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Ni(II)octadecylphosphonate: an inorganic/organic layered weak-ferromagnet

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Abstract

$Ni[CH_3(CH_2)_{17}PO_3]\cdot H_2O$ was prepared and characterized by several techniques and the magnetic properties were measured by using a SQUID magnetometer. Preliminary refinement of the X-ray diffraction powder data by structure-less Le Bail fitting could be obtained and the compound was found to crystallise in the orthorhombic space group *Pmn2₁* with $a = 5.478(7)$ Å, $b = 42.31(4)$ Å, $c = 4.725(3)$ Å. Ni(II)*octadecyl* phosphonate is lamellar and the structure consists of alternating inorganic and organic layers. The inorganic layers are interspersed by by-layers of the octadecyl substituent and van der Waals contacts are established between them. IR spectroscopy revealed *all-trans* configuration of the hydrocarbonic chain. A tilt angle of 48.2° between the chain axis and the (*ac*) plane could be estimated. The temperature dependence of the molar susceptibility plotted as $1/\chi$ vs. T is linear above 100 K and it follows the Curie–Weiss law. The Curie, C, constant suggests the presence of Ni(II) ion in the $S = 1$ spin state and the negative Weiss, θ, constant is indicative of antiferromagnetic nearest neighbour exchange interactions. Zero-field and field-cooled χ vs. T plots were then recorded. The plots show no overlap below 20 K, thus indicating that the compound is in an ordered magnetic state. The critical temperature has been located at the onset of the χ vs. T plot and was found to be $T_N = 21$ K. The magnetization vs. field plots, measured at different temperatures, provide the indication that the compound is a *weak-ferromagnet* below T_N.

Keywords: Phosphonates; *Octadecyl*; Nickel(II) ion; Layered compounds; Magnetic properties; Weak ferromagnet

1. Introduction

Metal(II)-phosphonates, $M[RPO_3]\cdot H_2O$ and *bis*-phosphonates, $M_2[O_3P–R–PO_3]\cdot 2H_2O$ (where M = Cd, Mn, Fe, Co, Ni, Zn, and R is an alkyl or aryl group) represent an interesting class of lamellar metal salt compounds [1,2]. They crystallise mainly in layered structures composed of metal ions and the phosphonate oxygen atoms lying in puckered sheets. The pendent organic R-group occupies the interlamellar space and two organic layers having van der Waal contacts are interspersed to the inorganic ones. The number of carbon atoms in the organic chain can be varied and the interlayer distance can be then increased. It has been shown that the structures of divalent metal phosphonates tend to comprise zig-zag layers with the metal ion six-coordinated (see Scheme 1).

For each phosphonate group two oxygens form a bridge between a pair of metal atoms whereas the third oxygen is coordinated to only one metal atom. Each metal atom is thus coordinated by six oxygens in a distorted octahedral symmetry. The two-dimensional nature of the crystal lattice in paramagnetic metal(II) phosphonates favours the nearest neighbour exchange magnetic interaction and, at low temperatures, a long-range magnetic ordering is often observed [3].

Recently Hix and Harris [4] prepared and characterized a few nickel(II) organo-phosphonates, but the compounds were obtained by a solid state reaction of a stoichiometric mixture of phosphonic acid and nickel(II) hydroxide at the melting point of the ligand. In the latter study no crystal structure and magnetic properties of them were reported.

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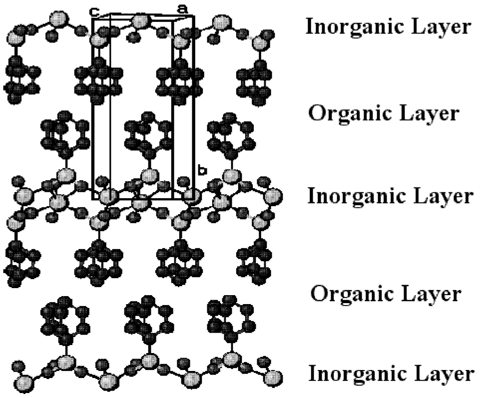


Scheme 1. Hybrid organic–inorganic network.

