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An Effect of the Supercell Calculation on Muon Positions and Local Deformations of Crystal Structure in La_2CuO_4

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Abstract. Muon positions in La_2CuO_4 were examined by using the density functional theory. Potential minimum positions near apical and plane oxygen have been determined as possible initial muon stopping positions. We found that final muon stopping positions were different from those initial positions due to effects of the local deformation of crystal structure which was induced by injected muons. This means that injected muons relax their positions deforming local crystal structures and minimizing the total energy of the system. We also found that the estimation of those final muon positions had to be done in the large scale area as a supercell which contained 27 unit cells in order to achieve realistic situations of the system with the muon as a dilute impurity.

1. Introduction

Information of muon sites in materials is of importance to know about local hyperfine interactions in order to discuss detailed electromagnetic properties. The mother material of the Cu-based La high-T_c oxides, La_2CuO_4 (LCO), is one of good target material which has been investigated so well by muons. In general, it has been argued that muons prefer positions near to anion due to the attractive force between the positive charge of muon and the negative one of anion. In the case of LCO, muons are expected to stop near apical and/or plane oxygen of the CuO_6 octahedra. In order to estimate muon positions, one way is to estimate minimum electrostatic potential by the first principal calculation and then to regard those potential minimum points as muon positions [1]. In past studies on LCO [2, 3, 4, 5, 6, 7, 8, 9], efforts have been paid to estimate muon positions by the minimization of the electrostatic potential and also from nuclear

dipole field measurements. In addition to those information, the internal field coming from Cu spins at the muon site which is observed in an antiferromagnetically ordered state of LCO is a good indication to estimate the muon site. This has been measured in the beginning of the history of the μSR study on LCO to be about 415 G [10]. However, any numerical estimation has not yet succeeded to reproduce the experimental data and estimated muon positions were widely scattered as shown in Figure 1.

Recently, Suter *et al.* has shown an effect of the local deformation of the crystal structure by an injected muon which is a new concept to estimate the final position of the muon. They have indicated a possible relaxation of the muon position to the different final one pushing surrounding local atoms [11]. Following this result, we re-examined muon positions in LCO taking into account more parameters which have not been included in past studies for LCO, like the relaxation of the final muon position and the local deformation of the crystal structure induced by muons. Especially, we examined an effect of the size of the calculation area. This means that we compared results which were obtained from the single unit-cell calculation and supercell calculations which have never been tried in the past due to the limitation of performance and capacity of computing resources.

In this paper, we report the first result of our detailed estimation of final muon positions after taking into account the relaxation of the muon itself and the local deformation of the crystal structure. Especially, we emphasize in this paper the importance of the supercell calculation in order to estimate the final muon position in LCO.

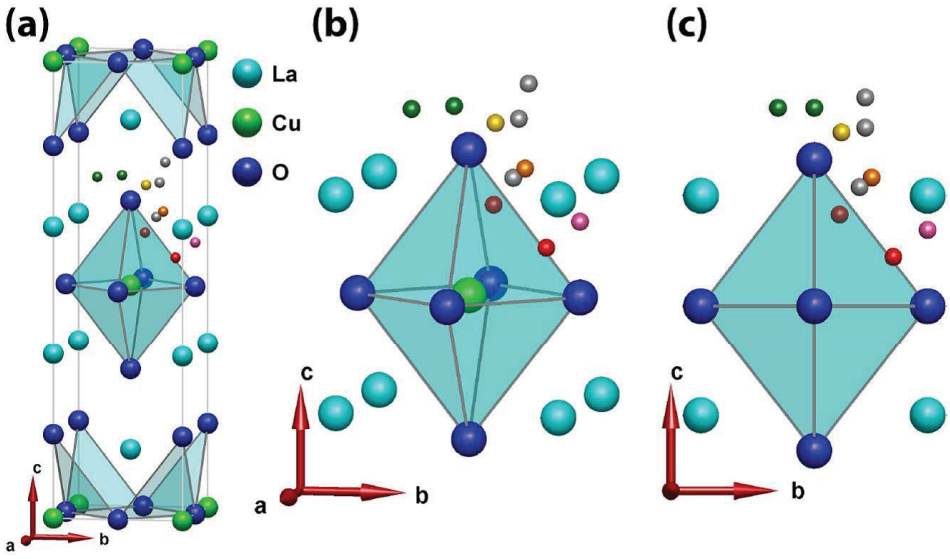

Figure 1. Muon positions in La_2CuO_4 which were suggested in past studies. (a) View with suggested muon positions in the past. (b) and (c) 3D and 2D views of CuO_6 octahedra with muon positions suggested in the past, respectively. Green marks are suggested from Saito *et al.* [2], a pink one is from McMillen *et al.* [3], an orange one is from Hitti *et al.* [4], grey ones are from Torikai *et al.* [5], and red ones are from S. Sulaiman *et al.* [6].

