln = Y, Ho, and Dy, respectively.

The YRu-1212 was prepared using the same procedure, except that for this compound it was necessary to start from a slightly Ru poor composition in order to obtain a single phase sample of the desired stoichiometry [10,11]. The lattice parameters obtained are $a = b = 3.818(1)$ Å and $c = 11.5222(3)$ Å. All samples are single phase within the XRD resolution, except for YRu-1222 which presents a small amount of $SrRuO_3$. All ac susceptibility measurements were performed in a commercial PPMS (Physical Properties Measurement System), while for the dc measurements a SQUID magnetometer MPMS-5 was employed, both equipments made by Quantum Design company.

3. Experimental results

The temperature dependence of the complex ac susceptibility ($\chi_{ac} = \chi' + i\chi''$) is presented in Fig. 1. The measurements performed for an applied field of $H = 50$ Oe for all samples present a well defined peak at temperatures $T_f = 87.4$, 103.3 and 101.5 K for Dy-, Ho- and YRu-1222, respectively, and $T_N = 140.6$ K for YRu-1212. This peak is strongly suppressed by increasing the magnetic field H for all three LnRu-1222 samples, and it almost vanishes for $H = 500$ Oe. Also, the peak position is shifted to higher temperatures at higher magnetic fields. The strong suppression of the peak in χ' at moderate fields is characteristic of the spin glass behavior. On the other hand, the peak for YRu-1212 presents a much weaker dependence with the magnetic field and it is slightly shifted to lower temperatures with the increase of H. Another important difference between LnRu-1222 samples and the YRu-1212 one is the presence of an anomaly in the ac susceptibility at $T_M = 150$ K for LnRu-1222, while no anomaly was observed for sample YRu-1212. This anomaly is more prominent for Y- and HoRu-1222 than for DyRu-1222, and is smeared out when H is increased. It is striking that the anomaly observed in LnRu-1222 samples occurs at the same temperature, independently of Ln, and also that this temperature is

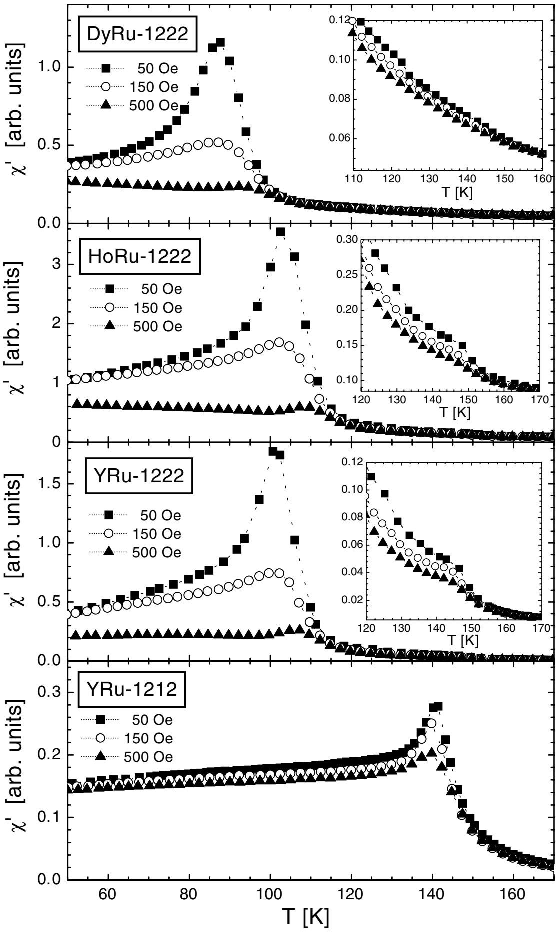

Fig. 1. Real part of the ac magnetic susceptibility as a function of temperature for different magnetic fields, for all four samples. Insets show the anomaly observed in the χ_{ac} measurements (for LnRu-1222 samples only) for $T_f < T < T_M$.

