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## Spin glass formation in Li-substituted $\text{Co}_2\text{TiO}_4$ spinel

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### Abstract

DC magnetization and AC susceptibility measurements point to the formation of a spin glass state in the ternary spinel-type compounds  $\text{Li}_{1.33x}\text{Co}_{2-2x}\text{Ti}_{1+0.67x}\text{O}_4$ . The dynamics of spin freezing was analysed with both the critical slowing down and the thermally activated dynamics models. The parameter values obtained, as well as the behaviour of the zero-field-cooled and field-cooled magnetization as a function of temperature, indicate the existence of a cluster glass state in disordered spinel samples with  $x = 0.25$  and  $0.40$ , and probably also in the ordered spinel with  $x = 0.50$ . Ordered spinel samples with  $x = 0.75$  and  $0.875$  were found to be paramagnetic down to the temperature of 1.7 K with a random distribution of  $\text{Co}^{2+}$  ions.

### 1. Introduction

Ternary spinels are widely recognized as versatile systems from both a technological and a fundamental point of view. By changing their chemical composition through cation replacement, many physical properties of these compounds can be altered in a controllable manner. From the magnetic point of view, cation substitution presents a good example of the frustration and randomness phenomena which are the basic concepts in disordered magnetism, and the spin glass phase in particular [1, 2]. In this work we present results on the magnetic properties of ternary  $\text{Li}_{1.33x}\text{Co}_{2-2x}\text{Ti}_{1+0.67x}\text{O}_4$  spinels over a wide concentration range of  $0.25 \leq x \leq 0.875$ . One end member ( $x = 1$ ) of this series is diamagnetic  $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$  and has excellent properties as an anode material in lithium rechargeable batteries [3], while  $\text{Co}_2\text{TiO}_4$  ( $x = 0$ ) possesses unusual magnetic properties [4, 5].

In most binary spinel compounds magnetic inter-sublattice A–B interactions are dominant (where A denotes tetrahedral and B octahedral crystallographic sites), so collinear

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ferrimagnetic order is commonly observed. However, in some cobalt spinels intra-sublattice interactions (A–A and B–B) are dominant, which can lead to a significant departure from the Néel collinear model. For instance,  $\text{Co}_3\text{O}_4$  oxide with the cation configuration of  $[(\text{Co}^{2+})_A(\text{Co}^{3+})_B]$  shows an antiferromagnetic phase transition at 33 K indicating a strong intra-sublattice A–A interaction [6]. On the other hand, the spinel compound  $\text{Co}_2\text{RuO}_4$  undergoes a spin glass transition at 16 K as a result of competing A–A and A–B interactions [7]. In that sense,  $\text{Co}_2\text{TiO}_4$  spinel is a highly interesting system with rich magnetic behaviour:

- (i) DC magnetization measurements revealed re-entrant magnetic properties with a paramagnetic–ferrimagnetic transition at  $T_N = 55$  K and formation of a spin glass phase at  $T_{SG} = 46$  K [4];
- (ii) another study done by the AC susceptibility technique has detected five peaks in the magnetic susceptibility versus temperature curve in the 1.7–50 K range [5].

This behaviour was attributed to either the coexistence of ferrimagnetic longitudinal and spin glass transverse components [4], or a partial freezing of half of each (A and B) sublattice as a consequence of a weak A–B interaction [5].

The aim of this work is to study the change of the magnetic properties of the parent  $\text{Co}_2\text{TiO}_4$  compound caused by partial cation substitution for the magnetic  $\text{Co}^{2+}$  ions with diamagnetic  $\text{Li}^+$  and  $\text{Ti}^{4+}$  ions, namely  $\frac{5}{2}\text{Co}^{2+} \rightarrow \text{Li}^+ + \text{Ti}^{4+}$ . The solubility of  $\text{Co}_2\text{TiO}_4$  and  $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$  is full [8], enabling the study of magnetic phenomena over a wide concentration range.

