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The Low Temperature Study of Ln[Fe(CN)$_6$]·xH$_2$O Rare-Earth Ferricyanides, Ln = Pr, La

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We present magnetic and structural properties of Ln[Fe(CN)$_6$]·xH$_2$O, Ln = Pr, La single crystals investigated by means of elastic neutron diffraction and heat capacity down to 0.03 K and susceptibility and magnetization measurements. The susceptibility data were taken on the commercial SQUID magnetometer (Quantum Design) in the range between 2 K and 30 K and in fields up to 5 T. Our low temperature neutron diffraction data taken in a zero field rules out some of antiferromagnetic models suggested in the literature.

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1. Introduction

The Ln[Fe(CN)$_6$]·xH$_2$O (Ln = rare-earth atom) compounds belong to a large family of molecular magnets where the magnetic interaction between Ln^{3+} and Fe^{III+} is mediated over large distances via Ln^{3+}–N≡C–Fe^{III+} exchange paths. The parent K$_3$[Fe(CN)$_6$] compound itself was extensively studied both theoretically and experimentally in the last century. The Fe atoms of [Fe(CN)$_6$]$^{III-}$ complexes, common for all studied systems, are located in the octahedral centers surrounded by six cyanides groups (CN)$^{I-}$ poiting radially away from the center. Due to a presence of a strong crystal field, five d-electrons of the Fe^{III+} cation occupy low lying t_{2g} orbitals leaving one electron spin uncompensated and results into a low spin state with an effective spin $S = 1/2$. The K$_3$[Fe(CN)$_6$] system itself orders antiferromagnetically below T_N = 128 mK [1]. In our low temperature study we focus on the chemically related system Ln[Fe(CN)$_6$]·xH$_2$O with Ln = Pr, La where exchange path(s) Ln^{3+}–N≡C–Fe^{III+} similarly as for Ln = Dy, Sm [2] could play a key role in promoting magnetic order. Our previous data in [2–4] indicated magnetic correlations: a maximum in AC susceptibility and in zero-field-cooled magnetization curves at about 12 K and a sharp lambda anomaly in temperature dependence of heat capacity ≈ 1.3 K [2].

2. Experimental and discussion

The Ln[Fe(CN)$_6$]·xH$_2$O, Ln = Pr, La single crystals were prepared at the Institute of Experimental Physics, SAS, Košice under optimized diffusion conditions, from mixing of saturated aqueous solution K$_3$[Fe(CN)$_6$] and aqueous solutions of PrCl$_3$ and LaCl$_3$, respectively. Depending on the water content in the structure, the Ln[Fe(CN)$_6$] system usually forms the pentahydrate complexes and adopts the hexagonal type of symmetry ($P63/m$) whereas tetrahydrate compounds adopt the orthorhombic type of structure ($Cmcm$) [5, 6].

Heat capacity data were taken on Ln[Fe(CN)$_6$], Ln = Pr, La single crystals of weight $m_{(\mathrm{Ln=Pr})}$ = 2.01 mg and $m_{(\mathrm{Ln=La})}$ = 2.32 mg, respectively, down to 280 mK using two low temperature systems: PPMS (Quantum Design) and CM-14.5 (Oxford Instruments) located at the HZB Berlin. Figure 1 shows heat capacity data of Ln[Fe(CN)$_6$], Ln = Pr and La that exhibit anomalies at ≈ 1.3 K and ≈ 0.39 K, respectively, together with data on Sm and Dy published [2] previously. The inset displays in detail three lambda-like anomalies at temperatures of 1.3, 0.47 and 0.4 K for Ln = Pr and at T = 0.39 and 0.35 K for Ln = La. Magnetic moment and susceptibility measurements were performed on MPMS — SQUID magnetometer in the range from 2 K to 292 K.

