

Biquadratic Interactions and Spin-Peierls Transition in the Spin-1 Chain LiVGe_2O_6

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The magnetic susceptibility of a new one-dimensional $S = 1$ system, the vanadium oxide LiVGe_2O_6 , has been measured. Contrary to previous $S = 1$ chains, it exhibits an abrupt drop at 22 K typical of a spin-Peierls transition, and it is consistent with a gapless spectrum above this temperature. We propose that this behavior is due to the presence of a significant biquadratic exchange interaction, a suggestion supported by quantum chemistry calculations that take into account the quasidegeneracy of the t_{2g} levels.

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The physics of one-dimensional (1D), spin-1 chains has attracted a considerable amount of attention after the prediction by Haldane that the 1D Heisenberg model has a spin gap for integer spins [1], a prediction confirmed since then by the observation of a gap in many spin-1 chains [2]. A lot of progress has been made by studying the most general Hamiltonian describing an isotropic coupling between neighboring spins 1, namely [3]

$$H = J' \sum_i \vec{S}_i \cdot \vec{S}_{i+1} + J'' \sum_i (\vec{S}_i \cdot \vec{S}_{i+1})^2. \quad (1)$$

The phase diagram of this model is extremely rich [4]. It is most easily described using the parametrization $J' = J \cos\theta$, $J'' = J \sin\theta$. The system has two gapped phases: the Haldane phase for $-\pi/4 < \theta < \pi/4$ and a dimerized, gapped phase for $-3\pi/4 < \theta < -\pi/4$. The two phases are connected by a critical point at $\theta = -\pi/4$ for which the model is solvable by Bethe ansatz and the spectrum gapless. In the following, we will use the other standard parametrization $J' = J$, $J'' = -\beta J$ because β is a direct measure of the relative strength of the biquadratic coupling to the bilinear one. With this parametrization, the Haldane phase is limited to $J > 0$ and $-1 < \beta < 1$, while the dimerized, gapped phase corresponds to $\beta > 1$ if $J > 0$ and $\beta < -1$ if $J < 0$. Hopelessly, it has not been possible so far to explore this phase diagram experimentally due to the lack of systems with a sizable biquadratic exchange: A well-admitted point of view is that β is always very small, and the quantitative interpretation of the experimental results obtained on many spin-1 chain compounds with the pure Heisenberg model has largely confirmed this assumption.

In this Letter, we study the magnetic properties of a compound which has forced us to abandon this point of

view, namely the vanadium oxide LiVGe_2O_6 . Although this system is clearly a spin-1 chain given its structure, its susceptibility is markedly different from that of other spin-1 chains, and, as we shall explain below, the most plausible explanation seems to be that there is a significant biquadratic exchange.

A powder sample of LiVGe_2O_6 was prepared by the solid state reaction method starting from a stoichiometric mixture of Li_2CO_3 , GeO_2 , and V_2O_3 which was placed in a platinum crucible and heated under vacuum 2 h at 200 °C and then 12 h at 900 °C. A second thermal treatment at 800 °C for 12 h was necessary to obtain the pure compound. Lithium vanadium metagermanate LiVGe_2O_6 is the end member of the solid solution $\text{LiV}(\text{Si}_{2-x}\text{Ge}_x)\text{O}_6$ ($0 \leq x \leq 2$) isolated and characterized by Satto *et al.* [5]. This compound belongs to the alkali metal pyroxene family denoted $AM^{3+}B_2O_6$ ($A = \text{alkali}$; $B = \text{Si, Ge}$; $M = \text{a variety of cations at a valence state } 3+$) which has been extensively studied since many compounds are naturally occurring minerals. The structure of LiVGe_2O_6 has been determined from x-ray powder diffraction Rietveld analysis at 295 K. It crystallizes in the monoclinic system, space group $P2_1/c$ compared to $C2/c$ for LiVSi_2O_6 with $a = 9.863(4)$ Å, $b = 8.763(2)$ Å, $c = 5.409(1)$ Å, and $\beta = 108.21(1)^\circ$. The structure, depicted in Fig. 1, is made of infinite isolated chains of edge sharing VO_6 octahedra linked together by chains of corner sharing GeO_4 tetrahedra. The consequence of the change in the space group is that the chains of tetrahedra equivalent in LiVSi_2O_6 are distorted in LiVGe_2O_6 with two distinct crystallographic sites Ge1 and Ge2. The geometric parameters are reported in Table I. Note that the chains are connected to their neighbors only through two GeO_4 tetrahedra so

