

Calculation of energy and magnetic susceptibility of Fe atomic system during dislocation motion in magnetic field

Energy and
magnetic
susceptibility

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Abstract

Purpose – The purpose is to calculate the change in the total energy of a small fragment of an idealized lattice of iron (in its pure form and with impurity atoms) containing an edge dislocation during its elementary motion at one interatomic spacing, both under the influence of a constant magnetic field and without it. The introduction of a magnetic field into the system is aimed at checking the adequacy of the description of the phenomenon of magnetoplasticity by changing the total energy of the atomic system.

Design/methodology/approach – The design procedure is based on a quantum-mechanical description of the switching process of the covalent bond of atoms in the dislocation core. The authors used the method of density functional theory in the Kohn-Shem version, implemented in the GAUSSIAN 09 software package. Using the perturbation theory, the authors modeled the impact of an external constant magnetic field on the energy of a system of lattice atoms.

Findings – The simulation results confirmed the effect of an external constant magnetic field on the switching energy of the covalent bond of atoms in the dislocation core, and also a change in the magnetic susceptibility of a system of atoms with a dislocation. This complements the description of the magnetoplastic effect during the deformation of metals.

Originality/value – The authors created quantum-mechanical models of the dislocation motion in the Fe crystal lattice: without impurities, with a substitutional atom Cr and with an interstitial atom C. The models take into account the influence of an external constant magnetic field.

Keywords Crystal lattice, Dislocation, Substitution atom, Interstitial atom, Energy, Magnetic field, Magnetoplasticity, Magnetic susceptibility

Paper type Research paper

1. Introduction

If we consider a body as an object motionless in space without external influences, then its total energy corresponds to the internal energy of interaction of elementary particles. Each specific property of the body is described by the amount of energy spent on the transformation of the system into a new energy state. The rheological properties of bodies are characterized by the level of energy spent on distortion and restructuring of the crystal structure under the influence of external stresses.

The bulk of deformable metals are steels. These are alloys of iron with carbon, chromium and other elements. Their crystal structure is a lattice of iron atoms with impurity atoms of alloying elements. Impurity atoms occupy positions in the crystal lattice in accordance with the ratio between their sizes and the atoms of the matrix. The chromium atom, the size of which is larger than the iron atom, replaces it at the sites of the crystal lattice. A small carbon atom is embedded in the space between the lattice sites. Carbon can occupy a position on the face of the Fe lattice and in its plane. For the study, we chose the option of placing a carbon atom in the plane, in the center of the unit cell of Fe atoms. Impurity atoms are located below the edge dislocation line. They form compressive stresses in the crystal lattice. The



dislocation edge forms a tension region in the crystal lattice, which compensates for the compressive stresses from impurity atoms, and therefore attracts them. This created a simplified semblance of the dislocation motion in the Cottrell atmosphere.

The crystal structure of Fe-based alloys has a significant number of linear and point defects. Their presence and interaction with each other form the strength and plasticity of bodies. At the micro and macro levels, this is expressed in the existence of a certain energy barrier, overcoming which ensures the transition of defects into a mobile state, plastic deformation of the body. Energy for the movement of defects is communicated from the outside by applying a mechanical load, which creates internal stresses in the system of atoms of the body, changes its energy.

The review (Golovin, 2004) proved the fact of the influence of a magnetic field (MF) on the mechanical properties of solids, but the mechanism of this effect is determined by various factors and is insufficiently studied. The weak magnetic fields cannot directly affect the mechanical properties of metals at the macroscopic level. The smallness of the energy of the magnetic field leads to the conclusion that the effect of the MF on the mechanical properties of solids occurs, most likely, at the electronic level. MF affects the value of the energy barrier overcome by the crystal structure defects during their motion. This phenomenon is called magnetoplasticity (Golovin, 2004; Gui-Rong *et al.*, 2016; Alshits *et al.*, 2016; Wang *et al.*, 2015; Zhang *et al.*, 2020; Morgunov *et al.*, 2018). The existing theoretical explanation of magnetoplasticity is based on the spin interaction between dislocation cores and point defects, described in the methods of magnetic resonance spectroscopy. The dislocation core with a size of 1–10 nm differs greatly from the defect-free region of the crystal in physical and chemical properties. Various stoppers (for example, impurity atoms) can hinder the dislocation motion. Overcoming obstacles by dislocation is accompanied by the formation and breaking of covalent bonds, and a change in the spin state of defects. MF can change the orientation of the spins and thereby resolve one or another bond of atoms in the crystal lattice. MF performs direction control function of the motion of dislocations.

