Triplet dimerization crossover driven by magnetic frustration in In$_2$VO$_5$

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In$_2$VO$_5$, containing magnetically frustrated zigzag chains, shows a remarkable crossover at 120 K between paramagnetic states with positive (17 K) and negative (-70 K) Weiss temperatures. Magnetic moment and entropy data show that the V^{4+} $S=1/2$ spins condense into $S=1$ triplet dimers below the crossover. A further freezing of the antiferromagnetically coupled triplet dimers into a global singlet state is observed at 2.5 K, with no long range magnetic order down to 0.42 K and in fields up to 9 T. No structural V-V dimerization is observed by high-resolution synchrotron x-ray diffraction down to 10 K, but a subtle lattice anomaly evidences a spin-lattice coupling in the triplet dimer state. This is assigned to longitudinal oxygen displacement modes that reduce frustration within the chains and so couple to the spin dimer fluctuations.

PACS number(s): 75.10.Pq, 61.50.Ks, 75.30.Wx

I. INTRODUCTION

The properties of low dimensional quantum magnets have been studied extensively, in particular, the one-dimensional antiferromagnetic (AF) $S=1/2$ chain, for which the susceptibility has been calculated to very high accuracy.[1] The addition of a next nearest neighbor, frustrating, AF exchange interaction (J_2) produces an array of exotic instabilities and ground states; this model is realized by the zigzag chain shown in Fig. 1. The much studied case with J_1, $J_2>0$ (AF-AF) is unstable with respect to a singlet dimerized state with a spin gap when the ratio $\alpha=|J_2/J_1|>0.2411$,[2,3] as exemplified by the spin-Peierls material CuGeO$_3$.[4] The zigzag chain with ferromagnetic J_1 and antiferromagnetic J_2 (F-AF) couplings has been less studied; however, recent work has shed new light on the phase diagram and thermodynamics of this model. The ground state is reported to be ferromagnetic for $0 \leq \alpha \lesssim 1/4$ and an antiferromagnetic helix for $\alpha > 1/4$,[5–7] which has been realized in several materials containing $S=1/2$ Cu^{2+}.[8–10]

In this paper, we report magnetic susceptibility, resistivity, heat capacity, synchrotron powder x-ray, and powder neutron diffraction results for In$_2$VO$_5$. These reveal a spin dimerization instability in an F-AF $S=1/2$ zigzag chain. Below 120 K, In$_2$VO$_5$ behaves as an unfrustrated chain of antiferromagnetically coupled $S=1$ triplet dimers which show a further condensation into a global singlet ground state at 2.5 K. In$_2$VO$_5$ has an orthorhombic structure (space group *Pnma*) consisting of edge-sharing VO$_6$ chains along the **b** axis, separated by sheets of diamagnetic InO$_6$ octahedra.[11] Two recent theoretical papers investigated magnetic exchange in In$_2$VO$_5$ (Ref. 12) and reported contradictory results of frustrated antiferromagnetic or ferromagnetic exchange interactions, prompting the present experimental study.[13]

II. SAMPLE PREPARATION

A high purity sample of In$_2$VO$_5$ was prepared by grinding small single crystals, grown by the previously reported method.[11] Our samples are black, and resistivity measurements between 350 and 150 K (below which the sample resistance was too high to be measured) showed In$_2$VO$_5$ to be semiconducting with a 300 K resistivity of 3.2 Ω cm and a band gap of 170 meV.

