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Exchange bias effect in sub-micrometric granulated composites of antiferromagnetic superconductor and ferromagnetic manganite

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Abstract

We report the synthesis of RuSr₂GdCu₂O₈-La_{0.67}Sr_{0.33}MnO₃ superconducting-magnetic composites with 50 vol.% of both RuSr₂GdCu₂O₈ and La_{0.67}Sr_{0.33}MnO₃ compounds. Structural characterization was performed by x-ray diffraction, which permitted to establish the absence of other crystallographic phases and the non reactive character of the compounds into the composite. Scanning electron microscopy showed the sub-micrometric size of grains of the system. Resistivity measurements evidenced the superconducting transition for the RuSr₂GdCu₂O₈ material, which has the value T_{sc}=39.2 K. Results of magnetization as a function of temperature corroborated the superconducting transition and showed the expected antiferromagnetic character of the RuSr₂GdCu₂O₈ perovskite, with a Néel temperature of T_N=132.7 K. Systematic measurements of applied magnetic field at up 5 kOe were performed at temperature regimes below the Curie temperature (T_C) of La_{0.67}Sr_{0.33}MnO₃ but above the Néel temperature (T_N) of RuSr₂GdCu₂O₈; below T_N of RuSr₂GdCu₂O₈ but above the superconducting critical temperature (T_{SC}) of RuSr₂GdCu₂O₈; and below T_{SC} of RuSr₂GdCu₂O₈. Our results reveal the ferromagnetic character of the composites at the temperature regime T_N < T < T_C. Exchange bias effect was observed for weak applied fields (H < 1.5 kOe) at the temperature regime T_{SC} < T < T_N. At the superconducting temperature regime (T < T_{SC}) weaker exchange bias is observed for low magnetic fields (H < 0.6 kOe). For strong magnetic fields (H > 2 kOe) the ferromagnetic character of the system is recovered. © 2007 Elsevier Science. All rights reserved

Keywords: Superconducting ruthenate, manganite, magnetic properties, exchange bias effect.

1. Introduction

Magnetic long-range order and superconductivity do not mutually exist within a single thermodynamical phase. Discovery of the coexistence of the superconducting character and antiferromagnetic (AFM) ordering in Ru-1212-type RuSr₂GdCu₂O₈ compound [1], has supplied a opportunity for studying these antagonic phenomenon in the same material [2-3]. RuSr₂GdCu₂O₈ ruthenocuprate (Ru-1212) is characterized by a triple perovskitic cell similar to that of YBa₂Cu₃O_{7-δ}, where Y and Ba are substituted by Gd and Sr, respectively, and the CuO₂ planes are separated from one another not by the Cu chains, but by

RuO₆ octahedra. It is known that this material exhibits a superconducting transition T_{sc}≈40 K and an antiferromagnetic ordering with Néel temperature T_N≈130 K [1-3].

Manganite perovskites La_{1-x}Sr_xMnO₃ are extensively studied because its evidence the phenomenon of colossal magnetoresistance [4]. When x=0.3, this material has a ferromagnetic character with Curie temperature T_c=378 K [5].

An important magnetic characteristic associated with the exchange anisotropy created at the interface between a ferromagnetic (FM) and an antiferromagnetic material occurs when materials FM (with high Curie temperature T_C) and AFM (with Néel temperature T_N<T_C) are cooled through the T_N [6-7]. This effect, which is known as

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exchange bias, produces an asymmetry in the AFM-FM hysteresis curve. This hysteresis loop at $T < T_N$ after the field cooling recipe, is shifted along the field axis generally in the negative direction [8].

In this work we present the synthesis of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ - $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ composites with sub-micrometric grains. We report structural, morphological, electrical and magnetic characterizations of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ and $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ compounds, and $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ - $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ composites. We attributed the observation of the exchange bias effect to AFM-FM interfaces due the AFM character of the $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ materials at low magnetic fields and the typical FM response of the $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ manganites.