This paper deals with the synthesis and magnetic properties of a new $Ni[CH_3(CH_2)_{17}PO_3]\cdot H_2O$. This compound was mainly studied for two reasons:

1) to investigate the influence of the organic thickness on its magnetic properties,
2) the synthesis of a truly 2D magnetic insulator.

Part of this work has been reported previously [5].

2. Experimental

2.1. Synthesis

A solution of $NiCl_2\cdot 6H_2O$ (1.0 g, 4.2 mmol) in 30 ml of water was filtered and added to a clean aqueous solution containing octadecyl phosphonic acid [6], (1.00 g, 3 mmol) and urea (0.37 g, 6 mmol). The resulting mixture was refluxed for a week at 80 °C. A greenish-yellow microcrystalline solid began to precipitate after few days. After complete reaction the compound was separated by filtration and washed three times with water, with hot methanol and finally dried to the air.

Anal. Calc. for $Ni[CH_3(CH_2)_{17}PO_3]\cdot H_2O$: C, 52.84; H, 9.11; H_2O, 4.40.

Found: C, 53.44; H, 9.87; H_2O, 4.29.

2.2. Characterizations and physical measurements

Elemental analyses were made by the Servizio di Microanalisi della Area di Ricerca di Roma del CNR. Thermogravimetric (TGA) data were measured in flowing dry nitrogen at a heating rate of 10° min^{-1} on a Stanton-Redcroft STA-781 thermoanalyzer. The FT-IR absorption spectra were recorded on a Perkin Elmer 621 spectrophotometer using KBr pellets. Static magnetic susceptibility measurements were obtained by using a Quantum Design MPMS5 SQUID magnetometer in fields up to 5 T. A freshly prepared sample was filled in a cellulose capsule and placed inside a polyethylene straw at the end of the sample rod. All the experimental data were corrected for the core magnetization using Pascal's constants. Room temperature X-ray powder diffraction data were recorded on a Seifert XRD-3000 diffractometer, Bragg–Brentano geometry, equipped with a curved graphite monochromator [λ(Cu $K\alpha_{1,2}$) = 1.54056/1.5444 Å] and a scintillation detector. The data were collected with a step size of 0.02°, $\Delta 2\theta$ and a counting time of 8s per step of 0.2° min^{-1} over the range $4^\circ < 2\theta < 80^\circ$. The sample was mounted on a flat glass plate giving rise to a strong preferred orientation. The diffractometer zero point was determined from an external Si standard.

2.3. Preliminary structural characterization of $Ni[CH_3(CH_2)_{17}PO_3]\cdot H_2O$

The X-ray powder diffraction spectrum of $Ni[CH_3(CH_2)_{17}PO_3]\cdot H_2O$ is shown in Fig. 1. The diffraction patterns in the low-angle region are dominated by the ($0\,k\,0$) reflections, which were used to estimate the interlayer spacing. The patterns could be indexed assuming the orthorhombic space group $Pmn2_1$, a space group found in the lamellar compound Ni(II)-*methyl*-phosphonate [5]. A good quality unit cell refinement was obtained by using the structure-less Le Bail fitting method [7]; the final results are the following unit cell parameters: $a = 5.478(7)$ Å, $b = 42.31(4)$ Å, $c = 4.725(3)$ Å. According to the packing model for Mg(II)-alkyl phosphonates reported by Mallouk and co-workers [8] the lattice constant b increases linearly with n, the number of carbon atoms in the alkyl chain. The tilt angle τ between the (ac) plane and the alkyl chain axis can be estimated by assuming an angle of 78.8° between the P–C bond and the c axis (taken from the Ni(II)-*methyl*-phosphonate structure), an average C–C-bond angle of 111–112° and the C–C single bond distance of 1.53 Å. Thus, the tilt angle τ of 48.2° was calculated for a double organic layer considering the following equation [8],

$$b = 2 \times [\delta + 1.27n \sin(\tau)]$$

where b is the lattice constant, n is the number of the C–C bonds and δ is the inorganic layer thickness (see Scheme 2).

