An investigation of muon sites in YBa$_2$Cu$_3$O$_6$ by using Density Functional Theory

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Abstract. The electrostatic potential has been investigated in YBa$_2$Cu$_3$O$_6$ by applying the density functional theory in order to estimate possible muon sites. We found five minimum potential positions around the apical oxygen of the CuO$_5$ polyhedral. In addition to those, we also found another minimum potential position near the yttrium atom which is in between the CuO$_2$ layers. Those estimated positions are different from those suggested from previous µSR studies on the basis of the dipole-field estimation.

1. Introduction

The mechanism of high-$T_C$ superconductivity is still beyond a dark shade and more investigations are ongoing by using a lot of techniques. One key direction of the investigation is to understand the magnetic properties of the system. The muon-spin relaxation (µSR) study has been applied to high-$T_C$ oxides and has achieved a lot of results and suggestions from the beginning of the history of high-$T_C$ oxides [1-4]. One advantage of the µSR technique is the magnetic phase diagram. For instance, a long-range antiferromagnetically ordered state of Cu spins in La$_2$CuO$_4$ has been detected by µSR [1]. The co-existing state between the superconductivity and the magnetically ordered state has been suggested [4] and an exotic spin alignment around the hole concentration of 1/8 per Cu. This so called 1/8 effect has been detected in La$_{2-x}$Ba$_x$CuO$_4$ [3]. Such a magnetically ordered state and the 1/8 effect have been confirmed in YBa$_2$CuO$_{6+\delta}$ by means of µSR studies [5-7]. Since µSR data can give us information of hyperfine fields, we can principally discuss magnetic properties of the system. For such discussions, we need to know the muon positions because relative positions of stopped muons to magnetic moments are necessary to clarify hyperfine couplings which are the key information to understanding the magnetic interactions.

We have been trying to clarify the muon sites in Cu-based high-$T_C$ oxides in order to understand the Cu spin states and hyperfine interactions in order to achieve new information on the magnetic properties. One useful way to know the muon positions are to estimate electrostatic interactions between the injected muon and surrounding atoms on the basis of...
computational techniques. We have carried out computational investigations on La$_2$CuO$_4$ (LCO) by using the density functional theory (DFT) method taken into account effects of the local crystal deformation and relaxation position of the injected muon itself which have not been included in past studies to estimate muon positions [8]. Another type of high-\(T_C\) oxides, YBa$_2$Cu$_3$O$_{6+\delta}$ (YBCO), is also a good target to apply our developed method to estimate muon positions. The hole concentration of YBCO can be changed by changing the oxygen content, \(\delta\), from 0 to 1 and the system changes from the antiferromagnetic state to the superconducting state [5-7]. The magnetic phase diagram of YBCO is similar to that of LCO. The electronic property is insulating and the antiferromagnetic ordered state appears in the underdoped regime. The antiferromagnetic transition temperature, \(T_N\), at \(\delta = 0\) is above the room temperature. Clearly, muon-spin precession components have been observed below \(T_N\) showing that there are some muon sites in YBCO [5]. The YBCO becomes metallic with increasing \(\delta\) and the antiferromagnetic ordered state disappears and the superconducting state appears.

Although DFT investigations on LCO have been carried out by some groups in the past, studies on YBCO to determine muon sites have not yet been done, especially in the underdoped regime near \(\delta = 0\). In this paper, we report the first and preliminary trial of the potential calculation by using the DFT method in order to estimate muon positions in YBCO with \(\delta = 0\). We found at least six minimum potential positions in the unit cell where the injected muon could be initially trapped. Five of them were around the apical oxygen as argued in previous studies [5,9,10] but the sixth is near the yttrium atom which is in between the CuO$_2$ layers and not yet discuss in the past.

2. Results and Discussions
Figure 1 shows the crystal structure of YBCO with \(\delta = 0\). The unit cell has the tetragonal structure with the space group P4/mmm. There are two Cu sites in the unit cell. One of the Cu is in the CuO$_2$ plane and the other is outside the CuO$_2$ plane. The Cu atom in the CuO$_2$ plane forms the polyhedral structure with five oxygen atoms and is named as Cu(II). The Cu(II) has a half spin with the charged state of Cu$^{2+}$. The other Cu atom forming the O-Cu-O linear bond is named as Cu(I). The Cu(I) does not have any magnetic moment and has a charged state of Cu$^{1+}$. Cell parameters of this system are \(a = b = 3.8715\ \text{Å}\) and \(c = 11.738\ \text{Å}\) [11].

