Electronic structure and lattice relaxation related to Fe in MgO

M. A. Korotin, A. V. Postnikov, T. Neumann, and G. Borstel

Universität Osnabrück – Fachbereich Physik, D-49069 Osnabrück, Germany

V. I. Anisimov

Institute of Metal Physics, Russian Academy of Sciences, Yekaterinburg GSP-170, Russia

M. Methfessel

Institut für Halbleiterphysik, P.O.Box 409, D-15204 Frankfurt an der Oder, Germany

(October 15, 2018)

Abstract

The electronic structure of Fe impurity in MgO was calculated by the linear muffin-tin orbital–full-potential method within the conventional local-density approximation (LDA) and making use of the LDA+U formalism. The importance of introducing different potentials, depending on the screened Coulomb integral $U$, is emphasized for obtaining a physically reasonable ground state of the Fe$^{2+}$ ion configuration. The symmetry lowering of the ion electrostatic field leads to the observed Jahn–Teller effect; related ligand relaxation confined to tetragonal symmetry has been optimized based on the full-potential total energy results. The electronic structure of the Fe$^{3+}$ ion is also calculated and compared with that of Fe$^{2+}$.

31.20.-d, 71.10.+x, 71.25.Tn

Typeset using REVTeX
I. INTRODUCTION

The electronic structure of defects in MgO has been the subject of a number of theoretical studies. Among the latest first-principles calculations, one should mention the study on anion vacancies by the muffin-tin Green’s function method [1] and in a mixed-basis pseudopotential supercell calculation [2]. In Ref. [3], the electronic structure of Fe, Co, and Ni impurities in MgO has been calculated making use of the Green’s-function method within the linearized-muffin-tin-orbitals (LMTO) – atomic-spheres-approximation (ASA) formalism. In this paper, the energy positions of the impurity 3d levels in the gap have been calculated for several charge states of the impurity ions. However, the effects of lattice relaxations around cation impurity atoms have been ignored (although the uniform relaxation around vacancies and substitutional hydrogen has been considered in Ref. [2]), and the main emphasis has been on the peculiarities of the electronic structure in these defect systems.

The present study is motivated by the fact that Fe impurity (as well as many other 3d ions) in MgO is a Jahn–Teller system, as has been observed in electron spin resonance experiments (see, e.g., Refs. [4] and [5]). However, the microscopic pattern of the underlying Jahn–Teller distortion is not clear from the experiment, nor did the \textit{ab initio} calculations performed up to now succeed in incorporating the essential effects of the interaction between orbital moment of the impurity ion and the displacements of ligand atoms. Based on an \textit{ab initio} electronic structure calculation scheme with no shape approximation for the potential, we attempted to study the effect of symmetry-lowering atomic displacements on the total energy and thus to optimize the positions of ligand atoms towards their relaxed local configuration around the impurity. In doing this, we realized the importance of going beyond the local density approximation (LDA) in describing the electronic states at the impurity site.

In Sec. II, we briefly specify the calculation scheme we used. In Sec. III, the results of a conventional calculation for the Fe:MgO system within the local-density approximation are outlined. In Sec. IV, we describe the effect of introducing the orbital-dependent potential within the so-called LDA+U approximation. In Sec. V, the lattice relaxation around Fe in
MgO is analyzed, basing on total-energy calculations for various geometries. In Sec. VI, we present a simplified way to model a metastable Fe$^{3+}$ ion configuration of the impurity in MgO and analyze the electronic structure corresponding to this configuration.

II. CALCULATION METHOD

We performed the calculations for the $2\times2\times2$ supercell of MgO (16 atoms), with one Mg atom substituted by Fe, making use of the full-potential LMTO method \[6,7\]. The space is divided into nonoverlapping muffin-tin spheres, the radii of which were chosen to be 1.65 a.u. for Mg (or Fe) and 2.13 a.u. for O. Mg $2p$ and Fe $3p$ states were treated as semicore, and all higher-lying states included in the valence band panel. Following the usual routine of geometry-optimizing full-potential calculations, we calculated the equilibrium lattice constant of the undistorted NaCl-type crystal lattice of perfect MgO, which was found to be 98% of the experimental value 4.21 Å. The band structure calculated for perfect MgO was found to be in agreement with earlier calculations \[1,2,3\]. The valence band is formed mainly by O $2p$ states and the conduction band by Mg $3p$ states, with the gap separating them equal to 0.43 Ry (5.85 eV). This value is somewhat bigger than in some other calculations, e.g. 4.36 eV \[2\], 4.65 eV \[1\], 4.98 eV \[8\], but well below the experimental estimate of about 7.8 eV \[8,9,10,11\], which is a typical error in calculating the band gap value within the LDA.

