Calculation of the exchange integrals for $\text{Co}_{1-x}\text{Ni}_x$ alloy by Korring-Kohn-Rostoker method

Sergey N. Budko and Marina V. Mamonova

Dostoevsky Omsk State University, Omsk, Russia

E-mail: mamonovamv@omsu.ru

Abstract. In this work we investigate the cobalt-nickel alloy magnetic properties. Calculations of lattice constants for Co, Ni and $\text{Co}_{1-x}\text{Ni}_x$ alloy with different concentrations were performed with the VASP framework. Calculations of the exchange integrals were carried out using the SPR-KKR package (spin-polarized relativistic Korring-Kohn-Rostoker method). For pure ferromagnets, the Co exchange interaction is ferromagnetic. For Ni, the exchange interaction of the nearest neighbors also is ferromagnetic, but the exchange interaction of the next nearest neighbors has a very weak antiferromagnetic character. In the $\text{Co}_{1-x}\text{Ni}_x$ alloy, the exchange interaction of the nearest neighbors decreases with increasing nickel concentration. The next nearest neighbors exchange interaction at a concentration of Ni $x \geq 0.5$ has an antiferromagnetic character.

1. Introduction

This article is devoted to the theoretical investigation of cobalt-nickel alloy magnetic properties. Cobalt, which has a hcp structure in its pure form, is poorly deposited on another metal of the fcc structure, for example, copper (copper is the most common example of an adsorbent), however cobalt is characterized by a high critical temperature. In turn, nickel has a small critical temperature but is well deposited on copper. Thus, the $\text{Co}_{1-x}\text{Ni}_x$ alloy is characterized by better magnetic and adsorption properties as compared to pure metals. Co and Ni are miscible and form stable alloys near room temperature. By varying the Co content, we can produce stable alloy materials with different bulk $T_c$ values [1]. As the cobalt concentration in the CoNi alloy increases, the critical temperature increases. In addition, these alloys are used in layered heterostructures with giant magnetoresistance, which are actively used in data storage technologies. The magnetic properties and resistivity of an alloy are highly dependent on its composition. The study of these materials provides valuable information on the values of the exchange integrals of ferromagnets, which can be used in numerical Monte Carlo simulations of the nonequilibrium behavior of multilayer magnetic nanostructures.

2. Korring-Kohn-Rostoker method

The SPRKKR-package is based on the KKR-Green’s function formalism that makes use of multiple scattering theory. The problem of setting up the electronic Green’s function $G(\vec{r}, \vec{r}’ E)$ for a solid on the basis of relativistic multiple scattering theory for arbitrary scalar and vector potentials has been investigated in great detail by T. Huhne, C. Zecha, and H. Ebert [2]. The corresponding expression for $G(\vec{r}, \vec{r}’ E)$ is given by

$$G(\vec{r}, \vec{r}’ E) = \sum_{\vec{r}”} \frac{1}{E - H(\vec{r}”)} G(\vec{r}, \vec{r}’ E)$$

where $H(\vec{r}”)$ is the Hamiltonian for the scattered state $\vec{r}”$.
Figure 1. Crystal structure of a) Co$_{0.75}$Ni$_{0.25}$ b)Co$_{0.5}$Ni$_{0.5}$ c)Co$_{0.25}$Ni$_{0.75}$ lattices. Number of unit real space Bravais lattice consist of four atoms: a) Co1, Co2, Co3, Ni1 b) Co1, Co2, Ni1, Ni2 c) Co1, Ni1, Ni2, Ni3.

\[ G(\vec{r}, \vec{r}'; E) = \sum_{\Lambda \Lambda'} Z^n_\Lambda(\vec{r}, E) \tau^{nm}_{\Lambda \Lambda'}(E) Z^{m\times}_N(\vec{r}', E) \]

\[ - \sum_{\Lambda} Z^n_\Lambda(\vec{r}, E) J^{m\times}_\Lambda(\vec{r}', E) \Theta(\vec{r}' - \vec{r}) \]

\[ + J^n_\Lambda(\vec{r}, E) Z^{m\times}_N(\vec{r}', E) \Theta(\vec{r} - \vec{r}') \delta_{nm} \]

for $\vec{r}, \vec{r}'$ within the cell $n(m)$. Here the normalization in analogy to the nonrelativistic formalism of Faulkner and Stocks for the wave functions $Z$ and $J$ has been used. The quantity $\tau^{nm}_{\Lambda \Lambda'}$ is the so-called scattering path operator. For an ordered system the site diagonal scattering path operator $\tau^{nn}$ can be obtained from the BZ integration of single-site $t$ matrix:

\[ \tau^{nn} = \frac{1}{\Omega_{BZ}} \int_{\Omega_{BZ}} d^3k [t(\vec{k})]^{n-1} - G(\vec{k}, E)]^{-1} \]

where $G(\vec{k}, E)$ is the matrix of the relativistic structure constants.