III. MAGNETIC MEASUREMENTS

The magnetic susceptibility of In$_2$VO$_5$, measured with a Quantum Design magnetic property measurement system in a 150 Oe field, and the inverse susceptibility are shown in Fig. 2. Two distinct linear regions are seen in the inverse susceptibility with a crossover at 120 K. A Curie-Weiss fit in the range of 140–300 K gives a Weiss temperature of $\Theta = 17$ K, and a moment of $1.81\mu_B$, consistent with an $S = 1/2$ system with $g = 2.09$. Below 120 K, the Weiss tempera-
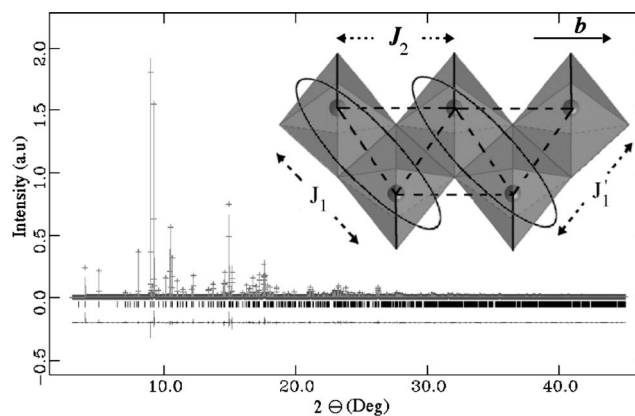

FIG. 1. Observed, calculated, and difference plots for the Rietveld fit to the synchrotron x-ray diffraction profile of In$_2$VO$_5$ at 10 K. The inset shows the zigzag chain arrangement of VO$_6$ octahedra with the magnetic exchange interactions and the triplet dimers formed below 120 K, as indicated. The short V-O bonds perpendicular to the chain direction are shown as solid lines.
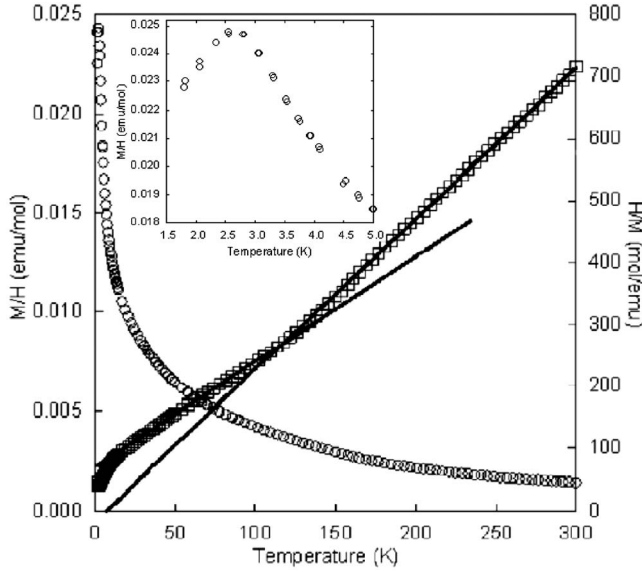
FIG. 2. Magnetic susceptibility of In_2VO_5 measured in a 150 Oe field and the inverse susceptibility with Curie-Weiss fits above and below the 120 K crossover shown. The inset shows the low temperature susceptibility maximum in zero field and field cooled measurements.

ture changes sign ($\Theta = -70$ K) and the paramagnetic moment increases to $2.2\mu_B$. A crossover between positive and negative Θ regimes is very unusual, and it could signify a transition at which the structure and hence the exchange pathways are significantly altered, but this is ruled out by the diffraction results below. Our alternative explanation, which is supported by the heat capacity measurements, is that the zigzag $S=1/2$ chains in In_2VO_5 undergo a crossover into a chain of triplet dimers, as shown in Fig. 1. This is a plausible ground state for the F-AF zigzag chain with $\alpha \sim 1$.[14] The paramagnetic moment of $2.1\mu_B$ calculated for the triplet ($S=1$) dimerized state, with $g=2.09$, is in good agreement with the observed value of $2.2\mu_B$ below the 120 K crossover.

IV. STRUCTURAL STUDIES

To determine whether In_2VO_5 undergoes a structural transition at 120 K, synchrotron powder x-ray diffraction data

were collected at temperatures of 10–280 K with wavelength $\lambda = 0.456\ 21$ Å, using the high-resolution instrument ID31 at the ESRF, Grenoble, and a 10 K neutron profile was also recorded using the Super-D2B diffractometer ($\lambda = 1.594$ Å) at the ILL, Grenoble. The data were fitted well by Rietveld refinements, starting from the previously reported 300 K *Pnma* structure[15] using the GSAS suite of programs.[16,17]

