Spin glass behavior in LaCo$_{1-x}$Rh$_x$O$_3$ ($x = 0.4$, 0.5, and 0.6)

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We studied the magnetic ground state of Co/Rh-disordered LaCo$_{1-x}$Rh$_x$O$_3$ ($x = 0.4$, 0.5, and 0.6) by means of powder neutron diffraction (PND), muon spin relaxation ($\mu$SR), ac susceptibility, isothermal magnetic relaxation, and heat capacity measurements. The dc magnetic susceptibility measurements exhibit a cusp around the freezing temperature $T_f$ of all studied compounds. PND measurements show no indications of long-range magnetic ordering down to 4 K in all studied samples. $\mu$SR experiments on these compounds show a peak in the muon spin relaxation rate around $T_f$. However, no spontaneous muon spin precession can be observed evidencing the short-range nature of the magnetic ordering. For the $x = 0.5$ sample ac susceptibility measurements show that $T_f$ shifts to higher temperatures with increasing frequency and becomes suppressed by a dc biasing field. All these observations indicate that the Co/Rh-disordered LaCo$_{1-x}$Rh$_x$O$_3$ system is a spin glass for $x = 0.4$, 0.5, and 0.6.

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I. INTRODUCTION

The spin state of the Co$^{3+}$ ions in LaCoO$_3$ has been studied extensively in the past as a function of temperature, pressure, magnetic field, and cation substitution [1–12]. For the octahedrally coordinated Co$^{3+}$ ions in LaCoO$_3$ a nonmagnetic low-spin (LS) configuration ($t_{2g}^6e_g^0$) can be observed at low temperatures (below about 100 K) due to the crystal field splitting that overcompensates the Hund’s coupling. On heating, a gradual transition to a paramagnetic state with magnetic Co$^{3+}$ ions can be observed. For higher temperatures the spin state of the Co$^{3+}$ ions is controversially discussed in the literature [3,10–12]. Polarized neutron scattering experiments indicate the thermal population of the high-spin (HS) configuration ($t_{2g}^4e_g^2$) above about 100 K [6], whereas theoretical calculation proposed also the occupation of an intermediate-spin (IS) state ($t_{2g}^3e_g^1$) [7] as supported by several subsequent experiments [8,9]. Finally, it was shown that the thermal population of a HS state is consistent with magnetic susceptibility, ESR, neutron scattering, and x-ray absorption spectroscopy data whereas the IS state is never favorable [12].

Recently, it was reported that the substitution of Rh for Co ions induces possible magnetic ordering in LaCo$_{1-x}$Rh$_x$O$_3$ [13–15]. LaCoO$_3$ and LaRhO$_3$ crystallize in the rhombohedral and orthorhombic structure with the space group $R\bar{3}c$ and $Pbnm$. The substitution of Rh for Co rapidly stabilizes the $Pbnm$ structure, and for $x > 0.2$ the pure orthorhombic phase appears [13,16]. Generally, no charge transfer between Co$^{3+}$ and Rh$^{3+}$ ions is expected. However, there exist proposals for a complex mixture of Co$^{2+}$, Co$^{4+}$, Rh$^{2+}$, and Rh$^{4+}$ ions in this system [17]. The ionic radius of Rh$^{3+}$ (0.665 Å) is larger than that of Co$^{3+}$ (0.545 Å for the LS state and 0.61 Å for the HS state) [18]. Due to the different ionic sizes of Co$^{3+}$ ions in the HS and in the LS state it can be expected that the Co$^{3+}$ HS state can be stabilized by a lattice expansion.

An anomalous cusp was observed in magnetic susceptibility measurements below $T_{\text{cusp}} \approx 15$ K for $0.1 \leq x \leq 0.4$. $T_{\text{cusp}}$ decreases with increasing $x$. A bifurcation between the zero-field-cooled (ZFC) and field-cooled (FC) data and a small hysteresis effect in the isothermal magnetization measurement was observed below $T_{\text{cusp}}$. It is, therefore, suggested that the system undergoes a weak ferromagnetic transition below $T_{\text{cusp}}$ [13].

