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Pseudo-gap and possible Spin-Peierls transition in the vanadium oxide $VOSb_2O_4$

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Abstract. We report on the magnetic susceptibility and electron spin resonance measurements on polycrystalline samples of the vanadium oxide $VOSb_2O_4$, a quasi-one-dimensional $S = 1/2$ Heisenberg system. The susceptibility vanishes at zero temperature, but there is no cusp at the onset of the susceptibility drop, and the ESR linewidth exhibits an increase characteristic of a phase transition at a much lower temperature. We show that this behaviour is consistent with the formation of a pseudo-gap in a spin-Peierls system in the adiabatic limit.

PACS. 75.45.+j Macroscopic quantum phenomena in magnetic systems – 75.50.Ee Antiferromagnetics – 75.40.Cx Static properties (order parameter, static susceptibility, heat capacities, critical exponents, etc.) – 76.30.-v Electron paramagnetic resonance and relaxation

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 [1,2], a major breakthrough in the field was the discovery in 1993 by Hase *et al.* [3] of the first inorganic system exhibiting a SP transition, namely $CuGeO_3$.

However $CuGeO_3$ is representative of only one class of spin-Peierls systems, namely systems in which there is no pseudo-gap in the spin-excitation spectrum above the transition. In such systems, the susceptibility exhibits a characteristic cusp at the transition temperature. The presence of a pseudo-gap was predicted on quite general grounds for 1D systems by Lee *et al.* [4], but it was shown later on by Cross and Fisher [5] that 3D phonons can lead to a significant suppression of the pseudo-gap.

The study of the other class of spin-Peierls systems has recently started with the careful analysis of the spin-Peierls transition in the organic system $(BCPTTF)_2X$ by Dumoulin *et al.* [6] in 1996 who convincingly showed the opening of a pseudo-gap above the spin-Peierls transition and the absence of any significant cusp in the susceptibility at the transition. The origin of the difference between the two kinds of spin-Peierls systems is still a matter of debate, but the observation of strong pretransitional fluctuations in $CuGeO_3$ far above the transition by Pouget *et al.* [7] clearly shows that the difference cannot be attributed to the absence of structural fluctuations above the transition. A more plausible explanation is that $CuGeO_3$ is in the non-adiabatic limit, *i.e.* that pretransitional structural fluctuations are too fast to lead to a pseudo-gap, as recently emphasized by Pouget [8].

Judging from the impact of $CuGeO_3$ 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_2CuO_3 [9] or $MgVO_3$ [10], while the transition observed in NaV_2O_5 [11] 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, $VOSb_2O_4$, which we believe is the first example of an inorganic spin-1/2 chain that undergoes a SP transition with the opening of a pseudo-gap far above the transition. This system is made of almost isolated chains of VO_5 pyramids. According to Darriet *et al.* [12] $VOSb_2O_4$ crystallizes in the monoclinic system, space group $C2/c$, 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 slightly distorted square pyramids. Along the [001] direction the apices of the VO_5 pyramids alternately point up and down relative to a plane of the square base (see Fig. 1a). 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

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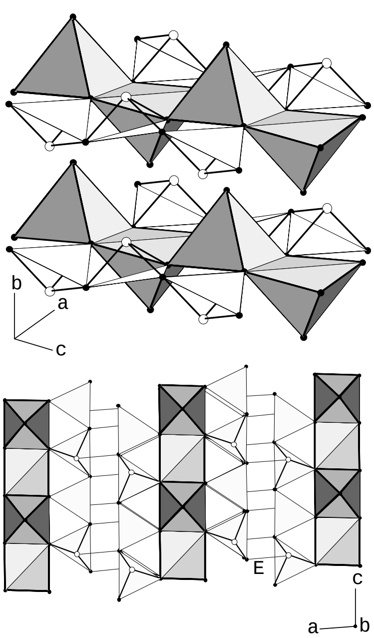

Fig. 1. (a) Polyhedral representation of the $VOSb_2O_4$ structure illustrating the infinite isolated chains of VO_5 pyramids. (b) the (*ac*) plan projection of the crystal structure of $VOSb_2O_4$.