2. Calculations

We carried out the potential calculation by using the VASP program [12, 13]. We used the density functional theory (DFT) using generalized gradient approximation (GGA) corrections with Perdew and Wang (PW91) parametrization [14]. The methodology for determining muon sites by DFT calculations in insulators has been described and tested in some ionic fluorides [15, 16]. The projector augmented wave (PAW) method was used for the pseudopotential [17] with cutoff energy 500 eV. The resolution for electrostatic potential grid was 60×60×140 in a-, b-, and c-axes. The crystal structure was optimized until the total energy and the total force were less than 1×10^{-4} eV and 1×10^{-3} eV/Å, respectively. At first, the electrostatic potential without the muon was calculated in order to estimate initial positions for injected muons. This first-step estimation showed that there would be more than two minimum potential positions [18]. After putting H^+ at those minimum potential positions as a model of the initially trapped muon, we estimated final muon positions taking into account effects of relaxation of the muon itself and the local deformation of the crystal structure. We repeated this operation on the single-unit cell and the supercell to see an effect of the calculation area to the final muon positions. The size of the supercell was 3×3×3 which contained 27 unit cells. We used a computer cluster system in RIKEN named RIKEN Integrated Cluster of Clusters (RICC) to achieve the stronger computing performance.

3. Results and Discussions

Figures 2-(a) and (b) show the results of potential calculations around the CuO_6 octahedra of LCO. These calculations were done on the single-unit cell taking into account the orthorhombic crystal structure. Similar minimum potential areas were drawn by isosurfaces. As has been already suggested in past studies, we can see one possible muon position near the apical oxygen. Since the CuO_6 octahedra is slightly bent from the CuO_2 plane due to the backling of CuO_6 octahedra which leads the orthorhombic crystal structure, minimum potential area near the apical oxygen was not symmetric in all direction and tend to stay in one side around the apical oxygen. We found that the typical distance of this area from the apical oxygen was more than 1 Å which was bigger than those predicted in past studies. This suggests a possibility that the muon near the apical oxygen would not form the typical hydrogen bonding with the apical oxygen. At this moment, we have no detail estimation of the electronic state around the muon, so that more calculations are needed to discuss the bounding state of the muon with the apical oxygen.

Other positions were new compared to past studies. One was nearly attached to the surface of the CuO_6 octahedra. The distance from the apical oxygen was also more than 1 Å. The other one is on the line between two plane oxygen and almost on the CuO_2 plane. This position had the closest distance to the Cu spin. This means that the larger internal field would be expected at this position in the magnetically ordered state compared to other positions.

Those estimated positions have similar minimum potential. Differences in the potential energy were not so big and in the order of a couple of ten kelvin. Thus, all of positions can be candidates to trap injected muons. In terms of the number of muon positions in LCO, it has been believed for a long time to be one because the first μSR data on LCO has been well analyzed by a single component function [10]. Our current result of the potential calculation seems to be against to this experimental result. But, if the fraction of the muon-stopping ratio on each position is different and one position has large fraction compared to other components, the time spectrum can be analyzed by a single component in case of that the statics of the data is not good enough to realize other components with small amplitude. The zero-point vibration of the muon itself can help and enhance this effect. Since the zero-point vibration energy of the muon is recently estimated to be in the order of a half eV [15], the muon can move around potential minimum positions if the potential barrier between those positions is not so high rather than

the zero-point vibration energy. At this moment, more numerical investigations are going on to estimate the difference of the fraction of stopping muons and the zero-point vibration energy.

