ЖЭТФ, 2016, том 149, вып. 2, стр. 389–392 

# ELECTRONIC STRUCTURE OF Gd-DOPED MgO

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Received June 8, 2015

The electronic structure of Gd-doped MgO is investigated using the LSDA+U (local spin density approximation with U-correction) method and compared to the MgO structure. The total density of states obtained accounting for the correlation effects in the $4f$ shell of gadolinium is found to be formed by the oxygen $2p$ states at the valence band and the $4f$ gadolinium occupied states, while the conduction band is represented by a mixture of empty electronic states. Magnetic properties of the calculated Gd-doped MgO are found to be formed solely by the Gd-$4f$-magnetic moment of about $7\mu_B$, in good agreement with recent experimental results suggesting a ferromagnetic coupling of the local magnetic moments induced by Gd.

**DOI:** 10.7868/S0044451016020164

## 1. INTRODUCTION

Spintronics aims to manipulate spin instead of (or in addition to) charge in solid-state systems, opening up the possibilities to use both charge and spin degrees of freedom of carriers in electronic devices [1, 2]. Diluted magnetic semiconductor (DMS) compounds introduce a dilute amount of magnetic transition metal (TM) ions into a semiconductor [3]. Among these materials, MgO is a very promising material for spintronics which with additional spin alignment may show more functionalities, such as spin filter, in addition to playing the role of an electronic-state filter [4]. For practical purposes, ferromagnetic ordering or coupling is desirable. Magnetic transition metals doping wide-gap semiconductors show ferromagnetism. Recently, ferromagnetic ordering above room temperature was also observed in a rare earth (RE) metal doped wide-gap semiconductors [5–9].

In this kind of doping, in contrast to transition-metal doping, the amount of ions to induce ferromagnetism is significantly reduced. MgO, a wide-gap insulator, is of huge interest as a tunnelling barrier in spintronics applications. A high magnetoresistance ratio was predicted theoretically [10, 11] and realized experimentally [12, 13] in magnetic tunnelling junctions with MgO single crystals as tunnelling barriers. In the tunnelling process, MgO single crystal acts as a state filter, only allowing half-metallic Bloch states with one symmetry pass, which leads to the giant MR effect. If MgO is made ferromagnetic via dilute magnetic doping, it may also work as a spin filter [1] or induce a large magnetic-field effect [4].

In [4], a dilute magnetic insulator based on MgO with an ordering temperature higher than room temperature was achieved, after implantation of 300 keV Gd ions into MgO. It was shown that the implantation of nonmagnetic ions (Ar and C) into MgO only results in enhanced paramagnetism; this implies that the observed ferromagnetism in Gd-implanted MgO is not due to the magnetic coupling between defects with local moments.

Doping MgO with transition metals, like vanadium in [14], shows that in a first-principle study of the energetic and magnetic properties of the V-doped MgO, V assumes a high-spin state with a local moment of about $3\,\mu_B$. Then the interaction between these local moments is very short-ranged and the antiferromagnetic (AFM) ordering is energetically more favorable. But the formation of V–$V_{Mg}$–V defect clusters was found to weaken the antiferromagnetic coupling in bulk MgO, degenerating the AFM and ferromagnetic state. It was also found that the formation energy of V at the surface is considerably higher than in the bulk and V is therefore expected to diffuse from the surface into the bulk of MgO.

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In this paper, we report the results of the electronic structure calculations for Gd:MgO with one Mg ion substituted by Gd using the LSDA+U (local spin density approximation with U-correction) method. We discuss the role of the Gd impurity in magnetic properties and electronic structure of Gd:MgO.

