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Origin of anomalous temperature dependence of the magnetic susceptibility of $BaVS_3$ and MgV_2O_5

R.J. Radwanski[a,b,*], R. Michalski[a,b], Z. Ropka[b]

[a] *Institute of Physics, Pedagogical University, 30-084 Krakow, Poland*
[b] *Center for Solid State Physics, S^nt Filip 5, 31-150 Krakow, Poland*

Dedicated to H.A. Bethe, the pioneer of the CEF theory, on his 95th birth anniversary (2 July 2001)

Abstract

We have shown that the V^{4+} ion with 1d electron can have almost non-magnetic ground state under the action of the octahedral crystal field in the presence of the spin–orbit coupling and off-cubic distortions. It causes anomalous temperature dependence of the magnetic susceptibility at low temperature region like observed in MgV_2O_5. The formation of the weakly magnetic ground state is caused by the substantial orbital moment that almost cancels the spin moment.

Keywords: Crystal electric field (CEF); Spin–orbit coupling; Orbital moment; MgV_2O_5

In compounds MgV_2O_5 and $BaVS_3$, that become nowadays very popular [1–3], the V^{4+} ion occurs with 1d electron. The V^{4+} ion is usually treated as $S=\frac{1}{2}$ system, i.e. with the spin-only degree of freedom. The usual neglect in the current literature of the orbital moment is consistent with the widely spread, but erroneous, conviction that the orbital magnetism plays rather negligible role due to the quenching of the orbital moment for 3d ions. The above-mentioned compounds are example of numerous compounds in which this $S=\frac{1}{2}$ behavior is drastically violated. One of this drastic violation experimentally observed is associated with the substantial departure of the temperature dependence of the paramagnetic susceptibility $\chi(T)$ from the Curie law at low temperatures marked by the finite susceptibility or even by its substantial decrease.

The aim of this paper is to present results of our studies of the influence of the local symmetry on $\chi(T)$ for the d^1 electronic system, but in the presence of the spin–orbit coupling. In our approach we take into account the spin and orbital momenta.

One d electron is described by quantum numbers $L=2$ and $S=\frac{1}{2}$. The term ^2D is 10-fold degenerated. We have considered the electronic structure of the d^1 electronic system under the action of the octahedral crystal field H_{CF} and the spin–orbit coupling Hamiltonian H_{s-o} resulting from the well-known single-ion-like Hamiltonian [4,5]

$$H_d = H_{CF}^{cub} + H_{s-o} = B_4(O_4^0 + 5O_4^4) + \lambda L \cdot S + B_2^0 O_2^0 + \mu_B(L + g_e S) \cdot B_{ext}.$$

All terms have the usual meaning—see Ref. [5], where the Fe^{2+} ion has been discussed. The cubic term has been separated owing to its usual dominance.

Exact computations reveal that $\chi(T)$ exhibits a very complex behavior as a function of the spin–orbit coupling and the lattice disortions, Fig. 1. The inclusion of the spin–orbit coupling (curve 2) to the octahedral field causes the complete breakdown of the Curie law and produces the finite, Pauli-like, susceptibility at low temperatures. Moreover, even a decrease of the susceptibility with decreasing temperatures can be obtained allowing the off-cubic distortion to occur as one can see from the curve 4 in Fig. 1. Then a maximum is formed at ambient temperatures. Despite of this complex low-temperature behavior, $\chi(T)$ at temperatures above, say,

*Corresponding author. Center for Solid State Physics, S^nt Filip 5, 31-150 Krakow, Poland. Tel.: +48-12-633-61-46; fax: +48-12-632-40-12.

E-mail address: sfradwan@cyf-kr.edu.pl (R.J. Radwanski).

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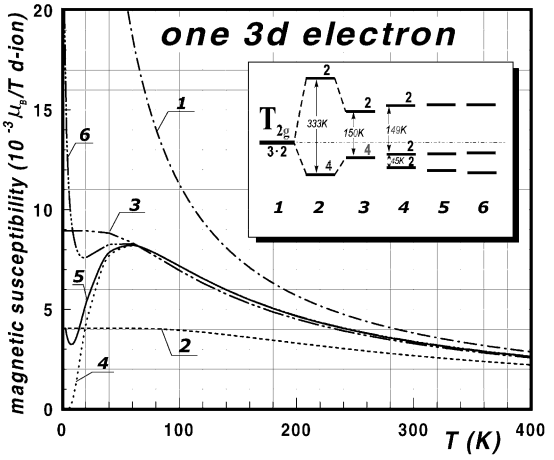