3. Results and discussion

Ni(II)-*octadecyl* phosphonate was prepared by the reaction of the phosphonic acid in water with $NiCl_2\cdot 6H_2O$ in the presence of urea at temperatures above 80–90 °C. The compound, precipitated as a greenish-yellow microcrystalline powder after days of reflux, has been characterized by elemental analyses and several techniques (TGA (DSC), XRPD, electronic and FT-IR

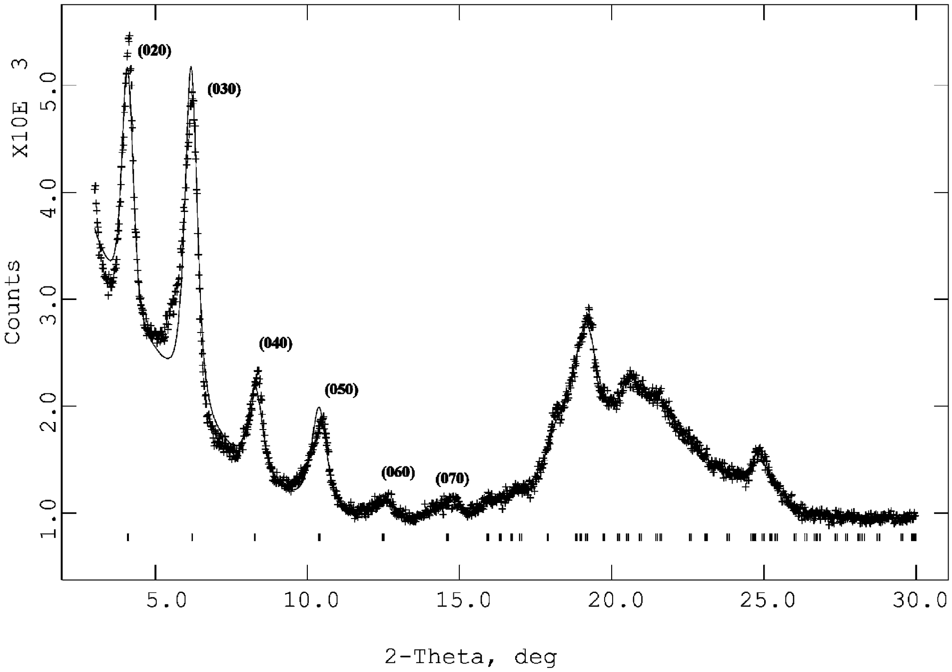
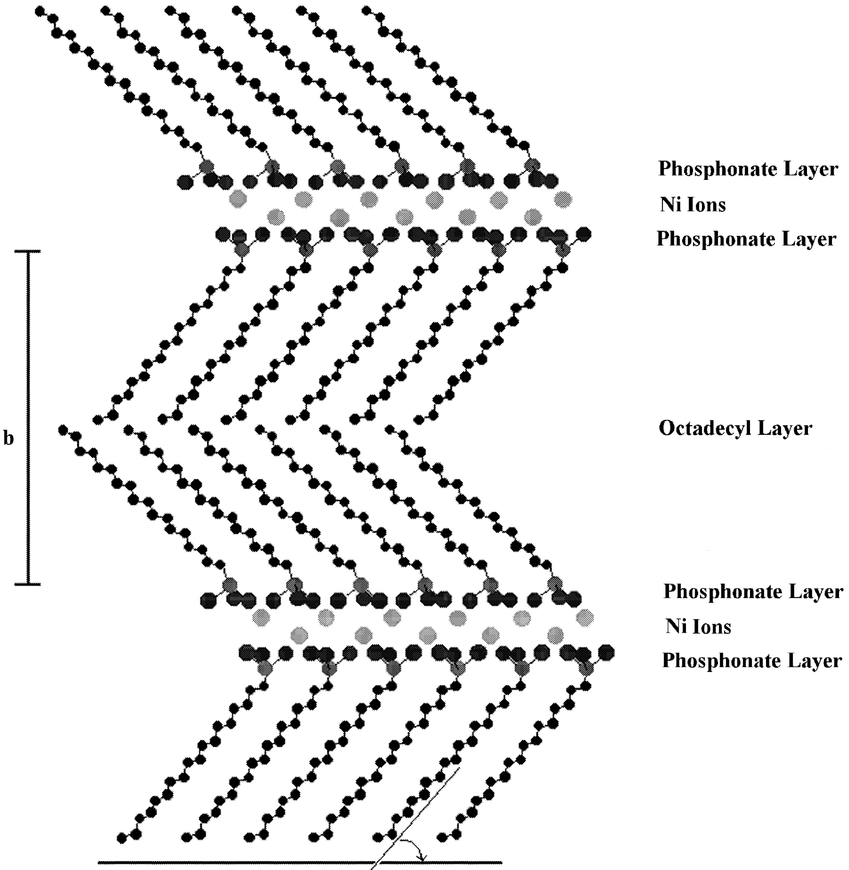


