Biquadratic interactions and spin-Peierls transition in the spin 1 chain LiVGe$_2$O$_6$

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The magnetic susceptibility of a new one-dimensional, S=1 system, the vanadium oxide LiVGe$_2$O$_6$, 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 behaviour is due to the presence of a significant biquadratic exchange interaction, a suggestion supported by quantum chemistry calculations that take into account the quasi-degeneracy of the t$_{2g}$ levels.

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 $\frac{1}{2}$, 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]

$$H = J' \sum_i \vec{S}_i \cdot \vec{S}_{i+1} + J'' \sum_i (\vec{S}_i \cdot \vec{S}_{i+1})^2$$  \hspace{1cm} (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 $\beta$ 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 $J < 0$. Hopefully, 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 $\beta$ 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$_2$O$_6$. 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$_2$O$_6$ was prepared by solid state reaction method starting from a stoichiometric mixture of Li$_2$CO$_3$, GeO$_2$ and V$_2$O$_5$ which was placed in a platinum crucible and heated under vacuum 2 hours at 200° C and then 12 hours at 900° C. A second thermal treatment at 800° C for 12 hours was necessary to obtain the pure compound. Lithium vanadium metager-

FIG. 1. Polyhedra representation of LiVGe$_2$O$_6$ structure down the a* axis.
manate LiVGe$_2$O$_6$ is the end member of the solid solution LiV(Si$_{2-x}$Ge$_x$)O$_6$ (0 ≤ x ≤ 2) isolated and characterized by Satto et al. This compound belongs to the alkali metal pyroxene family denoted AM$^{3+}$B$_2$O$_6$ (A=alkali, B=Si, Ge, M=a variety of cations at a valence state 3+) which has been extensively studied since many compounds are naturally occuring minerals. The structure of LiVGe$_2$O$_6$ has been determined from X-ray powder diffraction Rietveld analysis at 295 K. It crystallises in the monoclinic system, space group P2$_1$/c compared to C2$/c$ for LiVSi$_2$O$_6$ with a=9.863(4)Å, b=8.763(2)Å, c=5.409(1)Å and β=108.24(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$_2$O$_6$ are distorted in LiVGe$_2$O$_6$ with two distinct crystallographic sites Ge1 and Ge2. The geometric parameters are reported in Table 1. Note that the chains are only connected to their neighbours through two GeO$_4$ tetrahedra so that the coupling perpendicular to the chains must be very small.

![Figure 2](image2.png)

**FIG. 2.** Magnetic susceptibility of LiVGe$_2$O$_6$.

The magnetic susceptibility has been measured on a powder sample between 1.75 K 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 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 behaviour below that temperature is typical of a spin-Peierls system with impurities 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.

The first possibility is that although vanadium is in the oxydation state 3+, i.e. the electronic configuration is 3$d^2$, one could have an effective spin 1/2 model, as was advocated a long time ago by Castellani et al in the context of V$_2$O$_3$. To check this, we have fitted the high temperature data with the expression \( \chi(T) = \chi_0 + \frac{C}{T+\theta} \). A reasonable fit is obtained for \( \chi_0 = 5.3 \times 10^{-4} \text{ cm}^3/\text{mol} \), \( C = 0.80 \text{ cm}^3/\text{mol K} \) and \( \theta = 79K \). 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.

![Figure 3](image3.png)

