Research Article

The orbital-doublet E_g ground state of the Mn^{3+} ion in $LaMnO_3$

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The Mn^{3+} ion has been treated as a highly-correlated $3d^4$ system in contrary to often discussed one-electron approaches. From the octahedral position of the Mn^{3+} ion in $LaMnO_3$ the crystal-field (CEF) ground state of the $3d^4$ electronic system is inferred to be the orbital-doublet cubic E_g state. The cubic CEF parameter B_4^0 is derived to be -18 meV. The spin-orbit coupling produces, even in case of the cubic CEF interactions, a singlet ground state. Its magnetic moment grows rapidly with the applied magnetic field approaching 3 μ_B for the T_{2g} state and 4 μ_B for the E_g state. This latter value is in agreement with the experimental finding.

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A Mn^{3+} ion has 4 d electrons in the incomplete outer shell that form a highly-correlated electron system $3d^4$. This Letter has been motivated by the recent enormous increase of interest in $La_{1-x}Ca_xMnO_3$ compounds [1–3] - the appearance of a ferromagnetism with T_C of 360 K in Ca-doped compounds is indeed an extremely intryguing scientific problem not solved despite of the fact that the Ca-induced ferromagnetism effect is known by more than 50 years [4]. Surely a large magnetoresistance effect that enables technical applications, vivifies interest

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to $La_{1-x}Ca_xMnO_3$ compounds. In the parent $LaMnO_3$ compound the manganese atoms occur in the trivalent state anticipated from valences $La^{3+}Mn^{3+}O_3^{2-}$. This compound is an antifferomagnetic insulator with T_N of 140 K and the low-temperature magnetic moment of about 3.9 μ_B [5]. This value close to 4 μ_B is **thought to come from 4 largely independent** d **electrons having fully quenched orbital moments** [1–3]. This one-electron picture seems to be oversimplified as it ignores effect of spin-orbit (s-o) interactions and the 5-fold spin degeneracy of the ^{5}D term relevant to the $3d^4$ electronic system. In fact, this one-electron approach is questioned in this Letter as d electrons are known to form highly-correlated systems $3d^n$. For the notation and the analysis of crystal-electric-field (CEF) effects of $3d$ ions the reader is asked to consult a book of Abragam and Bleaney [6], ch. 7.

The aim of the present Letter is to analyse localized states of the $3d^4$ system under the action of the crystal-field and spin-orbit interactions mainly with respect to the local magneti moment. Although cubic CEF states are widely discussed [1–3, 6], here some consequences concerning the many-electron character of the CEF states, the spin degeneracy and the influence of spin-orbit interactions will be clarified. It provides strong arguments for the ground state of the Mn^{3+} ion of the E_g orbital-doublet ground state rather than the orbital-triplet T_{2g} state.

A modern approach to compound like $LaMnO_3$ is based on an idea of Mott that it is strong electron correlations that make electrons in the incomplete $3d$ shell to stay rather localized than itinerant (Mott insulators). In a zero-order approximation the electron correlations are accounted for by phenomenological Hund's rules that yield for the $3d^4$ electron configuration the term ^{5}D with S=2 and L=2 as the ground term. Following the intermediate crystal-field approach [6] the ground term ^{5}D, under the action of the crystal field of the cubic symmetry, splits into the orbital triplet Γ_5, denoted in the intermediate ligand field as T_{2g}, and the orbital doublet Γ_3 (E_g). The ^{5}D term is 25-fold degenerated; 5-fold degeneration occurs with respect to the orbital degree of freedom. Each orbital state contains the 5 spin-degree of freedom. This situation is accounted for if one considers the single-ion Hamiltonian of the $3d^n$ system of the $3d$-transition-metal ion of the form:

$$H_d = B_4^0\ (O_4^0 + 5\ O_4^4) + \lambda\ L{\cdot}S + \mu_B(L + g_eS){\cdot}B_{ext} \qquad (1).$$

The first term is the cubic CEF Hamiltonian with the Stevens operators O_n^m that depend on the orbital quantum numbers L, L_Z. The second term accounts for the spin-orbit interactions. The last term accounts for the influence of the magnetic field, the externally applied in the present case. The free-electron g_e value is taken as 2.0023. The

