Successive spin orderings of tungstate-bridged Li$_2$Ni(WO$_4$)$_2$ of spin 1

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1. Introduction

Low-dimensional and quantum magnetism has been an important topic since Haldane conjectured that a one-dimensional (1D) Heisenberg chain of integer spin has an exotic gapped ground state, while the non-integer spin systems are gapless [1]. In fact, the Haldane phase of an $S = 1$ chain has also been identified as a symmetry protected topological phase of long-range entangled quantum states [2]. The Haldane chain has often been described using the valence-bond-solid (VBS) model for integer spins [3], where a 1D spin liquid state implies that the spins remain quantum-disordered at $T = 0$ K and are separated from the excited states by a gap.

Several quasi-1D chain systems of $S = 1$ have been proposed to support the Haldane conjecture, such as, the organic Ni(C$_{2}$H$_{8}$N$_{2}$)$_{2}$NO$_{2}$ClO$_{4}$ (abbr. NENP) and the inorganic Y$_{2}$BaNiO$_{5}$ and Tl$_{2}$Ru$_{2}$O$_{7}$ [4–11]. Spin gap may also appear in the 1D systems due to dimerization caused by, e.g. Peierls or spin-Peierls effects and was observed in many compounds such as Li$_{2}$RuO$_{3}$ [12, 13], MoO$_{2}$ [14, 15], NaTiSi$_{2}$O$_{6}$ [16–18] and many others.

Zheludev et al clearly distinguished the $S = 1$ spin dynamics of Ni(C$_{6}$H$_{14}$N$_{3}$)$_{2}$Ni(PF$_{6}$)$_{2}$ (abbr. NDMAP) as a Haldane chain and of Ni(C$_{9}$H$_{24}$N$_{4}$)NO$_{2}$(ClO$_{4}$) (abbr. NTENP) as a dimer chain through neutron scattering studies [19, 20]. In contrast, an ideal Haldane chain system is...
difficult to find experimentally. Even if a spin gap is found in a quasi-1D integer spin chain system, it is not sufficient to claim the existence of a Haldane ground state, not to mention that the unavoidable weak interchain coupling produces a long-range ordering at sufficiently low temperatures. The Haldane gap has been suggested for a 1D $S = 1$ CsNiCl$_3$ spin chain system [21], but antiferromagnetic (AFM) long-range ordering below $T_N \sim 4.9$ K has also been found as a result of the weak interchain coupling [22]. A strong quadratic exchange interaction or interchain coupling has been proposed to close the Haldane gap in LiVGe$_2$O$_6$ [18, 23, 24]. In addition, even for the nearly ideal Haldane chain compound Y$_2$BaNiO$_5$, the existence of a non-Haldane or dimerization mechanism cannot be ruled out completely [10, 25].

Compounds with general formula Li$_2$TM(WO$_4$)$_2$, where TM is a transition metal ion have a 3D crystal structure composed of the TM$_6$ octahedra which are linked with pairs of the edge-shared inverted WO$_5$ pyramids, as shown in figure 1. The magnetic coupling between transition metal ions spins are expected to be corroborated by super–superexchange (SSE) interaction through tungstate-bridged indirect route of TM–O–W–O–TM. This makes, e.g. Li$_2$Co(WO$_4$)$_2$ a quasi one-dimensional system [26]. In this work, we report the magnetic properties of closely related system based on Ni and show using magnetic susceptibility, specific heat, and dielectric constant measurements that Li$_2$Ni(WO$_4$)$_2$ is as an interesting low-dimensional spin 1 system. It does not demonstrates the formation of the spin gap due to a sizeable interchain exchange, but there are three consecutive magnetic phase transitions (one is of short range and two are long-range order).

