Effect of Ising-type Tb$^{3+}$ ions on the low-temperature magnetism of La, Ca cobaltite

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Received 19 July 2013, revised 10 January 2014
Accepted for publication 21 January 2014
Published 3 March 2014

Abstract
Crystal and magnetic structures of the $x = 0.2$ member of the La$_{0.8-x}$Tb$_x$Ca$_{0.2}$CoO$_3$ perovskite series have been determined from powder neutron diffraction. Enhancement of the diffraction peaks due to ferromagnetic or cluster glass ordering is observed below $T_C = 55$ K. The moments first evolve on Co sites, and ordering of Ising-type Tb$^{3+}$ moments is induced at lower temperatures by a molecular field due to Co ions. The final magnetic configuration is collinear F for the cobalt subsystem, while it is canted F$_x$C$_y$ for terbium ions. The rare-earth moments align along local Ising axes within the ab-plane of the orthorhombic Pbnm structure. The behavior in external fields up to 70–90 kOe has been probed by magnetization and heat capacity measurements. The dilute terbium ions contribute to significant coercivity and remanence that both steeply increase with decreasing temperature. A remarkable manifestation of the Tb$^{3+}$ Ising character is the observation of a low-temperature region with an anomalously large linear term of heat capacity and its field dependence. Similar behaviors are detected also for other terbium dopings $x = 0.1$ and 0.3.

Keywords: perovskite cobaltites, neutron diffraction, magnetic ordering, Ising moments, linear specific heat

(Some figures may appear in colour only in the online journal)

1. Introduction

The properties of perovskite cobaltites are largely affected by closeness in energy of different local states of the octahedrally coordinated cobalt ions. The well-known example is LaCoO$_3$, in which a spin transition, or spin-state crossover, occurs in the course of temperature. It has been recognized that the LaCoO$_3$ ground state is based on non-magnetic low spin state of Co$^{3+}$ (LS, $S = 0$, $t_{2g}^6e_g^0$), while with increasing temperature above $\sim$40 K, the energetically close high spin Co$^{3+}$ (HS, $S = 2$, $t_{2g}^4e_g^2$) species start to be populated by thermal excitation [1]. The HS population is practically saturated above 150 K, reaching about 40–50%. Strong HS/LS nearest neighbor correlations or even short-range ordering are anticipated in that phase [2–5]. At still higher temperature the ordering melts. This process is accompanied by a drop of electrical resistivity centered at about 530 K, which can be interpreted as a transition from a Mott insulator to a quasi-metallic state. The high-temperature phase of LaCoO$_3$ should be regarded as inhomogeneous, since it essentially retains the LS/HS Co$^{3+}$ disproportionation, with only short visits to intermediate spin (IS, $S = 1$, $t_{2g}^5e_g^1$) configurations [5].

While pure LaCoO$_3$ is paramagnetic at all temperatures, the doping of holes by chemical substitution generally introduces ferromagnetic interactions and leads finally to long-range ferromagnetic (FM) order. This evolution is best documented for the La$_{1-x}$Sr$_x$CoO$_3$ system [6, 7]. The mildly
doped compounds exhibit a non-uniform ground state with hole-rich FM regions of IS/LS character for Co$^{3+}$/Co$^{4+}$, embedded in the hole-poor matrix with the main weight of LS Co$^{3+}$. The origin of such two-phase competition cannot be understood within any standard band picture, and is intimately associated with the strongly correlated nature of the materials [8, 9]. The transition to a more homogeneous state is observed at $x = 0.22$, as documented by the onset of metallic conductivity and a finite electronic heat with a linear coefficient $\gamma \approx 40 \text{ mJ K}^{-2}$ [10]. Above this critical concentration, the La$_{1-x}$Sr$_x$CoO$_3$ compounds show characteristics of conventional ferromagnets, namely the large $\lambda$-anomaly in the specific heat at $T_C$, the critical behavior manifested by a sharp peak in small-angle neutron scattering, and by critical exponents $\beta$, $\gamma$ and $\delta$ belonging to the universality class of the 3D Heisenberg model [6, 7, 11].

The situation in calcium-doped system La$_{1-x}$Ca$_x$CoO$_3$ is less explored. In this case a much more uniform FM phase seems to form, starting from weak doping, though the saturated moments are low and no metallic conductivity is reached [10, 12, 13]. There are, nevertheless, a few reports indicating a certain phase separation, similarly to what was reported earlier for some glasses or disordered and frustrated ferromagnets [15].