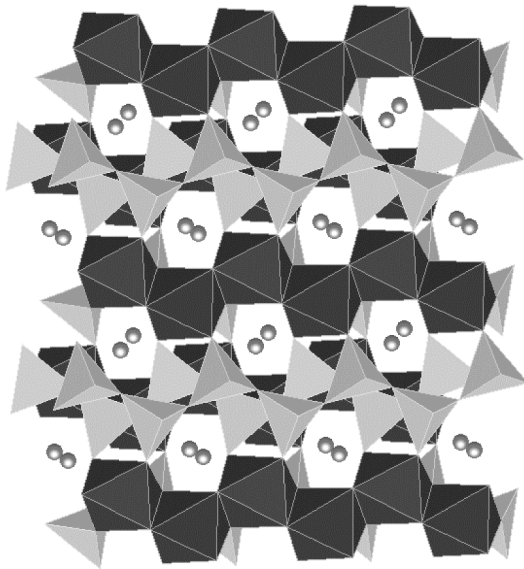


FIG. 1. Polyhedra representation of LiVGe_2O_6 structure down the a^* axis.

that the coupling perpendicular to the chains must be very small.

The magnetic susceptibility has been measured on a powder sample between 1.75 and 350 K and for magnetic fields ranging from 1 Oe to 7 T using a SQUID magnetometer. The results are insensitive to the magnetic field strength, and the data for $H = 1$ T are shown in Fig. 2. Although the impurity contribution at low temperature is not negligible, two features are clearly visible. The most spectacular one is an abrupt drop below 22 K. The behavior below that temperature is typical of a spin-Peierls system with impurities [6], and it is very likely that this is indeed a spin-Peierls transition. In particular, any explanation based on level crossings induced by the magnetic field can be excluded since the results are independent of the strength of the magnetic field. Besides, the susceptibility above this temperature is typical of gapless systems like the Heisenberg $S = 1/2$ chain, and not of spin 1 chains with a Haldane gap, in which case the susceptibility drops much faster below its maximum. In fact, since the spin-Peierls instability occurs in gapless systems because of the magnetic energy to be gained by opening a gap, both features are consistent with each other, and the main question is to understand the origin of the absence of a Haldane gap in the first place.

TABLE I. Selected geometrical parameters (Å).

V-O5	1.89(1)	Ge1-O5	1.73(1)	Li-O1	2.04(1)
O3	1.94(1)	O4	$1.74(1) \times 2$	O3	2.08(1)
O1	2.04(1)	O1	1.78(1)	O4	2.11(1)
O1	2.06(1)			O2	2.18(1)
O2	2.07(1)	Ge2-O6	$1.75(1) \times 2$	O5	2.33(1)
O2	2.08(1)	O3	1.76(1)	O6	2.49(2)
		O2	1.77(1)	V-V	3.149(3)

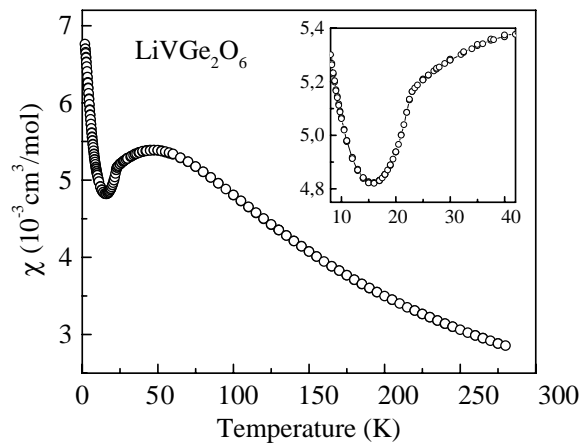


FIG. 2. Magnetic susceptibility of LiVGe_2O_6 . Inset: Enlargement around the abrupt drop at 22 K.

