DENSITY OF STATES OF Fe_3O_4

Jozef DRGA[1,2*] – Jozef CHOVANEC[3] - Stanislav ŠIMKOVIČ[4] – Jozef KÚDELČÍK[5]

[1]*Department of Engineering, Faculty of Special Technology, Alexander Dubček University of Trenčín, Pri Parku 19, 91150 Trenčín, Slovakia*

[2]*Institute of Physical Electronics, Faculty of Natural Sciences, Masaryk University.Kotlářská 267/2, 611 37 Brno, Czech Republic*

[3]*Vitrum Laugaricio – The join rearch center of glass science, Študentská 2, 91150 Trenčín, Slovakia*

[4]*High school of Piarists, Palackého 4, 91101 Trenčín, Slovakia*

[5]*Department of Physics, Faculty of Electrical Engineering, University of Žilina, Univerzitna 1, 010 26 Žilina, Slovakia*

**Corresponding author E-mail address: jozef.drga@tnuni.sk*

Abstract:

We present the investigation of Magnetite using density functional theory in this contribution, the properties of Fe3O4, which makes it usable for a material for nanoparticles in magnetic fluid, will be discussed. The Fermi Energy and Density of States were calculated.

Key words: magnetic fluids, nanoparticles, magnetite, density of states

1. Introduction

Magnetic fluids are interesting materials used in various technical applications. They consist of magnetic nanoparticles, base liquid and surfactant layer of ferromagetic or ferimagnetic particles [1]. The Fe_3O_4 is mostly used as a material for magnetic particles because it has chemically inert properties. The structure of Fe_3O_4 is inverse spinel at room temperature [2]. The structural formula in Fe_2O_3. FeO, where the (Y) is trivalent and the second atom (X) is divalent. The formula for spinel is XY_2O_4, it is possible to fill all the octahedral with Y (trivalent) atoms and the tetrahedral with X (divalent) atoms. We cannot reverse the roles of X and Y and fill all the sites. If we were to try, we could only fill half the octahedral with X, and thetetrahedral would only take up half the Y atoms. Such a structure is called an inverse spinel. In reality, most spinels are somewhere between the two end states [3].

In magnetite, the tetrahedral and octahedral sites form two magnetic sub lattices with the spin moments on the X sublattice antiparallel to those on the Y sublattice. The proposed electronic structure of the octahedralFe^{2+} cations corresponds to a situation where an extra electron resides in the lowest unoccupied t2g orbital located a Fermi level. Such an occupation then would give rise to the 100% spin-polarized charge carriers desired for spintronic applications [4, 5].

2. Program VASP

The Vienna Ab initio Simulation Package (VASP) is an application for atomic scale materials modelling; for example electronic structure calculations and quantum-mechanical molecular dynamics. It allows calculations of Born-Oppenheimer molecular Dynamics, Relaxation using conjugate gradient, Quasi-Newton or damped molecular Dynamics, Nudged elastic band methods (transitions states search) Climbing dimer method (transition state search), many optical and magnetic properties.

3. Little bit of theory

The magnetic properties depend of the electronic structure in the materials. To study electronic structure the Density functional theory (DFT) was used. The fundamental equation to solve is the time-independent Schrödinger equation

$$H\Psi = E\Psi \tag{1}$$

The Density functional theory consists of two fundamental Hohenberg-Kohn-Sham theorems

a.) The ground-state energyE_0 of a many-bodysystem is a unique functional of the particle density$n(\vec{r})$.

b.) The ground-state energy functional $E[n(\vec{r})]$ has its minimum relative to variations $\delta n(\vec{r})$ of the particle density at the equilibrium density $n_0(\vec{r})$

$$E_0 = E[n_0(\vec{r})] = \min\{E[n(\vec{r})]\} \tag{2}$$

$$\left.\frac{\delta E[n(\vec{r})]}{\delta n(\vec{r})}\right|_{n(\vec{r})=n_0(\vec{r})} = 0$$

The Hamiltonian H of a many electron-system in an external potential V is given by

$$H = T + V_{ee} + V, \tag{3}$$

Where V_{ee} is electron-electron interaction potential. The ground-state energyE_0can be expressed in the form

$$E_0 = \langle \Psi_0 | H | \Psi_0 \rangle \tag{4}$$

and the particle density

$$n_0(\vec{r}) = |\langle \Psi_0 | \vec{r} \rangle|^2 \tag{5}$$

4. Results

Density of states (DOS) of a system describes the number of states per interval of energy that are available to be occupied. The projector augmented-wave PAW pseudopotentials (PPs) [6, 7] and the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional were used. [8].We considered two steps. In the first stage we calculated the structure of materials with the ionic and electronic relaxation. The number of K-Points was 6. The second step was DOS calculation. All calculations were performed at zero temperature 0 K. In this case the number of K-Points increased to 18.

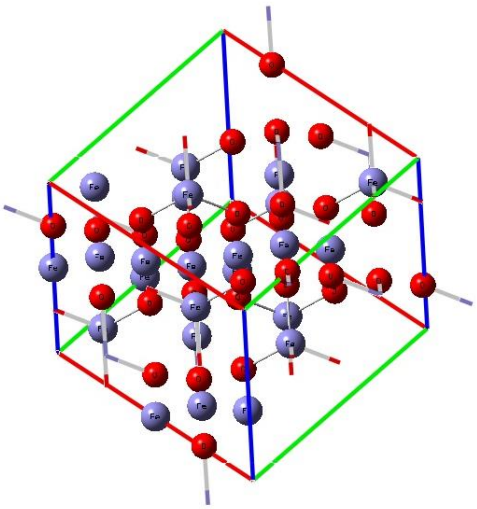

Fig. 1.Structure of elementary cell.

