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# Spin Polarization of CuO Nanowires

**Jisang Hong**

*Department of Physics, Pukyong National University, Busan 608-737, Korea*

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**Very recently, it was presented that the one dimensional (1D) CuO atomic chains can maintain large magnetic moments. In this work, we analyzed m-resolved density of states (DOS) to understand the peculiar spin polarization occurred in Cu atoms. It was found that the |m|=1 states play an essential role in the spin polarization of Cu atoms. In addition, we calculated magnetic anisotropy energy (MAE) and observed that the distribution of MAE is strongly sensitive to the interatomic distance between Cu and O atoms. Besides, it was revealed that the contribution to MAE comes for the second half of Brillouin zone (BZ).**

**Key words :** one dimensional CuO nanowire, ferromagnetism, magnetic anisotropy

## 1. Introduction

Magnetic properties of ultra small objects in low dimensional system have become the main research topics in the studies of magnetic materials. Indeed, the physics of nanostructured materials has become very rapidly growing and fascinating issue because of fundamental interests and device applications purposes. Especially, 1D structures are particularly of interest since they are the simplest systems in structural view point. Nonetheless, there were no available examples for pure 1D systems until very recently [1, 2].

The transport property of a 1D nanowire system manifests many interesting features. First of all, the electrons flow only in one direction due to the dimensionality of the nanowire, and this feature greatly simplifies the transport phenomena, but at the same time the quantum effect can dramatically affect the transport property. Therefore, a great amount of research effort has been focused on the quantum transport study of low dimensional nanostructured materials. It is well known that the electronic structure of ultra small object in low dimension substantially changes compared to that found in macroscopic size and this modification in underlying electronic structure provides many peculiar magnetic properties, not found in bulk materials. For instance, interesting transport property of Cu nanowires was presented by Gillingham [3, 4]. In these 1D Cu nanowires, they measured quantum conductance with and without applied magnetic field. Surprisingly, when a magnetic filed about 0.5 mT was applied to the perpendicular direction to the axis of Cu nanowires, roughly 70% of magneto-conductance effect was observed. It is obvious that the Cu has no magnetic moment in bulk phase. However, as remarked above in the reduced dimension there is a high probability to maintain magnetic phase in nanostructure.

The conductance measurement with Cu nanowires was made at room temperature in the air, hence the Cu nanowires were likely to adsorbe oxygen atom as the authors of Refs. 4 and 5 commented. Consequently, these authors concluded that the spin polarized effect of Cu nanowire is originated from oxygen adsorption. In fact, oxygen atom is well known to have a strong influence on the magnetic or electronic properties of materials. As an example, according to our recent investigation for the oxygen effect on the magnetic anisotropy of Ni/Cu(001), it was found that the oxygen can affect the direction of spin alignment causing from in-plane to out-of plane magnetization at certain critical thickness of Ni thin films on Cu(001) surface [5].

To reveal the peculiar spin polarization found in 1D Cu systems, we theoretically investigated the physical properties and found that the 1D Cu atomic chains have no magnetic phase regardless of Cu-Cu interatomic distance. Surprisingly, it was presented that the Cu and O atoms can maintain magnetic moments when the CuO nanowire is stretched from equilibrium state [6]. In this work, we

*Corresponding author: Tel: +82-51-620-6369,
Fax: +82-51-611-6357, e-mail: hongj@pknu.ac.kr

will thus explore the origin of spin polarization of Cu atoms. In addition, the distribution of MAE in the Brillouin zone for various 1D CuO atomic chains will be investigated as well.

## 2. Calculational Method

The full potential linearized augmented plane wave (FLAPW) method was employed [7]. Thus, no shape approximation in the charge, potential, and wavefunction expansions is assumed. The core electrons are treated fully relativistically, and the generalized gradient approximation (GGA) [8] was adopted to describe the exchange correlation function. Spherical harmonics with $\lambda_{max}$=8 were used to expand charge, potential, and wave functions in the muffin tin region. Energy cutoffs of 225 Ry and 25 Ry were used for the plane wave star functions and basis expansion in the interstitial region. We employed supercell geometry, hence 2D square lattice was assumed with 13 a.u. in the lateral direction. The CuO wires are placed along the z-axis.

