

Long-range antiferromagnetic order in the $S=1$ chain compound LiVGe_2O_6

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The phase transition in the compound LiVGe_2O_6 has been proposed as a unique example of a spin-Peierls transition in an $S=1$ antiferromagnetic chain. We report neutron- and x-ray-diffraction measurements of LiVGe_2O_6 above and below the phase transition at $T=24$ K. No evidence is seen for any structural distortion associated with the transition. The neutron results indicate that the low-temperature state is antiferromagnetic, driven by ferromagnetic interchain couplings.

The physics of one-dimensional (1D) spin systems has been a field of considerable theoretical and experimental interest in recent years. The enhanced importance of quantum fluctuations in these systems manifests itself in many exotic phenomena, two of which are the Haldane gap in integer spin chains and the spin-Peierls transition in 1D half-integer spin systems. Haldane predicted in 1983,¹ based on field-theoretical models, that Heisenberg, antiferromagnetic (AF), integer spin chains possess a spectrum of magnetic excitations in which lowest lying excited states are separated by a finite-energy gap from the ground state. This remarkable result contrasts the half-integer case where the excitation spectrum is gapless. However, in the presence of magnetoelastic coupling, the energy of 1D, AF, half-integer spin systems can be lowered by a dimerization of the uniform chains. The resulting alternating spin chains possess a gapped magnetic excitation spectrum separating a singlet ground state from the triplet of excited states. This structural phase transition, driven by gains in magnetic energy, from the uniform to dimerized spin chain is known as the spin-Peierls transition.²

Experimentally, the Haldane gap has been observed in numerous $S=1$ chain systems including CsNiCl_3 ,³ AgVP_2S_6 ,⁴ YBaNiO_5 ,⁵ $\text{Ni}(\text{C}_2\text{H}_8\text{N}_2)_2\text{NO}_2\text{ClO}_4$,⁶ and $\text{Ni}(\text{C}_3\text{H}_{10}\text{N}_2)_2\text{N}_3\text{ClO}_4$.⁷ The spin-Peierls transition has fewer experimental realizations most of which are organic, such as $\text{Cu}(\text{Au})\text{BDT}$ (Ref. 2) and $\text{MEM}(\text{TCNQ})_2$ (Ref. 2) with the only known inorganic example being CuGeO_3 .⁸ Recently, results were published on an $S=1$, chain material LiVGe_2O_6 (Ref. 9) which were interpreted as being a remarkable union of these two, seemingly unrelated, phenomena. Powder susceptibility measurements showed a rapid decrease on passing through a transition temperature of about 22 K reminiscent of the isotropic decrease in magnetization, associated with the opening of a singlet-triplet gap in the excitation spectrum, which accompanies a spin-Peierls transition.² However, the preexisting gapped excitation spectrum normally precludes the possibility of a spin-Peierls phase transition in integer spin chain systems. It was suggested⁹ that the Haldane gap was closed in LiVGe_2O_6 due to an anomalously large biquadratic exchange interaction and this now gapless integer spin chain system undergoes a spin-Peierls phase transition at $T=22$ K.⁹

However, very recent ⁷Li nuclear magnetic resonance (NMR) (Ref. 10) experiments produced results which

seemed to contradict this interpretation. These measurements indicated that the observed phase transition was not a spin-Peierls transition and that the low-temperature phase was antiferromagnetic in nature. Their results are also interpreted as being consistent with a discontinuous phase transition. In addition, these measurements suggest unusual behavior in the ordered phase including a gapped excitation spectrum with a gap $\Delta/k_B=83$ K,¹⁰ roughly twice the observed coupling constant $J/k_B\approx 45$ K,⁹ despite an anisotropy D/k_B of less than 20 K.⁹ The authors of this¹⁰ and a recent theory paper¹¹ discuss possible mechanisms for the low-temperature properties of LiVGe_2O_6 resulting from the splitting of the three t_{2g} orbitals which accommodate the two V^{3+} electrons. This splitting results from a small trigonal distortion⁹ and separates the d_{xz} orbital from the low-lying d_{xy} , d_{yz} doublet. Two scenarios are suggested, the first of which leads to a reduced intrachain coupling and subsequent enhancement of biquadratic and next-near-neighbor interactions.^{10,11} The second scenario leads to increased importance of orbital degrees of freedom¹⁰ and possible orbital ordering. However, until now, the precise nature of the ordered state was unclear.