Figure 1. Crystal structure of YBa$_2$Cu$_3$O$_6$.
The Cu(II) atom which is surrounded by five oxygen atoms and has a spin half with the charged state of Cu$^{2+}$. The Cu(II) influences the magnetism of this system and forms the antiferromagnetic structure in the magnetically ordered state, while the Cu(I) is in the non-magnetic state with zero spin and charged state of Cu$^{1+}$.

We have carried out the potential calculations by using the VASP program [12,13]. The total phonon energy of the model system was minimized changing the density of electrons with
the threshold energy of $1 \times 10^{-4}$eV. We adopted the plain wave function and the Perdew-Burke-Ernzerhof (PE) function for the electronic correlations. We meshed the unit cell to be $100 \times 100 \times 140$ along each crystal axes and calculated the electrostatic potential without muon in order to estimate the most probable initial positions for the injected muons. We adopted a supercell which contained $2 \times 2 \times 2$ unit cells. All calculations were performed on the RIKEN Integrated Cluster of Clusters (RICC) supercomputer.

Figure 2 indicates the results of the potential calculations. We searched for the local minimum potential throughout the unit cell and found a few possible positions. Fig. 2(a) shows the total view of the unit cell with isosurfaces which show areas of minimum potential positions. Differences in colours exhibit differences in minimum potentials. Fig. 2(b) and 2(c) are expanded views of sections surrounded by black and pink lines in Fig. 2(a). Minimum potentials are marked by M1 to M6, following the order of the depth of the potential energy. Accordingly, the M1 position has the lowest energy and the potential energy increases to M6. Differences of potential energy of those positions were not so large and in the order of 10 Kelvin. It was not possible to find more minimum positions in regions which have the higher potential energy than that of the M6 position.

Figure 2. Results of the potential calculation by using the DFT method. Minimum potential positions are drawn by isosurfaces with different colours. The M1 position has the lowest potential energy and the M6 one has slightly higher energy compared to that of M1, although the difference of the energy is at most the order of 10 Kelvin.

Positions of M1, M2 and M3 are located around the apical oxygen of the CuO$_5$ polyhedral. The position of M4 is closer to the CuO$_2$ plane with the distance of about 1.10 Å. The fifth minimum potential position M5, is located between the Cu(I) atoms with the distance from Cu(I) of about 1.89 Å. The sixth minimum potential M6, is near to the yttrium atom with the distance from the yttrium atom of about 1.95 Å. The angle of Y-M6-O was 94.26°. Detailed coordinates of all the estimated minimum potential positions and calculated potential energies at those positions were listed in Table 1.

Nishida et al. has suggested at least two muon positions in YBCO [5]. Plural muon positions in YBCO have also suggested by the other groups [9,10]. One is near the apical oxygen with a smaller internal field from Cu spins of about 300 G and the other is near the planar oxygen with a larger internal field of about 1300 G. Since the positions of M1, M2 and M3 are close
to the apical oxygen of the CuO$_5$ polyhedral with the distance to the apical oxygen of about 1 Å, one of those positions can possibly be regarded as the one suggested by Nishida et al. [5]. However, the other minimum potential positions from our investigate ions do not match with those near the planar oxygen as suggested by Nishida et al. In addition to this, the minimum potential positions of M6 and M5 are new and difficult to think about from the view point of the well-known argument on the muon-binding state with anions. The injected muon prefers to associate with anions and forms like the hydrogen binding state, thus, gaining the binding energy with anions. We tried to find more minimum potential positions in and near the CuO$_2$ plane by changing the calculation resolution. However, we have not yet succeeded to locate any muon positions near the planar oxygen which would correspond to those suggested by Nishida et al.. Such a conflict in muon sites between those suggested from the dipole-field calculations and those estimated from the potential calculation was also reported in the case of LCO [14]. This fact means that a simple estimation of the electrostatic potential is not sufficient to estimate muon stopping sites as have been done in previous studies [15]. We can propose to re-investigate the dipolar field interaction between the Cu and muon spins. This is because the Cu spin in high-$T_C$ oxides is strongly hybridized with neighboring oxygen atoms and could be spatially distributed throughout the CuO$_6$ octahedral. This effect could lead to Fermi-contact type interactions adding more hyperfine fields at the muon sites.

We are still carrying on more detailed potential calculations, including taking into account the local lattice deformations which are caused by the injected muon and the movement of the muon itself after being trapped at the minimum potential positions. The DFT method can include such conditions and shows the final position of the muon which is different from the initial stopping position. We hope to publish those results in a separate paper soon.