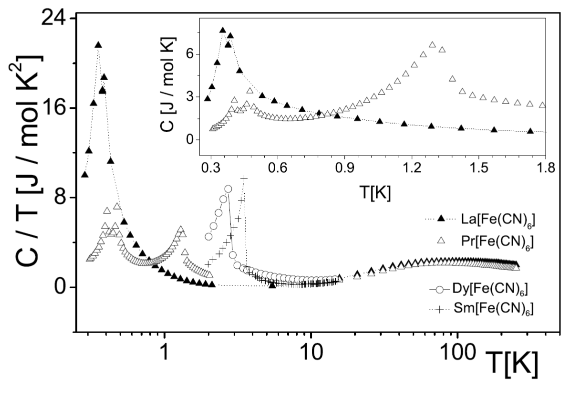

Fig. 1. Low temperature heat capacity data of selected rare-earth ferricyanides Ln[Fe(CN)$_6$]·xH$_2$O, Ln = Pr (≈ 1.3 K), La (≈ 0.39 K), Sm (T_N ≈ 3.5 K [2]), Dy (T_N ≈ 2.8 K [2]) in semilogarithmic scale. The inset shows lambda-like anomalies for Ln = Pr and La in C vs. T plot.

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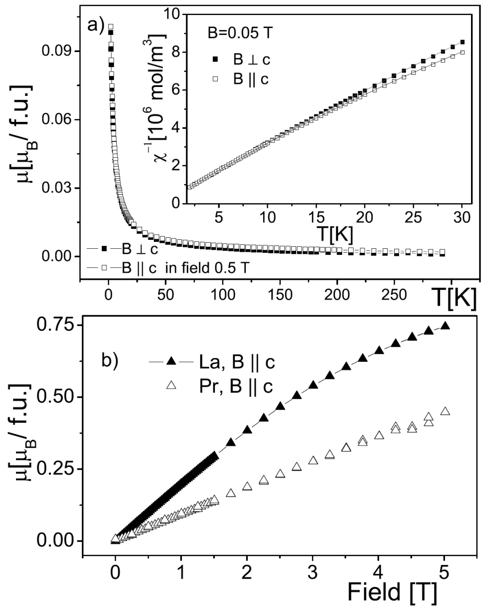

Fig. 2. (a) Magnetization curves of La[Fe(CN)$_6$] measured for $B \parallel c$ and $B \perp c$ ($B = 0.5$ T). The inset shows inverse susceptibility data $\chi^{-1}_{B\parallel c}(T)$ and $\chi^{-1}_{B\perp c}(T)$ measured in a low field of 0.05 T and the best fits. Part (b) displays the field dependence of magnetization for Ln[Fe(CN)$_6$], Ln = La, Pr measured at $T = 2$ K for field ramped up 5 T and back to 0 T.

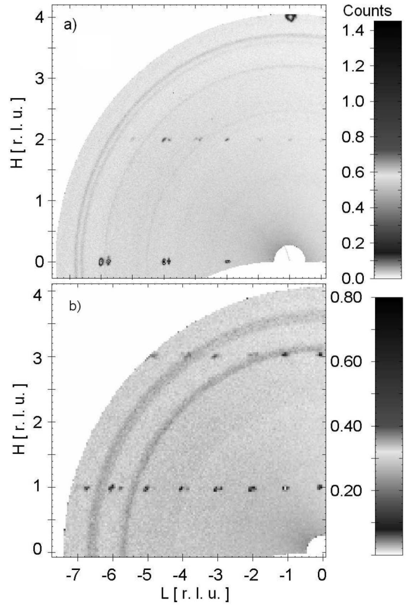

Fig. 3. (a) H0L reciprocal map of Pr[Fe(CN)$_6$] at $T = 0.03$ K. (b) H1L reciprocal map of Pr[Fe(CN)$_6$] at $T = 0.45$ K.