Each electronic and ionic contribution in energy and ionic contributions to sum of forces were calculated. The precision of total (free) energy between two ionic relaxation steps was set up 10^{-5}. The calculation was performed using 2201 points to ensure good resolution. Energy range from -10eV to 15 eV was used. The Fermi energy was calculated as 5.57 eV.

The structure of magnetite is shown on Fig 1. Fig. 2 shows density of states profile, the valence and conducting band. The density of states profile is in the summary state does not distinguish between spin up and down.

Fig. 3 shows the DOS in bands structure. System looks like insulator, but in temperature T=123 K the Verwey transition will occur and the system will be in conducting state. It depends on the change of the crystal and electronic structure [9].

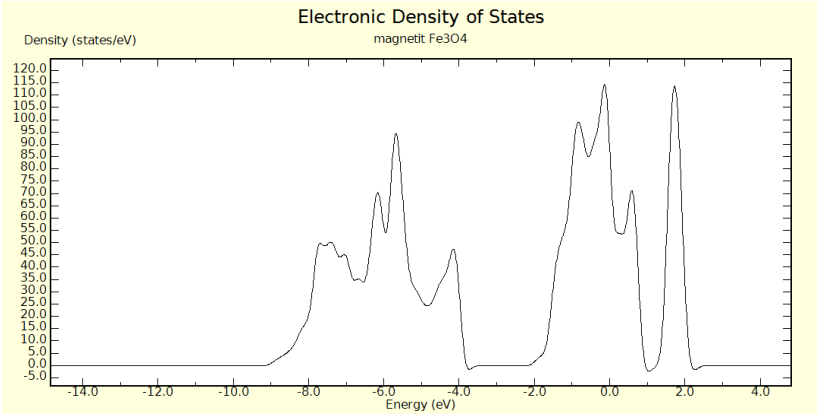

Figure 2. Summary Density of states of Fe3O4

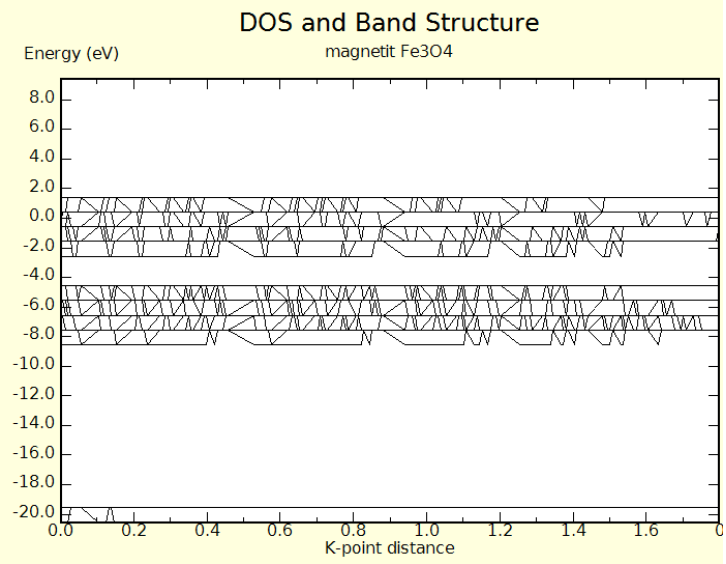

Fig. 3. DOS and Band structure

5. Conclusions

The Density of States of Magnetite was calculated below Verwey transition at temperature 0K. The Density of States curve shows insulator behaviour. The properties of Fe_3O_4 make it a suitable to a material for nanoparticles in magnetic fluids and is also usable in spintronics. The Fermi energy was obtained as 5.57 eV.

Acknowledgement

Európska únia
Európsky fond regionálneho rozvoja

Operačný program VÝSKUM a VÝVOJ

This contribution was created on the basis of the project "Research centre ALLEGRO" (ITMS project code: 26220220198), supported by Operational Programme Research and Development funded by the European Regional Development Fund.

6. Referencies

[1] J. Kúdelčík, P. Bury, J. Drga, P. Kopčanský, V. Závišová, M.Timko: Comparison of Theories of Anisotropy in Transformer Oil-Based Magnetic Fluids, Applied Physics, Vol.: 11, 2013, No: 2, p. 147

[2] S. Sasaki: Radial distribution of electron density in magnetite, Fe3O4, Acta Crystallographica B (vol 53, 1983, p. 762
[3] H. St. C. O'Neill, W. A. Dollase: Crystal structures and cation distributions in simple spinels from powder XRD structural refinements: MgCr2O4, ZnCr2O4, Fe3O4 and the temperature dependence of the cation distribution in $ZnAl_2O_4$, Physics and Chemistry of Minerals, Vol. 20, 1994, Is. 8, p. 541
[4] Z. Zhang, S. Satpathy: Electron states, magnetism, and the Verwey transition in magnetite, Physics. Review B, Vol. 44, 1991, p. 13319
[5] K. Jordan, A. Cazacu, G. Manai, S.F. Ceballos, S.Murphy, I.V. Shvets: Scanning tunnelling spectroscopy study of the electronic structure of Fe_3O_4 surfaces, Physics Review B Vol. 74, 2006, p. 085416
[6] P. Blöchl: Projector augmented-wave method, Physics. Review. B, Vol. 50, 1994, p. 17953
[7] G. Kresse, D. Joubert: From ultrasoft pseudopotentials to the projector augmented-wave method, Physics Review, Vol. 59, 1999, p. 1758
[8] J. Perdew, K. Burke, M. Ernzerhof: Generalized Gradient Approximation Made Simple, Physics Review Letters, Vol. 77, 1996, No. 18, p.3865
[9] S. de Jong at al.: Speed limit of the insulator–metal transition in magnetite, Nature Materials Vol, 12, 2013, p 882