The Brillouin zone integration in the course of iterations was performed over a mesh of special points; total-energy convergency over the $\mathbf{k}$ points has been achieved at 10 special points for the main valence band panel in the irreducible part of the Brillouin zone for tetragonal symmetry (most of the calculations have been performed in tetragonal symmetry for the reasons discussed below). Densities of states were calculated by the tetrahedron method with 75 $\mathbf{k}$ points in the irreducible part.
III. IRON IMPURITY IN MGO: ELECTRONIC STRUCTURE IN THE LDA

Fe impurities which substitute 1/8 of Mg atoms in the supercell give rise to narrow levels in the gap above the mostly O 2p-type valence band. In conventional LDA calculations, the potential acting on all d electrons of the same spin at Fe site is identical, and splitting of the impurity levels may occur due to spin polarization or the crystal field effect.

The interaction between nearest Fe atoms, which are separated only by one Mg atom in the [110] direction, gives rise to the formation of narrow $t_{2g}$ and $e_g$ bands split by the crystal field by $\sim 0.1$ Ry. The lower-lying $t_{2g}$ states become fully occupied by 3 spin-up and 3 spin-down electrons, and the Fe impurity is stripped of its 4s electrons, thus being left in the $^1A_1$ atomic configuration with ionicity 2+. The Fermi level falls, therefore, in the gap between the $t_{2g}$ and $e_g$ bands.

The density of states obtained by the full-potential LMTO calculation, in the option which incorporated spin-resolved potential and charge density within the Fe MT sphere, but in fact resulted in a zero spin moment, is shown in Fig. 1. A nonmagnetic configuration occurs quite seldom for Fe impurities, and in the present case the calculated result clearly contradicts the experimental observation that the ground state configuration of Fe in MgO is $^5T_2$ (2$e_g$, 4$t_{2g}$) – see the discussion in Ref. \[3\]. Therefore we were careful in additionally investigating the question of whether the obtained non-magnetic configuration of Fe is a drawback of LDA, or an artifact due to some particular cell geometry, choice of sphere radii, etc. In a series of calculations by the tight-binding (TB) LMTO method \[12\] it was proven that the first assumption is correct, since convergence to the same nonmagnetic configuration occurred irrespective of the cell size (as big as a 32-atom supercell of MgO:Fe has been tested), presence of empty spheres, and other starting conditions. The (0$e_g$, 6$t_{2g}$) configuration turned out to be very stable, as any attempt to remove electrons from $t_{2g}$ states to $e_g$ states energetically quite separated from them led to the situation when the Fermi level crosses two narrow peaks (spin-down $t_{2g}$ and spin-up $e_g$) and is therefore energetically very unfavorable.
The converged density of states determined for the 32-atom supercell by the TB-LMTO method was almost identical to that shown in Fig. 1, with the same position of $t_{2g}$ and $e_g$ impurity peaks in the energy gap, only that the widths of these peaks have been substantially reduced. We considered this similarity as an indication that our results from a full-potential calculation in regard to the structure optimization may be probably only slightly corrected by further increase of the supercell size.

An obvious drawback of conventional LDA calculations performed for potentially magnetic impurities in insulators is the implicit orbital degeneracy within the $d$ shell. In reality, one would expect that the potential acting on any particular electronic state depends on whether this state is occupied or empty. Being effectively of just marginal effect for strongly hybridized systems, this discrepancy becomes quite important as the degree of localization increases. This is exactly the case in the MgO:Fe system, and we discuss below how the results could be amended by lifting the orbital degeneracy.

