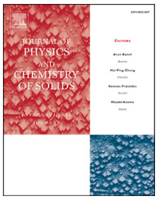
Journal of Physics and Chemistry of Solids 113 (2018) 194–200

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids

journal homepage: www.elsevier.com/locate/jpcs



Optical absorption spectra and g factor of MgO: Mn^{2+}explored by *ab initio* and semi empirical methods

E-L. Andreici Eftimie [a], C.N. Avram [a,*], M.G. Brik [b,c,d], N.M. Avram [a,e]

[a] Faculty of Physics, West University of Timisoara, V. Parvan 4, 300223, Timisoara, Romania
[b] College of Sciences, Chongqing University of Posts and Telecommunications, Chongqing, 400065, People's Republic of China
[c] Institute of Physics, University of Tartu, W. Ostwald Str. 1, Tartu, 50411, Estonia
[d] Institute of Physics, Jan Dlugosz University, ArmiiKrajowej 13/15, PL-42200, Częstochowa, Poland
[e] Academy of Romanian Scientists, Independentei 54, 050094, Bucharest, Romania

ARTICLE INFO

Keywords:
Mn^{2+}
MgO
ab initio calculations
Exchange charge model

ABSTRACT

In this paper we present a methodology for calculations of the optical absorption spectra, ligand field parameters and g factor for the Mn^{2+} ($3d^5$) ions doped in MgO host crystal. The proposed technique combines two methods: the *ab initio* multireference (MR) and the semi empirical ligand field (LF) in the framework of the exchange charge model (ECM) respectively. Both methods of calculations are applied to the $[MnO_6]^{10-}$cluster embedded in an extended point charge field of host matrix ligands based on Gellé-Lepetit procedure. The first step of such investigations was the full optimization of the cubic structure of perfect MgO crystal, followed by the structural optimization of the doped of MgO:Mn^{2+} system, using periodic density functional theory (DFT). The *ab initio* MR wave functions approaches, such as complete active space self-consistent field (CASSCF), N-electron valence second order perturbation theory (NEVPT2) and spectroscopy oriented configuration interaction (SORCI), are used for the calculations. The scalar relativistic effects have also been taken into account through the second order Douglas-Kroll-Hess (DKH2) procedure. *Ab initio* ligand field theory (AILFT) allows to extract all LF parameters and spin-orbit coupling constant from such calculations. In addition, the ECM of ligand field theory (LFT) has been used for modelling theoptical absorption spectra. The perturbation theory (PT) was employed for the g factor calculation in the semi empirical LFT. The results of each of the aforementioned types of calculations are discussed and the comparisons between the results obtained and the experimental results show a reasonable agreement, which justifies this new methodology based on the simultaneous use of both methods. This study establishes fundamental principles for the further modelling of larger embedded cluster models of doped metal oxides.

1. Introduction

The magnesium oxide single crystal, perhaps the simplest of oxides, doped with the $3d^n$ transition metal (TM) ions, displays interesting physical and chemical properties [1,2] and references therein. When a TM ion is embedded as an impurity, in a host matrix, a new material is formed that possesses additional properties which are very attractive from the technological and theoretical points of view [3,4]. The TM ions (Cr^{3+}, Mn^{4+}, V^{2+}, Ni^{2+} ,Fe^{2+}, etc.) doped in MgO have been studied in a large number of experiments, with several applications, especially as good candidates for tunable laser operation, luminescent materials, new photovoltaic materials, luminescent centers in white LED devices, etc. [3–5]. Many papers have investigated the Mn^{2+} doped MgO host crystal, but it should be pointed out that reports on both the *ab initio* and LF calculations are scarce. If for other $3d^n$ transition metal ions we find many theoretical studies regarding the energy levels and spin-Hamiltonian parameters, for Mn^{2+} we have encountered only a few published papers [6–8]. It is well known [2,4] that a great achievement of the semi empirical LFT methods has been that, with a minimum amount of empirical parameters, a great variety of properties could be explained and even reproduced with good accuracy.

