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Griffiths-Like Phase in Nanocrystalline Manganite $La_{0.85}Ca_{0.15}MnO_3$

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The ferromagnetic Curie temperatures T_C derived from a temperature derivative of AC susceptibility are equal to 106 K and 161 K for the nanocrystalline and polycrystalline manganites, respectively. The magnetic susceptibility and electron spin resonance confirm that the Griffiths-like phase exists above the Curie temperature in paramagnetic matrix of the nanocrystalline manganite. An analysis of electron spin resonance spectra allows to detect the upper temperature limit for an existence of Griffiths-like phase at temperature $T_{GI} = 290$ K, which is somewhat higher than the T_G of the magnetic susceptibility.

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1. Introduction

The theoretical and experimental investigation of the Griffiths phases was initiated several decades ago [1]. The Griffiths-like phase unveils a deviation from ideal paramagnetic structure described by the Curie–Weiss law. This deviation inherent for solids with the structural and/or magnetic disorder, appears below the Griffiths temperature T_G determining the onset of a ferromagnetic clustering processes.

The efforts to account for the experimental results pertaining the Griffiths-like phases are sometimes made by means of the λ exponents together with a critical temperature T_R. The main disadvantage of such an approach is related to some optionality in choosing these parameters, which in turn hampers a comparison between even similar materials. The fitting procedure supplies usually the T_R temperature located in a middle between the Curie and the Griffiths temperatures.

This paper continues and extends a previous investigation of the Griffiths phase [2] to the new mixed valence manganite $La_{0.85}Ca_{0.15}MnO_3$. It consists in the simultaneous application of the magnetic susceptibility and electron spin resonance studies. The applied method follows that one proposed by Marysko et al. [3, 4].

2. Experimental

The nano- and polycrystalline samples of single phase orthorhombic manganites $La_{0.85}Ca_{.15}MnO_3$, are prepared by the sol–gel method using high purity reagents. The average crystallite sizes for nano- and polycrystalline samples are estimated to about 9 nm and 110 nm, respectively. Magnetic characterization was made by means of magnetic AC susceptibility and electron spin resonance (ESR). The magnetic susceptibility was measured at magnetic field amplitude of 10 Oe. The ESR spectra were recorded for loose powder in a capillary using a Bruker spectrometer working at 9.44 GHz (X-band).

3. AC magnetic susceptibility

Figure 1 shows that the paramagnetic susceptibility of polycrystalline manganite approximately obeys the Curie–Weiss law with the Weiss temperature $T_W \approx 164$ K. This T_W value is close to the ferromagnetic Curie temperature $T_C = 161$ K, as determined from the minimum derivative $d\chi/dT$. The high temperature paramagnetic susceptibility of nanocrystalline manganite obeys the Curie–Weiss law with $T_W = 190$ K. The down-turn deviation from the Curie–Weiss law observed below $T_G = 280$ K is characteristic for the Griffiths-like phase. The ferromagnetic Curie temperature of nanocrystalline manganite $T_C = 106$ K is relatively lower, revealing that the exchange interaction is reduced by the structural and magnetic disorder. This observation is consistent with the core–shell model applicable for nanocrystalline manganites [5].

In order to get a deeper insight a plot of $d(1/\chi)/dT$ was analyzed (Fig. 2) showing a remarkable difference between the nano- and polycrystalline manganites studied. For the nanocrystalline manganite a pronounced maximum is located at 266 K. Its half width is about 24 K. A weakly fluctuating values of $d(1/\chi)/dT$ seen above 300 K correspond to a slope of the Curie–Weiss relation in pure paramagnetic phase. The upper limit of Griffiths-like phase is additionally evidenced by out of phase component χ'' of AC susceptibility. It is worth to notice that the high temperature edge of $d(1/\chi)/dT$ maximum is close to the high temperature limit of non zero χ'' susceptibility as plotted in Fig. 3. This χ'' susceptibility shows

