Anomalous temperature dependences of the susceptibility for the one-3d-electron cation

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Abstract
We have studied properties of the one-3d-electron cation (Ti\textsuperscript{3+}, V\textsuperscript{4+} ions) under the action of the low-symmetry crystal field in the presence of the spin-orbit coupling. Very anomalous temperature dependences of the magnetic susceptibility \(\chi(T)\) have been obtained as resulting from the off-cubic lattice distortion provided the intra-atomic spin-orbit coupling is taken into account. It indicates that, despite of the weakness of the spin-orbit coupling, the one 3d electron in a solid cannot be treated as a free S=1/2 spin. The same holds for compounds containing the Ti\textsuperscript{3+} and V\textsuperscript{4+} ions.

1 Introduction
The one-3d-electron cation occurs in such compounds as CaV\textsubscript{4}O\textsubscript{9}, MgVO\textsubscript{3}, LiV\textsubscript{2}O\textsubscript{4}, LaTiO\textsubscript{3}, NaV\textsubscript{2}O\textsubscript{5}, (VO\textsubscript{2})\textsubscript{2}P\textsubscript{2}O\textsubscript{5} that become nowadays very popular [1-5]. Compounds containing V\textsuperscript{4+} and Ti\textsuperscript{3+} ions are usually treated as a S=1/2 system i.e. with the spin-only magnetism. 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. However, this S=1/2 behavior is drastically violated in the above mentioned compounds [1-5]. One of
this drastic violation experimentally-observed is associated with substantial departure of the temperature dependence of the paramagnetic susceptibility from the Curie law at low temperatures marked by the anomalous temperature dependence of the magnetic susceptibility exhibiting a pronounced maximum centered at 20-100 K and low susceptibility at low temperatures.

The aim of this paper is to show that anomalous temperature dependences of the paramagnetic susceptibility can result from low-symmetry crystal-field (CEF) interactions of the one-3d-electron cation provided the intra-atomic spin-orbit (s-o) coupling is taken into account.

2 Theoretical outline

We have considered the electronic structure of the one-3d-electron cation under the action of the crystal-field interactions $H_{CF}$ and the spin-orbit coupling Hamiltonian $H_{s-o}$ as resulting from the single-ion-like Hamiltonian [6-9]

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

The crystal field has been divided into the cubic part, usually dominant in case of compounds containing 3d ions, and the off-cubic distortion written by the second-order leading term $B_2^0 O_2^0$. The last term allows the influence of the external magnetic field to be calculated. $g_e$ amounts to 2.0023. It is necessary for calculations, for instance, of the paramagnetic susceptibility - in fact the paramagnetic susceptibility is calculated [10] as the magnetization in an external field of, say, 0.1 T.

The detailed form of the Hamiltonian (1) is written in the LS space that is the 10 dimensional spin-orbit space. The L and S quantum numbers for one 3d electron are equal to $S=1/2$ and $L=2$. The Hamiltonian (1) is customarily treated by perturbation methods [6] owing to the weakness of the s-o coupling for the 3d ions in comparison to the strength of the crystal-field interactions. We have accepted the weakness of the s-o coupling, what is reflected by the sequence of terms in the Hamiltonian (1), but we have performed direct calculations treating all shown terms in the Hamiltonian (1) on the same foot. The separate figures, if presented are shown for the illustration reasons.

Calculations [10] have been performed for physically relevant values of $\lambda_{s-o}$ close to +220 K ($=150 \text{ cm}^{-1}$) - such the value is given for the Ti$^{3+}$ ion [6 p.399]. The cubic CEF parameter $B_4$ is taken as +200 K. The positive
sign refers to the octahedral ligand surrounding of the 3d cation. For these parameters the overall effect of the s-o coupling amounts to about 30 meV what is only 1.5 % of the octahedral CEF splitting. It turns out that despite of so small s-o coupling its effect on properties is enormous, on the magnetic properties, in particular. It is related with the fact of almost perfect compensation of the spin moment by the orbital moment for the realized ground state.

3 Results and discussion

In Fig. 1 the temperature dependence of the paramagnetic susceptibility $\chi(T)$ is shown for different strength of the s-o coupling and different off-cubic distortions. The inclusion of the s-o coupling breaks down the Curie law at low temperatures as one can see comparing the curve 1 (no s-o coupling) with curves 2 and 3, where $\lambda_{s-o}$ amounts to $+220$ K and $+100$ K, respectively. In contrary to the curve 1, resembling the Curie law expected for the free $S=1/2$ spin, the susceptibility shown by curves 2 and 3 exhibits at low temperatures a saturated behaviour resembling the Pauli paramagnetism. The low-temperature saturation value decreases with increasing the strength of the s-o coupling. For $\lambda_{s-o}$ of $+220$ K it saturates at level of $4 \cdot 10^{-3}$ $\mu_B/T$ per d-ion. It corresponds to $2.2 \cdot 10^{-3}$ emu/mole provided that all spins in the lattice contribute identically to the macroscopically observed susceptibility. Values of this order are experimentally observed, indeed [1-5]. It can be noted that despite of very anomalous behavior at low temperatures, all $\chi(T)$ curves converge at temperatures above 300 K. Above this temperature the temperature dependence can be approximated by the Curie-Weiss law though the non-linearity of the $\chi^{-1}(T)$ plot is visible if too large temperature interval is considered.

