IOPscience iopscience.iop.org

Home Search Collections Journals About Contact us My IOPscience

Low temperature magnetic structure of the quasi 1-dimensional magnet Ni_2SiO_4

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2009 J. Phys.: Conf. Ser. 145 012037

(http://iopscience.iop.org/1742-6596/145/1/012037)

View the table of contents for this issue, or go to the journal homepage for more

Download details:

IP Address: 93.180.53.211
This content was downloaded on 11/02/2014 at 10:30

Please note that terms and conditions apply.

Low temperature magnetic structure of the quasi 1-dimensional magnet Ni_2SiO_4

R H Colman[1], **T Fennell**[1,2], **C Ritter**[2], **G Lau**[3], **R J Cava**[3] **and A S Wills**[1]

[1]University College London, 20 Gordon Street, London, WC1H 0AJ, UK
[2]Institut Laue-Langevin, BP 156, 38042 Grenoble Cedex 9, France
[3]Princeton Materials Institute and Department of Chemistry, Princeton University, Princeton, New Jersey, USA

E-mail: `a.s.wills@ucl.ac.uk`

Abstract. Ni_2SiO_4, Liebenbergite, is an example of a quasi-one-dimensional magnet made up of frustrated corner sharing triangles of Ni^{2+} ($S = 1$) ions that propagate parallel to the b axis. Ni_2SiO_4 is isostructural with olivine, a common mineral of varying composition $Fe_{2-x}Mg_xSiO_4$, and is described in the orthorhombic space group *Pnma*. A synthetic polycrystalline sample of Ni_2SiO_4 was studied using powder neutron diffraction with spectra taken above and below the antiferromagnetic ordering transition ($T_N \approx 34\,K$). Analysis of the magnetic structure was carried out using the symmetry models of corepresentation theory. The refined spin structure evidences both ferromagnetic and antiferromagnetic inter-chain interactions, and ferromagnetic intra-chain coupling. The competition between the magnetic interactions can be seen in the canting of the moments away from a collinear arrangement.

Current theories of magnetism are challenged by highly correlated systems that show degeneracies and fluctuations. The characterisation of ground states of new model systems is an important step for testing and confirming predictions, and geometrically frustrated magnets provide important opportunity for this. A triangle of antiferromagnetically coupled spins is the archetypal example of a geometrically frustrated motif, due to the competing exchange interactions between the three moments. There are many ways to link these triangles into extended structures, with particular interest in those with low connectivity, such as the vertex-sharing triangular and tetrahedral geometries of the kagome [1] and pyrochlore [2] lattices.

The olivine family of minerals (XYO_4 where X = an M^{2+} transition metal ion and Y = a group III or group IV atom, most commonly Si) consist of a one dimensional array of metal ions which form zig-zag chains of corner-sharing triangles. In Ni_2SiO_4 there are two symmetry distinct metal sites: Ni(1) form linear chains of ions propagating parallel to the b-axis, and Ni(2) make up the apex of the triangles zig-zagging along the linear chains within the ab-plane (figure 1B). These metal sites are coordinated by an octahedra of oxygen, and the tetrahedral interstitial sites between the chains are occupied by group III or IV atoms (figure 1A). Preliminary inelastic powder neutron studies of this material showed it to behave like a quasi-one dimensional integer spin chain [3], with a spin gap below $T = 35\,K$ the transition temperature for magnetic order.[4]

Diffraction spectra from 15 g of Ni_2SiO_4 [4], were taken with the D1A powder neutron diffractometer at the ILL, both above and below the Néel transition using neutrons of wavelength $\lambda = 1.91$ Å. The sample temperature was controlled using a standard 'orange' cryostat and the

