

Supplemental materials at articles

“Magnetic properties of Au–Mn nanowires”

Theoretical study of quantum and atomic properties of one dimensional metallic nanowires was carried out using the first principle code VASp, based on the density functional theory (DFT) [14, 15]. DFT leads the many particle problem to the one particle problem in effective potential. Instead of many particle wave functions one variable is introduced – electronic density of the system. The main positions of DFT are introduced into the Thomas–Fermi theory. The Thomas–Fermi method – a method of search of the electron density directly from the potential without first finding the wave functions which are the solutions of many-particle Schrödinger equation.

The Density Functional Theory (DFT) – TF theory developed and updated by Kohenberg and Kohn. The main innovation in a theory is the claim that all the properties of the electronic structure in the non-degenerate state is completely determined by its electron density:

$$n(r) = \sum_{j=1}^N |\phi_j|^2. \quad (1)$$

The density functional theory establishes a one-to-one correspondence between the electron density and the wave function of the ground state (1). Effective potential, takes into account all many particles effects presented as the sum of the total electrostatic potential and the exchange-correlation potential

$$v_{\text{eff}}(r) \equiv v(r) + \int \frac{n(r')}{|r - r'|} dr + v_{xc}(r). \quad (2)$$

Thus, we get the following Schrödinger equation for determination of ground state of the system:

$$\left(-\frac{1}{2} \nabla^2 + v_{\text{eff}}(r) - \varepsilon_j \right) \phi_j = 0 \quad (3)$$

is a one-electron Schrödinger equation. Here

$$\sum_j \varepsilon_j = T[n(r)] + \int v_{\text{eff}}[n(r)] n(r) dr. \quad (4)$$

Further improvement of the density functional theory belongs to Kohn and Sham [14, 15], which introduce an explicit form for the exchange-correlation interaction. Equation (3) is a Kohn–Sham equation, ϕ_j – Kohn–Sham spin-orbitals. The exchange-correlation potential is the variational derivative the exchange-correlation energy on the electron density, it depends on the electron density for a homogeneous electron gas. For inhomogeneous system the value of the exchange-correlation potential at the point defined by the radius vector \mathbf{r} , depends not only on the value of the electron density at this point, but also on the variation of the coordinate near this point.

$$v_{xc}(r) \equiv \frac{\delta}{\delta \tilde{n}(r)} E_{xc}[\tilde{n}(r)] \Big|_{\tilde{n}} = n(r). \quad (5)$$

For the calculations in the article it was used the generalized gradient approximation (GGA) exchange-correlation interaction, because it more accurately describes the quantum properties of systems with highly irregular distribution of electron density. The GGA exchange-correlation functional depends not only on the density, but also on its first spatial derivative:

$$E_{xc}^{\text{GGA}}[n_{\uparrow}, n_{\downarrow}] = \int d^3r f(n_{\uparrow}, n_{\downarrow}, \nabla n_{\uparrow}, \nabla n_{\downarrow}). \quad (6)$$

For the calculation of solids, the most widely used approximation of the GGA approximation, proposed by a Perdew scientific group [14, 15]. The system of equations (1)–(6) is complete system of Kohn–Sham equations, which is solved iteratively in the chosen basis. In the program code VASP is implemented a self-consistent solution of the Kohn–Sham equations in the plane-wave basis.

The program of Vienna Ab-initio Simulation Package (VASP) [14, 15] implements the self-consistent solutions of system of Kohn–Sham equations in the plane-wave basis for determination the equilibrium density of the electronic system. System of Kohn–Sham equations is solved iteratively in a predetermined basis for the determination of the electron density of the system. The integration through reciprocal space by a special grid of k -points $k - 1 \times 1 \times 7$ constructed according to the scheme proposed by Monkhorst and Pack were carried out to accurately calculation of the energy of a system [16]. The integration over the Brillouin zone was performed using the tetrahedron method with Blohl correction [17, 18]. After solving a system of Kohn–Sham equations – finding all the single-particle eigenfunctions of the ground state and the calculation of the total energy of the system – the force in the unit cell are calculated by Hellman–Feynman theorem [15].

All the presented calculations are performed using the generalized gradient approximation for the potential exchange-correlation interaction and PAW (Projector Augmented-Wave)-potential [15, 18].

Mixed Au-Mn nanowire modeled by constructing of periodic supercell with Born–Karman boundary conditions as a chain of four atoms: two atoms of Au and two Mn atoms along the z -axis. To exclude the interaction of the wire with its image at translation over the entire space the cell size in the x and y was chosen $> 10 \text{ \AA}$. In this paper, a series of calculations on stretching and contraction of evenly mixed Au–Mn nanowires was performed that simulates processes taking place in the atomic structure of the wire during its formation by MCBJ technic [19] or with help of STM method [20].

To study the magnetic properties of low-dimensional systems is used the Stoner criterion for ferromagnetism:

$$IN^0(\varepsilon_F) > 1. \quad (7)$$

The stability of the magnetic solution depends on the overlap between the two spin energy bands, that is, the magnitude of the displacement Δ the spin splitting of the density of states $N^0(\varepsilon)$ at the Fermi level. In the Stoner theory the offset value Δ determined by the value of the exchange integral I , where the value of the exchange integral I is determined from an *ab initio* calculations within the DFT. According to the Stoner criterion the magnetic solution may be stable for systems with a large quantity of non-magnetic density of state (DOS) at Fermi level. If antiferromagnetic susceptibility greater than ferromagnetic ones the expression $\chi_{\text{AFM}} - \chi_{\text{FM}}$ changes sign, the antiferromagnetic state stabilizes in the system. The magnetic moment, in turn, can be calculated as the difference between the spin DOS at the Fermi level.