In order to achieve final muon positions, we put H^+ as a model of μ^+ and repeated calculations taking into account effects of the muon-position relaxation and the local deformation of the crystal structure. Since the muon position near the apical oxygen has been argued to be the most possible one in past studies, we concentrated on this position to estimate as the first trial. Figure 3 shows the estimated final state of this position. Figure 3-(a) indicates the result of the single unit-cell calculation and Figure 3-(b) shows the one of the supercell calculation. Light-red marks are initial positions of the muon which are corresponding to the minimum potential position as indicated in Figure 2. Deep-red marks are final positions after the calculation including all effects. Red lines and blue lines show the initial and final positions of the CuO_2 plane before and after the calculation, respectively. Arrows in Figure 3 exhibit directions of the local deformation of the CuO_6 octahedra induced by the muon. The magnitude of each arrow is corresponding how much distance each atom is shifted from its initial place.

In the case of the single unit-cell calculation, as shown in Figure 3-(a), the injected muon can induce the local modification of the crystal structure. The apical oxygen which was the nearest to the muon was pushed up along the c-axis. The CuO_2 plane was forced to be rotated to the same direction with the buckling direction of the CuO_6 octahedra. Following this movement, the apical oxygen at the opposite site to the muon rotates along the buckling direction also. It can be said that the injected muon tends to make the buckling angle bigger on the basis of this single unit-cell calculation. A change in the potential state was expected to be induced due to this deformation of the local crystal structure causing the muon position to be relaxed and become stable after the muon found out the final position in order to make the total energy of the system minimized. Accordingly, the muon moved from the initial position to the up-right direction approaching to the apical oxygen.

We have to note that the single unit-cell calculation condition is corresponding to the case of that each unit cell has the muon at the crystallographcally same position. Accordingly, due to this single unit-cell periodicity, the local deformation of the next neighbor unit cell should be treated to be rotated in the opposite direction by the muon leading that the degree of the orthorhombicity of the crystal structure stronger. This operation could change the crystal structural axis by the injected muons. In addition to this, the single unit-cell calculation assumes that each unit cell has one muon, indicating that the injected muon is no longer as a dilute impurity and exists in all unit cells However, these conditions are not realistic. The density

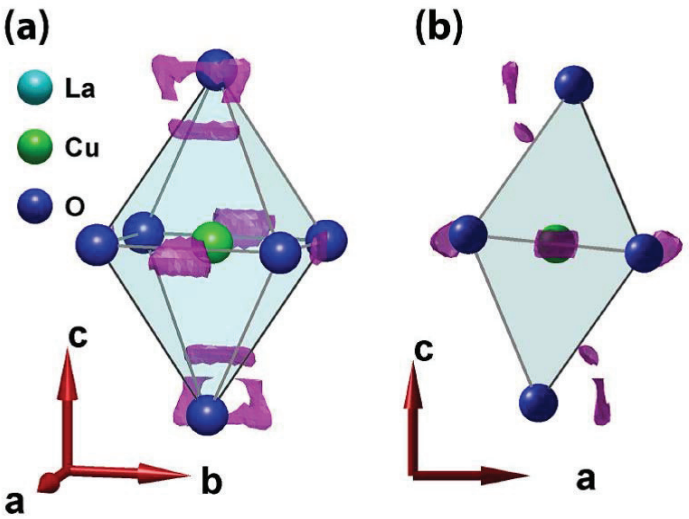

Figure 2. Estimated minimum potential positions around the CuO_6 octahedra of LCO. (a) A view in the 3 D state and (b) a view along the b axis. The similar minimum potential positions are drawn as isosurfaces with energy scales of about 0.25 eV.

of the muon is very small in materials as very dilute impurities and the crystal structure must not be changed by the injection of muons. Past computational studies adopted this single-unit cell condition and resulted in the scattering of estimated muon positions. Therefore, the single unit-cell calculation could lead to an inappropriate result in terms of the final state of the muon and the local crystal deformation.

