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RE-ENTRANT SPIN GLASS TRANSITION IN $\text{LiCr}_{0.175}\text{Mn}_{1.825}\text{O}_4$ SPINEL

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Abstract

Magnetic properties of Cr^{3+} substituted LiMn_2O_4 spinel have been investigated by measuring both temperature and field dependence of DC magnetization, as well as temperature dependence of AC susceptibility. Obtained results point to the re-entrant spin glass behavior in the low temperature region where system undergoes long range antiferromagnetic transition at $T_N=42$ K followed by the spin glass transition at $T_F=22$ K. High temperature behavior is of the Curie-Weiss type with effective magnetic moment corresponding to the sample's chemical composition.

Introduction

During the last decade LiMn_2O_4 spinel compound and its metal cation substitutes $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ ($M=\text{Al}^{3+}$, Zn^{2+} , Ti^{4+} , Cr^{3+} , Co^{2+} , Ni^{2+}) have been attracting extensive attention from both application-oriented and fundamental reasons. The primary interest had been provoked by LiMn_2O_4 as the promising cathode material for rechargeable lithium-ion batteries [1], while its metal substitutes were investigated in order to reduce capacity fading upon electrochemical cycling [2].

From the magnetic viewpoint LiMn_2O_4 is an intriguing system due to a several key intrinsic properties: (i) magnetic Mn^{3+} and Mn^{4+} ions are placed at the corners of a network of corner-sharing tetrahedras ("pyrochlore network") that leads to a spin frustration in case of antiferromagnetic (AF) interactions [3]; (ii) Mn^{3+} ions in a high-spin state ($t_{2g}^3 e_g^1$) are well known example of Jahn-Teller (JT) ions that can produce the distortion of $\text{Mn}^{3+}\text{O}_6^{2-}$ octahedras [4]; (iii) superexchange 90° Mn-O-Mn interactions can be ferromagnetic (FM) for pair of Mn^{4+} ions or AF for both $\text{Mn}^{3+}/\text{Mn}^{3+}$ and $\text{Mn}^{3+}/\text{Mn}^{4+}$ combinations [3]. These properties lead to a complex magnetic behavior at low temperatures [5,6]. In addition, the substitution of manganese ions by some other 3d cation (Cr^{3+} , Ti^{4+}) [7] offers the possibility to study effects of bond and/or site disorder on the geometrically frustrated magnetic system. In this work we focus our attention on the magnetic properties of Cr^{3+} substituted spinel compound $\text{LiCr}_{0.175}\text{Mn}_{1.825}\text{O}_4$.

Results and Discussion

The powder $\text{LiCr}_{0.175}\text{Mn}_{1.825}\text{O}_4$ sample was prepared by a rapid glycine-nitrate method (GNM), described elsewhere [8]. The XRPD experiments were performed on the Philips 1050 diffractometer by using $\text{CuK}\alpha_{1,2}$ radiation. All reflections of the

obtained XRPD pattern correspond to pure spinel phase. For the crystal structure refinement $15 \leq 2\theta \leq 115^\circ$ range was used with the 0.02° step and 10 seconds exposition. Refinement was done using the FullProf computing program based on the Rietveld full profile method. The structure has been refined in the space group $Fd3m (O_h^7)$ in well-known spinel type. The refinement results show that all Cr^{3+} ions substitute Mn^{3+} ions only, while no migration of lithium ions in the octahedral cation sites was obtained within the refinement accuracy.

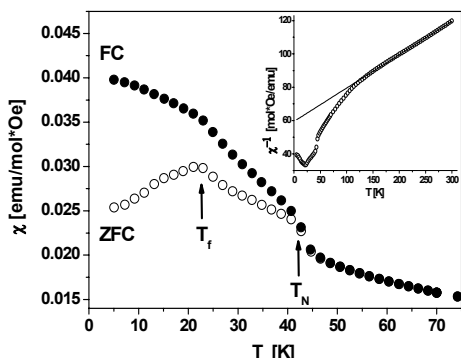


Fig. 1. Molar magnetic susceptibility χ in ZFC and FC regimes. *Inset:* Experimental (dots) and fitted (line) ZFC χ^{-1} values.