In Stoner theory electrons are considered as free particles moving in the periodic field of the crystal. Since the orbital angular momentum of the electron in this case is suppressed by the crystal field, the electron states are described by spin moment and the moment \mathbf{k} . Stoner theory of ferromagnetism is based on three main principles:

1. Carriers of the magnetic properties are uncompensated spins of electron in the d energy band.
2. Exchange effects caused by the molecular field.
3. The Fermi-Dirac statistics is used to describe the system.

The stability of nonmagnetic solutions for the system can be estimated as the possibility of electrons moving between energy bands with different spin polarization. Thus the stability of the magnetic solution depends on the overlap between the two spin energy bands, that is, the magnitude of the displacement Δ of the spin splitting of the density of states. In Stoner theory the displacement Δ determined by the value of the exchange integral I $\Delta = Im$. So the spin density of states $N^\sigma(\varepsilon)$ can be represented as a non-magnetic DOS shifted by $\Delta/2$

$$N^\uparrow(\varepsilon) = N^0\left(\varepsilon + \frac{Im}{2}\right), \quad N^\downarrow(\varepsilon) = N^0\left(\varepsilon - \frac{Im}{2}\right). \quad (8)$$

The number of occupied states can be calculated by integration of the spin of the DOS at the Fermi level. The magnetic moment, in turn, can be calculated as the difference between the spin DOS at the Fermi level.

These two equations can be represented as a system of

$$m = F(m), \quad (9)$$

$$F(m) = \int_{-\infty}^{\varepsilon_F} \left[N^0 \left(\varepsilon + \frac{Im}{2} \right) - N^0 \left(\varepsilon - \frac{Im}{2} \right) \right] d\varepsilon, \quad (10)$$

which is solved by the self-consistent. The stability of the magnetic solutions can in turn be estimated as

$$F'(m) = \frac{I}{2} \left[N^0 \left(\varepsilon_F + \frac{Im}{2} \right) + N^0 \left(\varepsilon_F - \frac{Im}{2} \right) \right] + \left[N^0 \left(\varepsilon_F + \frac{Im}{2} \right) - N^0 \left(\varepsilon_F - \frac{Im}{2} \right) \right] \frac{d\varepsilon_F}{dm}. \quad (11)$$

In the case the expression $m = 0$ is much simpler to

$$F'(0) = IN^0(\varepsilon_F). \quad (12)$$

A sufficient condition for the existence of magnetism in the system

$$F'(0) > 1, \quad (13)$$

finally Stoner criterion for the existence of ferromagnetism:

$$IN^0(\varepsilon_F) > 1, \quad (14)$$

where the exchange integral I can be found from *ab initio* calculations with help of DFT method. According to the Stoner criterion the magnetic solution may be stable for systems with a large quantity of non-magnetic DOS at Fermi level. If antiferromagnetic susceptibility greater than ferromagnetic ones the expression $\chi_{\text{AFM}} - \chi_{\text{FM}}$ changes sign, the antiferromagnetic state stabilizes in the system. The magnetic moment, in turn, can be calculated as the difference between the spin DOS at the Fermi level. The spin polarization of the system considered in the LSD (local spin density) approximation. Instead, the local density of a system used the functional of spin density of a system.

$$n(r) \rightarrow \rho(r) = \frac{n(r)}{2} \mathbf{1} + \frac{m(r)}{2} \vec{\sigma}, \quad (15)$$

$\mathbf{1}$ – unit matrix, $\vec{\sigma} = (\vec{\sigma}_x, \vec{\sigma}_y, \vec{\sigma}_z)$ – Pauli matrices. Accordingly, the wave function of the system is represented already as a second order spinor

$$\Psi_i(r) = \begin{pmatrix} \alpha_i(r) \\ \beta_i(r) \end{pmatrix}. \quad (16)$$

Then the matrix of the electronic density of a system is defined as

$$\rho(r) = \sum_{i=1}^N \begin{pmatrix} |\alpha_i(r)|^2 & \alpha_i(r)\beta_i(r)^* \\ \alpha_i(r)^*\beta_i(r) & |\beta_i(r)|^2 \end{pmatrix}. \quad (17)$$

The charge and magnetic density are determined in accordance with the expressions

$$n(r) = \text{Tr}(\rho(r)) = \sum_1^N |\Psi_i(r)|^2, \quad m(r) = \sum_1^N \Psi_i(r)^+ \sigma(r) \Psi_i(r). \quad (18)$$

Schrödinger equation in a system of self-consistent Kohn–Sham equations, which takes into account the spin polarization of the system have the form

$$\sum_{\beta} (-\delta_{\alpha\beta} \nabla^2 + v_{\text{eff}}^{\alpha\beta} f(r)) \Psi_{i\beta}(r) = \varepsilon_i \delta_{\alpha\beta} \Psi_{i\beta}(r) \alpha = 1, 2. \quad (19)$$

The Hamiltonian of the system can be presented as the sum of non-magnetic and magnetic components

$$H = (-\nabla^2 + v_{\text{NM}}) \mathbf{1} + b \vec{\sigma}. \quad (20)$$

The nonmagnetic component of the Hamiltonian is diagonal, the magnetic part can be as diagonal (in the case of collinear magnetism), and take nondiagonal form.

Magnetization is calculated as

$$M = N_u - N_d. \quad (21)$$

The total energy of the system is now a function of the magnetization M of the system

$$E_T(M, \{R_p\}) = \sum_{i,j} \varepsilon_{ij} - \frac{1}{2} \int_V n(r) \Phi_{\text{elec}}(r) d^3r + \int_V \left(n(r) \varepsilon_{xc}(r) - \sum_j n_j(r) \Phi_{xc}(r) \right) d^3r. \quad (22)$$