Here, we reanalyzed the magnetic ground state of LaCo$_{1-x}$Rh$_x$O$_3$ around $x = 0.5$. Therefore, we studied the magnetic properties of LaCo$_{1-x}$Rh$_x$O$_3$ ($x = 0.4$, 0.5, and 0.6) by means of dc and ac magnetic susceptibility, powder neutron diffraction (PND), and muon spin relaxation ($\mu$SR) methods. Our structural refinement indicates that the Rh and Co ions are randomly distributed in all our studied samples. In the magnetic susceptibility measurements an anomalous cusp could be observed for all studied compositions $x$. However, there is no indication of static long-range magnetic ordering in PND and $\mu$SR measurements. In ac susceptibility measurements $T_{\text{cusp}}$ shifts to higher temperatures with increasing frequency and is suppressed by a biasing magnetic field. Thus, our results are indicative of a spin glass ground state in Co/Rh-disordered LaCo$_{1-x}$Rh$_x$O$_3$.

II. EXPERIMENT

Polycrystalline samples of LaCo$_{1-x}$Rh$_x$O$_3$ with $x = 0.4$, 0.5, and 0.6 were synthesized by solid state reaction. Stoichiometric amounts of La$_2$O$_3$, Co$_3$O$_4$, and Rh$_2$O$_3$ were mixed and ground thoroughly in an agate mortar and sintered for 2 days at 1200°C in air with several intermediate grindings. The phase purity was confirmed by both x-ray diffraction (XRD) and PND. Powder x-ray diffraction measurements were performed on a Bruker D8 Discover A25 powder x-ray diffractometer.

The dc magnetic susceptibility, $\chi(T)$, was measured using the magnetic property measurement system (MPMS; Quantum Design) in a temperature range between 2 K and 380 K. The ac susceptibility was measured using the vibrating sample magnetometer (VSM; Quantum Design). The ac magnetic
driven field, $H_{ac}$, was fixed to 4 Oe, and $\chi$ was recorded with frequencies $f = 3, 13, 57, 113, 317,$ and 898 Hz. A dc biasing magnetic field, $H_{dc} = 0, 200, 1000,$ and 5000 Oe, was also applied with $f$ fixed at 57 Hz. For all ac susceptibility measurements, the sample was first zero-field cooled to the base temperature and $\chi(T)$ was recorded in the heating run. Isothermal magnetization relaxation measurements were performed using the VSM system. The samples were cooled from room temperature to the measuring temperature with a magnetic field of 1000 Oe. Then, the field was switched off and the time dependence of the magnetization was recorded. Heat capacities were measured using the physical property measurement system (PPMS; Quantum Design). The contributions from grease and sample holder were measured separately and subtracted from the total capacity.

PND was performed on the high-resolution powder diffractometer SPODI at the FRM-II in Garching, Germany ($\lambda$ of 2.536 Å; 8 hours counting time for each diffraction pattern). Muon spin relaxation ($\mu$SR) experiments were performed at the GPS spectrometer at the PSI in Villigen, Switzerland. The decay positrons from the injected muons were accumulated by the forward and backward counters located before and after the sample. The asymmetry of the muon spin polarization is defined as $A(t) = \frac{[F(t) - \alpha B(t)]/[F(t) + \alpha B(t)]}{2}$, where $F(t)$ and $B(t)$ are the number of positrons detected at the forward and backward counters at time $t$, respectively. The parameter $\alpha$ is a correction of the counting efficiency for the forward and backward counters, which was determined by a transverse (perpendicular to the initial muon spin direction) field (TF) measurement in the high-temperature paramagnetic state. A small longitudinal (parallel to the initial muon spin direction) field (LF) of 20 Oe was applied in order to decouple the muon spin from the nuclear moments during the experiments. A LF of 500 and 2000 Oe was also applied at 1.55 K in order to distinguish whether the internal field is static or dynamic. The data were analyzed with the free software package WIMDA [19].