The origin of such interesting temperature behavior of the paramagnetic susceptibility is related with the low-energy electronic structure. In Fig. 2c the discrete low-energy electronic structure, computed for the octahedral crystal-field parameter $B_4 = +200$ K and the spin-orbit coupling constant $\lambda_{s-o} = +220$ K is shown. Fig. 2d shows further splitting into three Kramers doublet states (A,B,C) by the tetragonal distortion of $B_2^0 = +10$ K. It is obvious that the existence of such the discrete energy spectrum will affect enormously electronic and magnetic properties, in particular at low temperatures.
For magnetic properties the existence of the Kramers doublet ground state with the very small magnetic moment and of the substantial moment at the excited state is extremely important. With increasing temperature the excited states become thermally populated and owing to drastically different values of the magnetic moment the conventional Boltzmann distribution function produces the maximum in the $\chi(T)$ plot. In Fig. 3 the population of the three lowest states (A,B,C) from Fig. 2d is shown.

We would like to point out that the exotic properties are not associated with the shown parameters. Surely they do not result from a special choice of parameters. Very similar low-energy structure and the $\chi(T)$ curve is obtained for other parameters - of course the energy separations and the magnetic moments will be different. We point out that the discussed by us parameters are physical measurable parameters and they are related with the atomic physics and the local symmetry.

Very important outcome is that the 3d$^1$ electron system in the octahedral oxygen surrounding, a MO$_6$ complex, has a very weakly-magnetic ground state. This weakly-magnetic ground state results from almost perfect compensation of the orbital and spin moments. We have calculated that the ground state of the scheme shown in Fig. 2d has $S=\pm0.50$ and $L=\mp1.00$ and its Kramers-like eigenfunction is given as (the z component of L and S are shown)

$$\psi_o = 0.9999 \left| \pm1, \mp \frac{1}{2} \right> - 0.01 \left| 0, \pm \frac{1}{2} \right>$$

where the sign $\pm$ refers to two conjugate Kramers states.

The eigenfunction of the first excited Kramers-like doublet is given as

$$\psi_1 = 0.72 \left| xy, \mp \right> + 0.68 \left| \pm1, \pm \frac{1}{2} \right> ,$$

where $\left| xy, \mp \right>$ function has the usual meaning in the CEF theory for the 3d cubic states [6-9] extended for the spin component as $\left| xy, \mp \right> = \sqrt{1/2} \left( \left| 2, \mp \frac{1}{2} \right> - \left| 2, \mp \frac{3}{2} \right> \right)$. Making use of the other functions orbital functions $\left| xz \right>$ and $\left| yz \right>$ the eigenfunctions $\psi_o$ and $\psi_1$ can be written as

$$\psi_{o+} = \left| xz, - \right>$$
$$\psi_{o-} = \left| yz, + \right>$$
$$\psi_{1+} = 0.72 \left| xy, - \right> + 0.68 \left| +1, \mp \frac{1}{2} \right> ,$$
$$\psi_{1-} = 0.72 \left| xy, + \right> + 0.68 \left| -1, \mp \frac{1}{2} \right> .$$

From the shape of these functions one can easily see that for the functions $\psi_{o+}$ and $\psi_{o-}$ spin and orbital moments cancels each other. For the $\psi_1$
functions the resultant moment equals $0.68^2(3) - 0.72^2(-1)$ i.e. $0.43 \, \mu_B$ as is shown in Fig. 2d.

The formation of the very-weakly magnetic state the 3d$^1$ electron system is really interesting result owing to the Kramers doublet ground state. The compensation of the spin moment by the orbital moment obviously is related with taking into account the intra-atomic spin-orbit coupling. The removal of the Kramers-doublet ground-state degeneracy will produce further interesting phenomena in ultra low temperatures. Their description goes, however, beyond the present study.

