# Proceedings of the 16th Czech and Slovak Conference on Magnetism, Košice, Slovakia, June 13–17, 2016 Spin-Glass Behavior in $LaCu_4Mn$ Compound

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The experimental results of the X-ray powder diffraction, magnetic susceptibility, electrical resistivity, and specific heat measurements of the LaCu<sub>4</sub>Mn compound are presented. LaCu<sub>4</sub>Mn is an intermetallic compound that crystallizes in the hexagonal CaCu<sub>5</sub>-type structure (space group P6/mmm, No. 191), where the atoms on the 3g (1/2, 0, 1/2) site create a kagome lattice, which can cause the spin frustration and leads to a variety of interesting states of matter, such as spin-ice, spin-liquid, and spin-glass states. The Rietveld refinement reveals a random distribution of Mn and Cu atoms on the 3g and 2c site, where about 80% of Mn atoms occupy the 3g site. The lattice parameters are a = 5.252(1) Å and c = 4.176(1) Å. The low-field zero-field-cooled and fieldcooled DC magnetic susceptibilities show splitting below the spin freezing temperature  $T_f \approx 33$  K. At 2 K the magnetization M(H) exhibits hysteresis with coercivity field of  $\approx 5$  kOe. The AC susceptibility measurements exhibit a frequency-dependent cusp, associated with a frequency-dependent freezing temperature. Moreover, there is no clear sign of long range magnetic order in specific heat and resistivity measurements.

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#### 1. Introduction

Intermetallic compounds and alloys with the CaCu<sub>5</sub>type crystal structure reveal a variety of interesting physical properties. In recent works we observed how the disorder and the geometrical frustration in Ce- and Mnbased materials lead to the spin-glass (SG) and other complex glassy behaviors [1–3], which are still topical [4]. For better understanding of those effects, in this article we report detailed studies on LaCu<sub>4</sub>Mn compound, where only the Mn ions show magnetic moment. Dhar et al. has suggested that LaCu<sub>4</sub>Mn does not show the long range magnetic ordering and reveals a spin-glass-like behavior [5].

## 2. Experimental detail

The polycrystalline LaCu<sub>4</sub>Mn sample was prepared by induction melting of pure elements. The preparation process took place under the protective argon atmosphere. The sample was turned and remelted several times to ensure homogeneity.

The quality of the sample was verified by means of X-ray powder diffraction (XRD) and energy dispersive spectroscopy (EDS). The magnetic, thermodynamic, and transport properties of the compound were studied at temperatures ranging from room temperature down to 2 K at ambient conditions, using a commercial Quantum Design physical property measurement system.

### 3. Results and discussion

The X-ray diffraction pattern obtained at room temperature is presented in Fig. 1, where experimental data are refined with the Rietveld method using the FULL-PROF software. XRD revealed a phase pure sample with hexagonal structure belonging to the P6/mmm space group and a disorder due to the random distribution of Mn and Cu atoms on the 3g and 2c site. Lattice parameters, a = 5.252(1) Å and c = 4.176(1) Å, are in agreement with previous studies [5]. The chemical composition was confirmed by the EDS measurements and it agrees almost perfectly with the nominal one.



Fig. 1. Room temperature XRD pattern for  $LaCu_4Mn$  compound.

Figure 2 shows the temperature dependence of the field cooled (FC) and ZFC (zero-field cooled) DC magnetic susceptibility  $\chi_{DC}$  in an external field H = 1 kOe. ZFC curve shows a clear peak near 33 K, defined as the freezing temperature  $T_f$ . There is also the divergence between ZFC and FC curves. When higher magnetic field is applied the position of the peak moves towards lower temperatures.

The high temperature magnetic susceptibility follows the modified Curie–Weiss (C–W) law  $\chi(T) = \chi_0 + C/(T - \theta_p)$ . A linear fit to the inverse susceptibility  $\chi^{-1}(T)$  (solid line in Fig. 3) in the temperature range

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Fig. 2. The temperature dependence of the ZFC and FC magnetic susceptibility for the  $LaCu_4Mn$  compound in the field of 1 kOe. Inset shows the isothermal magnetization plots at 2 and 300 K.

of 100–350 K gives the C–W paramagnetic temperature  $\theta_p = -16.4(4)$  K, temperature independent susceptibility  $\chi_0 = 2.2(1) \times 10^{-3}$  emu/mol, and the effective magnetic moment  $\mu_{\rm eff} = 2.37(1) \ \mu_{\rm B}$ . Negative  $\theta_p$  suggests an antiferromagnetic type of interaction between the Mn ions. The reduced value of  $\mu_{\text{eff}}$ , compared to the free  $Mn^{2+}$  ion (5.92  $\mu_B$ ), is typical of many frustrated systems. By comparing  $\theta_p$  with the temperature at which the order freezes,  $T_f$ , the frustration parameter  $\varphi$  is obtained:  $\varphi = |\theta_p|/T_f \approx 0.5$ . Such a small value of  $\varphi$ indicates lack of frustration in the LaCu<sub>4</sub>Mn compound. Therefore, we have fitted  $\chi^{-1}(T)$  with standard C–W law in the temperature range between 280 and 350 K to avoid the low temperature effects (dashed line in Fig. 3). From that fit we get:  $\mu_{\text{eff}} = 4.69(1) \ \mu_{\text{B}}$  and  $\theta_p = -323(3)$  K. In this scenario the value of the frustration parameter  $\varphi = 9.8$  is much higher and indicates a strong frustration. Moreover, the  $\mu_{\text{eff}}$  shows smaller deviation from the theoretical values.



Fig. 3. The inverse ZFC DC magnetic susceptibility  $\chi^{-1}$  versus T plot for LaCu<sub>4</sub>Mn. The lines are the C–W law fits as described in the text.

