To the origin of large reduction of the effective moment in Na$_2$V$_3$O$_7$

Z. Ropka
Center for Solid State Physics, S$^2$Filip 5, 31-150 Krakow, Poland

R.J. Radwanski
Center for Solid State Physics, S$^2$Filip 5, 31-150 Krakow, Poland,
Institute of Physics, Pedagogical University, 30-084 Krakow, Poland

We have shown that the observed large reduction of the effective moment in Na$_2$V$_3$O$_7$ may be caused by conventional crystal-field interactions and the intra-atomic spin-orbit coupling of the V$^{4+}$ ion. The fine discrete electronic structure of the 3$d^1$ configuration with the weakly-magnetic Kramers-doublet ground state, caused by the large orbital moment, is the reason for anomalous properties of Na$_2$V$_3$O$_7$. Moreover, according to the Quantum Atomistic Solid-State Theory (QUASST) Na$_2$V$_3$O$_7$ is expected to exhibit pronounced heavy-fermion phenomena at low temperatures.

Keywords: crystal-field interactions, spin-orbit coupling, orbital moment, Na$_2$V$_3$O$_7$

PACS: 71.70.E, 75.10.D

Gavilano et al. \cite{Gavilano} have discovered that the effective moment of the V$^{4+}$ ion in Na$_2$V$_3$O$_7$ is reduced by 1 order of magnitude upon reducing the temperature from 100 to 10 K. The moment reduction is inferred from the experimentally measured temperature dependence of the magnetic susceptibility. After taking into account the diamagnetic contribution the inverse susceptibility shows in the temperature range 100-300 K a straight line behaviour with the effective moment $p_{eff}$ of 1.9 $\mu_B$ per V ion. A straight line between 20 and 1.9 K implies $p_{eff}$ of 1 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 "the compensation of eight out of the nine V spins ..." in order to reproduce the observed reduction of the effective moment by 1 order of magnitude. It is worth to add that Na$_2$V$_3$O$_7$ shows no sign of the magnetic order down to 1.9 K.

The aim of this Letter is to propose an explanation for this reduction of the effective moment in Na$_2$V$_3$O$_7$. We can reproduce very well the observed temperature dependence of the paramagnetic susceptibility by considering the electronic structure associated with the V$^{4+}$ ion (3$d^1$ configuration) under the action of the crystal field (CEF) taking into account the spin-orbit (s-o) coupling. It turns out that, despite of the Kramers doublet ground state, a state with quite small magnetic moment can be obtained as an effect of the spin-orbit coupling, that involves quite large orbital moment. In our present explanation we have been oriented by our earlier calculations for the V$^{4+}$ ion presented in Refs \cite{Ref1, Ref2}.

We assume that one 3$d$ electron in the V$^{4+}$ ion is described by quantum numbers $L=2$ and $S=1/2$. The ground term $^2D$ is 10-fold degenerated. Its degeneracy is removed by the intra-atomic spin-orbit interactions and in a solid by crystal-field interactions. This situation can be exactly traced by the consideration of a single-ion-like Hamiltonian

$$H_d = H_{CEF} + H_{s-o} + H_{CF} + H_Z = B_4(O_4^0 + 5O_4^0) + \lambda L \cdot S + B_3^0O_2^0 + \mu_B(L + g_e S) \cdot \mathbf{B}$$

in the 10-fold degenerated spin-orbital space. The last term allows to calculate the influence of the external magnetic field $\mathbf{B}$ and enables calculations of the paramagnetic susceptibility. Such type of the single-ion Hamiltonian has been widely used in analysis of electron-paramagnetic resonance (EPR) spectra of 3$d$-ion doped systems \cite{Ref1, Ref2}. Here we use this Hamiltonian for systems, where the 3$d$ ion is the full part of the crystal. Although we know that the local symmetry in Na$_2$V$_3$O$_7$ is quite complex we approximate, for simplicity, the CEF interactions by considering dominant octahedral interactions with a trigonal distortion. For the octahedral crystal field we take $B_4=+200$ K. The sign "+" comes up from ab initio calculations for the ligand octahedron. The spin-orbit coupling parameter $\lambda_{s-o}$ is taken as +360 K, as in the free V$^{4+}$ ion \cite{Ref1}.