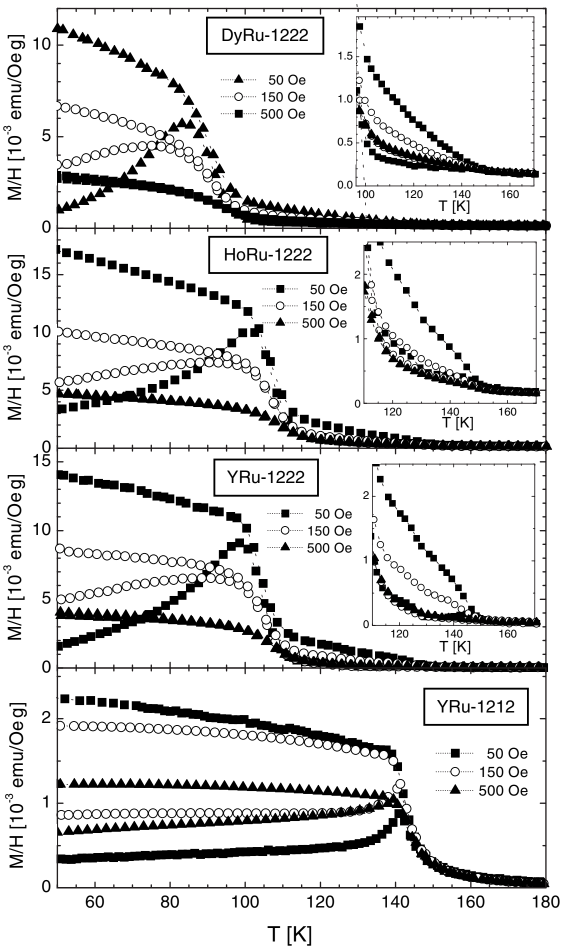

Fig. 2. DC magnetic susceptibility as a function of temperature for different magnetic fields, for all four samples. Insets show the irreversibility observed in the measurements (for LnRu-1222 samples only) for $T_f < T < T_M$.

close to the position of the peak observed for YRu-1212.

In Fig. 2 we present the dc magnetic susceptibility as a function of temperature for different magnetic fields. The curves for all LnRu-1222 show similar behaviors. The field cooled (FC) measurements present a ferromagnetic-like shape, while the zero-field cooled (ZFC) curves present a peak at the temperatures $T_p = 83.7$, 101.8 and 98.9 K for Dy-, Ho- and YRu-1222 respectively, for $H = 50$ Oe. The ZFC/FC curves branch apart twice, first at $T_M \approx 150$ K (for all LnRu-1222 samples), and again at $T_{irr} \approx T_f \sim 100$ K (Y- and HoRu-1222) or 84 K (DyRu-1222). At $H = 50$ Oe the ZFC and FC curves are not exactly reversible for any temperature below T_M, so T_{irr} is not well determined. As the applied magnetic field is increased to 500 Oe, a significant reduction in the irreversibility is observed and both, ZFC and FC curves, tend to a ferromagnetic-like behavior. The irreversibility observed at temperatures above the peak in the ZFC curve is also greatly affected by the increase of the applied field, being hardly distinguishable at $H = 500$ Oe. Comparing the results for dc magnetization with the ac susceptibility, we

