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The first study of antiferromagnetic eosphorite-childrenite series $(Mn_{1-x}Fe_x)AlP(OH)_2H_2O$ (x=0.5)

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ABSTRACT

This study presents for the first time the antiferromagnetic structure of the eosphorite-childrenite series $(Mn_{1-x}Fe_x)AlPO_4(OH)_2H_2O$ (x=0.5), based on neutron single crystal diffraction at 3 K in combination with group theoretical representation analysis. The new magnetic structure is described in the magnetic space group $\mathbf{P_C}$mnb, maintaining the atomistic unit cell size ($a\times b\times c$) with a ~6.9 Å, b ~10.4 Å, c ~13.4 Å. Mn-rich and Fe-rich zones within solid solution crystals are expanded up to several hundred micrometers, as seen in electron microprobe and polarisation microscopy. Magnetic susceptibility and specific heat measurements on two different eosphorite-childrenite crystals show the magnetic transition temperature between 6.5 K and 6.8 K as the Mn^{2+}/Fe^{2+} ratio varies over single compositional zones. Below the Néel temperature, a magnetic field between 1.5 T and 2 T parallel to the a-axis causes a 180° spin-flip, reaching the saturation (5.25 μ_B pfu) toward high magnetic fields.

1. Introduction

Eosphorite and childrenite are the respective Mn- and Fe-enriched end-members of the solid solution $MAlPO_4(OH)_2H_2O$ ($M=Mn^{2+}$ and Fe^{2+}) occurring from hydrothermal phosphatisation of metasediments and granitic pegmatites [1,2]. These minerals are coloured in various pinkish and brown tones mainly depending on the Mn/Fe ratio [2]. The eosphorite-childrenite series crystallizes at room temperature (*RT*) in the space group **C**mca (#64) [2–4] (i.e. **C**mce used present with 'double' glide planes *e* oriented 'normal' and 'inclined' to the plane of projection [5]). As shown in Fig. 1**a**, this solid solution structure is built up with two types of 1-dim. octahedral chains along [100], i.e. chains made of strongly distorted octahedra of $MO_4(OH, H_2O)_2$ and those of more regular octahedra of $AlO_2(OH)_2(OH, H_2O)_2$ [4]. Both M- and Al-chains are connected to each other via PO_4 tetrahedra and hydrogen bonds to give rise to a 3-dim. network (Fig. 1**b**). Three interesting issues are found in this combined octahedral and tetrahedral framework: (1) the presence of 1-dim. chains confining two different magnetic *3d* transition metal cations (Mn^{2+} and Fe^{2+}), making a complete solid-solution series; (2) the presence of protons at various crystallographic sites governed by different hydrogen bonding interactions; (3) the coexistence of OH and H_2O groups involved in the framework. In this context, Gatta et al. investigated eosphorite using neutron single crystal diffraction to precisely determine three unique hydrogen positions, explaining the absence of both atomistic and magnetic ordering of Mn/Fe at 20 K [4]. The existent of a magnetic phase of eosphorite was proven in Mössbauer spectra acquired at 4.2 K [6].

However, the magnetic structure of eosphorite-childrenite solid solution is unknown up to date. The present study reports the antiferromagnetic structure resulted from neutron single crystal diffraction of $(Mn_{1-x}Fe_x)AlPO_4(OH)_2H_2O$ with x=0.5 at 3 K in combination with group theoretical representation analysis. Furthermore, magnetic susceptibility and specific heat measurements with two different eosphorite-childrenite compounds show a variation in the Néel temperature between 6.8 K and 6.5 K, which seems to be due to compositional zones with different Mn/Fe ratios. Indeed, this work confirms macroscopic Mn-rich and Fe-rich zones over up to several hundred micrometers by means of electron microprobe and polarisation microscopy. Three different hydrogen bondings are briefed in

