Spin-Peierls transition with strong structural fluctuations in the vanadium oxide 
VO\textsubscript{3}Bi\textsubscript{2}O\textsubscript{4}

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We report on the magnetic susceptibility and electron spin resonance measurements on polycrystalline samples of the vanadium oxide VO\textsubscript{3}Bi\textsubscript{2}O\textsubscript{4}, a quasi-one dimensional S=1/2 Heisenberg system.

We show that the susceptibility vanishes at zero temperature, as in a gapped system, and we argue that this is due to a spin-Peierls transition with strong structural fluctuations.

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Although the study of the spin-Peierls (SP) transition in S = 1/2 antiferromagnetic (AF) Heisenberg chains has started a long time ago with the discovery of the first SP transition in the organic system TTFCuBDT in 1975 \cite{1}, a major breakthrough in the field was the discovery in 1993 by Hase et al. \cite{2} of the first inorganic system exhibiting a SP transition, namely CuGeO\textsubscript{3}. The possibility to grow large single crystals has led to a very intense experimental activity, and the understanding of the properties of such systems, in particular in strong magnetic fields, has been dramatically improved.

However CuGeO\textsubscript{3} is representative of only one class of spin-Peierls systems, namely systems in which structural fluctuations are to a certain extent negligible. In such systems, the dimerization of the lattice is very brutal, and the susceptibility exhibits a characteristic cusp at the transition temperature. The irrelevance of structural fluctuations in a 1D system is very surprising, and the first theories actually predicted a strongly fluctuating regime above the transition \cite{3}. This discrepancy was resolved by Cross and Fisher \cite{4}, who showed that an appropriate treatment of 3D phonons can lead to a significant suppression of fluctuations.

The study of fluctuations in spin-Peierls systems has recently restarted however with the careful analysis of the spin-Peierls transition in the organic system (BCPTTF)\textsubscript{2}X by Dumoulin et al. \cite{5} in 1996 who convincingly showed the presence of very strong structural fluctuations above the spin-Peierls transition. Judging from the impact of CuGeO\textsubscript{3} on the field, the search for inorganic systems with similar properties is a real challenge. However the inorganic spin 1/2 chains synthetized so far do not seem to fill this gap. Most of them just do not show any sign of a SP instability, like Sr\textsubscript{2}CuO\textsubscript{3} \cite{6} or MgVO\textsubscript{3} \cite{7}, while the transition observed in NaV\textsubscript{2}O\textsubscript{5} \cite{8} is very abrupt and is now believed to involve charge degrees of freedom as well.

In this paper we report on the magnetic properties of a vanadium oxide, VO\textsubscript{3}Bi\textsubscript{2}O\textsubscript{4}, which we believe is the first example of an inorganic system that undergoes a SP transition with very strong fluctuation effects. This system is made of almost isolated chains of VO\textsubscript{3} pyramids. According to Darriet, Bovin and Galy \cite{9} VO\textsubscript{3}Bi\textsubscript{2}O\textsubscript{4} crystallizes in the monoclinic system, space group C2\textsubscript{1}c, with the unit cell dimensions a=18.03 Å, b=4.800 Å, c=5.497 Å, \beta=94.58° (Z=4). The vanadium atoms are fivefold coordinated in a slightly distorted square pyramids with one characteristic short vanadyl bond V-O close to 1.59 Å towards its apex and 2×2 longer bonds at 1.91 and 2.04 Å with the oxygens of the square base. Along the [001] direction the apices of the VO\textsubscript{3} pyramids alternately point up and down relative to a plane of the square base (see Fig. 1(a)). The smallest in-chain V-V distance is approximately 3.01 Å. The distances between the chains are 4.80 and 18.03 Å for the [010] and the [100] direction, respectively. Thus from a magnetic point of view, the VO\textsubscript{3}Bi\textsubscript{2}O\textsubscript{4} structure can be viewed as infinite isolated chains of V\textsuperscript{4+} ions running along the [001] direction. The antimony atoms exhibit the typical one-sided threefold coordination of the oxygen atoms having a stereactive lone pair E \cite{10} (see Fig. 1(b)).