## 2. Experimental details

The samples of  $\text{Li}_{1.33x}\text{Co}_{2-2x}\text{Ti}_{1+0.67x}\text{O}_4$  ( $0.25 \leq x \leq 0.875$ ) have been synthesized by a ceramic procedure, and details were already given in [8]. The DC magnetization of the samples obtained was measured in the 1.7–295 K temperature range and an applied field of 1 kOe by using a SQUID magnetometer. In the vicinity of magnetic phase transitions the magnetization was measured both in ZFC (zero-field-cooled) and FC (field-cooled) regimes. The AC susceptibility was measured in the temperature region of 1.7–30 K in the 7–1500 Hz frequency range and at applied DC fields of 50 Oe and 1 kOe. The experimental data were corrected for the temperature independent diamagnetic contribution.

## 3. Results and discussion

### 3.1. Crystal structure

The structure properties of  $\text{Li}_{1.33x}\text{Co}_{2-2x}\text{Ti}_{1+0.67x}\text{O}_4$  samples were studied in detail and results have been reported in [8]. We shall here briefly summarize the crystal structure peculiarities which are essential for the consideration of magnetic properties.

In  $\text{Li}_{1.33x}\text{Co}_{2-2x}\text{Ti}_{1+0.67x}\text{O}_4$  spinels a change of crystal symmetry with concentration  $x$  occurs: samples with  $0 \leq x \leq 0.40$  and  $x = 1$  crystallize in the space group (SG)  $Fd\bar{3}m$  (disordered spinels), whereas samples with  $0.50 \leq x \leq 0.875$  crystallize in the SG  $P4_332$  (ordered spinels) [8]. In disordered spinels the cations occupy two non-equivalent sites: tetrahedral 8a with local symmetry  $\bar{4}3m$  (A sites) and octahedral 16d with local symmetry  $\bar{3}m$  (B sites). In the ordered spinel structure there are three non-equivalent cation sites, one tetrahedral 8c site (local symmetry 3) and two octahedral sites, 4b (local symmetry 32) and 12d (local symmetry 2) [8].

**Table 1.** Cation distribution and cation ordering in Li<sub>1.33x</sub>Co<sub>2-2x</sub>Ti<sub>1+0.67x</sub>O<sub>4</sub> spinels.

Sample	Space group	Cation distribution
Co <sub>2</sub> TiO <sub>4</sub> ( $x = 0$ )	$Fd\bar{3}m$	(Co) <sub>8a</sub> [CoTi] <sub>16d</sub>
Li <sub>0.33</sub> Co <sub>1.50</sub> Ti <sub>1.17</sub> O <sub>4</sub> ( $x = 0.25$ )	$Fd\bar{3}m$	(Li <sub>0.09(1)</sub> Co <sub>0.91(1)</sub> ) <sub>8a</sub> [(Li <sub>0.24(1)</sub> Co <sub>0.59(1)</sub> )Ti <sub>1.17</sub> ] <sub>16d</sub>
Li <sub>0.53</sub> Co <sub>1.20</sub> Ti <sub>1.27</sub> O <sub>4</sub> ( $x = 0.40$ )	$Fd\bar{3}m$	(Li <sub>0.20(1)</sub> Co <sub>0.80(1)</sub> ) <sub>8a</sub> [(Li <sub>0.34(1)</sub> Co <sub>0.40(1)</sub> )Ti <sub>1.27</sub> ] <sub>16d</sub>
Li <sub>0.665</sub> CoTi <sub>1.335</sub> O <sub>4</sub> ( $x = 0.50$ )	$P4_332$	(Li <sub>0.31(1)</sub> Co <sub>0.69(1)</sub> ) <sub>8c</sub> [(Li <sub>0.38(1)</sub> Co <sub>0.12(1)</sub> ) <sub>4b</sub> (Co <sub>0.17(1)</sub> Ti <sub>1.335</sub> ) <sub>12d</sub> ]
LiCo <sub>0.50</sub> Ti <sub>1.50</sub> O <sub>4</sub> ( $x = 0.75$ )	$P4_332$	(Li <sub>0.51(1)</sub> Co <sub>0.49(1)</sub> ) <sub>8c</sub> [(Li <sub>0.495(1)</sub> Ti <sub>0.02(1)</sub> ) <sub>4b</sub> (Co <sub>0.04(1)</sub> Ti <sub>1.48(1)</sub> ) <sub>12d</sub> ]
Li <sub>1.16</sub> Co <sub>0.25</sub> Ti <sub>1.59</sub> O <sub>4</sub> ( $x = 0.875$ )	$P4_332$	(Li <sub>0.75(1)</sub> Co <sub>0.25(1)</sub> ) <sub>8c</sub> [(Li <sub>0.29(1)</sub> Ti <sub>0.21(1)</sub> ) <sub>4b</sub> (Li <sub>0.12(1)</sub> Ti <sub>1.38(1)</sub> ) <sub>12d</sub> ]
Li <sub>1.33</sub> Ti <sub>1.67</sub> O <sub>4</sub> ( $x = 1$ )	$Fd\bar{3}m$	(Li) <sub>8a</sub> [Li <sub>0.33</sub> Ti <sub>1.67</sub> ] <sub>16d</sub>