[010] and the [100] direction, respectively. Thus from a magnetic point of view, the $VOSb_2O_4$ structure can be viewed as infinite isolated chains of V^{4+} ions running along the [001] direction. The antimony atoms exhibit the typical one-sided threefold coordination of the oxygen atoms having a stereoactive lone pair E [12] (see Fig. 1b).

Polycrystalline samples of $VOSb_2O_4$ having a light-green color were synthesized by solid-state reaction [12]. ESR X-band spectra were collected using a Bruker ESP300 spectrometer equipped with a standard TE_{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.

The temperature dependence of the magnetic susceptibility $\chi_{\rm raw}(T)$ of a 100 mg polycrystalline sample of $VOSb_2O_4$ in a field of 2 T is shown in Figure 2. Below room temperature, when the temperature is lowered, $\chi(T)$ passes through a broad maximum at $T_{\rm max} \approx 160$ K, which is typical of a $S = 1/2$ Heisenberg chain with $J/k \simeq 250$ K. However, on further cooling the sample, there is a rapid decrease which starts around 40 K, and the slope exhibits a clear maximum at $T_{\rm c} = 13$ K. Finally, there is a minimum at 10 K followed by an increase of the susceptibility indicating the presence of magnetic impurities. The drop that starts around 40 K is reminiscent of a SP transition, but there is a dramatic difference with $CuGeO_3$: there is no cusp in the susceptibility around the temperature where it becomes much smaller than the Bonner-Fisher prediction. On the contrary, the susceptibility drops rapidly but smoothly below 35 K, very much like in $(BCPTTF)_2X$.

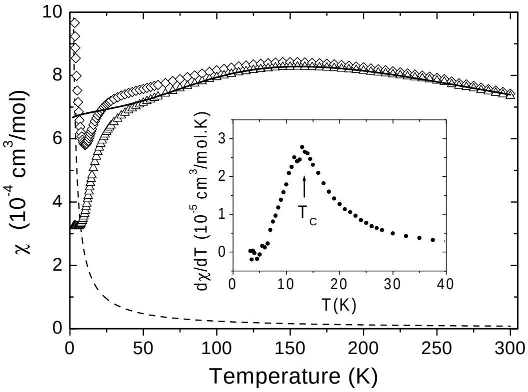

Fig. 2. The temperature dependence of the magnetic susceptibility of a 100 mg $VOSb_2O_4$ polycrystalline sample $\chi_{\rm raw}(T)$ at $H = 2$ T (open diamonds). Open triangles, dashed line and solid line represent the corrected for the impurity contribution $VOSb_2O_4$ susceptibility $\chi_{\rm cor}(T)$, the impurity contribution to $\chi_{\rm raw}(T)$ and the best fit to the $\chi(T)$ of $S = 1/2$ HAF according to equation (50), reference [18] ($J/k = 245 \pm 5$ K, $\chi_0 = 0.00021$ cm^3/mol, $g = 1.66$), respectively. The insert details low temperature behavior of $d\chi_{\rm cor}(T)/dT$.

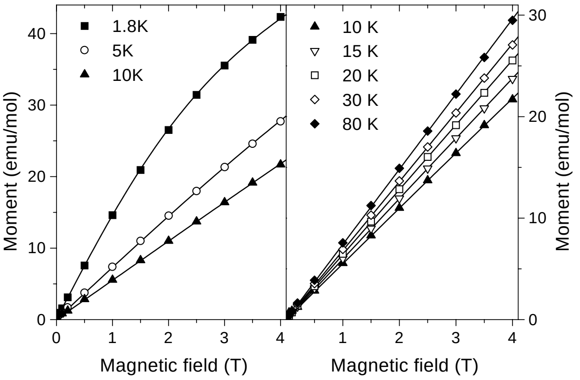

Fig. 3. The magnetization of $VOSb_2O_4$ *vs.* magnetic field at different temperatures. The symbols are experimental data, the solid lines are the fit results according to the equation of $M(H,T)$ discussed in the text.

