Low Temperature Magnetic Ordering of the Magnetic Ionic Plastic Crystal, Choline[$FeCl_4$]

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Abstract. We report on the nature of the low temperature magnetic ordering of a magnetic ionic plastic crystal, Choline[$FeCl_4$]. This investigation was carried out using heat capacity measurements, neutron diffraction experiments and muon spin relaxation (μSR) spectroscopy. The calorimetric measurements show the onset of an unusual magnetic ordering below 4 K with a possible second magnetic phase transition below 2 K. Low temperature neutron diffraction data reveal a three dimensional antiferromagnetic ordering at 2 K compatible with the previous magnetometry results. The analysis of μSR spectra indicates a magnetic phase transition below 2.2 K. At 1.6 K, the analysis of the shape of the μSR spectra suggests the existence of an additional magnetic phase with features of a possible incommensurate magnetic structure.

1. Introduction

Plastic crystal materials were described by Timmermans in the 1960s. These compounds, composed entirely of ions, display an intermediate phase between the solid and the liquid state called plastic phase. It is reached by one or more solid–solid phase transitions on warming the fully ordered crystalline phase from low temperatures [1]. This phase is characterized by a state presenting both long-range order and short-range disorder. Such as short-range is originated by rotational motions of the molecules. The plastic behaviour, with a negligible vapour pressure and high ionic conductivity at room temperature, reinforce their interest as solid state ion conductors [2, 3].

The introduction of structural functionalities on the cationic or anionic part has eased the design of new plastic crystal phases with targeted properties. Transition metal-containing plastic phase, such as organic inorganic plastic crystals (OIPCs) [4] could be auspicious new emergent materials, which will favourably combine the properties of ionic plastic crystals with the magnetism, originated from the metal incorporated in the complex anion. This is the case of the N,N,N-trimethylethanolammonium tetrachloroferrate (III), Choline[$FeCl_4$], which combines a three-dimensional magnetic ordering with a

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high solid-state-conduction [5], becoming a promising candidate for its use as electrolyte in solid state lithium batteries.

A structural and magnetic investigation of Choline[$FeCl_4$] was carried out using Raman spectroscopy and time-resolved X-ray thermodiffractometry. The most striking features are an enhancement of the rotational motion of [Choline]$^+$ and [$FeCl_4$]$^-$ anions with increasing temperature up to the melting point, 490 K, and the presence of a three-dimensional magnetic ordering below 4 K [5]. In this contribution we focus on the nature of the low temperature magnetic ordering of this compound combining heat capacity measurements, neutron diffraction data and muon spin relaxation (μSR) spectroscopy.

2. Results and discussion

Heat capacity (Cp) measurements were carried out with a standard QD PPMS device by a relaxation method using a two-tau model. Data were collected from 2 to 10 K at several magnetic fields between 0 and 50 kOe (Figure 1). In absence of an external magnetic field, when the temperature is lowered, the Cp value starts to increase below 5 K, showing a shoulder around 3.4 K. Then, a strong increase down to 2 K (ΔC_p=13 J/Kmol) is detected. The first anomaly (3.4 K) does not have the typical behaviour of a second-order transition, but it can be associated with the establishment of a three-dimensional antiferromagnetic ordering, in good agreement with magnetic susceptibility measurements [5]. In addition, the strong increase down to 2 K could be related to a possible additional magnetic transition at lower temperatures. By applying magnetic fields, the shoulder remains up to 30 kOe, but vanishes for larger fields. This vanishing shoulder corroborates the presence of the weak magnetocrystalline anisotropy detected in the magnetization data [5]. Furthermore, the second magnetic anomaly decreases its magnitude as the magnetic field increases, and probably shifting to lower temperatures, as is expected for an antiferromagnetic ordering. Therefore, neutron and muon studies were performed in order to understand the origin of this unusual magnetic behaviour.