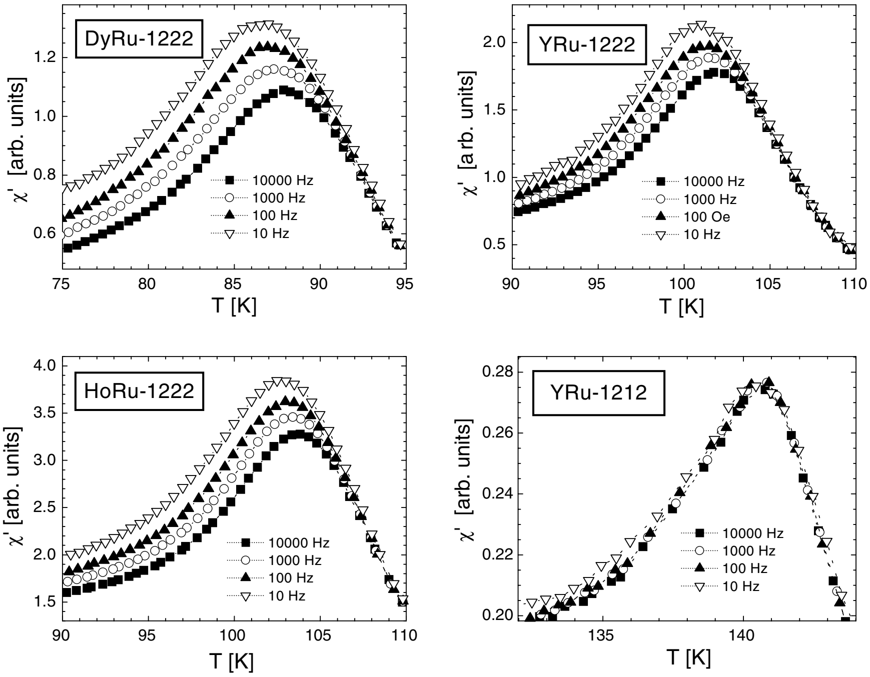

Fig. 3. Real part of the ac susceptibility as a function of temperature for $H = 50$ Oe and for four different frequencies, for all four samples. The peak position defines the freezing temperature T_f (for the LnRu-1222 samples).

observe: (1) the anomaly in χ' occurs at the same temperature, $T_M \approx 150$ K, of the deviation from the paramagnetic behavior in the magnetization data; (2) the peak position in χ' roughly coincides with T_{irr}. The coincidence of the peak temperature in χ' with T_{irr}, the drastic reduction of irreversibility and the ferromagnetic-like behavior of both ZFC and FC curves with small applied fields, are all consistent with the expected behavior of a spin-glass system. Now we turn our attention to the YRu-1212 sample again. The ZFC/FC irreversibility is also suppressed with the increase of H, but a significant irreversibility remains present even at $H = 500$ Oe. Also, the peak in the ZFC curve is broadened at higher H, but it does not disappear (up to 500 Oe). Once more, the behavior of the YRu-1212 is quite different from the observed for LnRu-1222, which by its turn is very similar for Ln = Dy, Ho and Y.

The most clear and conclusive way to experimentally separate an antiferromagnet from a spin-glass is to probe the frequency dependence of the peak in χ'. As can be observed in Fig. 3, the peak shifts to lower temperatures and its intensity increases as the frequency of the excitation field is decreased, for all three LnRu-1222 samples. This frequency dependence of χ' is one of the fingerprints of a spin-glass transition [12]. To distinguish a spin glass from a superparamagnet, it is necessary to analyze the peak shift with frequency in a quantitative way, which can be achieved by evaluating $\Delta T_f/[T_f \log(\omega)]$. From the FC ac susceptibility measurements at different frequencies (Fig. 3) we could estimate $\Delta T_f/[T_f \log(\omega)] \approx 0.0031$, 0.0021 and 0.0018 respectively for Dy-, Ho- and YRu-1222, which is consistent with the expected behavior for spin-glasses [12]. On the other hand, no significant changes in the peak are observed for the YRu-1212 sample, which is the expected behavior for an antiferromagnet.