The results on cation distribution and cation ordering, obtained according to the refined occupation number values [8], are given in table 1. It can be seen that magnetic Co<sup>2+</sup> ions in disordered spinel samples ( $x = 0.25, 0.40$ ) are randomly distributed between two cation sites, 8a and 16d. In ordered spinel samples the situation depends on the  $x$  value: for  $x = 0.50$  there is a random distribution of Co<sup>2+</sup> among all cation sites (8c, 4b and 12d); for  $x = 0.75$  and 0.875 samples, Co<sup>2+</sup> ions preferentially occupy tetrahedral 8c sites. The sample with  $x = 0.75$  is a fully ordered spinel with a 1:3 ratio at octahedral sites: that is, Li<sup>+</sup> ions occupy exclusively 4b sites while Ti<sup>4+</sup> ions occupy only 12d sites (within the experimental error). Samples with  $x = 0.50$  and 0.875 are partially ordered spinels where two cations can simultaneously occupy both 4b and 12d sublattices (table 1).

### 3.2. DC susceptibility

The data obtained for the temperature dependence of the DC susceptibility are depicted in figures 1(a) and (b). The differences in magnetic behaviour between samples with different concentration,  $x$ , and cation distribution of magnetic Co<sup>2+</sup> ions are obvious:

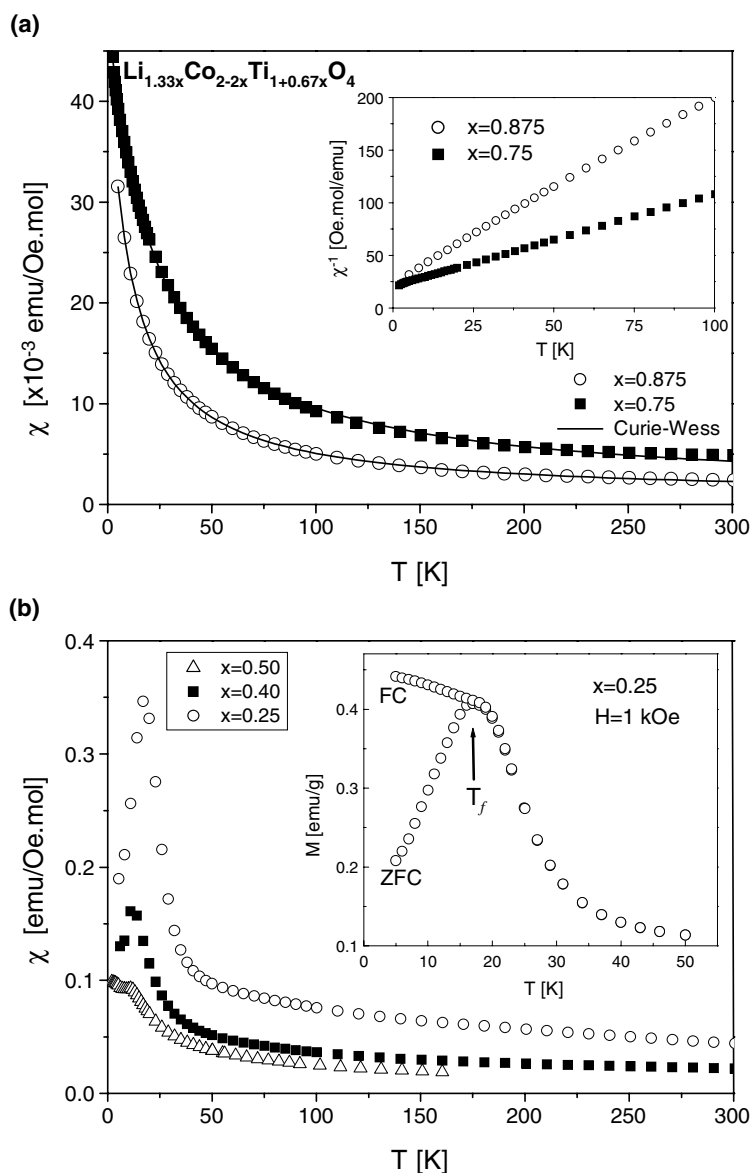
- (i)  $x = 0.25$  and 0.40 samples (Co<sup>2+</sup> ions occupy both cation sites in SG  $Fd\bar{3}m$ ) show a magnetic phase transition at approximately 17 and 11 K, respectively;
- (ii) the  $x = 0.50$  sample (Co<sup>2+</sup> occupy all three cation sites in SG  $P4_332$ ) has a magnetic phase transition at  $T \approx 11$  K; however, the increase in the susceptibility below this temperature can be attributed to a presence of a small quantity of paramagnetic impurities, and in the following analysis we shall omit this sample;
- (iii)  $x = 0.75$  and 0.875 samples (Co<sup>2+</sup> occupy only tetrahedral 8c sites in SG  $P4_332$ ) are paramagnetic down to  $T = 1.7$  K.