To elucidate the nature of the low-temperature ordered state, we have performed temperature-dependent neutron-diffraction studies, and complementary x-ray-diffraction studies, above and below the transition temperature. These measurements indicate a commensurate, antiferromagnetic, long-range ordered low-temperature phase and provide no evidence for a structural distortion associated with the transition.

LiVGe_2O_6 crystallizes in a monoclinic unit cell with space group $P2_1/c$ and room-temperature lattice constants $a=9.863(4)$ Å, $b=8.763(2)$ Å, $c=5.409$ Å, and $\beta=108.21(1)^\circ$.⁹ The structure is composed of chains of edge sharing VO_6 octahedra which are connected by GeO_4 tetrahedra. Previous measurements^{9,10} have indicated that the V ions exist in a 3+ oxidation state with an effective $S=1$ magnetic moment.

Polycrystalline samples of LiVGe_2O_6 were prepared using a slightly different method than reported by Millet *et al.*⁹ Stoichiometric quantities of GeO_2 , Li_2O , V_2O_5 , and V metal were sealed in evacuated Pt tubes and heated for 2 days at 900 °C. The samples were single phase according to powder x-ray diffraction. To reproduce the magnetization results reported previously, a small amount of powder was

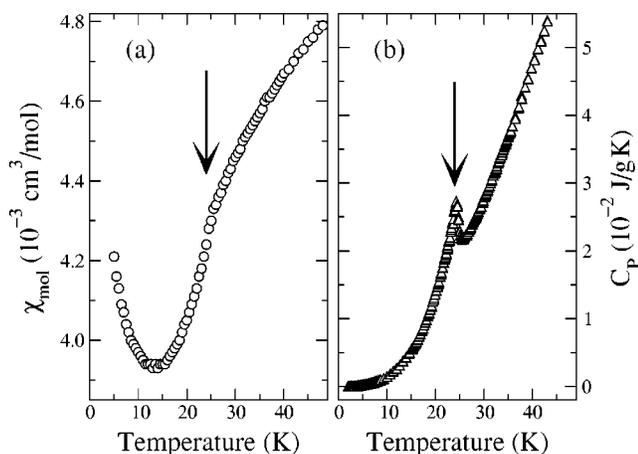


FIG. 1. dc molar susceptibility (a) and specific heat (b) as a function of temperature for temperatures in the vicinity of T_N . The dc magnetization was measured in an applied field of 2.5 kOe while the specific heat was a zero-field measurement. Both measurements clearly show the presence of a phase transition at a temperature of about 24 K indicated by the arrows.

loaded in a Quantum Design superconducting quantum interference device magnetometer and the dc magnetization was measured as a function of temperature in an applied magnetic field of 2.5 kOe; the magnetization varied linearly with H for fields up to 65 kOe. The results are shown in Fig. 1(a) for temperatures up to 50 K and clearly demonstrate the same rapid decrease in magnetization, below a transition temperature of about 24 K, reported previously.^{9,10} The Curie tail below 10 K corresponds to less than 40 ppm of 3d impurity content. In addition, specific heat measurements were performed on a 13.7 mg cold-pressed pellet of LiVGe_2O_6 using a commercial heat-pulse, Quantum Design calorimeter, the results of which are shown in Fig. 1(b). These results show a clear phase transition at a temperature of about 24 K, consistent with the magnetization results.

For the neutron-diffraction measurements, approximately 10 g of LiVGe_2O_6 powder was loaded in an aluminum sample can in the presence of He exchange gas and attached to the cold finger of a closed-cycle He refrigerator. The neutron-diffraction measurements were performed on the HB1 triple-axis spectrometer at the High Flux Isotope Reactor, Oak Ridge National Laboratory. Neutrons of wavelength 2.44 Å were selected using a pyrolytic graphite (PG) (002) monochromator crystal and elastically scattered neutrons were measured using a second PG (002) analyzer crystal. To prevent higher-order contamination, a graphite filter was placed in the incident beam. The intensity of diffracted neutrons was measured for scattering angles between 5° and 100° for temperatures of 50 and 11 K, well above and below the transition temperature, respectively.