## 2. COMPUTATIONAL DETAILS

The calculation of the electronic structure of MgO without doping was done first. The electronic structure of MgO was calculated in the local spin density approximation (LSDA) in the framework of the band calculation package TB-LMTO-ASA (tight-binding, linear muffin-tin orbitals, atomic sphere approximation) [15]. A simple rocksalt structure was taken. The radii of MT (muffin-tin) spheres for LMTO (linear muffin-tin orbitals) calculations were $R(\mathrm{Mg}) = 2.4$ a. u. and $R(\mathrm{O}) = 2.1$ a. u.; empty spheres (atomic spheres with zero nuclear charge) were added to fill the space. The following muffin-tin orbitals were taken: O ($2s$-, $2p$-, $3d$-), Mg ($3s$-, $3p$-, $3d$-). The muffin tin orbitals Gd ($6s$-, $6p$-, $5d$-, $4f$-) were taken in Gd:MgO. In a supercell containing 8 ions ($2 \times 2 \times 2$), one Mg ion was substituted by one Gd ion. In previous studies (see, e. g., Ref. [16]), it was clearly demonstrated that the influence of Gd when substituting Zn in an insulator like the ZnO lattice is confined to the nearest O neighbors [16]. For this reason, the densities of states for different Gd:MgO supercells are very close, and no sizing effects related to the number of atoms in the supercell were found [16]. In our work, integration in the reciprocal space was performed using the total number of $k$-points $6 \times 6 \times 6 = 216$. Empty atomic spheres without nuclear charge were inserted to fill the interstitial regions.

Then the band structure of Gd-doped MgO was further calculated in the LSDA+U method [17, 18]. In this method, a Hubbard-like correction for a particular shell (in our case, Gd-$4f$) is included as an orbital-dependent potential in the calculations to enhance the electron–electron interaction (underestimated in the local density approximation) with parameters U for direct and J for exchange interactions (see Ref. [18] for further details). For the Gd $4f$ shell, this results in the presence of occupied and unoccupied narrow bands [17] far away from the Fermi energy, in agreement with the experimental data of spectroscopy for elemental Gd [18] and other gadolinium compounds [19]. The capability of the LSDA+U method to correctly reproduce the electronic structure of other rare-earth compounds can be found, for example, in [20]. For doped MgO compounds, the LSDA+U method in comparison with other computational approaches was demonstrated in [14] to be efficient in describing characteristics of V-doped MgO.

## 3. RESULTS AND DISCUSSIONS

In Fig. 1, the calculated densities of states for MgO are shown. The valence band is formed mainly by the oxygen $2p$-orbital contribution from $-5$ eV to the Fermi energy ($E_F$), and the conduction band by a mixture of empty states with a dominating Mg $3p$ broad band above 15 eV. The LSDA calculation gave the band gap value equal to about 5 eV, which underestimates the experimental value. At $-18$ eV, a separate band is composed of O $2s$ states. This is the well-known problem of band gap underestimation in the L(S)DA approach, where the potential is orbital-independent. The estimate can be improved by means of the LSDA+U method, where the orbital-dependent potential acts on the occupied and unoccupied orbitals differently [17].

The electronic structure of Gd-doped MgO was calculated in the LSDA+U method [17, 18] in the framework of the band calculation package TB-LMTO-ASA. A supercell of 8 atoms was taken, where the central Mg was replaced by the Gd ion with the same radius

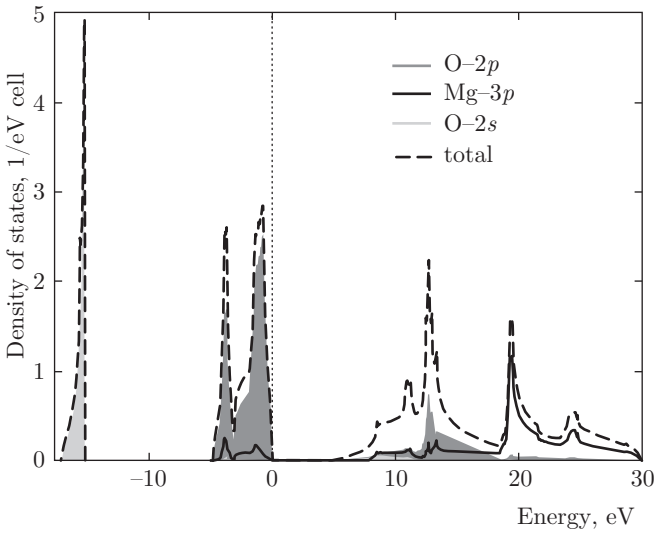


**Fig. 1.** The total and partial densities of states of MgO from the LSDA calculation. The dashed curve shows the total density of states, the dark shaded area — the Mg-$3p$-states, the O-$2p$-states are given with the solid curve, while the light shaded area below $-15$ eV denotes the O-$2s$-states. The Fermi energy corresponds to zero