Polycrystalline samples of VO\textsubscript{3}Bi\textsubscript{2}O\textsubscript{4} having a light-green color were synthesized by solid-state reaction \cite{10}. ESR X-band spectra were collected using a Bruker ESP300 spectrometer equipped with a standard TE\textsubscript{102} cavity and a continuous helium flow cryostat that allows temperature scans between 4 and 300 K. The temperature and the field variation of the magnetization was measured with a Quantum Design SQUID magnetometer from 300 to 1.8 K in fields up to 4 T.

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The temperature dependence of the magnetic susceptibility \( \chi_{\text{raw}}(T) \) of a 100 mg VOSb\(_2\)O\(_4\) polycrystalline sample \( \chi_{\text{raw}}(T) \) at \( H = 2 \) T (open diamonds). Open triangles, dashed line and solid line represent the corrected for the impurity contribution VOSb\(_2\)O\(_4\) susceptibility \( \chi_{\text{cor}}(T) \), the impurity contribution to \( \chi_{\text{raw}}(T) \) and the best fit to the \( \chi(T) \) of \( S = 1/2 \) HAF according to Eq. (50), Ref. 18 ( \( J/k = 245 \pm 5 \) K, \( \chi_0 = 0.00021 \) cm\(^3\)/mol, \( g = 1.66 \)), respectively. The insert shows low temperature behavior of \( d\chi_{\text{cor}}(T)/dT \).

Before we can start discussing the physical origin of this unusual behaviour, the first thing we must check is whether the susceptibility indeed goes to zero at zero temperature, as in a SP transition. Let us first study in more details the impurity contribution. To characterize more quantitatively this impurity contribution \( \chi_{\text{imp}}(T) \) to \( \chi_{\text{raw}}(T) \), particularly with an idea to separate it from the intrinsic susceptibility of the VOSb\(_2\)O\(_4\) phase, which we will call \( \chi_{\text{cor}}(T) \), we have carried out magnetization measurements vs. \( H \) at various fixed temperatures from 80 K to 1.8 K. The results are shown in Fig. 3. An important information about \( \chi_{\text{imp}}(T) \) is contained in the low temperature nonlinear dependence of \( M_{\text{imp}}(H,T) \) when \( \mu H > kT \). Therefore we have to examine the data in Fig. 3 using the following equation \( M(H, T) = M_{\text{imp}}(H,T) + \chi_{\text{cor}}(T) \cdot H \), where \( M_{\text{imp}}(H, T) \) is expressed in a standard way as \( M_{\text{imp}}(H, T) = \mu_{\text{imp}} N_A g \mu_B S \cdot B_S(g\mu_B S H/kT) \), \( B_S \) is the Brillouin function, \( S \) is an impurity spin value and \( \mu_{\text{imp}} \) defines the relative impurity concentration. The results of a fit of the experimental data with this equation are shown in Fig. 3 as solid lines. The following parameters \( S = 1/2 \), \( \mu_{\text{imp}} = 0.00573(5) \) were extracted ( \( g = 1.975 \) was fixed in the fit procedure) together with the AF Curie-Weiss constant \( \theta \approx 0.6 \) K obtained from the low-T dependence of \( \chi_{\text{raw}}(T) \). We are now in a position to correct \( \chi_{\text{raw}}(T) \) for the impurity contribution. In Fig. 2 \( \chi_{\text{imp}}(T) = p_{\text{imp}} C/(T + \theta) \) \( (C = 0.366 \) cm\(^3\)/K/mol) is plotted (dashed line) along with the \( \chi_{\text{cor}}(T) = \chi_{\text{raw}}(T) - \chi_{\text{imp}}(T) \). This behaviour is consistent with a zero contribution to the spin sus-

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FIG. 1. (a) Polyhedral representation of the VOSb\(_2\)O\(_4\) structure illustrating the infinite isolated chains of VO\(_4\) pyramids. (b) the (ac) plan projection of the crystal structure of VOSb\(_2\)O\(_4\).