© 2009 IOP Publishing Ltd

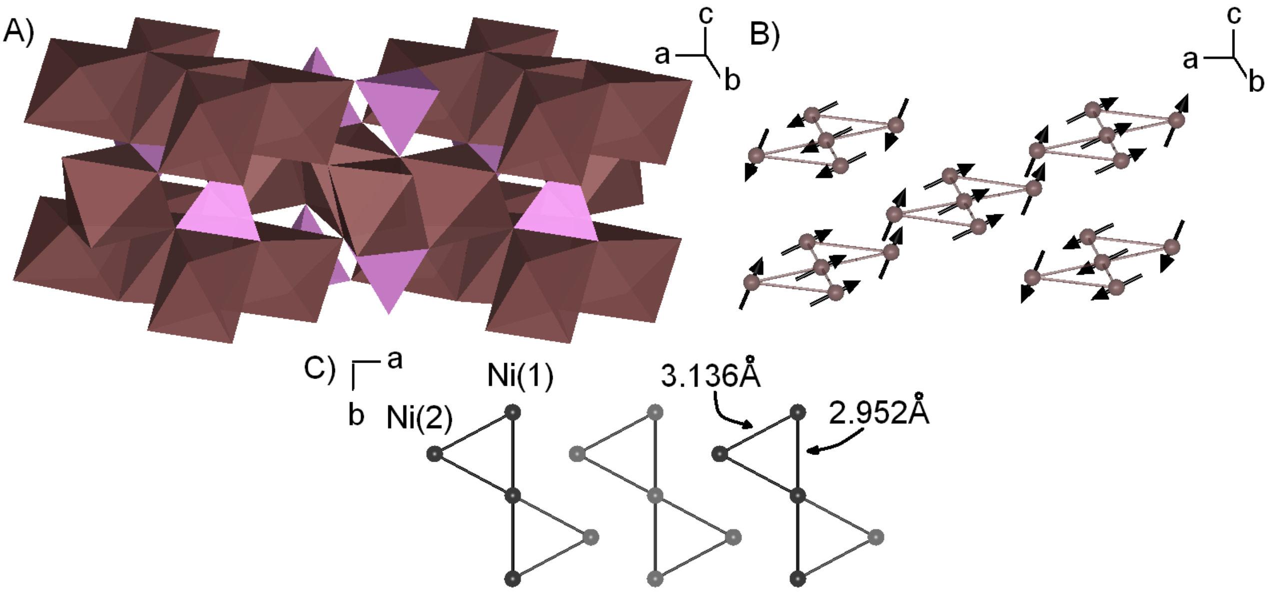

Figure 1. **A**: A polyhedral representation of Ni_2SiO_4 with NiO_6 displayed as dark edge-sharing octahedra and SiO_4 displayed as light tetrahedra occupying the interstitial sites between the chains; **B**: The magnetic structure of Ni_2SiO_4 refined from neutron diffraction data collected at 2 K and $\lambda = 1.91$ Å showing the zig-zag chain arrangement of corner sharing isosceles triangles of Ni^{2+} ions propagating along the b-axis; **C**: A view parallel to the b-axis giving the edge-lengths of the isosceles triangles formed from the Ni^{2+} ions (Generated using FPStudio [9]).

sample was contained within a vanadium can. Refinement of spectra collected at 39 K and 2 K was carried out using GSAS[5] together with the symmetry analysis program SARAh[6].

The refined nuclear structure of Ni_2SiO_4 at 39 K was consistent with previously published powder diffraction results [4] and the low temperature diffraction pattern contained new magnetic Bragg peaks that could be indexed with a magnetic propogation vector $\mathbf{k}_{24}$=$(\frac{1}{2}, 0, \frac{1}{2})$ in Kovalev's notation [7], also consistent with previously published results [11], although the refined magnetic structure was found to differ from that reported. The different symmetry-types of magnetic structure were determined using corepresentation analysis[12], an extension to the commonly used representational theory,[13] and the program SARAh [6]. Refinement of the magnetic structure was performed in terms of the basis vectors, ψ_ν, of a given irreducible corepresentation multiplied by a (weighting) coefficient, C_ν. In this formalism the set of refined moments, m_j, is generated from the linear combination of the basis vectors: $m_j = \sum_\nu C_\nu \psi_\nu$.

The data could only be well fitted using a corepresentation formed by the combination of the representations $\Gamma_3 \oplus \Gamma_7$ from Kovalev's tables (table 1) [7, 8]. It is notable that the 4 equivalent positions of each of the Ni crystallographic sites form distinct groups, or *orbits*, formed from positions (1+3) and (2+4) and the combination of these representations defines moment components on all of the symmetry related positions. The equivalence of these orbits prevents the sizes of the moments from being separately refined, and those moments of a given Ni site were constrained to be equal in magnitude. The refinement (figure 1C) was not improved by the presence of components parallel to the b-axis, and the moments of both the Ni(1) and Ni(2) sites were subsequently restricted to the ac-plane. The inter-chain couplings are shown to be antiferromagnetic along the $< -1\ 0\ 1 >$ direction, and ferromagnetic along the $< 1\ 0\ 1 >$ direction, with ferromagnetic interactions dominating between the intra-chain spins.