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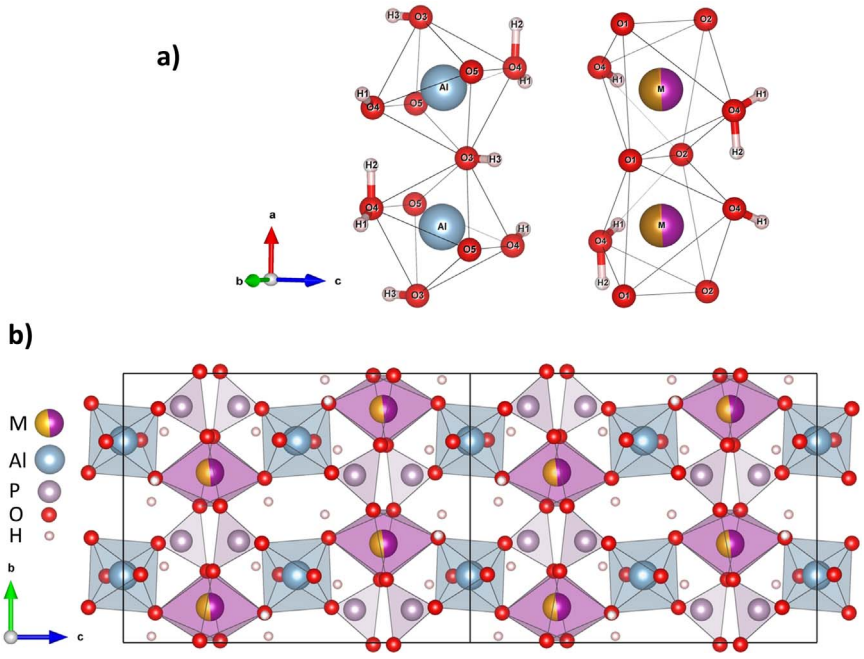

Fig. 1. The crystal structure of eosphorite-childrenite series is made of chains of alternating $MO_4(OH, H_2O)_2$ and $AlO_2(OH)_2(OH, H_2O)_2$ octahedra **(a)** which are connected to each other via PO_4 tetrahedra **(b)**.

Table 1
Experimental and refinement parameters in X-ray and neutron diffraction studies.

Sample	**S2**	**S1**		**S1**	**S1**
Refinements	Atomistic structure model	Joint refinement for atomistic structure model		Atomistic structure model	Magnetic structure model
Radiation source	X-ray	X-ray	Neutron	Neutron	
Wavelength [Å]	0.71073	0.71073	1.03854	1.03854	
Data collection temperature [K]	300	300	300	3	
Crystal size	40×80×40 μm^3	80×80×50 μm^3	3×2.7×7 mm^3	3×2.7×7 mm^3	
Theoretical density [g/cm^3]	3.1491	3.1334	3.2541	3.2275	
Lattice parameters [Å]	a=6.915 (1)	a=6.921 (1)	a=6.844 (3)	a=6.843 (3)	
	b=10.420 (1)	b=10.418 (1)	b=10.294 (3)	b=10.327 (3)	
	c=13.432 (1)	c=13.432 (1)	c=13.294 (2)	c=13.306 (2)	
Maximal sin(θ)/λ	0.690	0.859	0.587	0.699	
k-vector					(0, 1, 0)
h k l ranges	−9 < h < 9	−11 < h < 11	−7 < h < 7	−7 < h < 7	
	−14 < k < 14	−17 < k < 17	−10 < k < 5	−5 < k < 12	
	−18 < l < 18	−22 < l < 22	−4 < l < 14	−15 < l < 12	
Condition for observed reflections	I > 3 σ(I)	I > 3 σ(I)	I > 3 σ(I)	I > 3 σ(I)	
Number of unique/total observed reflections	531/ 2912	1160/ 72142	280/ 1243	331/ 1834	58/ 302
Absorption correction factors [7]	A_{min}=0.937 A_{max}=1.053	A_{min}=0.966 A_{max}=1.031	None	None	None
R_{ini}	3.95	6.26	11.39	8.46	16.58
Number of refinement parameters	54	81		37	4
Extinction factor	none	none	0.0013(1)	0.0013(2)	5.1(12)
R(F)	2.87	2.08	7.20	5.40	9.33
wR(F^2)	6.37	5.59	14.92	13.08	18.76
Goodness-of-Fit (S)	1.57	1.86	5.68	4.94	4.76
Shift/σ_{max} Shift/σ_{av}	−0.0081; 0.0011	−0.0136; 0.0016	−0.0136; 0.0016	0.0042; 0.0012	0.0410; 0.0187
(Δ density)$_{max}$	0.46	0.62	1.3	0.94	
(Δ density)$_{min}$	−0.53	−0.55	−1.11	−1.31	

$R(F)=[\Sigma||F_o|-|F_c||/\Sigma|F_o|]$; $wR(F^2)=[\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_c^2]^{1/2}$; Weighting $w=1/(\sigma^2(I)+0.0004*I^2)$.
$S=[\Sigma w(F_o^2-F_c^2)^2/(M-P)]^{1/2}$, where F_o and F_c are observed and calculated structure factors, respectively, M is number of reflections, and P is number of parameters.

connection with bonding valences in the last part of this research report.

2. Experimental

2.1. Sampling, optical, chemical, and thermal analyses

Crystal samples of two different eosphorite-childrenite solid solutions were characterized in this study. Two samples (labeled as **S1** and