2. Experimental

Single phase polycrystalline samples of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ and $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ perovskite materials were prepared by the standard solid state reaction method from high purity (99.99%) powder precursor oxides. Mixture 50 vol% $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ and 50 vol% $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ was solid-reacted to form the composite material. Structural analysis of pure compounds and the composite material were performed by x-ray diffraction (XRD) experiments in a Siemens D5000 diffractometer ($\lambda_{\text{CuK}}=1.5406 \text{ \AA}$). Microstructural characterization of compounds and composite were carried out by Scanning Electron Microscopy (SEM). Electrical resistivity was measured by an AC low-noise low-frequency technique and magnetization measurements were performed by using a QD 2000 MPMS SQUID.

3. Results and discussion

In figure 1, XRD patterns show the single crystallographic phases for $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ (a), $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ (b) and two separate phases for the composite samples without any trace of chemical reaction between the respective compounds (c). For figure 1(a), all diffraction peaks of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ could be indexed on the basis of a tetragonal lattice with cell parameters $a=3.822(5) \text{ \AA}$ and $c=11.473(2) \text{ \AA}$. For diffractogram of figure 1(b), we refine to obtain the crystallographic values $a=5.483(1) \text{ \AA}$, $b=5.532(2) \text{ \AA}$ and $c=7.7912(4) \text{ \AA}$, corresponding to the monoclinic structure of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$. In the case of the cubic LaMnO_3 , differences between holes (occupied by cations) and cations, give rise to a distortion because the minimum in the free energy is obtained through the rotation of octahedra around one or various crystallographic axis of the initial lattice. When the rotation occurs around the [100] axis, one tetragonal distortion is produced; for a rotation around the [110] axis, the distortion is orthorhombic and when around the [1 1 1] axis is rhombohedral [9]. In

the $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ case, the monoclinic feature is introduced by the partial substitution of Sr into the La sites.

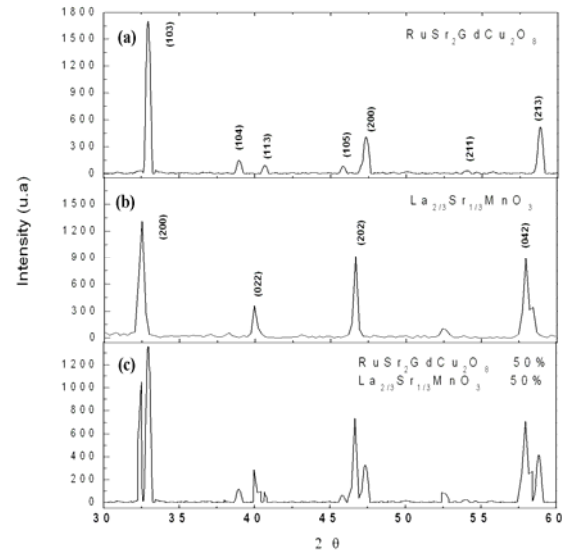


Fig. 1. XRD patterns for (a) $\text{RuSr}_2\text{GdCu}_2\text{O}_8$, (b) $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ and (c) composites 50 vol.% $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ and 50 vol.% $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$.

SEM images of figure 2 reveal the sub-micrometric character of grains for the composite system. The mean grain size, estimated from the SEM image is $0.5 \mu\text{m}$ for $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ and 0.1 - $0.2 \mu\text{m}$ for $\text{RuSr}_2\text{GdCu}_2\text{O}_8$.

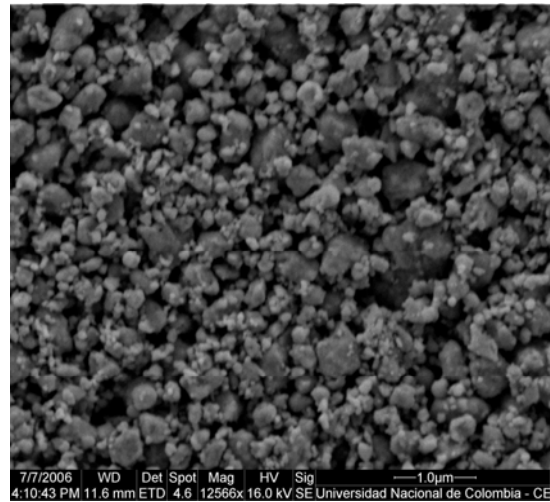


Fig. 2. SEM image for $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ - $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ composites. Minor grains correspond to the ruthenocuprate system.

