Li$_2$ZnV$_3$O$_8$: a vanadium-based geometrically frustrated spinel system

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Abstract

We report the synthesis and characterization of Li$_2$ZnV$_3$O$_8$, which is a new Zn-doped LiV$_2$O$_4$ system containing only tetravalent vanadium. A Curie–Weiss susceptibility with a Curie–Weiss temperature of $\theta_{CW} = -214$ K suggests the presence of strong antiferromagnetic correlations in this system. We have observed a splitting between the zero-field cooled (ZFC) and field cooled (FC) susceptibility curves below 6 K. A peak is present in the ZFC curve around 3.5 K, suggestive of spin-freezing. Similarly, a broad hump is also seen in the inferred magnetic heat capacity around 9 K. The consequent entropy change is only about 8% of the value expected for an ordered $S = 1/2$ system. This reduction indicates the continued presence of large disorder in the system in spite of the large $\theta_{CW}$, which might result from strong geometric frustration in the system. We did not find any temperature $T$ dependence in our $^7$Li nuclear magnetic resonance shift down to 6 K (an abrupt change in the shift does take place below 6 K), though considerable $T$-dependence has been found in the literature for LiV$_2$O$_4$—undoped or with other Zn/Ti contents. Consistent with the above observation, the $^7$Li nuclear spin-lattice relaxation rate $1/T_1$ is relatively small and nearly $T$-independent, except for a small increase close to the freezing temperature which, once again, is small compared to undoped or 10% Zn or 20% Ti-doped LiV$_2$O$_4$.

Keywords: geometric frustration, B-site doped spinel, LiV$_2$O$_4$

(Some figures may appear in colour only in the online journal)

1. Introduction

Cubic spinel materials AB$_2$O$_4$ with non-magnetic ions at the A-site and magnetic ions at the B-site are interesting due to the existence of a geometrically frustrated [1, 2] B-sublattice (corner-shared tetrahedra) in them. Perhaps the most studied compound in this category is LiV$_2$O$_4$ which exhibits d-electron-derived, heavy Fermi liquid behavior [3–5]. In Villain’s work [6] LiV$_2$O$_4$, doped with a non-magnetic impurity at the V-site or with a magnetic impurity at the A-site, has been studied extensively [7–11]. Likewise, the structure of Na$_2$Ir$_3$O$_8$ or [Na$_{1.5}$(Na$_{0.25}$Ir$_{0.75}$)$_2$O$_3$]$_2$O$_3$ is also derived from the spinel structure [12]. Here, the Na$_{1.5}$ are at the A-sites, whereas Ir and Na at the B-sites have distinct positions and the Ir ions form corner-shared triangles in three dimensions. This has been dubbed the hyperkagome lattice, which is proposed to have a quantum spin liquid ground state.

Motivated by the above we have been searching for new $S = 1/2$ spinel systems which might exhibit interesting properties. Li$_2$ZnTi$_3$O$_8$ has the same space group as Na$_4$Ir$_3$O$_8$, i.e. $P4_332$; and Zn and Ti ions exist at distinct B-sites, hence the Ti ions form a hyperkagome lattice. This compound is unfortunately nonmagnetic due to the +4 oxidation state of the titanium. We therefore set out to prepare Li$_2$ZnV$_3$O$_8$, which would have a $^7$Li nuclear magnetic resonance shift down to 6 K (an abrupt change in the shift does take place below 6 K), though considerable $T$-dependence has been found in the literature for LiV$_2$O$_4$—undoped or with other Zn/Ti contents. Consistent with the above observation, the $^7$Li nuclear spin-lattice relaxation rate $1/T_1$ is relatively small and nearly $T$-independent, except for a small increase close to the freezing temperature which, once again, is small compared to undoped or 10% Zn or 20% Ti-doped LiV$_2$O$_4$.
The magnetic susceptibility of Li2ZnV3O8 is measured to be 99.99% purity, ZnO (Aldrich 99.99% purity), and VO2, pelletized it, and then fired it in a tubular furnace at 650°C for 28 h under a dynamical vacuum (better than 10−5 mbar) at 800°C for 24 h. In the next step we mixed Li2CO3 (Alpha Aesar 99.995% purity), ZnO (Aldrich 99.99% purity) and VO2, pelletized it, and then fired it in a tubular furnace at 650°C for 24 h. Then we prepared VO2 by mixing this V2O3 with VO2 in a 1:1 molar ratio, pelletizing and firing in a dynamical vacuum (better than 10−5 mbar) at 800°C for 24 h. In the next step we mixed Li2CO3 (Alpha Aesar 99.995% purity), ZnO (Aldrich 99.99% purity) and VO2, pelletized it, and then fired it in a tubular furnace at 650°C for 24 h. Then we prepared VO2 by mixing this V2O3 with VO2 in a 1:1 molar ratio, pelletizing and firing in a dynamical vacuum (better than 10−5 mbar).

