Available online at www.sciencedirect.com
SCIENCE DIRECT®
ELSEVIER
Journal of Magnetism and Magnetic Materials 284 (2004) 92–96
Journal of magnetism and magnetic materials
www.elsevier.com/locate/jmmm

Neutron diffraction study of the magnetic ordering of jamesonite ($FePb_4Sb_6S_{14}$)

Philippe Léone[a,*], Gilles André[b], Charlotte Doussier[a], Yves Moëlo[a]

[a] *Laboratoire de Chimie des Solides, Institut des Matériaux Jean Rouxel, UMR 6502 CNRS-Université de Nantes, 2 rue de la Houssinière, BP 32229, 44322 Nantes cedex 03, France*

[b] *Laboratoire Léon Brillouin, CEA-CNRS, CEA-Saclay, 91191 Gif-s-Yvette cedex, France*

Received 5 May 2004; received in revised form 11 June 2004
Available online 10 July 2004

Abstract

Jamesonite, $Fe^{2+}Pb_4Sb_6S_{14}$, is a natural sulfide in which Fe octahedra form single chains, that would favor a quasi-one-dimensional magnetism. The susceptibility shows an antiferromagnetic behavior with a broad maximum at 30 K and an irregularity at 5 K. A neutron powder diffraction study has been undertaken between 1.4 and 44 K. In the diffractograms, below 5 K, supplementary peaks of magnetic origin and characteristic of a three-dimensional long-range magnetic ordering appear. The magnetic structure corresponds to a canted antiferromagnet with a propagation wave-vector $k = [0.5, 0, 0]$ and a magnetic ordered magnetic moment on Fe atoms of 3.3(1) μB at 1.4 K. Below 30 K one-dimensional magnetic ordering or correlations are visible in the diagrams and persist down to 1.4 K.

PACS: 75.25. +z

Keywords: Jamesonite; Sulfide; Iron; Neutron diffraction; Magnetic structure

1. Introduction

Jamesonite, $Fe^{2+}Pb_4Sb_6S_{14}$, is a natural sulfide in which Fe octahedra form single chains parallel to *a* axis, 12.3, 15.7 and 19.1 Å apart (Fig. 1), that would favor a quasi-one-dimensional magnetism. The crystal structure was first determined and refined by Niizeki and Buerger [1]. Two new determinations were performed recently [2,3]. We showed that natural jamesonite exhibits an antiferromagnetic behavior with a broad maximum of susceptibility at 30 K and an irregularity at 5 K (Fig. 2) [2]. Expecting an $S = 2$ Haldane system compound, Matshushita and Ueda [3] synthetized jamesonite and fitted susceptibility versus temperature curve as an $S = 2$ 1D-HAF system. To

*Corresponding author. Tel.: +33-2-40-37-39-34; fax: +33-2-40-37-39-95
E-mail address: Philippe.Leone@cnrs-imn.fr (P. Léone).

0304-8853/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jmmm.2004.06.031

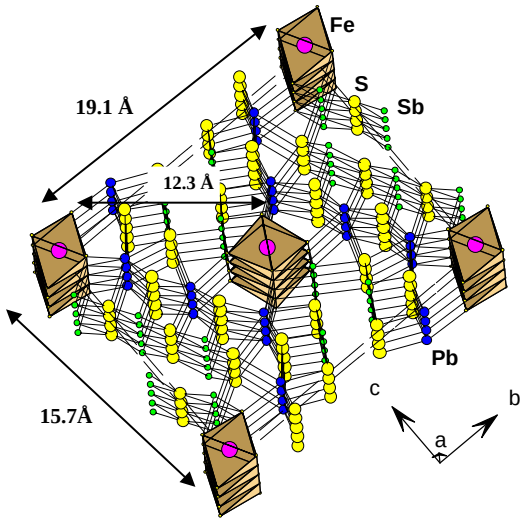

Fig. 1. Crystal structure of jamesonite.