The known models do not take into account the entire set of possible spin-dependent processes affecting plasticity. The description of the elementary process of motion of a dislocation in a magnetic field remains relevant. The dynamics of the defect structure of a solid is based on the relationship between the changes in the state of electrons, which alone can be affected by the MF. These processes cannot be considered within the framework of the popular string dislocation model, which ignores the atomic structure of its core. Therefore, the interpretation of magnetoplasticity requires an appeal to related fields of knowledge, in particular, to quantum chemistry, which describes spin-dependent processes.

2. The model

The quantum-mechanical approach makes it possible to describe the processes of plastic deformation of the crystal lattice of atoms in weak magnetic fields on the electronic level. This requires taking into account a variety of physical phenomena: the motion of electrons in the field of nuclei, the interaction of electrons with each other, spin and other effects. The simultaneous consideration of these phenomena is impossible. There are used mathematical models that take into account the simplest and important effects. One of the most widespread models of an isolated molecule is the nonrelativistic stationary many-electron Schrödinger equation in the Born-Oppenheimer approximation:

$$H\psi(\vec{r}) = E\psi(\vec{r}) \quad (1)$$

where $\psi(\vec{r})$ is the wave function, which depends explicitly on the coordinates of all electrons and depends on the coordinates of the nuclei as parameters; H is the nonrelativistic

Hamiltonian of the molecule. This model does not take into account the relativistic increase in the mass of electrons, the influence of electrons on the motion of nuclei, and the influence of the external environment on the behavior of an individual molecule. At the same time, it takes into account the most significant molecular energy effects: the interaction of electrons with the nuclei of the molecule and the mutual repulsion of electrons.

The Hartree–Fock method is often used to solve [equation \(1\)](#). However, this method does not take into account cross-correlation in the motion of electrons (an electron in a molecular orbital moves in the averaged field of a molecule, not noticing changes in the coordinates of other electrons). Considering correlation computationally is very difficult. A relatively simple approach is the density functional theory (DFT) method. Instead of the wave function, it uses the electron density $\rho(\vec{r})$ to calculate the main characteristics of the system. Any property of the ground state of a molecule can be expressed in terms of the electron density. Therefore, the total electron energy in the DFT is:

$$E[\rho] = T[\rho] + V_{en}[\rho] + V_{ee}[\rho] \quad (2)$$

where $T[\rho]$ is the kinetic energy, $V_{en}[\rho]$ is the potential energy of electron-nuclear interactions, $V_{ee}[\rho]$ is the energy of interelectronic interactions, which can be written as:

$$V_{ee}[\rho] = V_c[\rho] + V_{xc}[\rho] \quad (3)$$

where $V_c[\rho]$ is the energy of the Coulomb interaction of electrons, and $V_{xc}[\rho]$ is exchange-correlation energy, that is, that part of the potential energy of interaction of electrons with each other, which takes into account the correlation energy. The functionals $T[\rho]$, $V_{en}[\rho]$ and $V_c[\rho]$ can be found quite accurately; the simplest way is the so-called Kohn-Sham method. In this method, ρ is represented as the sum of the contributions of individual electrons described by some auxiliary self-consistent orbitals (Kohn-Sham orbitals):

$$\rho(\vec{r}) = \sum_{i=1}^N |\varphi_i(\vec{r})|^2 \quad (4)$$

where $\varphi(\vec{r})$ is the one-electron Kohn-Sham (atomic) orbital, the index i runs over all states that are filled with electrons in accordance with the Pauli principle and denotes the spatial indices.

Thus, the total electronic energy of a system of N electrons can be represented as:

$$\begin{aligned} E(\rho) = & -\frac{1}{2} \sum_{i=1}^N \int \varphi_i^*(\vec{r}) \nabla^2 \varphi_i(\vec{r}) d\vec{r} - \\ & - \sum_K Z_K \int \frac{\rho(r)}{|r - R_K|} dr + \frac{1}{2} \int \int \frac{\rho(r)\rho(r')}{|r - r'|} dr dr' + V_{xc}[\rho] \end{aligned} \quad (5)$$

where Z is the nuclear charge (in atomic units); r is the radius vector of the electron; R is the radius vector of the nucleus.

