Calculation of the electronic structure of the Mott insulator NiO, LaMnO$_3$ and of GaN:Mn

R. J. Radwanski$^{1,2}$, Z. Ropka$^1$

$^1$ Center of Solid State Physics, S"{u}n Filip 5, 31-150 Krakow, Poland  
$^2$ Institute of Physics, Pedagogical University, 30-084 Krakow, Poland

E-mail: sfradwan@cyf-kr.edu.pl; www.actaphysica.eu.

Abstract. 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. We claim that the $d-d$ splitting is of the (almost) purely electrostatic origin and it has been calculated from first principles. Finally, contrary to the band-theory, we claim the existence of the discrete electronic structure, in a meV scale, in 3$d$-atom containing compounds.

1. Introduction

Theoretical description of the magnetism and the electronic structure of compounds containing 3$d$ transtition-metal atoms is still a challenging problem in the modern solid-state physics. In last years we put our contribution to the theoretical research starting from the simplest compounds. We have managed to consistently describe properties of NiO, reconciling its insulating ground state and a strong (antiferro-)magnetism with $T_N$ of 525 K [1, 2]. We exactly calculated electronic structure associated with eight 3$d$ electrons at each Ni site in the incomplete 3$d$ shell. We solved a problem of origin of electron correlations in NiO. We calculated value of the magnetic moment and its temperature dependence. We derived the orbital moment to be substantial of 0.54 $\mu_B$. We calculated the low-energy electronic structure of NiO from first principles [2, 3]. We take it as a remarkable result because NiO has been considered by more than 60 years as a prominent Mott insulator exhibiting very strong electron correlations. In our calculations we include spin-orbit interactions - thanks it our description goes beyond commonly made text-book spin-only/quenched-orbital-moment approximation [4], p.71.

In this contribution the same procedure is applied to the Mn doped GaN compounds. The obtained electronic structure is compared to the one found in LaMnO$_3$. We have found that the electronic structure in these two different compounds with manganese atoms can be consistently theoretically described. Good description of NiO, LaMnO$_3$ and Mn-doped GaN allows better understanding of interplay of electron correlations, magnetism, localized states and the detailed crystal structure.
2. Theoretical outline and discussion

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 3$d$-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 of the Mn-O bonds) and 196 pm (Mn-N distance) in the doped GaN. We work in the frame of the Quantum Atomistic Solid-State Theory (QUASST) [5, 6] assuming that the involved 3$d$ atoms (becoming ions in the solid) preserve their atomic-like integrity, and consequently the respective atomic-like electronic structure, becoming the full part of a solid. In other words, we assume that a better physical start for description of electronic and magnetic properties of any compound containing 3$d$/4$f$/5$f$ atoms is single-ion phenomena than solid-state effects.

LaMnO$_3$ crystallizes in the perovskite-based structure (regular) and belongs 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 [7, 8]. Its magnetism and the electronic structure is quite well understood within the crystal-field approach with the 10$Dq$ of 2.1 eV, if completed with the spin-orbit coupling and the detailed
description of off-octahedral distortions [9, 10]. This value of 10Dq is in perfect agreement with the reality taking an experimentally-observed excitation at 2.06 eV as related with the $t_{2g}$-$e_g$ excitation [11]. 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. Recently this sharp line was identified with the intra-atomic $d-d$ transition, $^5T_2 - ^5E$, of the $d^4$ configuration [12, 13].

In both these completely different compounds manganese atoms occur as the trivalent ions Mn$^{3+}$ [9, 10, 11, 12, 13] with four outer electrons. In the many-electron CEF approach these $d$ 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 as is shown in Fig. 1b and 1c. 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 [14] is well known that the crystal-field coefficient $A_1$, 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 nearest-neighbour Mn-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 La$^{3+}$Mn$^{3+}$O$_3$ - a value of 1.373 eV for the Mn$^{3+}$ ion in Ga$^{3+}$N$^{3-}$ - it is in very good agreement with the observed value of 1.41 eV [12, 13]. In fact, one comes to a perfect agreement taking into account a slightly smaller Mn-N distance in GaN. Very good reproduction of the ratio of the octupolar crystal-field interactions with the up-side-down electronic structure of the Mn-doped GaN compared to LaMnO$_3$ 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$_3$ and the $^5E_g$ ground subterm can be calculated from the ordinary point-charge model with the O$^{2-}$ ions forming the octahedron and taking into account the mean value $\langle r_d^2 \rangle$ as 17.4 a$_B^2$ [15]. For the same value of $\langle r_d^4 \rangle$ and the local N$^{3-}$-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) as it was discussed in Refs [9, 10]. Also in these papers we have discussed formation of the (anti-)ferromagnetic state in LaMnO$_3$ below $T_N$ of 140 K.