Figure 2a shows the temperature dependence of the La[Fe(CN)$_6$] magnetization measured in field of 0.5 T parallel and perpendicular to the c-axis. No significant anisotropy for La[Fe(CN)$_6$] has been found. This result is in contrast to the anisotropy of Pr[Fe(CN)$_6$] reported earlier [2]. The inset shows inverse susceptibility data taken from 2 K to 30 K in an external field of 0.05 T and best fits to $\chi = C/(T-\theta)$ formula with following parameters: $\chi_0^{\perp} = 1.14(4) \times 10^{-8}$ m^3/mol, $C_{\perp} = 3.253(6) \times 10^{-6}$ m^3 K/mol, $\theta_{\perp} = -0.86(5)$ K and $\chi_0^{\parallel} = 2.324(3) \times 10^{-8}$ m^3/mol, $C_{\parallel} = 3.114(5) \times 10^{-6}$ m^3 K/mol, $\theta_{\parallel} = -0.74(4)$ K. The effective moments $\mu_{\rm eff}^{\perp} = 1.44(2)\mu_{\rm B}$ and $\mu_{\rm eff}^{\parallel} = 1.41(2)\mu_{\rm B}$ are to be compared with a value calculated for the low spin state of free Fe$^{\rm III+}$, $\mu^{\rm Fe^{III+}} = g\sqrt{S(S+1)} \approx 1.73\ \mu_{\rm B}$. The field dependence of Ln[Fe(CN)$_6$], Ln = La, Pr magnetic moment is displayed in Fig. 2b. Data taken at temperature of 2 K with field along the c-axis show a linear increase of magnetization as field increases up to 1.5 T (Ln = La), followed by a slow tendency towards saturation. However, the field of 5 T is not enough to reach the full saturation. Only linear field dependence is observed for Ln = Pr sample.

Neutron data were taken on Ln[Fe(CN)$_6$], Ln = Pr, La single crystals at several temperatures at E4-diffractometer with a setup (40′-open-$\frac{\lambda}{2}$FILT-sample-2Ddet) and E10-diffractometer with (open-60′-$\frac{\lambda}{2}$FILT-sample-^{3}HeDet) using neutron wavelength of 2.45 Å and 1.41 Å, respectively. In addition, the E2-diffractometer was used to map (H0L) and (H1L) reciprocal space of Pr[Fe(CN)$_6$] sample at several temperatures: above 1.3, at 0.7, 0.45 and 0.03 K. The typical (H0L) and (H1L) reciprocal maps are shown in Fig. 3a,b. The crystal of composition Ln = Pr used in the neutron scattering experiment, in fact, consists of two single crystals with nuclear reflections well separated in the reciprocal space. Both crystals have common a-axis with the value that agrees well with literature data [4, 5] but differ in the c lattice parameter. While one crystal has the literature value, the second exhibits the value that is by 3% larger. The reason is unclear at present. The low temperature scans taken at E2-diffractometer at several temperatures did not reveal any additional magnetic signal neither within scattering (H0L) plane, nor within the first layer above the (H0L) scattering plane. Data collected on Pr[Fe(CN)$_6$] at the E4-diffractometer show a small increase of the intensities at (004) and (400) nuclear reflections, however, no clear magnetic signal is observed at respective low-2θ reflections that should be more sensitive to magnetism. Similar conclusions can be made for La[Fe(CN)$_6$] ($a = 7.554$ Å and $c = 14.452$ Å) where the differences of signals at 0.28 K and 0.7 K at nuclear positions were not statistically significant. No additional signal of magnetic origin was observed at (1/2 0 1/2), (1 0 1/2), (1/2 0 1), (3/2 0 1/2), (3/2 0 1/2) and (003), (005) reflection positions.

In summary, the lambda-like anomalies observed via heat capacity measurements indicate that cooperative effects occur at temperatures of 1.3, 0.47, 0.4, and 0.39, and 0.35 K for Ln = Pr and La, respectively. Their origin becomes an open question. Our neutron results discriminate some of antiferromagnetic models suggested in literature [3]. However, due to the absence of a clear magnetic signal no final statement about the magnetic structure can be made. This result calls for a new powder experiments and new single crystal growth activities.

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