Figure 1. Unit cell of Li2ZnV3O8. The Li+, Zn2+, V4+ and O2− ions are shown in indigo, blue, yellow and red, respectively. The B-sites form a corner-shared tetrahedral network but are shared by Li+ and Zn2+ ions.

2. Experimental details

Li2ZnV3O8 was prepared by standard solid state reaction methods. First we prepared V2O3 by reducing V2O5 (Aldrich—99.99%) in a hydrogen atmosphere at 650°C for 16 h. Then we prepared VO2 by mixing this V2O3 with VO2 in a 1:1 molar ratio, pelletizing and firing in a dynamical vacuum (better than 10−5 mbar) at 800°C for 24 h. In the next step we mixed Li2CO3 (Alpha Aesar 99.995% purity), ZnO (Aldrich 99.99% purity) and VO2, pelletized it, and then fired it in a tubular furnace at 650°C for 28 h under a dynamical vacuum (better than 10−5 mbar). X-ray diffraction (XRD) patterns were collected with a PANalytical x-ray diffractometer using Cu Kα radiation (λ = 1.54182 Å). The Rietveld refinement of the XRD pattern (see figure 1) was carried out using the ‘Fullprof’ [14] software. The lattice parameter was found to be 8.332 Å in the F d -3 m space group. The formula of Li2ZnV3O8 could be written in two different ways, [Li2(Zn0.25V0.75)2O4]2 or [(Li0.5Zn0.5(Li0.25V0.75)2O4]2. Out of the two possible site arrangements in Li2ZnV3O8, the second one is possibly the right site assignment since Zn is known to prefer the tetrahedral site in spinels [15]. In both these possibilities V is at the B-site. We refined the XRD data of Li2ZnV3O8 to determine the site occupation. The best refinement was obtained with the formula Li2(Zn0.25V0.75)2O4]2 which implies some Zn-deficiency at the A-site. The results of the refinements are shown in table 1 below. The goodness of the Rietveld refinement is defined by the following parameters. R_p = 19.6%, R_wp = 16.9%, R_exp = 5.30% and χ^2 = 11.3. There were some extra phases of Li2V2O5, Li3VO4 and VO2 present at the 1% level. The Rietveld refinement is done considering all four phases.
Using inductively coupled plasma-atomic emission spectroscopy we determined the ratio of lithium with zinc and vanadium. From this analysis we found the molar formula unit of the compound to be Li$_{1.98}$Zn$_{0.86}$V$_3$O$_8$. This result is consistent with our ‘Fullprof’ refinement since there we also found that zinc is deficient at the A-site.

In the structure of Li$_2$ZnV$_3$O$_8$ the B-sites (shared by Zn$^{2+}$ and V$^{4+}$ in the 1 : 3 ratio) form a corner-shared tetrahedral network (see figure 2). In the case of random/statistical occupations of 0.24 of the B-sites by Zn and V, there will be missing magnetic atoms in the triangular network. This disruption/dilution of the corner-shared tetrahedral network is likely to lead to a relieving of frustration, which might then lead to a spin-glass-like state at low temperature.