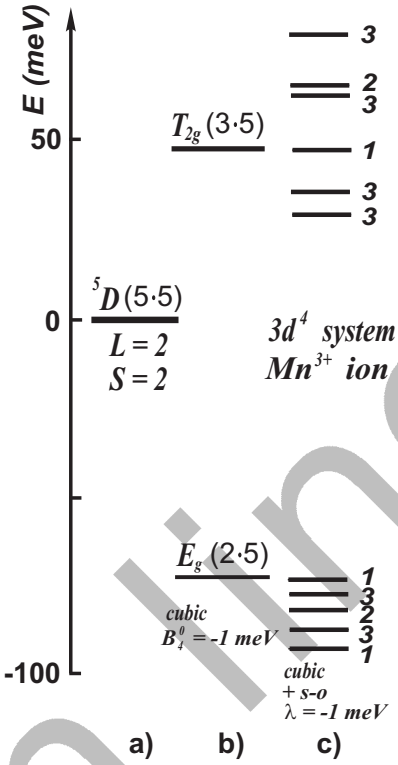

FIG. 1: Schematic splitting of the 25-fold degenerated ^{5}D term (a) of the $3d^4$ system, expected to be realized for the Mn^{3+} ion in $LaMnO_3$. b) The energy level scheme of the $3d^4$ system under the action of CEF interactions of the cubic symmetry, produced by octahedrally arranged O^{2-} ligands, $B_4^0<0$, with the orbital-doublet E_g ground state. All the levels 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, $\lambda = +10$ meV, on the localized states of the $3d^4$ system; a singlet ground state should be noticed. In $LaMnO_3$ B_4^0 is expected to be - 18 meV.

calculations of the many-electron states of the $3d^4$ system have been performed by the diagonalization of a 25·25 matrix associated with the Hamiltonian (1) considered in the $|LSL_ZS_Z\rangle$ base [7].

As a result of the diagonalization one obtains the energies of the 25 states and the eigenvectors containing information e.g. about the magnetic properties. These magnetic characteristics are computationally

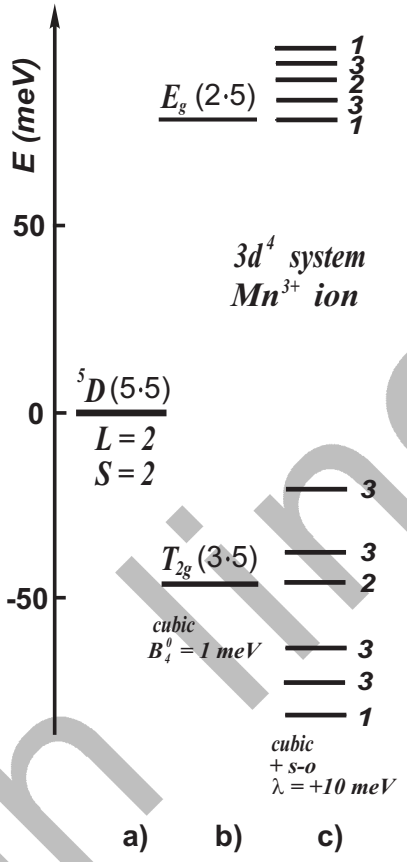

FIG. 2: The same as Fig. 1 but for the tetrahedral cubic CEF interactions, $B_4^0 > 0$, that lead to the orbital-triplet T_{2g} ground state.

revealed under the action of the external magnetic field. Obviously due to the spin-orbit coupling the states are no longer purely orbital states $|LL_Z\rangle$.

The present calculations have been directed in order to account for the magnetic moment and its formation by the magnetic field. The calculations have been performed for the spin-orbit constant λ for the Mn^{3+} ion of +10 meV taken after ref. [6], p.399, and different, negative and positive, alues for B_4^0. For a $B_4^0 > 0$ the orbital triplet T_{2g} is the CEF ground state whereas for $B_4^0 < 0$ the orbital doublet E_g is the ground state. All orbital states have 5-fold degeneracy with respect to

