

## Crystal-field interactions in LaMnO<sub>3</sub> and in GaMnN: evidence for an applicability of the point-charge model

R. J. Radwanski\*

Center of Solid State Physics; *S<sup>nt</sup> Filip 5, 31-150 Krakow, Poland*  
Institute of Physics, Pedagogical University, 30-084 Krakow, Poland

Z. Ropka

Center of Solid State Physics; *S<sup>nt</sup> Filip 5, 31-150 Krakow, Poland*

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We have shown that energy values of the  $d-d$  splittings of 2.06 eV in LaMnO<sub>3</sub> 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<sup>2-</sup> and N<sup>3-</sup> ions with  $\langle r_d^4 \rangle$  as 17.4 a<sub>B</sub><sup>4</sup>.

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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<sub>3</sub> 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

\* <http://www.e-physica.pl>; Email: [sradwan@cyf-kr.edu.pl](mailto:sradwan@cyf-kr.edu.pl)

$3d$ -ion (Mn) is the same and practically the same is the distance to the nearest-neighbour (n-n) anions; 200 pm in  $\text{LaMnO}_3$  (the mean value) and 196 pm in the doped GaN.

$\text{LaMnO}_3$  crystallizes in the perovskite-based structure (regular) and belong to the class of compounds known as Mott insulators. The scientific interest to  $\text{LaMnO}_3$ -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  $\text{O}^{2-}$  and  $\text{N}^{3-}$  ions.

## II. THEORETICAL OUTLINE AND DISCUSSION

In both these completely different compounds manganese atoms occur as the trivalent ions  $\text{Mn}^{3+}$  [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  $\text{Mn}^{3+}$  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 LaMnO<sub>3</sub> 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 LaMnO<sub>3</sub> and the  ${}^5E_g$  ground subterm can be calculated from the ordinary point-charge model with the O<sup>2-</sup> 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 N<sup>3-</sup> 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 LaMnO<sub>3</sub> 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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