The paramagnetic susceptibilities of  $x = 0.75$  and 0.875 samples were fitted with the Curie–Weiss law in the form

$$\chi(x, T) = \frac{C(x)}{T - \Theta(x)} + \chi_{\text{VV}}, \quad (1)$$

where  $\chi_{\text{VV}}$  denotes a temperature independent Van Vleck contribution. The best-fit curves obtained are depicted in figure 1(a), and from the values of the fitted parameters ( $C$ ,  $\theta$ ,  $\chi_{\text{VV}}$ ) we have found that:

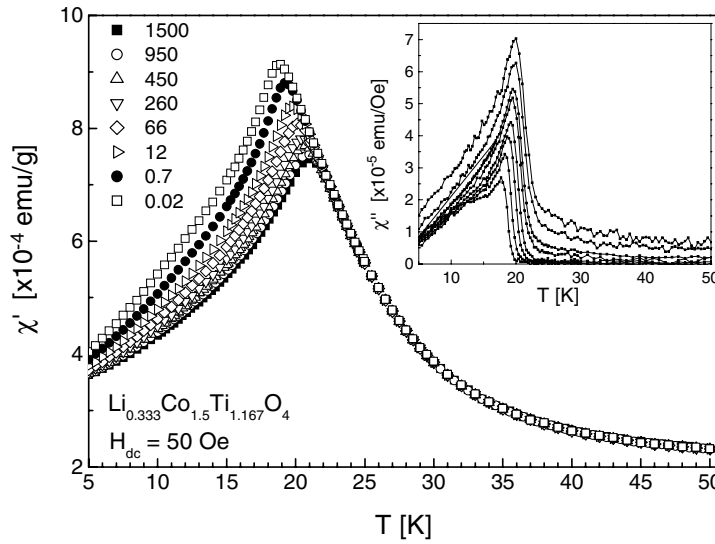
- (i) the effective magnetic moments were  $\mu_{\text{eff}} = 3.9(1) \mu_{\text{B}}$  and  $\mu_{\text{eff}} = 4.1(1) \mu_{\text{B}}$  for  $x = 0.875$  and 0.75 samples respectively, and these values are typical for tetrahedrally coordinated Co<sup>2+</sup> ions [9];
- (ii) from  $\theta(x)$  values and the well-known mean field relation  $\Theta(x) = -\frac{1}{3}S(S+1)\frac{J_{\text{NN}}}{k_{\text{B}}}Z_{\text{NN}}x$ , where  $Z_{\text{NN}}$  denotes the number of nearest magnetic neighbours, we have found that the value of the nearest-neighbour exchange integral for A–A magnetic cations is  $J_{\text{NN}} = -8$  K.