Fig. 1. X-ray powder diffraction patterns of Ni[$CH_3(CH_2)_{17}PO_3$]·H_2O.



Scheme 2. Packing model for Ni[$CH_3(CH_2)_{17}PO_3$]·H_2O.

absorption spectroscopy). The TGA shows the first mass loss between 50 and 100 °C (2.3%) due to the water of crystallization or adsorbed water. It then starts to lose coordinated water at ~130 °C and it stops at 270 °C. The observed weight loss at this stage is 5.2%, a value that corresponds roughly to one water molecule per formula unit. The calculated weight loss for one water molecule is 4.40%. Above 280 °C the compound starts to decompose and stops at 570 °C, loosing 52.89% of the weight, corresponding to the aliphatic chain of the ligand.

3.1. Optical properties

The IR absorption spectrum of $Ni[CH_3(CH_2)_{17}PO_3]\cdot H_2O$ is reported in Fig. 2 and shows some remarkable differences when compared with that of $Ni[CH_3PO_3]\cdot H_2O$ [5]. Intense peaks were found at 2954, 2916, 2848 cm^{-1} together with a shoulder at 2870 cm^{-1} and assigned to the asymmetric methyl, [$\nu_a(CH_3)$], and to a symmetric methyl, [$\nu_s(CH_3)$], (i.e. 2954 and 2870 cm^{-1}), to asymmetric methylene, [$\nu_a(CH_2)$], and symmetric methylene, [$\nu_s(CH_2)$], stretches (i.e. 2916 and 2848 cm^{-1}), of the octadecyl group. It is well known that the position and the shape of the [$\nu_a(CH_2)$] and [$\nu_s(CH_2)$] absorption bands reflects the conformational order and packing of the aliphatic chains in monolayers [9]. For long-chain hydrocarbons when the aliphatic chain is in *all-trans* conformation the energy of the [$\nu_a(CH_2)$] band ranges between 2918 and 2920 cm^{-1}. The observed position of the [$\nu_a(CH_2)$] band at 2918 cm^{-1} implies that alkyl chains are in a fully extended *all-trans* conformation [10]. Another indication of the state of the hydrocarbon chains comes from the [$\nu_s(CH_2)$] band. The peak position of the latter band for crystalline hydrocarbons lies at 2850 cm^{-1} and shifts to a higher value, 2856 cm^{-1}, as the organic chains become less packed. The appearance of the band at 2848 cm^{-1} is consistent with a high density crystalline phase. The presence of two bands at 3430 cm^{-1} and a shoulder at 3396 cm^{-1} and a band at 1660 cm^{-1} in the spectrum indicates that water is coordinated to the metal ion [11]. In the region 900–1800 cm^{-1} of the infrared spectrum a medium intense peak at 1468 together with a weak band at 1408 cm^{-1} are assigned to the methylene scissor deformation. An intense peak at 1150 cm^{-1} and a progression of weak peaks up to 1400 cm^{-1} are assigned to the CH_2 rocking and wagging modes of *all-trans* alkyl chains in this compound [12]. The band at 1096 cm^{-1} is assigned to the asymmetric $[PO_3]^{-2}$ stretch and bands between 1066 and 962 cm^{-1} to the symmetric $[PO_3]^{-2}$ stretches, which split as a result of lower than C_{3v} local symmetry of the phosphonate groups.

