Ab-initio calculation and μSR study of the covalency effect in $YBa_2Cu_3O_6$

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Since the first discovery of high-T_c in cuprates over three decades ago, extensive studies of their magnetic properties have been carried out in order to explain the mechanism of superconductivity. $YBa_2Cu_3O_6$ ($YBCO_6$), which is the mother compound of the high-T_c cuprate $YBa_2Cu_3O_{6+x}$, shows long-range antiferromagnetic (AF) ordering with the Néel temperature T_N = 420 K. The AF ordering in this system arises from the strong on-site coulumb repulsion between electrons, and it is destroyed by changing the oxygen content, which results in superconductivity. A detailed understanding of the electronic structures and magnetic states regarding the mother compound and its chemical derivatives is the key to understand the nature of superconductivity.[1)]

We studied the covalency effect on the magnetic properties of $YBCO_6$ by *ab-initio* calculations through the density functional theory (DFT) and the muon-spin resonance (μSR) technique. The μSR experiment involves the implantation of muons into the system, and this provides information on the internal field at the muon site, which is very important when discussing the electronic and spin states of the system.

We have carried out μSR experiments on single crystals of $YBCO_6$ and detected three distinct muon-spin precession components. This result suggests that three different muon sites exist in $YBCO_6$ with internal fields of 117.7 G, 295.5 G, and 220.4 G. In order to get a deeper understanding of this result, we tried to estimate the muon-sites by *ab-initio* calculations and calculate the internal fields at these muon sites. Since DFT fails to consider the strong correlation effect in a system such as $YBCO_6$, an additional Hubbard parameter, U, was incorporated into our *ab-initio* calculations (DFT+U).[2)] The DFT+U calculations found three local minima in the potential, which can be regarded as initial muon sites in the system since muon has a positive charge. These positions, marked as M1, M2, and M3, are shown in Fig. 1.

The muon perturbation to the host system was calculated by placing one muon at each initial muon site in a large $4 \times 4 \times 2$ supercell and allowing all ions in the supercell to relax. The large supercell is required to accomodate the behaviour of the muon as an ultra dilute impurity in the host system. In the last step, we calculated the internal field at each relaxed muon position on the basis of dipolar interaction between the muon and the magnetic ions. The calculated internal fields at the muon sites on the basis of ionic picture of magnetism, where spins reside in particular ions, are larger than those deduced from the experiments, although the zero point vibration energy of muons was carefully considered.

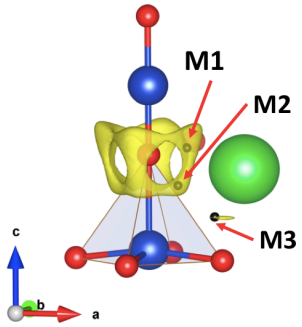

Fig. 1. The muon site positions from DFT+U calculations.

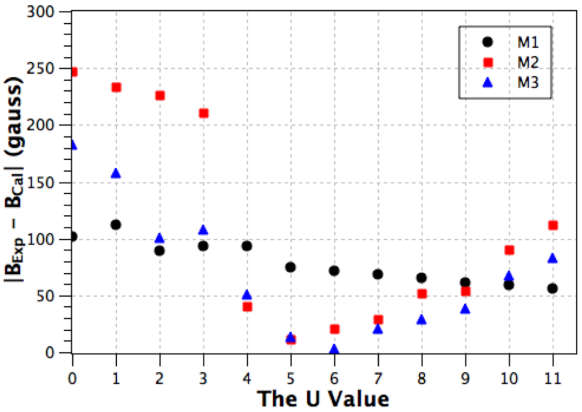

Fig. 2. The differences between the calculated and experimental values of the internal fields as functions of the U value.

The covalency effect, which arises from the strong hybridization between the Cu 3*d* and the O 2*p* orbitals, is thought to play a crucial role in this discrepancy. This effect causes the extention of spin density in the real space, although it is contradictory to the ionic picture of magnetism. The DFT+U calculations have the capability to provide the spin density and have successfully explained the ambigous missing intensity in copper oxide compounds.[3)] Finally, we examined the internal fields at the muon sites on the basis of the spin density criterion. The internal field at each site has a strong dependence on the U value. Careful tuning of the U value was required. The differences between the calculated and experimental values of the internal fields are shown as functions of the U value in Fig. 2.

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