In order to understand better the behavior of LaCoO$_3$-related compounds with the calcium doping, we have undertaken the study of the La$_{0.8-x}$Tb$_x$Co$_{0.2}$O$_3$ system. We have selected Tb$^{3+}$ ions since they show complex magnetic behavior due to crystal field effects, and can be effectively used as a local probe of the low-temperature magnetism produced by the cobalt subsystem. We have found, with the help of the neutron diffraction, magnetic measurements and investigation of the low-temperature heat capacity, that the magnetic ground state is highly non-uniform and Ising-type Tb$^{3+}$ moments have a critical influence on the magnetic properties.

2. Experimental details

Samples of La$_{0.8-x}$Tb$_x$Co$_{0.2}$O$_3$ ($x = 0.1$, 0.2 and 0.3) were synthesized by a sol–gel procedure followed by annealing at $1000 \, ^\circ\text{C}$ under air for at least 24 h. The starting materials included stoichiometric amounts of La$_2$O$_3$, Tb$_2$O$_7$, CaCO$_3$ and Co(NO$_3$)$_2$$_2$ solutions with a chemically determined metal content, while ethylene glycol was used to prepare the gel precursor. The final products were checked for phase purity by x-ray diffraction. The perovskite crystal structures are of the orthorhombic $Pbnm$ type, except for a small coexistence of the $R3c$ phase in the $x = 0.1$ sample. More detailed structural investigation was performed by neutron diffraction in LLB (Saclay, France) on the G41 diffractometer using a wavelength of 2.422 Å. The neutron diffraction data, obtained at selected temperatures down to 1.8 K, were analyzed by a Rietveld method with the help of the FULLPROF program (version 4.80/2010).

For a complex physical characterization the $x = 0.2$ compound (La$_{0.6}$Tb$_{0.2}$Co$_{0.2}$O$_3$) was selected. The magnetic moment was measured on a SQUID magnetometer (MPMS-XL; Quantum Design) over the range 2–400 K under various fields in the range 100 Oe–70 kOe. Zero-field-cooled (ZFC) and field-cooled (FC) runs were performed. The hysteresis loops were measured up to a maximum field of 70 kOe at selected temperatures, starting from $T = 2$ K upwards. The remanent magnetization versus $T$ dependence was measured after recording the hysteresis loop $T = 2$ K and decreasing $H$ to zero. The ZFC long-time relaxation experiments were performed by cooling the sample from $T = 300$ K to a target temperature $T$ and keeping it for a certain wait time $t_w$, typically $10^3$ s, before setting the field $H = 10$ Oe and starting the measurement. The time evolution of the magnetic moment was then recorded between $t = 0$ and $t = 4900$ s. The AC susceptibility measurements were carried out with the amplitude of driving field 3.9 Oe and frequency 0.3–300 Hz.

The specific heat was measured by a PPMS device (Quantum Design) using the two-$\tau$ model. The data at zero field and under fields up to 90 kOe were collected generally on sample cooling. The experiments at very low temperatures (down to 0.4 K) were done using the He$^3$ option.

3. Results and discussion

3.1. Transport properties

As a first physical characterization of the La$_{0.6}$Tb$_{0.2}$Co$_{0.2}$O$_3$ system, the basic transport phenomena were probed. Figure 1 presents the temperature dependence of electrical resistivity, thermoelectric power and thermal conductivity. The displayed data show that the electronic transport is of a transitional behavior between the strongly activated semiconductor LaCoO$_3$ and the doped ferromagnetic metallic compounds La$_{1-x}$Sr$_x$Co$_3$O$_7$. The actual regime, manifested by the activated resistivity and linear (metallic-like) thermopower at the lowest temperatures, can be described as variable range hopping. This type of behavior is typical for systems with localized electronic states forming a quasi-continuous band around the Fermi level; for doped cobalitites see e.g. [16]. The resistivity above $\sim 15$ K follows a non-standard power-law dependence, similarly to what was reported earlier for some polycrystalline specimens of electron-doped LaCoO$_3$ [17] or mixed systems LaCo$_{1-x}$Cu$_x$O$_3$ [18].