2. Experimental

Polycrystalline Li$_2$Ni(WO$_4$)$_2$ powder sample was prepared using mixtures of stoichiometric amounts of high purity (>99.95%) NiO, Li$_2$CO$_3$ and WO$_3$ via conventional solid-state reaction method. Following the preparation procedure reported by Alvarez-Vega et al [27] the homogenized mixture of oxides was heated to 550 °C and 650 °C for 24 h each with intermittent grinding and pelletizing, and the final annealing procedure was performed at 700 °C for 160 h in the air. Because of the low temperature reaction that is necessary to prevent Li losses and to prevent the sample from melting, a prolonged grinding and annealing procedure is necessary to eliminate the impurity phase completely. The phase purity and structure refinement have been examined and confirmed using powder diffraction with synchrotron x-rays of $\lambda = 0.619$ Å (NSRRC, Taiwan) at room temperature (RT). The neutron diffraction measurements were conducted at the Bragg Institute, ANSTO, using the high-resolution powder diffractometer Echidna ($\lambda = 1.6215$ Å) defined by Ge (3 3 5) crystals) for the crystalline structure analysis at low-temperature, 2 K (LT). Both dc and ac magnetic susceptibilities were measured using a SQUID-VSM magnetometer (Quantum Design, USA). The heat capacity was measured using a standard relaxation method with PPMS (Quantum Design, USA). For the dielectric and polarization measurements, the powder was first pressed into dense pellets and sintered at 600 °C for 24h. The sintered pellets are then polished into thickness of 0.4–0.5 mm. Silver paint was applied to both sides of the pellet as electrodes to form a parallel plate capacitor. We glued the sample on the
cryostat. Four low-loss coaxial cables connected the sample to a high-precision LCR meter (Agilent, E4980A). This so-called four-terminal pair configuration cancels out the mutual coupling between coaxial cables. Furthermore, the residual impedance of the whole circuit was excluded by using correction function of this LCR meter before the measurement, i.e., the impedance of the system with ‘empty’ capacitor and shorted samples were measured. The acquired residual impedance was automatically subtracted in later measurements and the LCR meter read the sample’s capacitance directly. We have tested our measurement system with commercial standard capacitors (1-100pF) with high accuracy. The dielectric permittivity (\(\varepsilon\)) and sample geometric parameters \(\varepsilon_0\) = \(Cd/\varepsilon_0\) where \(C\) is the capacitance, \(d\) is the thickness, \(A\) is the area of the sample, and \(\varepsilon_0\) is the permittivity of free space (8.85 \times 10^{-12} \text{ F m}^{-1}). The corresponding electric polarization was measured via a pyroelectric method. After cooling specimens in a static poling electric field of 300kV m^{-1}, the poling field was removed and short circuited for at least one hour to avoid possible trapped stray charges before measurement upon warming. Pyroelectric currents were measured at a rate of 4 K s^{-1}.

### 3. Parameters of calculations

The refined crystal structures for \(\text{Li}_2\text{Ni(WO}_4\text{)}_2\) at room-temperature (RT) and low-temperature (LT) phases are listed below in table 1, which were used for \textit{ab initio} band structure calculations. We applied the linearized muffin-tin orbitals method (LMTO) [28, 29] with the von Barth–Hedin exchange correlation potential. [30] The \(\text{W(6s, 6p, 5d), Ni(4s, 4p, 3d), O(2s, 2p)}\) and \(\text{Li(2s, 2p)}\) states were included to the basis set. The muffin-tin (MT) sphere radii were taken to be 2.30 a.u., 2.50 a.u., 1.60 a.u., and 2.78 a.u. for \(\text{W, Ni, O, and Li}\), respectively. The calculations were carried out taking into account the strong Coulomb interaction on the 3d-shell of \(\text{Ni}^{2+}\) ions within LSDA+U approximation [31], where onsite Coulomb repulsion parameter \(U = 8 \text{ eV}\) and Hund’s rule coupling parameter \(J_H = 0.9 \text{ eV}\) were applied [32, 33]. The Brillouin-zone (BZ) integration in the course of self-consistency iterations was performed over a mesh of 96 \(k\)-points in the full BZ.