The resulting electronic structure of the 3$d^1$ ion contains 5 Kramers doublets separated in case of the dominant octahedral CEF interactions into 3 lower doublets, the $T_{2g}$ cubic subterm, and 2 doublets, the $E_g$ subterm, about 2 eV above (Fig. 1). The $T_{2g}$ subterm in the presence of the spin-orbit coupling is split into lower quartet and excited doublet (Fig. 1.2). Positive values of the trigonal distortion parameter $B_3^0$ yields the ground state that has

\*URL: http://www.css-physics.edu.pl  
Electronic address: sftradwan@cyf-kr.edu.pl

\[
\text{http://www.css-physics.edu.pl} \quad \text{Electronic address: sftradwan@cyf-kr.edu.pl}
\]
small magnetic moment (Fig. 1.3). For $B_0^0 = +6 \mathrm{K}$ the ground state moment amounts to $\pm 0.15 \mu_B$. It is composed from the spin moment of $\pm 0.42 \mu_B$ and the orbital moment of $\mp 0.27 \mu_B$ (antiparallel). The sign $\pm$ corresponds to 2 Kramers conjugate states. The excited Kramers doublet lies at $38 \mathrm{K}$ ($3.3 \mathrm{meV}$) and is almost non-magnetic - its moment amounts to $\pm 0.03 \mu_B$ only ($= \pm 1.03 \mu_B + 2 \cdot (\mp 0.50 \mu_B)$) due to cancellation of the spin moment by the orbital moment. So small and different moments for subsequent energy levels is an effect of the spin-orbit coupling and distortions.

![Diagram](image_url)

**FIG. 1:** The localized states of the 3$d^1$ configuration in the V$^{4+}$ ion under the action of the crystal field and spin-orbit interactions originated from the 10-fold degenerated $^2D$ term; (1) the splitting of the $^2D$ term by the octahedral CEF surroundings with $B_1 = +200 \mathrm{K}$, $\lambda_{\text{oct}} = 0$; (2) the splitting by the combined octahedral CEF and spin-orbit interactions; (3) and (4) the effect of the trigonal distortions. The states are labelled by the degeneracy in the spin-orbital space and the value of the magnetic moment.

Having the electronic structure, the state energies and eigenfunctions, we calculate the Helmholtz free energy $F(T, B)$. By definition, known from statistical physics, we calculate the paramagnetic susceptibility, as $\chi(T) = -\partial^2 F(T, B)/\partial B^2$, and its temperature dependence. In Figs 2 and 3 the calculated results for the paramagnetic susceptibility are shown for different physical situations of the V$^{4+}$ ion: line (1) for the purely octahedral crystal field; line (2) shows $\chi(T)$ in extra presence of the spin-orbit coupling; lines (3), (4), (5) in extra presence of trigonal distortions $B_0^0$ of different strength. One can see that all these curves are completely different from the $S=1/2$ behaviour, expected for a free spin. The V$^{4+}$ ion with one 3$d$ electron is usually treated as $S=1/2$ system i.e. with the spin-only magnetism and with taking into account the spin degree of freedom only. The neglect in the current literature of the orbital moment is consistent with the widely-spread conviction that the orbital magnetism plays rather negligible role due to the quenching of the orbital moment for 3$d$ ions. Na$_2$V$_3$O$_7$ is an example of numerous compounds in which the $S=1/2$ behavior in the temperature dependence of the paramagnetic susceptibility is drastically violated (CaV$_4$O$_9$, MgVO$_3$, (VO)$_2$P$_2$O$_7$, ...). It is seen in the substantial departure of $\chi(T)$ from the Curie law at low temperatures. The spin-orbit coupling and small distortion of the local surroundings of the V$^{4+}$ ion causes drastic change of the slope of the $\chi^{-1}(T)$ plot below 100 K (Fig. 3, lines (2) and (5)). Such change of the slope is usually treated as the change of the effective moment. In Fig. 4 the temperature dependence of the effective moment per the V ion, calculated as $p_{\text{eff}} = \sqrt{3} \chi T$, are presented for different physical situations shown in Fig. 2. The strong temperature dependence is seen below 100 K, Fig. 4 lines (2) and (5). It means, that the strong temperature dependence results from the spin-orbit coupling and distortions. It is worth to add that negative values of the $B_0^0$ yields the temperature dependence of the susceptibility with a broad maximum due to the almost non-magnetic ground state and excited magnetic doublet, similarly as we calculated in Ref. 2.
FIG. 2: The calculated temperature dependence of the atomic-scale paramagnetic susceptibility $\chi(T)$ for the 3$d^1$ configuration in the V$^{4+}$ ion for different physical situations: line (1) - $\chi(T)$ for the purely octahedral crystal field with $B_4=+200$K ($\lambda_{s-o}=0$); line (2) - in combination with the spin-orbit coupling $\lambda_{s-o}=+360$ K; lines (3) and (4) show the influence of the off-cubic trigonal distortions $B_{02}=+6$ K (3) and $B_{02}=+12$ K (4); curve (5), with $B_{02}=+9$ K, reproduces very well measured experimental data (o, after Refs [1, 6]) after taking into account a diamagnetic term (x).

