^{1}H NMR on $(Ni_xMn_{1-x})_3[Cr(CN)_6]_2 \cdot nH_2O$

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We report on ^{1}H NMR of $(Ni_xMn_{1-x})3[Cr(CN)_6]_2 \cdot 15H_2O$ hexacyanochromates, where x changes from 0 to 1. The decay time constants of the free induction decay signals described by an effective spin–spin relaxation time $T_{2\text{eff}}$ obtained from $M(t) = M_0 \exp(t/T_{2\text{eff}})$ decrease as the local magnetic moments increase produced by the magnetic transition metal ions at the sites of the resonant ^{1}H nuclei. The recovery of the magnetization in the spin–lattice relaxation time (T_1) experiments was single-exponential.

1. Introduction

Magnetic properties of prussian blue analogues (PBA) have been intensively studied in the last two decades. A large variety of attractive phenomena has been observed during this period, such as spin glass like behavior, photomagnetic behavior, piezomagnetic behavior and magnetic pole inversion [1–5]. The simple face centered cubic lattice of PBA's is however far from being free of defects and vacancies, part of metal ion positions are vacant, while some of them are filled with the water molecules. The water content, which can be modified during synthesis, influences significantly the resultant magnetic properties of prepared PBA, namely the value of the Curie temperature and the value of saturated magnetization [6]. High level of disorder present in the PBA crystal lattice leads to the increased importance of experimental techniques enabling to study the local magnetic structure in investigated compounds. Magnetic local structures of different PBA have been studied previously by solid state ^{13}C and ^{2}H NMR in [7, 8].

It has been shown that the NMR spectrum of $(Ni_{0.4}Mn_{0.6})_3[Cr(CN)_6]_2 \cdot nD_2O$, is not a simple superposition of the two spectra of $Mn_3[Cr(CN)_6]_2 \cdot nD_2O$ and $Ni_3[Cr(CN)_6]_2 \cdot nD_2O$. The crystal water molecules of the mixed system sense an averaged hyperfine field of Ni and Mn ions and they are tightly bound neither to Ni nor Mn ions at high temperatures [8]. In our paper we present the ^{1}H NMR spectra for $(Ni_xMn_{1-x})_3[Cr(CN)_6]_2 \cdot nH_2O$ at room temperature for different values of x.

2. Experimental

Polycrystalline $(Ni_xMn_{1-x})_3[Cr(CN)_6]_2 \cdot 15H_2O$ hexacyanochromates ($x =$ 0, 0.32, 0.34, 0.38, 0.42, 0.46, 1) were prepared by mixing of $K_3[Cr(CN)_6]$ and $MnCl_2$ aqueous solutions. The fraction of x was varied from 0 to 1 by using of equivalent volume of reactants. The Cr, Mn, and Ni amount was verified by atomic absorption spectroscopy. The crystal structure symmetry was confirmed as cubic, space group $Fm-3m$ (No. 225) by X-ray diffraction measurements. Magnetization measurements were carried out with a SQUID magnetometer (MPMS). The proton magnetic resonance measurements were accomplished by a Bruker SXP 4-100 pulse NMR spectrometer of $\approx 10^{-6}$ resolution at frequency of $\nu_0 \equiv \omega_0/2\pi = 82.55$ MHz. [1]H free induction decay (FID) signals and spin echoes generated by the pulse sequence $(\pi/2)_X - \tau - (\pi)_Y$ were detected. Spin–lattice relaxation times (T_1) were measured with the inversion-recovery method. Hydrogen content was determined by extrapolation of the FID signal amplitudes to $t = 0$.

3. Results

Substitution of Mn ions in the lattice by Ni leads to the decrease in the elementary cell volume (Fig. 1a). The presence of two magnetic sub-lattices, ferromagnetic interaction between Ni and Cr and anti-ferromagnetic between Mn and Cr, results in the occurrence of the so-called compensation temperature T_{comp}, that means the temperature at which the two magnetic sub-lattices are fully compensated. The position of the compensation temperature shifts with increasing x to lower values, and for $x = 0.42$ no T_{comp} was observed (Fig. 1b). Figure 2a shows that the compensation temperature decreases with increasing magnetic field. The ^{1}H nuclei in the water molecules served as local probes in the NMR experiments. The amplitude of the time-domain FID signal at $t = 0$ is proportional to the number of ^{1}H nuclei in the sample. This makes possible to determine the amount of resonant water molecules i.e. the molar ratio $n_{NMR}/n_{formula}$ (Table). The resonance frequency of the protons in water molecules near to the magnetic metal ions is shifted by the local magnetic moments so far from the applied frequency that the signal of these protons is not detected and we obtain $n_{NMR}/n_{formula} < 100\%$. The decay time constants of the FID signals described by an effective spin–spin relaxation time T_{2eff} obtained from $M(t) = M_0 \exp(t/T_{2eff})$ decrease as the local magnetic moments produced by the magnetic transition metal ions at the sites
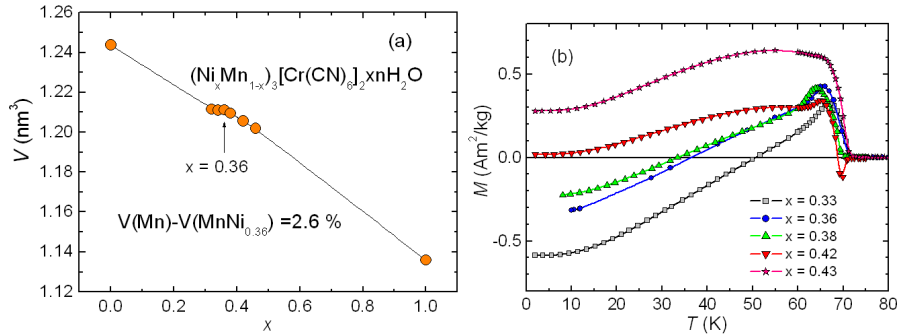
Fig. 1. (a) The effect of x on the volume of the elementary cell. (b) The effect of x on the compensation temperature T_{comp}.
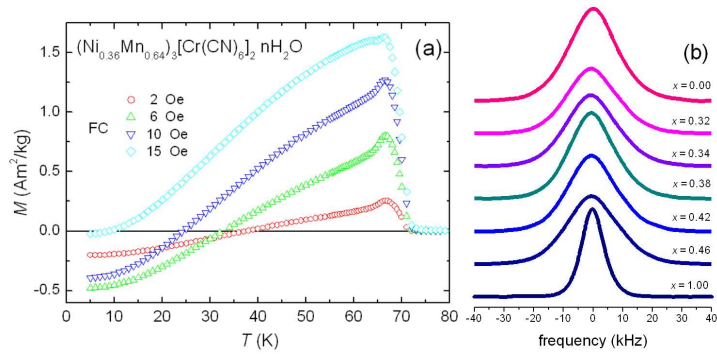