For the exchange-correlation potential $V_{xc}[\rho]$, the exact representation is unknown and additional approximations are required. In the works of [Masrour et al. \(2015a, b, 2016, 2017, 2018\)](#), [Kadim et al. \(2021\)](#) and [El Krimi et al. \(2020\)](#), magnetic properties of a number of iron compounds with various additives were calculated using the method of linear augmented plane wave based on DFT and Monte Carlo simulations within generalized gradient approximation GGA, Hubbard approximation and modified Becke-Johnson potential. In this work, the B3LYP hybrid functional was also used as the exchange correlation potential. It

consists of the exchange three-parameter Slater Baker functional–B3, including the density gradient, and the Li-Yang-Parr correlation functional LYP. The choice of this functional is due to the presence of a limited number of empirical parameters and is used to take into account various types of electron correlation in the calculations of metal complexes.

Quantum calculations are performed with a finite basis set functions that are used to construct molecular orbitals. In the simplest case, they represent the wave functions of atomic orbitals (AO) occupied by electrons in the ground state. Such a basis set is called minimal. In extended basis sets, valence orbitals are described by several basis functions, which, in turn, can be represented by a different number of Gaussian functions and are called split-valence bases. To take into account the polarization of the electron cloud, the basis set includes functions with higher values of the orbital quantum number (d-, f-types). Among polarization basis sets, the most popular is the 6–31 g (d) atomic orbital basis. This is a split-valence basis in which the AOs of the inner shell are represented by six Gaussian functions. Valence AOs are represented by three and one functions, respectively.

The influence of the magnetic field in the first order of perturbation theory was taken into account by modelling the 6–31 g (d) -jske AO basis set constructed in [Kapusta *et al.* \(2018\)](#), with allowance for deformation of the electron density by an external perturbation. The applied method of Green's function ([Voronkov and Rossikhin, 1981](#)) helped to determine explicit analytical expressions for the correction wave functions of the first order of the perturbation theory. Additional basis functions generated by this perturbation operator were extracted from their structure.

The widespread use of the DFT method is associated with a fairly good agreement between the calculated and experimental data, previously unattainable within the Hartree–Fock approximation. There are a number of available quantum chemical program, which includes DFT method. The time spent in calculations by this method increases as N^3 , which makes it possible to calculate large polyatomic systems. The leader in the market of quantum chemical programs is the GAUSSIAN package, which is used to complete about 80% of all publications on quantum chemical research.

3. Results and their discussion

We calculated the change in the total energy of a small fragment of an idealized crystal lattice of iron with a moving edge dislocation. The considered variants of the crystal lattice of iron included its pure form and that with impurity atoms. The calculations were performed for conditions of external influence of a constant magnetic field and without it. The calculations were carried out by the DFT method in the Kohn-Shem version using the GAUSSIAN 09 software package ([Frisch *et al.*, 2009](#)). The temperature in the calculations was chosen to be 295 K.

[Figure 1](#) shows models of an idealized crystal lattice reflecting an elementary act of motion of an edge dislocation. Its motion is represented in the form of interatomic bond switching (dashed line in [Figure 1](#)), which leads to the displacement of the dislocation at one interatomic spacing. We considered three models of the crystal lattice: with only Fe atoms ([Figure 1a and b](#)), with one substitutional atom Cr ([Figure 1c and d](#)), with one interstitial atom C ([Figure 1e and f](#)).

We compared the energy of the system of pure Fe atoms in initial configuration 1 with the systems containing impurity atoms. The substitution atom Cr reduced the energy by 1.3%, the interstitial atom C increased by 0.2%. Under the influence of MF, the deviation of energies between these types of atomic systems retained their values.

The calculation showed a change in the energy of a system of atoms during the movement of a dislocation ([Figure 2](#)). The change in energy characterizes the change in the stability of the system of atoms of the crystal lattice. Stability increases with decreasing energy.