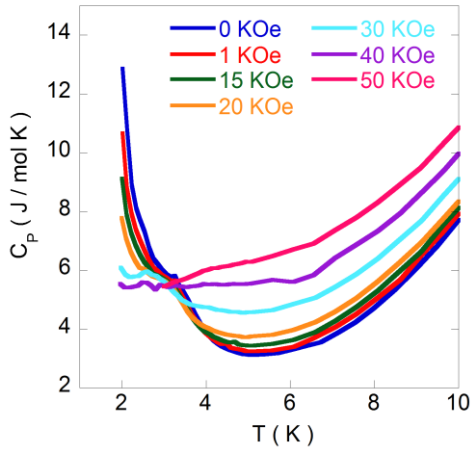

Figure 1. Temperature dependence of the heat capacity of Choline[$FeCl_4$] under external magnetic fields ($0 \leq H \leq 50$ kOe).

Powder neutron diffraction measurements were performed on the D1B diffractometer, at the Institute Laue-Langevin of Grenoble, using a neutron wavelength of 2.525 Å. About 3 g of Choline[$FeCl_4$] was employed in the neutron diffraction experiments, placed in a cylindrical vanadium container and held in a liquid helium cryostat. The temperature evolution of the D1B patterns between 2 and 10 K shows the presence of extra elastic intensity at temperatures below around 4 K, corroborating the onset of a magnetic ordering. A comparative view of the patterns above (10 K) and below (2 K) the magnetic ordering temperature is shown in Figure 2 (a). The most significant feature being the presence of an

extra magnetic signal (2θ ≈ 15º), which could be attributed to the establishment of a three-dimensional antiferromagnetic ordering. A satisfactory monoclinic solution with unit cell parameters of a = 15.376(1) Å, b = 15.234(1) Å, c = 8.742(1) Å, β = 99.20(1) and V = 2021.52 (1) Å^3 was found using the WINPLOTR programme. The additional magnetic peak at 2 K was indexed with the propagation vector k = (0, 0.17, 0) indicating that the magnetic structure is incommensurate. The experimental, calculated and difference diffraction profiles are displayed in Figures 2 (b). However, with only one visible magnetic peak, we cannot determine univocally the magnetic propagation vector. As observed in other hybrid organic–inorganic materials based in tetrahaloferrate cation such as Dimim[FeX_4] [6, 7, 8], Edimim[FeX_4] [9] or Emim[FeX_4] (X = Cl and Br) [10, 11] the magnetic structure should consist of an arrangement of iron metal complex groups, stabilizing the overall antiferromagnetic ordering without direct Fe··Fe interactions, but through the superexchange interactions, Fe-Cl··Cl-Fe.

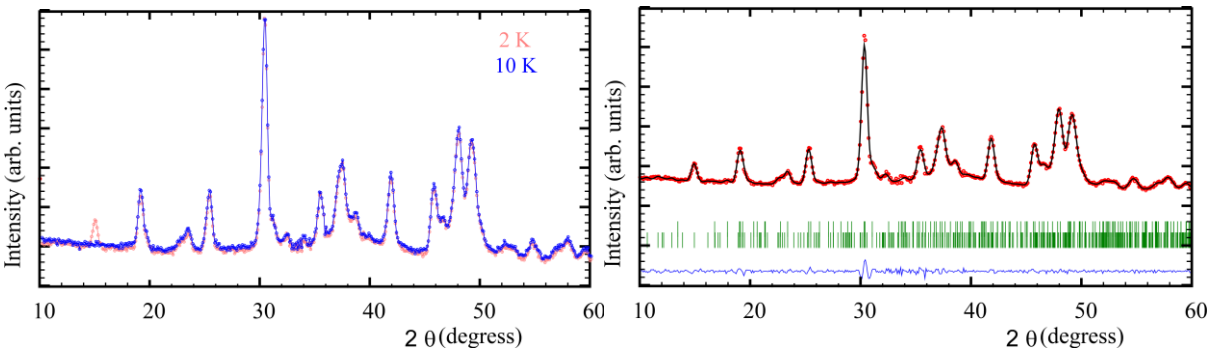

Figure 2. (a) Neutron patterns at 10 and 2 K for Choline[$FeCl_4$] in D1B difractometer. The (*) dot show the magnetic contributions. (b) Neutron diffraction profiles for Choline[$FeCl_4$] phase at 2 K. Positions of the magnetic (second row) profile are also presented.