Also, we have verified the existence of a spin-glass behavior through the measurement of the remanent magnetization. Fig. 4 shows both thermoremanent magnetization (TRM) and

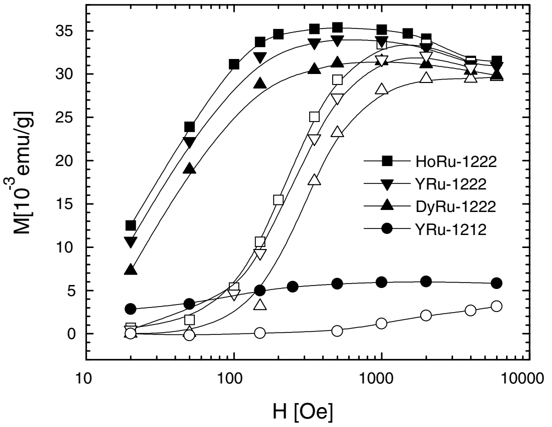

Fig. 4. Thermoremanent magnetization (TRM, solid symbols) and isothermal remanent magnetization (IRM, open symbols) for all samples, measured as a function of the applied magnetic field, at $T = 30$ K. The solid lines are only guides for the eyes.

isothermal remanent magnetization (IRM) measurements [8,12] for the three LnRu-1222 and the YRu-1212 samples. For the TRM experiments, all curves present an abrupt increase at lower fields, going through a small maximum just before reaching its saturation, while the IRM experiments, all curves present a much more gentle increase up to the saturation value. These results are again in agreement with the expected behavior of a spin-glass [12]. The TRM and IRM results for the YRu-1212 sample present a much less pronounced dependence on the applied field, although it also increases with H.

4. Discussion

The results presented in the previous section show that all LnRu-1222 studied samples present a spin-glass transition at T_f, while the YRu-1212 sample is an antiferromagnet. It is important to notice that the spin glass behavior is strongly dependent on sample quality, so the observation of the spin glass behavior in a single sample is not necessarily a clear proof that it is an intrinsic property of the studied compound. However, a systematic observation of the spin glass phase in several high quality samples of the same compounds family is indeed a strong indication that these materials present an intrinsic glassy behavior. By comparing the results on the LnRu-1222 samples with those of the YRu-1212 sample, which were all prepared and handled exactly in the same way, we obtain further evidence that the spin glass phase is a common property of the LnRu-1222 family. Following, we first discuss the results for the LnRu-1222 samples to check for possible influences of the specific Ln ion on their spin-glass properties. A second and more important discussion is to find out why LnRu-1222 and LnRu-1212 present such distinct magnetic properties.

It is well known that only the Ru spins in the RuO_2 planes order magnetically, while the Ln ions present a paramagnetic response down to the lowest probed temperature [1]. Then it is expected that the Ln layers play a less important role in determining the magnetic ordering in these ruthenates. In fact, it could be inferred from the data presented in Figs. 1–4 that the change of the Ln ion did not change qualitatively the magnetic behavior of the LnRu-1222 samples. However, a few differences between them can be pointed out, the more obvious being the diminution of the freezing temperature following the order Ho–Y–Dy–Gd [8]. As shown in Fig. 5, this can be related to the changes in volume of the unit cell [9], due to the different ionic radii of the Ln ions. Fig. 5 also shows a plot of T_M, which is almost constant for

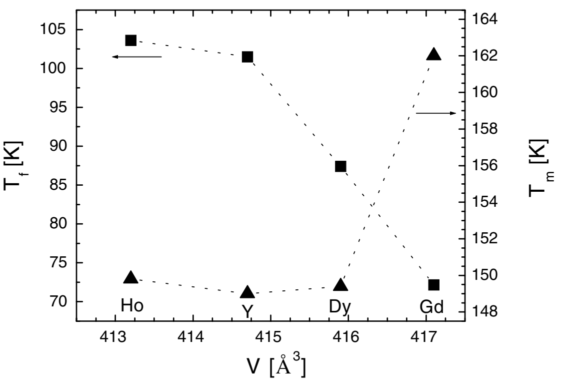

Fig. 5. Variation of the freezing temperature T_f and the magnetic transition T_M as a function of the volume of the unit cells for LnRu-1222 compounds. The results for GdRu-1222 were extracted from Ref. [8].

the samples studied in this work, but is much higher for the GdRu-1222 sample previously studied [8]. Because the GdRu-1222 sample was prepared by a different technique [13], it could also be that this difference is a consequence of the synthesis process. Also, the irreversibility observed in ZFC/FC magnetization curves for temperatures $T_f < T < T_M$ is very small for GdRu-1222 and becomes more prominent for compounds with smaller Ln ions. Both, different ionic radii and synthesis process, seem to affect this irreversibility.