The first possibility is that although vanadium is in the oxidation state 3+, i.e., the electronic configuration is $3d^2$, one could have an effective spin-1/2 model, as was advocated a long time ago by Castellani *et al.* [7] in the context of V_2O_3 . To check this, we have fitted the high temperature data with the expression $\chi(T) = \chi_{VV} + C/(T + \theta)$. A reasonable fit is obtained for $\chi_{VV} = 6.3 \times 10^{-4} \text{ cm}^3/\text{mol}$, $C = 0,80 \text{ cm}^3/\text{mol}$, and $\theta = 79 \text{ K}$. This value of C is consistent with a spin-1 system with an average g value of 1.79, a value typical of spin-1 V^{3+} . Besides, we have performed an ESR investigation of this system. The only signal that we could detect is typical of V^{4+} , but this signal corresponds to the small, paramagnetic contributions at low temperature. The fact that the main signal has not been detected is consistent with a spin-1 state originating from V^{3+} since any single-ion anisotropy pushes the resonance frequency outside the experimental range unless one works in a sufficiently high magnetic field. So it is clear that this is indeed a spin-1 system.

Taking for granted that the main contribution comes from spin 1 originating from V^{3+} , the possible explanations for the absence of a gap are (i) the coupling between the chain; (ii) a strong uniaxial, easy plane anisotropy; (iii) a significant biquadratic interaction. To review these various possibilities, it is useful to start with a brief description of the quantum chemistry of the vanadium ions. In this compound, the vanadium atoms are sitting in a distorted oxygen octahedron (see Fig. 3) with two neighboring VO bonds shorter than the other four. This situation is very similar to the distortion of the sulfur octahedron surrounding vanadium in AgVP_2S_6 [8], and the three t_{2g} orbitals are split into a low-lying doublet (d_{xy} , d_{yz}) and a single orbital (d_{xz}) at an energy Δ above the doublet. *Ab initio* calculations of the energy levels have been performed for a single ion embedded in a crystal, and the estimates for Δ are in the range 270–300 meV depending on the embedding. The degeneracy between the d_{xz} and d_{yz} orbitals is actually lifted due to the low symmetry, but

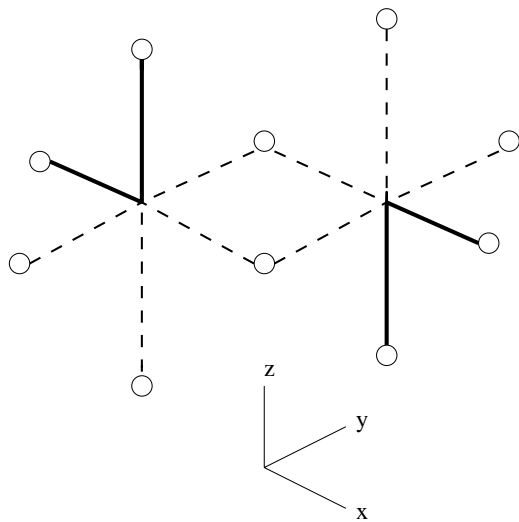


FIG. 3. Schematic representation of two-neighboring V^{3+} ions with their surrounding oxygen octahedra. The solid (dashed) lines correspond to short (long) bonds.