As shown in figure 3, DC resistivity measurement evidences the superconducting feature of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$. The critical temperature ($T_{\text{SC}} = 39.2 \text{ K}$) was determined by the criterion of the maximum of higher temperature in the temperature derivative of resistivity, as schematized in the inset of figure 3.

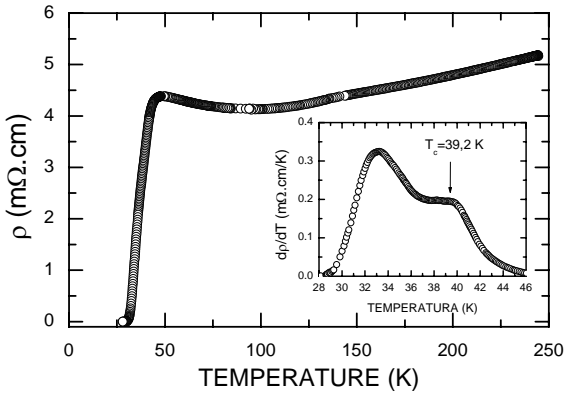


Fig. 3. Characteristic behavior of the superconducting transition for the Ru-1212 material. Inset corresponds to numerical temperature derivative of resistivity. Critical temperature is shown as the maximum of higher temperature.

Results of magnetization as a function of temperature for the same Ru-1212 material reveal a magnetic ordering with AFM transition for $T_N = 132.7$ K. Figure 4 shows the magnetic response when we vary temperature by the zero field cooling (ZFC) and field cooling (FC) recipes, for an applied field of 2 Oe. The superconducting transition is also observed in this picture and the respective value is in agreement with that of the resistivity result.

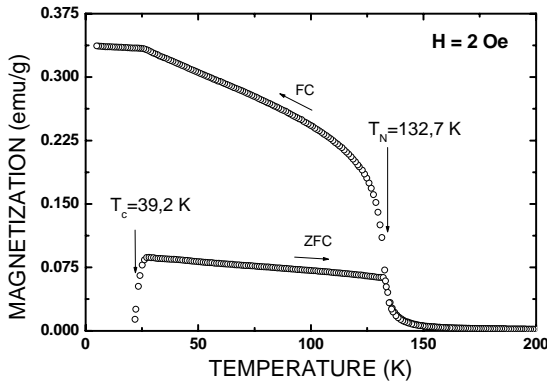


Fig. 4. ZFC and FC procedures in magnetization as a function of temperature for Ru-1212.

The magnetic field dependence of the magnetization revealed the characteristic FM behavior of $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$. We perform a FC measure of magnetization up to reach the temperature value $T=250$ K. Then, curves of magnetization as a function of applied field were carried out as shown in figure 5, which exhibits the hysteretic behavior of magnetization for $\text{RuSr}_2\text{GdCu}_2\text{O}_8\text{-La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ composites for a temperature value above T_N of the AFM $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ but below T_C of the FM $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ material ($T_N < T < T_C$).

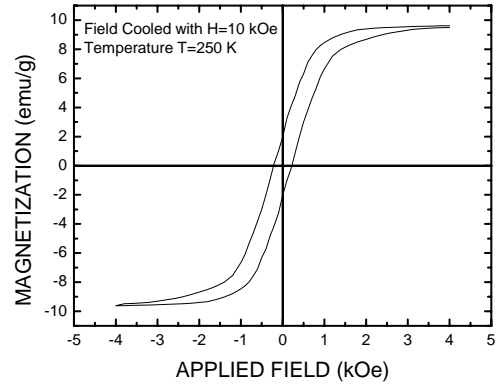


Fig. 5. Hysteretic FM behavior of $\text{RuSr}_2\text{GdCu}_2\text{O}_8\text{-La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ composites at $T=250$ K.

At the temperature regime $T < T_N$, we observe a weak exchange bias behavior for low applied magnetic fields ($H < 1.5$ kOe), with an exchange field $H_E = 60$ Oe. The characteristic asymmetric curve of this exotic phenomenon is showed in figure 6. We notice that this effect is not observed for magnetic fields higher than 2 kOe. At the superconducting regime ($T < T_{SC}$), we effectively observe a weaker exchange bias effect for low applied fields ($H < 600$ Oe) with a exchange field $H_E = 40$ Oe. This behavior is shown in the inset of figure 6. When the applied field is increased, we recover the FM curve characteristic of the single $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ material. This behavior may be evidence that the AFM ordering in the $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ only occurs for low magnetic fields. For high applied fields we could be expecting a competition between superconductivity and FM behavior in this interesting material.