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

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 chains; 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 neighbouring VO bonds shorter than the other four. This situation is very similar to the distortion of the sulfur octahedron surrounding vanadium in AgVP₂Se₆ [9], and the three t₂g orbitals are split into a low-lying doublet (dₓᵧ, dᵧz) and a single orbital (dₓz) 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 dₓz and dᵧz orbitals is actually lifted due to the low symmetry, but 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 (resp. different) orbitals U (resp. U₂). Typical values are J_H = 0.5 – 1 eV, U₁ = 4–6 eV and U₂ = U₁−2J_H. Vanadium first neighbours sit in edge-sharing octahedra, the short bonds being opposite to each other and not involved in the common edge (see Fig. 3). If we denote by tᵢᵢ the hopping integrals between Wannier states corresponding to the t₂g orbitals with i, j = 1, 2 and 3 for dₓᵧ, dᵧz and dₓz, respectively, then t₁₂ = t₁₃ = 0 by symmetry while t₁₁, t₂₂ and t₃₃ involve direct overlaps between 3d orbitals and can be estimated from standard tables [9]: t₁₁ = 0.3 eV and t₂₂ = t₃₃ = −0.1 eV. Finally t₂₃ 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 t₂₃ = 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 [11]. However, to have a significant effect on the susceptibility in the range 22-55K, 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 was 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 ∑ᵢ (Sᵢₓ)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 V³⁺, the spin-orbit coupling λL·S gives rise to a uniaxial, easy-plane anisotropy of order λ²/Δ and a reduction of the perpendicular g factor: gₚ = 2(1 − λ/Δ). In the isolated ion V³⁺, λ = 104 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∥ has the typical value 1.9, this implies that gₚ = 1.73, i.e. λ/Δ = 0.3. With λ = 104 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 V³⁺ in this kind of environment [22]. 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 t₂g orbitals. This turns out to be a rather complicated problem with very different results in different situations. So we will only present a summary of the results relevant for LiVGe₂O₆. 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[S₁·S₂ − β(S₁·S₂)²] are given by E₀ = −J(2 + 4β), E₁ = −J(1 + β) and E₂ = J(1 − β) for Sₜₒₜ = 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 Δ = 300 meV, U₁ = 5 eV, J_H = 5 eV, t₁₁ = 0.3 eV and t₁₂ = t₁₃ = −0.1 eV, β is already equal to .7 if t₂₃ = .5 eV and increases with t₂₃ until it diverges when the bilinear exchange vanishes and becomes ferromagnetic.

This remarkable behaviour is best understood in the context of a perturbation expansion in the hopping integrals. In the non-perturbed 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: t₁₁ and t₁₂ yield an AF contribution J_AF = (1/2)(t₁₁² + t₁₂²)(1/E₂ + 1/E₃) >
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 $J_F = (2/3)t_{23}^2(1/E_2 - 1/E_3) < 0$ with $E_1 = U_3 + \Delta$ and $E_4 = U_2 + 2J_H + \Delta$ due to the Hund’s rule coupling that favours 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, $\beta$ becomes substantially large when the coupling from the second order contribution, $|J_{AF} + J_F|$, is comparable to $t^4/(U_2^2\Delta)$, with $t$ the largest of the hopping integrals. The parameters we estimate for LiVGe$_2$O$_6$ 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, like e.g. in AgVP$_2$S$_6$, where it is of the order of 400 K [4]. As a consequence of this relatively small value of the nearest neighbour coupling, the relative magnitude of the next-nearest neighbour 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, favour a dimerized groundstate, it does not close the Haldane gap [4] 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 $\beta$. In particular, the susceptibility is quite flat below the maximum, which is consistent with a very small gap, i.e. with a value of $\beta$ around 1 [16]. Besides, the gapped phase that occurs beyond $\beta = 1$ corresponds to a two-fold, dimerized ground state, very much like for the spin 1/2 chain with large enough second neighbour 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 LiVGe$_2$O$_6$. 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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| V-O5 | 1.89(1) | Ge-O5 | 1.73(1) | Li-O1 | 2.04(1) |
| O3  | 1.94(1) | O4   | 1.74(1)x2 | O3  | 2.08(1) |
| O1  | 2.04(1) | O1   | 1.78(1) | O4   | 2.11(1) |
| O1  | 2.06(1) | O2   | 1.78(1) | O2   | 2.18(1) |
| O2  | 2.07(1) | Ge-O6 | 1.75(1)x2 | 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) |

TABLE I. Selected geometrical parameters (Å)