III. RESULTS AND DISCUSSION

A. Structure and magnetization

The $x = 0.4, 0.5,$ and 0.6 compounds have been measured at 4 K and 300 K by means of powder neutron diffraction. A typical diffraction pattern for $x = 0.5$ is shown in Fig. 1(a). The obtained diffraction patterns were refined by the Rietveld method using the FullProf software package. The crystal structure can be described by the orthorhombic space group $Pbnm$. The very weak (1 0 1) Bragg peak indicates that the Co and Rh ions are randomly distributed in the sample [20,21]. The Rh-doping dependence $x$ of the lattice constants is shown in Fig. 1(e). Due to the larger Rh$^{3+}$ ionic radius the lattice constants along three crystallographic directions all increase with increasing Rh content $x$ [18]. Our results are consistent with previous studies [13,16]. Especially, also the crossover of the $a$ and $b$ lattice parameters can be observed at $x = 0.5$.

In Fig. 2(a) the dc magnetic susceptibility measurements of LaCo$_{1-x}$Rh$_x$O$_3$ are shown. All studied samples exhibit a cusp in the ZFC measurement at about 5 K, 4 K, and 3 K for $x = 0.4, 0.5,$ and 0.6 respectively. As can be seen, $T_{cusp}$ shifts towards lower temperature with increasing Rh content $x$ which is consistent with a scenario where the Co ions are substituted by nonmagnetic Rh ions. The FC measurements diverge from the ZFC measurements at temperatures higher than $T_{cusp}$. The magnetization measurement at different temperatures are shown for the $x = 0.5$ sample in Fig. 2(b). At 2 K a weak
FIG. 2. (a) Magnetic susceptibility measurements for \( x = 0.4, 0.5, \) and 0.6. Open and solid symbols: ZFC/FC measurements. For clarity, the data sets for the \( x = 0.4 \) and 0.5 samples are shifted with the dashed lines indicating the shifted zero values. (b) Isothermal magnetization measurements for \( x = 0.5 \) at different temperatures. (c) Comparison of isothermal magnetization measurements at 2 K for \( x = 0.4, 0.5, \) and 0.6. The hysteresis effect is observable with a remanence of 0.01 \( \mu_B/\text{f.u.} \) and a coercivity of 600 Oe. At 10 K, which is somewhat higher than \( T_{\text{cusp}} \), the hysteresis effect is absent, and, finally, the magnetization curve is straight at 50 K as typical for a paramagnetic state. The magnetization per formula unit, remanence, and coercivity measured at 2 K decrease with increasing \( x \) as can be seen in Fig. 2(c).

The temperature dependence of the inverse magnetic susceptibility \( \chi^{-1}(T) \) is shown in Fig. 3(a). Note that previous studies \[13\] fit a Curie-Weiss function \( \chi^{-1}(T) \) between 200 K and 300 K to the data:

\[
\chi^{-1}(T) = \frac{T - \theta_{\text{CW}}}{C},
\]

where \( C \) is the Curie constant and \( \theta_{\text{CW}} \) is the Curie-Weiss temperature. We fitted our data in the same temperature range as well as in the high-temperature regime between 300 K and 380 K; see Fig. 3(a). The obtained effective moment \( \mu_{\text{eff}} = \sqrt{8C} \) and Curie-Weiss temperature \( \theta_{\text{CW}} \) are plotted in Fig. 3(b). \( \chi^{-1}(T) \) deviates from the fitted curve above 300 K for the \( x = 0.4 \) and 0.5 samples, thus indicating that the magnetic susceptibility is not Curie-Weiss like. This might originate from a thermal population of the HS state in LaCo\(_{1-x}\)Rh\(_x\)O\(_3\). While the substitution of Rh for Co might stabilize the Co\(^{3+}\) HS state due to the expansion of the lattice [see Fig. 1(e)], the remaining Co\(^{3+}\) ions in the LS state could still be thermally excited to the HS state with the increasing unit cell volume for rising temperature. Previous studies proposed that the magnetic ground state below \( T_{\text{cusp}} \) is weak ferromagnetic \[13\]. Although a hysteresis effect was observed below \( T_{\text{cusp}} \), as shown in Figs. 2(b) and 2(c), the magnetization is very small compared to the effective moment. In order to unveil possible magnetic ordering, we also performed PND at 4 K for all these compounds. However, no enhancement of any Bragg peaks, or extra peaks due to magnetic ordering, could be observed; see Figs. 1(b)–1(d).