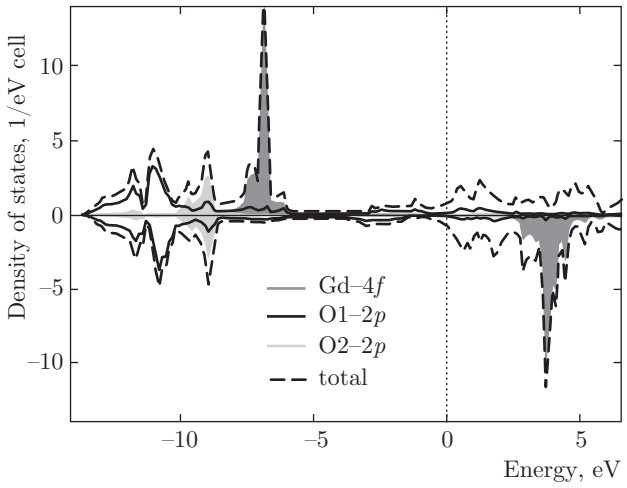


**Fig. 2.** The total and partial densities of states of Gd:MgO from the LSDA+U calculation. The dashed curve shows the total density of states, the dark shaded area — the Gd-4$f$-states, the O2-2$p$-states are given with the solid curve, while the light shaded area — the O1-2$p$-states. The Fermi energy corresponds to zero.

of the muffin-tin sphere. In the LSDA+U method, the Coulomb interaction for Gd $4f$ orbitals was taken into account via the parameters of direct (U) and exchange (J) Coulomb interactions of the $4f$ electrons in Gd as $U(\mathrm{Gd}) = 6.7$ eV and $J(\mathrm{Gd}) = 0.7$ eV, in agreement with the values for elemental Gd metal [18].

In the LSDA+U calculation, we found the Gd-$4f$-spin moment equal to $6.8\mu_B$ as expected for the Gd ion in metals with the ferromagnetic coupling to the other Gd ions, in agreement with recent experimental data on Gd-implanted MgO samples [4]. The Gd $5d$ states have a negligible spin polarization, whereas other states of gadolinium are almost empty.

In Fig. 2, the LSDA+U-calculated density of states taking the correlation effects in the Gd $4f$ shell into account are shown. The $4f$-gadolinium occupied states manifest themselves with a sharp band structure at $-7$ eV below the Fermi energy, while the empty $4f$ states are well separated and can be found near 4 eV above $E_F$. As in pure MgO, the oxygen $2p$ states in Gd:MgO form the ground part of the valence band from $-14$ to $-8$ eV below $E_F$. But due to the Gd ion in the supercell, some oxygen atoms remain of the same type (we let them be denoted by O2), surrounding Gd, whereas one oxygen ion (O1) is located far from Gd and becomes inequivalent, with a different energy position from about $-8$ to $-10$ eV below the Fermi level.

Noteworthy, in the conduction band Gd-doped MgO is composed of a mixture of empty electronic states and empty Gd states. In general, the insulating character of MgO changes to a metallic one with some low density of states at the Fermi energy. These states are given by a mixture of states, similar to the conduction band in MgO.

## 4. CONCLUSION

In summary, using the LSDA+U approach, we have investigated the role of the Gd impurity in Gd-doped MgO. We found that magnetic properties are formed by the Gd-$4f$-spin moment equal to $6.8\mu_B$ and expected to form ferromagnetic interaction among impurities in agreement with recent experimental data. Taking into account the correlation effects, the density of states is found to be formed by oxygen $2p$ states at the valence band and $4f$-gadolinium occupied states, while the conduction band is composed by a mixture of empty electronic states.