With the Green’s function $G(\vec{r}, \vec{r}'; E)$ available the charge and spin density can be obtained via

\[ n(\vec{r}) = -\frac{1}{\pi} \text{Im} \text{Tr} \int_{E_F}^{E} dE G(\vec{r}, \vec{r}, E) \]

\[ m(\vec{r}) = -\frac{1}{\pi} \text{Im} \text{Tr} \int_{E_F}^{E} dE \beta \sigma_z G(\vec{r}, \vec{r}, E) \]

From the Green’s function most electronic properties can be derived straightforwardly. For example the spin magnetic moments and orbital magnetic moment are obtained from:

\[ \mu_{\text{spin}} = -\frac{\mu_B}{\pi} \text{Im} \text{Tr} \int_{E_F}^{E} dE \int_{V} d^3r \beta \sigma_z G(\vec{r}, \vec{r}, E) \]

\[ \mu_{\text{orb}} = -\frac{\mu_B}{\pi} \text{Im} \text{Tr} \int_{E_F}^{E} dE \int_{V} d^3r \beta l_z G(\vec{r}, \vec{r}, E) \]
Using the SPR-KKR package it is possible to calculate the exchange coupling parameters $J_{ij}$ of the Heisenberg model:

$$ H = -\frac{1}{2} \sum_{i \neq j} J_{ij} S_i S_j $$

(7)

where $S_i$ and $S_j$ are vectors having the directions of corresponding local magnetic moments on sites $i$ and $j$. The exchange coupling parameter $J_{ij}$ can be found from ab initio calculations based on the KKR Green’s function method using the formulation of Lichtenstein et al. [3]:

$$ J_{ij} = \frac{1}{4\pi} \text{Im} \int dE \text{Tr}(t_{ij}^{-1} - t_{ji}^{-1}) t_{ij}^{-1} (t_{ij}^{-1} - t_{ji}^{-1}) t_{ij}^{-1} $$

(8)

3. Result of calculations

First, calculations of lattice constants for Co, Ni, and Co$_{1-x}$Ni$_x$ alloy with different concentrations were performed in the framework of VASP [4], the projection augmented wave (PAW) method and GGA PBE pseudopotential approximation. The lattice constants were calculated from the condition of minimum total energy as the functions of convergence parameters. We confined ourselves to values of the plane waves cut-off energy $E_{\text{cut}} = 500$ eV and Monkhorst Pack grid size 15x15x15. The magnetic moment of atoms is directed collinearly. The crystalline cells with translation of fcc Co$_{1-x}$Ni$_x$ alloy structure with different Ni concentrations are shown in figure 1.

| Table 1. Calculated equilibrium lattice constants for fcc Co, fcc Ni and Co$_{1-x}$Ni$_x$ alloy. |
|--------------------------------------------------|
| $a_{\text{vasp}}, \text{Å}$ | $a_{\text{lit}}, \text{Å}$ |
| Co      | 3.517 | 3.55 [5] |
| Co      | 3.514 | 3.42 [6] |
| Co$_{0.75}$Ni$_{0.25}$ | 3.514 |
| Co$_{0.5}$Ni$_{0.5}$ | 3.516 |
| Co$_{0.25}$Ni$_{0.75}$ | 3.510 |
| Ni      | 3.513 | 3.52 [7] |
|         |      | 3.47 [8] |

The calculated values of equilibrium lattice constants are presented in table 1. It can be seen that good agreement is obtained between our calculated values and the range of values of the lattice constant given in other articles. For Co$_{1-x}$Ni$_x$, a very small, less than 1%, dependence of the lattice constant on the Ni concentration is observed.