3.2. Crystal structure

The crystal and magnetic structures of La$_{0.6}$Tb$_{0.2}$Co$_{0.2}$O$_3$ perovskite were determined from the powder neutron diffraction, measured at temperatures from 1.8 to 300 K. Let us note that, without terbium substitution, the crystal structure of La$_{1-x}$Ca$_x$CoO$_3$ changes from rhombohedral (space group $R3c$) for $x < 0.1–0.2$ to orthorhombic (space group $Pbnm$).
for $x > 0.2–0.3$, with both phases coexisting in the intermediate doping range [19, 20]. For La$_{0.6}$Tb$_{0.2}$Ca$_{0.2}$CoO$_3$ the single orthorhombic Pbnm structure is observed over the whole experimental temperature range. For three selected temperatures the complete data including atomic coordinates are presented in table 1. The occupancy of oxygen sites is refined to 1.009 ± 0.003, indicating an oxygen content in the La$_{0.6}$Tb$_{0.2}$Ca$_{0.2}$CoO$_3$ sample slightly above the ideal stoichiometry. This result may suggest that the cobalt valence in La$_{0.6}$Tb$_{0.2}$Ca$_{0.2}$CoO$_3$ is shifted from the formal mixture 0.2 Co$^{3+}$/0.8 Co$^{4+}$ to an actual 0.25 Co$^{3+}$/0.75 Co$^{4+}$. The goodness of Rietveld fit is characterized by values $R_p = 2.03\%$, $R_w^p = 2.77\%$ and $R_{Bragg} = 1.92\%$ at 300 K, and $R_p = 2.85\%$, $R_w^p = 4.01\%$, $R_{Bragg} = 2.06\%$ and $R_{mag} = 9.17\%$ at 1.8 K.

The temperature evolution of lattice parameters and cell volume/f.u. is displayed in the upper panel of figure 2. The relation between lattice parameters, $a > b - c/\sqrt{2}$, is different from the situation in perovskites ABO$_3$ with smaller A cations (and smaller tolerance factor), for which the tilting of the octahedra network is the dominant source of the orthorhombic distortion, and the relation between lattice parameters $b > c/\sqrt{2} > a$ is typical. The present type of orthorhombic deformation should thus be related to a small shear distortion of the CoO$_6$ octahedron, namely the deviation of O–Co–O angles from 90°, that prevails over the effects of the octahedral tilting.

The extent of octahedral tilting is quantified by the average bond angle Co–O–Co, which makes 160° at room temperature, decreases to 159.5° at 100 K and then to 159.2° at the lowest temperature. The average Co–O bond distance decreases from 1.930 Å at 300 K to 1.926 Å at 100 K, but then remains approximately constant down to the lowest temperature. The CoO$_6$ octahedron is almost regular, the difference between the longest and shortest Co–O distance does not exceed 0.02 Å. The three non-equivalent O–Co–O angles in the Pbnm structure range between 88.8°–89.6°.

The change of CoO$_6$ tilting incurred by lowering temperature is also reflected in the temperature evolution of the

![Figure 1. Resistivity, thermoelectric power and thermal conductivity of La$_{0.6}$Tb$_{0.2}$Ca$_{0.2}$CoO$_3$. The linear part of the resistivity versus $T^{-1/4}$ dependence, seen in the inset of the upper panel for $T < 15$ K, is characteristic of variable range hopping.](image1)

![Figure 2. (a) Temperature dependence of the lattice parameters and cell volume/f.u. (b) The relative changes of short and long A–O bonds, $A = $ La$_{0.6}$Tb$_{0.2}$Ca$_{0.2}$, together with average values of Co–O bonds and O–Co–O angles.](image2)

| $T$ (K) | 1.8 | 100 | 300 |
|---------|-----|-----|-----|
| $a$ (Å) | 5.3686(5) | 5.3693(6) | 5.3852(6) |
| $b$ (Å) | 5.3539(4) | 5.3567(6) | 5.3713(6) |
| $c$ (Å) | 7.5674(6) | 7.5732(7) | 7.5945(8) |
| $x$, LaTbCa | $-0.0005(11)$ | $-0.0075(8)$ | $-0.0077(8)$ |
| $y$, LaTbCa | 0.0294(5) | 0.0279(4) | 0.0262(5) |
| $x$, O1 | 0.0750(13) | 0.0634(9) | 0.0618(9) |
| $y$, O1 | 0.4911(7) | 0.4912(6) | 0.4930(7) |
| $x$, O2 | $-0.2775(8)$ | $-0.2793(7)$ | $-0.2803(7)$ |
| $y$, O2 | 0.2813(7) | 0.2793(6) | 0.2770(8) |
| $z$, O2 | 0.0303(6) | 0.0345(4) | 0.0339(4) |

Table 1. The crystallographic data summary for La$_{0.6}$Tb$_{0.2}$Ca$_{0.2}$CoO$_3$ at 1.8, 100 and 300 K. Space group Pbnm. Atom coordinates: LaTbCa 4c(x, y, 1/4), Co 4b(1/2, 0, 0), O1 4c(x, y, 1/4), O2 8d(x, y, z).
Figure 3. Magnetic moment of La$_{0.6}$Tb$_{0.2}$Ca$_{0.2}$CoO$_3$ measured under various fields in the FC (□) and ZFC (○) regimes. The insets show the corresponding inverse susceptibility graphs.

coordination sphere of the large cation (La$_{0.6}$Tb$_{0.2}$Ca$_{0.2}$) in the A site of the perovskite structure. The twelve bonds could be divided into two groups of eight shorter and four longer distances, having different evolution with temperature, see the lower panel of figure 2. The eight shorter bonds shorten relative to room temperature values, whereas the four longer bonds elongate compared to room temperature. The temperature evolution of the shorter A–O bonds closely resembles that of the Co–O–Co bond angle.