Fig. 1. The calculated temperature dependence of the atomic-scale paramagnetic susceptibility $\chi(T)$ for the $3d^1$ system on the spin–orbit coupling and the lattice off-cubic distortions (1) in the purely octahedral crystal field ($B_4 = +200\,\mathrm{K}$), (2) in the presence of the spin–orbit coupling $\lambda_{s-o} = +220\,\mathrm{K}$ and 3) $\lambda_{s-o} = +100\,\mathrm{K}$, (4),(5),(6) show the influence of the off-cubic distortions (4) the tetragonal $B_2^0 = +10\,\mathrm{K}$, (5) and (6) with additional orthorhombic distortions B_2^2 of $+5\,\mathrm{K}$ (5) and of $+10\,\mathrm{K}$ (6). In the inset the associated low-energy electronic structures are schematically shown.

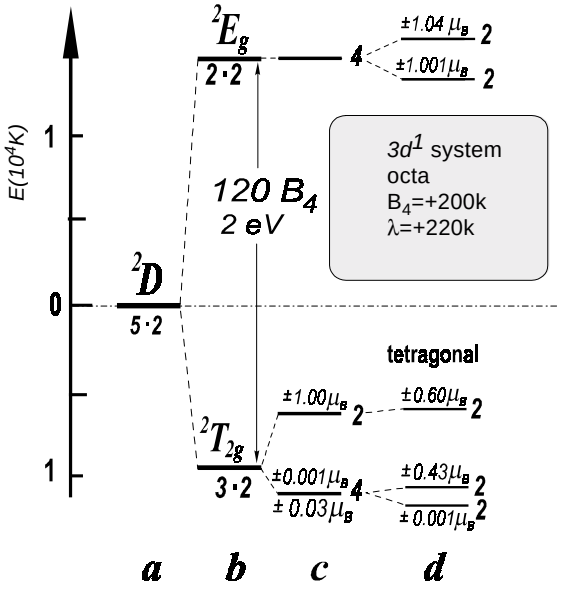

Fig. 2. The localized states of the $3d^1$ electron under the action of the crystal field and spin–orbit interactions: (a) the 10-fold degenerated ^2D term realized in the absence of the CEF and the s–o interactions; (b) the splitting of the ^2D term by the octahedral CEF surrounding, $\lambda_{s-o} = 0$; (c) the splitting by the combined octahedral CEF and spin-orbit interactions; (d) the effect of the tetragonal distortion. The splittings in (c) and (d) are not to the left-hand scale.

250 K can be quite well approximated by the Curie–Weiss law, though with the effective p_{eff} moment of 2.2–2.8μ_B, much larger than the $S = \frac{1}{2}$ value of 1.73μ_B. These calculated values are close to those typically experimentally observed. But we would like to point out that the appeared Curie–Weiss behavior is purely CEF and spin–orbit coupling effect.

In Fig. 2c is shown the low-energy electronic structure computed for the octahedral crystal-field parameter $B_4 = +200\,\mathrm{K}$ and the spin–orbit coupling constant $\lambda = +220\,\mathrm{K}$ (a value typical for the Ti^{3+} ion, for the V^{4+} ion a value of $+360\,\mathrm{K}$ is expected, [4 p.399]). This value of B_4 yields the E_g–T_{2g} splitting of 2.07 eV in agreement with optical experiments that reveal the absorption line at 2–3 eV in a number of 3d ion compounds. The ground state in the purely octahedral oxygen (MO_6) surrounding is only very weakly magnetic. This weakly magnetic state results from the almost perfect compensation of the orbital and spin moments. The formation of the very weakly magnetic state in the atomic scale is really interesting result owing to the Kramers doublet ground state.

In conclusion, the spin–orbit coupling and the departure of the local crystal-field symmetry from the octahedron cause complex behavior at low temperatures like finite or even zero low-temperature susceptibility with a rounded maximum at ambient temperatures. The intra-atomic spin–orbit coupling forms the weakly magnetic ground state of the V^{4+} ion on the atomic scale. According to the quantum atomistic solid-state theory (QUASST) these atomic discrete energy states are preserved when the paramagnetic atoms becomes the part of the solid [6].

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