No superstructure is observed for In_2VO_5 between 10 and 280 K, and the coordinates from the combined x-ray and neutron refinement at 10 K (Table I) confirm that no gross structural transition (e.g., V-V dimerization) occurs. The lattice parameters are shown in Table II. The *a* and *c* parameters and the volume do not show a clear 120 K anomaly. However, *b* goes through a minimum at this temperature (Fig. 3), evidencing a coupling between the lattice and the magnetic crossovers. Within error, no significant change to the atomic coordinates, and hence to the bond angles that influence the exchange pathways, is observed around the 120 K crossover. The lattice microstrain parallel to *b*, $s_\parallel[010]$, which quantifies local variations in the axis length, is larger than the perpendicular component and increases on cooling below 300 K but then decreases at low temperatures [Fig. 3(b)]. This is consistent with a more highly correlated spin state if spin-lattice coupling is significant.

V. HEAT CAPACITY MEASUREMENTS

The heat capacities (C_p) of In_2VO_5 and the diamagnetic analog In_2TiO_5 were measured using a Quantum Design physical property measurement system and are plotted in Fig. 4. A C_p/T peak is seen at 5 K for In_2VO_5 and a broad feature is also observed around 120 K. The magnetic heat capacity of In_2VO_5 was estimated by subtracting the In_2TiO_5 data and the resulting $C_p(\text{mag})/T$ and magnetic entropy S_{mag} are also shown. Two magnetic entropy releases are observed. On warming up to ~ 100 K, the entropy tends toward the $1/2R \ln 3 \approx 4.5$ J/mol K value expected for 1/2 mole of $S=1$ dimers. Above 120 K, an additional contribution increases the total magnetic entropy to approximately the $R \ln 2 \approx 5.8$ J/mol K value for the monomeric $S=1/2$ state. Hence, the magnetic heat capacity variation for In_2VO_5 con-

TABLE I. Refined coordinates and components of the anisotropic thermal *U*-tensor (Å^2) from the combined x-ray and neutron refinement of the In_2VO_5 structure at 10 K in space group *Pnma*. Atoms In(1), V, O(1), O(2), and O(3) are at (x, 1/4, z), and In(2), O(4), and O(5) are at (x, 3/4, z).

| Atom	x	z	U_{11}	U_{22}	U_{33}	U_{13}
In(1)	0.0979(5)	0.08391(2)	0.0024(2)	0.0006(2)	0.0009(1)	−0.0015(1)
In(2)	0.32998(5)	0.23758(2)	0.0028(1)	0.0020(2)	0.0025(1)	−0.0019(1)
V	0.1096(1)	0.42345(6)	0.0023(3)	0.0026(4)	0.0027(3)	−0.0010(3)
O(1)	0.2406(4)	0.3224(2)	0.008(1)	0.006(2)	0.001(1)	0.000(1)
O(2)	0.3457(4)	0.4959(1)	0.004(1)	0.007(2)	0.001(1)	0.000(1)
O(3)	0.3699(3)	0.1504(2)	0.002(1)	0.003(2)	0.003(1)	−0.001(1)
O(4)	0.0602(3)	0.1770(2)	0.002(1)	0.003(2)	0.002(1)	0.000(1)
O(5)	0.0687(4)	0.4515(2)	0.008(2)	0.003(2)	0.006(1)	0.000(1)
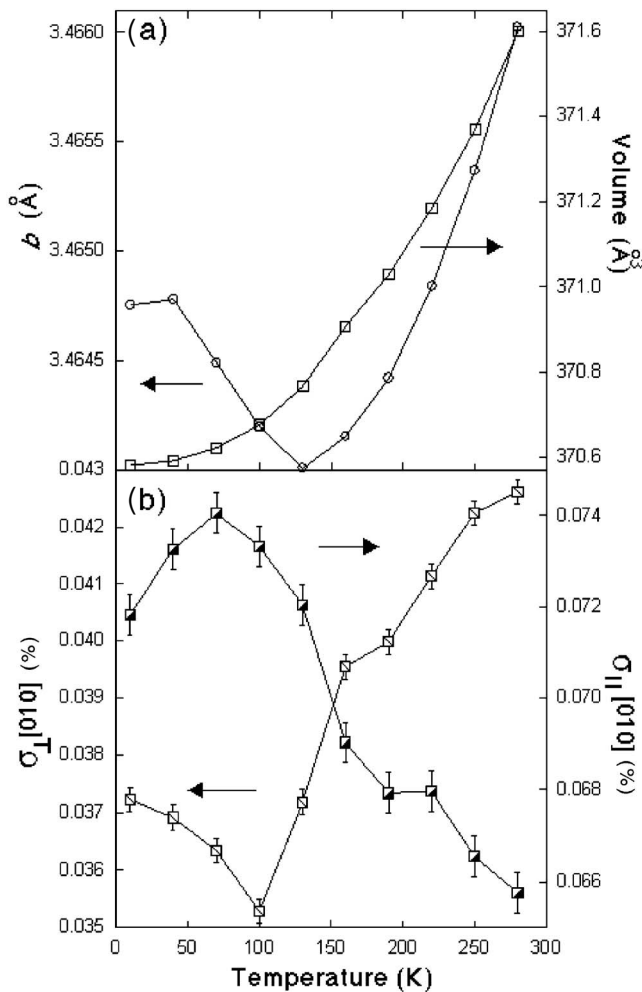
FIG. 3. Temperature evolution of (a) the **b**-axis length and cell volume and (b) the lattice microstrains parallel and perpendicular to [010] from the high-resolution synchrotron x-ray diffraction study of In_2VO_5.

