DFT+U Calculations of Transition Metal Doped AlN

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The electronic structure of transition metal (TM = V, Cr, Mn, Fe) doped aluminium nitride was presented. The calculations were made within the DFT and DFT+U approach and the supercell approximation. The effective interaction parameter Hubbard U for mentioned compounds was determined within linear response approach in contrast to the other type of calculations which treated this factor as an adjustable parameter.

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1. Introduction

The diluted magnetic semiconductors (DMSs) are formed by replacing cations of the semiconductor crystal with $3d$ transition metal (TM) dopants such as for instance V, Cr, Mn or Cu. Recently the DMSs are widely studied both experimentally and theoretically due to their possible applications in spintronics [1, 2]. Theoretical investigation of DMSs are based mostly on the density functional theory with local density approximation (LDA) or generalized gradient approximation (GGA)[3, 4]. It is a well known fact that those approximations fail in the description of the magnetic properties of some TM compounds such like TM monoxides for example. To improve calculations of such materials the DFT+U method was developed [5]. In this method the on-site d–d Coulomb interaction U is added to the LDA or GGA functional. However the value of the Hubbard U parameter is not known and often is taken from the experiments to adjust calculations to them. Recently some methods [6] to evaluate this parameter from the first principles have been found and we used one of them in this paper. DMSs like ZnO:Co [7, 8] or GaN:Mn and GaAs:Mn [9] were investigated within DFT+U approach but method presented here was used only in case of ZnO:Co [8] and there are no other papers (according to our knowledge) which contain the DFT+U calculations of AlN:TM.

This letter is organized in the following way: we present the short description of method of calculation in Sect. 2, the results and the discussion are given in Sect. 3, finally the short summation will be presented.

2. Method of calculations

All calculations were done using the plane-wave Quantum-Espresso package [10] and the ultrasoft pseudopotential method [11]. In the calculations we used the generalized gradient approximation (GGA) based on Perdew, Burke and Ernzerhof (PBE)[4]. The cut-off radius was equal to 60 Ry for energy and 720 Ry for charge density. The Brillouin zone integrations were performed by using $6 \times 6 \times 4$ Γ-centered k-point grid and Methfessel–Paxton smearing with smearing width of 0.005 Ry. The electronic and magnetic properties of TM doped AlN were investigated in $2 \times 2 \times 2$ supercell which contained 32 atoms. Substitution of one Al atom gives realistic experimental dopant concentration of 6.25%. The calculations were performed within the theoretical lattice constants which were equal to $a = 5.887$ a.u. and $c = 9.451$ a.u. This values are in good agreement with the experimental data ($a = 5.880$ a.u., $c = 9.407$ a.u.) [12]. The atomic coordinates were fully relaxed until the forces acting on a single atom were less than 10^{-3} Ry/a.u.

The Hubbard U value was computed from constrained density functional calculations. We computed numerically the total energy as a function of the localized-states occupations of the "Hubbard" site q_I. This function has a form

$$E\left[\{q_I\}\right] = \min_{n(r),\alpha_I} \left\{E\left[n(r)\right] + \Sigma_I \alpha_I \left(n_I - q_I\right)\right\},$$

where n_I is the total localized-states occupations and Lagrange multipliers α_I are small shifts of the potential which plays a role of our constraints. The Hubbard U parameter

$$U = \left(-\frac{\partial \alpha_I}{\partial q_I}\right) - \left(-\frac{\partial \alpha_I^{\mathrm{KS}}}{\partial q_I^{\mathrm{KS}}}\right).$$

The last term is connected with rehybridization of the localized orbitals in noninteracting Kohn–Sham band structure. This procedure is repeated until self-consistency will be obtained i.e. evaluated value of the U parameter in first iteration is used as a starting parameter in second and so on (Fig. 1, left). The detailed description of this method is presented in Refs. [6, 8].