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 $\chi_{\rm imp}(T)$ to $\chi_{\rm raw}(T)$, particularly with an idea to separate it from the intrinsic susceptibility of the $VOSb_2O_4$ phase, which we will call $\chi_{\rm cor}(T)$,we have carried out magnetization measurements *vs.* H at various fixed temperatures from 80 K to 1.8 K. The results are shown in Figure 3. An important information about $\chi_{\rm imp}(T)$ is contained in the low temperature nonlinear dependence of $M_{\rm imp}(H,T)$ when $\mu H > kT$. Therefore we have to examine the data in Figure 3 using the following equation $M(H,T) = M_{\rm imp}(H,T) + \chi_{\rm cor}(T)\,H$, where $M_{\rm imp}(H,T)$ is expressed in a standard way as $M_{\rm imp}(H,T) = p_{\rm imp}N_A g\mu_B S\,B_S(g\mu_B SH/kT)$, B_S is the Brillouin function, S is an impurity spin value and $p_{\rm imp}$ defines the relative impurity concentration. The results of a fit of the experimental data with this equation are shown in Figure 3 as solid lines. The following parameters $S = 1/2$, $p_{\rm imp} = 0.00573(5)$ 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 $\chi^{-1}_{\rm raw}(T)$. We are now in a position to correct $\chi_{\rm raw}(T)$ for the impurity contribution. In Figure 2 $\chi_{\rm imp}(T) = p_{\rm imp}C/(T+\theta)$ ($C = 0.366$ cm^3 K/mol) is plotted (dashed line) along with the $\chi_{\rm cor}(T) = \chi_{\rm raw}(T) - \chi_{\rm imp}(T)$. This behaviour is consistent with a zero contribution to the spin susceptibility $\chi_{\rm spin}(T) = \chi_{\rm cor}(T) - \chi_0$ at zero temperature if the sum of the diamagnetic and Van Vleck contributions χ_0 is equal to $\chi_{\rm cor}(T = 0)$. While the diamagnetic contribution can be estimated from standard tables ($\chi_{\rm dia} \simeq -1.01 \times 10^{-4}$ cm^3/mol [13]), 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 Figure 4a. 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 ± 0.002 already reported for low-dimensional vanadates [10,14]. 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 ± 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 $\chi_{\rm spin}(T) + \chi_{\rm imp}(T)$ and then using an appropriate procedure for the subtraction of $\chi_{\rm imp}(T)$ to restore the T-dependence of $\chi_{\rm spin}(T)$. In the case of $VOSb_2O_4$ the subtraction of $\chi_{\rm imp}(T)$ 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 $\chi_{\rm imp}(T)$ so, we can use this information to check the correctness of the subtraction at each T. We drop out the technical details of this procedure and postpone them to our forthcoming paper. The $\chi^{\rm ESR}_{\rm spin}(T)$ data as extracted from ESR are given in an inset of Figure 4b. It is clearly seen that the spin magnetic susceptibility of $VOSb_2O_4$ 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 Figure 4a. For example, the 7.3 K ESR spectrum is almost for 95% an impurity one. Note that this temperature dependence is consistent with that deduced from the susceptibility measurements after subtraction of the impurity contributions and assuming that the Van Vleck contribution is such that $\chi_{\rm cor} = 0$ (see inset of Fig. 4b).