The exchange constants were computed for the Heisenberg Hamiltonian, which is written in the following form of

\[ H = \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j \]  

where the summation runs twice over each pair of \(ij\). We utilized Green’s function method to compute exchange constants \(J_{ij}\), where one finds \(J_0\) as a second derivative of the total energy with respect to the small spin rotation [33, 34]. We used the supercell containing 8 magnetic \(\text{Ni}^{2+}\) ions to calculate the exchange integrals. The lowest total energy corresponds to the AFM structure, where local magnetic moments are ordered antiferromagnetically along Ni–Ni bond with lengths of 4.89 Å and 5.62 Å in the \(\text{ab}\) quasi-triangular plane and also along the \(c\)-axis.

### 4. Results and discussions

The double tungstate \(\text{Li}_2\text{Ni(WO}_4\text{)}_2\) crystal structure can be simplified as a 3D network of \(\text{NiO}_6\) octahedra connected by pairs of edge-shared inverted \(\text{WO}_3\) pyramids, as shown in figure 1(b). The symmetry is quite low, triclinic, and there are several different Ni–Ni distances for each coordination sphere, which will lead to a number of inequivalent exchange couplings. Figure 1(d) shows the Rietveld refinement of a synchrotron x-rays diffraction pattern of \(\text{Li}_2\text{Ni(WO}_4\text{)}_2\) taken at room temperature using the General Structure Analysis System (GSAS) software package. All diffraction peaks are fitted to a triclinic symmetry of space group \(\text{P1}\) satisfactorily and consistent with earlier report [27], as tabulated in table 1. The refinement result for data collected at 2 K was based on a neutron diffraction study, which is also shown in table 1.

The magnetic susceptibilities of \(\text{Li}_2\text{Ni(WO}_4\text{)}_2\) polycrystalline sample under an applied field of \(H = 1 \text{ T}\) as a function of temperature are shown in figure 2(a). No thermal hysteresis
is found between the measurements of the field-cooled and zero-field-cooled sequences within instrument resolution, and the ac-susceptibility measurement with $H_{ac} = 3$ Oe and frequencies of 10–750 Hz does not show frequency-dependence (not shown). The broad peak at $\sim 20$ K suggests a transition from the high-temperature paramagnetic (PM) state to a low-temperature antiferromagnetic (AFM)-like ordering, but the peak near 20 K is too broad for a typical 3D long-range AFM ordering. The low temperature enlarged view of $\chi(T)$ (inset of figure 2(a)) indicates that there are two small drops below the broad peak near 20 K, and the low temperature upturn below $\sim 5$ K could be coming from the PM contribution of the localized spins coming from impurities and defects. The first derivative of $\chi(T)$, $d(\chi(T))/dT$ as shown in figure 2(b), shows two peaks at $T_{N1} \sim 18$ K and $T_{N2} \sim 13$ K, which correspond to the two tiny drops in $\chi(T)$ below the broad peak near 20 K.

Based on $\chi(T)$ data alone, we can assign the features of $\chi(T)$ peak near 20 K and the $d(\chi(T))/dT$ peaks near $T_{N1}$ and $T_{N2}$ to AFM-like couplings of short and long range nature tentatively. While the $\chi(T)$ peak near 20 K is broad for a 3D AFM long range ordering, it could be due to a short range AFM ordering of low dimension. In addition, the peak of $d(\chi(T))/dT$ at $T_{N1} \sim 18$ K is relatively broader than that of $T_{N2}$, which strongly suggests that an actual magnetic ground state could exist only below $T_{N2} \sim 13$ K. For Li$_2$Ni(WO$_4$)$_2$ with Ni$^{2+}$ spins distributed unevenly along $a$-, $b$-, and $c$-directions of triclinic cell (see figure 1), it is reasonable to assume that this is the super-superexchange coupling between Ni$^{2+}$ spins, which is responsible for the formation of short-range (SRO) and 3D long-range orderings (LRO).