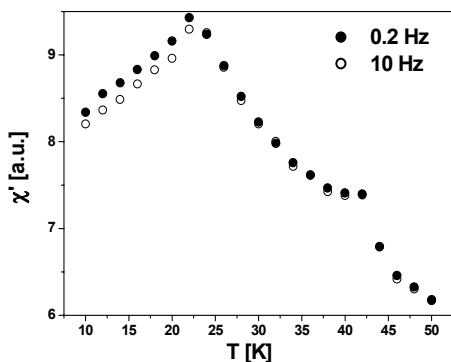


Fig. 2. Real part χ' of the AC susceptibility.

ability is a signature of the re-entrant spin glass behavior which means that spin-glass (SG) phase develops from the magnetically ordered state with the decrease in temperature [9]. Further information on the nature of the ordered phase can be gained from the isothermal $M(H)$ measurements, Fig. 3. The magnetization dependence versus field recorded at 40 K (i.e. below the phase transition at 42 K) is linear up to ± 5 T field which is a signature of a long-range AF order. Consequently, the temperature of 42 K is a Néel temperature of the sample under consid-

DC magnetic measurements were done in the applied field of 100 \AA in both zero-field-cooled (ZFC) and field-cooled (FC) regimes in the 4-300 K range. Obtained molar magnetic susceptibilities corrected for underlying ionic diamagnetism are reported in Fig. 1. Bifurcation between ZFC and FC curves is obvious for temperatures below 45 K. In the ZFC branch below this temperature two singularities can be observed: the first one at about 42 K and the second one at 22 K. In order to clarify the origin of these singularities we have conducted AC susceptibility measurements in the low temperature region. The AC susceptibility was measured in the zero applied DC field and with the AC driven field of $H_{ac}=4$ \AA . The obtained real part χ' for field frequencies of 0.2 Hz and 10 Hz are depicted in Fig. 2. One can see that frequency dependence of χ' can be observed only below the singularity at 22 K, while signals for both frequencies coincide above this temperature. Consequently, χ' singularity at 42 K is frequency insensitive i.e. this points to the presence of the magnetically ordered phase below this temperature. Such a dependence of the in-phase AC susceptibility

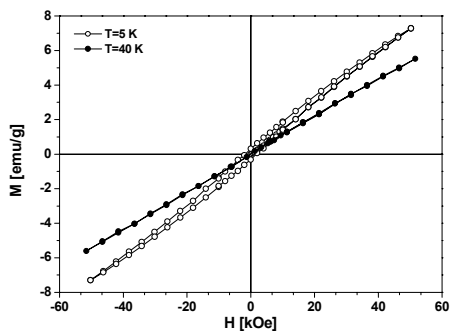


Fig. 3. $M(H)$ dependence recorded at 5 K and 40 K in the field range of ± 5 T.

eration. $M(H)$ curve recorded at 5 K (i.e. below the SG freezing temperature of $T_f = 22$ K) shows considerable hysteretic behavior with the coercive field of $H_c \approx 1700$ Oe. This can be caused by the following two phenomena: (i) weak ferromagnetism due to the canted magnetic moments as a result of frustrated AF ordering on the pyrochlore magnetic sublattice [5,6]; (ii) FM superexchange Mn^{4+} -O- Mn^{4+} interactions in the charge ordered Mn^{4+} regions [6]. Both phenomena provoke the emergence of the SG phase [9].

From the fit to a Curie-Weiss law in the high temperature region (200-300 K), shown in the inset of Fig. 1, the effective magnetic moment of $\mu_{\text{eff}} = 4.40 \mu_B$ was found. This value is in good agreement with the calculated moment of $\mu_{\text{eff}}^{\text{calc}} = 4.32 \mu_B$ obtained under the assumption that Cr^{3+} ions replace Mn^{3+} ions only. In addition, this confirms the findings of the crystal structure refinement.

Conclusion

In pure $LiMn_2O_4$ the charge ordering of manganese ions is accompanied by the collective JT effect which leads to the removal of the spin frustration on the pyrochlore network. This results in the emergence of the long range AF ordering below $T_N \approx 65$ K [10]. The partial substitution of the Mn^{3+} (JT ion) by the Cr^{3+} (non-JT ion) causes the emergence of the partial system frustration that leads to the re-entrant SG behavior - the Néel temperature is lowered to 42 K and the formation of the SG phase occurs below $T_f = 22$ K.

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