3. Conclusions

We claim that the energy values of the $d-d$ splittings, of 2.06 eV in LaMnO$_3$ 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. We claim that the $d-d$ splitting is predominantly of the purely electrostatic origin, contrary to a textbook knowledge of a significant contribution due to the $3d$ (TM) - $2p$ (O) hybridization [4]. Finally, contrary to the band-theory we claim the existence of the discrete electronic structure, in a meV scale, in 3d-atom containing compounds. A discrete electronic structure with such large accuracy has been calculated by us for a quite great number of 3d compounds, not mentioning 4f and 5f compounds, like FeBr$_2$ [16], LaCoO$_3$ [17], CoO, FeO [3]. At present the Resonant Inelastic X-ray Scattering (RIXS) experiments allow to reveal such $d-d$ excitations [18] - a theoretical explanation of the observed
1-2 eV excitations used by authors of Ref. [18] is quite similar to our approach. In such a situation we can express a large satisfaction developing a theoretical approach which becomes step by step confirmed in novel experiments.

References
[1] R. J. Radwanski and Z. Ropka, Acta Phys. Pol. A 97, 963 (2000).
[2] R. J. Radwanski and Z. Ropka, Acta Physica 1, 26 (2006).
[3] R. J. Radwanski and Z. Ropka, Physica B 403, 1453 (2008).
[4] J. M. D. Coey - this Conference; http://confer.uj.edu.pl/jems2010/JEMS_tutorial_Coey.pdf.
[5] R. J. Radwanski and Z. Ropka, Acta Phys. Pol. B 31, 3079 (2000).
[6] R. J. Radwanski and Z. Ropka, in: New development of in Field Theory, Ed. O. Kovras, Nova Science Publ., New York 2006, p. 93 arXiv/cond-mat/0404713 (2004).
[7] Y. Tokura and N. Nagaosa, Science 288, 462 (2000).
[8] D. D. Sarma, N. Shanthi, S. R. Barman, N. Hamada, H. Sawada, and K. Terakura, Phys. Rev. Lett. 75, 1126 (1995).
[9] R. J. Radwanski and Z. Ropka, Acta Physica 9-10, 1 (2007).
[10] R. J. Radwanski and Z. Ropka, Acta Physica 9-10, 39 (2007).
[11] M. W. Kim, P. Murugavel, S. Parashar, J. S. Lee, and T. W. Noh, New J. Phys. 6, 156 (2004).
[12] A. Wolos, A. Wysmolek, M. Kaminska, A. Twardowski, M. Bockowski, I. Grzegory, S. Porowski, and M. Potemski, Phys. Rev. B 70, 245202 (2004).
[13] S. Marcet, D. Ferrand, D. Halley, S. Kuroda, H. Mariette, E. Gheeraert, F. J. Teran, M. L. Sadowski, R. M. Galera, and J. Cibert, Phys. Rev. B 74, 125201 (2006).
[14] A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions (Clarendon, Oxford) 1970.
[15] R. J. Radwanski and Z. Ropka, Acta Physica 25, 34 (2008).
[16] Z. Ropka, R. Michalski, and R. J. Radwanski, Phys. Rev. B 63, 172404 (2001).
[17] Z. Ropka and R. J. Radwanski, Phys. Rev. B 67, 172401 (2003).
[18] M. Moretti Sala, V. Bisogni, C. Aruta, G. Balestrino, H. Berger, N. B. Brookes, G. M. de Luca, D. Di Castro, M. Grioni, M. Guarise, P. G. Medaglia, F. Miletto Granozio, M. Minola, P. Perna, M. Radovic, M. Salvuzzo, T. Schmitt, K. J. Zhou, L. Braicovich, G. Ghiringhelli, arXiv:1009.4882v4.