The 50 K data was refined using Rietveld analysis and the observed pattern was found to be consistent with the previously determined crystal structure⁹ with low-temperature lattice constants of $a = 9.800$ Å, $b = 8.709$ Å, $c = 5.364$ Å, and $\beta = 108.21^\circ$.

A portion of the resulting diffraction pattern is shown in the two upper panels of Fig. 2 for temperatures of 11 and 50 K. We see clear, excess scattering at positions which can be described by Miller indices (110) and (001). These two re-

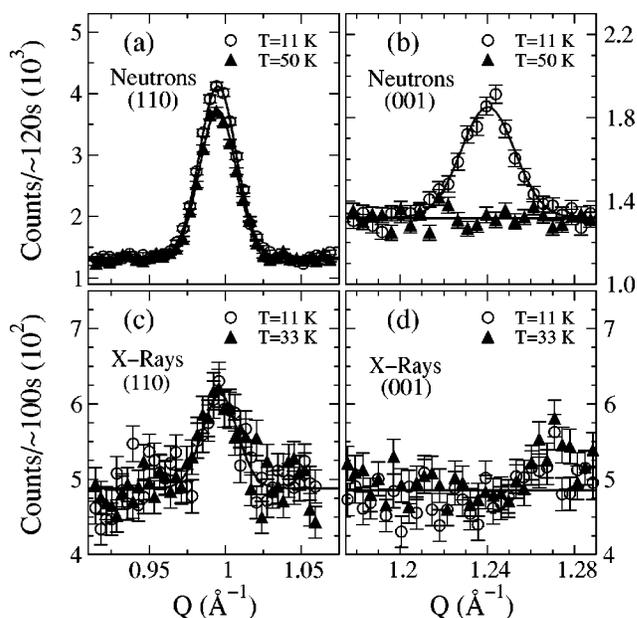


FIG. 2. The upper panels show powder neutron-diffraction data for the (110) and (001) reciprocal lattice positions at temperatures above and below T_N . The lower panels show identical scans performed using x-ray-diffraction techniques. The neutron-diffraction data indicate the presence of additional scattering below the transition temperature. The absence of excess scattering seen in the x-ray-diffraction results confirms the magnetic nature of the scattering.

flections were the most pronounced but other, weaker reflections were seen at (111) and (220) positions with possible reflections at $(\bar{1}\bar{1}1)$ and (020). No additional scattering was observed for reflections with scattering angles in excess of about 50°. This enhancement of the scattering at low angles is consistent with it being magnetic in origin.

To further confirm the magnetic nature of the scattering, the measurements were repeated using x-ray-diffraction techniques. Approximately 2 g of LiVGe_2O_6 powder was pressed into a pellet and loaded in a Be can in the presence of He exchange gas. This can was then connected to the cold finger of a closed-cycle He refrigerator and mounted in a Huber four-circle diffractometer. The incident radiation was $\text{Cu-K}\alpha$ x rays from an 18 kW rotating anode x-ray generator which were further monochromatized by Bragg reflection from a PG monochromator crystal. To allow comparison with the neutron-diffraction results, the intensity of diffracted x rays was measured for scattering angles between 5° and 70° at temperatures of 33 and 11 K, again above and below the transition temperature. The resulting data in the vicinity of the (110) and (001) reflections is shown in the lower two panels of Fig. 2. Clearly, no additional scattering is seen on passing through the transition temperature and, in fact, no excess scattering was observed at any angle. This further confirms the magnetic nature of the excess scattering observed in the neutron-diffraction experiment. This coupled with the resolution limited nature of the excess neutron intensity, indicates that the low-temperature phase is, in fact, a long-range ordered, commensurate magnetic state.

