Influence of spin-orbit interactions on the cubic crystal-field states of the $d^4$ system*

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Original submission: 27.01.1997

It has been shown that for the highly-correlated $d^4$ electronic system the spin-orbit interactions produce, even in case of the cubic crystal-field interactions, a singlet ground state. Its magnetic moment grows rapidly with the applied magnetic field approaching $4 \mu_B$ for the $E_g$ state, but only $3 \mu_B$ for the $T_{2g}$ state. The applicability of the present results to the Mn$^{3+}$ ion in LaMnO$_3$ is discussed.

4 $d$ electrons of paramagnetic ions form a highly-correlated electron system $3d^4$ as their orbital and spin movements are correlated within the incomplete outer shell. This Letter has been motivated by the recent enormous increase of interest in La$_{1-x}$Ca$_x$MnO$_3$ compounds [1–3]. Surely a large magnetoresistance effect, that enables wide technical applications, vivifies interest to La$_{1-x}$Ca$_x$MnO$_3$ compounds. In the parent LaMnO$_3$ compound the manganese atoms occur in the trivalent state anticipated from valences La$^{3+}$Mn$^{3+}$O$_2$$^-$. This compound is an antiferromagnetic insulator with $T_N$ of 140 K and the low-temperature magnetic moment of about 3.9 $\mu_B$ [1]. The presently discussed electronic structure [1–3] of LaMnO$_3$ completely ignores the effect of spin-orbit interactions and the 5-fold spin degeneracy of the $^5D$ term relevant to the $3d^4$ electronic system.

The aim of the present Letter is to analyze the influence of spin-orbit interactions on the
localized states of the $3d^4$ system produced by crystal-field (CEF) interactions of the cubic symmetry. The $3d^4$ system is realized in paramagnetic ions like Mn$^{3+}$, Cr$^{2+}$, Ru$^{4+}$ ($4d^4$). The Mn$^{3+}$ state is realized in the antiferromagnetic insulator LaMnO$_3$ that recently has got large interest as the parent compound of La$_{2/3}$Ca$_{1/3}$MnO$_3$ shows the Ca-induced ferromagnetism and the enormous magnetoresistance effect at the vicinity of room temperature.

One can be surprised but the influence of the spin-orbit interactions has not been systematically studied though CEF effect is already known by more than 65 years, after the works of Bethe and Kramers at 1930. It is only generally accepted that in 3$d$ ions spin-orbit interactions are much weaker than CEF interactions - such the statement, however, has led to the ignorance of spin-orbit interactions. Nowadays performed band-structure calculations usually ignore spin-orbit interactions with a (wrong) justification by the quenching-orbital-moment effect. The forgetting of the spin-orbit interactions is, however, very dangerous. It will be shown in this Letter that they produce a number of new physical phenomena like the singlet ground state, for instance.

The physical situation of the $3d^n$ system of a 3$d$-transition-metal ion is taken to be accounted for by considering the single-ion Hamiltonian containing the electron-electron d-d interactions $H_{el-el}$, the crystal-field $H_{CEF}$, spin-orbit $H_{s-o}$ and Zeeman $H_z$ interactions:

$$H_d = H_{el-el} + H_{CEF} + H_{s-o} + H_z$$  (1)

The electron-electron and spin-orbit interactions are intra-atomic interactions whereas crystal-field and Zeeman interactions account for interactions of the unfilled 3$d$ shell with charge and spin surrounding. These interactions are written in the decreasing-strength succession.

In a zero-order approximation the electron-electron correlations among the $d$ electrons are accounted for by phenomenological Hund’s rules that yield for the $3d^4$ electron configuration the term $^5D$ with $S = 2$ and $L= 2$ as the ground term. Under the action of the crystal field of the cubic symmetry, the term $^5D$ splits into the orbital triplet $\Gamma_5$, denoted also as $T_{2g}$, and the orbital doublet $\Gamma_3$ ($E_g$). Crystal field (CEF) effects of 3$d$ ions the reader is asked to consult.
The $^5D$ term is 25-fold degenerated. The 5-fold degeneration occurs with respect to the orbital degree of freedom and each orbital state contains the 5 spin-degree of freedom. This situation is accounted for if one considers the single-ion Hamiltonian (1) written in the explicit form for the Hund’s rule $|LS⟩$ term:

$$H_d = B_4(O^4_L + 5O^4_z) + \lambda L \cdot S + \mu_B(L + g_eS) \cdot B_{ext}$$  \hspace{1cm} (2)

The first term is the cubic CEF Hamiltonian with the Stevens operators $O^m_n$ that depend on the orbital quantum numbers $L$ and $L_z$ and $B_4$ is CEF parameter. The second term is the spin-orbit interactions where $\lambda$ is the intra-atomic spin-orbit coupling. The last term accounts for the influence of the magnetic field, the externally applied in the present case. For simplicity the free-electron $g_e$ value is taken as 2.0 instead of 2.0023. The calculations of the many-electron states of the 3$d^4$ system have been performed by the diagonalization of a 25x25 matrix associated with the Hamiltonian (2) considered in the $|LSL_zS_z⟩$ basis.