4 Conclusions.

The very strong influence of the spin-orbit coupling and of the lattice off-cubic distortions on the temperature dependence of the local paramagnetic susceptibility has been revealed for the one-3d-electron cation (the 3d$^1$ system). The highly-coupled spin-orbital 3d$^1$ system is thought to be realized in Ti$^{3+}$ and V$^{4+}$ ions existing in ionic compounds like CaV$_4$O$_9$, MgVO$_3$, LiV$_2$O$_4$, NaV$_2$O$_5$. These off-cubic distortions cause very anomalous temperature dependences of the local paramagnetic susceptibility resembling very much those experimentally found in these presently-in-fashion compounds. We would like to point that these anomalous $\chi(T)$ curves are obtained within the localized-electron approach provided that the (weak) intra-atomic spin-orbit coupling is taken into account. Although weak it has enormous influence on the low-energy electronic structure and low-temperature magnetic and electronic properties. We are aware that the calculations have to be extended to take into account other effects - first of them seems to be geometrical effects associated with the non-collinearity of the local symmetry axes. The most important result of this study is that the one 3d electron cannot be treated as the free $S=1/2$ spin. The same holds for compounds containing the Ti$^{3+}$ and V$^{4+}$ ions.

References

[1] M.P.Gelfand, Z.Weihong, R.R.P.Singh, J.Oitmaa and C.J.Hamer, Phys.Rev.Lett. 77 (1996) 2794.
Figure Captions

Fig. 1. Calculated influence of the spin-orbit coupling and the lattice off-cubic distortions on the temperature dependence of the paramagnetic susceptibility $\chi(T)$ for the one-3d-electron cation (the 3d$^1$ system) in the dominant octahedral crystal field ($B_4=+200K$). 1) $\chi(T)$ in the presence of the octahedral CEF but in the absence of the spin-orbit coupling - it shows the Curie law but with $\mu_{\text{eff}}$ of 2.29 $\mu_B$, instead of 1.73 $\mu_B$ expected for the free S=1/2 spin; 2) $\chi(T)$ in the presence of the octahedral CEF and the spin-orbit coupling $\lambda_{s-o} = +220$ K; 3) the same as 2) but for $\lambda_{s-o}$ of +100 K. 4, 5, 6) show the influence of the off-cubic lattice distortions in the presence of the octahedral CEF ($B_4=+200K$) and the spin-orbit coupling $\lambda_{s-o}$ of +100 K; 4) with the tetragonal distortion $B_{2}^0=+10$ K; 5) and 6) with additional orthonmobic distortion $B_{2}^2$ of +5 K (5) and +10 K (6). In the inset the associated low-energy electronic structures are schematically shown.

Fig. 2. The localized states of the one-3d-electron cation under the action of the crystal field and spin-orbit interactions: a) the 10-fold degenerated $^2$D term realized in the absence of the CEF and the s-o interactions; b) the splitting of the $^2$D term by the octahedral CEF surrounding $B_4=+200$ K (
\( \lambda = 0 \) yielding the \( ^2T_{2g} \) cubic subterm as the ground state; c) the splitting of the lowest \( ^2T_{2g} \) cubic subterm by the combined octahedral CEF and spin-orbit interactions (\( \lambda = +220 \) K, \( B_4 = +200 \) K); the degeneracy and the associated magnetic moments are shown; d) the further splitting by the tetragonal distortion of \( B_2^0 = +10 \) K to three Kramers doublet states (A, B, C); the degeneracy and the associated magnetic moments are shown - the very small moment of the Kramers doublet ground state and the substantial moment of the excited doublet is worth to note.

Fig. 3. The temperature dependence of the population of the localized states A, B and C shown in Figure 2d.
One 3d electron

magnetic susceptibility \(10^{-3} \mu_B/T \text{d-ion}\)

\(T_{2g}^{3/2}\)

\(333\text{K}\)

\(150\text{K}\)

\(49\text{K}\)

\(45\text{K}\)

\(1\)

\(2\)

\(3\)

\(4\)

\(5\)

\(6\)
$E \left( 10^4 K \right)$

$\frac{2E_g}{2 \cdot 2}$

$120 B_4 \frac{2 eV}{2 \cdot 2}$

$\frac{2D}{5 \cdot 2}$

$\frac{2T_{2g}}{3 \cdot 2}$

$3d^1$ system
octa

$B_4 = +200 \text{ K}$

$\lambda = +220 \text{ K}$

$\pm 1.04 \mu_B$

$\pm 1.001 \mu_B$

$\pm 1.00 \mu_B$

$\pm 0.60 \mu_B$

$\pm 0.001 \mu_B$

$\pm 0.03 \mu_B$

$\pm 0.43 \mu_B$
The thermal population of the three lowest states is shown in the graph. The population of states is plotted against temperature (T) in Kelvin (K). The states A, B, and C are labeled on the graph, with state A having the highest population decrease as temperature increases, followed by state B, and state C having a minimal change in population with temperature. The energy levels (E) are indicated at specific temperatures, with 314 K and 354 K showing significant changes in population distributions.