3. Results

Using the method presented above we evaluated a Hubbard U parameter for both ferromagnetic (FM) and nonmagnetic (NM) systems. From the values listed in Table
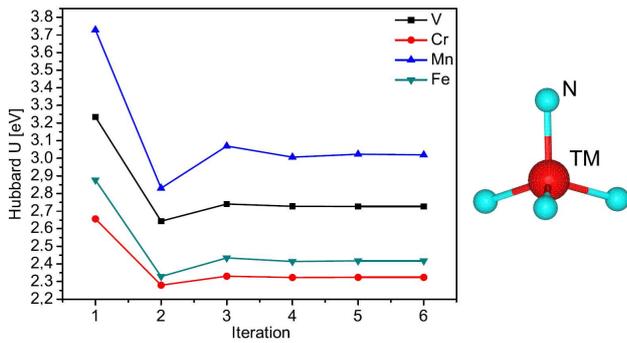
Fig. 1. Self-consistent calculations of Hubbard U parameter for spin-polarized TM doped AlN (left) and TMN_4 tetrahedra with three equidistance nitrogen atoms in basal plane and one in c-axis (right).

we see that there is a difference between U for FM (spin-polarized) and NM (without spin-polarization) state. This difference is probably connected with different occupations of localized levels in the spin-polarized case and this had an influence on response matrices. It is expected according to [6]. The largest difference between U_{NM} and U_{FM} was observed for Fe (1.4 eV) and the smallest for Cr atom (0.3 eV).

TABLE

Hubbard U parameter for TM in both non-spin-polarized and spin-polarized case.

Transition metal	U for NM [eV]	U for FM [eV]
V	3.11	2.73
Cr	2.60	2.32
Mn	3.59	3.02
Fe	3.83	2.42

If we put a magnetic ion into nonmagnetic host, then the neighbouring anions should be polarized ferro- or antiferromagnetically to this ion. We investigated a behaviour of the magnetic moment in the TMN_4 tetrahedron (Fig. 1, right) without and with U parameter. For vanadium the distances in basal plane and in c-axis were equal, respectively, to 1.93 Å and 2.03 Å.

The magnetic moment on V ion was 1.91 μ_B without U and 2.02 μ_B after included U corrections. However the magnetic moment on neighbouring nitrogen atoms changed in basal plane from -0.01 μ_B to -0.03 μ_B and in c-axis from -0.006 μ_B to -0.02 μ_B (without and with U parameter, respectively). In case of chromium the distances was 1.92 and 1.97 Å (in basal plane and c-axis, respectively).

The magnetic moment on Cr ion changed from 2.85 μ_B to 3.06 μ_B after adding U parameter. Magnetic moment on neighbouring atoms changed from -0.02 μ_B to -0.07 μ_B in both basal plane and c-axis direction. For Mn ion Mn–N bond were equal to 1.91 Å in plane and 1.94 Å in c-axis direction.

The magnetic moment on Mn ion changed from 3.68 μ_B to 4.03 μ_B and moments on nitrogen changed from 0.01 μ_B to -0.08 μ_B in plane and from 0.06 μ_B to 0.02 μ_B in perpendicular direction after included Coulomb interaction.

In Fe ion bonds had the same length as in Mn case. The magnetic moment changed from 3.66 μ_B to 3.72 μ_B on iron atom and did not change in basal plane and decreased from 0.24 μ_B to 0.23 μ_B in c-axis direction on nitrogen atoms. From these calculations we have seen that applying U corrections have changed a magnetic behaviour in case of V, Cr and Mn and there were no significant changes in AlN:Fe compound. The most important changes were connected with increase in the absolute value of the magnetic moment on the neighbouring anions. Taking into account on-site interaction the range of the exchange interaction increases. This suggests that d–d Coulomb interaction can play an important role in description of DMS's. In all cases spin-polarized systems were energetically more favorable than non-spin-polarized ones.

In Fig. 2 we presented total and partial density of states from Mn d-states for AlN:Mn. From the figure we have seen that delocalization of d-states slighty increases after applying U. Similar situation takes place in a case of w-GaN:Mn [9], however in GaN:Mn partially occupied states were mixed with valence states but in AlN:Mn these states were still located in band gap.
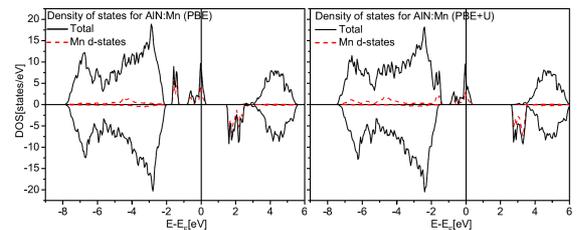

Fig. 2. The total and partial density of states of Mn d-states for AlN in the ferromagnetic state without (left) and with U (right).

4. Conclusions

In this paper the DFT+U calculations of AlN doped with TM were presented. The values of Hubbard U parameter were evaluated from first principles. Taking into account in the calculations on-site Coulomb interaction, the range of magnetic interaction increases in V, Cr, Mn cases but in case of iron the situation does not change so much.

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