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Thermally and field-driven spin-state transitions in $(Pr_{1-y}Y_y)_{0.7}Ca_{0.3}CoO_3$

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The first-order character of the transition from the low-to-intermediate spin state in the system $(Pr_{1-y}Y_y)_{0.7}Ca_{0.3}CoO_3$ ($y = 0.075$–0.15) has been verified by magnetization measurements. For $y = 0.075$, the transition manifests itself in $\chi(T)$ steps at temperatures depending on external fields. In this case, isothermal measurements show a field-driven transition exhibiting a field hysteresis. The entropy contribution is evaluated and discussed. Qualitative analysis based on a two-level model suggests that the observed influence of the magnetic field can be explained only by assuming the presence of exchange interactions. © *2011 American Institute of Physics*. [doi:10.1063/1.3559485]

I. INTRODUCTION

The spin-state transitions (SST) in $LaCoO_3$−type cobaltites concern the Co^{3+} ions, which may occur in the low-spin (LS) $s = 0$, intermediate (IS) $s = 1$, or high-spin $s = 2$ states. A specific case of simultaneous first-order SST and metal–insulator transition, accompanied by a large volume change, was reported on the mixed valency cobaltite $Pr_{0.5}Ca_{0.5}CoO_3$ (Ref. 1) and related systems of lower calcium doping with Pr substituted by smaller rare earths (see, e.g., Ref. 2). Recently, the exclusive role of praseodymium for such a type of transition has been elucidated.[3–5] Based on the electronic structure calculations and detailed analysis of the structural, electrical, magnetic, and specific heat data, it has been found that the transition is accompanied by a significant charge transfer between cobalt and praseodymium ions. In particular for the system $(Pr_{1-y}Y_y)_{0.7}Ca_{0.3}CoO_3$, about one-third of the Pr^{3+} ions changes their valency to Pe^{4+} during the SST on decreasing temperature.[4] In the present contribution we follow previous works[2,4] and bring a detailed study of the first-order SST and its dependence on the applied magnetic field, taking a special emphasis on the composition y=0.075. The new result is the observation of a field-driven SST, which can be explained by the presence of the exchange interaction acting on the paramagnetic IS Co^{3+} ion.

II. EXPERIMENT

In our experiments we used the ceramic samples of $(Pr_{1-y}Y_y)_{0.7}Ca_{0.3}CoO_3$ ($y = 0.075$, 0.1, 0.15) described previously in Ref. 4. The magnetic measurements were carried out by means of the superconducting quantum interference device magnetometers MPMS XL and MPMS-5S. The temperature dependence of the susceptibility χ under an applied field 1 kOe was measured between 5 and 300 K using a temperature sweep rate of 2 K/min. In increasing temperature the SST manifests itself in an increase of the susceptibility by $\Delta\chi = \Delta m/H$. In Fig. 1(a) the results are shown between 20 and 200 K, where we observe the SST at the temperatures $T_s \approx 64$, 93, and 132 K with $\Delta\chi \approx 0.020$, 0.0093, and 0.0058 emu mol^{-1} Oe^{-1} for $y = 0.075$, 0.1, and 0.15, respectively. At the same temperatures a pronounced peak of the specific heat has been observed, very sharp for the former two samples and more diffuse for the latter one (see Ref. 4).

As a second step, we carried out the measurements around T_s employing smaller sweep rates that enable the precise determination of thermal hysteresis. For the $y = 0.075$ sample, where the SST is very sharp, we found that the reliable results, which are not dependent on the sweep rate, can be achieved with the rate 0.007 K/min. An example of thermal hysteresis curve (THC) is given in Fig. 1(b), which shows the $\chi(T)$ plot measured at $H = 10$ kOe during warming and subsequent cooling. At the temperatures T_{su} and T_{sd} we see an almost step increase and decrease of the susceptibility with the thermal hysteresis $\Delta T = T_{su} - T_{sd}$ and the average SST temperature $T_s = 0.5(T_{su} + T_{sd})$. Here, we obtained $T_s = 64.04$ and $\Delta T = 0.35$ K. The same type of experiment was then performed for several static magnetic fields, including $H = 0$, where the THC was evaluated from the real part of the ac susceptibility measured with a driving ac field 3.9 Oe (the imaginary part was too small to be detected). In accordance with expectation, T_s decreases with increasing field H and the dependence can be well approximated by the relation $T_s(H) = T_s(0) - AH^2$ [inset of Fig. 1(b)]. The value of ΔT increases with increasing field H from 0.19 Oe ($H = 0$) to 0.48 ($H = 70$ kOe). The data on $T_s(0)$, A, and the average value of ΔT are listed in Table I.

For $y = 0.1$ and 0.15 the character of the SST becomes more continuous as can be seen in Fig. 1(a). Analogously as in the case of $y = 0.075$, we performed the measurements of the THC around T_s using the sweep rates of 0.15 K/min ($y = 0.1$) and 0.2 K/min ($y = 0.15$). In both cases, ΔT and A are very small (Table I). The results for $y = 0.15$ are exemplified in Fig. 1(c).