Although the LFT has been widely successfully applied to the interpretation of the optical spectra and the multiplets energies of TM ions in crystals [9], it cannot predict the optical properties of unknown or hypothetical materials. Consequently, the LFT is not an accurate method because it does not allow one to compute the properties of TM complexes without recourse to the experimental data.

The *ab initio* calculations of theoptical absorption spectra and the g

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[*] Corresponding author. West University of Timisoara, Bd.V.Parvan No.4, 300223, Timisoara, Romania.
E-mail address: calin.avram@e-uvt.ro (C.N. Avram).

https://doi.org/10.1016/j.jpcs.2017.10.033
Received 22 August 2017; Received in revised form 22 September 2017; Accepted 20 October 2017

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factors for impurity ions in solid state materials became, in the last two decades, a very attractive tool used to analyse various properties of doped solids without using any fitting or empirical parameters. They have a high predictive power and allow for estimations of various physical and optical properties for the materials yet unknown.

The fully relativistic first-principles discrete variational multielectron (DVME) method [10] is based on the numerical solutions of Dirac equation, with the local density approximation, whereas *ab initio* model potential (AIMP) [11], as an embedded cluster method [12], is capable of calculating local structures and spectroscopic properties of ionic crystals. The MR *ab initio* calculations, including the embedded cluster model, have been proven to be a methodological alternative for the investigation of the electronic structure and optical spectra of TM doped crystals [13–15].

In the present work we perform a theoretical investigation of the local coordination structure, the optical absorption spectra, the LF parameters and g factor for Mn^{2+} ($3d^5$) ions doped in MgO host crystal, in the frame of a new methodology. We have combined the MR *ab initio* calculations with the semi empirical ECM [16]. The calculations were carried out for a quantum cluster $[MnO_6]^{-10}$ embedded in an extended point charge field, in order to reproduce properly the Madelung potential, separated by a boundary region composed of repulsive capped effective core potentials, according to the Gellé-Lepetit procedure [17].

The first step in applying the new methodology was the optimization of the structure of the perfect cubic MgO crystal. The next step was the modelling of optimized new MgO geometry by a 2 × 2 × 2 supercell [18]. The third step consists in doping this supercell with divalent manganese ion, one of the 32 Mg ions being replaced by a divalent Mn ion. This new supercell was fully relaxed using different DFT functionals (PBE0, B3LYP, SOGGAXC, etc.), as implemented in the Crystal 09 software [18]. Based on the DFT-optimized supercell geometries, the last step of this new methodology consists in the generation a manganese centered $[MnO_6]^{-10}$cluster, immediate surrounded by point charges at lattice sites. These charges, having fractional values are obtained according Gellé -Lepetit procedure [17] which consists in calculation of the Madelung potential and the environmental associated charges for a given crystal fragment, by the cancellation of a number of multipolar moments in an elementary cell. The charges account for electrostatic, exchange and Pauli interactions of the cluster with their environments and produce the same electrostatic potential as the method of Ewald [19].

In order to calculate the optical absorption spectra, ligand field parameters and g factor for this cluster, by *ab initio* MR method, we have used the state average CASSCF [20], NEVPT2 [21,22] and SORCI [23] methods. The scalar relativistic effects through DKH2 procedure and spin-orbit effects with effective spin-Hamiltonian method [24] have also been taken into account.

The results of each step of the above-described methodology are discussed and the agreement with the experimental data [25,26] is quite satisfactory, which justifies the simulation scheme used for the title system. The AILFT [27], a user-friendly method applied to studied system, gave us unambiguously the ligand field Dq parameter, B and C Racah parameters and ξ spin-orbit constant of Mn^{2+} doped in magnesium oxide.

The embedded octahedral cluster $[MnO_6]^{10-}$ was also used for semi empirical calculations of optical absorption spectra in the ECM framework [16] and g factor by perturbation theory.