3.2. Magnetic properties

Static magnetic susceptibility measurements were performed on a polycrystalline sample in the applied magnetic field of 200 Oe and in the temperature range of 5–270 K, both in zero and field cooled modes. The temperature dependence of the molar magnetic susceptibility plotted as $1/\chi$ vs. T is reported in Fig. 3. The plot is linear above 100 K and it obeys to the Curie-Weiss law. The deduced C-value, i.e. 1.25 cm^3 K mol^{-1}, is in agreement with the expected value for a Ni(II) d^8 ($S=1$) electronic configuration. The Weiss constant is negative in value, i.e. $\theta = -24$ K. The χT vs. T plot decreases slowly on lowering the temperature down to

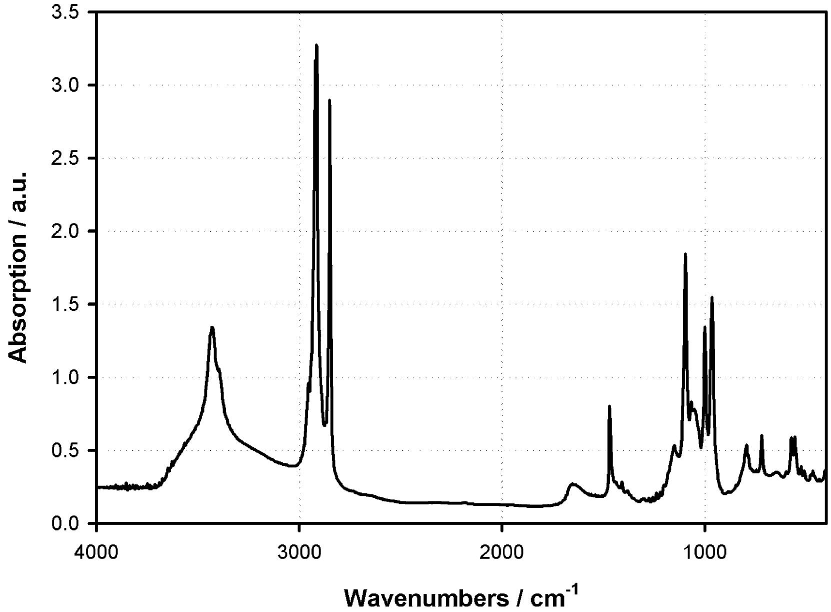


Fig. 2. Absorption FTIR spectrum of $Ni[CH_3(CH_2)_{17}PO_3]\cdot H_2O$ in the KBr region.