firms the triplet dimerization model proposed above.

A separate magnetic freezing transition below 5 K is evidenced in the low temperature magnetic susceptibility and

TABLE II. Lattice parameters for In_2VO_5 at temperatures between 10 and 280 K.

| T (K)	a (Å)	b (Å)	c (Å)	Volume (Å^3)
10	7.2252(1)	3.46475(6)	14.8034(2)	370.583(1)
40	7.2252(1)	3.46478(6)	14.8038(2)	370.593(1)
70	7.2251(1)	3.46449(6)	14.8064(2)	370.623(1)
100	7.2253(1)	3.46420(6)	14.8094(2)	370.677(1)
130	7.2255(1)	3.46401(6)	14.8133(2)	370.767(1)
160	7.2260(1)	3.46415(6)	14.8173(2)	370.907(1)
190	7.2264(1)	3.46442(6)	14.8202(2)	371.029(1)
220	7.2271(1)	3.46484(6)	14.8233(2)	371.185(1)
250	7.2279(1)	3.46542(6)	14.8267(2)	371.370(1)
280	7.2291(1)	3.46602(6)	14.8307(2)	371.600(1)
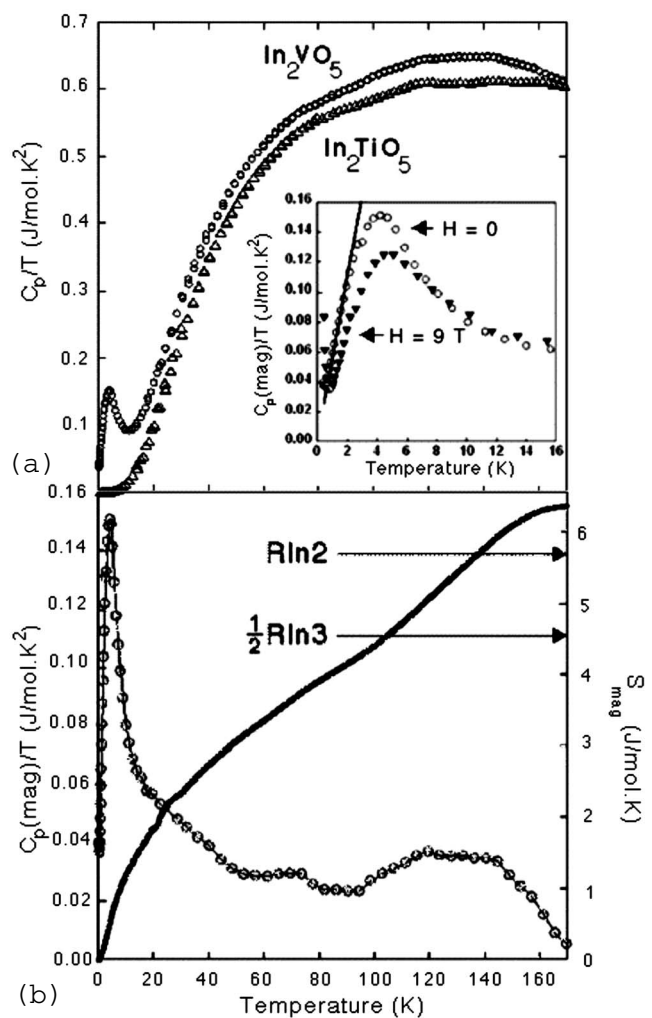
FIG. 4. Heat capacity data for In_2VO_5 at low temperatures. (a) Measured heat capacities for In_2VO_5 and In_2TiO_5 plotted as C_p/T. The inset shows the magnetic part of the heat capacity of In_2VO_5 measured in 0 and 9 T fields, with a power law fit to the zero field data below 2 K. (The upturn in the 9 T data is due to a trace of paramagnetic impurity.) (b) Magnetic heat capacity [shown as $C_p(\mathrm{mag})/T$] and the integrated entropy for In_2VO_5, showing the expected limits for triplet dimer $(1/2R \ln 3)$ and $S=1/2$ monomer $(R \ln 2)$ states.