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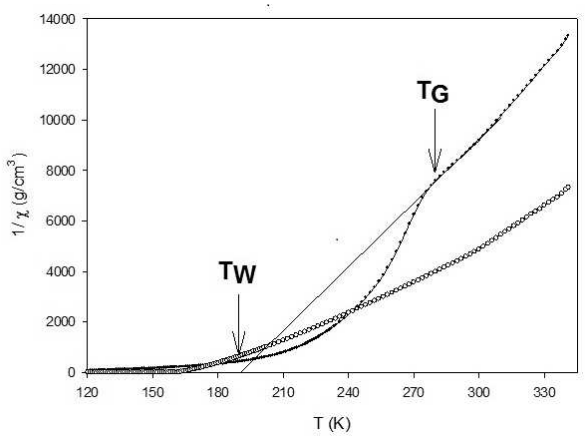

Fig. 1. Temperature variation of inverse magnetic susceptibility for the nano- (solid symbols) and polycrystalline (open symbols) manganites. Solid line corresponds to the Curie–Weiss law for nanocrystalline manganite.

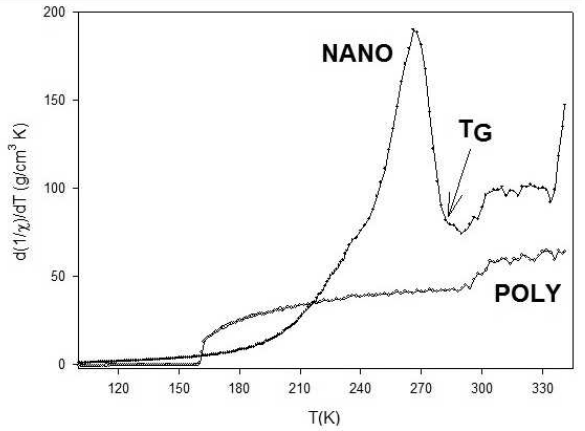

Fig. 2. Temperature variation of a derivative of inverse magnetic susceptibility for the nano- (solid symbols) and polycrystalline (open symbols) manganites.

that the energy dissipation decays above 276 K, when the Griffiths phase disappears and the manganite becomes a pure paramagnet.

Such a behavior is in contrast to the polycrystalline manganite exhibiting a slowly diminishing variation of $\mathrm{d}(1/\chi)/\mathrm{d}T$ with a decrease of temperature observed at higher temperature. It is followed by an abrupt drop down at 160 K — in vicinity of the Curie temperature $T_{\mathrm{C}} = 161$ K. The $\mathrm{d}(1/\chi)/\mathrm{d}T$ dependence of both the nano- and polycrystalline manganites described above is in good accordance with that analyzed by Marysko et al. for the $La_{0.75}Sr_{0.25}MnO_3$ manganites [3].

4. Electron spin resonance spectra

The intensity of electron spin resonance signal is known to be proportional to magnetic susceptibility [6]. Unfortunately, a direct comparison of absolute values of AC magnetic susceptibility and magnetic susceptibility determined from electron spin resonance is not possible due

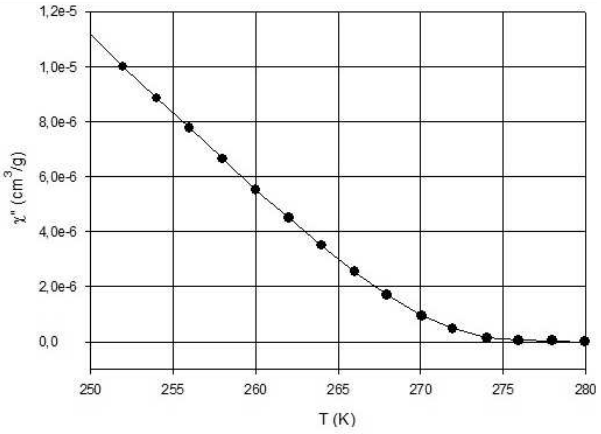

Fig. 3. Temperature variation of out of phase magnetic susceptibility χ'' for the nanocrystalline manganite.