**IV. RESULTS OF LDA+$U$ CALCULATIONS**

In a simple way, the orbital- (and occupation-) dependent potential is introduced in the so-called LDA+$U$ approach [13][14]. The correction to the potential enters as a constant term, determined primarily by the screened effective Coulomb integral $U$ and the screened exchange parameter $J$ (see Ref. [14]).

The first parameter for the system in question has been estimated from self-consistent full-potential calculation within the LDA using the scheme of Gunnarsson *et al.* [15] to be $U=0.489$ Ry. The value of $J$ for Fe in MgO is expected to be the same as in FeO and was taken from Anisimov *et al.* [13].

In an earlier application [13], the LDA+$U$ method has been applied to a number of oxide systems, making it possible to obtain reasonable *ab initio* estimations of the band gap value and magnetic moments that were otherwise not possible within the LDA. When applying this scheme to MgO, however, it was not possible to correct the underestimated value of the
band gap in a similar way, because of rather weak localization of the Mg 3p states forming
the conduction band. Therefore, the effect of LDA+U was confined in our case only to
the Fe impurity, for which the conventional LDA approach predicts an essentially incorrect
charge configuration.

On introducing the occupation-dependent potential acting on each Fe 3d orbital inde-
dependently as is described above, the energy positions of the impurity levels in the gap were
drastically changed (Fig. 2). As the filled and empty states of $t_{2g}$ symmetry are no longer
forced to reside at the same energy position, as was the case in the LDA calculation, the
system finds its way in the course of iterations to a more stable configuration where the
Fermi level falls in the gap between filled $(xy)$ and empty $(xz, yz)$ states of $t_{2g}$ symmetry
and thus the Hund’s rule is satisfied. Majority-spin $e_g$ states are then completely filled,
in contrast to what was predicted by the LDA calculation, and the atomic configuration
becomes $(2e_g, 4t_{2g})$.

It was essential to perform the Brillouin zone integration over at least 1/16, i.e. over the
irreducible wedge corresponding to the tetragonal structure, and not over 1/48 as for cubic
symmetry, in order to account for the difference which appears now between $xy$ and $(xz,
yz)$ states which are differently occupied. This does not mean that we force the system to
split the $d$ state in this particular way. The use of the appropriate symmetry is just a means
to save effort in the integration over the whole Brillouin zone, which would give the same
scheme of splitting for the $d$ states.

It is seen from Fig. 2 that the degeneracy pattern of Fe 3d levels in the ligand field
of nominally cubic symmetry looks like that corresponding to a tetragonal crystal field,
because of the symmetry-lowering effect of filled $xy$ states. As is known, $t_{2g}$ states should
split into $b_{2g}$ and $e_g$, and this is consistent with the remaining degeneracy of $xz$ and $yz$
states. Then, $e_g$ should split into $a_{1g}$ and $b_{1g}$, which is seen as the lifted degeneracy between
$(3z^2 - 1)$ and $(x^2 - y^2)$ states; however, they both are either filled (for majority spin) or
empty (for minority spin) and therefore are acted on by the same $U$-dependent correction
to the potential.
The tetragonal-symmetry electrostatic field at the Fe site may affect the relaxation of the ligand atoms around the impurity. In addition to the totally symmetric uniform relaxation which was studied, e.g., around vacancies in Ref. [2], we should now consider the effect of symmetry-lowering tetragonal displacements of oxygen atoms. The results of corresponding total-energy calculations are discussed below.

V. OPTIMIZATION OF THE LIGAND GEOMETRY

Not much is known about the structural microscopic configuration of atoms in the MgO crystal around the Fe impurity, apart from the mere fact that this system exhibits dynamic Jahn–Teller behavior. The origin of the Jahn–Teller displacement seems to be essentially the tetragonal electrostatic field related to the ground-state configuration of the Fe$^{2+}$ ion as discussed above, and the dynamical character reveals merely an exchange between three equivalent directions of the tetragonal axis in the initially cubic crystal.