In our previous work [6], the main issue was to theoretically investigate if one can find magnetic phase in Cu nanowires since unexpected spin polarized effect in Cu was found [3, 4]. Due to the unknown structural information for Cu nanowires employed in experimental measurement, the calculations were performed in two different ways. First, we examined that possibility of ferromagnetism in pure one dimensional Cu atomic chain. The ferromagnetism in 1D pure Cu nanowire varying the Cu-Cu interatomic distance from 4.4 a.u. to 6.0 a.u. was investigated and found that the unsupported 1D pure Cu nanowires have no magnetic moment within a wide range of Cu-Cu distances. Overall, the conclusion was drawn that the Cu atom cannot become magnetic just by reducing number of neighboring atoms. As commented in experimental works [3, 4], the conductance measurement was performed in air and active element such as oxygen was expected to be present in the nanowire. Hence, we considered 1D CuO atomic chains and conducted numerical calculations.

## 3. Results and Discussions

Since the Cu nanowire used in experimental measurement was prepared by using a mechanical method, i.e. stretching bulk Cu to very thin wire, we elongated the CuO diatomic chain along the z-axis from equilibrium state to simulate the stretch in the experimental procedures. The total energy calculations (not shown here) showed that the 1D CuO atomic chain reaches equilibrium state at $d_{Cu-O}$=3.25 a.u. and the maximum elastic deformation occurred about $d_{Cu-O}$=3.80 a.u. Now, we present magnetic moments of Cu and O atoms as a function of inter-atomic distances in Figs. 1. Astonishingly, it was found that both Cu and O atoms have large magnetic moments when the CuO nanowire is stretched from its equilibrium state as shown in Fig. 1(a). These results may account for the following experimental findings [3, 4]. When the contact is stretched, a CuO chain is formed with an elongated Cu-O distance. In turn, the wire is magnetic as shown in Fig. 1(a) and one may detect spin dependent quantum transport. In contrast, the chain loses magnetization when the contact closes up, either because of the depletion of O or crushing of Cu-O chain. The magnetic moments for Cu and O are very sensitive to the inter-atomic distance. Nonetheless, very interestingly their sum appears to be very stable in the range of elastic deformation. This finding is of key importance in explaining why spin polarized effects are observed in practice because the nanowires that form in the experiment are

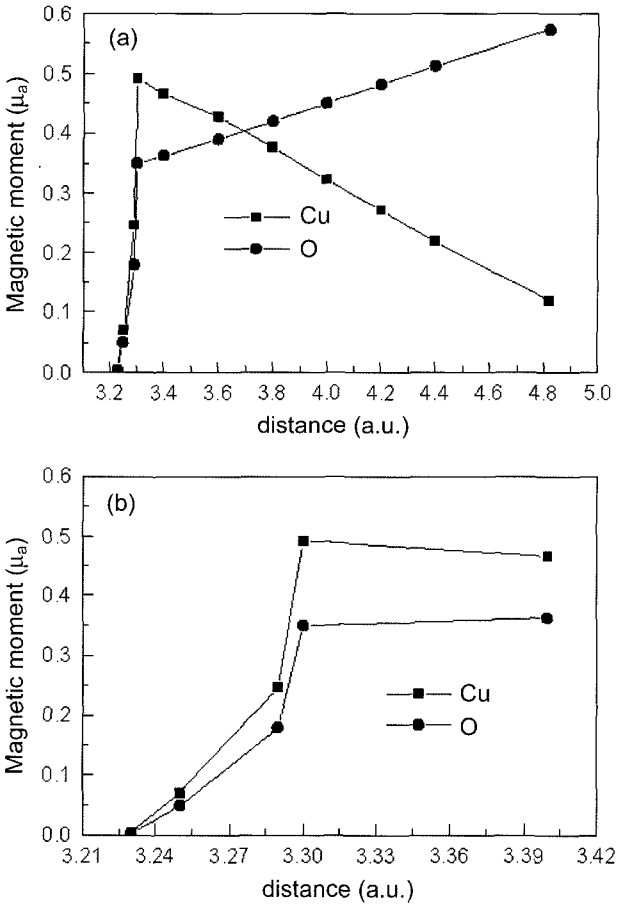


**Fig. 1.** (a) Calculated magnetic moments of Cu and O atoms. (b) Trend of magnetic moments of Cu and O in short ranges of Cu-O distance.

likely to undergo a range of strain values. The orbital magnetic moments for both Cu and O are very small (< 0.01 $\mu_B$). From Fig. 1(a), one can see that the magnetic moment jumps from zero to finite value when the inter-atomic distance changes slightly. We thus further investigated more details of magnetic moments of Cu and O atoms in small ranges and the results are presented in Fig. 1(b). It was found that the magnetic moments of both Co and O atoms occur not in the infinitesimal increase of strain, but above certain critical distance, for instance about 3.29 a.u. and the transition from non-magnetic to ferromagnetic state displays similar to first order transition. Here, we should remark that the possibility of anti-ferromagnetic ground state in the CuO nanowire is also investigated. Such a state, however, did not appear even as a meta-stable phase because the different initial magnetic configurations all converged to the ferromagnetic ground state.