Table 1. Position of minimum potentials in YBa$_2$Cu$_3$O$_{6+\delta}$.

| Minimum potential | Estimated muon coordinate | Energy ($eV$) |
|-------------------|----------------------------|--------------|
| M1                | 1.051 0.000 1.510          | $-4.310 \times 10^{-2}$ |
| M2                | 0.000 0.798 2.600          | $-4.292 \times 10^{-2}$ |
| M3                | 1.051 0.000 2.100          | $-4.185 \times 10^{-2}$ |
| M4                | 0.000 1.848 3.350          | $-4.127 \times 10^{-2}$ |
| M5                | 0.000 1.868 0.168          | $-4.032 \times 10^{-2}$ |
| M6                | 0.000 1.770 5.701          | $-3.991 \times 10^{-2}$ |

3. Conclusion

We have applied the DFT calculation to the Cu-based high-$T_C$ oxide YBa$_2$Cu$_3$O$_{6+\delta}$ in order to clarify possible muon sites. We found at six minimum potential sites and since the difference in potential energy among those sites are small (in the order of 10 Kelvin), all sites can be candidates to trap injected muons. Comparing with the experimentally suggested positions [5], it can be concluded that three positions with the lowest energies, which are located close to the apical oxygen of the CuO$_5$ polyhedral can be regarded as the positions that have been suggested experimentally. However, we still cannot explain the other estimated muon positions in order to match with the experimental data. More detailed calculations including the effects of the local crystal deformations caused by the injected muon and the relaxation position of the muon itself to the final state are now ongoing.
4. Acknowledgement
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5. References

[1] Uemura Y J 1987 Phys. Rev. Lett. 59 1045
[2] Uemura Y J, Luke G M, Sternlieb B J, Brewer J H, Carolan J F, Hardy W N, Kadono R, Kempton J R, Kieff R F, Kreitzman S R, Mulhern P, Riseman T M, Williams D L, Yang B X, Uchida S, Takagi H, Gopalakrishnan J, Sleight A W, Subramanian M A, Chien C L, Cieplak M Z, Xiao G, Lee V Y, Statt B W, Stronach C E, Kossler W J and Yu X H 1989 Phys. Rev. Lett. 62 2317
[3] Watanabe I, Kawano K, Kumagai K, Nishiyama H and Nagamine K 1992 J. Phys. Soc. Jpn. 61 3058
[4] Niedermayer Ch, Bernhard C, Blasius T, Golnik A, Moodenbaugh A and Budnick J I 1988 Phys. Rev. Lett. 80 3843
[5] Nishida N, Miyatake H, Shimada D, Okuma S, Ishikawa M, Takabatake T, Nakazawa Y, Kuno Y, Keitel R, Brewer J H, Riseman T M, Williams D L, Watanabe Y, Yamazaki T, Nishiyama K, Nagamine K, Ansaldo E J and Torikai e 1987 Jpn. J. Appl. Phys. 26 L1856
[6] Sanna S, Allodi G, Concas G, Hillier A D and Renzi R De 2004 Phys. Rev. Lett. 93 207001
[7] Akoshima M, Koike Y, Watanabe I and Nagamine K 2000 Phys. Rev. B 62 6761
[8] Adiperdana B, Dharmawan I A, Siregar R E, Watanabe I, Ohishi K, Ishii Y, Suzuki T, Kawamata T, Risdiana, Sheuermann R, Sedlak K, Tomioka Y, Waki T, Tabata Y and Nakamura H 2012 Physics Procedia 30 109-112.
[9] Weber M, Birrer P, Gygax F N, Hitti B, Lippelt E, Maletta H, and Shenck A 1990 Hperfine Interact. 63 207
[10] Pinkpank M, Amato A, Adhreica D, Gygax F N, Ott H R, and Shanck A 1999 Physica C 317-318 299
[11] Bordet P, Chaillout C, Capponi J J, Chenavas J and Marezio M 1987 Nature. 327 687
[12] Kresse G and Furthmiller J 1996 Phys. Rev. B 54 11169
[13] Kresse G and Furthmiller J 1996 Comput. Mat. Sci. 6 15
[14] Sulaiman S, Sahoo N, Srinivas S, Hagelberg F, Das T P, Torikai E and Nagamine K 1994 Hyperfine Interact. 84 87
[15] Stilp E, Suter A, Prokscha T, Morenzoni E, Keller H, Wojek B M, Luetkens H, Gozar A, Logvenov G and Bozovic I 2013 Phys. Rev. B 88 064419