**B. ZF and LF \( \mu \)SR**

In order to get further insight in the magnetic properties of LaCo\(_{1-x}\)Rh\(_x\)O\(_3\), \( \mu \)SR experiments were performed for the samples with \( x = 0.4 \) and 0.5. Since \( \mu \)SR is very sensitive to small magnetic moments, static long-range magnetic ordering can be easily detected. Figure 4 shows the typical time spectra measured with a tiny LF of 20 Oe in order to decouple the
muon spins from the nuclear moments. The spectra for the two samples show a similar line shape. At high temperatures, an exponential-like decay can be observed which is expected for a paramagnetic state. With decreasing temperature a fast relaxation component develops and coexists with the slow relaxation component. At low temperatures, e.g., at 1.55 K, it can be observed that the muon spin relaxation rate decreases. Such behavior might suggest the slowing down of magnetic fluctuations and the appearance of static magnetism. However, no spontaneous muon spin precession can be observed. Our observations are reminiscent of a spin glass state [22] with short-ranged spin correlations and $T_{cusp}$ corresponding to the spin freezing temperature $T_f$. In order to extract the muon spin relaxation rate, the spectra in Fig. 4 are fitted to a two-component exponential function,

$$A(t) = A_s \exp(-\lambda_s t) + A_f \exp(-\lambda_f t),$$

(2)

where $A(0)$ is the initial asymmetry fixed to the value measured at high temperature, $A_s$ and $A_f$ are the amplitudes of the slow and fast relaxation components, and $\lambda_s$ and $\lambda_f$ are the muon spin relaxation rates for the slow and fast components, respectively. The fitted curves are shown in Fig. 4 in red. A two-component relaxation behavior was also observed in other spin glass systems [23,24], suggesting a distribution of the relaxation rate in the sample. We also tried to fit the spectra using the stretched exponential function, $A(t) = A(0)\exp(-\lambda t^\beta)$. As shown in the inset of Fig. 4(b), this function cannot describe the entire spectrum (especially at low temperatures in the early-time region). In addition, we also tried to fit the spectrum using a formula derived by Uemura et al. (Eq. (17) in Ref. [25]) for modeling a spin glass system. However, also these approaches fail to describe our spectra properly.

The temperature dependence of the extracted parameters is shown in Fig. 6. The two compounds show very similar behavior. From Figs. 6(a) and 6(b), it can be seen that the amplitude of the slow relaxation component decreases with decreasing temperature and levels off below $\sim 8$ K and $\sim 6$ K for $x = 0.4$ and 0.5, respectively, while the fast relaxation component shows opposite behavior. The ratio of $A_f/A_s$ is almost constant below $T_f$ and amounts to roughly 4:1 which also shows the presence of dynamic volumes in the sample since for a static specimen a ratio of 0.666/0.333 is expected. The temperature dependence of $\lambda_s$ and $\lambda_f$ is shown in Figs. 6(c) and 6(d). $\lambda_s$ increases with decreasing temperature and shows a peak at $\sim 6$ K ($\sim 8$ K) for $x = 0.4$ and 0.5, which reflects the critical slowing down of the spin fluctuations in LaCo$_{1-x}$Rh$_x$O$_3$. On the other hand, $\lambda_f$ continuously increases with decreasing temperature, and tends to be temperature independent at low temperatures.
The peak position of $\lambda_s$ is very close to $T_{\text{cusp}}$ observed in dc magnetization measurements and indicates the spin freezing temperature $T_f$ observed by $\mu$SR. The somewhat higher value of $T_f$ compared to $T_{\text{cusp}}$ might arise from the faster fluctuation scale probed by $\mu$SR. Hence, the $A_s$ component observed here corresponds to the 1/3 longitudinal relaxation component in an ideal quasistatic powder sample, and the 2/3 transverse relaxation component is included in $A_f$. Here, the ratio between $A_f$ and $A_s$ is not exactly 2:1 as expected for an ideal quasistatic case for a powder sample. This indicates that some part of the sample is still fluctuating; i.e., the sample is inhomogeneous. The increase of $\lambda_f$ below $T_f$ also suggests that the internal field distribution becomes broader at low temperatures.