The results of the calculation of exchange integrals and lattice constants obtained by us and taken from literary sources are given in the table 2. $\bar{J}$ denotes the averaging of the values of the exchange integral for atoms at the nodes of the unit cell located at the same distance from each other. A change of the lattice constant significantly affects the parameters of the exchange interaction. So for Co, with $\Delta a = |a_{\text{lit}} - a_{\text{vasp}}| = 0.1 \text{Å}$, it causes $J_1$ to change to $\Delta J_1 = 0.2 \times 10^{-14}$ erg, which corresponds to 10%; for Ni, with $\Delta a = 0.007 \text{Å} \Delta J_1 = 0.2 \times 10^{-14}$ erg, which corresponds to 54%.

According to the results of the calculations given in table 2, we can get the following conclusions: for pure Co, the exchange interaction is ferromagnetic, and for pure Ni, the exchange interaction of the next nearest neighbors has a very weak antiferromagnetic character $J_2 = -0.009 \times 10^{-14}$ erg. The exchange integrals values obtained by us are in good agreement with the values obtained in the framework of the first-principles tight-binding linear muffin-tin orbital method (TB-LMTO) [9].
Table 2. Calculated exchange integrals for fcc Co and fcc Ni.

|        | Co     | Ni     | Co     | Ni     |
|--------|--------|--------|--------|--------|
| \( J_1 \) | 1.000  | 1.000  | 2.000  | 2.000  |
| \( J_2 \) | 0.000  | 0.000  | 0.000  | 0.000  |

Table 3. Calculated magnetic moments per atom for fcc Co, fcc Ni and Co\(_{1-x}\)Ni\(_x\) alloy.

|        | \( \mu_{\text{spin}}^\text{Co}, \mu_B \) | \( \mu_{\text{arb}}^\text{Co}, \mu_B \) | \( \mu_{\text{spin}}^\text{Ni}, \mu_B \) | \( \mu_{\text{arb}}^\text{Ni}, \mu_B \) |
|--------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| Co     | 1.5827             | 0.0713             |                                |                                |
| Co\(_{0.75}\)Ni\(_{0.25}\) | 1.6644             | 0.0799             | 0.6287             | 0.0380             |
| Co\(_{0.5}\)Ni\(_{0.5}\)  | 1.6906             | 0.0811             | 0.6874             | 0.0428             |
| Co\(_{0.25}\)Ni\(_{0.75}\) | 1.7267             | 0.1016             | 0.6649             | 0.0489             |
| Ni     | 0.5985             | 0.0497             |                                |                                |

In the framework of the SPR-KKR method, a spin \( \mu_{\text{spin}} \) and an orbital magnetic moments \( \mu_{\text{arb}} \) were obtained with the lattice constant values calculated in VASP and presented in table 1. Analyzing the result of these calculations in table 3, we can conclude that an increase in Ni concentration leads to an increase in magnetic moments. Orbital magnetic moments do not exceed 5\%-10\% of the spin moment values. The values of the magnetic moments of the alloy and, consequently, the magnetization are greater than the corresponding values in pure metals. Thus, the Co\(_{1-x}\) Ni\(_x\) alloy is characterized by better magnetic properties as compared to pure metals.

Table 4. Calculated exchange integrals for Co\(_{1-x}\)Ni\(_x\) alloy.

| \( J_1, 10^{-14}\text{erg} \) | Co\(_{0.75}\)Ni\(_{0.25}\) | Co\(_{0.5}\)Ni\(_{0.5}\) | Co\(_{0.25}\)Ni\(_{0.75}\) |
|-------------------------------|-----------------|-----------------|-----------------|
| \( J_{1}(\text{Ni-Co}) \)    | 0.843(4)        | 1.211(1)        | 1.338(7)        |
| \( J_{1}(\text{Co-Co}) \)    | 2.885(3)        | 3.411(1)        |                 |
| \( J_{1}(\text{Ni-Ni}) \)    | 0.471(1)        | 0.419(3)        |                 |
| \( J_1 \)                     | 1.864(1020)     | 1.363(942)      | 0.878(459)      |
| \( J_{2}(\text{Co-Co}) \)    | 0.015(78)       | -0.026(32)      | -0.058(8)       |
| \( J_{2}(\text{Ni-Ni}) \)    | -0.037(1)       | -0.069(6)       | -0.056(16)      |
| \( J_2 \)                     | 0.002(71)       | -0.047(31)      | -0.057(14)      |