The temperature dependence of magnetization $M$ was measured in a 1 kOe magnetic field $H$ in the temperature range 2–300 K using a vibrating sample magnetometer attached with a Quantum Design Physical Property Measurement System (PPMS). The temperature dependence of heat capacity has also been measured in the temperature range 2–300 K using a vibrating sample magnetometry we determined the ratio of lithium with zinc and vanadium. From this analysis we found the molar formula unit of the compound to be Li$_{1.98}$Zn$_{0.86}$V$_3$O$_8$. This result is consistent with our ‘Fullprof’ refinement since there we also found that zinc is deficient at the A-site.

The heat capacity data of Li$_2$ZnV$_3$O$_8$ are shown in figure 5. We fit the data to 1/($\chi' - \chi_0$) = ($T - \theta_{CW}$)/$C$ in the range 190–300 K, where we took $\chi_0$ as the sum of the core diamagnetic susceptibilities for all the atoms in Li$_2$ZnV$_3$O$_8$ [16] and the Van–Vleck paramagnetic susceptibility $\chi_{VV} = 2.048 \times 10^{-4}$ cm$^3$/mole based on the vanadium-based $S = 1/2$ spinel compound Li$_2$V$_2$O$_4$ [17]. From the Curie constant obtained from the fit (0.30 cm$^3$ K/mole V$^{4+}$), the effective number of Bohr magnetons is found to be 1.55 which is slightly smaller than the value for a $S = 1/2$ system ($\mu_{eff} = 1.73$ $\mu_B$). Whereas no sharp anomaly is seen in the susceptibility data down to 2 K, a difference between the ZFC and FC susceptibilities is seen below about 6 K, suggestive of freezing of moments or glassy behavior. Such ZFC/FC bifurcation has been seen in Zn or Ti doped Li$_2$V$_2$O$_4$ at around the same temperature. The asymptotic Curie–Weiss temperature is large and negative ($\theta_{CW} \approx -214$ K), in comparison to the freezing temperature, indicating strong antiferromagnetic interactions. Note that the peak of the ZFC curve (at $T \sim 3.5$ K) is less than the temperature where the ZFC/FC bifurcation starts. The ZFC/FC split is possibly linked with the onset of spin-cluster formation; the peak of the ZFC curve indicates the freezing temperature ($T_1$). These anomalies point to the fact that the freezing phenomena might already set in above $T_1$. A similar kind of behavior has also been observed in Li$_{1-x}$Zn$_x$V$_2$O$_4$ (for $x \geq 0.8$ [13]) and in Li(V$_{1-y}$Ti$_y$)$_2$O$_4$ (for $y = 0.2$ [10]). The inherent geometric frustration of the spinel system coupled with the random occupation of the B-sites by magnetic V$^{4+}$ and nonmagnetic Li$^{+}$ is suggested to be responsible for the observed susceptibility behavior. Note that, in comparison, the $\theta_{CW}$ values for the Li(V$_{1-y}$Ti$_y$)$_2$O$_4$ ($y = 0.05 - 1$) system are less than 100 K [10]. In our ac susceptibility measurements as well, a hump-like anomaly was observed at 4 K in the real part of the susceptibility $\chi'$ (see figure 4). In the range of frequencies of the ac field considered by us (20–1000 Hz), no shift in the peak position of $\chi'$ was observed. This is different from the conventional spin-glass behavior observed in the Zn-doped (at A-site) Li$_{1-x}$Zn$_x$V$_2$O$_4$ [7]. This suggests that there exists some kind of spin freezing in this compound, though it is not conventional spin glass behavior.