to the technical factors limiting a spectra recording. The recorded electron spin resonance spectra allowed to calculate the signal intensity $I(T) = AH_{PP}^2$, where A and H_{PP} stand for an amplitude and signal peak to peak width, respectively. An alternative double integration approach could not be used due to the ESR base line shift. The temperature variation of inverse signal intensity $1/I(T)$ plotted in Fig. 4 resembles a plot of inverse AC susceptibility of Fig. 1. However, the Weiss temperature T_{WI} becomes 150 K, being smaller as compared to $T_{\mathrm{W}} = 190$ K derived from a susceptibility. This points to the relatively weaker interaction between magnetic moments responding to the high frequency field in electron spin resonance experiment. Moreover, this plot shows the somewhat enhanced Griffiths temperature $T_{\mathrm{GI}} = 290$ K. The same $T_{\mathrm{GI}} = 290$ K was also found for the nanocrystalline manganite $La_{0.50}Ca_{0.50}MnO_3$ [2]. This temperature coincidence points to the high similarity between the finest fractions of the Griffiths-like phase present in both the manganites, as detected by ESR spectra.

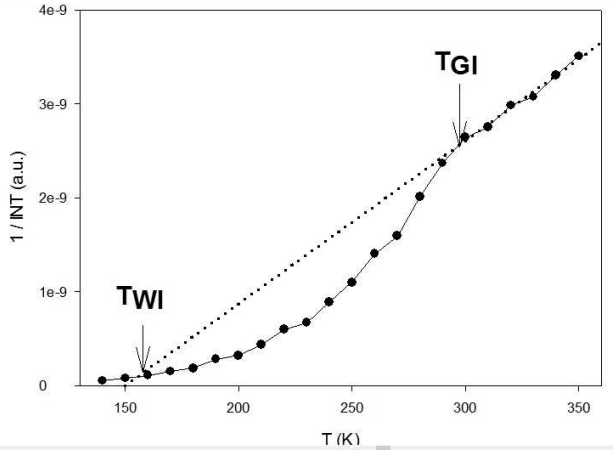

Fig. 4. Temperature variation of inverse signal intensity for the nanocrystalline manganite. Dotted line corresponds to the Curie–Weiss law.

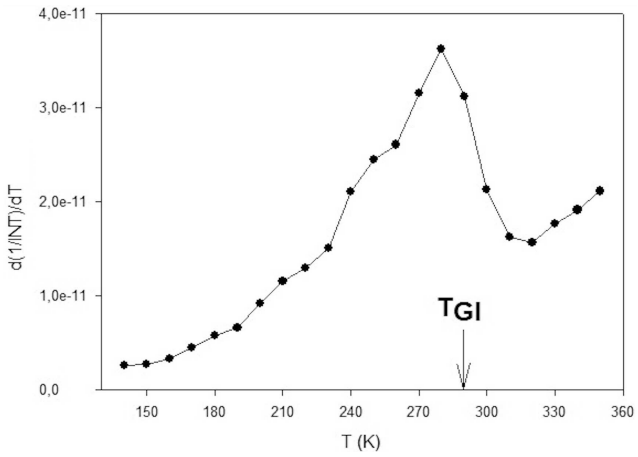

Fig. 5. Temperature derivative of inverse signal intensity for the nanocrystalline manganite.

In order to inspect a fine structure related to the Griffiths-like phase the $\mathrm{d}(1/I)/\mathrm{d}T$ variation is plotted in Fig. 5 for the nanocrystalline manganite. The pronounced $\mathrm{d}(1/I)/\mathrm{d}T$ maximum at 280 K is located 13 K above that of $\mathrm{d}(1/\chi)/\mathrm{d}T$. Moreover, the half width of almost 50 K is twice broader than for AC susceptibility. The above behavior seems to be characteristic for the nanocrystalline mixed valence manganites as the similar differences in $\mathrm{d}(1/I)/\mathrm{d}T$ and $\mathrm{d}(1/\chi)/\mathrm{d}T$ variation are also reported for the nanocrystalline manganite $La_{0.50}Ca_{0.50}MnO_3$ [2].

5. Conclusion

The existence of the Griffiths-like phase in nanocrystalline $La_{0.85}Ca_{0.15}MnO_3$ manganite is independently revealed using two complementary experimental methods: magnetic susceptibility and electron magnetic resonance. The collected results confirm that the Griffiths-like phase extends in the relatively broad temperature interval up to about 290 K as indicated by the electron spin resonance spectra. This proves that the high frequency field is able to excite the relatively smaller magnetic clusters/systems responsible for the Griffiths-like phase in the nanocrystalline manganite studied. The frequency dependence of the Griffiths anomaly will be studied separately.

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