

Crystal-field interactions in LaMnO_3 and in GaMnN : evidence for an applicability of the point-charge model

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We have shown that energy values of the $d-d$ splittings of 2.06 eV in LaMnO_3 and 1.41 eV in Mn-doped GaN can be consistently explained within the ordinary crystal-field theory. Moreover, these values can be calculated from the ordinary point-charge model with the O^{2-} and N^{3-} ions with $\langle r_d^4 \rangle$ as $17.4 a_B^4$.

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I. INTRODUCTION

The crystal-field theory of Bethe, Van Vleck, Kramers is well-known to be adequate for a theoretical description of magnetic, electronic and spectroscopic properties for rare-earth compounds. There is growing evidence for its high adequateness also for $3d$ transition-metal ions containing compounds, both with $3d$ cation as impurities and as being the full part of the crystal lattice. These two compounds, LaMnO_3 and Mn-doped gallium nitride GaMnN , have been chosen owing to their completely different crystallographic structure, different character of bonds and different formal valences but in both compounds the involved

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$3d$ -ion (Mn) is the same and practically the same is the distance to the nearest-neighbour (n-n) anions; 200 pm in LaMnO_3 (the mean value) and 196 pm in the doped GaN.

LaMnO_3 crystallizes in the perovskite-based structure (regular) and belong to the class of compounds known as Mott insulators. The scientific interest to LaMnO_3 -based compounds has increased considerably about 1995 after revealing its colossal magnetoresistance properties [1–5]. Its magnetism and the electronic structure is quite well understood with the crystal-field approach with the $10Dq$ of 2.06 eV, if completed with the spin-orbit coupling and the detailed description of off-octahedral distortions [6–8]. Mn-doped gallium nitride GaMnN is a wide-band semiconductor with the wurzite hexagonal structure but with a sharp energy structure peaked at 1.4116 eV. It is quite recent when this sharp line was identified with the intra-atomic $d-d$ transition, ${}^5T_2-{}^5E$, of the d^4 configuration [9, 10].

The aim of this paper is to show up that these two values are fully understood within the crystal-field theory. Moreover, these splitting values can be calculated from the ordinary point-charge model with the O^{2-} and N^{3-} ions.

II. THEORETICAL OUTLINE AND DISCUSSION

In both these completely different compounds manganese atoms occur as the trivalent ions Mn^{3+} [6–10] with four outer electrons. In the many-electron CEF approach these four d electrons form a strongly-correlated intra-atomic $3d^4$ electron system. The strong correlations among the $3d$ electrons are accounted for, in a zero-order approximation, by two Hund's rules. These two Hund's rules yield for the d^4 system the ground term 5D with $S=2$ and $L=2$. Its 25-fold degeneracy is removed by the crystal field and spin-orbit interactions. Under the action of the dominant cubic crystal field, the 5D term splits into the orbital triplet ${}^5T_{2g}$ and the orbital doublet 5E_g with the energy separation $\Delta = 10Dq$ of about 1-3 eV.

From the crystal-field theory [11] is well-known that the crystal-field coefficient A_4 , originating from the charge surroundings in the lattice, for the tetrahedral site (in GaMnN) is 4/9 of that for the octahedral site (and of the opposite sign). Taking into account the trivalency of the N ions with respect to the divalent oxygen ions, one comes to a conclusion that for the same n-nMn-anion distance the value of the CEF splitting, $10Dq$, in case of the tetrahedral site should be 2/3 of that for the octahedral site.

Thus one expects on basis of 2.06 eV in $\text{La}^{3+}\text{Mn}^{3+}\text{O}_3$ a value of 1.373 eV for the Mn^{3+} ion in $\text{Ga}^{3+}\text{N}^{3-}$ - it is in very good agreement with the

observed value of 1.41 eV (one comes to even better agreement taking into account a slightly smaller distance in GaN). Very good reproduction of the ratio of the octupolar crystal-field interactions with their up-side-down electronic structure of GaMnN compared to LaMnO₃ gives very strong argument for **the purely electrostatic origin of the crystal-field splittings** in these both compounds.

The strength of $10Dq$ of 2.06 eV in LaMnO₃ and the 5E_g ground subterm can be calculated from the ordinary point-charge model with the O²⁻ ions forming octahedron and taking into account the mean value $\langle r_d^4 \rangle$ as $17.4 a_B^4$. For the same value of $\langle r_d^4 \rangle$ and the local N³⁻ tetrahedron one gets 1.41 eV for the 5T_2 - 5E splitting in the Mn-doped GaN with the 5T_2 ground subterm, i.e. exactly as is observed. A necessary removal of large degeneracies of the ground subterm (10 and 15-fold) goes via the spin-orbit coupling and the lattice distortions (Jahn-Teller effect) [7, 8], but it goes beyond the present paper.

III. CONCLUSIONS

Energy values of the $d-d$ splittings, of 2.06 eV in LaMnO₃ and 1.41 eV in Mn-doped GaN, with their up-side-down ground subterms can be consistently explained within the ordinary crystal-field theory. It simultaneously proves purely electrostatic origin of the $d-d$ splitting.

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