this splitting is very small according to *ab initio* calculations (in the range 3–7 meV) and physically unimportant, so we will neglect it for simplicity. The other on-site parameters are the Hund's rule coupling J_H and the repulsion between electrons on the same (different) orbitals U_1 (U_2). Typical values are $J_H = 0.5$ –1 eV, $U_1 = 4$ –6 eV, and $U_2 = U_1 - 2J_H$. Vanadium first neighbors sit in edge-sharing octahedra, the short bonds being opposite each other and not involved in the common edge (see Fig. 3). If we denote by t_{ij} the hopping integrals between Wannier states corresponding to the t_{2g} orbitals with $i, j = 1, 2$, and 3 for d_{xy} , d_{yz} , and d_{xz} , respectively, then $t_{12} = t_{13} = 0$ by symmetry while t_{11} , t_{22} , and t_{33} involve direct overlaps between $3d$ orbitals and can be estimated from standard tables [9]: $t_{11} = 0.3$ eV and $t_{22} = t_{33} = -0.1$ eV. Finally t_{23} will have a contribution from indirect hopping through the oxygen $2p$ orbitals and is expected to be the largest hopping parameter in the problem, presumably in the range $t_{23} = 0.5 - 1$ eV. Let us now discuss the possible explanations for the absence of a gap.

(i) *Interchain coupling*.—It is well known that a relatively modest interchain coupling can close the gap [10]. However, to have a significant effect on the susceptibility in the range 22–55 K, the interchain coupling should be in that range. Such a large ratio of the interchain to intrachain coupling seems very unlikely given the very one-dimensional structure of the compound. Besides, if the interchain coupling were of the order of 20 K or larger, one should find a transition to long range order in the same temperature range, not a spin-Peierls transition. So we believe that the interchain coupling plays no significant role in the present system.

(ii) *Uniaxial anisotropy*.—Several theoretical studies have shown that the presence of an easy plane, uniaxial anisotropy of the form $D \sum_i (S_i^z)^2$ can close the Haldane

gap, the critical value being $D = J$ if the coupling between the spins is purely Heisenberg and isotropic in spin space [11]. Can D be of the order of 50 K in the present system? The answer is clearly negative on both experimental and theoretical grounds. Given the electronic structure of V^{3+} in the present compound, the spin-orbit coupling $\lambda \vec{L} \cdot \vec{S}$ gives rise to a uniaxial, easy-plane anisotropy of order λ^2/Δ and a reduction of the perpendicular g factor: $g_{\perp} = 2(1 - \lambda/\Delta)$. In the isolated ion V^{3+} , $\lambda = 104 \text{ cm}^{-1}$, which can be considered as an upper bound to its value in a crystal due to covalency effects. Now the average g factor determined from the high temperature susceptibility is equal to 1.79. Assuming that g_{\parallel} has the typical value 1.9, this implies that $g_{\perp} = 1.73$, i.e., $\lambda/\Delta = 0.13$. With $\lambda = 104 \text{ cm}^{-1}$, this leads to $D = 20$ K, a value clearly too small to close the gap. Besides, the actual value of λ , hence the value of D , is certainly smaller than that. A careful analysis with single crystal NMR would be very useful in getting more precise estimates. Theoretically, the large value of Δ also points to a very small value of D , of the order of a few K. This value is typical of V^{3+} in this kind of environment [12]. So the explanation in terms of uniaxial anisotropy can be discarded.

(iii) *Biquadratic interaction*.—Thus, the only remaining possibility to explain the absence of a Haldane gap is the presence of a significant biquadratic interaction. Since the presence of a biquadratic interaction of significant magnitude has never been reported in any system, the most important task is to see whether such an interaction could indeed occur in the present case. So we have considered the general problem of the effective coupling between two spins 1 in almost degenerate t_{2g} orbitals. This turns out to be a rather complicated problem with very different results in different situations. So we will present only a summary of the results relevant for LiVGe_2O_6 . The details will appear in a forthcoming paper [13]. Since the Hilbert space has a total of 495 states, this problem can be easily diagonalized numerically. As long as the energy Δ is not too small, the low energy sector contains 9 states organized in 3 levels with degeneracy 1, 3, and 5, typical of an isotropic coupling between spins 1. Now the splitting between these levels can be used to determine both the bilinear and biquadratic exchange integrals since the energy levels of two spins 1 coupled by the Hamiltonian $J[\vec{S}_1 \cdot \vec{S}_2 - \beta(\vec{S}_1 \cdot \vec{S}_2)^2]$ are given by $E_0 = -J(2 + 4\beta)$, $E_1 = -J(1 + \beta)$, and $E_2 = J(1 - \beta)$ for $S_{\text{tot}} = 0, 1$, and 2, respectively. It turns out that in a large parameter range, and in particular for physically relevant parameters, β can be larger than 1, i.e., the biquadratic interaction can be significant and even dominant. For instance, if we take $\Delta = 300$ meV, $U_1 = 5$ eV, $J_H = 0.5$ eV, $t_{11} = 0.3$ eV, and $t_{22} = t_{33} = -0.1$ eV, β is already equal to 0.7 if $t_{23} = 0.5$ eV and increases with t_{23} until it diverges when the bilinear exchange vanishes and becomes ferromagnetic.