C. ac susceptibility

In order to unambiguously determine the spin glass ground state in this system, we also performed ac susceptibility measurements as a function of frequency and dc biasing magnetic field. Figure 7(a) shows the temperature dependence of the in-phase component, $\chi'$, of the ac susceptibility measured at different frequencies (no dc biasing field was applied). With increasing frequency the freezing temperature $T_f$ shifts towards higher temperatures which is indicative for a spin glass system. The frequency dependence of $T_f$ is estimated by the quantity $K = \Delta T_f / T_f \Delta \log_{10} f$, where $\Delta$ refers to the difference. The obtained value for $K$ amounts to $\sim 5.3\%$ for $x = 0.5$ which resembles values for other spin glass systems [26]. The out-of-phase component $\chi''$ also becomes nonzero below $T_f$ as can be seen in Fig. 7(b) for the selected frequency $f = 57$ Hz, indicating a dissipative process which can be suppressed by a dc biasing field. The frequency dependence of $T_f$ can be well described by the conventional critical slowing down behavior, and fitted by the function

$$
\tau_f = \tau_0 (T_f / T_g)^{-z_v},
$$

where $\tau_f = 1 / f$ corresponds to the maximum relaxation time of the system at temperature $T_f$, $\tau_0$ is the intrinsic relaxation time of the spin dynamics, $T_g$ is the freezing temperature for $f = 0$ which is fixed to $T_{\text{cusp}}$ as obtained from ZFC dc magnetic susceptibility measurements, and $z_v$ is the dynamic exponent. A fit to Eq. (3) yields $\tau_0 = 1.6(7) \times 10^{-8}$ s and $z_v = 8.3(3)$ for the $x = 0.4$ compound; $\tau_0 = 6(1) \times 10^{-8}$ s and $z_v = 9.8(2)$ for the $x = 0.5$ compound; $\tau_0 = 6(1) \times 10^{-7}$ s and $z_v = 9.0(4)$ for the $x = 0.6$ compound. The goodness of the fit is shown in the inset of Fig. 7(a). The intrinsic relaxation time $\tau_0$ is found to be 5–6 orders of magnitude larger than that of typical single-ion spin glass systems which is of the order $\sim 10^{-13}$ s. This suggests that the relaxation in LaCo$_{1-x}$Rh$_x$O$_3$ is dominated by domains rather than by single ion effects. The dynamic exponent $z_v$ is in agreement with that of Ising spin glasses [27,28].

Spin glass behavior has been observed in several cation-doped LaCoO$_3$ systems such as La$_{1-x}$Sr$_x$CoO$_3$ [29] and LaCo$_{1-x}$Ni$_x$O$_3$ [30]. In the former, the competition between antiferromagnetic Co$^{3+}$-Co$^{4+}$/Co$^{5+}$-Co$^{4+}$ and ferromagnetic Co$^{3+}$-Co$^{4+}$ superexchange interaction was proposed as the origin. In the latter system, a charge transfer between the Co and Ni ions has been observed, and the competition...
between ferromagnetic and antiferromagnetic interactions is responsible for the spin glass behavior in this system. For Co/Rh disordered LaCo$_{1-x}$Rh$_x$O$_3$ we expect no charge transfer between Co$^{3+}$ and Rh$^{3+}$ ions. But, the disorder induced by the random distribution Co-rich and Rh-rich clusters of different sizes might be the origin of the spin glass behavior in Co/Rh disordered LaCo$_{1-x}$Rh$_x$O$_3$. The competition between the (antiferromagnetic according to Kanamori’s rule [31]) nearest-neighbor and next-nearest-neighbor interactions might also be (partly) responsible for the spin glass behavior [32].