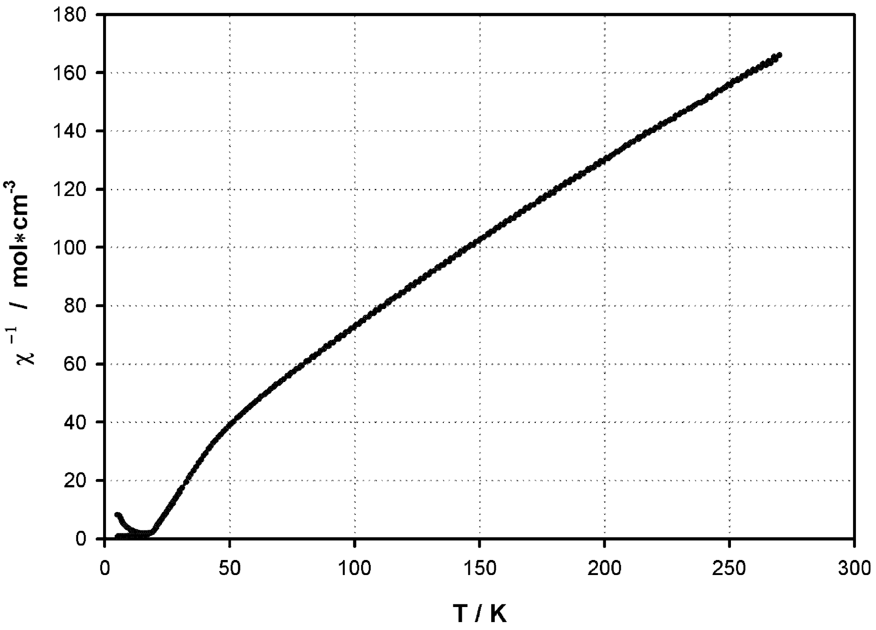


Fig. 3. Temperature dependence of $1/\chi$ vs. T for $Ni[CH_3(CH_2)_{17}PO_3]\cdot H_2O$.

30 K and then starts to rise again. Below this temperature the magnetic behaviour is different from that observed in $Ni[CH_3PO_3]\cdot H_2O$ [5]. Zero-field (zfc) and field-cooled (fc) M vs. T plots under an applied field of 10 Oe have been measured and they are reported in Fig. 4. The two plots do not overlap and the bifurcation point is at $T \sim 21$ K. The zfc magnetization increases up to ~ 16 K reaching a broad maximum and then decreases again slowly down to 5 K. The fc magnetization shows a continuous increase on lowering the temperature. The experiment provides the indication that the compound is magnetically ordered below $T =$ 21 K. The difference between the fc and zfc magnetizations, depicted in Fig. 4, represents the irreversible magnetization, ΔM_{fc-zfc}. ΔM_{fc-zfc} starts to increase on lowering the temperature and it reaches the value of 60 cm^3 Oe mol^{-1} at $T \sim 5$ K. The temperature at the onset of the zfc plot is taken as the critical temperature T_N. Hysteresis loops were observed at different temperatures below $T \leqslant 20$ K for applied magnetic fields < 1 T. The plot recorded at $T = 5$ K reported in Fig. 5 is not characteristic of a ferromagnetically ordered material. In fact, at 3 T, the magnetization does not saturate and the value at that field is 18% of that expected for the

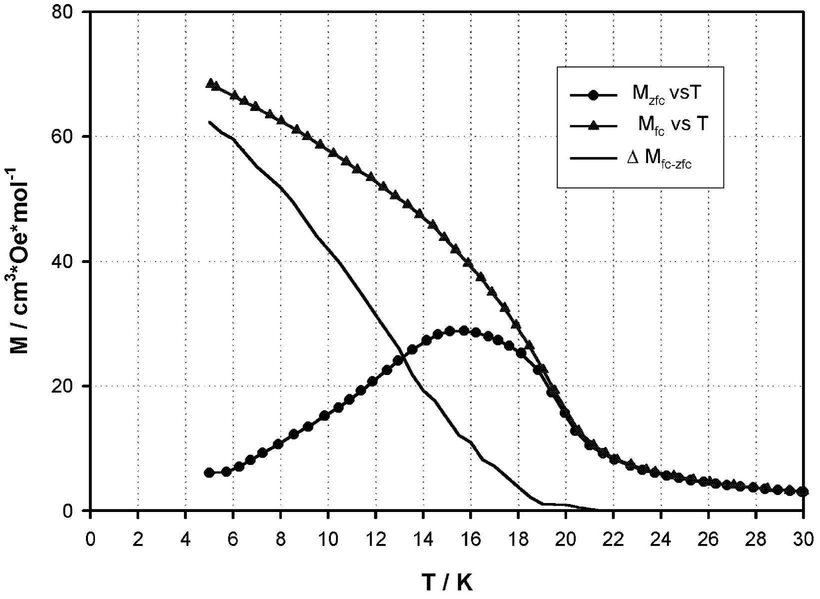


Fig. 4. Temperature dependence of M vs. T plot for $Ni[(CH_3(CH_2)_{17}PO_3)]\cdot H_2O$ in the temperature range 5–30 K in zero-field (●—●—●) and field cooling modes (–▲–▲–). Irreversible magnetization, ΔM_{fc-zfc} as obtained from the difference of the fc and zfc plots (——).