FIG. 3: The calculated temperature dependence of the atomic-scale paramagnetic susceptibility shown in the $\chi^{-1}$ vs $T$ plot for the 3$d^1$ configuration in the V$^{4+}$ ion for different physical situations defined in Fig. 1 and in the main text. The significant departure from the Curie law as well as from the S=1/2 behavior is seen due to the spin-orbit coupling and distortions.

For comparison we show in Figs 2 and 3 the experimental data (empty circles) taken from Refs [1, 6] for the measured paramagnetic susceptibility. These data have been used for calculations of the effective moment from the Curie law - they are shown in Fig. 4 as empty circles. The data, shown as "x" in Figs 2-4 have been obtained from measured experimental data of Refs [1, 6] by taking into account a diamagnetic term $\chi_o$ of $\mu B/T$ V-ion ($=-0.0004$ emu/mol V). These data (x) coincide well with our calculations shown as line 5 obtained for a set of parameters: $B_4=+200$ K, $\lambda_{s-o}=+360$ K and $B_{02}^2=+9$ K. For this set of parameters the energy level scheme contains 2 excited
FIG. 4: Temperature dependence of the effective magnetic moment $p_{eff}$ calculated from the Curie law for the $3d^4$ configuration in the $V^{4+}$ ion for different physical situations defined in Fig. 1 and in the main text. The significant reduction from a value of 1.73 $\mu_B$, expected for the free spin $S=1/2$, is seen due to the spin-orbit coupling and distortions.

doublets at 58 and 580 K and the ground-state moment amounts to 0.21 $\mu_B$. We treat this coincidence as not fully physically relevant owing to the much more complex local symmetry of the $V^{4+}$ ion in Na$_2$V$_3$O$_7$, a large uncertainty in the evaluation of the diamagnetic term and of the paramagnetic susceptibility measured on a polycrystalline sample. But we take the reached agreement 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. Extremely important is that we can reproduce not only the overall $\chi(T)$ dependence in the full measured temperature range but we also reproduce its absolute value.

In conclusion, we argue that the experimentally-observed temperature dependence of the paramagnetic susceptibility of Na$_2$V$_3$O$_7$ can be explained in single-ion approach, extended to the Quantum Atomistic Solid-State Theory QUASST 

It is further indication for the high physical adequacy of the QUASST conjecture that the electronic and magnetic properties of the $3d$-ion containing compounds are determined by the fine electronic structure of the $3d$ ion. Moreover, we would like to point out that according to QUASST the Kramers spin-like degeneracy of the ground state, not removed down to 1.9 K, has to be removed somewhere - we expect it to occur at very low temperatures. Thus our theory predicts Na$_2$V$_3$O$_7$ to exhibit heavy-fermion-like properties in the specific heat at ultra-low temperatures.

[1] J. L. Gavilano, D. Rau, S. Mushkolaj, H. R. Ott, P. Millet, and F. Mila, Phys. Rev. Lett. 90, 167202 (2003).
[2] R. J. Radwanski, R. Michalski, and Z. Ropka, Physica B 312-313 628 (2002).
[3] Z. Ropka, R. Michalski, and R. J. Radwanski, Anomalous temperature dependences of the susceptibility for the one-3d-electron cation, http://xxx.lanl.gov/abs/cond-mat/9907141.
[4] A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions (Clarendon, Oxford, 1970).
[5] C. Ballhausen: Ligand Field theory (McGraw-Hill, 1962); W. Low: Paramagnetic Resonance in Solids (Academic, 1960).
[6] J. L. Gavilano, D. Rau, S. Mushkolaj, H. R. Ott, P. Millet, and F. Mila, Physica B 312-313 622 (2002).
[7] R. J. Radwanski, R. Michalski, and Z. Ropka, Acta Phys. Polonica B 31 3079 (2000).
[8] R. J. Radwanski and Z. Ropka, Quantum Atomistic Solid State Theory, http://xxx.lanl.gov/abs/cond-mat/0010081.