**Figure 1.** Temperature dependences of the DC susceptibility of  $\text{Li}_{1.33x}\text{Co}_{2-2x}\text{Ti}_{1+0.67x}\text{O}_4$  spinels: (a) for  $x = 0.75$  and  $0.875$  samples; (b) for  $x = 0.25$ ,  $0.40$  and  $0.50$  samples.

This shows that A–A exchange is of considerable strength. The inset of figure 1(a) points to the fact that the intersections of both  $\chi^{-1}(T)$  curves with the y axis coincide, which means that the distributions of magnetic ions in both samples are random [10]. The best-fit values of the Van Vleck contribution  $\chi_{\text{VV}}$ ,  $7 \times 10^{-4}$  and  $9 \times 10^{-4}$  emu Oe $^{-1}$  mol $^{-1}$  for  $x = 0.875$  and  $0.75$  respectively, are rather high but not uncommon for systems containing Co $^{2+}$  ions [7].

The observed maxima in the  $\chi(T)$  data for  $x = 0.25$  and  $0.40$  samples (figure 1(b)) have been the subject of a more detailed study in order to identify the character of this phase transition. DC zero-field-cooled (ZFC) and field-cooled (FC) magnetization curves in an applied field of 1 kOe for the  $x = 0.25$  sample were measured in the 1.7–50 K temperature



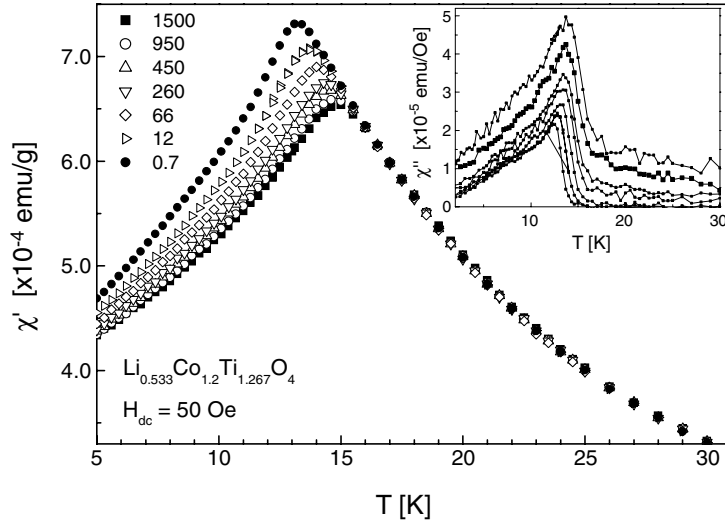
**Figure 2.** The real  $\chi'$  component of the AC susceptibility as a function of temperature and frequency for the  $\text{Li}_{0.333}\text{Co}_{1.5}\text{Ti}_{1.167}\text{O}_4$  ( $x = 0.25$ ) sample. Inset: the frequency dependence of the imaginary  $\chi''$  component of the AC susceptibility versus temperature.

range and the data obtained are depicted in the inset of figure 1(b). The existence of a maximum in the ZFC magnetization curve at  $T_f = 17.0(5)$  K, just below the separation point of the ZFC and FC curves at the irreversibility temperature  $T_{ir}$ , serves as an indication of the spin glass phase. The irreversibility temperature  $T_{ir}$  is usually determined as the point where the ratio  $(M_{FC} - M_{ZFC})/M_{ZF}$  is less than 1% [11]. By using this criterion we have found that  $T_{ir}|_{x=0.25} \approx 19$  K. The FC magnetization continues to increase below  $T_{ir}$ , while the ZFC magnetization prominently decreases below  $T_f$ . Such behaviour, as well as the large difference between the ZFC and FC magnetization, is commonly ascribed to the formation of a cluster glass state, as shown in various cluster glass systems [11, 12]. In canonical spin glass systems FC magnetization has an almost constant value below  $T_{ir}$ , or it decreases [13].