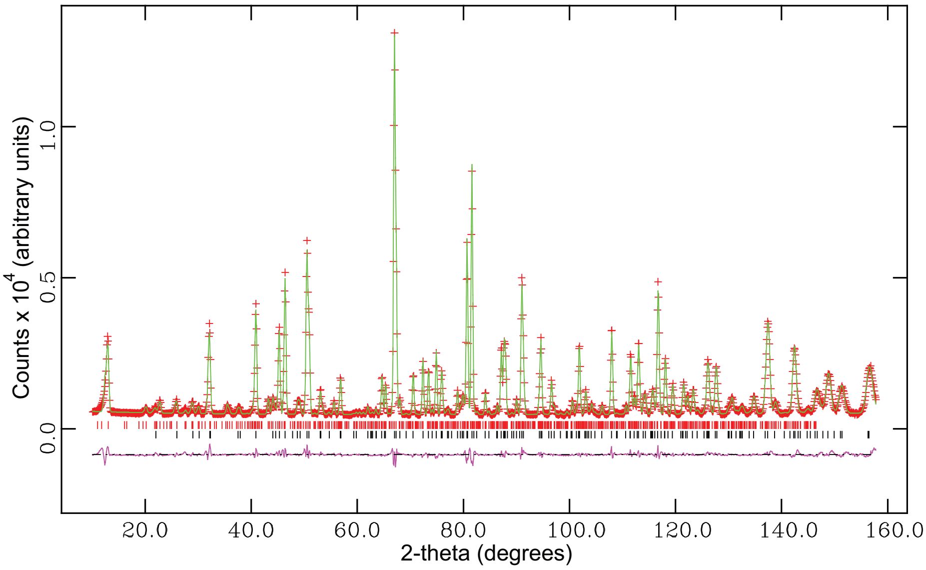

Figure 2. The observed and calculated neutron diffraction spectrum of Ni_2SiO_4 with nuclear and magnetic reflections, collected on D1A of the ILL at 2 K using neutrons of $\lambda = 1.91$ Å[10]. The crosses correspond to experimental data; the lines correspond to calculated values and the upper and lower tick-marks indicate the positions of the magnetic and crystallographic reflections respectively. Refined lattice parameters were $a = 10.114362(10)$ Å, $b = 5.912301(6)$ Å and $c = 4.729040(5)$ Å. The goodness of fit parameters were $\chi^2 = 12.52$ and $R_{wp} = 0.0461$ for 35 parameters.

The moments on the two sites form a non-collinear structure, with the canting of Ni(1) and Ni(2) moments away from the a-axis being 26.26° and 69.42° respectively. The moments of the Ni(1) and Ni(2) sites refined to 2.03(3) and 2.08(4) μ_B, respectively, in good agreement with expectations for $S = 1$ Ni^{2+}.

The refined structure differs from that previously reported in two respects.[11] Firstly, the refinement was significantly improved with the moments of the two crystallographically distinct Ni^{2+} sites were allowed to refine to different values. Secondly, symmetry analysis shows that Γ_1 and Γ_5 would need to be used to describe the previously reported structure, in contrast to Γ_3 and Γ_7 from our results. The differences in the diffraction pattern between these two structures are subtle but the fit to our data was noticeably worsened if the previously reported structure[11] was used to model the data. The subtle differences could easily have been masked by the resolution of the previously reported pattern along with the limited angular range reported, $5 \leq 2\theta(°) \leq 30$, in comparison to our high resolution data collected over the range $5 \leq 2\theta(°) \leq 160$.

In conclusion, we report a low temperature powder neutron diffraction study of Ni_2SiO_4, a quasi-1-dimensional magnet made up of zig-zagging chains of Ni^{2+} triangles. The magnetic structure reveals evidence of frustrated interactions with a significant canting away from collinearity. We note also that corepresentations are required to fully describe the symmetry of the spin configuration which is found to be subtlety different to that previously reported.