The heat capacity data of Li$_2$ZnV$_3$O$_8$ are shown in figure 5. It is clear that no sign of long-range ordering is observed down to 2 K. At around 5 K a small hump is seen in the $C_p/T$ data, which changes slightly with the change in the magnetic field; however, this change of magnetic field is not due to the Schottky effect. This hump in the heat capacity data is close to the temperature where ZFC and FC curves are split in the $\chi(T)$ versus $T$ data. Since we do not have a suitable non-magnetic

| Atoms   | Co-ordinates | Occupancy |
|---------|--------------|-----------|
| Li1(8a) | 0.000 0.000 0.000 | 0.46      |
| Zn1(8a) | 0.000 0.000 0.000 | 0.43      |
| Li2(16d)| 0.625 0.625 0.625 | 0.24      |
| V(16d)  | 0.625 0.625 0.625 | 0.75      |
| O1(32e) | 0.594 0.594 0.594 | 1.00      |

![Figure 3](image-url)
analogue for this system we tried to extract the magnetic specific heat of Li2ZnV3O8 by subtracting the lattice contribution using a combination of Debye and Einstein heat capacities, $C_{\text{Debye}}$ and $C_{\text{Einstein}}$, respectively. In the $T$-range 27–125 K, the measured heat capacity $C_p$ could be fit with a combination of one Debye and two Einstein functions of the type given below, where the coefficient $C_\theta$ stands for the relative weight of the acoustic modes of vibration and the coefficients $C_\alpha$ and $C_\gamma$ are the relative weights of the optical modes of vibration.

\[
C_{\text{Debye}} = C_\theta \times 9 n R (T/\theta_\theta)^3 \int_0^{\theta_\theta/T} (x^4 e^x / (e^x - 1)^2) \, dx
\]

\[
C_{\text{Einstein}} = 3 n R \left[ \sum C_{\alpha} \times x_\alpha \times e^{x_\alpha} / (e^{x_\alpha} - 1)^2 \right], \quad x = \frac{\text{hv}_\alpha}{kT}
\]

In the above formula, $n$ is the number of atoms in the primitive cell, $k_B$ is the Boltzmann constant, $\theta_\theta$ is the relevant Debye temperature and $m$ is an index for an optical mode of vibration. In the Debye–Einstein model the total number of modes of vibration (acoustic plus optical) is equal to the total number of atoms in the primitive unit cell. For Li2ZnV3O8 this number is 14. In this model we have considered the ratio of the relative weights of acoustic modes and the sum of the different optical modes to be $1 : 2$ for $C_{\alpha}$ and $C_{\gamma}$ due to having two light atoms (lithium, oxygen) and two comparatively heavier atoms (vanadium and zinc) in this compound we considered two different optical modes of vibrations. The fit yields a Debye temperature of 157 K and Einstein temperatures of 293 K and 698 K with relative weights $C_\theta : C_\alpha : C_\gamma = 1 : 4.3 : 8.7$. Upon subtracting the lattice heat capacity with the above parameters, we obtain the magnetic contribution to the heat capacity $C_m(T)$. The entropy change ($\Delta S$) was calculated by integrating the $C_m/T$ data (see figure 5). The entropy change from about 25 K to 2 K is about 1.4 J K$^{-1}$ (calculated for one formula unit containing three V$^{4+}$ ions) which is about 8% of the value for an S = 1/2 system ($R ln (2S + 1)$), which indicates the presence of many degenerate low-energy states at low temperatures. The value of the entropy change in our system is within the range of values inferred for other doped Li2V2O4 systems [10]. This large reduction in the value of $\Delta S$ down to temperatures much lower than the Weiss temperature ($\theta_W$) is typical of disordered systems and a consequence of the presence of strong geometric frustration in Li2ZnV3O8. We observed a broad maximum in the $C_m(T)$ versus T data at 9 K. Although we have not observed any frequency dependence in the $\chi'$ susceptibility data, which is the main characteristic feature of canonical spin-glasses, the maximum of $C_m(T)$ is observed to be above the freezing temperature ($T_f$). At low $T$, in the range of 2–5 K $C_m(T)$ follows a power law ($C_m(T) = \gamma T^\alpha$) with $\gamma = 98.4$ mJK$^{-1}$mol$^{-1}$ and $\alpha = 1.24$ dependence with temperature. This is similar to what has been observed in other strongly correlated spin-glasses [10, 18]. All these facts tie together to point out that there might be some formation of a cluster-glass-like state in the system around 9 K which ultimately drives the system in the metastable frozen state below $T_f$.