As a result of the diagonalization we obtain the energies of the 25 states and the eigenvectors containing information e.g. about the magnetic properties. These magnetic characteristics are computationally revealed under the action of the external magnetic field. Due to the spin-orbit coupling the states are no longer purely cubic orbital states $|L, L_z⟩$ denoted as $|x^2 - y^2⟩$, $|3z^2 - r^2⟩$, $|xy⟩$, $|zx⟩$, $|yz⟩$ states. In case of purely cubic CEF interactions two first states form the orbital-doublet $E_g$ state whereas the three last states form the orbital-triplet $T_{2g}$ state. These states are shown in Fig. 1b for an exemplary value $B_4=-10$ K. (In reality, $B_4$ amounts to 100 K - 300 K; here this small value of $B_4$ has been taken to show in the same scale the crystal-field and spin-orbit interactions). In fig. 1c the effect of the spin-orbit interactions with $\lambda$ of $+120$ K ( $+85$ cm$^{-1}$, such the value is given for the Mn$^{3+}$ ion in ref. on p. 399). Inspecting Fig. 1 one can see that spin-orbit interactions i) largely remove the degeneracies of the 10-fold $E_g$ state and of the 15-fold $T_{2g}$ state and yield ii) the singlet ground state. This singlet ground state is produced always, i.e. independently on the sign of the parameter $B_4$ as seen in Figs 1 and 2. In Fig. 2 the same results are shown but for a positive value $B_4 = +10$ K. For a $B_4>0$ the orbital triplet $T_{2g}$ is the CEF ground state whereas for $B_4<0$ the orbital doublet $E_g$ is the ground state.
The reason for the formation of the singlet ground state is very simple. It is, somehow, the manifestation of the 3rd Hund rule, that becomes valid in case of the strong spin-orbit coupling (the situation realized in rare-earth ions). The strong spin-orbit coupling is realized in Figs 1 and 2 by weakening of CEF interactions (going from left to right). The 3rd Hund rule says that the ground multiplet of the \((L=2, S=2)\) term is \(5D_0\) with \(J=L-S=0\) as the incomplete 3d shell is less than half filled. The \(5D_0\) multiplet is a singlet. Such the singlet \(5D_0\) multiplet occurs for the \(d^4\) system where \(\lambda>0\). The formation of the localized singlet ground state by the spin-orbit interactions in the \(d^4\) system, even in case of the doublet \(E_g\) state, is a new and extremely surprising result owing to a general conviction that the orbital-doublet state \((E_g)\) is unaffected by the spin-orbit coupling. It comes from this Letter that this is true for the \(2D\) term applicable to the \(d^1\) and \(d^9\) system but not for the \(d^4\) and \(d^6\) systems where \(S = 2\). This effect has been signalized by Abragam and Bleaney, who wrote that the \(E_g\) state can be split by second-order effects, in the perturbation method, of the s-o coupling. Now it has been proved by direct calculations that these second-order effects have to be taken into account from the beginning. For comparison of the effect of the spin-orbit coupling on the cubic CEF states as has been calculated by Abragam and Bleaney and in the present Letter the reader is asked to compare Fig. 1c and Fig. 7.19b on p.404 of ref. It allows for revealing of the novelty of the present calculations. As mentioned already the Figs 1 and 2 have been made for small values of \(B_4\) parameters. The CEF splitting amounts usually to \(\sim 25000 \text{ K}\), the spin-orbit splitting of the \(T_{2g}\) state - to 600 K \((5\lambda)\). Then the splitting of the \(E_g\) state amounts to 14 K only.

It is worth noting that despite of the singlet nature of the ground state its magnetic moment grows rapidly with applying field as is shown in Fig. 3. In case of the \(E_g\) CEF ground state this induced moment approaches the saturation to an integer value of 4 \(\mu_B\). Fig. 3, curve 1. Such the value is somehow manifestation of the well-known quenching of the orbital moment in 3d paramagnetic ions as just this value one expects for 4 electrons with the spin-moment only. For the \(T_{2g}\) state the moment saturates at level of 3 \(\mu_B\) as one can see from Fig. 3, curves 3 and 4. This strong influence is due to van Vleck term and occurs
so easily because of the presence of a large number of low-energy localized states close to the singlet ground state.