Following this result on the single unit-cell calculation, we re-tried the muon-position estimation on the basis of the super-cell calculation. We calculated 27 unit cells which were the limit of the acceptance of RICC at this moment. We put one H^+ as the model of the muon in the central unit cell of the 3×3×3 supercell block. We tested the same position with that adopted in the unit-cell calculation which was the nearest to the apical oxygen. No H^+ was allocated in neighboring unit cells, although the density of the muon in the supercell was still higher rather than any realistic cases. As shown in Figure 3-(b), the movement of the muon and the local deformation estimated from the supercell calculation were fairly different from those estimated in the single unit cell. The apical oxygen which was nearest to the muon moved to the up-right direction. The rotation angle of the CuO_2 plane became bigger rather than the case of the single unit-cell calculation, showing that the injected muon would push the rotation of the CuO_6 octahedra more. On the other hand, it was found that almost no local deformation was induced in other neighboring unit cells. Especially, all atoms near the edge of the supercell have almost no local deformation. Those facts mean that the deformation of the crystal structure induced by the injected muon is very limited in one unit cell which contains the muon as an impurity nearby and that this local deformation effect disappears quickly in neighboring unit cells. After the injected muon stopped at the initial position, the muon moved from the initial position to the right and slightly went down approaching to the surface of the CuO_6 octahedra. Since the apical oxygen was escaping to the up direction from the initial position, the distance between the apical oxygen and the muon did not change so much. This is naturally understood like that the muon would like to keep the distance to the oxygen not to change the relative potential energy higher.

We are now trying to explain the experimental result of the hyperfine field from Cu spins at the muon site in the magnetically ordered state [10] on the basis of the dipole-field calculation in order to confirm our calculation results. However, we have not yet achieved good agreement. In parallel, we are examining other muon positions which are shown in Figure 2 by using the same method to try to explain experimental results. Since LCO is a good insulator, we believe that the dipole-dipole interaction can explain the experimental data on the basis of our estimated

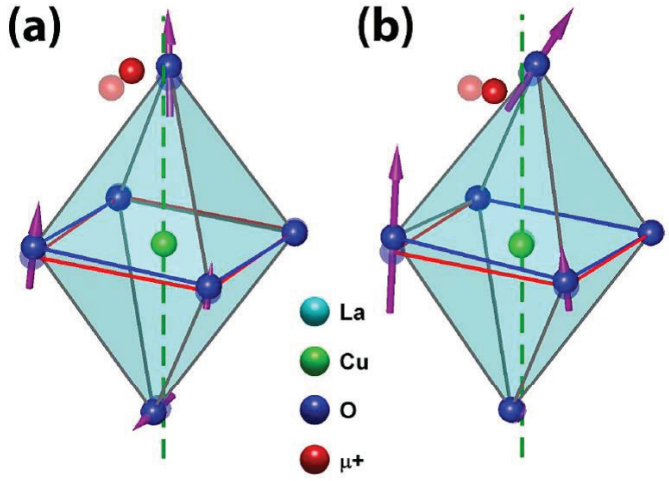

Figure 3. Initial and final states of estimated muon positions and local deformation of the CuO_6 octahedra. The muon position near the apical oxygen was investigated. Light-red and deep-red marks are the initial and final positions of the muon, respectively. Red and blue lines are positions of CuO_2 plane before and after the calculation, respectively. (a) In the case of the unit-cell calculation and (b) in the case of the supercell calculation.

muon positions. If our current trial finally fails, we have to move to think about a different hyperfine interaction which is the Fermi-contact type interaction. In order to think about such a type of the hyperfine interaction, we need to argue the electronic state of the muon which means the charged state of the muon itself and interactions with surrounding electronic orbitals. In parallel, we will try to include the magnetic interaction between ordered spins by using the spin-polarized DFT estimations in order to tune final muon positions which will take more calculation time and not the main matter to discuss in this paper at this moment.

4. Conclusion

We have examined possible muon sites in La_2CuO_4 (LCO) by using density functional theory calculations. Minimum electrostatic potential positions in the unit cell of LCO were estimated to be as initial positions of injected muons. We found some possible positions which have the similar potential energy. One of them was very similar with that discussed in past computational studies and close to the apical oxygen of the CuO_6 octahedra. Taking into account effects of the relaxation of the muon position and the local deformation of the crystal structure induced by the injected muon, final state of the muon was calculated in two models. One was the single unit-cell model and the other is the $3\times3\times3$ supercell one. We found that the single unit-cell calculation would lead to inappropriate results which were different from a realistic situation. It was better to estimate muon positions by adopting the supercell with a single muon as an impurity. We confirmed that the injected muon can deform the local crystal structure. This effect was very limited around the muon and disappeared quickly in neighboring unit cells. One of estimated final muon positions was near the apical oxygen as has been argued in the past. However, this position still cannot explain the experimental result. More estimations on other muon positions are going on.

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