Almost non-magnetic ground state of the V^{4+} ion: the case of $BaVS_3$

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We have shown that the V^{4+} ion with 1 d 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. Such the situation occurs in the hexagonal $BaVS_3$. The fine discrete electronic structure with the weakly-magnetic Kramers-doublet ground state is the reason for anomalous properties of $BaVS_3$.

The V^{4+} ion is realized in such compounds as CaV_4O_9, $MgVO_3$, $(VO)_2P_2O_7$, $BaVS_3$ that become nowadays very popular [1–9]. The V^{4+} ion with one 3d electron, a $3d^1$ system, is usually treated as S=1/2 system i.e. with the spin-only magnetism and with taking into account the spin degrees of freedom only [1–9]. 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 3d ions. The above mentioned compounds are example of numerous compounds in which this S=1/2 behavior is drastically violated [1–9]. One of this drastic violation

experimentally-observed is associated with the substantial departure of the temperature dependence of the paramagnetic susceptibility from the Curie law at low temperatures and the formation of a non-magnetic state at low temperatures.

The aim of this Letter is to study the magnetic moment of the V^{4+} ion in $BaVS_3$ by consideration of the eigen-states and eigen-functions of the $3d^1$ electron system under the action of the octahedral crystal field (CEF) in the presence of the spin-orbit (s-o) coupling and a small off-cubic distortion. It turns out that, despite of the Kramers doublet ground state, a ground state with quite small magnetic moment can be obtained as an effect of the off-cubic distortions.

One $3d$ electron is described by L=2 and S=1/2. The term ^{2}D is 10-fold degenerated. Its degeneracy in a solid is removed by crystal-field interactions and the intra-atomic spin-orbit interactions. The latter is described by a well-known Hamiltonian $H_{s-o} = \lambda L \cdot S$. The crystal-field Hamiltonian is related with the local symmetry of the V^{4+}-ion site. This local symmetry can be quite low as well as there can be a few cationic sites. In case of the hexagonal structure of $BaVS_3$ (the $CsCoCl_3$ type) the nearest cationic surrounding is formed by 6 sulphur anions. This sulphur surrounding is close to the octahedral surrounding [7, 8] - the hexagonal axis of the elementary cell lies along the main diagonal of the local octahedron. Thus, the crystallographic structure of $BaVS_3$ suggests the start for the analysis of the crystal-field interactions from the dominant octahedral CEF interactions supplemented by an off-cubic trigonal distortion.

This situation can be exactly traced by the consideration of a single-ion-like Hamiltonian

$$H_d = H_{CF}^{octa} + H_{s-o} + H_{CF}^{tr} =$$
$$B_4(O_4^0 + 5O_4^4) + \lambda L \cdot S + B_2^0 O_2^0 + \mu_B(L + g_e S) \cdot B_{ext} \qquad (1)$$

in the 10-fold degenerated spin+orbital space. The last term allows to calculate the influence of the external magnetic field. It allows also the calculations of the paramagnetic susceptibility. Such type of the Hamiltonian has been widely used in analysis of electron-paramagnetic resonance (EPR) spectra of $3d$-ion doped systems [10, 11]. Here we use this Hamiltonian for systems, where the $3d$-ion is the real part of the crystal.

The resulting electronic structure of the V^{4+} ion contains 5 Kramers doublets separated in case of the dominant cubic CEF interactions into 3 lower doublets (originated from the T_{2g} cubic sub-term) and 2 doublets (from the E_g sub-term) 2-3 eV above (T_{2g}-$E_g = 120 \cdot B_4$; we take

B_4= +200 K, the sign + corresponds to the ligand octahedron). The 3 lower doublets are spread over 1.5·λ_{s-o} (λ_{s-o} is taken as +360 K, after [10]). The octahedral CEF states in the presence of the spin-orbit coupling have been shown in Ref. 12 - for the $3d^1$ system the T_{2g} subterm is split into lower quartet and a doublet at 1.5·λ_{s-o}. The quartet states, that are in fact two Kramers states, have very small magnetic moments [12]. Negative values of the trigonal distortion parameter B_2^0 yields the ground state that is almost non-magnetic. Here we focus on the trigonal distortion as the tetragonal distortion has been studied in Ref. 13. For B_2^0 = -20 K the ground state moment amounts to ±0.06 μ_B. It is composed from the orbital moment of ±0.74 and the spin moment of ∓68 μ_B (antiparallel). The sign ± corresponds to 2 Kramers conjugate states. The excited Kramers doublet lies at 110 K (=10 meV) and is strongly magnetic - its moment amounts to ±0.45 μ_B (=±0.46+2·(∓0.005)). We ask ourselves for the origin of the trigonal distortion. Obviously, it has the main source in the lattice trigonal distortion. In fact, it can be quite easily realized in the hexagonal structure via the elongation or the contraction along the hexagonal axis without the change of the overall hexagonal symmetry. The trigonal distortion of the crystal field, with the negative value of B_2^0, is additionally produced by the positive charges located on the V ions in the hexagonal plane.

The existence of such the discrete electronic structure with such strange magnetic characteristics causes enormous effect in the temperature dependence of magnetic and electronic properties like it was calculated for $LaCoO_3$ [14]. In particular, the susceptibility is very small at low temperatures and exhibits a maximum at ambient temperatures. Moreover, we would like to point out that the Kramers spin-like degeneracy of the ground state has to be removed somewhere - we expect it to occur at very low temperatures. Thus our theory predicts $BaVS_3$ to exhibit heavy-fermion like properties in the specific heat at ultra-low temperatures.

In conclusion, the very strong influence of the spin-orbit coupling on the realized ground state and its magnetic moment has been proved for the V^{4+} ion within the CEF theory. Almost non-magnetic Kramers doublet ground state can be formed by off-cubic crystal-field distortions. Such conditions are realized in the hexagonal structure of $BaVS_3$. The crystal-field effect of a low symmetry and the spin-orbit coupling is, according to us, the reason for experimentally-observed anomalous behavior of $BaVS_3$. In our atomic-like approach there is very strong correlation between the local symmetry and the realized magnetic moment. This atomic-like approach, extended to the quantum atomistic

solid-state theory (QUASST), points out that such considerations are physically meaningful as the whole crystal $BaVS_3$ is built up from the face-sharing VS_6 octahedra stacking along the hexagonal axis. In order to avoid a undeserved critique we would like to say that we do not claim that everything can be explained in a solid state by atomic physics but more subtle effects known from atomic physics have to be employed for the understanding of solid-state properties. It means, in particular, that compounds with V^{4+} ions cannot be simplified as S=1/2 systems, despite of consideration of spin ladders or spin chains. It means also that the intra-atomic spin-orbit coupling has to be taken into account for any meaningful description of electronic and magnetic properties of $3d$-ion containing compounds.

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