It is quite apparent that the realization of spin polarization of Cu and O atoms stems from 3d and 2p orbitals, respectively. Since the Cu wire alone has no magnetic moment, we attribute the spin polarization of CuO nanowire to the effect of oxygen atom. Hence, it will be interesting to explore the inter-atomic distance dependent features of density of states (DOS). Three different systems are selected as shown in Figs. 2. The solid lines are the DOS of Cu atom, and the low lying dotted lines are for the O atom. With the inter-atomic distance of 3.25 a.u. where the CuO nanowire is in equilibrium state, the DOS both of majority and minority spin electrons are symmetric as expected from the magnetic moment calculations. One can also see that large number of holes are present up to 1 eV above the Fermi level indicating conventional non-magnetic metallic behavior. When $d_{Cu-O}$=3.29 a.u., the spin polarized state appears and there are still sizable states for both majority and minority spin electrons at the Fermi level. When the distance becomes 3.80 a.u. at which almost the maximum plastic deformation occurs, the behavior of the DOS is significantly different from the previous cases. The most striking feature is that the CuO nanowire has half metallic character since the majority spin electrons are filled, while the minority spin bands still contain appreciable number of holes. As a result, we observed large magnetic moments in CuO nanowire. If we increase further the inter-atomic distance from shown in Fig. 2(c), the half metallic feature is still conserved, but the major peak of DOS above the Fermi level for Cu in the minority spin band is shifted to the lower energy. This character results in large suppression of Cu magnetic moment compared to that for an inter-atomic distance of 3.80 a.u..

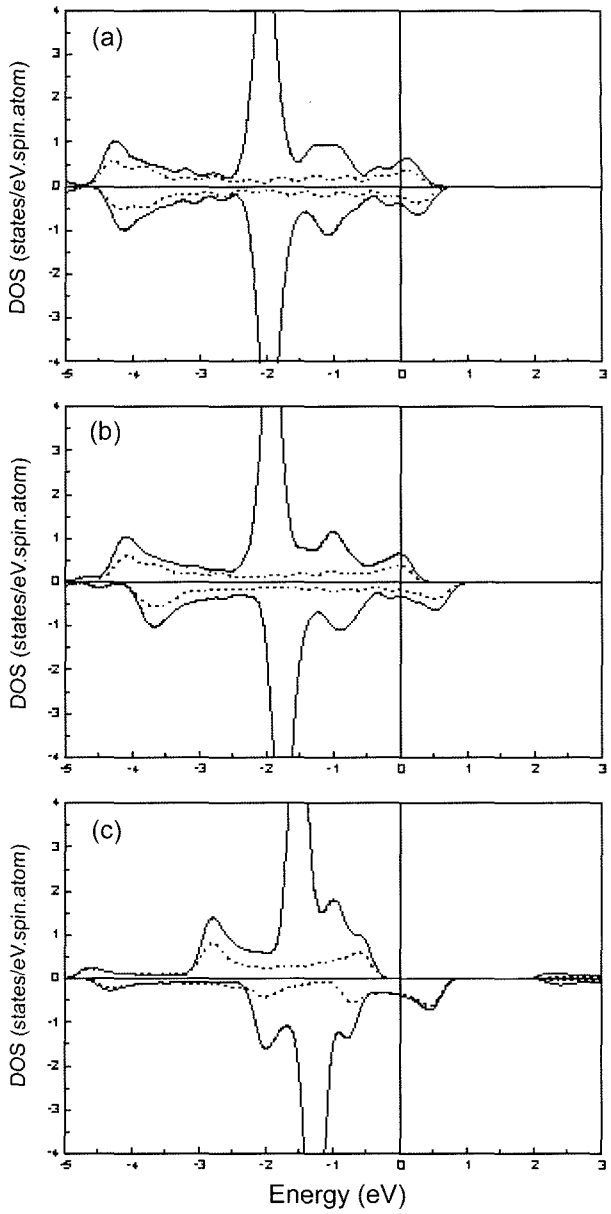


**Fig. 2.** DOS of CuO nanowires (a) $d_{Cu-O}$=3.25 a.u. (b) $d_{Cu-O}$=3.29 a.u., $d_{Cu-O}$ and (c) $d_{Cu-O}$=3.80 a.u..