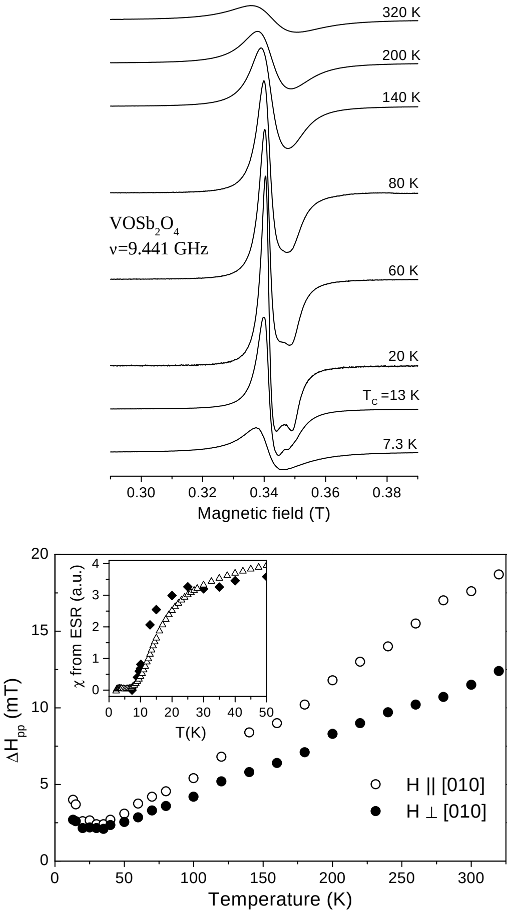

Fig. 4. (a) The temperature evolution of ESR spectra in the $VOSb_2O_4$ polycrystalline sample from 320 to 7.3 K; (b) the temperature dependence of the peak-to-peak linewidth $\Delta H_{\rm pp}$ in $VOSb_2O_4$ extracted from computer simulation of experimental spectra. The insert shows the double integrated ESR spectra intensity $\chi^{\rm ESR}_{\rm spin}(T)$ (solid diamonds). $\chi_{\rm spin}(T) = \chi_{\rm cor}(T) - \chi_0$ deduced from Figure 2 is also shown scaled with $\chi^{\rm ESR}_{\rm spin}(T)$ so, that $\chi_{\rm spin}(T_{\rm max}) = \chi^{\rm ESR}_{\rm spin}(T_{\rm max})$.

Another very important information is contained in the temperature dependence of the line width. As seen in Figure 4b, the peak-to-peak linewidth $\Delta H_{\rm pp}$ shows a characteristic V-like temperature dependence (a strong decrease of ΔH replaced at $T \approx 13$ K by the beginning of a rapid increase of ΔH). Note that such a behaviour has been previously observed in both SP materials NaV_2O_5 and $CuGeO_3$ [15], 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 the dramatic suppression of magnetic fluctuations at low temperature: Frustration or dimerization due to a SP transition. Let us analyze both possibilities [16].

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 [17,18]. 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 $\chi_{\mathrm{spin}}(T)$ 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 [10], 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 $VOSb_2O_4$ than in $MgVO_3$, especially in the *a*-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 $VOSb_2O_4$ 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 [19–21] is possible (see Fig. 2), although with an effective *g*-factor smaller than the actual one measured in ESR.

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, ESR is a dynamical probe, and it indicates that there is a change of regime between fast and slow fluctuations, but it does not allow to conclude that we have a static order. Clear signatures of the transitions, like new Bragg peaks or new phonons lines below 13 K, are not available yet. In fact, if 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 [4], 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 pseudo-gap opens in the quasi-1D vanadium oxide $VOSb_2O_4$ from susceptibility, magnetization and ESR data. The most original aspect of this system with respect to other inorganic spin 1/2 chains is that the drop of the susceptibility starts at a temperature much higher than the temperature where an actual phase transition seems to take place. Given the very one-dimensional structure of the compound, we believe that the most likely explanation of this behaviour is that the drop of the susceptibility is due to the opening of a pseudo-gap due to pretransitional structural fluctuations, and that the dramatic change of behaviour of the ESR signal at lower temperature is due to a spin-Peierls transition. 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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16. *A priori*, one could also try to explain the observed magnetic behaviour in $VOSb_2O_4$ on the basis of either: (i) an AFM phase transition, or (ii) the alternating Heisenberg chain. However an AFM transition at low temperature would be in strong contradiction with our EPR experiments: In this case, one should observe a critical line broadening when approaching T_c from above instead of a strong line narrowing as observed experimentaly and shown in Figure 4b. The alternating Heisenberg chain cannot be considered as a plausible explanation either in the case of $VOSb_2O_4$: According to the crystal structure analysis the V^{4+} ions occupy equivalent positions in the $VOSb_2O_4$ lattice which gives rise to a uniform distribution of exchange integrals in the V-O-V chains.
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