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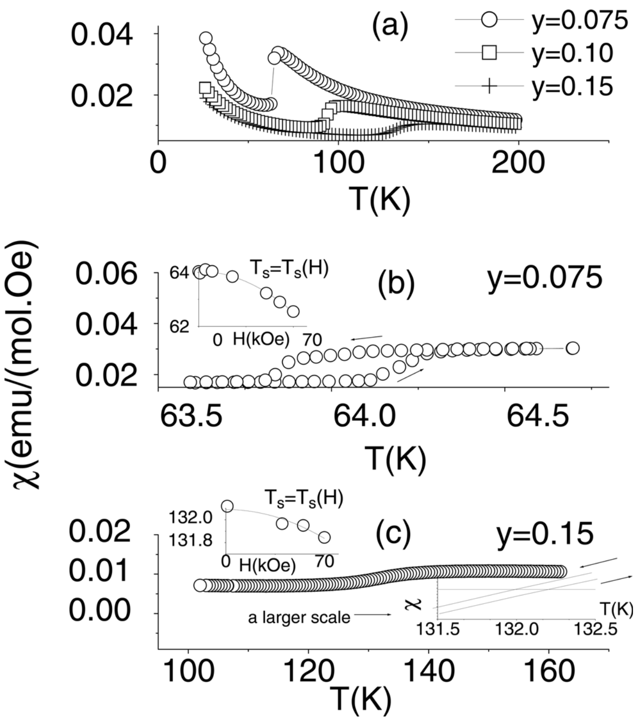

FIG. 1. (a) Temperature dependence of the molar susceptibility measured under an applied field 1 kOe; (b) thermal hysteresis for $y = 0.075$ at $H = 10$ kOe, in the inset the dependence of average T_s on magnetic field H; (c) the same for $y = 0.15$ and, in the right inset, the part of the thermal hysteresis curve displayed on a larger scale.

Now we focus our attention on the isothermal $m(H)$ dependencies taken at temperatures near $T_s(0)$. In contrast to the $y = 0.1$ and 0.15 samples, we find that for $y = 0.075$ the hysteresis curves indicating field-driven SST transitions. At $T = 64$ K the dependence $m(H)$ is linear, corresponding to the field-independent susceptibility m/H of paramagnetic ions Co^{3+}, Co^{4+}, and Pr^{3+} [Fig. 2(a)]. With decreasing temperature, a metamagnetic-like transition becomes evident and, due to hysteresis, the $m(H)$ dependence transforms into a closed loop. The contribution of the SST, obtained by subtracting linear dependence corresponding to the paramagnetic background, is illustrated by a dotted line in Fig. 2(b). At $T = 63.3$ K, the average field hysteresis makes $\Delta H \approx 13$ kOe.

III. DISCUSSION

The finite values of ΔT and ΔH seen in Figs. 1(b) and 2(b) indicate the first-order character of SST. In this case, when increasing temperature a latent heat Δq must be transferred to a system and its entropy increases by $\Delta S = \Delta q/T$. The entropy change ΔS can be determined using the Clausius–Clapeyron equation $dT_s/dH = T\Delta m/\Delta q$. After

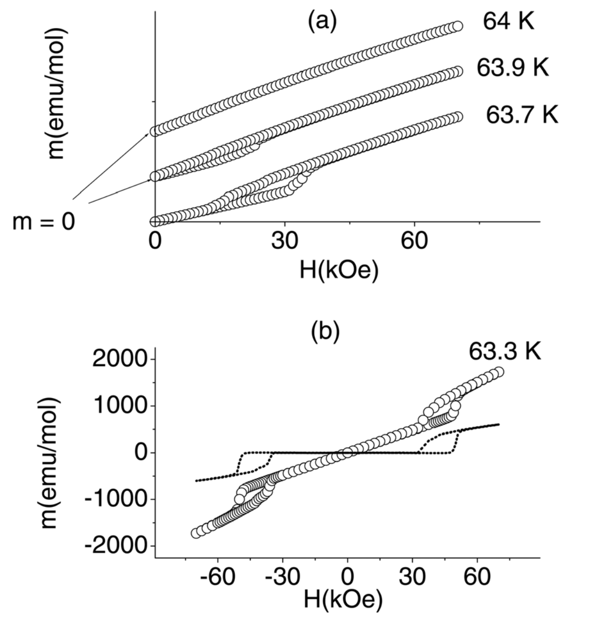

FIG. 2. The hysteresis loops for $y = 0.075$ measured at several temperatures near $T_s(0)$; the hysteresis loop corrected for a paramagnetic background is shown by the dotted curve.

setting $\Delta m = H\Delta\chi$ and integrating, the Clausius–Clapeyron equation transforms to $T_s = T_s(0) - AH^2$, where $A = \Delta\chi/(2\Delta S)$ and $T_s(0)$ is the SST temperature for $H = 0$. The determined values of ΔS are included in Table I.

