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Ground state, electronic structure and magnetism of $LaMnO_3$

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Abstract

We argue that in $LaMnO_3$ there exists a low-energy electronic structure originating from the atomic-like states of the strongly correlated $3d^4$ electronic system occurring in the Mn^{3+} ion. Our studies indicate that the intra-atomic spin–orbit coupling and the orbital magnetism are indispensable for the physically adequate description of electronic and magnetic properties of $LaMnO_3$.
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The present study is a continuation of our systematic investigations on the electronic structure and magnetic properties of compounds containing transition-metal atoms. Problem of the Mn^{3+} ion containing compounds is of particular interest. $LaMnO_3$ is an insulating antiferromagnet with the Neel temperature of 140 K [1–4]. Recently, in $LaMnO_3$ the problem of the orbital ordering is widely discussed. The orbital ordering appears much above Neel temperature. The Mn ions in the perovskite structure sit in the distorted oxygen octahedron. The basis for all theories is the description of the Mn^{3+} ion and its electronic structure. There is no consensus about the description of this electronic structure.

The aim of this paper is to present a consistent description of the low-energy electronic structure and of the magnetism of $LaMnO_3$. In our understanding, formulated as the quantum atomistic solid state theory (QUASST) [5,6], the low-energy electronic structure is related to the atomic-like electronic structure of the strongly-correlated $3d^4$ electronic system occurring in the Mn^{3+} ion. In our description the orbital magnetism and the intra-atomic spin–orbit coupling play a fundamentally important role.

The four d electrons of the Mn^{3+} ion in the incomplete 3d shell in $LaMnO_3$ form the strongly correlated intra-atomic $3d^4$ electron system. These strong correlations among the 3d electrons we account for by two Hund's rules, yield the ^5D ground term, Fig. 1a. In the oxygen octahedron surroundings, realized in the perovskite structure of $LaMnO_3$, the ^5D term splits into the orbital doublet ^5E_g as the ground subterm, Fig. 1b, and the excited orbital triplet $^5T_{2g}$.

The E_g ground subterm comes out from ab initio calculations for the octupolar potential, the A_4 CEF coefficient acting on the Mn^{3+} ion from the oxygen negative charges. Such atomic-like $3d^4$ system interacts with the charge and spin surroundings in the solid. The interaction with the charge surroundings, we approximate by means of the crystal-field interactions. As shown in Fig. 1c, energy level scheme of the $3d^4$ system in the octahedral crystal field and in the presence of the spin–orbit coupling contains 25 states in the spin–orbital space. The dominating octahedral crystal field leaves 10 lowest states well separated from others. These 10 states are split in two quintets by the tetragonal distortion, see Fig. 1d. The splitting of two quintets is of the order of 120 meV and we think that this splitting has been revealed in Raman spectra [7]. This fine electronic structure predominantly governs the electronic and

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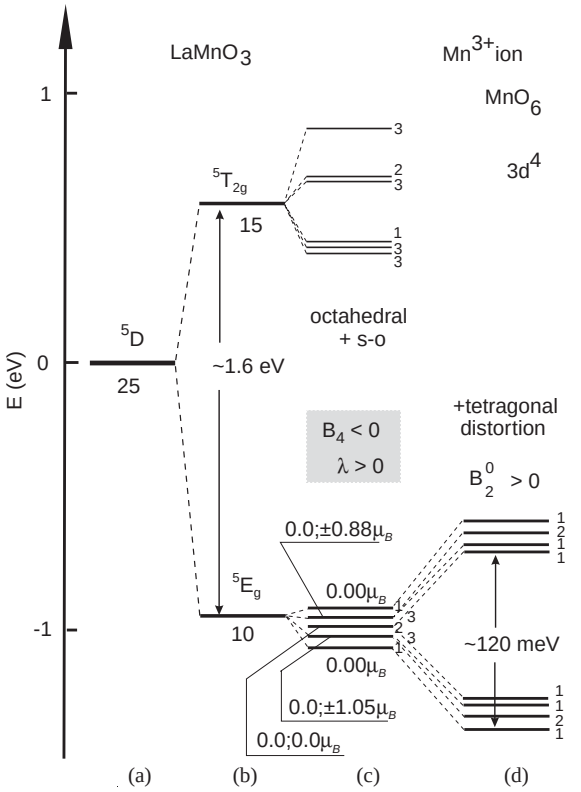


Fig. 1. Calculated electronic structure of the lowest ^{5}D term (a) of the $3d^4$ electronic system occurring in the Mn^{3+} ion realized in $LaMnO_3$, produced by the octahedral crystal field (b), the intra-atomic spin–orbit coupling (c) and the tetragonal distortion (d). The degeneracy and the magnetic moment of the states are shown. The fine splitting is not to the left-hand scale.