The temperature dependence of the (110) and (001) magnetic Bragg reflections was measured from 11 to about 40 K and the resulting data are shown in the upper panel of Fig. 3.

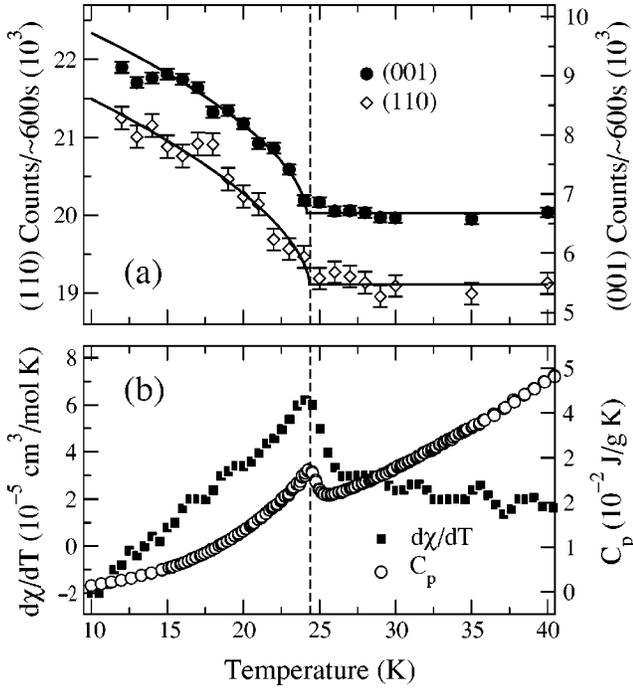


FIG. 3. The upper panel (a) shows the temperature dependence of the diffracted neutron intensity for the (001) and (110) magnetic Bragg reflections. The solid lines represent fits to a power law in the reduced temperature, $t = |T - T_N|/T_N$. For reference, the lower panel (b) shows the temperature derivative of the susceptibility and the specific heat. The dashed line represents the transition temperature (about 24 K). This clearly shows that the extra magnetic neutron scattering disappears upon passing through the transition temperature.

For reference, we have plotted the temperature derivative of the molar susceptibility and replotted the specific heat data in the lower panel of Fig. 3. The excess neutron intensity clearly disappears on passing through the transition temperature indicating its association with the phase transition. The temperature dependence can be well described by a power law in the reduced temperature suggestive of a continuous phase transition. In addition, no hysteresis has been observed in either the magnetization or the specific heat and, thus, in contrast to the NMR results,¹⁰ we conclude that the transition is continuous in nature. While we can rule out the possibility of the transition being strongly first order in nature, it is impossible to rule out a weakly first-order phase transition from the existing data.

Despite the small number of observed reflections, we have sufficient information to determine the spin arrangement in the ordered state. As all reflections can be indexed with integer indices, the magnetic unit cell is identical in size to the nuclear unit cell and, hence, contains four magnetic V^{3+} sites. The observed magnetic peak intensities, coupled with the absence of (100) and (010) reflections, are most consistent with the arrangement of spins shown in Fig. 4 where we have superimposed the spins on the known crystal structure. In comparing various magnetic structures, an analytical approximation for the V^{3+} magnetic form factor was employed.¹² The observed spin structure has spins aligned antiferromagnetically along the chain direction with ferromagnetic alignment between neighboring chains suggestive

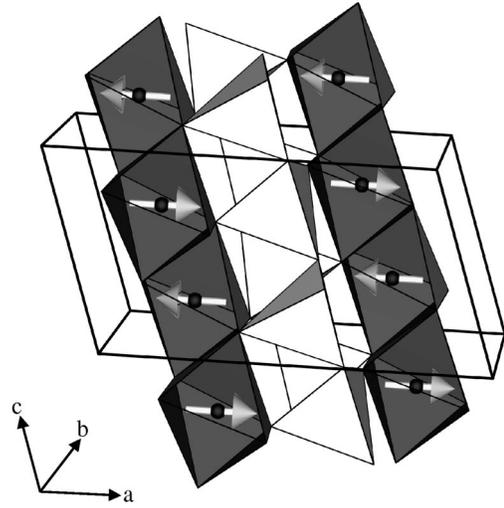


FIG. 4. The structure of LiVGe_2O_6 is shown for two neighboring chains of edge-sharing VO_6 octahedra together with the connecting GeO_4 tetrahedra. Superimposed on the VO_6 octahedra is the arrangement of spins determined from the powder neutron-diffraction data showing antiferromagnetic alignment along the chains and ferromagnetic alignment between chains. The spin direction could not be determined unambiguously due to insufficient data and the indicated directions are for demonstration purposes only.