We were unable to detect the NMR signal associated with the $^{51}$V nucleus of Li2ZnV3O8. This could be due to the fact that there is a strong, on-site, local moment which naturally couples well with its own nucleus. The fluctuations of this moment are very effective in causing a fast relaxation of the nuclear magnetization. This makes the detection of its NMR signal difficult. In Cs2CuCl4

3 Depending on the temperature range chosen for the fit, the inferred lattice heat capacity is a bit different. Also, since this system has a large $\theta_W$ (= $214$ K), entropy release might take place in a broad temperature range below about 200 K. Due to the large lattice contribution at high temperatures it is nearly impossible to accurately determine the magnetic contribution to the heat capacity in this range. Consequently, there is likely to be a significant uncertainty in the entropy change estimation.
The 7Li NMR linewidth increases with decreasing temperature, as shown in the inset of figure 6. Down to about 100 K, the full-width-at-half-maximum (FWHM) of the 7Li spectrum for Li2ZnV3O8 is similar to that for pristine LiV2O4 and also not much different from the other doped-LiV2O4 systems. With a decrease in temperature, the spectrum of Li2ZnV3O8 broadens at a significantly slower rate compared to LiV2O4 and the doped-LiV2O4 systems [11].

We now discuss the origin of the 7Li NMR linewidth in Li2ZnV3O8. There are two contributions to the NMR linewidth. The first one originates from the nuclear–nuclear dipolar interaction, while the second arises from the demagnetizing field due to the neighboring powder grains [21]. By using the Gaussian approximation we can write the 7Li linewidth (FWHM) as

\[ \Delta \approx 2.35 \sqrt{\langle \Delta \nu^2 \rangle + \left( B_{\text{g}} H_{\text{f}} / 2\pi \right)^2} \]  

(1)

where \( \langle \Delta \nu \rangle \) is the dipolar interaction term calculated from the internuclear interaction, \( \chi \nu \) is the volume susceptibility (\( \chi \nu = \chi_{\text{mud}} M, d = 4.134 \text{ g cm}^{-3} \) is the density and \( M = 360.09 \text{ g mol}^{-1} \) is the molar mass), \( \gamma/2\pi = 1654.6 \text{ Hz G}^{-1} \), \( H = 93954.3 \text{ Oe} \) and \( B \) is the fractional root-mean-square deviation of the local field from the applied field \( H \). The temperature independent dipolar contribution was calculated for

For Li2ZnV3O8, lithium \((L=3/2)\) is in the tetrahedral \((A\)-site\) and octahedral \((B\)-site\) environment with oxygen. At least at the tetrahedral sites (but also at the octahedral sites in the case of distortions) a non-zero electric field gradient quadrupolar splitting is expected. However, down to 4 K, we were able to irradiate the full spectrum. We have measured the recovery of the longitudinal 7Li nuclear magnetization \( M_t \) after a saturating comb and fitted it using the following stretched exponential function,

\[ 1 - M_t / M_s = A \times e^{-t/\tau^\beta} \]  

(2)