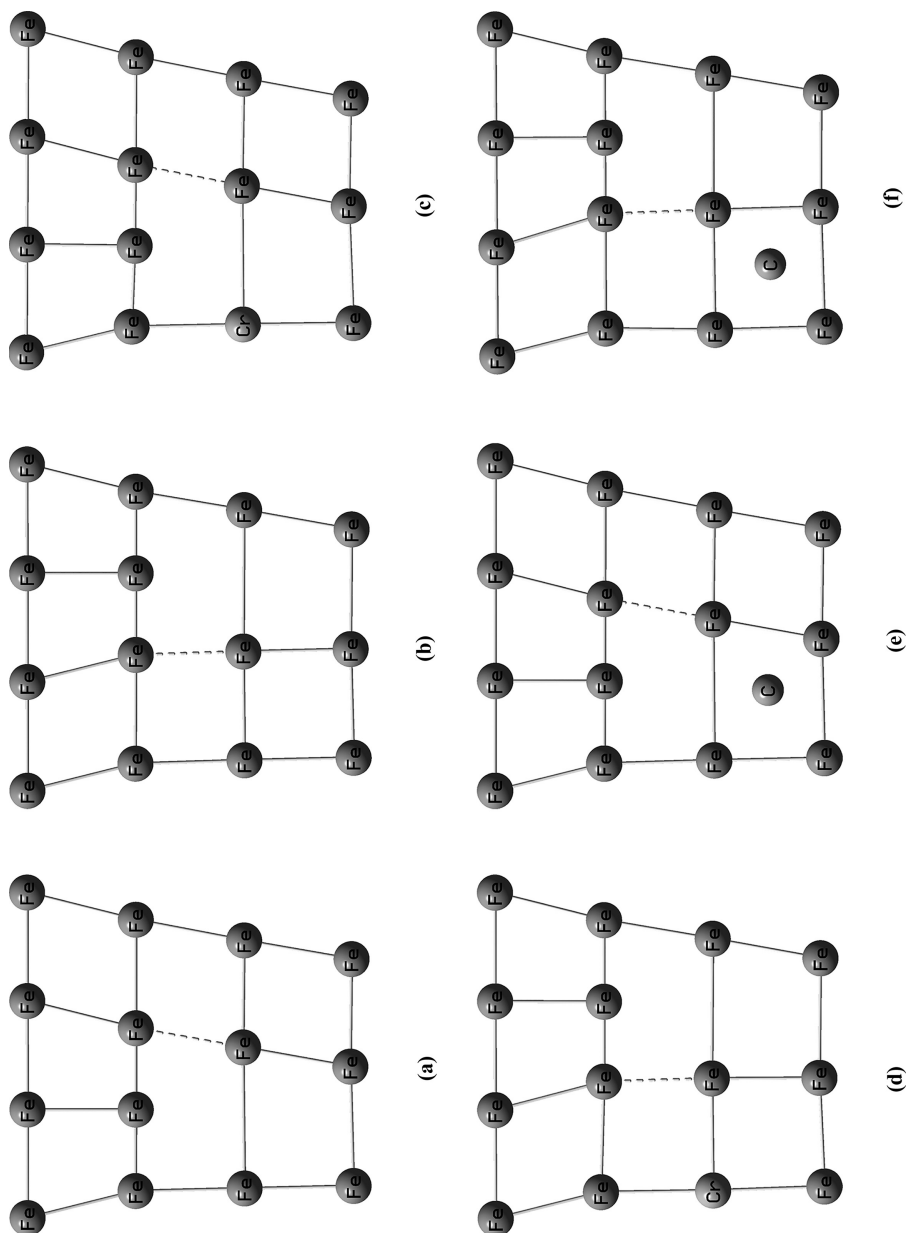
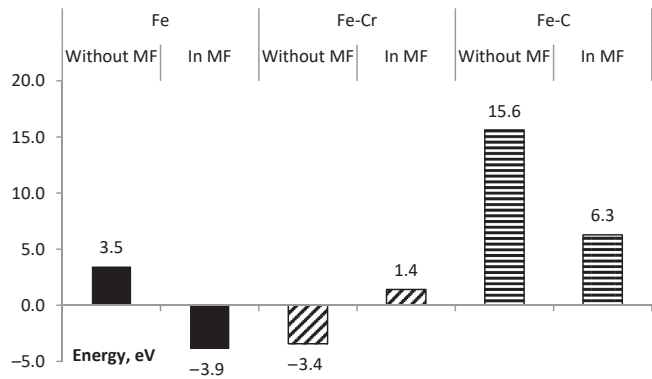