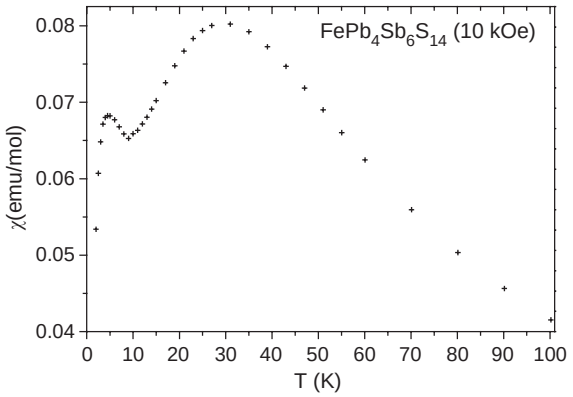

Fig. 2. Jamesonite single crystal susceptibility versus temperature.

elucidate this magnetic behavior and determine the magnetic structure of natural jamesonite, we have undertaken a powder neutron diffraction study in function of temperature.

2. Experimental

The sample comes from an unknown deposit in Siberia; it forms massive group of parallel fibres, up to several cubic centimetres in volume, with very high mineralogical purity [2]. The neutron diffraction experiments were performed at the Laboratoire Léon Brillouin (CEA-CNRS in Saclay) using the G4.2 and G4.1 diffractometers. The high-resolution powder diffractometer G4.2 ($\lambda = 2.343$ Å) was used for the refinement of the nuclear structure at 300 K and the high-flux multi-detector (800 cells) G4.1 ($\lambda = 2.4266$ Å) for the determination of the magnetic structure and the thermal evolution of the low temperature patterns. Ten diagrams were collected between 1.4 K and 44 K in the 2θ range 7–86.9°. The powder sample was set in a cylindrical vanadium can and held in a liquid helium cryostat. Nuclear and magnetic structures were refined using the Rietveld-type [4] fullprof [5] program. The nuclear scattering lengths and iron magnetic form factor were those included in this program.

3. Results

3.1. Neutron diffraction

The neutron diffraction pattern recorded at 300 K on G4.2 fully confirms the known jamesonite structure: monoclinic symmetry, space group $P\ 2_1/c$ (N° 14); cell parameters $a = 4.034$ Å, $b = 19.081$ Å, $c = 15.710$ Å and $\beta = 91.80°$; $Z = 2$. Iron atoms occupy only one Wyckoff site of multiplicity two: $2b$.

The pattern recorded at 44 K on G4.1 is characteristic for the only nuclear scattering with slightly smaller parameters $a = 4.011$ Å, $b = 19.081$ Å, $c = 15.704$ Å and $\beta = 91.70°$.

Fig. 3 shows neutron diffraction patterns collected at 1.4, 6 and 44 K. A series of extra peaks is present at 1.4 K corresponding to the three-dimensional (3D) long-range magnetic ordering of the iron magnetic moments. These magnetic peaks can be indexed in doubling the a parameter of the crystal cell. These extra peaks have disappeared at 6 K. Moreover at around $2\theta = 17°$, corresponding to the nuclear peak (0 2 1), the background of all neutron diagrams exhibits a step which disappears at around 30 K.

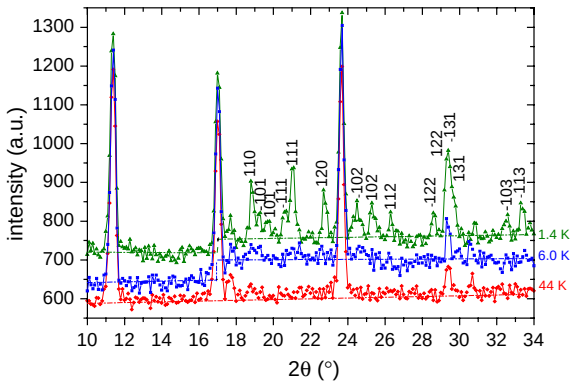

Fig. 3. Part of the neutron diffraction patterns of jamesonite at 1.4, 6.0 and 44 K. Relatively to the diagram at 6.0 K, those at 1.4 and 44 K have been shifted up and down, respectively.