All *ab initio* calculations were performed with the computer program ORCA 4.0.1 package [28] in conjunction with DKH-def2-TZVP basis set [29].

The results of our calculations through aforementioned methodology lead us to point out the reliability of this theoretical *ab initio* and semi empirical approaches and the fact that a combination of such methods is a powerful tool for deeper studies of doped crystals with TM ions. The purpose of this new methodology is not only to understand the d−d transitions in monomeric embedded clusters but also to build the basis for further studies of larger embedded clusters for which experimental data is unavailable or unreliable.

2. Computational methods

2.1. Geometry optimizations of crystal structure

Magnesium oxide, a white hygroscopic solid mineral that occurs naturally as periclase, is a cubic crystal with a lattice of the Mg^{2+} and O^{2-} ions held together by ionic bonding. MgO belongs to the space group $Fm\overline{3}m$ (No. 225 in the International Table of Crystallography) with the lattice constant a = 4.211 Å and equilibrium distance d(Mg^{2+} - O^{2-}) equal to 2.1055 Å [30]. The unit cell has four formula units with eigth ions, 4 Mg^{2+}at the (4a) and 4 O^{2-}at the (4b) Wyckoff positions, respectively.

The crystal strucure of MgO shows that each Mg^{2+} ion is surrounded by six oxygens ions, in a perfect octahedral symmetry (Fig. 1).

Periodic *ab initio* calculations based on DFT have been carried out by means of the CRYSTAL 09 packages [18]. All ions have been described using all electron triple-zeta with polarization (TZVP) basis sets of reasonably high quality [32].

Firstly, we have computed the equilibrium geometry of pure MgO bulk, relaxing all atomic positions and lattice constants (full geometry optimization). We probed the performance of different functionals in order to check out which of them describes the experimental geometry best of all. The threshold of the self-consistent field (SCF) energy was set to 10^{-7}, a (75 974) point grid was used, shrinking factor of the reciprocal-space net was set to 8 and for accelerating convergence we chose the Broyden scheme [33].

Table 1 shows that results which were obtained using the LDA/VWN [34–36] local density approximation, combining the Dirac−Slater LDA exchange with the Vosko−Wilk−Nusair VWN correlation functional. Also, PWGGA [37–39] the gradient corrected exchange-correlation potential by Perdew and Wang ,and the Becke B3LYP [40,41], three-parameter hybrid exchange functional in combination with the Lee−Yang−Parr [42] gradient corrected correlation functional, provide rough results.

However, a good agreement with the experimental data was achieved using the hybrid exchange-correlation functional like PBE0 [43,44] based on the GGA PBE functional, B3PW [45] functional, involving a hybrid of nonlocal HF exact exchange, LDA exchange and Becke's gradient corrected exchange functional combined with the nonlocal PWGGA, SOGGAXC [46] exchange SOGGA correlate PBE and PBEsol [47] modified Perdew−Burke−Ernzerh of generalized gradient approximation functional. Overall, hybrid exchange correlation functional SOGGAXC emerged with an average absolute deviation of about 0.03% only on the unit cell volume. The theoretical results for lattice parameters, distances and volumes, after full optimization of undoped MgO pure crystal are shown in Table 1.

Secondly, after we had chosen the best functional, we have carried out full geometry optimization for the same host lattice doped with the

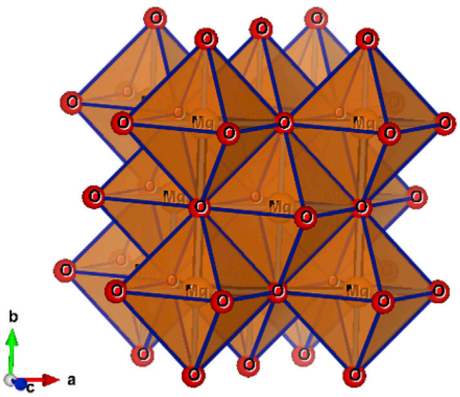

Fig. 1. Crystal strucure of MgO (drawn by Vesta [31]).

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