3.3. Magnetic properties

Magnetic properties of La$_{0.6}$Tb$_{0.2}$Ca$_{0.2}$CoO$_3$ were probed by DC magnetization measurements and by frequency-dependent AC susceptibility experiments. Temperature curves of the magnetic moment measured under various fields from 100 Oe to 70 kOe are presented in figure 3. The moments observed above $\sim 60$ K are proportional to the applied field, which is a signature of a paramagnetic state. The paramagnetic properties are more apparent in the insets of figure 3, where data are plotted in terms of inverse susceptibility. With increasing temperature the Curie–Weiss dependence $\chi = C/(T - \theta)$ is approached, where the molar value of Curie constant depends on the effective paramagnetic moment, $C = N\mu^2_{\text{eff}}/3k$. The fit yields $\mu^2_{\text{eff}} = 28.6 \mu_B^2/\text{f.u.}$ and a Weiss temperature $\theta = 23$ K. The square value of the effective moment agrees with a theoretical expectation, namely the weighted sum of $\mu^2_{\text{eff}}$ for 0.2 Tb$^{3+}$ (the free-ion value $\mu_{\text{eff}} = 9.72 \mu_B$) and the valence mixture 0.25 Co$^{4+}$/0.75 Co$^{3+}$, both in the intermediate spin state ($S = 1.5$ and 1, respectively), which gives a total $\mu^2_{\text{eff}} = 28.7 \mu_B^2$. The positive Weiss $\theta$ is attributed to FM interactions between Co ions, since the interaction between more diluted Tb ions is supposedly weak and of antiferromagnetic (AFM) type.

Below $\sim 60$ K the magnetic moment increases rapidly. The low-temperature diverging tail of the FC curves, clearly observed in figure 3 up to 10 kOe, can be assigned mainly to the magnetic response of Tb$^{3+}$ ions. There is an inflection point at about 20 K, which suggests that this paramagnetic-like term is superimposed on another term due to Co$^{3+}$/Co$^{4+}$ ions, having a form close to the Brillouin curve. This latter contribution and its gradual saturation in high fields resembles the behavior of a conventional ferromagnet. However, the bifurcation between ZFC and FC curves, which shifts with increasing field to lower temperatures, indicates rather the formation in La$_{0.6}$Tb$_{0.2}$Ca$_{0.2}$CoO$_3$ of a non-uniform state of glassy character. This conclusion is further supported by AC susceptibility measurements over the frequency range 0.3–300 Hz, presented in figure 4. As shown in the inset, the characteristic temperature $T_f$, at which the real part $\chi'$ passes through a maximum, exhibits with increasing frequency $\nu$ of the applied AC field an upward shift that can be quantified by a semiempirical dimensionless parameter $K = \Delta T_f/[T_f\Delta(\log \nu)] = 0.0016$. Such a weak frequency dependence, compared to much larger $K$-values in canonical spin-glass systems [21], suggests that the FM clusters that freeze near $T_f \sim 55$ K are relatively large.
The typical manifestation of the frustrated magnetic state is the long-time relaxation of magnetization and ageing effects. The data we obtained are nearly identical to the results of Nam et al on polycrystalline La$_{0.5}$Sr$_{0.5}$CoO$_3$, exhibiting a similar non-uniform magnetic state in which the FM and glassy behaviors coexist [22]. In particular, for $T = 40$ K, i.e. slightly below the freezing temperature, the relaxation of moments after application of the probing field $H = 10$ Oe could be described by a stretched exponential function and the maximum of the derivative of $m(T)$ with respect to $\ln(T)$ is attained at an elapsed time close to the wait time $t = t_w$ ($t_w = 1000, 2000$ and $3000$ s).

The magnetization curves for $T \leq 40$ K are presented in figure 5. In the temperature range down to $\sim 15$ K the magnetization shows a rapid rise at lower fields, but the next increase is more gradual and lacks saturation in the highest field of $70$ kOe. All these features differ from the conventional behavior of bulk FM and are typical for a cluster glass with a broad size distribution of FM domains and strong AFM interactions between them. Below $\sim 15$ K, an anomalous behavior is observed. The virgin magnetization curves are specified by a linear initial part followed by a break, after which a steep rise, resembling a metamagnetic transition, occurs. The critical field corresponding to the break increases with decreasing temperature in a hyperbolic way, as seen in the inset of figure 5. Since our neutron diffraction study does not indicate any change of the magnetic ground state below $15$ K, the existence of the metamagnetic transition can be discarded. Instead, we relate the observed character of the magnetization curves to the low-temperature effect of Tb$^{3+}$ moments. Namely, the local anisotropy connected with the presence of Tb$^{3+}$ ions may lead to the pinning of domain walls in FM ordered regions, which influences both the coercivity seen in the hysteresis loops (figure 6) and the metamagnetic-like form of the virgin curves. Let us note that the coercive field reaches $\sim 7$ kOe at $2$ K, and the above-mentioned ‘metamagnetic transition’ is observed at the same field.

