Comment on ”Low-dimensional spin $S=1/2$ system at the quantum critical limit: Na$_2$V$_3$O$_7”$ 

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From the experimentally measured temperature dependence of the magnetic susceptibility $\chi(T)$ of Na$_2$V$_3$O$_7$, exhibiting at temperatures below 100 K drastic violation of the Curie-Weiss law, Gavilano et al. [1] have inferred that the effective moment of the V$^{4+}$ ion in Na$_2$V$_3$O$_7$ is reduced by the one order of magnitude upon reducing the temperature from 100 to 10 K. In the figure 1 of Ref. [1] it is seen that after taking into account the diamagnetic contribution $\chi_o (= -0.0005 \text{ emu/mol f.u.})$ the inverse susceptibility shows in the temperature range 100-300 K a straight line behavior with the effective moment $p_{\text{eff}}$ of 1.9 $\mu_B$ per V ion. Another straight line between 20 and 1.9 K implies $p_{\text{eff}}$ of one order of magnitude smaller. Gavilano et al. provide an explanation that ”The reduction of the effective magnetic moment is most likely due to a gradual process of moment compensation via the formation of singlet spin configurations with most but not all of the ions taking part in this process. This may be the result of antiferromagnetic interactions and geometrical frustration.” They further conjectured, recalling the structural speciality (nanotubes), ”the compensation of eight out of the nine V spins ...” in order to reproduce the observed reduction of the effective moment by one order of magnitude. Moreover, they also found that Na$_2$V$_3$O$_7$ shows no sign of the magnetic order down to 1.9 K - we find this experimental observation to be in sharp contradiction with the earlier conclusion about the presence of strong antiferromagnetic interactions.

In this Comment [2] we would like to argue that this drastic violation of the Curie-Weiss law can be understood as caused by well-known conventional phenomena like the crystal field

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(CEF) interactions but with taking into account the intra-atomic spin-orbit (s-o) coupling for the V$^{4+}$ ion ($3d^1$ configuration). There is the general agreement that in Na$_2$V$_3$O$_7$ there are V$^{4+}$ ions. Calculations, motivated by Gavilano et al.’s paper, of the electronic structure of the V$^{4+}$ ion ($3d^1$ configuration) under the action of the CEF and s-o interactions with the resulting $\chi(T)$ dependences are presented in Ref. [3]. These calculations followed our earlier results [4, 5, 6]. Refs [3] and [6] have been devoted to the $3d^1$ configuration. Our calculations prove the enormous influence of the spin-orbit coupling and of crystal-field interactions on the temperature dependence of the paramagnetic susceptibility (and other thermodynamical properties) revealing the drastic violation of the Curie-Weiss law at low temperatures. We think that our results are quite obvious for some people, in particular for those having experience with CEF effects in rare-earth compounds and knowing a 70-year-old book of Van Vleck [7]. This Comment is motivated by the subsequent rejection by the Editor of Phys. Rev. Lett. of our paper "Spin-orbit origin of large reduction of the magnetic moment in Na$_2$V$_3$O$_7"$ [3], in which we propose our CEF+s-o-based explanation.

In Fig. 1 we present the calculated influence of the spin-orbit coupling and crystal-field interactions on the atomic-scale susceptibility. From this figure the significant departure from the Curie law as well as from the $S=1/2$ behavior due to the spin-orbit coupling and distortions is clearly seen, in particular at low temperatures. Curve 3, calculated for the octahedral crystal field $B_1=+200$ K, the spin-orbit coupling $\lambda_{s-o}= +360$ K and an off-octahedral trigonal distortion $B_2^0=+9$ K, reproduces very well measured experimental data (shown as x in Fig. 1, after Refs [1, 8]) with taking into account the diamagnetic term $\chi_o$ of -0.0007 $\mu_B/T$ V-ion ($\simeq -0.0004$ emu/mol V)). We treat this coincidence as not fully relevant owing to the much more complex local symmetry of the V$^{4+}$ ion in Na$_2$V$_3$O$_7$, to a large uncertainty in the evaluation of the diamagnetic term and of the paramagnetic susceptibility measured on a polycrystalline sample. We take, however, the reached agreement as strong argument for the high physical adequacy of our CEF+s-o approach and as strong indication for the existence of the fine electronic structure in Na$_2$V$_3$O$_7$, originating from the V$^{4+}$ ion, determined by crystal-field and spin-orbit interactions. Very important is the fact that our approach is able to reproduce the overall $\chi(T)$ dependence in the full measured temperature range and that it reproduces the absolute value (it is really not trivial result) of the macroscopic magnetic susceptibility. For the recalculation of the microscopic atomic-scale susceptibility we take into account only the number of the V ions involved - here for
the molar susceptibility simply the Avogadro number is taken.