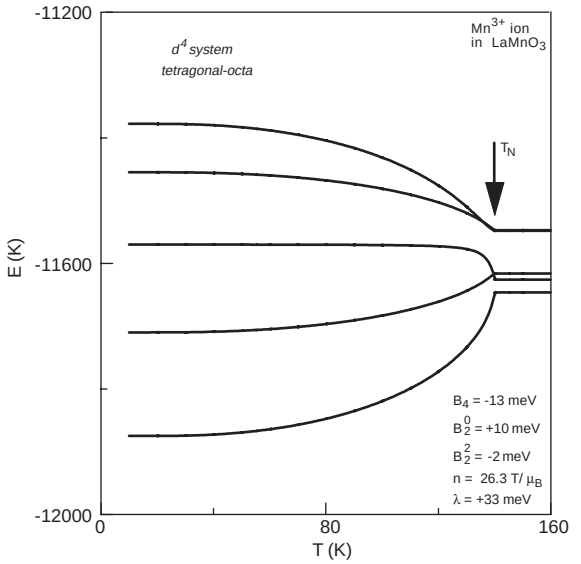


Fig. 2. Calculated temperature dependence of the energy of the 5 lowest levels of the Mn^{3+} ion in $LaMnO_3$ in the paramagnetic ($T > T_N = 140$ K) and the magnetic ($T < T_N$) state with the magnetic moments along the *a*-axis. Parameters are shown in the figure.

magnetic properties of real 3d-ion systems. To such electronic structure we superimpose the spin-dependent interactions to account for the macroscopically observed magnetic state. The appearance of the magnetic state is associated with the spin polarization and the temperature dependence of the energy of levels as is seen in Fig. 2. The self-consistent calculations have been performed similarly to that presented in Ref. [8] for $FeBr_2$. With the octahedral CEF parameter $B_4 = -13$ meV, $B_2^0 = +10$ meV, the spin–orbit coupling parameter $\lambda_{s-o} = +33$ meV and the molecular-field coefficient $n = 26.3\ T/\mu_B$ we get a value of 3.72 μ_B for the Mn^{3+}-ion-ordered magnetic moment. This value is in good agreement with the experimental datum. $LaMnO_3$ has been calculated to order magnetically along the *a*-axis within the tetragonal plane. The magnetic interactions set up at 0 K the molecular field of 108 T. The calculated magnetic moment of 3.72 μ_B is built up from the spin moment of $+3.96\ \mu_B$ and from the orbital moment of $-0.24\ \mu_B$. Although the orbital moment is relatively small its presence modifies completely the electronic structure. The Mn^{3+} ground-state wave function calculated by us is given as $\psi = 0.87|x^2 - y^2, -2\rangle + 0.48|z^2, -2\rangle$.

Having electronic structure, both in the magnetic and paramagnetic state, we can calculate the free Helmholtz energy and the resulting thermodynamical properties by means of statistical physics. The calculated electronic structure differs fundamentally from those presented in the current literature [1–4]. Contrary to the one-electron description we work with many-electron functions of $S = 2$ and $L = 2$.

In conclusion, we argue that in $LaMnO_3$ there is a preserved low-energy electronic structure originating from the atomic-like states of the strongly correlated $3d^4$ electronic system occurring in the Mn^{3+} ion. Our approach provides a microscopic mechanism for the electron–lattice and the spin–lattice coupling as well as for the electron–electron correlations. We are convinced that the orbital degree of freedom (L) and the intra-atomic spin–orbit coupling are indispensable for physically adequate description of electronic and magnetic properties of $LaMnO_3$. QUASST enables calculations of the value and direction of the local magnetic moment and reveals that they are predominantly governed by the local lattice symmetry. We get a value of 3.72 μ_B for the Mn^{3+} ion magnetic moment—this value is very sensitive to the local distortions and contains the substantial orbital moment. Our approach accounts for the insulating state as well as for a number of transitions observed in the Raman-scattering experiment on $LaMnO_3$ and

provides the symmetry of the ground state eigenfunction in agreement with the expected one.

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