We may conclude this section by a statement that the chemically highly inhomogeneous compound La$_{0.6}$Tb$_{0.2}$Ca$_{0.2}$CoO$_3$ shows a spectrum of behaviors, some of which are typical for bulk FM and others reminiscent of glassy systems.
The opposite changes on these peaks suggest that also the terbium moments at A sites adopt AFM ordering, and their orientation is parallel to the cobalt moments. Namely, the intensity of the neutron diffraction peak 110 + 002 drops since it is given by the square of $m_{Co} - m_{Tb}$, while the intensity 112 + 020 + 200 given by the square of $m_{Co} + m_{Tb}$ rises.

The second, well-marked change below 20 K is the appearance of new magnetic peaks at 100 + 010 and 102 + 012 positions. These peaks are indicative of the C-type AFM arrangement in the sample and may originate either in magnetic phase coexistence or in spin canting. Although a partial AFM order of cobalt spins was already detected by neutron diffraction for some cobaltites of similar doping, such as La$_{1-x}$Ba$_x$CoO$_3$ ($x = 0.17$–$0.19$) [23], we relate the present observation to the canted arrangement of Tb$^{3+}$ moments within the FM phase. Let us note that the canting is an inevitable consequence of the Ising character of the Tb$^{3+}$ moments and alternation of the easy axes in the $ab$-plane of the orthoperovskite structure [24]. A better known example is the TbCoO$_3$ cobaltite with non-magnetic LS Co$^{3+}$, which below $T_N \sim 3.5$ K shows a spontaneous Tb$^{3+}$ ordering also of cantled type, $A_xG_y$ in Bertaut’s notation [25, 26].

The results of the Rietveld refinement are presented in figure 8. The spontaneous ordering is established at first on Co sites, and the ordering of the Tb moments arises gradually at lower temperatures by the action of the molecular field induced by Co ions. The crystallographic orientation of Co moments cannot be unambiguously determined due to a small splitting of the reflections of the pseudocubic perovskite cell. We suppose that the magnetic axes of FM domains are distributed rather randomly, but below 20 K the Co spins align in accordance with the easy local axes of Ising-type Tb$^{3+}$ ions, which are within the $ab$-plane, inclined to $\pm 36^\circ$ out of $b$-direction. Based on this angle, found actually on the related perovskite system TbAlO$_3$ [24], and using the observed moments at 1.8 K in figure 8, we may conclude that the final configuration is of collinear $F_g$ type with a long-range ordered moment of 0.55 $\mu_B$/Co, and the rare-earth ordered moments form the canted arrangement $F_gC_g$ with average components per site of $m_T = 0.75$ $\mu_B$ and $m_C = 0.5$ $\mu_B$, or per rare-earth ion of $m_T = 3.8$ $\mu_B$/Tb and $m_C = 2.5$ $\mu_B$/Tb. This means that the terbium moments are inclined from the $a$-axis to $34^\circ$ and their ordered magnitudes are 4.5 $\mu_B$. The orientation of the canted arrangement with respect to the crystallographic axes then shows that the AFM diffraction lines observed at 100 + 010 and 102 + 012 positions in the $T = 1.8$ K diffraction pattern in figure 7 are in fact the (100) and (102) intensities, while (010) and (012) are extinguished. As far as the bulk magnetic moment is concerned, the sum of FM components of the Co and Tb ions, 1.3 $\mu_B$/f.u. at 1.8 K, seems to correspond very well to the magnetization data in figures 5 and 6 when an intuitive extrapolation to zero field is done.

The same set of FM and AFM reflections and, consequently, very similar magnetic structures (see figure 12) have been observed also for other terbium dopings in our La$_{0.8-x}$Tb$_x$Co$_2$O$_3$ series. For a comparison, the low-angle parts of the neutron diffraction patterns of $x = 0.1$, 0.2 and 0.3 at 1.8 K are presented together in figure 9. The refined moments at cobalt sites and the magnitudes of terbium moments and their inclination from the orthorhombic axis $a$ are summarized in table 2.