This remarkable behavior is best understood in the context of a perturbation expansion in the hopping integrals. In the nonperturbed ground state each site carries two electrons in a triplet state built out of the two low-lying orbitals. Then the degeneracy is in general lifted at second order, as for kinetic exchange, and the coupling is of the Heisenberg form, i.e., purely bilinear. What is important, however, is that it contains both ferromagnetic and antiferromagnetic contributions: t_{11} and t_{22} yield an AF contribution $J_{AF} = (1/2)(t_{11}^2 + t_{22}^2)(1/E_2 + 1/E_3) > 0$, with $E_2 = U_1 + \Delta$ and $E_3 = U_1 + 2J_H + \Delta$ due to Pauli exclusion principle, while t_{23} yields a ferromagnetic contribution $J_F = (2/3)t_{23}^2(1/E_4 - 1/E_1) < 0$ with $E_1 = U_2 + \Delta$ and $E_4 = U_2 + 2J_H + \Delta$ due to the Hund's rule coupling that favors intermediate states with high spin. Then if these couplings are of the same order, one has to go to fourth order to calculate the exchange integrals. It turns out that at this order the coupling is no longer purely bilinear but has a biquadratic contribution with a negative sign, and the ratio of this contribution to the bilinear one diverges at the transition between antiferromagnetic and ferromagnetic bilinear exchanges. The explicit expressions are very long and will be given in a forthcoming paper. In general, β becomes substantially large when the coupling from the second order contribution $|J_{AF} + J_F|$ is comparable to $t^4/(U_1^2\Delta)$, with t the largest of the hopping integrals. The parameters we estimate for LiVGe₂O₆ fall in this range. So, whereas all other explanations could be discarded on the basis of elementary but robust arguments, it seems that the presence of a significant biquadratic interaction is a natural consequence of the relatively small splitting of the t_{2g} levels, i.e., of the quasi-orbital-degeneracy of the system.

Note that the order of magnitude of the exchange integral supports by itself this explanation: Without any competition between J_F and J_{AF} the exchange integral would be much larger, as, e.g., in AgVP₂S₆, where it is of the order of 400 K [14]. As a consequence of this relatively small value of the nearest neighbor coupling, the relative magnitude of the next-nearest neighbor interaction, which has been implicitly neglected so far, might actually not be as small as what a naive guess based on the geometry suggests. While such a term will, if anything, favor a dimerized ground state, it does not close the Haldane gap [15] and cannot by itself account for the properties of the present system.

The presence of a biquadratic interaction has several interesting consequences. First of all, it will modify the temperature dependence of the susceptibility, and the data above the spin-Peierls transition are indeed consistent with a large value of β . In particular, the susceptibility is quite flat below the maximum, which is consistent with a very small gap, i.e., with a value of β around

1 [16]. Besides, the gapped phase that occurs beyond $\beta = 1$ corresponds to a twofold, dimerized ground state, very much like for the spin-1/2 chain with large enough second neighbor exchange, and a Peierls transition with a dimerization of the lattice is of course a very likely instability of the system. So an explanation in terms of a biquadratic interaction of the same order but larger than the bilinear one is at the present stage the simplest and most natural explanation of the very peculiar properties of LiVGe₂O₆. Further experimental investigations of this material to confirm the Peierls nature of the transition and to study its magnetic properties with and without magnetic field is likely to be an active field of research in the next few years.

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