### 3.3. AC susceptibility

In order to get a better insight into the nature of a spin glass state we have performed AC susceptibility measurements under the conditions already given in the experimental section. In figures 2 and 3 we depicted both the in-phase part  $\chi'$  and the out-of-phase part  $\chi''$  of the dynamic susceptibility  $\chi_{ac} = \chi' - i\chi''$ , for  $x = 0.25$  and  $0.40$  samples, respectively. As can be seen, the peak values of both  $\chi'$  curves increase and shift to lower temperatures with decreasing frequency, i.e. there is a frequency dependence  $T_f(f)$  of the freezing temperatures. Contrary to this, the imaginary part  $\chi''$  of the dynamic susceptibility exhibits lowering of the peak values and a shift to higher temperatures with the frequency decrease (insets in figures 2 and 3). The dependences obtained for both  $\chi'$  and  $\chi''$  are characteristic of the spin glass state [14].

The relative shift of the maximum peak temperature  $T_f$  per decade of frequency, i.e.  $\Psi = (\Delta T_f / T_f) / \Delta(\log f)$ , for the in-phase part  $\chi'$  was determined to be 0.02 and 0.03 for the  $x = 0.25$  and  $0.40$  samples, respectively. These values are in the range of those obtained in both canonical spin glass and cluster glass systems,  $\sim 10^{-3}$ – $10^{-2}$  [12, 14, 15]. In the case of a superparamagnet (non-interacting magnetic particles) the  $\Psi$  parameter is larger, of the order of  $10^{-1}$  [14].



**Figure 3.** The real  $\chi'$  component of the AC susceptibility as a function of temperature and frequency for the  $\text{Li}_{0.533}\text{Co}_{1.2}\text{Ti}_{1.267}\text{O}_4$  ( $x = 0.40$ ) sample. Inset: the frequency dependence of the imaginary  $\chi''$  component of the AC susceptibility versus temperature.

To analyse the frequency shift of freezing temperatures  $T_f(f)$  obtained we have used two approaches: (i) the Vogel–Fulcher law (often used in cluster glass systems) and (ii) dynamic scaling theory. The empirical Vogel–Fulcher law is given by the expression

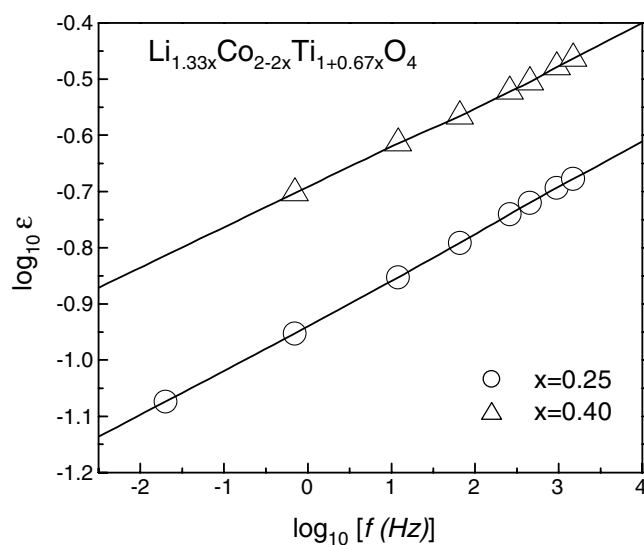
$$f = f_0 \exp(-E_a/(T_f - T_0)), \quad (2)$$

where parameter  $T_0$  is a measure of inter-particle interaction strength, and  $E_a$  denotes an activation energy parameter. The frequency parameter  $f_0$  is connected with the relaxation time  $\tau$  of the magnetization vector in the region  $T \rightarrow T_f^+$  by the relation  $\tau = 1/f_0$ . The best-fit values obtained for the parameters were:  $E_a = 92$  K,  $T_0 = 15.5$  K and  $f_0 = 2.65 \times 10^{10}$  Hz for  $x = 0.25$ ; and  $E_a = 110$  K,  $T_0 = 9.2$  K and  $f_0 = 5.3 \times 10^{11}$  Hz for the  $x = 0.40$  sample. The relaxation time  $\tau$  is connected with the cluster size in such a manner that  $\tau$  increases with the increase in cluster size. In cluster glass systems  $\tau$  is found to cover a wide range of values, from  $10^{-6}$  s [16] to  $10^{-13}$  s [12]. The relaxation times observed in our samples (of the order of  $10^{-10}$ – $10^{-11}$ ) could indicate the presence of small interacting clusters that are randomly frozen. Also, in systems with larger clusters a cluster growth occurs during the freezing process, which is not the case in our system.

