Estimation of Muon Stopping Site in CoCr$_2$O$_4$ Using Density Functional Theory

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Abstract. Spinel material Cobalt Chromite (CoCr$_2$O$_4$) is a ferrimagnetic material with $T_C$ of about 93 K. This compound has attracted much attention due to the presence of electrical polarization which related to spiral magnetic transition at $T_S = 26$ K. [Physical Review B, 70, 214434, 2004]. This spiral magnetic transition phenomena could be explored by experiment using Muon Spin Rotation, Relaxation, and Resonance ($\mu$SR). Positive muon in $\mu$SR plays a role as a local magnetic probe thus, we need to determine the muon stopping site information. In this study, we investigate the muon stopping site of CoCr$_2$O$_4$ with ferrimagnetic ground state using spin polarized Density Functional Theory implemented in Full-potential Linearized Augmented Plane Wave (FLAPW) method. The exchange-correlation effect was considered in the scheme of GGA+$U_{eff}$ approximation. Based on the minimum energy of electrostatic potential, we obtain the muon stopping site around the three Oxygen ions in the tetrahedral site of Cobalt.

Keywords: Muon stopping site, electrostatic potential, CoCr$_2$O$_4$, DFT, FLAPW

1. Introduction

Cobalt Chromite, CoCr$_2$O$_4$, is a ferrimagnetic material with $T_C$ of about 93 K. There has been a high interest in this compound due to the presence of electrical polarization which related to spiral magnetic transition $T_S$, at around 26 K [1]. The presence of the clamping between the magnetization and electrical polarization makes CoCr$_2$O$_4$ belong to the class of multiferroic material [2]. The coexistence of ferromagnetism and ferroelectricity in multiferroic material could be applied to some potential devices such as a magnetic field sensor [3], modulator [4], memory devices [5], gyrator [6], and energy harvesting device [7].

CoCr$_2$O$_4$ crystallizes in the cubic spinel structure with the lattice constant of 8.3346 Å [8] as shown in Fig.1. The A site of the spinel occupied by Co$^{2+}$ ion while the B site occupied by Cr$^{3+}$ ion [1]. Due to the magnetism of Co$^{2+}$ cation in A site, the geometric frustration inside CoCr$_2$O$_4$ cannot be released by lowering the crystal symmetry. The alternative way to get rid the geometrical frustration is through the temperature dependent magnetic structure mechanism [9]. The magnetic structure of CoCr$_2$O$_4$ is changing from collinear ferrimagnetic to be a complex noncolinear spiral magnetic configuration at 26 K [10]. Due to the complexity of noncolinear spiral configuration, this paper only considers the collinear ferrimagnetic structure (the temperature region from 93 K down to 26 K).

The magnetic transition phenomena in CoCr$_2$O$_4$ can be measured by experiment using Muon Spin Rotation, Relaxation, and Resonance ($\mu$SR) technique. Since the $\mu$SR is a local probe to measure the internal magnetic fields, therefore it is necessary to find the positions of the muon stop in the
material. This paper reports the muon stopping site in CoCr$_2$O$_4$ crystal based on the local minima of the electrostatic potential obtained from density functional theory (DFT) implemented in Full-potential Linearized Augmented Plane Wave (FLAPW) method.

2. Computational method
The positive muon which is commonly used in the experiment would prefer to stop in the minimum of the electrostatic potential near the negative ions [11]. In term to know the muon stopping site, firstly we need to calculate the electrostatic potential felt by the muon inside of CoCr$_2$O$_4$ using:

\[ V_{\mu}(\vec{r}) = -\frac{e^2}{2} \int \frac{n(\vec{r}^\prime)}{\vec{r} - \vec{r}^\prime} d\vec{r}^\prime + \sum Z_i e^2 \frac{R_i}{\vec{r} - \vec{R}_i}, \]

where the first term in this expression is a Hartree term with \( n(\vec{r}^\prime) \) is the density of electron, and the second term is a nuclei term. \( V_{\mu}(\vec{r}) \) value inside of materials can be calculated using ab-initio strategy [11-13].

![Figure 1. Crystal structure of CoCr$_2$O$_4$ conventional cell.](image)

The electrostatic potential of the muon inside CoCr$_2$O$_4$ was obtained from equation (1) utilizing the electron density provided by DFT calculation implemented in FLAPW method [14-16]. The Linearized Augmented Plane Wave (LAPW) function used a cutoff of \(|\vec{k} + \vec{G}| \leq 3.9 \text{ a.u.} \) and muffin-tin sphere radii of 2.0, 2.1, and 1.6 a.u. for Co, Cr, and O ions, respectively. These radii were considered to avoid overlap among the muffin-tin spheres and to ensure the loss of electron from the core is less than 0.05 with the respect of the total electron. We used generalized gradient approximation (GGA) [17] for exchange-correlation and \( U_{\text{eff}} \) value for strong correlation effect [10]. The \( U_{\text{eff}} \) term consist of a subtraction between \( U \) value denoting as the Coulomb interaction and \( J \) as Hund’s coupling [18]. The \( U \) value for Co and Cr ion was set to be 5 eV and 3 eV, for the \( J \) value both of Co and Cr was set to be 1 eV [10]. The minimum electrostatic potential of the muon was calculated based on Eq. 1 for the CoCr$_2$O$_4$ conventional cell as show in Fig. 1 with the mesh of 101×101×101.

3. Results and discussion
In order to determine the local minima of the electrostatic potential sites of the muon inside the CoCr$_2$O$_4$, we draw an isosurface potential of 0.15 eV greater than the global minimum potential in all positions of the grid. We obtain the isosurface forms a ring around three Oxygen ions of tetrahedral side of Cobalt as shown in Fig. 2. It is noted that the distance between Oxygen ions at the tetrahedra side of Cobalt (3.20604 Å) is bigger than at the octahedral side of Chromium (2.95243 Å). Figure 3 shows the tetrahedra symmetry of the Cobalt ions and the tetrahedra symmetry of the ring at the Cobalt sides.

The possibility to find another local minimum around the Cobalt site was carried out by varying the isosurface potential value from 0.1 to 1 eV. Figure 4 shows that the result of increasing the
isosurface potential value. It is interesting to note that there are no other minima outside the cluster. In order to find the local minimum, we will focus only the position inside the ring cluster and yields to minimum positions with a distance of 2.01 Å from the Cobalt site. All of these six positions are also located near three Oxygen positions around the Cobalt ion.

![Figure 2](image1.png) **Figure 2.** Electrostatic potential isosurfaces with 0.15 eV greater than the global minimum value.

![Figure 3](image2.png) **Figure 3.** A tetrahedra symmetry applies for both the ring of electrostatic potential isosurfaces and Cobalt ion.

![Figure 4](image3.png) **Figure 4.** Ring-shaped clusters of electrostatic potential isosurfaces around A site (Co ion) with isosurfaces value of (a) 0.1, (b) 0.5, and (c) 1 eV greater than the global minimum value of electrostatic potential energy.

All of those six positions described above cannot be considered as final muon stopping sites because there is a possibility that muon can still move away from the minimum positions due to the arrangement of the crystal structure in the presence of muon. This will be resolved by considering the relaxation of the local structure caused by muon and the muon zeropoint motion (ZPM) [11,13,19].

4. Conclusion
The position of the minimum electrostatic potential position in \( \text{CoCr}_2\text{O}_4 \) has been determined using density functional analysis based on FLAPW method with correlation effects. Electrostatic potential

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isosurface plot from the resulted calculation shows that there are six minimum positions with 2.01 Å radius from the Cobalt tetrahedral site.

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