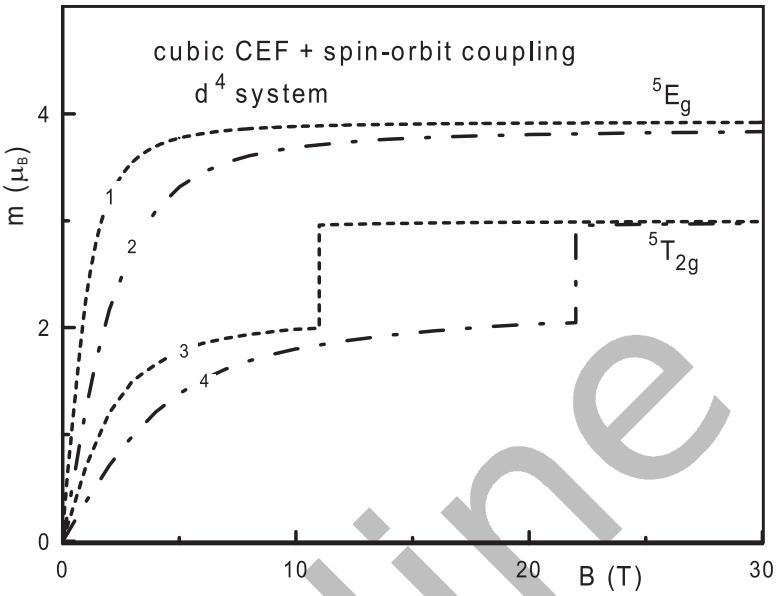

FIG. 3: The magnetic-field induced magnetic moment of the $3d^4$ system, expected to be realized in the Mn^{3+} ion, placed at the octahedral (the E_g ground state) and the tetrahedral (the T_{2g} ground state) crystal electric field. The spin-orbit constant $\lambda = +10$ meV. The calculations have been performed for realistic values (negative and positive) of $B_4^0 = 10$ (dashed-point line) and 18 meV (dashed line). The negative values yield the orbital-doublet E_g ground state whereas positive values - to the orbital-triplet T_{2g} ground state. The induced- moment somehow saturates to 2, 3 and 4 μ_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.

the spin S = 2. The inclusion of the spin-orbit coupling largely removes the degeneracy, see Figs 1 and 2. One sees that the CEF+s-o ground state is a singlet, independently on the sign of B_4^0. Despite of this fact its magnetic moment grows rapidly with applying field as is shown in Fig. 3. This induced moment approaches the saturation with integer values of 4 μ_B, 2 or 3 μ_B what is somehow manifestation of the well-known quenching of the orbital moment in $3d$ paramagnetic ions. The largest moment of 4.0 μ_B is attained for the negative value of B_4^0 and the E_g CEF ground state. In case of the T_{2g} state a moment of 3 μ_B is attained after a moment jump associated with the level crossing. In $LaMnO_3$ the experimentally found Mn-ion moment amounts to 3.9-4.0 μ_B [5]. It indicates for the orbital-doublet E_g as the CEF ground state.

To make it clear, the T_{2g} state cannot produce the moment 4.0 μ_B unless the field is bigger than 200 T. From value of 140 K for T_N in $LaMnO_3$ I have found that the molecular field amounts about 100 T [8].

From analysis of the lattice structure we know that the Mn ion in $LaMnO_3$ is placed in the octahedral position formed by six O^{2-} ligands. Abragam and Bleaney (p.374) wrote that then B_4^0 should be negative. It yields just the orbital-doublet ground state in agreement with earlier finding from the magnetic moment considerations. Finally one can ask about the size of crystal-field interactions, namely the value of B_4^0 parameter. The $d-d$ separation has been measured to be 2.0 eV [3] (between the center of two peaks) or 2.2 eV [2]. The $d-d$ separation in the case of a D term amounts to 120 B_4^0 - so B_4^0 should be close to (minus) 18 meV.

Such strong effect of spin-orbit interactions on the doublet E_g state leading to the formation of the localized singlet ground state is a somehow 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 ^{2}D 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 [6], p. 435, who wrote that the E_g state is split by second-order effects, in the perturbation method, of the s-o coupling. Now it has been proved by the direct calculations. The present calculations reveal also that the description of the influence of the s-o coupling on the triplet T_{2g} state by the perturbation method with an effective $\tilde{\lambda}$ and $\tilde{J}$ values, as shown in Fig. 7.19b of ref. [6] is very approximate. In fact, the 7-fold degeneracy of the ground $\tilde{J}$=3 state is always lifted. One can recognize this pseudo-$\tilde{J}$ structure in Fig. 2 where the real energy structure contains closely lying 7, 5 and 3 localized levels. Thus, the influence of the s-o coupling on the cubic orbital E_g and T_{2g} states is very essential introducing new physics to the problem. From this point the present direct calculations of the influence of the spin-orbit coupling are superior to the perturbation methods [6] what is not surprise owing to the general accessibility of desk computers at present.

In conclusion, the Mn^{3+} ion has been treated as a highly-correlated system $3d^4$. From the octahedral position of the Mn ion in $LaMnO_3$ the CEF ground state is inferred to be the orbital-doublet E_g state. The cubic CEF parameter B_4^0 is derived to be -18 meV. The spin-orbit interactions produce, even in case of the cubic CEF interactions, a singlet ground state. Its magnetic moment grows rapidly with the applied magnetic field approaching for the E_g state a value of 4.0 μ_B. It is in

agreement with the experimental finding as in antiferromagnetic state there exists at zero-temperature the molecular field of about 100 T. The present description is based on the $3d$ paramagnetism theory successfully used in the description of EPR and optical spectra [6].

Added after 3 referee reports. The author is fully aware of the importance of lattice distortions and the Jahn-Teller effect but author is convinced that these distortions can be properly accounted for if the spin-orbit coupling is taken **before** into account. Moreover, physical properties of $LaMnO_3$, like temperature dependence of the magnetic susceptibility will be much affected by the zig-zag structure of Mn^{3+} ions.

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[7] the computer program is available on the written request.
[8] R. J. Radwanski - to be published.