The Low Temperature Study of Ln[Fe(CN)₆]·xH₂O
Rare-Earth Ferricyanides, Ln = Pr, La

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1. Introduction

The Ln[Fe(CN)₆]·xH₂O (Ln = rare-earth atom) compounds belong to a large family of molecular magnets where the magnetic interaction between Ln³⁺ and Fe³⁺ ions is mediated over large distances via Ln⁻→Fe²⁺ exchange paths. The parent K[Fe(CN)₆] was extensively studied both theoretically and experimentally in the last century. The Fe atoms of [Fe(CN)₆]³⁻ complexes, common for all studied systems, are located in the octahedral centers surrounded by six cyanides groups (CN)⁻ poiting radially away from the center. Due to a presence of a strong crystal field, five d-electrons of the Fe³⁺ cation occupy low lying t₂g orbitals leaving one electron spin uncompensated and results into a low spin state with an effective spin S = 1/2. The K₃[Fe(CN)₆]₃ system itself orders antiferromagnetically below Tᵢ = 128 mK [1]. In our low temperature study we focus on the chemically related system Ln[Fe(CN)₆]·xH₂O with Ln = Pr, La where exchange path(s) Ln¹⁺→N≡C-Fe²⁺ 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]·xH₂O, 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 K₃[Fe(CN)₆] and aqueous solutions of PrCl₃ and LaCl₃, respectively. Depending on the water content in the structure, the Ln[Fe(CN)₆] system usually forms the pentahydrate complex 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]₃, Ln = Pr, La single crystals of weight mₖ(Ln=Pr) = 2.01 mg and mₖ(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]₃, 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.

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Fig. 1. Low temperature heat capacity data of selected rare-earth ferricyanides Ln[Fe(CN)₆]·xH₂O, Ln = Pr (≈ 1.3 K), La (≈ 0.39 K), Sm (Tᵢ ≈ 3.5 K [2]), Dy (Tᵢ ≈ 2.8 K [2]) in semilogarithmic scale. The inset shows lambda-like anomalies for Ln = Pr and La in C vs. T plot.
Figure 2a shows the temperature dependence of the La[Fe(CN)$_6$]$_x$ magnetization measured in a field of 0.5 T and best fits to the $\chi(T)$ formula with the following parameters: $\chi_0 = 1.14(4) \times 10^{-8}$ m$^3$/mol, $C_\perp = 3.253(6) \times 10^{-6}$ m$^3$/K/mol, $\theta_\perp = -0.86(5)$ K and $\chi_0 = 2.324(3) \times 10^{-8}$ m$^3$/mol, $C_\parallel = 3.114(5) \times 10^{-6}$ m$^3$/K/mol, $\theta_\parallel = -0.74(4)$ K. The effective moments $\mu_\perp = 1.44(2) \mu_B$ and $\mu_\parallel = 1.41(2) \mu_B$ are to be compared with a value calculated for the low spin state of free Fe$^{III+}$, $\mu_{Fe^{III+}} = g\sqrt{S(S+1)} \approx 1.73 \mu_B$. The field dependence of Ln[Fe(CN)$_6$]$_x$, Ln = La, Pr magnetic moment is displayed in Fig. 2b. Data taken at temperatures 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)$_6$]$_x$, Ln = Pr, La single crystals at several temperatures at E4-diffractometer with a setup (40'-open-$\frac{1}{2}$ FILT-sample-2Ddet) and E10-diffractometer with (open-$\frac{1}{2}$ FILT-sample-4HeDet) and E10-diffractometer with (open-$\frac{1}{2}$ FILT-sample-2Ddet) and E10-diffractometer with (open-$\frac{1}{2}$ FILT-sample-4HeDet) 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)$_6$]$_x$ 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)$_6$]$_x$ 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-2$\theta$ angles that should be more sensitive to magnetism. Similar conclusions can be made for Ln[Fe(CN)$_6$]$_x$ (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 1/2), (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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References