The μSR experiments were performed in zero applied field at the Laboratory for Muon Spin Spectroscopy of the Paul Scherrer Institute, Switzerland using the GPS spectrometer in the temperature range 2–200 K. Above 4 K, the whole sample volume is in the paramagnetic phase. For the entire temperature range, the μSR data were fitted using the sum of an exponentially damped – Kubo-Toyabe depolarization function [12], first term in eq. (1), with a term describing the μ^+ behaviour in the magnetic phase:

$$A_{para}e^{-\lambda t}\left(\frac{1}{3}+\frac{2}{3}\left(1-\sigma^2t^2\right)e^{-\frac{\sigma^2t^2}{2}}\right)+A_{magn}P_{magn}(t) \quad (1)$$

σ can be expressed in terms of the interaction between the muon spin and the spins of the compound and the characteristics of the latter spins; $A_{magn}+A_{para}=A$ where A is a parameter called asymmetry that can be obtained from a calibration run, in the paramagnetic phase, in weak transverse field. The first term in Eq. (1) describes a double channel depolarization of the muon ensemble, in the paramagnetic phase: one arising from the fluctuating electronic magnetic moments, the exponential relaxation, and the other one from the static (for the time window of the μSR experiments) depolarization due to the nuclear magnetic moments, the so-called Kubo-Toyabe depolarization function. The second term of the sum in Eq. (1) describes the magnetic volume and has different T dependencies, which are dependent of the temperature range. $A_{magn}=0$ for $T>4\,\mathrm{K}$ while $A_{para}=0$ at lower temperatures.

As one can see from Figure 3, below 4 K, a fast relaxing component sets in, confirming the onset of a magnetic ordering detected by heat capacity and neutron powder diffraction measurements. Down to about 2.4 K, the "magnetic part" of the μSR spectra could be described by a purely exponential $A_{magn}P_{magn}(t)$, i.e. no oscillations are observed in the μSR spectra. The temperature dependence of A_{para} in this temperature range is displayed in the inset of Figure 3 (right). Below 2.4 K there is clear indication of a (broad) non-zero average field at the muon site: oscillations are observed in the μSR spectra. $A_{magn}P_{magn}(t)$ that fits best the μSR spectra has the following expression:

$$A_{magn}P_{magn}(t) = A_1 e^{-\lambda_1 t} J_0(2\pi\nu_1) + A_2 e^{-\lambda_2 t} J_0(2\pi\nu_2) + A_3 e^{-\lambda_3 t} \quad (2)$$

where $A_1 + A_2 + A_3 = A_{magn}$, $A_3 = \frac{A_1 + A_2}{2}$ and $J_0(2\pi\nu)$ is a 0'st order Bessel function.