FIG. 2. The temperature dependence of the magnetic susceptibility of a 100 mg VOSb\(_2\)O\(_4\) polycrystalline sample \( \chi_{\text{raw}}(T) \) at \( H = 2 \) T (open diamonds). Open triangles, dashed line and solid line represent the corrected for the impurity contribution VOSb\(_2\)O\(_4\) susceptibility \( \chi_{\text{cor}}(T) \), the impurity contribution to \( \chi_{\text{raw}}(T) \) and the best fit to the \( \chi(T) \) of \( S = 1/2 \) HAF according to Eq. (50), Ref. 18 ( \( J/k = 245 \pm 5 \) K, \( \chi_0 = 0.00021 \) cm\(^3\)/mol, \( g = 1.66 \)), respectively. The insert shows low temperature behavior of \( d\chi_{\text{cor}}(T)/dT \).
ceptibility $\chi_{\text{spin}}(T) = \chi_{\text{cor}}(T) - \chi_0$ at zero temperature if the sum of the diamagnetic and Van Vleck contributions $\chi_0$ is equal to $\chi_{\text{cor}}(T = 0)$. While the diamagnetic contribution can be estimated from standard tables ($\chi_{\text{dia}} \approx -1.01 \times 10^{-4} \text{cm}^3/\text{mol}$ [1]), an unbiased estimate of the Van Vleck susceptibility would require susceptibility data at temperatures much larger than the typical exchange integrals, a regime which is not accessible.

To go around this difficulty, we have performed extensive ESR measurements. A representative series of X-band ESR spectra recorded from 320 to 7.3 K on a polycrystalline sample (12 mg) is presented in Fig. 4(a). We note the axial symmetry of the obtained spectra, especially apparent at $T = 20$ K, reflecting the axial symmetry of the crystal field acting on $V^{4+}$ ions in the fivefold pyramidal environment. The computer spectra simulations over the temperature range 13 - 320 K give two $T$-independent $g$-factors: $g_\perp = 1.978$, $g_\parallel = 1.930$ with the average value of $1.962 \pm 0.002$ already reported for low-dimensional vanadates [8,12]. At low $T$ it is found that the measured spectra contain an additional ESR signal. The intensity of this additional signal roughly follows Curie law and the average $g$-factor is found to be $1.975 \pm 0.005$. We ascribe this signal to the magnetic impurities which are responsible for the steep increase of the magnetic susceptibility at low temperatures (see above).

To extract information from these ESR spectra, we have proceeded in the following way. Since the ESR is insensitive to the diamagnetic and Van Vleck contributions to the susceptibility, we are able, by double integration of the ESR spectra, to reconstruct the sum $\chi_{\text{spin}}(T) + \chi_{\text{imp}}(T)$ and then using an appropriate procedure for the subtraction of $\chi_{\text{imp}}(T)$ to restore the $T$-dependence of $\chi_{\text{spin}}(T)$.

FIG. 3. The magnetization of VOSb$_2$O$_4$ vs. magnetic field at different temperatures. The symbols are experimental data, the solid lines are the fit results according to the equation of $M(H,T)$ discussed in the text.

FIG. 4. (a) The temperature evolution of ESR spectra in the VOSb$_2$O$_4$ polycrystalline sample from 320 to 7.3 K; (b) the temperature dependence of the peak-to-peak linewidth $\Delta H_{pp}$ in VOSb$_2$O$_4$ extracted from computer simulation of experimental spectra. The insert shows the double integrated ESR spectra intensity $\chi_{\text{spin}}^{ESR}(T)$ (solid diamonds). $\chi_{\text{spin}}(T) = \chi_{\text{cor}}(T) - \chi_0$ deduced from Fig. 2 is also shown scaled with $\chi_{\text{spin}}^{ESR}(T)$ so, that $\chi_{\text{spin}}(T_{\text{max}}) = \chi_{\text{spin}}^{ESR}(T_{\text{max}})$.

In the case of VOSb$_2$O$_4$ the substraction of $\chi_{\text{imp}}(T)$ is a rather tedious but unambiguous procedure because i) the impurity ESR spectra have quite different line parameters (such as the linewidth, g-factor and the temperature dependence of spectra intensity) as compared to the main spectra; ii) from the magnetization measurements we know the $T-$evolution of $\chi_{\text{imp}}(T)$ so, we can use this information to check the correctness of the substraction at each $T$. We drop out the technical details of this procedure and postpone them to our forthcoming
paper. The $\chi_{\text{spin}}^{\text{ESR}}(T)$ data as extracted from ESR are given in an inset of Fig. 4(b). It is clearly seen that the spin magnetic susceptibility of VOSb$_2$O$_4$ goes to zero in the limit $T \to 0$, a result which is qualitatively apparent from the examination of ESR spectra at 20, 13 and 7.3 K in Fig. 4(a). For example, the 7.3 K ESR spectrum is almost for 95% an impurity one. The fact that $\chi_{\text{spin}}(T \to 0)$ is 0 clearly evidences that the VOSb$_2$O$_4$ ground state at low temperature is a nonmagnetic singlet. The limit $S = 0$. Note that the temperature dependence is consistent with that deduced from the susceptibility measurements after substraction of the impurity contributions and assuming that the Van Vleck contribution is such that $\chi_{\text{cor}} = 0$ (see inset of Fig. 4(b)).