3.2. Magnetic structure

In order to determine the magnetic structure, to limit the number of parameters, we used group theory. The calculation of the irreductible representations of the 'little' group is based in the subroutine ZAK provided with the program KAREP [6]. The basis vectors, which describe the possible couplings between the components of magnetic moment of the two iron equivalent crystallographic sites, were calculated with BasIreps program included in Fullprof program.

The character table for $P2_1/c$ group and $k=[0.5,0,0]$ wave-vector, and the decomposition into irreducibles representations for iron site are given in Table 1. There are, a priori, two possible magnetic structures associated with representations 'Γ_2' and 'Γ_4', being defined by three parameters. Basis vectors for these representations are given in Table 2. The best fit is observed for representation Γ_2. The magnetic reliability factor is 12.6% for the Γ_2 model against 32.0% for the Γ_4 one.

Magnetic moments and reliability factors of the best refinement at 1.4 K are included in Table 3. Fig. 4 shows observed, calculated and difference neutron diffraction patterns. Fig. 5 represents the magnetic structure at 1.4 K. The magnetic moment reaches 3.3(1) μ_B at 1.4 K. At 6 K, magnetic reflections have disappeared.

Table 1
Character table for $P2_1/c$ group, $k=[0.5,0,0]$, and decomposition into irreducible representations for the iron site

	E	2_y	i	m_y
Γ_1	1	1	1	1
$\Gamma 2$	1	1	−1	−1
Γ_3	1	−1	1	−1
Γ_4	1	−1	−1	1
Γ	6	0	−6	0

$\Gamma = 3\ \Gamma_2 + 3\ \Gamma_4$

Table 2
Basis vectors for Γ_2 and Γ_4 irreducible representations for the iron site

	M_x	M_y	M_z
Γ2	+ +	+ −	+ +
Γ4	+ −	+ +	+ −

4. Discussion

Contrary to the conclusions of Matsushita and Ueda [3], we have shown that the irregularity of susceptibility at 5 K is clearly due to a 3D long-range magnetic ordering of the iron magnetic moments of jamesonite. For $AgVP_2S_6$ ($S=1$) [7] and $MnCl_3$(bipy) ($S=2$) [8] no long-range magnetic ordering could be detected; on the other hand, like jamesonite, $CsNiCl_3$ ($S=1$) [9] and $CrCl_2$ ($S=2$) [10] show 3D ordering at low temperature.

Jamesonite is a canted antiferromagnet. Iron magnetic moments are mainly oriented along the a-axis. For two chains 12.3 Å apart, the coupling between M_x and M_z components are ferromagnetic, and between M_y components, antiferromagnetic. Fe^{2+} ions have a magnetic moment of 3.3(1) μ_B. Usually, the Fe^{2+} ion is expected to have a moment of approximately 4 μ_B. The difference between this value and the experimental results has been already observed for such a compound, as for example $CsNiCl_3$ [9].

The significative step observed around $2\theta=17^\circ$ in the neutron diffraction patterns background

Table 3
Magnetic moments of iron atoms and refinement reliability factors at 1.4 K

Atom	X	y	z	M_x	M_y	M_z	M (μ_B)
Fe1	0.5	0	0	2.8 (1)	1.5 (1)	−0.5 (2)	3.3 (1)
Fe2	0.5	0.5	0.5	2.8 (1)	−1.5 (1)	−0.5 (2)	3.3 (1)
Phase 1		Crystalline structure		$R_{Bragg} = 7.88$		$R_f = 4.59$	
Phase 2		Magnetic structure		$R_{magnetic} = 12.6$			

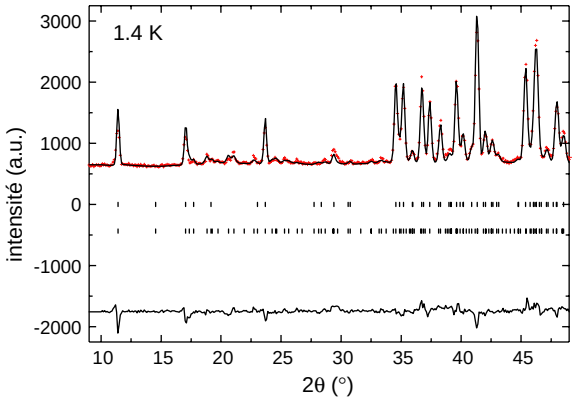

Fig. 4. Observed (cross), calculated (solid line) and difference (solid line at the bottom) neutron diffraction patterns at 1.4 K. The first series of Bragg reflexion markers corresponds to the nuclear structure, and the second series to the magnetic structure.