### Table 2. Data summary on magnetic ordering in the La$_{0.8-x}$Tb$_x$Co$_2$O$_3$ series.

| $x$    | $T_C$ (K) | $\mu_B$/Co | $\mu_B$/Tb | $\phi$ (deg) |
|-------|-----------|------------|------------|--------------|
| 0.1   | 80        | 1.05       | 8.4        | 33           |
| 0.2   | 55        | 0.55       | 4.5        | 34           |
| 0.3   | 30        | 0.35       | 3.0        | 31           |

Figure 7. The low-angle part of neutron diffraction patterns taken on La$_{0.6}$Tb$_{0.4}$Co$_2$O$_3$ at temperatures 1.8–20 K. The FM ordering is deduced from the hardly visible enhancement of 110 + 002 and 112 + 020 + 200 lines, the C-type AFM order is manifested by the additional magnetic reflections, 100 + 010 and 102 + 012.

Figure 8. FM ordered magnetic moments of Co and Tb and the C-type AFM ordered magnetic moments of Tb. Error bars for the partial FM components are similar to those shown for the overall Co + 0.2Tb moment, $\sim \pm 0.2 \mu_B$. 

![Graph showing magnetic moment as a function of temperature](image_url)
temperatures, for transition metal oxides. The dominant term is the lattice can be fitted by a sum of common contributions, known as parameters, which is complemented by a rather large linear specific heat component, whereas the temperature range of linear regime expands. We note that a linear specific heat is a general property of glassy systems, both the dielectrics and spin glasses. However, in the present system this term should be attributed to Tb nuclei present in FM regions, and argue by the very large electronic moment of Tb ions ~8.4 μB and hyperfine coupling constant 400 kOe/μB, compared to ~1.7 μB and 80 kOe/μB for Co3+/Co4+ in [7].

Let us turn now to the specific heat excess that emerges in lower fields. In the difference graph in figure 10(b), it is seen that the entropy associated with excessive heat at zero field is seemingly transformed, at 90 kOe, to a larger linear specific heat contribution of 159Tb nuclei present in FM regions, and argue by the very large electronic moment of Tb ions ~8.4 μB and hyperfine coupling constant 400 kOe/μB. The temperature range of linear regime expands. We note that a linear specific heat is a general property of glassy systems, both the dielectrics and spin glasses. However, in the present system this term should be attributed to Tb3+ ions in FM regions, where they experience, even in the absence of an external field, a non-zero randomly oriented field.

3.5. Heat capacity

The heat capacity measurements on La0.8-xTbxCa0.2CoO3 showed no observable λ-anomaly around their Curie temperatures $T_C = 80$ K, 55 K and 30 K for $x = 0.1$, 0.2 and 0.3, respectively. This means that critical fluctuations associated with magnetic ordering are distributed over a much larger temperature range than they are for conventional ferromagnets. Let us mention an analogous lack of criticality at the apparent $T_C$ of Pr0.7Ca0.3CoO3, which was attributed by El-Khatib et al to a magnetic/electronic phase separation where FM clusters (presumably hole-rich objects), preformed at temperatures as high as ~250 K, coexisted with the hole-poor paramagnetic matrix [27]. The behavior at the lowest temperatures is exemplified by the heat capacity data for La0.6TbxCa0.4CoO3, presented in figure 10(a). There is a marked component that is spanning below 10 K and seems to be proportional to the terbium doping. It decreases with applied field and apparently vanishes in the maximum field of 90 kOe. The residual heat or background can be fitted by a sum of common contributions, known for transition metal oxides. The dominant term is the lattice heat $\beta T^3$, which is complemented by a rather large linear specific heat $\gamma T$ and a marked Schottky anomaly at the lowest temperatures, $\alpha T^{-2}$. To improve the fit, a small quadratic term $\delta T^2$ is included. Let us note that a similar but somewhat larger quadratic term was observed earlier for the phase separated systems La1-xSrxCaO3 with $x < 0.22$ and was attributed to the non-FM regions [7]. The exact mechanism, remained, however, unclear. In the same work the Schottky anomalous term $\alpha T^{-2}$ due to 59Co nuclei experiencing a hyperfine field in FM regions was also analyzed. It appears that the present value of the coefficient $\alpha = 0.044$ J K mol$^{-1}$ is an order of magnitude larger, so that its nature should be different. We ascribe such an enhanced $\alpha T^{-2}$ term to the contribution of 159Tb nuclei present in FM regions, and argue by the very large electronic moment of Tb ions ~8.4 μB and hyperfine coupling constant 400 kOe/μB, compared to ~1.7 μB and 80 kOe/μB for Co3+/Co4+ in [7].