The results of calculations of the exchange interaction integrals for the nearest \( J_1 \) and the next nearest neighbors \( J_2 \) for various concentrations of the alloy components are given in table 4. The interaction of the nearest neighbors is additionally described by the Ni-Co interaction, but the
interaction the next nearest neighbors is described only by the interaction of atoms of the same type. It can be seen that the values of exchange interaction integrals $J_1^{(Ni-Co)}$ and $J_1^{(Co-Co)}$ increases with increasing Ni concentration in the alloy. The values of exchange interaction integrals $J_1^{(Co-Co)}$ and $J_1^{(Ni-Ni)}$ are positive and more than the corresponding values in the pure metals (table 2).

From the calculation results of the exchange integrals for the Co$_{1-x}$Ni$_x$ alloy, it follows that $J_1 > 0$ contributes to the ferromagnetic ordering of magnetic moments of the nearest neighbors, and $J_2 < 0$ at Ni concentration $x > 0.5$ contributes to the appearance of the antiferromagnetic configuration magnetic moments of the next nearest neighbors, but its value is significantly smaller than the constant $J_1$.

![Figure 2.](image)

**Figure 2.** The average values of exchange integrals for Co$_{1-x}$Ni$_x$ alloy as a function of the distance R between the atoms.

The figure 2 contains the plot of average values of exchange integrals depending on the distance between the atoms. Distances are represented in units of lattice constants. We can see that there is a similar behavior of the J functions for any Ni concentrations.

### 4. Conclusions

In this work, calculations of lattice constants for pure Co, Ni metals and for Co$_{1-x}$Ni$_x$ alloy were carried out in the VASP software complex. Using the calculated equilibrium lattice constant values, we calculated the spin and orbital magnetic moments and exchange integrals within the SPR-KKR package. A change in the constant of crystal structure significantly affects the parameters of the exchange interaction. The calculation results allow us to draw the following conclusions:

For pure ferromagnets, the Co exchange interaction is ferromagnetic. For Ni, the exchange interaction of the nearest neighbors also is ferromagnetic, but the exchange interaction of the next nearest neighbors has a very weak antiferromagnetic character $J_1 = -0.004 \times 10^{-14}$ erg.

In the Co$_{1-x}$Ni$_x$ alloy with increasing nickel concentration, the exchange interaction of the nearest neighbors $J_1^{(Ni-Co)}$ and $J_1^{(Co-Co)}$ increases, while $J_1^{(Ni-Ni)}$ and $J_2^{(Co-Co)}$ decreases. Exchange interaction of the next nearest neighbors at a concentration of Ni $x \geq 0.5$ has an antiferromagnetic character. The obtained values of the $J_1$ and $J_2$ integrals of the exchange interaction can be used to compare the results of Monte Carlo calculations [10] with the experiment.
Acknowledgments
This work was supported by RFBR according to the research projects 17-02-00279, 18-42-550003 and grant MD-6868.2018.2 of the President of Russia. Shared Facility Center Data Center of FEB RAS (Khabarovsk) is acknowledged for computational resources.

References
[1] Huang F, Kief M T, Mankey G J and Willis R F 1994 Phys. Rev. B 49 3962
[2] Huhne T, Zecha C and Ebert H 1998 Phys. Rev. B 58 10238
[3] Liechtenstein A I, Katsnelson M I and Gubanov V A 1984 J. Phys. F: Met. Phys. 14 L125
[4] Kresse P G and Furthmuller J 1996 Phys. Rev. B 54 11169
[5] Wuttig M and Liu X 2004 Ultrathin metal films (Berlin: Springer)
[6] Haglund J, Fernandez Guillermet A, Grimvall G and Korling M 1993 Phys. Rev. B 48 11685
[7] Wijn H P J 1991 Magnetic Properties of Metals (Berlin: Springer)
[8] Moruzzi V L, Janak J F and Williams A R 1978 Calculated Electronic Properties of Metals (New York: Pergamon)
[9] Pajda M, Kudrnovsky J, Turek I, Drchal V and Bruno P 2001 Phys. Rev. B 64 174402
[10] Prudnikov V V, Prudnikov P V and Mamonova M V 2017 Phys. Usp. 60 762