Figure 1.
Models of a fragment of
Fe crystal lattice with
an edge dislocation

Figure 2.
Energy change
between the initial and
final configurations of
systems of atoms



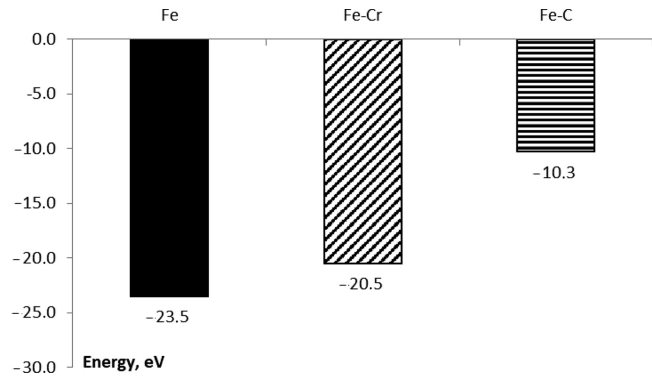
Therefore, the calculated data on the decrease in the energy between the configurations of the atoms will be considered favorable for the motion of the dislocation.

Let us consider the results of calculations without the influence of MF. For the crystal lattice of pure Fe without MF, the energy of configuration 2 is higher than 1, and the dislocation motion is resisted. The substitutional atom Cr without MF is not a stopper for dislocation motion; the energy of configuration 2 is less than 1. This does not mean that the dislocation motion occurs spontaneously without an external mechanical load, but such a motion will not encounter additional resistance and will be energetically favorable. The interstitial atom C, located in the center of the plane of Fe atoms, creates the largest energy barrier for the dislocation motion. Configuration 2 energy is higher than 1.

MF influenced the total electronic energy of the atomic system. In the presence of an MF, the energy of the atomic system decreases (Figure 3), and the ratio of the energies of configurations 1 and 2 changes. This result can be one of the rationales magnetoplasticity effect in a ferromagnetic material. The largest change occurred in the system of pure Fe atoms. Impurity atoms reduce the efficiency of the MF action.

The MF also changes the ratio of the energies of the configurations of atoms 1 and 2 (Figure 2). For a system of pure Fe atoms, the energy decreases, in contrast to the motion of a dislocation without an MF. The impurity atoms form an additional resistance to dislocation motion in the case of MF exposure. The energy of systems of atoms increases. However, the

Figure 3.
Reduction of the
energy of the initial
configuration of
systems of atoms in
the MF



initial decrease in the energy of configuration 1 in the MF significantly exceeds its increase in configuration 2. Therefore, there is a general positive effect of the MF action.

There is a relationship between the electronic structure of a system of atoms, its energy and physical properties, including magnetic ones. Magnetic properties are also an indicator of the conditions of dislocation mobility. The electrons localized in the core of the dislocation create high values of the local electron density and therefore significantly affect the magnetic properties of the atomic system. The magnetic susceptibility is directly proportional to the electron concentration. Without the influence of the MF for all configurations 2, the magnetic susceptibility increases (Figure 4), which means that the local electron density also increases. The influence of the magnetic field smoothes out the inhomogeneous distribution of electrons. The growth rate of the local electron density of the system of pure Fe atoms decreases. For the systems of atoms with impurities, the magnetic susceptibility and electron density even decrease.

The relationship between local electron density and dislocation can be demonstrated using electron density isolines. In the dislocation core, a high electron density is observed between atoms 5, 6, 7 of configuration 1 (Figure 5a) and atoms 6, 7, 8 of configuration 2 (Figure 5b).