It may be expected that the strongest effect on the total energy will be from the totally symmetric uniform adjustment of ligand shells as the Mg$^{2+}$ ion is substituted by Fe$^{2+}$. On top of this uniform relaxation, the Jahn–Teller effect is expected to emerge in the form of symmetry lowering due to additional displacements of ligand atoms consistent with the tetragonal symmetry. In order to reduce the computational effort for examining the effect of various independent atomic displacements on the total energy, we restricted ourselves to considering the displacement of the nearest oxygen atoms only. That means that we considered only uniform breathing of the O$_6$ octahedron and the additional axial displacement of its two apical atoms.

The total energy as a function of uniform O$_6$ breathing is shown in Fig. 3. Open circles mark the energy values obtained in the LDA+U calculation, and closed triangles the results from the conventional LDA calculation, with nonmagnetic configuration of the Fe$^{2+}$ ion. The latter values correspond to other absolute values of the total energy, but the plot is shifted so as to coincide with the LDA+U curve for zero breathing, for better comparison. One can
see that the outward expansion of the octahedron by $\sim 1\%$ of the lattice constant (1.15% in the LDA+$U$ calculation) is obtained in the calculation in both cases, so it is mostly a purely electrostatic effect, related to the different electronegativity of Fe and Mg. However, the magnitude of the energy lowering is substantially larger in the LDA+$U$ calculation.

Subsequent squeezing of the O$_6$ octahedron along [001] by 0.5% of the lattice constant lead to further decrease of the total energy. The corresponding densities of states (DOS’s) obtained in the LDA+$U$ calculation are presented in Fig. 2.

VI. CALCULATION FOR Fe$^{3+}$ ION

Although substitutional Fe in MgO exists mostly as a 2+ ion, the Fe$^{3+}$ configuration is also known to exist, at least as a metastable state. It was pointed out by Schultheiss [16] that upon irradiation with x rays or electrons, Fe$^{3+}$ ions are formed due to the trapping of holes at Fe$^{2+}$ sites. Since the origin of the holes to be trapped is most probably related to the lack of Mg atoms, an adequate modeling of such a defect should in principle incorporate this effect somehow in the construction of the supercell. In a simplified attempt to get some insight into the rearrangement of electronic states at the Fe site due to the absorption of an extra hole, we performed a self-consistent LDA+$U$ calculation with the option that the Fermi level was searched for at one electron less per supercell than should exist from the electroneutrality condition. This means physically that an electron is removed from the Fe site (since the band just below the Fermi level is of essentially Fe 3d character), and no charge compensation is nominally introduced. If we consider then the possible effect of restoring the charge neutrality in the simplest form, i.e., due to the introduction of compensatory charge uniformly distributed over the crystal, it will obviously lead merely to a slight rigid shift of all bands which have been calculated as described above. Therefore this simplified approach will be probably of no use for the study of relaxation where the spatial distribution of the compensating charge is really important, but it is expected to provide an adequate description of electronic states at the impurity site.
The resulting DOS is shown in Fig. 4. It is rather different from the DOS of the Fe$^{2+}$ ion, and the origin of this difference is that as the minority-spin $xy$ state, i.e., the highest occupied one, is stripped of its electron, it becomes equivalent, with respect to the potential acting on them, to $xz$ and $yz$ states, and the threefold degeneracy of the $t_{2g}$ state is restored in the course of iterations, even as we solved the band structure problem in nominally tetragonal symmetry. At the same time (as the half-filled $d$ shell possesses full cubic symmetry), the twofold degeneracy of $z^2$ and $x^2 - y^2$ states is restored. Larger exchange splitting, corresponding now to almost $5\mu_B$, shifts Fe majority-spin states down within the valence band region, and crystal-field-split minority-spin states are situated now at $\sim$0.2 Ry and $\sim$0.3 Ry above the Fermi level.