A more intriguing question to be answered is why all LnRu-1222 samples we have studied present a clear spin-glass behavior while the YRu-1212 sample is an antiferromagnet. It is worth noticing that structural differences between both compounds are restricted just to the Ln plane, which is isolated from the RuO_2 planes that order magnetically. Therefore, one possibility is that the Ln plane could affect the magnetic behavior of the compound by indirectly affecting the RuO_2 planes. To produce a spin-glass state it is necessary to frustrate the magnetic order, which is accomplished by disorder. One could first try to find this disorder in the mixing of Ce and Ln ions, which is only present in the LnRu-1222 family. A random distribution of Ln could cause small local perturbations in the crystalline structure in such a way that the RuO_6 octahedra could be distorted, thus inducing the frustration of Ru magnetic moments. Another simple explanation could come from an oxygen non-stoichiometry, which could directly affect the RuO_2 planes. The different magnetic behavior of the two families (LnRu-1212 and LnRu-1222) could only be explained if the LnRu-1222 family is more susceptible to present oxygen vacancies than the LnRu-1212 family. In fact, a recent work [4] reports that GdRu-1212 can be obtained with a near stoichiometric oxygen content, while the GdRu-1222 phase is clearly oxygen-deficient even after a 100-atm O_2 annealing. Changes observed in the valence of Ru in GdRu-1222 as the oxygen content varies suggest that the vacancies occur in the RuO_2 layers. The same work [4] has also shown that the oxygen content in GdRu-1212 is almost constant upon various annealings, while for GdRu-1222 a wider range of oxygen content is accessible. These results lead us to conclude that the most reasonable origin for the glassy behavior observed in our LnRu-1222 samples is the presence of oxygen vacancies. If this is the case, our results would be showing, in a quite dramatic way, the influence of the oxygen content on the magnetic properties of the LnRu-1222 samples. It is likely that some of the contradictory results reported on the LnRu-1222 system can be correlated to the difficulty to fully oxygenate samples of this system. Although we did not observe any indication of a spin glass phase in the studied YRu-1212, we believe that an oxygen-depleted Ru-1212 sample may also present a glassy behavior. It is important to notice that the samples we have studied in this work (as well as the GdRu-1222 sample, reported in Ref. [8]) were synthesized by routes which allow a higher oxygen content than other more usual procedures.

5. Concluding remarks

In this work we have shown that the frequency-dependent peak observed in the temperature dependence of the ac susceptibility χ_{ac}, as well as its suppression by a small magnetic field, combined with remanent magnetization results, provide strong evidence of the existence of a spin glass phase in polycrystalline LnRu-1222, Ln = Dy, Ho and Y. This is valid for samples with different Ln and prepared by two different routes (considering also the GdRu-1222 sample, previously reported [8]), indicating that the glassy behavior is a characteristic feature of the LnRu-1222 family, being not restricted to a single sample. This is to be contrasted with the existence of long-range antiferromagnetic order for the YRu-1212 sample. Although the change of the Ln ion did not change qualitatively the magnetic behavior of the LnRu-1222 samples, the freezing temperature is reduced with the increase of the Ln ionic radius.

We propose that oxygen vacancies could frustrate the long-range order of the Ru spins, leading to a spin glass phase. Recently [4] it was shown that the LnRu-1222 phase is usually oxygen deficient, while the LnRu-1212 family can be synthesized with near stoichiometric oxygen content. These results corroborate our ideas and provide a possible explanation for the contradictory behavior found in the literature, related to these two families of rutheno-cuprates.

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