When a dislocation moves, the atom of its core becomes more electronegative (Figure 5). So, atom №6 reduced the negative charge by 0.296 charge units leaving the dislocation core of configuration 1. And atom №7 acquired a larger negative charge by 0.087 charge units,

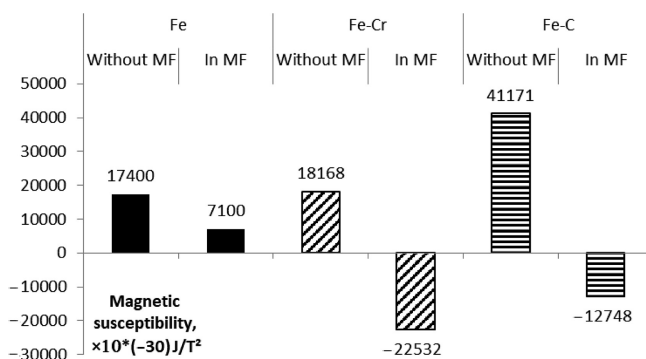


Figure 4.
Change in magnetic
susceptibility between
the initial and final
configurations of
atomic systems

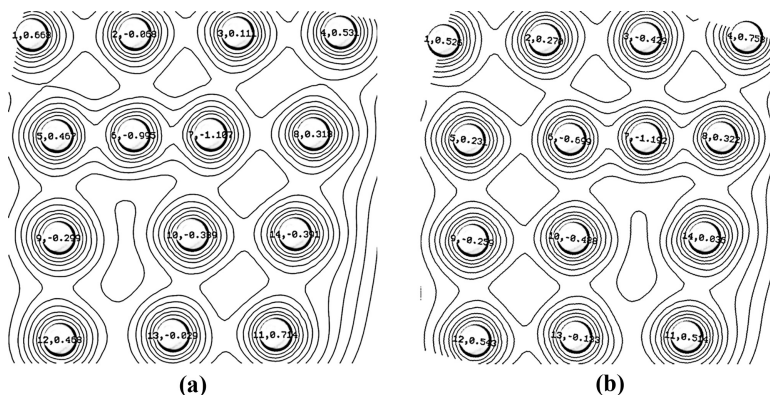


Figure 5.
Isolines of electron
density and charges on
atoms in a fragment of
the Fe crystal lattice

becoming the dislocation core in configuration 2. An increase in the negative atomic charge may result from an excess of negatively charged electrons, that is, an increase in the local electron density.

Based on the simulation results, it was determined that magnetoplasticity is an effect that acts only in certain atomic configurations, and therefore in the structures of real metals and alloys. This may serve as one of the explanations for the inconsistency of numerous experimental data on magnetoplasticity studies.

4. Conclusions

- (1) The paper presented the crystal structure of Fe-based alloys. We considered the process of dislocation motion, mechanical and magnetic properties of a crystalline body and the associated phenomenon of magnetoplasticity at the atomic level.
- (2) We described a quantum-mechanical method for calculating the total energy of a system of Fe atoms representing a fragment of a crystal lattice. The applied Kohn-Shem density functional theory, implemented in the GAUSSIAN 09 software package, allowed us to calculate the energy consumption for switching the covalent chemical bond of atoms in the dislocation core. The process simulates the dislocation motion at one interatomic spacing. The calculated models of dislocation advancement in the Fe crystal lattice included those without impurities, with a substitutional atom Cr and an interstitial atom C. Using perturbation theory, we simulated the influence of an external constant magnetic field on the energy of the system of lattice atoms.
- (3) Calculations have shown that in the initial state the presented variants of crystal lattices do not have significant differences in the value of the total energy of the atomic system. The dislocation motion increases the energy of the Fe atomic system and increases it to even greater extent in the presence of an interstitial atom C. That is, the dislocation motion encounters resistance. In a lattice with a substitutional Cr atom, there is no additional resistance to dislocation motion (the energy of the atomic system decreases). The effect of a magnetic field reduces the energy of a system of atoms in various configurations of their arrangement.
- (4) The dislocation motion increases the magnetic susceptibility of the atomic system of all the studied models. While the dislocation moves in the magnetic field, decreases either the magnetic susceptibility of the atomic system or the intensity of its growth. A magnetic field has a positive effect on the uniformity of the distribution of electrons within the system of atoms with distortion of the crystal lattice, especially in the presence of impurity atoms.
- (5) The positive and negative influence of the magnetic field on the dislocation mobility creates the prerequisites for the development of conditions for the realization of magnetoplasticity in real Fe-based alloys.

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