MÖSSBAUER STUDY OF A NEW CRYSTALLINE FLUORIDE: NaPbFe2F9

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Mössbauer spectrometry was carried out over the temperature range 4.2 K–300 K on a crystalline fluoride NaPbFe2F9, which orders antiferromagnetically below 116 K. The hyperfine data are discussed in terms of the position and the environment of iron sites.

1. Introduction

The crystalline NaPbFe2F9 compound results from the recrystallization of the analogous glass obtained by heating an anhydrous fluoride mixture [1]. The cell is monoclinic (space group C2/c). As shown in fig. 1, the structure, determined “ab initio” from its X-ray powder pattern and refined by the Rietveld method, consists in corner-sharing octahedra chains running along the c axis and along the [110] and [110] directions. Furthermore, the octahedra exhibit the usual shortening of the terminal bonds.

In the present communication, we report susceptibility measurements and a Mössbauer study over the temperature range 4.2 K–300 K.

Fig. 1. (001) projection of the crystalline structure of NaPbFe2F9: different FeF6 octahedra at z = 0 are hatched, those at z = ½ are not. 4b and 4d stand for the different types of octahedra. Small circles (on the top of hatched octahedra) represent Na atoms, large circles stand for Pb atoms.
2. Susceptibility measurements

The magnetic susceptibility was measured between 4.2 K and 300 K using the Faraday method. The sample of NaPbFe$_2$F$_9$ was cooled from room temperature to liquid helium temperature in the absence of an external magnetic field and subsequently heated in a 1.0 T applied field. An antiferromagnetic behaviour of the Fe–Fe interactions is evidenced by the negative value of the paramagnetic Curie temperature $\theta_p = -190$ K; the Néel temperature of NaPbFe$_2$F$_9$ is estimated at 115 K.

In addition, an inflexion point of the $\chi^{-1}(T)$ curve is observed below 90 K; it is due to the magnetic ordering temperature of the ferrimagnetic phase Na$_5$Fe$_3$F$_{14}$, always present as an impurity ($< 5\%$) [1].

3. Mössbauer spectroscopy

The $^{57}$Fe Mössbauer spectra were recorded in transmission geometry using a constant acceleration spectrometer with a $^{57}$Co source diffused in a rhodium matrix. The sample was made of powdered NaPbFe$_2$F$_9$ containing 5 mg Fe/cm$^2$.

Mössbauer experiments were performed over the temperature range 4.2 K–300 K using a bath cryostat, with a standard regulator (accuracy estimated at 1 K); the temperature was controlled by a linearized sensor calibrated at liquid helium and liquid nitrogen temperatures. The hyperfine data were refined with the Mosfit program [2].

The hyperfine structure observed on NaPbFe$_2$F$_9$ at 120 K and at room temperature shows the presence of pure electric quadrupolar interactions. The spectra presented in fig. 2 consist of a quadrupole doublet composed of two broad lines exhibiting a weak asymmetry: it reveals the presence of two paramagnetic ferric iron ions in two different sites at least.

A magnetic hyperfine structure is evidenced below $T_N = 116$ K, the magnetic ordering temperature established by thermal scanning. By following the thermal evolution of both positions and intensities of the different lines of the magnetic spectra, a definitive refinement was obtained by accounting for four components: such a procedure leads to the fitted spectra presented in fig. 3 and to the hyperfine parameters of the two main magnetic contributions as reported in table 1.

The isomer shift values confirm the presence of six-fold coordinated trivalent high-spin iron ions. In addition, their similarity leads to a unique interpretation of the paramagnetic spectra assuming only two quadrupolar components: the hyperfine data are also reported in table 1.

Let us examine the structure (as shown in fig. 1) [1] of a pure NaPbFe$_2$F$_9$, in order to discuss the Mössbauer data. One can distinguish two kinds of iron octahedra according to their neighbourhood: a first iron site, denoted 4b, is