1. Acknowledgments

We would like to thank Clemens Ritter for his invaluable help with data collection and the EPSRC (grant number EP/C534654) for funding.

IR	BV	Atom	BV components					
			Ni(1)			Ni(2)		
			$m_{\parallel a}$	$m_{\parallel b}$	$m_{\parallel c}$	$m_{\parallel a}$	$m_{\parallel b}$	$m_{\parallel c}$
Γ_3	ψ_1	1	1	0	0	1	0	0
		2	0	0	0	0	0	0
		3	1	0	0	1	0	0
		4	0	0	0	0	0	0
	ψ_2	1	0	1	0	0	0	1
		2	0	0	0	0	0	0
		3	0	-1	0	0	0	1
		4	0	0	0	0	0	0
	ψ_3	1	0	0	1			
		2	0	0	0			
		3	0	0	1			
		4	0	0	0			
Γ_7	ψ_1	1	0	0	0	0	0	0
		2	1	0	0	-1	0	0
		3	0	0	0	0	0	0
		4	1	0	0	-1	0	0
	ψ_2	1	0	0	0	0	0	0
		2	0	-1	0	0	0	1
		3	0	0	0	0	0	0
		4	0	1	0	0	0	1
	ψ_3	1	0	0	0			
		2	0	0	-1			
		3	0	0	0			
		4	0	0	-1			

Table 1. Basis vectors for representations Γ_3 and Γ_7 of the space group *Pnma* with $\mathbf{k}_{24}$=$(\frac{1}{2}, 0, \frac{1}{2})$ following Kovalev's notation[7]. The equivalent positions of Ni(1) are defined according to 1: (0, 0, 0), 2: (.5, .5, .5), 3: (0, .5, 0), 4: (.5, 0, .5); and for Ni(2) according to 1: (.27404, .25, .99123), 2: (.77404, .25, .50877), 3: (.72596, .75, .00877), 4: (.22596, .75, .49123)

2. References

[1] Shores M P, Nytko, E A *et al.* 2005 *J. Am. Chem. Soc.*, **127**, 13462; Wills A S 2001 *Can. J. Phys.* **79** 1501; Wills A S, Depuis V *et al* 2000 *Phys. Rev. B* **62**, R9264; Frunzke J, Hansen T, *et al.* 2001 *J. Mater. Chem.* **11** 179

[2] Wills A S, Zhitomirsky M E *et al.* 2006 *J. Phys.:Condens. Matter.* **18** L37; Stewart J R, Ehlers G,*et al.* 2004 *J. Phys. : Condens. Matter.* **16** L1; Poole A, Wills A S, Leliévre-Berna E 2007 *J. Phys. Condens. Matter.* **19** 452201

[3] Haldane F D M 1983 *Phys. Rev. Lett.* **50** 1153

[4] Hagemann I S, Khalifah P G, Ramirez A P and Cava R J 200 *Phys. Rev* B **62** R771

[5] Larson A C, Von Dreele R B 2004 *General Structure Analysis System (GSAS)* (Los Alamos National Laboratory Report LAUR 86-748)

[6] Wills A S 2000 *Physica* B **276** 680, *program available from www.ccp14.ac.uk*

[7] Kovalev O V 1993 *Representations of the crystallographic space groups Ed.2* (Gordon and Breach Science Publishers, Switzerland)

[8] Davies Z L and Wills A S 2008 *J. Phys. Condens. Matter.* **20** 104232

[9] Chapon L C and Rodríguez-Carvajal J, *program available from www.ccp14.ac.uk*

[10] Larson A C and Von Dreel R B 1994 *Los Alamos National Laboratory Report* 86-748

[11] Newnham R, Santoro R, Fang J and Nomura S 1965 *Acta. Cryst.* **19** 147

[12] Wigner E P 1959 *Group Theory and its Application to the Quantum Mechanics of Atomic Spectra* (London: Academic)

[13] Wills A S 2001 *Phys. Rev* B **63** 064430; Bradley C. J. and Cracknell A. P., 1972 *The Mathematical Theory of Symmetry in Solids* (Clarendon Press, Oxford).