Judging from the small difference between lattice parameters (and thus the Ni–Ni distance) along the three crystalline axes, the consecutive phase transitions at low temperature must be closely related to the anisotropic magnetic couplings along the three crystal axes. The decrease of the spin susceptibility $\chi(T)$ at $T_{N2} \sim 13$ K indicates an AFM-like coupling. The spin structure below $T_{N2}$ has been described as antiferromagnetically coupled FM chains. Neutron powder diffraction study has confirmed the existence of a commensurate AFM long range ordering (LRO) below $T_{N2} \sim 13$ K. On the other hand, the spin structure between $T_{N1}$ and $T_{N2}$ remains to be solved, although it may be a LRO of incommensurate AFM type, similar to that proposed in the iso-structural Li$_2$Co(WO$_4$)$_2$ of $S = 3/2$ [26].

The $\chi(T)$ data above 100 K can be fitted with the Curie–Weiss law $\chi(T) = \chi_0 + C/(T - \Theta)$ and yields $\Theta = -27.04(4)$ K suggesting paramagnetism of antiferromagnetic couplings among the nearest neighbor spins, and the temperature-independent $\chi_0 = 5.73 \times 10^{-4}$ cm$^3$ mol$^{-1}$ is the sum of core diamagnetism and Van Vleck paramagnetism. The effective magnetic moment $\mu_{\text{eff}}$ calculated from the fitted Curie constant $C = 1.17(2)$ cm$^3$ K mol$^{-1}$ is 3.06 $\mu_B$, which is slightly larger than the theoretical spin-only value of 2.83 $\mu_B$ for Ni$^{2+}$ with $S = 1$, which suggests the anisotropic orbital contribution to the spin system [36].

The upturn of $\chi(T)$ at low temperature below $\sim 5$ K is reminiscent of a typical paramagnetic contribution from localized spins due to isolated impurities or defects as often observed in many different transition metal oxides, e.g. in TiOCl [37], Y$_2$BaNiO$_5$ [25], or Ba$_2$Mn$_2$O$_6$ [38]. Because of the existence of 3D long range AFM-like ordering as discussed above, and since the finite value of $\chi$ at the lowest temperature is unknown, the correction to the low temperature $\chi(T)$ data that contains PM contribution due to the isolated impurities cannot be estimated accurately. The overall behavior of the measured $\chi(T)$ data represents a series of phase transitions from a high-temperature paramagnetic state ($T \gg 20$ K), to a short-range AFM-like ordering near 20 K, and an incommensurate ($T_{N1} \sim 18$ K) to commensurate ($T_{N2} \sim 13$ K) AFM-like long range orderings in 3D are developed.

Figure 3 shows the temperature dependence of the specific heat ($C_p$) for Li$_2$Ni(WO$_4$)$_2$ measured at zero field. The $C_p$ reveals a sharp maximum at $T_{N2} \sim 13$ K and a $\lambda$-type anomaly at $T_{N1} \sim 18$ K, which are indicative of 3D long-range magnetic orderings and have also been reflected in the $d(\chi(T))/dT$ plot (figure 2(b)). The magnetic specific heat ($C_{\text{mag}}$) is obtained by subtracting the phonon contribution ($\beta T^3$) from $C_p/T = \alpha + \beta T$ as shown in figure 3(b). The magnetic entropy ($\Delta S_m$) can be obtained by integrating $C_{\text{mag}}/T$ over temperature as shown in the inset of figure 3(b). Because the entropy gained at $T_{N1}$ is as high as $\sim 49$% and saturates above $\sim 55$ K to the saturation value $\Delta S = R \ln(2S + 1) = 9.13 J \cdot mol^{-1} \cdot K^{-1}$ for Ni$^{2+}$ of $S = 1$, which implies that a reduced dimensionality is present. The significant amount of residual entropy that is released only well above $T_{N1}$ must be related to the short-range magnetic correlation at high temperatures, which is a characteristic feature of a lower-dimensional spin system and consistent to the observed crystal structure of quasi 2D nature [39]. At low-temperature below $T_{N2}$, the magnetic heat

![Figure 2](image-url)
capacity ($C_{\text{mag}}$) reveals a $T^3$-behavior that agrees with the spin-wave contribution of the antiferromagnetic magnon for a 3D antiferromagnet [40].