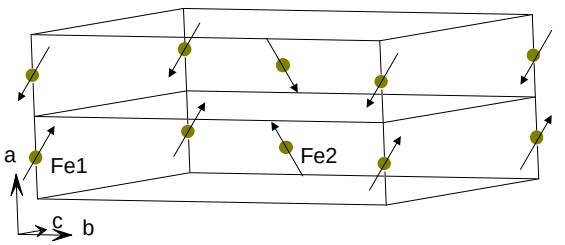

Fig. 5. Jamesonite magnetic structure.

below 30 K (Fig. 3) can be most probably attributed to a one dimensional (1D) magnetic ordering or correlations. At 1.4 K and up to 5 K, it is superposed upon the 3D long-range ordering. This 1D magnetic ordering disappears around 30 K, temperature at which is observed the broad maximum in the magnetic susceptibility curve. It can be suggested that the experimental observation of this 1D magnetic ordering is probably due to the magnetic ordering of the iron octahedra which form single chains in the structure (Fig. 1). Below 5 K a majority of these chains ordered three-dimensionally with the previously described magnetic structure. A few chains remain uncorrelated down to 1.4 K giving rise to this 1D magnetic signal. The coexistence below 5 K of these two types of magnetic ordering probably explains the smaller, 3.3 μ_B, than expected, 4 μ_B, iron maximum magnetic moment value.

Like jamesonite, berthierite, $FeSb_2S_4$, presents a crystal structure with 1D organization [11] in which iron octaedra form single chains parallel to the c-axis. The distances beetwen neighboring chains are smaller (6.19 Å), so the interactions are stronger leading to a 3D long range magnetic ordering at higher temperature ($T_N = 50$ K) [12]. The magnetic structure of berthierite is a spiral; the moments, 4.1 μ_B at 5 K, are in the (0 0 1) plane; no short range magnetic order was detected on neutron diagrams.

We intend to perform a neutron powder diffraction study of the Mn-isotype of jamesonite, benavidesite ($Mn^{2+}Pb_4Sb_6S_{14}$) [2], to compare its magnetic behavior with jamesonite one and to determine its magnetic structure.

References

[1] N. Niizeki, M.J. Buerger, Z. Kristallogr. 109 (1957) 161.
[2] P. Léone, L.M. Le Leuch, P. Palvadeau, P. Molinié, Y. Moëlo, Solid State Sci. 5 (2003) 771.
[3] Y. Matsushita, Y. Ueda, Inorg. Chemi. 42 (2003) 7830.
[4] H.M. Rietveld, J. Appl. Crystallogr. 2 (1969) 65.
[5] J. Rodriguez Carvajal, Abstracts of the Satellite Meeting of the XVth Congress of the International Union of Crystallography, Toulouse, 1990, p. 127.

[6] E.R. Hovestreydt, M.I. Arroyo, S. Slatter, H. Wonchatescheck, J. Appl. Crystallogr. 25 (1992) 544.
[7] C. Payen, H. Mutka, J.L. Soubeyroux, P. Molinié, P. Colombet, J. Magn. Magn. Mater. 104-107 (1992) 797.
[8] G.E. Granroth, M.W. Meisel, M. Chaparala, T. Jolicoeur, B.H. Ward, D.R. Talham, Phys. Rev. Lett. 77 (1996) 1616.
[9] V.J. Minkiewicz, D.E. Cox, G. Shirane, Solid State Commun 8 (1970) 1001.
[10] M. Hagiwara, K. Katsumata, J. Magn. Magn. Mater. 140–144 (1995) 1665.
[11] M.J. Buerger, T. Hahn, Am. Mineral. 40 (1955) 226.
[12] M. Winterberger, G. André, Physica B 162 (1990) 5.