The inset in Fig. 2 shows isothermal magnetization curves at 2 and 300 K. Large hysteresis is observed in the M(H) data at 2 K with the coercivity field of  $\approx 5$  kOe, but no hysteresis is observed above  $T_f$ . In addition, there is no saturation within the accessible magnetic field range. All those features are typical of the SG systems.

To confirm the SG effect we performed an AC susceptibility measurement at the frequency range 10 Hz < $f \leq 10$  kHz with the AC field  $H_{AC} = 5$  Oe. Tiny, but clearly visible shift of both the real (Fig. 4) and the imaginary part (not shown) of the AC magnetic susceptibility peaks close to  $T_f$  was observed. The initial frequency shift  $\Delta T_f / (T_f \log f) = 0.008(2)$  is comparable to the typical values for most spin glasses. In order to further parametrize the spin glass behavior, we have analyzed the frequency dependence of  $T_f$  by using the empirical Vogel–Fulcher [6] law  $f = f_0 \exp(-E_a/k_{\rm B}(T_f - T_0))$ and the standard expression for the conventional critical slowing down,  $\tau = 1/f = \tau_0 [(T_f - T_g)/T_g]^{z\nu}$  and we estimated the dynamical parameters: the activation energy  $E_a/k_B = 77(2)$  K, the characteristic temperature  $T_0 = 31.4(1)$  K, the static freezing temperature  $T_g = 33.4(2)$  K, and the critical exponent zv = 8.7(2). In both cases we assumed that the value of the characteristic frequency,  $f_0 = 1/\tau_0$ , is equal to  $10^{13}$  Hz. The fits of the experimental data by a Vogel–Fulcher and critical slowing down law are shown in Fig. 4b and c.



Fig. 4. (a) The temperature and frequency dependences of AC susceptibility (real part), (b) critical slowing down and (c) Vogel–Fulcher law fit.

Further characterization of the freezing of the spins was performed via isothermal remanent magnetization measurements. The sample was cooled in a magnetic field H = 10 kOe from 300 K to 5 K, and after waiting time of  $10^3$  s the field was switched off and the decay of magnetization was recorded for  $10^4$  s. Figure 5 shows the normalized isothermal remanent magnetization M(t)/M(t=0) curves at 5 and 10 K, where experimental data are fitted with the usually used logarithmical dependence  $M(t) = M_0(T) - S(T) \ln(t/t_0)$ . The obtained fitting parameters are: the initial magnetization  $M_0 = 0.013(1)$  and 0.011(1) emu/g, the magnetic viscosity  $S = 7.40(4) \times 10^{-5}$  and  $2.61 \times 10^{-4}$  emu/g, and the characteristic time  $t_0 = 8.5(5)$  and 27(2) s for T = 5 and 10 K, respectively.



Fig. 5. Magnetic relaxation of LaCu<sub>4</sub>Mn at 5 and 10 K after field cooling in 10 kOe and waiting time  $10^3$  s. The solid lines show the fitting to the equation  $M(t) = M(T) - S(T) \ln(t/t_0)$ .



Fig. 6. The specific heat of  $LaCu_4Mn$ . The nonmagnetic reference compound  $LaCu_4Al$  is also included for comparison.

To confirm the lack of long-range magnetic order we performed the specific heat and the electrical resistivity measurements (not shown here). As indicated in Fig. 6 there is no sign of the long-range magnetic order in the whole measured temperature range. The electronic specific heat coefficient  $\gamma = 50 \text{ mJ/(mol K}^2)$  is enlarged due to the disorder and the 3*d* Mn states near the Fermi level. The residual resistivity shows a quite large value  $\rho_0 = 125 \ \mu\Omega$ cm, which is also related to the disorder.

Next, we have used the isostructural LaCu<sub>4</sub>Al [7–9] compound as a nonmagnetic analog to determine the magnetic part of the specific heat and electrical resistivity. The magnetic part of the specific heat was calculated according to the equation:  $C_{mag} = C_p(\text{LaCu}_4\text{Mn}) -$ 

 $C_p(\text{LaCu}_4\text{Al}) \times (\text{m.w.}_{\text{LaCu}_4\text{Mn}}/\text{m.w.}_{\text{LaCu}_4\text{Al}})^{3/2}$ , including the necessary mass correction. It shows a broad maximum in the low temperature range. Similar behavior is visible in the magnetic part of the electrical resistivity (not shown). Broad maximum in the magnetic part of the specific heat and electrical resistivity is typical of the canonical SG.

The random distribution of the Mn atoms on the 3g and 2c sublattices does not let a well-defined long-range magnetic order to develop in the LaCu<sub>4</sub>Mn compound. The type of the magnetic interaction (ferromagnetic or antiferromagnetic) between Mn atoms strongly depends on the distances between them. Due to the disorder the Mn–Mn bonds have different lengths and the type of the magnetic interaction can be different, therefore a competition of the interactions occurs. Small negative  $\theta_p$  (from broad temperature C–W law fit) indicates that the antiferromagnetic type of interaction slightly dominates in LaCu<sub>4</sub>Mn. Moreover, 3g sublattice creates the kagome lattice, which can lead to the magnetic frustration.

 $LaCu_4Mn$  fulfills criteria for "canonical" SG [4]. It would be interesting to check if the  $LaCu_4Mn$  can be described by the theoretical models and considered as "ideal" SG.

### 4. Conclusions

LaCu<sub>4</sub>Mn compound was synthesized and characterized by AC/DC magnetic susceptibility, electrical resistivity, and heat capacity measurements. All the measurements and analyses have confirmed the lack of typical long-range magnetic ordering and revealed the existence of the SG state. The XRD and electrical resistivity results point to the disorder on the 3g and 2c lattice sites in the crystal structure as the origin of the SG behavior.

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