Li$_2$Ni(WO$_4$)$_2$ offers a rare opportunity to study the two-steps magnetic ordering of triangular-lattice antiferromagnet (TLAF) system via additional degree of freedom for symmetry breaking. Normally, the successive magnetic phase transitions often occur in equilateral TLAF system. Theoretically, it was predicted that two-step magnetic transition occurs in TLAF when the magnetic anisotropy is of the easy-axis type, while a single-step transition for TLAF with easy-plane anisotropy [41, 42]. In TLAF, $T_{N1}$ and $T_{N2}$ are associated with spin ordering of $c$-axis and $ab$ plane spin components, respectively. In the intermediate phase ($T_{N2} \leq T \leq T_{N1}$), one-third of the spins are aligned parallel to $c$ and the reminder are canted way from the $c$ with a canting angle $\theta$. The magnitude of intermediate phase is thus related to the ratio of easy-axis anisotropy to the intralayer exchange interaction, i.e. proportional to $(T_{N1} - T_{N2})/T_{N1}$ [41, 42]. Large intermediate phase is shown in Li$_2$Ni(WO$_4$)$_2$, i.e. $(T_{N1} - T_{N2})/T_{N1} \sim 0.28$, indicates that the easy-axis anisotropy is larger than the intralayer interaction, in contrast to the very narrow intermediate phase observed in Ba$_3$CoNb$_2$O$_9$ where $(T_{N1} - T_{N2})/T_{N1} \sim 0.19(T_{N1} \sim 1.39$ K and $T_{N2} \sim 1.13$ K), which indicates that easy-axis anisotropy is significantly smaller than the intralayer interaction [43].

Figure 4 depicts $C_p$ versus $T$ measured in several magnetic fields up to 8 T. Both the magnetic transition temperatures $T_{N2}$ and $T_{N1}$ are slightly shifted toward lower temperatures with increasing magnetic fields, as shown in the inset of figure 4. The shifting behavior of $T_{N1}$ and $T_{N2}$ is significantly different from the quasi-2D TLAF systems with easy-axis anisotropy, such as Rb$_2$Mn(MoO$_4$)$_3$ and Ba$_3$MnNb$_2$O$_9$ [44, 45], where $T_{N2}$ shifts to lower temperature but $T_{N1}$ shifts to higher temperature initially with increasing field. Instead, present $T_{N1}$ and $T_{N2}$ shifting behavior is similar to that of Ba$_3$CoNb$_2$O$_9$ as a 3D TLAF system with easy-axis anisotropy [43], as proposed theoretically by Plumer et al [46, 47]. Current observation of both $T_{N2}$ and $T_{N1}$ shift toward lower temperature with increasing field implies that Li$_2$Ni(WO$_4$)$_2$ responds to the impact of magnetic field via mostly electron-phonon coupling, instead of spin-only coupling mechanism, presumably with the help of a more flexible relative local distortion among Ni-O-W-O-Ni in 3D. In fact this unique property has also been reflected on the observed negative thermal expansion phenomenon recently [35].