heat capacity measurements. The broad magnetic susceptibility maximum at 2.5 K (Fig. 2, inset) shows that the global magnetic ground state of In_2VO_5 is a spin singlet, as expected for an antiferromagnetic $S=1$ chain. $C_p(\mathrm{mag})/T$ also shows a shoulder around 4 K [Fig. 4(a), inset], which decreases slightly in magnitude and moves to higher temperature in a 9 T field. The breadth of this peak and its robustness to a 9 T field show that it does not signify a long range magnetic ordering transition. (For long range order, a field estimated as $k_B T_{peak}/g\mu_B \approx 4$ T would be sufficient to suppress the peak.) We have also collected high intensity neutron powder diffraction data, using ILL instrument D20, which show no evidence for long range magnetic order down to 1.7 K (Fig. 5). The heat capacity shows a power law scaling, $C_p(\mathrm{mag}) \sim T^{1.89(2)}$, between 0.42 and 2 K. Linear scaling is expected for a truly one-dimensional system, but similar
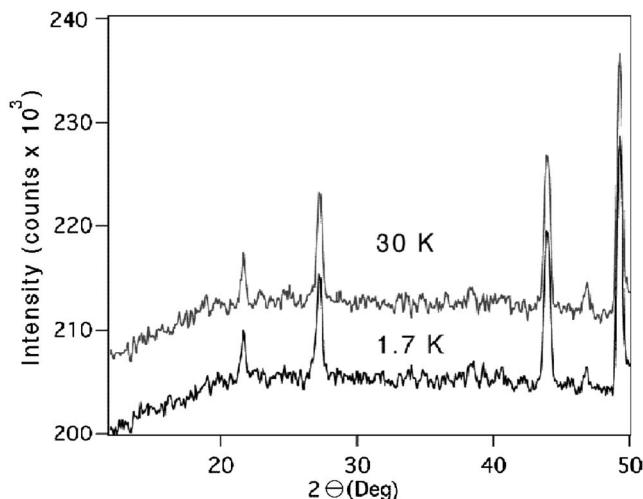
FIG. 5. Low angle region of neutron powder diffraction patterns for In$_2$VO$_5$ at 30 and 1.7 K (λ=2.42 Å), showing no additional peaks to evidence long range spin order below the 5 K magnetic transition.

values of 1.7–1.8 are reported in several quasi-one-dimensional systems (see footnote 21 in Ref. [10]).