VII. CONCLUSION

In the course of studying the electronic structure of Fe in MgO from first principles, we have found that an electronic-structure calculation within the conventional LDA erroneously predicts the ground-state configuration of Fe in MgO to be nonmagnetic, with the $(0e_g, 6t_{2g})$ configuration. In order to amend this drawback and to go beyond the LDA, an occupation-dependent correction to the potentials of different impurity states has been implemented in the LDA+$U$ scheme. The resulting electronic configuration of the Fe$^{2+}$ ion was found to be consistent with the Hund’s rule, and the lifting of the orbital degeneracy between occupied and empty $d$ states resulted in a local field of tetragonal symmetry at the impurity site. This symmetry-lowering affects the relaxation of the ligand atom around the impurity, making it a combination of a 1.15% (in units of the lattice constant) totally symmetric outward expansion of the $O_6$ octahedron and a 0.5% inward squeezing of two apical oxygen atoms. For the Fe$^{3+}$ ionic configuration of the impurity, the orbital splitting only persists between $t_{2g}$ and $e_g$ states of the $d^5$ shell, and the local cubic symmetry is retained.
ACKNOWLEDGMENTS

Financial support of the Deutsche Forschungsgemeinschaft is gratefully acknowledged. AVP thanks G. Sawatzky for useful discussions. MAK and VIA gratefully acknowledge financial support from the Netherlands NWO special fund for scientists from the former Soviet Union.
REFERENCES

* On leave from: Institute of Metal Physics, Russian Academy of Sciences, Yekaterinburg, Russia

[1] B. M. Klein, W. E. Pickett, L. L. Boyer and R. Zeller, Phys. Rev. B35, 5802 (1987).

[2] Q. S. Wang and N. A. Holzwarth, Phys. Rev. B41, 3211 (1990).

[3] G. Timmer and G. Borstel, Phys. Rev. B43, 5098 (1991).

[4] F. S. Ham, in Electron Paramagnetic Resonance, ed. by S. Geschwind (Plenum, New York, 1972), p.1.

[5] C. A. Bates, Phys. Rep. 35, 187 (1978).

[6] M. Methfessel, Phys. Rev. B38, 1537 (1988).

[7] M. Methfessel, C. O. Rodriguez, and O. K. Andersen, Phys. Rev. B40, 2009 (1989).

[8] D. M. Roessler and W. C. Walker, Phys. Rev. 159, 733 (1967).

[9] M. W. Williams and E. T. Arakawa, J. Appl. Phys. 386, 5272 (1967).

[10] A. S. Rao and R. J. Kerney, Phys. Status Solidi B 95, 243 (1979).

[11] L. Fiermans, R. Hoogewijs, G. de Mayer, and J. Vennik, Phys. Status Solidi A 59, 569 (1980).

[12] O. K. Andersen, O. Jepsen, and D. Glötzle, in Highlights of Condensed-Matter Theory, edited by F. Bassani, F. Fumi, and M. P. Tosi (North-Holland, New York, 1985); O. K. Andersen and O. Jepsen, Phys. Rev. Lett. 53, 2571 (1984).

[13] V. I. Anisimov, J. Zaanen, and O. K. Andersen, Phys. Rev. B 44, 943 (1991).

[14] V. I. Anisimov, I. V. Solovyev, M. A. Korotin, M. T. Czyzyk, and G. A. Sawatzky, Phys. Rev. B 48, 16929 (1993).
[15] O. Gunnarsson, O. K. Andersen, O. Jepsen, and J. Zaanen, Phys. Rev. B 39, 1708 (1989).

[16] T. E. Schultheiss, Med. Phys. 13, 361 (1986).
FIGURES

FIG. 1. Total DOS per unit cell from the FeMg$_7$O$_8$ supercell calculation (LDA result, converged to nonmagnetic configuration). The Fermi level is indicated by the vertical dashed line.

FIG. 2. Spin-resolved total DOS per unit cell and local orbital-resolved DOS at the Fe site in FeMg$_7$O$_8$ for the optimized geometry (LDA+U result).

FIG. 3. Total energy (per 16-atom unit cell) versus uniform breathing (circles) and tetragonal squeezing (squares) of the O$_6$ octahedron. Triangles: effect of breathing on the total energy in the LDA calculation (see text).

FIG. 4. Total DOS per unit cell and local orbital-resolved DOS on the Fe site for the Fe$^{3+}$ configuration in FeMg$_7$O$_8$. 