In conclusion, it has been shown that the spin-orbit interactions produce for the highly-correlated $d^4$ system, even in case of the cubic CEF interactions, the fine electronic structure with a singlet ground state both for the octahedral ($B_4<0$) and tetrahedral ($B_4>0$) sites. As spin-orbit interactions are intra-atomic interactions it means that one always deals with the singlet ground state in case of cubic CEF interactions. Despite of its singlet nature the calculations show that its magnetic moment grows rapidly with the applied magnetic field approaching for the $E_g$ state ($B_4<0$) a value of $4.0 \mu_B$. Such the state is expected to be realized in LaMnO$_3$ for which $B_4$ is anticipated for -200 K (and the $i$ ratio of 0.05) from the measured $d - d$ separation of 2.0-2.2 eV. The negative sign of $B_4$ is also consistent with the octahedral ligand surrounding of the Mn$^{3+}$ ion in LaMnO$_3$. From the value of 140 K for $T_N$ in LaMnO$_3$ a molecular field of about 100 T has been inferred. The present calculations clearly prove that for the meaningful discussion of properties of 3$d$ paramagnetic-ion compounds the spin-orbit and CEF interactions have to be taken into account at the starting point of a physical analysis.

* This paper has been submitted to Phys.Rev.Lett. on 27 January 1997 but has been rejected despite of our argument that our electronic structure is basically different from that published in Phys.Rev.Lett., Refs 1-3. A pretty long and intensive discussion has led to a scientific bet for 1 million dollars between the authors and the Editors. The reader is asked to see our later papers.

References

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[6] the computer programme is available on the written request.

[7] one of our papers has been rejected by the Editor of Phys. Rev. B at beginning of 1997 on an argument that our computer program yielding the splitting of the $E_g$ subterm must be wrong. Our long explanations did not help and we were forced to propose, as the real responsibility of Phys.Rev.Lett., a scientific bet for 1 million dollars, if similar discrete structures appear in Phys.Rev.Lett..

[8] R. J. Radwanski and Z. Ropka - to be published (Physica B 186-188, 507 (2000)).

Figure Captions

Fig. 1. Influence of spin-orbit interactions on the localized CEF states of the $3d^4$ system, that is expected to be realized in the Mn$^{3+}$, Cr$^{2+}$ and Ru$^{4+}$ ($4d^4$) ions, placed in the octahedral ligand field, a) The $^5D$ term has 25-fold degeneracy; b) The energy level scheme of the $3d^4$ system under the action of CEF interactions of the cubic symmetry, produced by octahedrally arranged $O^{2-}$ ligands, with $B_4=-10$ K, with the orbital-doublet $E_g$ ground state. All the levels would have the internal 5-fold spin-degree of freedom that could be revealed in the paramagnetic state by applying external fields; c) the effect of the spin-orbit interactions with $\lambda=+120$ K on the localized states of the $3d^4$ system; the states are labelled with the degeneracy - a singlet ground state should be noticed; d) the same as c but for smaller $|B_4|$, i.e. $B_4=-2$ K; e) the multiplet structure obtained for the extremely large spin-orbit coupling realized here by the absence of CEF interactions; $i$ denotes the ratio of the overall spin-orbit splitting ($=10\lambda$) and of the overall CEF splitting ($=120 |B_4|$). In real LaMnO$_3$, $i$ amounts to $\approx 0.05$, i.e. CEF interactions largely prevail the spin-orbit coupling.

Fig. 2. The same as Fig. 1 but for the tetrahedral cubic CEF interactions, i.e. $B_4>0$, 6
that lead to the orbital-triplet $T_{2g}$ ground state.

Fig. 3. The magnetic-field induced magnetic moment of the $3d^4$ system at 0 K with the $E_g$ ($B_4 < 0$, curves 1 and 2) and the $T_{2g}$ ($B_4 > 0$, curves 3 and 4) ground state calculated for $\lambda = +120$ K. The dashed-point lines show results for $|B_4| = 100$ K (curves 2, 4) and the dashed line for $|B_4| = 200$ K (curves 1, 3). The induced-moment somehow saturates to 2, 3 and 4 $\mu_B$ even in the case of magnetic fields so large as 200 T. In LaMnO$_3$ the molecular field at 0 K is anticipated for 100 T.
Fig. 1
Fig. 2