of ferromagnetic interchain coupling. Unfortunately, the limited amount of data makes it impossible to uniquely determine the spin direction but the strength of the (001) reflection indicates a small spin component along that direction. By considering several plausible spin directions an ordered moment ($\mu = g\mu_B \langle S \rangle$) of $1.14(8)\mu_B$ was extracted. This is reduced from the expected value of $1.79\mu_B$ [for $g = 1.79$ (Ref. 9) and $\langle S \rangle = 1$] and this difference is likely due to the importance of quantum fluctuations in the low-dimensional system. In fact, the observed ordered moment is similar to that seen in other Haldane chain systems which order magnetically: CsNiCl_3 is found to possess an ordered moment of $1.05\mu_B$ (Ref. 13) and the set of systems $R\text{BaNiO}_5$, which if $R \neq Y$ order magnetically, display an ordered moment of about $1.1\mu_B$.¹⁴

The observed ordering in LiVGe_2O_6 is very simple and, as mentioned above, exhibits properties consistent with other Haldane chain systems which order magnetically due to significant interchain couplings. These interchain interactions are the likely cause of the phase transition in LiVGe_2O_6 and the parallel alignment of neighboring spin chains suggests that they are ferromagnetic in nature. The strength of the interchain coupling is estimated, using the Ginzberg-Landau theory of Scalapino, Imry, and Pinkus,¹⁵ to be $J_{\perp} \approx 1.4$ K (assuming $J_{\parallel} = 45$ K, four neighboring chains, and $T_N = 24$ K). These interchain interactions suggest that LiVGe_2O_6 is a quasi-1D system with $J_{\perp}/J_{\parallel} \approx 0.03$ (it is important to note that this mean-field calculation results in an underestimated value of J_{\perp}). We note that this lower bound on the value of J_{\perp}/J_{\parallel} lies just above the critical value of 0.026, determined using various theoretical techniques,¹⁶⁻¹⁸ above which long-range order is expected in a system of coupled $S = 1$ chains. The observed ratio of interchain to intrachain coupling may be slightly larger than expected

given the 1D nature of the crystal structure, but is very similar to that observed in the quasi-1D Haldane system CsNiCl_3 (Ref. 3) and certainly seems feasible. Clearly, both quantum chemistry calculations and further experiments are needed to investigate the actual magnitude of the interchain couplings in LiVGe_2O_6 .

We cannot rule out more exotic mechanisms for the ordering in this system and if the transition is discontinuous, as suggested by NMR studies, a simple ordering mediated by interchain coupling may be unlikely. However, of the theoretical ideas postulated to date, the notion of weakened intrachain coupling resulting from crystal-field splitting is particularly intriguing.^{10,11} Perhaps, in addition to enhancing interactions such as next-near-neighbor coupling or biquadratic exchange,^{10,11} this reduction of intrachain coupling also increases the relative strength of the interchain interactions leading to a rather conventional ordering phase transition. In other words, the weakened intrachain interaction

makes the system less one-dimensional. The mechanism involved in this phase transition clearly deserves further study and several properties, such as the large magnetic gap observed in the low-temperature phase¹⁰ remain unexplained.

In summary, we have performed neutron diffraction, and complimentary x-ray-diffraction, measurements on LiVGe_2O_6 and see clear evidence for simple, commensurate long-range antiferromagnetic order below a temperature of 24 K. In addition, we see no evidence for structural changes at this temperature. These results contradict the complicated picture of an $S=1$ spin-Peierls system originally proposed⁹ and seems to indicate surprisingly large interchain interactions.

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