Since an interesting spin polarization phenomenon was found in 1D CuO atomic chains, it will be of interest to explore the origin of spin polarization occurred in Cu and O atoms. It is obvious that the spin polarization in Cu and O atoms originated from the spin splitting in d and p orbitals, respectively. There are many studies that the O atom can achieve magnetic moment under various conditions, but the examples of spin polarization in Cu atom are very rare. Hence, we analyzed m-resolved DOS behaviors for Cu atom for more comprehensive understanding and the results are presented in Figs. 3. The m-resolved DOS behaviors for $d_{Cu-O}$=3.29 a.u., $d_{Cu-O}$=3.30 a.u.,

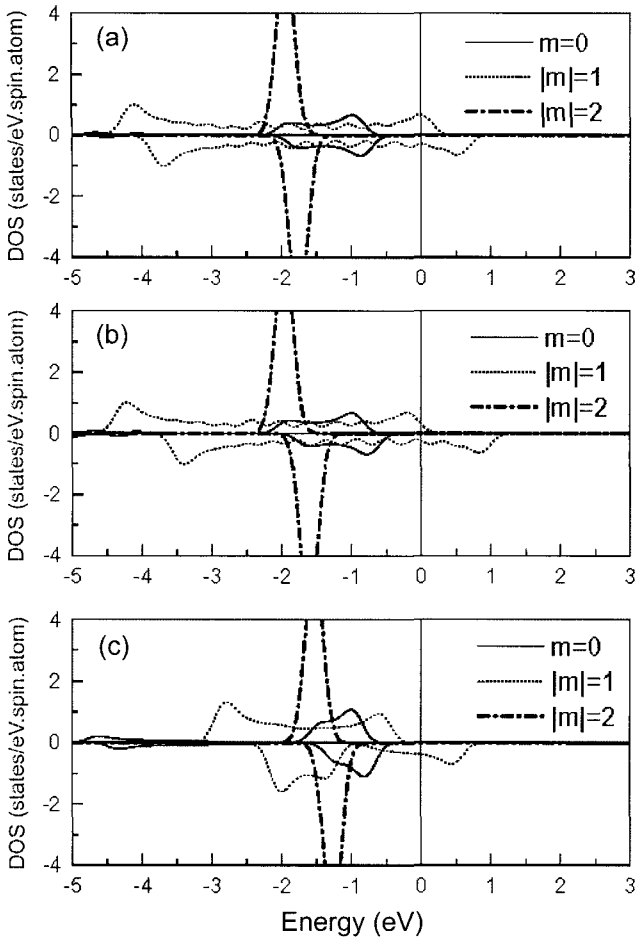


**Fig. 3.** m-resolved DOS of CuO nanowires (a) $d_{Cu-O}$=3.259 a.u. (b) $d_{Cu-O}$=3.30 a.u., and (c) $d_{Cu-O}$=3.80 a.u..

and $d_{Cu-O}$=3.80 a.u. are shown in Figs. 3(a), (b), and (c), respectively. One can clearly see that the m=0 and |m|=2 have rather narrow band widths and both majority and minority spin states are completed filled below the Fermi level indicating no sign of spin polarization in these orbitals. In the mean time, it was found that the |m|=1 states have quite broad band width and furthermore the spin asymmetry is realized. The common feature of spin polarization in |m|=1 states can be seen in all three different cases. In addition, the narrowing of band width is also observed with increasing interatomic distance. Overall, we can conclude that the interesting spin polarization in Cu atom stems from the peculiar physical property of |m|=1 orbitals.