In the second approach, the in-phase component  $\chi'$  of the AC susceptibility has been analysed according to conventional power-law dynamics. In the  $T \rightarrow T_f^+$  temperature region, the relaxation times  $\tau$  of the individual magnetic moments show a critical slowing down described by the relation  $\tau = \tau_0 \varepsilon^{-z\nu}$ , where  $\varepsilon = (T - T_f)/T_f$  denotes a reduced temperature,  $\tau_0$  is the microscopic relaxation time,  $z$  is the dynamical scaling exponent and  $\nu$  is the correlation length scaling exponent. Thus, the frequency dependent maxima should follow the expression

$$f = f_0 \varepsilon^{z\nu}. \quad (3)$$

A log–log plot of  $\varepsilon(f)$  gives an excellent linear dependence, as shown in figure 4. Best-fit values of the parameters are:  $f_0 = 5.6 \times 10^{13}$  Hz,  $z\nu = 13.9$  and  $T_f = 17.3$  K for the  $x = 0.25$  sample; and  $f_0 = 4.6 \times 10^{13}$  Hz,  $z\nu = 17.7$  and  $T_f = 11.0$  K for the  $x = 0.40$  sample. For canonical spin glasses such as CuMn and AuMn, typical  $f_0$  values



**Figure 4.** A log–log plot of the reduced temperature  $\varepsilon = (T - T_f)/T_f$  versus driven frequency for  $x = 0.25$  and  $0.40$  samples.

are within the  $10^{11}$ – $10^{12}$  Hz range [14]. The values of the critical exponents  $z\nu$  obtained are large in comparison with those found in diluted magnetic semiconductors [15, 17, 18] and other spin glasses where  $z\nu$  parameters are in the range 4–10 [14]. On the other hand, parameters that we obtained by using the Vogel–Fulcher law have reasonable values. We could suppose the existence of small magnetic clusters in our systems instead of a random distribution of individual magnetic ions, so deviations from typical parameter values found in canonical spin glasses are probably due to the formation of magnetically interacting clusters. It is well known that, for systems of non-interacting, single-domain magnetic particles, the frequency dependence of the blocking temperature  $T_b(f)$  can be well described by a thermally activated (Arrhenius) law [12]. However, recent works on magnetic nanoparticles with strong interaction, high local disorder and/or broad particle size distributions have reported power-law dynamics near  $T_b$ , with exponents  $z\nu$  within the  $10 \leq z\nu < 24$  range [19, 20].

### 3.4. Hysteresis

To further investigate the nature of the spin glass state, we performed measurements of the field dependence of the magnetization for the  $x = 0.25$  sample at two different temperatures. At the temperature  $T = 50$  K, above the glass transition temperature  $T_f \sim 17$  K, magnetization versus field is linear as expected (figure 5). At the temperature of 5 K a hysteresis loop was recorded. The value obtained for the coercive field  $H_c = 6.5$  kOe is larger than those commonly found in spin glasses [16, 21] but of the same order of magnitude as detected in the cluster glass  $\text{Co}_{0.2}\text{Zn}_{0.8}\text{Fe}_2\text{O}_4$  spinel which has been attributed to the random freezing of magnetic clusters in locally canted states [22]. The above result is also an indication of the cluster glass behaviour in the spinels under consideration.