VI. DISCUSSION

The S=1 dimer chain is one of the ground states predicted by the F-AF alternating Heisenberg S=1/2 chain model. The ground state varies smoothly from the dimerized (triplet) S=1 Haldane chain to the dimerized (singlet) S=0 chain as the ratio of exchange interactions changes.[18,19] Composite S=1 behavior has also been reported in the asymmetric spin ladder compound IPACuCl$_3$, which shows a susceptibility and excitations characteristic of an S=1 chain with a Haldane gap, and field induced Bose-Einstein condensation.[20–22] Spontaneous triplet dimerization has not been reported in other frustrated networks and so the unconventional ground state of In$_2$VO$_5$ is notable. Cu^{2+} zigzag chains with comparable exchange interaction ratios α=0.25−3 instead form incommensurate spin ordered ground states.[10]

We propose that the ground state found in In$_2$VO$_5$ evidences a high sensitivity of the J_1 interaction to small fluctuating lattice distortions. A weak spin-lattice coupling accompanying the dimer formation in the inset of Fig. 1 leads to inequivalent J_1 (intradimer) and J_1' (interdimer) interactions. Displacements that give J_1/J_1' > 1 reduce magnetic frustration and so the spin dimer fluctuations will couple to these modes. The small anomalies observed in the **b**-axis parameter and microstrain around the 120 K dimerization crossover are consistent with changes of longitudinal [010] phonon modes. The sensitivity of the J_1 exchange interactions to local distortion lies in the orientation of the magnetic orbitals in In$_2$VO$_5$. The unpaired electrons are localized in d_{xy}-type orbitals, perpendicular to the short V-O bonds (marked on Fig. 1, inset), which are effectively orthogonal within the J_1 pathways in a symmetric zigzag chain, leading to ferromagnetic superexchange. A small distortion such as displacement of oxygen atoms parallel to the chain direction removes the orthogonality and introduces a kinetic exchange component that rapidly decreases the strength of one of the now-inequivalent ferromagnetic interactions (J_1'). Hence, longitudinal oxygen vibrations can couple to variations in J_1/J_1' and the corresponding triplet dimer fluctuations. The freezing of the S=1 dimers below 5 K may be accompanied by the ordering of local displacements, and further studies of the low temperature properties of In$_2$VO$_5$ will be worthwhile to discover whether a Haldane gap or lattice distortions are observed. High field investigation of possible Bose-Einstein condensation, similar to that in IPACuCl$_3$,[22] also merits investigation.

In summary, In$_2$VO$_5$ shows a crossover between S=1/2 and S=1 dimer phases at 120 K. This instability reveals a ground state for the frustrated zigzag chain. Spin-lattice coupling is evidenced by subtle changes in the cell parameters and strains around the crossover, and this is ascribed to coupling between triplet dimer spin fluctuations and longitudinal oxygen vibrations within the zigzag chains. The spin dimers freeze into a global singlet state below 5 K without apparent long range magnetic order.

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[14] Applying the mean field expression $\Theta = -S(S+1)\Sigma J_{ij}/3k_B$ for Heisenberg exchange $J_{ij}\mathbf{S}_i\mathbf{S}_j$ (positive J corresponds to AF exchange) to the spin monomer regime >120 K ($S=1/2$, $\Theta = 17$ K, $\Sigma J_i = 2J_1 + 2J_2$) and below the dimerization crossover ($S=1$, $\Theta = -70$ K, $\Sigma J_i = J_1 + 2J_2$), assuming the exchange interactions are constant, gives $J_1/k_B = -173$ K and $J_2/k_B = 139$ K, hence $\alpha = 0.8$.

[15] All of the ID31 data were Rietveld fitted and a combined x-ray and neutron powder diffraction refinement at 10 K in which all thermal factors were refined anisotropically gave residuals $_wR_p = 0.118$ and $R_p = 0.0947$. The oxygen sites refined to within error of full occupancy. Microstrains (root-mean-squared variations in lattice strain) parallel, $s_\parallel[010]$, and perpendicular, $s_\perp[010]$, to the b axis were found by fitting the full widths at half maxima Γ_{hkl} of the Lorentzian synchrotron x-ray diffraction peaks as Γ_{hkl} (rad)$=s_\perp[010]+(s_\parallel[010]-s_\perp[010])\cos\phi+s_i\tan\theta$ where ϕ is the angle between [010] and the normal to the (hkl) diffraction plane. $s_i = 0.036\%$ is the instrumental broadening contribution found by fitting peaks from a standard silicon powder.

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