Figure 5 shows the temperature dependence of dielectric constant ($\varepsilon_r$) at 100kHz with its derivative ($d\varepsilon_r/dT$) shown in the inset. Two anomalies are observed near $T_{N1}$ and $T_{N2}$ at zero magnetic field, which are concurrent with the long range AFM magnetic transitions. These anomalies are related to the emergence of local electric dipole moments [48]. In principle, the dielectric constant anomaly could be related to the changes of various order parameters, including structural phase transition (lattice), polarization (para-ferro or para-antiferro electric transition), magnetization (magnetic phase transition via magneto-electric coupling) [49]. In multiferroic materials, more than one primary ferroic order parameters exhibit simultaneously.
We have measured pyroelectric current as a function of temperature, as shown in figure 5(b). It is found that the pyroelectric current is too weak to substantiate a detectable remnant polarization, i.e. Li$_2$Ni(WO$_4$)$_2$ cannot be categorized as a multiferroic material. Since the low-temperature diffraction data do not indicate any structural transition down to 2 K [35], it is consistent to the missing symmetry breaking as a result of electric dipole formation with concomitant magnetophonon coupling. On the other hand, a negative thermal expansion is observed below $T_{N2}$, which seems to correlate to the larger $\epsilon_r$ drop as a result of weakened local dipoles. The dielectric anomaly near the magnetic phase transition is a common phenomenon and has been observed in several AFM systems such as MnO, BaNiF$_4$, BaMnF$_4$, and MnF$_2$, etc [50, 51]. It was argued by Seehra et al that the dielectric anomaly in MnO and MnF$_2$ is due to phenomenon of exchange striction-induced lattice change. The change in the lattice constant, i.e. negative thermal expansion found in Li$_2$Ni(WO$_4$)$_2$ could be responsible for the existence of dielectric anomalies near the magnetic orderings.

It has been puzzling to note that systems showing clear dielectric constant anomaly without polarization have also been observed in the rock salt structure compounds ACrO$_2$ (A = Li and Na) [48], whereas polarization was observed in the isostructural delafossite compounds TCrO$_2$ (T = Cu and Ag). While all these samples are having the same rhombohedral structure of space group $R 3 m$, the stacking pattern of O-A-O layers differs from each other. Neutron diffraction studies suggested that two magnetic modulation vectors $q_1 = (1/3, 1/3, 0)$ and $q_2 = (-2/3, 1/3, 1/2)$ stack in alternation so that Cr$^{3+}$ layer with opposite spin chirality were observed in LiCrO$_2$ [52], on the other hand, the alternate stacking of opposite chirality layers, $q_2$, have not been observed in delafossite compounds TCrO$_2$ (T = Cu and Ag) [53, 54]. At current stage, it is difficult to conclude the existence of (anti)ferroelectric phase in Li$_2$Ni(WO$_4$)$_2$ without using single crystal sample for detailed spin dynamic measurements.

![Figure 5.](image)

**Figure 5.** The temperature dependence of the dielectric constant ($\epsilon_r$) under an applied frequency 100kHz in Li$_2$Ni(WO$_4$)$_2$. Upper inset: The first order derivative of the $\epsilon_r$ as a function of temperature. Lower inset: The temperature dependence of pyroelectric current.

5. *Ab initio* calculations

According to the present LSDA+$U$ calculations Li$_2$Ni(WO$_4$)$_2$ is an insulator with an energy gap $E_g \sim 2.7$ eV as seen from figure 6, where the partial densities of states (DOS) are presented. The top of the valence band is formed by Ni-3$d$ and O-2$p$ states, while the bottom of the conduction band is mostly of Ni-3$d$ character. The width of the valence band is quite large about $\sim$6.5 eV. The Ni $e_g$ orbitals are nondegenerate. The crystal field splitting between two $e_g$ orbitals is about 0.1 eV as obtained from the auxiliary LDA calculations. The magnetic moment of Ni$^{2+}$ ion was found to be $\pm 1.77 \mu_B$, this value corresponds to the high spin (HS) state $S = 1$ configuration and indicates strong hybridization between Ni-3$d$ and O-2$p$ states.