Here \( A \) stands for the amount of saturation and \( \beta \) denotes the stretching exponent. The systems which are driven into a spin-glass-like state possess a distribution of spin-lattice relaxation times due to different relaxation channels with different \( T_1 \). In these situations \( \beta \) is a measure for the width of the distribution.
systems, this is possibly the first compound where all the vanadium ions are in the $4^+$ oxidation state. Whereas the B-sites form a frustrated lattice, only 75% are occupied by V$^{4+}$ and the others have non-magnetic ions. A Curie–Weiss fit of the magnetic susceptibility data yields a Curie constant close to that expected for $S = 1/2$. The Curie–Weiss temperature $\theta_{CW} = -214$ K (greater than in the other LiV$_2$O$_4$ variants) is suggestive of antiferromagnetic correlation in the system. Spin freezing is observed below 6 K, similar to that in other LiV$_2$O$_4$ variants. The peak of the ZFC curve ($T \sim 3.5$ K) appears lower than the bifurcation point of the ZFC/FC curves ($T \sim 6$ K), indicating that with decreasing temperature there might be an onset of spin-cluster formation before the system is ultimately driven into the frozen state. In the heat capacity measurement an anomaly is seen around 9 K and the entropy change $\Delta S$ is only 8% of that expected for an ordered $S = 1/2$ system. This is likely due to the presence of strong geometric frustration in the system. We were unable to detect the NMR signal associated with the $^{51}$V nucleus of Li$_2$ZnV$_3$O$_8$ due to strong on-site local moment, so we worked with the $^7$Li nucleus. No temperature dependence of the $^7$Li NMR shift (except near the freezing temperature of 4 K) was observed, which might indicate a weak hyperfine coupling with the magnetic V$^{4+}$. The saturation recovery of the spin-lattice relaxation data has been fitted well using a stretched exponential function as might happen with a distribution of magnetic environments. In the temperature dependence of the spin-lattice relaxation rate we observed an increase close to the freezing temperature ($4$ K), though the magnitude of the anomaly close to the freezing temperature is 2-3 orders of magnitude smaller than for Li$_{1-x}$Zn$_x$V$_2$O$_4$ and Li(V$_{1-x}$Ti$_x$)$_2$O$_4$.

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Figure 8. The temperature dependence of the $^7$Li spin-lattice relaxation rate ($1/T_1$). The inset shows the variation of the stretching exponent $\beta$ with temperature.

This stretched exponential behavior of the saturation recovery of the spin-lattice relaxation data gives an indication of the presence of the local moments, although sensed very weakly through the window of the lithium nucleus. The $^7$Li NMR $1/T_1$ is nearly unchanged with temperature which is again surprising in light of the published data on pure and doped LiV$_2$O$_4$ (see figure 7 where the literature data are shown along with our data). We observed an increase in our $^7$Li NMR $1/T_1$ data for Li$_2$ZnV$_3$O$_8$ near the spin-glass/freezing temperature (4 K) and a small hump-like anomaly around 50 K (see figure 8). Likewise in the case of Li$_{1-x}$Zn$_x$V$_2$O$_4$ and Li(V$_{1-x}$Ti$_x$)$_2$O$_4$, an anomaly/peak in the $T$-dependence of $^7$Li NMR $1/T_1$ was seen near the spin-glass/freezing temperature. Note that the typical value of $^7$Li NMR $1/T_1$ data in Li$_2$ZnV$_3$O$_8$ ($\sim 8$ s$^{-1}$) is vastly smaller than in any of the other vanadium based spinels stated above. In $^7$Li NMR, the only indication of the presence of local moments in Li$_2$ZnV$_3$O$_8$ is in the temperature dependence of the linewidth and in the stretched exponential behavior in the spin-lattice relaxation.

Very recently $^7$Li NMR studies of a newly found valence-bond geometrically frustrated ($S = 1/2$) cluster magnet system (LiZn$_2$Mo$_3$O$_8$) with strong correlation ($\theta_{CW} \simeq -220$ K) between Mo$_3$O$_{13}$ clusters via oxygen bridges have been reported where no shift has been observed down to 4.2 K and an almost temperature-independent spin-lattice relaxation rate ($1/T_1$) of the order of 4 s$^{-1}$ has been observed for the main peak [23], which is similar to what we have seen in Li$_2$ZnV$_3$O$_8$.

4. Conclusion
In this work we have reported a new vanadium-based cubic spinel (AB$_2$O$_4$) system Li$_2$ZnV$_3$O$_8$, its preparation, crystal structure, magnetic properties, specific heat properties and NMR measurements. Among the B-site doped LiV$_2$O$_4$

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4 The small change in $\beta$ seen around 80 K might be an artifact related to the changing of cryogen from nitrogen to helium and the need to use a lower rf power at lower temperatures.
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