In the various physical properties observed in magnetic materials, the magnetic anisotropy energy (MAE) which is related to the direction of magnetization is one of the most important quantities. Indeed, there are two physical origins for magnetic anisotropy such as magnetic dipolar interaction and magneto crystalline anisotropy (MCA)

**Table 1.** Magnetic anisotropy energies in meV/cell for various nanowires.

| distance (atomic units) | $E_{dip}$ | $E_{SOC}$ |
|---|---|---|
| 3.29 | 0.004 | −0.936 |
| 3.30 | 0.016 | −1.732 |
| 3.80 | 0.010 | −1.176 |
| 4.20 | 0.006 | −0.073 |
| 4.40 | 0.004 | −0.039 |
| 4.82 | 0.002 | 0.207 |

due to spin-orbit interaction. The magnetic anisotropy from dipole interaction, so called shape anisotropy, always prefers the magnetization along the chain axis for 1D (z-direction in our structure), while the MCA depends on the behaviors of spin-orbit coupling (SOC). It is straightforward to calculate the MAE from dipolar interaction, but the MAE resulting from SOC requires very accurate numerical method. In our calculations, we employ torque method [9]. Since the CuO nanochain is placed along the z-axis, we can write the expression of MAE arising from SOC as $E = E_0 + E_1 \sin^2\theta + E_2 \sin^4\theta$, where $\theta$ is a polar angle measured from the chain axis. Then, one can easily obtain the MAE defined by the relation $E_{SOC} = E_x - E_z = E_1 + E_2$. A positive (negative) MAE means that the direction of magnetization is parallel (perpendicular) to chain axis. In Table 1, we present the calculated MAE for

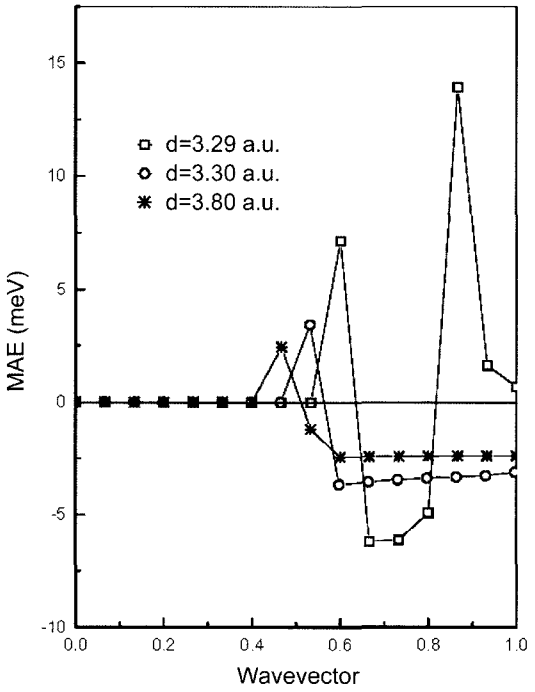


**Fig. 4.** Distribution of MAE along 1D BZ for three different cases (the wavevector has the unit of $\pi/a$ where a is the lattice constant.

various 1D CuO nanowires.

As one can see, the magnitude of MAE due to dipolar interaction is quite small compared to $E_{SOC}$ and we found that the MAE is strongly sensitive to the Cu-O interatomic distance. Nonetheless, the direction of magnetization in the wide ranges of $d_{Cu-O}$ was always perpendicular to the chain axis. Since we realized that the MAE has oscillatory behavior and strong sensitivity of magnetic anisotropy to the interatomic distance, the distribution of MAE in the one dimensional Brillouin zone (BZ) has been investigated. Fig. 4 displays the calculated distribution of MAE for three different systems. This figure tells us the character of spin-orbit coupling. In other words, the positive (negative) MAE means that the spin-orbit interaction causes parallel (perpendicular) to the chain axis at the particular k-mesh. First of all, it appeared that the first half of BZ does not contribute to the MAE in all cases. Instead, in the last half of BZ quite huge oscillatory trend with large magnitude of MAE was found when the $d_{Cu-O}$=3.29 a.u., but the overall strength of MAE is substantially suppressed due to the oscillation. For other case, we can find that each k-mesh has almost the same contribution to magnetic anisotropy.

## 4. Summary

In conclusion, we have explored the possibility of magnetic phase in 1D Cu nanowires. We presented that the CuO nanowires can display ferromagnetic phase when the CuO nanowire is elongated from equilibrium state. The m-resolved DOS results show that the spin polarization occurred in Cu atom is originated from the spin splitting only in |m|=1 states, while no sign of spin polarization found in other states. We observed that the contribution to MAE came from the second half of BZ and the MAE at each k-mesh was uniformly distributed, except for $d_{Cu-O}$=3.29 a.u. nanowire.

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