D. Isothermal relaxation

Figure 8 shows the isothermal relaxation of the three studied compounds below $T_f$. The data have been fitted with a stretched exponential function

$$M(t) = A \exp\left(-t/\tau\right)^\beta + B,$$  

where $A$ and $B$ are constants, $\beta$ the exponent, and $\tau$ the relaxation time. The resulting curves are shown as red lines in Fig. 8. Here, both $\tau$ and $\beta$ are characteristic for a glassy transition. Whereas $\beta$ amounts to 1 for systems with uniform energy barriers, glassy magnetic systems contain many local minima in the energy valley and $\beta$ varies from 0 to 1. Our extracted parameters are listed in Table I. Interestingly, $\beta$ attains a small and nearly temperature-independent value for all the LaCo$_{1-x}$Rh$_x$O$_3$ samples as is usually expected for typical glassy magnetic samples. On the other hand the relaxation time $\tau$ drastically falls with increasing temperature. This behavior is indicative for the presence of spin clusters in the system.

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<tr>
<th>Table I. Extracted isothermal relaxation time $\tau$ and exponent $\beta$ at different temperatures for the $x = 0.4$, 0.5, and 0.6 compounds.</th>
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<td>$T$ = 1.8 K</td>
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<td>$\beta$</td>
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E. Heat capacity

Figure 9 shows the zero-field specific heat, $C_p$, measurements for the LaCo$_{1-x}$Rh$_x$O$_3$ compounds. There is no sharp $\lambda$-like anomaly at $T_f$ for all the three samples, indicating no long-range magnetic ordering. In order to obtain the magnetic entropy, the data between 30 K and 100 K were fitted to a five-term polynomial function, as shown in Fig. 9, and the extrapolated low-temperature phonon contribution was then subtracted from the raw data in order to obtain the magnetic component $C_M$. The magnetic entropy was then calculated by $S(T) = \int_{T_0}^{T} C_M/\tau d\tau$, where $T_0$ is the base temperature. The results are shown in the inset of Fig. 9. The obtained $S$ at 20 K for all three compounds is much smaller than the expected value for a HS Co$^{3+}$ system. In this case $S$ would
amount to 8.0, 6.7, and 5.3 J mol$^{-1}$ K$^{-1}$ for the $x = 0.4$, 0.5, and 0.6 compounds, respectively. Apart from a possibly lower occupation of the HS state of Co$^{3+}$ ions at low temperatures the much lower value that we observe is indicative of substantial residual entropy in this Co/Rh-disordered system which is consistent with the glassy nature of the magnetic ground state in LaCo$_{1-x}$Rh$_x$O$_3$.

IV. CONCLUSION

We have investigated the magnetic ground state of Co/Rh-disordered LaCo$_{1-x}$Rh$_x$O$_3$ around half doping within a comprehensive study of magnetic susceptibility, PND, $\mu$SR, ac susceptibility, isothermal magnetic relaxation, and heat capacity measurements. Our structural analysis confirms that the Co$^{3+}$ and Rh$^{3+}$ ions are randomly distributed in our studied LaCo$_{1-x}$Rh$_x$O$_3$ samples. Our PND and $\mu$SR results exclude the appearance of long-range magnetic ordered states as recently proposed for this system. Instead, we observed a short-ranged correlated spin glass state. The spin glass state in these Co/Rh-disordered samples can be characterized by the freezing of domains.

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