## 4. Conclusion

Ternary  $\text{Li}_{1.33x}\text{Co}_{2-2x}\text{Ti}_{1+0.67x}\text{O}_4$  ( $0.25 \leq x \leq 0.875$ ) spinel compounds can be considered as diluted magnets originating from the partial substitution of magnetic  $\text{Co}^{2+}$  ions with



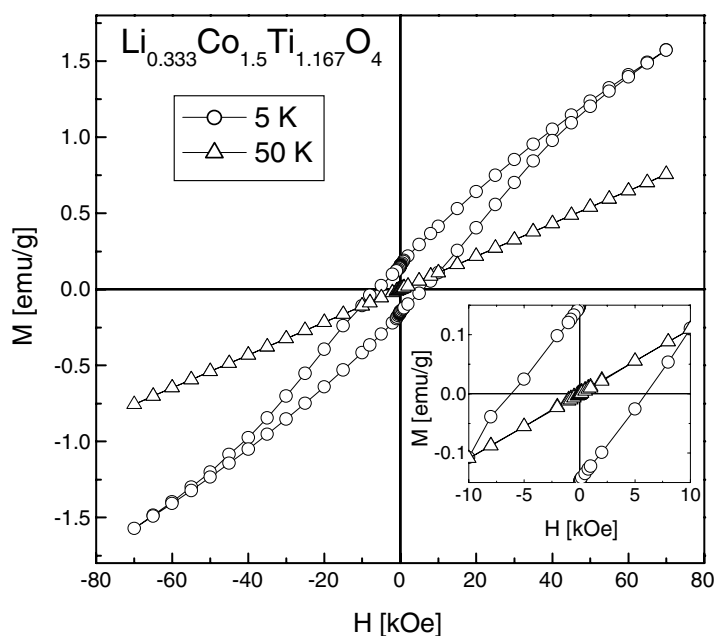


Figure 5. Hysteresis loops measured at  $T = 5$  and  $50$  K for the  $x = 0.25$  sample.

diamagnetic  $\text{Li}^+$  ions in the parent  $\text{Co}_2\text{TiO}_4$  ( $x = 0$ ) spinel. Since this binary spinel possesses complex magnetic properties [4, 5] our goal was to investigate their changes with the magnetic ion dilution.

For  $x = 0.25$  and  $0.40$  samples, the crystal symmetry of the diluted samples does not change from the starting  $\text{Co}_2\text{TiO}_4$ , and for these two compositions the development of spin glass order was found at low temperatures. With further dilution ( $x = 0.50$ ) a change in crystal symmetry occurs,  $Fd\bar{3}m \leftrightarrow P4_332$ , but the magnetic transition temperature remains almost unchanged with respect to the  $x = 0.40$  sample. The type of spin glass state was determined by analysing the frequency dependence of the AC susceptibility data. Results obtained by using different criteria point to the formation of a cluster glass state. Samples with the smallest  $\text{Co}^{2+}$  concentrations ( $x = 0.75$  and  $0.875$ ) are paramagnetic down to  $1.7$  K.

In the spinel systems under consideration superexchange can be considered as the dominant interaction mechanism among magnetic ions. In disordered spinels with  $x = 0.25$ ,  $0.40$  there are three superexchange paths:  $8a-8a$ ,  $8a-16d$  and  $16d-16d$ . In the ordered spinel with  $x = 0.50$  there are even more superexchange paths. Having in mind the angle–distance dependence of the superexchange mechanism [23, 24] the most important interactions should be between tetrahedral and octahedral sites: cation(8c)–anion–cation(12d) and cation(8c)–anion–cation(4d) [25]. In  $x = 0.75$  and  $0.875$  samples there is only one cation(8c)–cation(8c) interaction which occurs via more than one anion [25] and consequently it should be much weaker. As a result, these samples are in the paramagnetic phase down to  $1.7$  K.

The crystallographic distribution of  $\text{Co}^{2+}$  ions is random in samples with  $x = 0.25$ ,  $0.40$  and  $0.50$ , while for the  $x = 0.75$  and  $0.875$  samples  $\text{Co}^{2+}$  ions occupy only 8c sites. In diluted magnetic systems, another type of magnetic ion distribution can be considered in addition to crystallographic distribution; namely, magnetic ions can either form clusters or they can be randomly distributed with respect to each cation sublattice [25]. Magnetic measurements show that in our samples formation of clusters occurs in samples with  $x = 0.25$ ,  $0.40$  and (probably)

$x = 0.50$ . On the other hand, in the  $x = 0.875$  and  $0.75$  samples magnetic ions do not display clustering tendencies.

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