Another very useful information is contained in the temperature dependence of the line width. As seen from Fig. 4(b), the peak-to-peak linewidth $\Delta H_{\text{pp}}$ shows a characteristic V-like temperature dependence (a strong decrease of $\Delta H$ replaced at $T \approx 13$ K by a rapid increase of $\Delta H$). Such a behaviour has been previously observed in both SP materials NaV$_2$O$_5$ and CuGeO$_3$, the minimum temperature being equal to the SP transition temperature.

Let us now discuss the various possibilities to explain this behaviour. Assuming that the chains are well isolated magnetically, which is very reasonable given the geometry, we can think of only two possibilities to explain a vanishing susceptibility, hence the presence of a spin gap, at zero temperature: Frustration or dimerization due to a SP transition. Let us analyze both possibilities.

**Frustration:** It is well known that a coupling $J_2$ to second neighbours can lead to a spin gap if its ratio to the first-neighbour coupling $J_1$ is larger than 0.24. However the presence of a significant coupling between second neighbours will not just open a gap at low temperature, but will modify the temperature dependence of the susceptibility at high temperature as well. We have thus tried to fit $\chi_{\text{spin}}(T)$ with a significant value of $J_2$. The resulting fit is very bad, and much worse actually than without $J_2$ between 40 K and 300 K. So this possibility seems unlikely. Besides, if we compare with MgVO$_3$, another quasi-1D vanadium oxide which does not show any anomaly at low temperature, the chains have the same structure. But the magnetic measurements performed on MgVO$_3$ show no indication whatsoever of intra-chain frustration. So it seems more plausible that the difference between the magnetic properties of these systems comes from the interaction between the chains. In fact, the chains are further apart in VOSb$_2$O$_4$ than in MgVO$_3$, especially in the $c$ direction, where most of the residual coupling is believed to occur in MgVO$_3$. So it is not surprising that typical 1D effects show up in VOSb$_2$O$_4$ and not in MgVO$_3$.

**Dimerization due to SP transition:** In principle, a $S = 1/2$ chain is always unstable towards dimerization, but the transition temperature can be strongly reduced due to fluctuations of the lattice, especially if the system is very one-dimensional. In the present case, a good fit of the high-temperature susceptibility with the susceptibility of the $S=1/2$ chain is possible (see Fig. 2), although with an effective $g$-factor smaller than the actual one measured in ESR. This discrepancy is actually ubiquitous in V$^{4+}$ vanadates, whose properties are quite well understood otherwise, and it seems legitimate not to worry too much about it. It might come from different factors ranging from a poor determination of the weight due to the absorption of water by the sample to the presence of some non-magnetic impurity phase.

The next question is whether we do have a SP transition. From the susceptibility measurements alone, it is not possible to conclude. But if there is a transition, it seems likely that it does not take place at the onset of the drop, like in CuGeO$_3$, but at the temperature where the derivative of the susceptibility is maximal, i.e. 13 K. This scenario is actually favoured by ESR measurements since the line-width changes dramatically at the same temperature. However, clear signatures of the transitions, like new Bragg peaks or new phonons lines below 13 K, are not available yet.

If on the contrary the system remains fluctuating with a pseudo-gap down to zero temperature, as in the Lee-Rice-Anderson theory of the Peierls transition in metallic systems, the susceptibility is expected to decrease smoothly to zero. This would be consistent with our data. The behaviour of the line-width under such circumstances is not known however, and more work is needed to check whether our data can exclude this possibility.

To summarize, we have presented clear evidence that a spin gap opens in the quasi-1D vanadium oxide VOSb$_2$O$_4$ from susceptibility, magnetization and ESR data. The overall behaviour strongly suggests that this is due to the inherent SP instability of this spin 1/2 chain, but with very strong fluctuations. Given the lack of inorganic materials exhibiting this physics so far, the properties of this system are likely to attract a lot of attention in the future.

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