Let us turn now to the specific heat excess that emerges in lower fields. In the difference graph in figure 10(b), it is seen that the entropy associated with excessive heat at zero field is seemingly transformed, at 90 kOe, to a larger linear specific heat contribution of 159Tb nuclei present in FM regions, and argue by the very large electronic moment of Tb ions ~8.4 μB and hyperfine coupling constant 400 kOe/μB. The actual change of coefficient $\gamma$ is about 0.010 J K$^{-2}$ mol$^{-1}$, and we suppose it scales with applied field and modifies the background. After subtracting the background terms, the excessive heat contribution is plotted in the $C_p/T$ versus $T$ graph in figure 11. The characteristic feature is the large roughly constant part, which becomes obvious in applied fields and corresponds in fact to an additional linear term $C_p = \gamma_m T$. The value of $\gamma_m$ decreases with increasing external field, whereas the temperature range of linear regime expands. We note that a linear specific heat is a general property of glassy systems, both the dielectrics and spin glasses. However, in the present system this term should be attributed to Tb3+ ions in FM regions, where they experience, even in the absence of an external field, a non-zero randomly oriented field.
It is essential for the existence of such a linear specific heat that the Tb$^{3+}$ ions possess finite moments of Ising character [28]. This issue will be discussed below.

The entropy associated with Tb$^{3+}$ ions in La$_{0.6}$Tb$_{0.2}$Ca$_{0.2}$CoO$_3$ can be calculated by integration of excessive $C_p/T$. The data plotted in the inset of figure 11 show that the entropy change at zero field actually reaches $\sim$1.3 J K$^{-1}$ mol$^{-1}$. This value is in reasonable agreement with the theoretical $S_{\text{total}} = 8 \cdot \ln 2$ per ion, which gives 1.15 J K$^{-1}$ mol$^{-1}$ for a population of 0.2 Tb$^{3+}$/f.u. Nonetheless, the integral value over the temperature range of figure 11 is not conserved and decreases quickly with increasing external field. As mentioned above, the low-temperature entropy is transferred to a larger linear specific heat at intermediate temperatures or to a modified stiffness of the system.

4. Discussion

Our comprehensive investigation of the La$_{0.6}$Tb$_{0.2}$Ca$_{0.2}$CoO$_3$ system provides a significant amount of information on the role of rare-earth ions. No signatures for the eventual presence of Tb$^{4+}$ ions are observed and we may also argue that this valence state is unfavorable since it would greatly increase the size disorder on the perovskite A sites. The rare-earth ions are thus in the Tb$^{3+}$ state in the electronic configuration 4$f^6$, which is a non-Kramers ion. The lowest lying free-ion term is $^2$F$_6$ ($L = 3$, $S = 3$, $J = 6$), and it is split by the low-symmetry crystal field to 13 singlets. The calculations available for TbAlO$_3$ of the same Pbnm symmetry show that the ground and first excited states of the Tb$^{3+}$ ion are formed of 90% by two conjugate wavefunctions, $|6, +6\rangle + |6, -6\rangle$ and $|6, +6\rangle - |6, -6\rangle$, and their eigenenergies differ by only 0.025 meV, representing a quasi-doublet [24]. This specific kind of accidental degeneracy has important consequences. Firstly, a relatively modest magnetic field of external or molecular nature will mix the eigenstates into a form of two pseudospins with the main weight of $|6, +6\rangle$ and $|6, -6\rangle$, respectively. This results in a large magnetic moment of Tb$^{3+}$ ions, of approximately 8.4 $\mu_B$. Secondly, these moments essentially have an Ising-like character, which is a source of large local anisotropy and makes La$_{0.6}$Tb$_{0.2}$Ca$_{0.2}$CoO$_3$ the strongly coercive system. This property is reflected in the virgin magnetization curves by the apparent ‘metamagnetic transition’, and in the hysteresis loop by the remanent moment and coercive field both gradually increasing below $\sim$20 K.

The local Ising axes are oriented in the ab-plane of the Pbnm perovskite structure. Since there are two crystallographically equivalent sites of Tb$^{3+}$ ions related by reflection in the ac-plane, their Ising axes make an angle $\pm \varphi$ with the orthorhombic axis $a$. The angle $\varphi = 36^\circ$ has been determined for TbAlO$_3$ and, in the absence of spectroscopic data, we suppose a similar inclination also for the present La$_{0.6}$Tb$_{0.2}$Ca$_{0.2}$CoO$_3$, though the energy splitting of electronic levels might here be reduced due to smaller octahedral tilting. Let us note that the $x$- and $y$-components of moments deduced from the neutron diffraction, $m_x = 3.8$ $\mu_B$/Tb and $m_y = 2.5$ $\mu_B$/Tb, correspond in fact to $\varphi = 34^\circ$, and a similar inclination is determined also for La$_{0.8-x}$Tb$_x$Ca$_{0.2}$CoO$_3$ systems with other terbium dopings. What is varied are the magnitudes of the ordered cobalt and terbium moments, which rapidly decrease with $x$. The data in table 2 show that Tb$^{3+}$ in $x = 0.1$ exhibits the full theoretical moment 8.4 $\mu_B$/Tb, which signifies a complete long-range ordering in this sample, while the moments observed by neutron diffraction in samples with higher terbium contents, namely our target composition La$_{0.6}$Tb$_{0.2}$Ca$_{0.2}$CoO$_3$ ($x = 0.2$) and sample $x = 0.3$, drop gradually. By the comparison, we may conclude that the population of long-range ordered domains (\textgreek{g}100 nm) in the latter samples is reduced to 50% and 33%, respectively.

