Low temperature magnetic structure of the quasi 1-dimensional magnet Ni₂SiO₄

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Abstract. Ni₂SiO₄, Liebenbergite, is an example of a quasi-one-dimensional magnet made up of frustrated corner sharing triangles of Ni²⁺ (S = 1) ions that propagate parallel to the b axis. Ni₂SiO₄ is isostructural with olivine, a common mineral of varying composition Fe₂₋ₓMgₓSiO₄, and is described in the orthorhombic space group Pnma. A synthetic polycrystalline sample of Ni₂SiO₄ was studied using powder neutron diffraction with spectra taken above and below the antiferromagnetic ordering transition (T_N ≈ 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 (XYO₄ where X = an M²⁺ 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 Ni₂SiO₄ 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 Ni₂SiO₄ [4], were taken with the D1A powder neutron diffractometer at the ILL, both above and below the Néel transition using neutrons of wavelength λ = 1.91 Å. The sample temperature was controlled using a standard ‘orange’ cryostat and the
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$_2$SiO$_4$ 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 propagation vector $k_{24}=(\frac{1}{2}, 0, \frac{1}{2})$ 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, $\psi_\nu$, of a given irreducible corepresentation multiplied by a (weighting) coefficient, $C_\nu$. 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$_2$SiO$_4$ 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) $\mu_B$, 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 $\Gamma_1$ and $\Gamma_5$ would need to be used to describe the previously reported structure, in contrast to $\Gamma_3$ and $\Gamma_7$ 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$_2$SiO$_4$, 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.

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IR BV Atom | BV components

| | Ni(1) | Ni(2) |
|---|---|---|
| | $m_{||a}$ | $m_{||b}$ | $m_{||c}$ | $m_{||a}$ | $m_{||b}$ | $m_{||c}$ |
| $\Gamma_3 \psi_1$ | 1 | 0 | 0 | 0 | 1 | 0 | 0 |
| 2 | 0 | 0 | 0 | 0 | 0 | 0 |
| 3 | 1 | 0 | 0 | 0 | 1 | 0 | 0 |
| 4 | 0 | 0 | 0 | 0 | 0 | 0 |
| $\psi_2$ | 1 | 1 | 0 | 0 | 0 | 1 |
| 2 | 0 | 0 | 0 | 0 | 0 |
| 3 | 0 | -1 | 0 | 0 | 0 | 1 |
| 4 | 0 | 0 | 0 | 0 | 0 | 0 |
| $\psi_3$ | 1 | 0 | 0 | 1 |
| 2 | 0 | 0 | 0 |
| 3 | 0 | 0 | 1 |
| 4 | 0 | 0 | 0 |
| $\Gamma_7 \psi_1$ | 1 | 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 |
| $\psi_2$ | 1 | 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 |
| $\psi_3$ | 1 | 0 | 0 | 0 |
| 2 | 0 | 0 | -1 |
| 3 | 0 | 0 | 0 |
| 4 | 0 | 0 | -1 |

Table 1. Basis vectors for representations $\Gamma_3$ and $\Gamma_7$ of the space group $Pnma$ with $k_{24} = (\frac{1}{2}, 0, \frac{1}{2})$ 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

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