The calculated exchange coupling parameters of Li$_2$Ni(WO$_4$)$_2$ are presented in table 2. The strongest exchange coupling $J_3$ does not correspond to the shortest Ni–Ni bond length. Other values of the exchange integrals between the next nearest-neighbour Ni–Ni ions were not included in the table 2 because they are negligibly small. We can use the values of $J_1$, $J_3$, and $J_5$ to estimate the Weiss temperature as $\Theta = J_5 \sum_{J_i} S_i(S_i + 1)$ for Ni$^{2+}$ ion with $S = 1$ and find that $\Theta = -33.3 K$, which agrees reasonably with the experimental estimation of $\Theta = -27 K$ from the Curie-Weiss law fitting.

The topology of the exchange interaction in Li$_2$Ni(WO$_4$)$_2$ is similar to that of Li$_2$Co(WO$_4$)$_2$ [26]. Crystal structure of Li$_2$Ni(WO$_4$)$_2$ is somewhat different from that of Li$_2$Co(WO$_4$)$_2$. This is due to slightly larger ionic radius of Co$^{3+}$ (HS 0.745 Å vs 0.722 Å for Ni$^{2+}$).
orbitals $K$ and $K$. $K$ and $\sim 13 T$ undergo a two-step magnetic transition, and the Weiss temperature is approximately twice as large as $J_1$ and $J_3$ and the system Li$_2$Ni(WO$_4$)$_2$ could be considered as a set of coupled spin chains running along the $J_3$ direction. This exchange interaction is also super-superexchange, which occurs between the half-filled $2z^2 - r^2$ orbitals of Ni ions and goes through O-2$p$ and W-6$s$ states. Although Ni$^{2+}$ and Co$^{2+}$ have integer and half-integer spins, respectively, the magnetic behavior is very similar. Both systems undergo a two-step magnetic transition, and the Weiss temperature is practically the same; $\Theta = -27 K$. On the other hand, the transition temperatures of Li$_2$Ni(WO$_4$)$_2$ ($T_N 1 \sim 18 K$ and $T_N 2 \sim 13 K$) are higher than those of Li$_2$Co(WO$_4$)$_2$ ($T_N 1 \sim 9 K$ and $T_N 2 \sim 7 K$). Indeed, the absolute values of the exchange interaction parameters obtained from \textit{ab initio} calculations for Li$_2$Ni(WO$_4$)$_2$ are $\sim 2$ times larger than those of Li$_2$Co(WO$_4$)$_2$.

Another interesting feature is that the strongest exchange $J_3$ of Li$_2$Co(WO$_4$)$_2$ is twice as large as $J_2$, and $J_3$ is twice as large as $J_1$ in turn, which implies that Li$_2$Co(WO$_4$)$_2$ could be considered as a set of more weakly coupled 1D chains (as opposed to Ni counterpart). On the other hand, Li$_2$Ni(WO$_4$)$_2$ shows the strongest exchange $J_2$ being twice as large as $J_1$, but $J_3$ is nearly equal to $J_1$, which may explain why Li$_2$Ni(WO$_4$)$_2$ shows higher Néel temperatures comparing to those of Li$_2$Co(WO$_4$)$_2$. The obtained $J$ values are in a good agreement with SSE interaction parameters proposed by Whangbo \textit{et al} [55].

6. Conclusion

In summary, we have investigated the physical properties of spin 1 system Li$_2$Ni(WO$_4$)$_2$. It exhibits a short-range ordering at $\sim 20 K$ and develops into two successive long-range 3D antiferromagnetic orderings at $T_{N1} \sim 18 K$ and $T_{N2} \sim 13 K$. Dielectric anomalies are observed near the $T_{N1}$ and $T_{N2}$ indicate significant spin-phonon coupling. The magnetic entropy analysis of the specific heat measurement results shows that the short-range antiferromagnetic correlations are established well above $T_{N1}$, which suggests that Li$_2$Ni(WO$_4$)$_2$ could be viewed as a low dimensional spin system above $T_{N1}$.

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