FIG. 1: The calculated temperature dependence of the atomic-scale paramagnetic susceptibility shown in the $\chi^{-1}$ vs $T$ plot for the $3d^1$ configuration in the $V^{4+}$ ion for different physical situations: line (1) - for the purely octahedral crystal field with $B_4=+200$ K ($\lambda_{s-o}=0$); line (2) - the octahedral crystal field with $B_4=+200$ K in combination with the spin-orbit coupling $\lambda_{s-o}=+360$ K; line (3) shows the influence of the off-octahedral trigonal distortion $B_0^2=+9$ K. Curve (3) reproduces very well measured experimental data ($\chi_o$ after Refs [1, 8] with taking into account the diamagnetic term $\chi_o$ of $-0.0007 \mu_B/\text{V-ion}$ ($\simeq -0.0004$ emu/mol V)).

The ground state has weak magnetic moment due to the large orbital moment compensating the spin moment. In $\text{Na}_2\text{V}_3\text{O}_7$ there is a low-energy electronic structure originating from the $V^{4+}$-ion fine structure like that shown in Fig. 1(4) of ref. [3]. The energy level scheme contains 2 close excited doublets at 58 and 580 K and the Kramers-doublet ground-state moment amounts to $\pm 0.21 \mu_B$ ($=2(-0.23)\pm 0.25$). It is important to realize that whatever lower symmetry is in case of the $V^{4+}$ ion 5 Kramers doublets always are. The used parameters $B_4$ (+200 K), $\lambda_{s-o}$ (+360 K $\simeq$ 31 meV) and $B_0^2$ (+9 K) have clear physical meaning.
These both theoretical approaches can be experimentally distinguished. In the approach of Ref. 1 only 1/9 vanadium atoms contribute to the susceptibility at low temperatures whereas in the QUASST approach all vanadium atoms basically equally weakly contribute to $\chi$. But for searching for the truth the open exchange of information and the open discussion must be guaranteed. Moreover, our approach allows to calculate a number of zero-temperature properties, the low-energy electronic structure and other thermodynamical properties like has been presented in Refs 5, 6, 7, 9, 10, 11, 12, 13. All of them can be experimentally verified, the low-energy electronic structure by the EPR spectroscopy for instance, in contrary to explanation of Ref. [1]. We hope that this discussion will help to solve the very serious scientific problem about the role played by the spin-orbit interactions and by orbital magnetism in 3d-atom containing compounds.

In conclusion, we argue that well-established phenomena like the spin-orbit coupling, even quite weak, crystal-field interactions of low symmetry and the orbital magnetism have to be taken into consideration for explanation of non-trivial electronic and magnetic properties of Na$_2$V$_3$O$_7$ before other exotic mechanisms are proposed.

[1] J. L. Gavilano, D. Rau, S. Mushkolaj, H. R. Ott, P. Millet, F. Mila, Phys. Rev. Lett. 90, 167202 (2003).

[2] We are not in favour of writing of Comment, in which as the editorial obligation one has to criticize or correct somebody’s paper - thus please treat Comment as an extended normal scientific discussion. We are forced to write Comment due to a hardly understandable and unacceptable politics of the Editors of Phys. Rev.Lett., who find papers on the electronic structure and the magnetism of 3d-ion compounds, pointing out the importance of the spin-orbit coupling and the orbital moment, as inappropriate for the publication.

[3] R.J. Radwanski and Z. Ropka, Spin-orbit origin of large reduction of the effective moment in Na$_2$V$_3$O$_7$, [http://xxx.lanl.gov/abs/cond-mat/0309460](http://xxx.lanl.gov/abs/cond-mat/0309460). It has been rejected by the Editor of Phys.Rev.Lett. with the use of the referee argument that the s-o coupling is only a small perturbation. This paper followed original submission of 11-07-2003 "To the origin of large reduction of the effective moment in Na$_2$V$_3$O$_7" that can be found in [http://xxx.lanl.gov/abs/cond-mat/0307272](http://xxx.lanl.gov/abs/cond-mat/0307272).
[4] R. J. Radwanski and Z. Ropka, *Relativistic effects in the electronic structure for the 3d paramagnetic ions*, http://xxx.lanl.gov/abs/cond-mat/9907140.

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[13] Z. Ropka and R. J. Radwanski, Phys. Rev. B **67**, 172401 (2003).