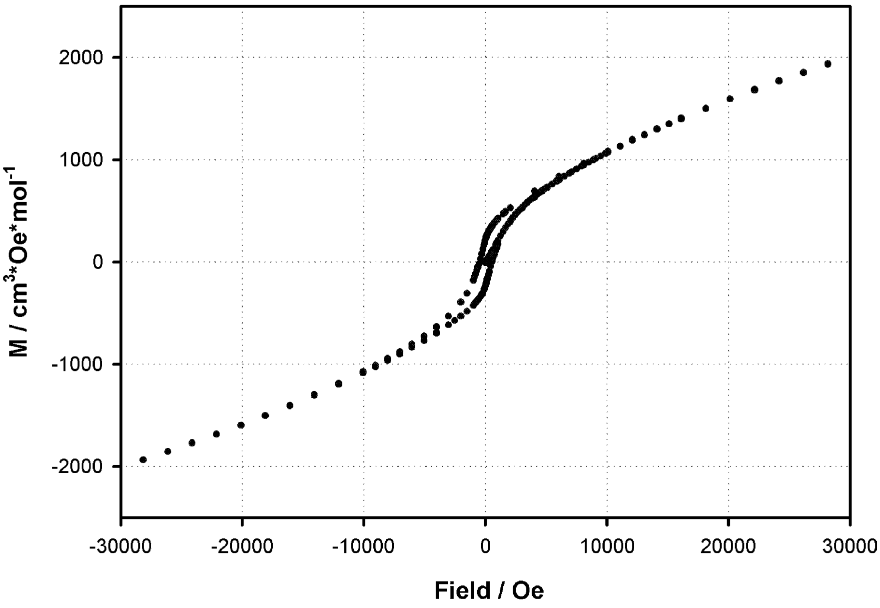


Fig. 5. Hysteresis loop of Ni[$CH_3(CH_2)_{17}PO_3$]·H_2O measured at $T = 5$ K.

fully aligned moment of Ni^{2+} (i.e. 11 170 cm^3 Oe mol^{-1}). This behaviour is typical of a weak-ferromagnet. The presence of the weakly ferromagnetic state is due to the 'spin-canting' [13]. The local spins in this ordered state are not perfectly antiparallel leading to a net spontaneous magnetization which saturates in a small field.

The value of magnetization increases non-linearly up to 3.0 T, the highest measured field. From the plot the values of the remnant magnetization, M_{remn}, and of the coercive field, H_c, can be directly obtained and they are 220 cm^3 Oe mol^{-1} and 516 Oe, respectively. The estimation of the value of M_s (5 K) from the equation [14]:

$$M(H, T) = M_s(T) + \chi(T) \times H$$

is difficult to be made. If we approximate the value of M_s to the M_{remn} found at 5 K then a canting angle of ~1° is estimated.

4. Concluding remarks

The Ni[$CH_3(CH_2)_{17}PO_3$]·H_2O has been prepared for the first time and characterized by X-ray diffraction and IR spectroscopy. It shows a lamellar structure made of alternating organic and inorganic layers and the interlayer distance is 42.31 Å; a distance which is lower than that observed in films of bilayers of Mn(II)-*octadecyl* phosphonates (i.e. 48.5 Å) obtained by LB technique [12]. This structure is also confirmed by IR spectra. The magnetic behaviour of Ni(II)-*octadecyl* phosphonate at low temperatures is peculiar because it is typical of a weak-ferromagnet. The broad maximum in the χ vs. T plot expected for a low-dimensional magnetic system is absent at low temperatures and an estimation of the *intra*-planar super-exchange J/k value is thus prevented. The presence of the weakly ferromagnetic state is due to the 'spin-canting' [13,14].

Acknowledgements

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