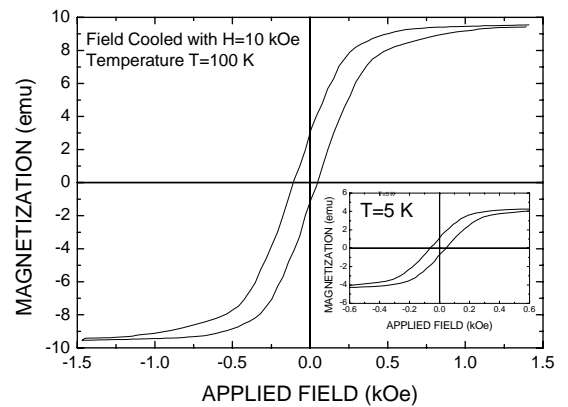


Fig. 6. Exchange bias effect of $\text{RuSr}_2\text{GdCu}_2\text{O}_8\text{-La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ composites at $T=100$ K ($T_{SC} < T < T_N$). The inset show the very weak exchange bias observed at $T < T_{SC}$ for low magnetic fields.

4. Conclusions

We have performed a complete characterization of the magnetic of $\text{RuSr}_2\text{GdCu}_2\text{O}_8\text{-La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ composites, constituted by sub-micrometric grains. Due the granular interfaces between the AFM $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ and FM $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ grains, it is observed that the exchange bias effect occurs for low applied magnetic fields at the $T_{\text{SC}} < T < T_{\text{N}}$ temperature regime. The H_{E} values obtained in this work, for composites of antiferromagnetic superconductor and ferromagnetic manganite, are extremely small when compared with reports for other systems, as $\text{FeF}_2\text{-Fe}$ bi-layers, which exhibit $H_{\text{E}} \approx 400$ Oe [8].

An interesting result is that of the absence of exchange bias for strong applied fields, still in the temperature regime $T_{\text{SC}} < T < T_{\text{N}}$. One possible explanation consists in to consider the singular magnetic structure of $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ as conform for both majority-AFM and minority-FM domains. On the other hand, the occurrence of exchange bias for low fields and the respective absence for strong fields, below the superconducting transition, is interpreted as a non conventional magnetic ordering in $\text{RuSr}_2\text{GdCu}_2\text{O}_8$ perovskite material.

Acknowledgments

This work was partially supported by the COLCIENCIAS Colombian agency on the projects Nos. 1101-06-17622, 1101-333-18707 and contract 043-2005 of Centro de Excelencia en Nuevos Materiales.

References

- [1] L. Bauernfeind, W. Widder, H.F. Braun, *Physica C* 254 (1995) 151.
- [2] J. W. Lynn, B. Keimer, C. Ulrich, C. Bernhard, J.L. Tallon, *Phys. Rev. B* 61 (2000) R14964.
- [3] I. I. Mazin, D.J. Singh, *Phys. Rev. Lett.* 82 (1999) 4324.
- [4] R. M. von Helmholt, J. Wecker, B. Holzapfel, L. Schultz and K. Samwer, *Phys. Rev. Lett.* 71 (1993) 2331.
- [5] M. Ziese, *Physica Stat. Sol. b* 243 (2006) 1389; M. C. Martin, G. Shirane, Y. Endoh, K. Hirota, Y. Moritomo, Y. Tokura, *Phys. Rev. B* 53 (1996) 14285.
- [6] W. H. Meiklejohn, C.P. Bean, *Phys. Rev.* 102 (1956) 1413.
- [7] S. Mangin, G. Marchal, B. Barbara, *Phys. Rev. Lett.* 82 (1999) 4336.
- [8] J. Nogués, Ivan K. Schuller, *J. Magn. Magn. Mater.* 192 (1999) 203.
- [9] E. L. Nagaev, *Phys-Usp* 39 (1996) 781.