The Ising character of Tb$^{3+}$ pseudospins elucidates also the character of the low-temperature specific heat of La$_{0.6}$Tb$_{0.2}$Ca$_{0.2}$CoO$_3$, namely it provides an explanation for the anomalously large linear term. In the FM phase of

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**Figure 11.** The Tb$^{3+}$ related term of the specific heat in La$_{0.6}$Tb$_{0.2}$Ca$_{0.2}$CoO$_3$. The inset shows the calculated entropy change within the temperature range 0.4–25 K.

**Figure 12.** Projection of La$_{0.6}$Tb$_{0.2}$Ca$_{0.2}$CoO$_3$ structure along the c-axis, showing the F$_{4c}$ ordering of cobalt moments located in the $c = 0$ level and the canted F$_{4c}$ ordering of rare-earth moments located on the mirror plane at $c = 0.25$. (The moment orientation in successive layers $c = 0.5$ and 0.75 are identical.)
mixed-valence cobaltites, each Tb\(^{3+}\) ion experiences certain molecular field causing Zeeman splitting of the quasi-doublet, \(\Delta E = g \cdot \mu_B \cdot H_m\), where \(g\) is the anisotropic gyromagnetic factor. The thermal population of the two electronic levels gives a standard Schottky peak in specific heat. As pointed out by Coey and von Molnar, when molecular and applied fields are randomly oriented, making an angle \(\theta\) with respect to local Ising axes, the Zeeman splitting varies as \(\cos \theta\) and, instead of two sharp levels, the system as a whole exhibits a continuous spectrum of excitations with a constant density of states from \(\Delta E = 0\) to \(\Delta E_{max}\). Namely, the constant density of states is a prerequisite for the strictly linear specific heat \([28]\). We believe that the same mechanism applies for the present \(\text{La}_{0.6}\text{Tb}_{0.2}\text{Ca}_{0.2}\text{CoO}_3\). Although the molecular field orientation at zero external field will depend on the details of the non-uniform FM phase, the randomness is guaranteed at increased applied fields because of the polycrystalline nature of our sample.

5. Conclusions

The perovskite cobaltite \(\text{La}_{0.6}\text{Tb}_{0.2}\text{Ca}_{0.2}\text{CoO}_3\) is a highly inhomogeneous chemical system with a large size disorder of A-site cations (La, Tb, Ca). The magnetic interactions of \(\text{Co}^{3+}/\text{Co}^{4+}\) ions have a clear prevalence for FM exchange, which is evidenced by the FM-like susceptibility transition, although typical \(\lambda\)-anomaly in heat capacity is absent. We presume that the formation of the FM phase starts as the nucleation of many FM regions that grow progressively and align according to anisotropy axes defined by local strains and local fluctuations of the charge carrier density. A non-uniform magnetic state with the coexistence of ordered and disordered regions, varying with the temperature, is thus anticipated. The neutron diffraction detects, nonetheless, a long-range FM order of cobalt moments below \(T_C = 55\ \text{K}\). This spontaneous alignment of cobalt spins is the source of a molecular field that acts on the Tb\(^{3+}\) ions, which are randomly distributed over the A sites of perovskite structure together with the non-magnetic \(\text{La}^{3+}\) and \(\text{Ca}^{2+}\) ions. As a result of this molecular field, the terbium pseudospins are gradually polarized and their static arrangement becomes observable below \(\sim 20\ \text{K}\). The experiments show that the effective cobalt–terbium interaction is ferromagnetic, but the resulting arrangement of terbium moments is canted due to alternating orientation of their local Ising axes. To summarize, the kind of magnetic structure actually observed (see figure 12) and the anomalous low-temperature linear term of the specific heat indicate a strong effect of Tb\(^{3+}\) ions with large Ising-type moments on the low-temperature magnetic behavior of La, Ca-based cobaltites.

Acknowledgments

This work was supported by project no. P204/11/0713 of the Grant Agency of the Czech Republic. We acknowledge the Laboratoire Leon Brillouin (Saclay, France) for providing access to the neutron beams and for all technical support during the experiments.

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