The important experimental fact is a step-like increase of χ in increasing both temperature and field. To elucidate this finding, we restrict our study to the Co^{3+} ion and its transition from the LS to IS state. We start from a thermodynamic two-level model of SST.[6–8] Using the notation in Ref. 7 the system can be characterized by two energy parameters E and ε, where E is the distance between the lowest LS singlet level and excited IS level with triple orbital and triple spin degeneracy. The parameter ε represents an energy gain due a change of the interatomic distances. The model calculation yields population n of the IS Co^{3+} ions, which should be proportional to $\Delta\chi$. The essential point is that the excitation is accelerated compared to simple Boltzmann statistics (the LS–IS gap shrinks gradually) and becomes even of first-order type, because the lattice volume adjusts to increasing number n. For $y = 0.075$ the calculation with spin $s = 1$, $g = 2$, $2l + 1 = 3$, $r = \varepsilon/E = 0.51$, and E (Table I) yields the function $n(T)$ exhibiting a step at $T = 64$ K, but its dependence on H field is very small (0.16 K for $\delta H = 70$ kOe). A reasonable agreement with experiment can be achieved only if we take into account a positive molecular field (ferromagnetic exchange interaction) acting on the paramagnetic IS Co^{3+} ion. This interaction can be approximately included

TABLE I. Parameters $T_s(0)$, A, $\Delta\chi$, ΔS, and ΔT deduced from experiment and E/kB used in the model calculation.

y	$T_s(0)$ (K)	$A \times 10^4$ (K kOe^{-2})	$\Delta\chi$ (emu mol^{-1} Oe^{-1})	ΔS (J mol^{-1} K^{-1}1)	ΔT (K)	E/kB (K)
0.075	64.04	3.10	0.02	3.23	0.35	280.3
0.1	93.13	1.43	0.0093	3.25	0.35	365.4
0.15	132.32	0.51	0.0058	5.68	0.23	538.4

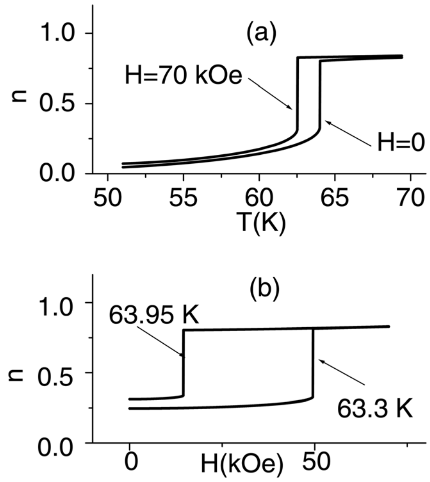

FIG. 3. Results of the calculations according to the two-level model: the temperature (a) and field (b) dependence of the occupation number n.

by changing the factor $\mu_B H/kT$ [see expression (35) in Ref. 7] by replacing T by $T-\vartheta$, where ϑ is a temperature characterizing the interaction. Using $\vartheta = 42$ K we obtain the functions $n(T)$, for which $T_s(0) = 64$ K and $T_s(70\ \text{kOe}) = 62.5$ K [Fig. 3(a)]. In Fig. 3(b) we show that the calculated functions $n(H)$ for $T = 63.3$ and 63.95 K exhibit step changes at 49.5 and 5.5 kOe, respectively. For $y = 0.1$ and 0.15 the calculated $n(T)$ dependencies were in a relatively good agreement with experiment for parameters for $r = 0.44$ and 0.46 and $\vartheta = 51$ and 48.6 K, respectively.

The final comment concerns the ΔS values presented in Table I. They are significantly lower than the two-level model of local excitations predicts for $(Pr_{1-y}Y_y)_{0.7}Ca_{0.3}CoO_3$—$\Delta S = 0.7R\ \ln 9 = 12.78$ J mol^{-1} K^{-1}. This discrepancy can be understood considering the metallic character of phase above T_s. We note that the excited IS states do not exist as bare Co^{3+} species. They provide e_g carriers that are delocalized over surrounding Co^{4+} sites, forming a droplet of the metallic phase of $t_{2g}^5\sigma^*$ character. In that case the relevant entropy retains only the spin degeneracy part and instead of common configuration term, $S = R(0.7 \ln 0.7 + 0.3 \ln 0.3)$, it contains a term that derives from density of states of the final phase, $S = \gamma T$ with γ of about 0.040 J mol^{-1} K^{-2} (see, e.g., Ref. 9). For $y = 0.075$ with $T_s \approx 64$ K one may, therefore, estimate $\Delta S = \gamma T + 0.7R\ \ln 3 - R(0.7 \ln 0.7 + 0.3 \ln 0.3) = 2.56 + 6.40 - 5.08 = 3.88$ J mol^{-1} K^{-1}, in reasonable agreement with the experimental value of 3.23 J mol^{-1} K^{-1}.

In summary, the spin-state transitions in $(Pr_{1-y}Y_y)_{0.7}Ca_{0.3}CoO_3$ with $y = 0.075$–0.15 exhibit a finite small hysteresis and the transition temperature depends on the magnetic field. The latter dependence enables the determination of the entropy contribution which is compared with the theoretical value. For $y = 0.075$ a field-driven transition is observed for cobaltites. The simple two-level model modified for the presence of the exchange interaction is used to qualitatively describe a step-like dependencies of the susceptibility on temperature and magnetic field.

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