This work was supported by the Ministry of Education and Science of the Russian Federation (No. 14.Z50.31.0025), the Russian Foundation for Basic Research (Project No. 13-02-00050), and the UrB RAS project 15-8-2-4. A. V. L. acknowledges support of the Dynasty Foundation.

## REFERENCES

**1**. S. A. Wolf, D. D. Awschalom, R. A. Buhrman, J. M. Daughton, S. von Molnar, M. L. Roukes, A. Y. Chtchelkanova, and D. M. Treger, Science **294**, 1488 (2001).

**2**. H. Toyosaki, T. Fukumura, Y. Yamada, K. Nakajima, T. Chikyow, T. Hasegawa, H. Koinuma, and M. Kawasaki, Nature Mater. **3**, 221 (2004).

**3**. T. Dietl, H. Ohno, F. Matsukura, J. Cibert, and D. Ferrand, Science **287**, 1019 (2000); T. Fukumura, Y. Yamada, H. Toyosaki, T. Hasegawa, H. Koinuma, and M. Kawasaki, Appl. Surf. Sci. **223**, 62 (2004).

**4**. Lin Li, Xiangming Fang, Changgan Zeng, J. Phys. D: Appl. Phys. **42**, 155003 (2009).

**5**. S. Dhar, O. Brandt, M. Ramsteiner, V. F. Sapega, and K. H. Ploog, Phys. Rev. Lett. **94**, 037205 (2005).

**6**. S. Dhar, T. Kammermeier, A. Ney, L. Perez, K. H. Ploog, A. Melnikov, and A. D. Wieck, Appl. Phys. Lett. **89**, 062503 (2006).

**7**. J. Hite, G. T. Thaler, R. Khanna, C. R. Abernathy, S. T. Pearton, J. H. Park, A. J. Steckl, and J. M. Zavada, Appl. Phys. Lett. **89**, 132119 (2006).

**8**. J. M. Zavada, N. Nepal, C. Ugolini, J. Y. Lin, H. X. Jiang, R. Davies, J. Hite, C. R. Abernathy, S. J. Pearton, E. E. Brown, and U. Hömmerich, Appl. Phys. Lett. **91**, 054106 (2007).

**9**. K. Potzger, S. Zhou, F. Eichhorn, M. Helm, W. Skorupa, A. Mucklich, J. Fassbender, T. Herrmannsdorfer, and A. Bianchi, J. Appl. Phys. **99**, 063906 (2006).

**10**. W. H. Butler, X. G. Zhang, T. C. Schulthess, and J. M. MacLaren, Phys. Rev. B **63**, 054416 (2001).

**11**. J. Mathon and A. Umerski, Phys. Rev. B **63**, 22040 (2001).

**12**. S. S. P. Parkin, C. Kaiser, A. Panchula, P. M. Rice, B. Hughes, M. Samant, and S. H. Yang, Nature Mater. **3**, 862 (2004).

**13**. S. Yuasa, T. Nagahama, A. Fukushima, Y. Suzuki, and K. Ando, Nature Mater. **3**, 868 (2004).

**14**. C. Arhammar, C. Moyses Araujo, K. V. Rao, S. Norgren, B. Johansson, and R. Ahuja, Phys. Rev. B **82**, 134406 (2010).

**15**. O. K. Andersen, Z. Pawlowska, and O. Jepsen, Phys. Rev. B **34**, 5253 (1986).

**16**. I. Bantounas, S. Goumri-Said, M. Benali Kanoun, A. Manchon, I. Roqan, and U. Schwingenschlögl, J. Appl. Phys. **109**, 083929 (2011).

**17**. V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B **44**, 943 (1991).

**18**. V. I. Anisimov, F. Aryasetiawan, and A. I. Lichtenstein, J. Phys.: Condens. Matter **9**, 767 (1997).

**19**. A. V. Lukoyanov, E. E. Kokorina, M. V. Medvedev, and I. A. Nekrasov, Phys. Rev. B **80**, 104409 (2009).

**20**. Yu. V. Knyazev, A. V. Lukoyanov, Yu. I. Kuz'min, and A. G. Kuchin, Phys. Stat. Sol. B **249**, 824 (2012).