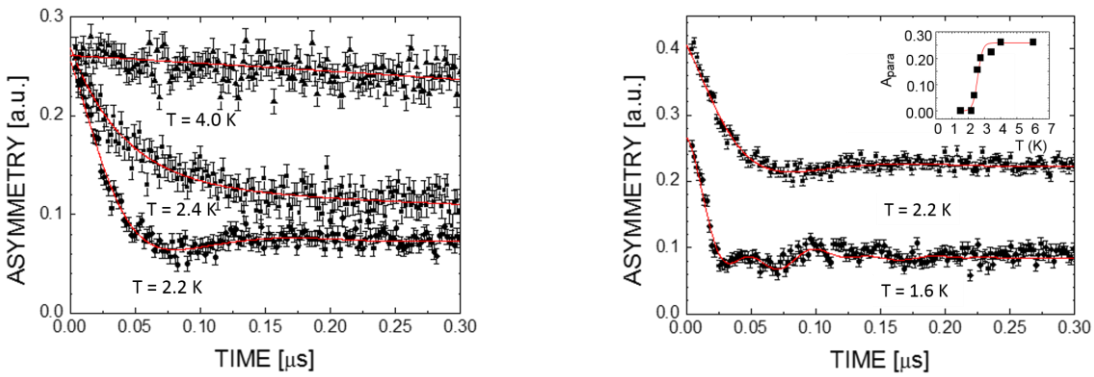

Figure 3. μSR spectra recorded on Choline[$FeCl_4$] at different temperatures between 1.6 and 4 K. In the left figure the 2.2 K spectra was shifted up for clarity. The solid lines represent the fitting according the Eq. (1) and (2). The inset shows the temperature dependence of A_{para}. The solid line is a guide to the eye.

Usually, a Bessel function fit of the μSR spectra is an indication of an incommensurate magnetic ordering (spin density wave). However, another fully plausible explanation would be the existence of a wide, non-symmetric field distribution at the muon site. Therefore, μSR results alone cannot decide whether the magnetic ordering of Choline[$FeCl_4$] below 2.2 K is incommensurate or not.

3. Conclusions

Heat capacity measurements show that the magnetic ionic plastic crystal Choline[$FeCl_4$] exhibits two successive magnetic transitions below 4 K. Neutron diffraction data confirms the antiferromagnetic nature of the long-range magnetic order whereas muon spin relaxation spectroscopy experiments, although not conclusive, are compatible with a possible additional incommensurate magnetic structure below 2 K.

4. Acknowledgements

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5. References

[1] Timmermans J 1961 *J. Phys. Chem. Solids* **18** 1
[2] Howlett P. C, Shekibi Y, MacFarlane D. R and Forsyth M 2009 *Adv. Eng. Mater.* **11** 1044
[3] MacFarlane D. R, Huang J and Forsyth M 1999 *Nature* **402** 792
[4] Lee M, Choi U. H, Wi S, Slebodnick C, Colby R. H and Gibson H. W 2011 *J. Mater. Chem.* **21** 12280
[5] de Pedro I, García-Saiz A, González J, de Larramendi I. R, Rojo T, Afonso C. A and Rodríguez Fernández J. 2013 *Phys. Chem. Chem. Phys.* **15(30)** 12724
[6] García-Saiz A, de Pedro I, Migowski P, Vallcorba O, Junquera J, Blanco J. A and Rodríguez Fernández, J 2014 Inorg. Chem. **53(16)** 8384
[7] García-Saiz A, Migowski P, Vallcorba O, Junquera J, Blanco J. A, González J. A, Fernández-Díaz M. T, Rius J, Dupont J, Rodríguez Fernández J and de Pedro I 2014 *Chem. Eur. J.* **20** 72
[8] García-Saiz A, de Pedro I, Blanco J A González J. A and Rodríguez Fernández, J 2013 *J. Phys. Chem. B* **117** 3198
[9] García Saiz A, de Pedro I, Vallcorba O, Migowski P, Campo I, Barquin, L F, Abrahams I, Motevalli M, Dupont J, Gonzalez J A, Rodríguez Fernández, J 2015 *RSC Adv.* **5** 60835
[10] de Pedro I, Rojas D. P, Albo J, Luis P, Irabien A, Blanco J A and Rodríguez Fernández, J 2010 *J. Phys.: Condens. Matter* **22(29)** 296006
[11] de Pedro, I, Rojas D. P, Blanco J A and Rodríguez Fernández, J 2011 *J. Magn. Magn. Mater.* **323** 1254
[12] Hayano R. S, Uemura Y. J, Imazato J, Nishida N, Yamazaki T and Kubo R 1979 *Phys. Rev. B* **20(3)** 85