Fig. 2. (a) The effect of magnetic field on compensation temperature. (b) Room-temperature ^1H NMR spectra for $(Ni_xMn_{1-x})_3[Cr(CN)_6]_2 \cdot 15H_2O$ compounds.

of the resonant ^1H nuclei. The recovery of the magnetization in the spin–lattice relaxation experiments was single-exponential (Table).

Frequency-domain spectra were obtained by the Fourier transformation of the spin echo signals (Fig. 2b). The full widths at half maxima of them (Table) widens as the local magnetic moments produced by the magnetic transition metal ions at the sites of the resonant ^1H nuclei. The presence of more than one type of resonant ^1H nuclei belonging to different types of water molecules in the sample can result in spectral widening also. The detectable ^1H nuclei for the compound $Ni_3[Cr(CN)_6]_2 \cdot 15H_2O$ belong to metal ions at the sites of the resonant ^1H nuclei. The detectable ^1H nuclei for the compound $Ni_3[Cr(CN)_6]_2 \cdot 15H_2O$ belong to either the coordinated or the zeolitic water molecules. We suppose that they belong most probably to the nickel-coordinated waters by the following reasons. (i) There are six such water molecules per formula unit and their relative number of $6/15 = 0.4$ agrees with the measured ratio $n_{NMR}/n_{formula}$. (ii) Much higher ratio of ^1H nuclei are detectable in the $x < 1$ compounds and practically all of the protons are resonant for $Mn_3[Cr(CN)_6]_2 \cdot 15H_2O$ (Table). This can be understood if we assume

Room-temperature ^{1}H NMR parameters $n_{\mathrm{NMR}}/n_{\mathrm{formula}}$ — relative amount of resonant ^{1}H nuclei; T_1 — spin–lattice relaxation time; $T_{2\mathrm{eff}}$ — effective time constant of FID signal; FWHM — full width at half maximum of the spectrum.

Compound	$n_{\mathrm{NMR}}/n_{\mathrm{formula}}$ [%]	T_1 [ms]	$T_{2\mathrm{eff}}$ [μs]	FWHM [kHz]
$Mn_3[Cr(CN)_6]_2$	92±10	0.65±0.03	15.2	19.0±0.1
$(Ni_{0.32}Mn_{0.68})_3[Cr(CN)_6]_2$	66±10	0.86±0.04	14.0	20.1±0.1
$(Ni_{0.34}Mn_{0.66})_3[Cr(CN)_6]_2$	74±10	0.79±0.04	14.2	20.2±0.1
$(Ni_{0.38}Mn_{0.62})_3[Cr(CN)_6]_2$	80±10	0.85±0.04	15.6	18.0±0.1
$(Ni_{0.42}Mn_{0.58})_3[Cr(CN)_6]_2$	75±10	0.83±0.04	14.7	19.2±0.1
$(Ni_{0.46}Mn_{0.54})_3[Cr(CN)_6]_2$	70±10	0.78±0.04	13.7	20.3±0.1
$Ni_3[Cr(CN)_6]_2$	40±10	6.2±0.3	33.0	8.8±0.1
average ($0.32 \le x \le 0.46$)	73	0.82	14.4	19.6

that the magnetic moment of manganese ions and their magnetic interaction with chromium ions are dominant over the magnetic fields of nickel or chromium ions and over the Ni–Cr interaction. As an overall result, the protons in the manganese compounds experience more homogeneous spatial distribution of local magnetic field strength and nature than in $Ni_3[Cr(CN)_6]_2 \cdot 15H_2O$. (iii) The NMR parameters T_1, $T_{2\mathrm{eff}}$ and FWHM show that detectable ^{1}H nuclei in the manganese containing compounds are subjects of significantly greater local magnetic moments than in $Ni_3[Cr(CN)_6]_2 \cdot 15H_2O$.

Acknowledgments

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