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Research Article

On the Possibility of Ferromagnetism in Nanosized $CuCl_2$

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Copper chloride consists of parallel chains of $CuCl_2$. The chains are sufficiently far apart such that the electronic and magnetic properties of $CuCl_2$ have been approximated as arising from isolated chains. Density functional theory using the LANL2DZ/6-31G* basis set has been used to calculate the total energy of $CuCl_2$ chains having nanometer length. The calculations, which are performed as a function of chain length, predict that chains having ferromagnetic order have a lower energy than chains with no order. Calculations of the band gap as a function of length for the ferromagnetic chains indicate that chains greater than 6 nm may be semiconducting suggesting that nanosized $CuCl_2$ chains have the potential to be magnetic semiconductors.

1. Introduction

There is much interest in the materials research community in magnetic nanoparticles because of present and potential applications, such as data storage and targeted delivery of drugs to diseased tissue. One of the most interesting results is the observation that bulk materials which are not ferromagnetic can become ferromagnetic on nanosizing. For example, rhodium is paramagnetic at all temperatures but has shown to be ferromagnetic when it has less than 30 atoms [1]. Materials such as CuO and NiO which are antiferromagnetic in the bulk become ferromagnetic when they are of nanometer dimensions [2, 3].

In this work theoretical methods are used to show that nanoparticles of copper chloride could be ferromagnetic. The unit cell of copper chloride is shown in Figure 1. The structure consists of parallel one dimensional chains of $CuCl_2$. The distance between the chains is appreciably larger than the distance between the copper atoms within the chains so that the chains can be treated as noninteracting. Within the chains the copper atoms are linked together along the chain by bridging chlorine atoms from each copper. The exchange interaction is facilitated through these Cl atoms. The electronic and magnetic properties of the material can be approximated by treating isolated $CuCl_2$ chains. There is experimental evidence for this conclusion. Bulk $CuCl_2$ undergoes a paramagnetic to antiferromagnetic transition at 70 K. The temperature dependence of the measured susceptibility has been well accounted for by treating the chains as noninteracting using the Ising model of magnetism which has an exact solution in one dimension [4].

In this work density functional theory (DFT) is used to calculate the total energy of the paramagnetic and ferromagnetic state of $CuCl_2$ chains as a function of chain length. The band gap at $K = 0$ and the dependence of the gap on the K vector are also calculated. The results indicate that nanosized chains of $CuCl_2$ could be ferromagnetic and in some instances semiconductors.

2. Methods

Density functional theory is used to calculate the total energy of $CuCl_2$ chains versus chain length when the Cu spins are ferromagnetically ordered and not ordered. The band gap at the center of the Brillouin zone is calculated as a function of chain length. The band gap is also calculated as a function of K vector employing periodic boundary conditions. The structure of the nano-length chains is assumed to be the same as in the bulk material. The Cu-Cl distance is taken as 2.96 A, and the Cl-Cu-Cl angle is 90 degrees [5]. The calculation employs the LANL3DZ/6-31G* basis set using the Gaussian 2003 software [6]. This basis set has been developed to deal with transition metal ions such as copper [7]. The basis set

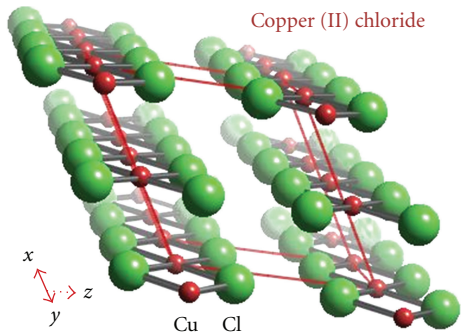

FIGURE 1: The unit cell of crystalline $CuCl_2$.

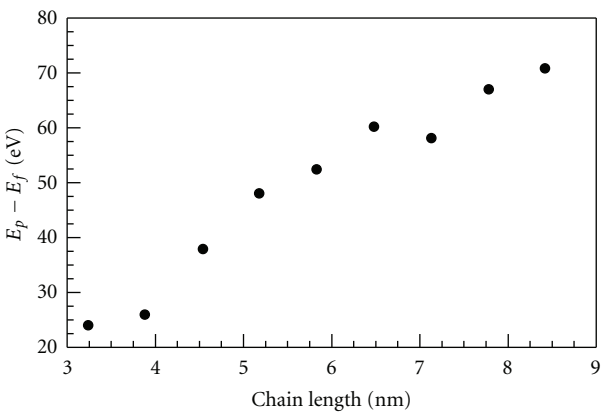

FIGURE 2: Plot of the difference in the total calculated energy versus chain length of ferromagnetic chains and paramagnetic chains. E_f is the total energy of the ferromagnetic chains, and E_p is the total energy of the paramagnetic chains. The ferromagnetic chains have lower energy.

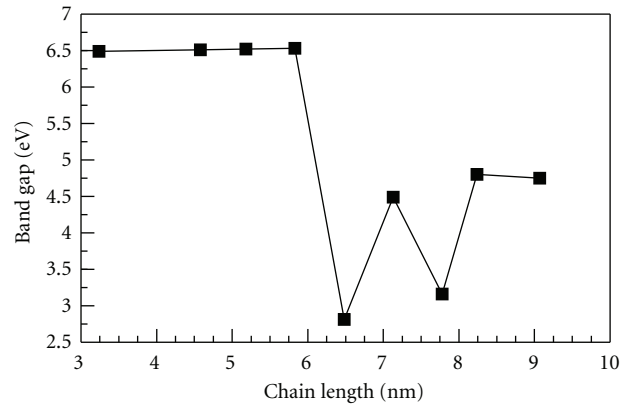

FIGURE 3: Plot of band gap at the center of the zone versus $CuCl_2$ chain length.

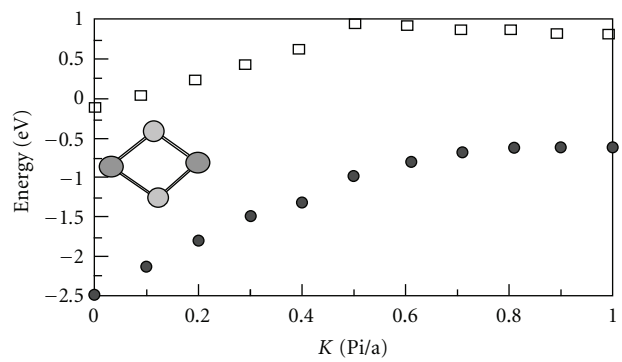

FIGURE 4: Calculation of the energy of the highest occupied orbital and the lowest unoccupied orbital of the spin-down energy gap versus the K vector. The insert is the unit cell of the chain used to calculate the band gap using periodic boundary conditions. The two copper ions have parallel spins.

employs effective core potentials to replace the coulomb, exchange, and core orthogonality effects of the chemically inert core electrons in the transitional metal ions. It has been shown to well predict the properties of materials containing transition metal ions.

3. Results

The calculations show that chains having ferromagnetic order that is a net spin Nx1/2 where N is the number of copper ions in the chain having a lower energy than a paramagnetic chain with no net spin. Figure 2 is a plot of the calculated difference in total energy between the paramagnetic state, E_p, and the ferromagnetic state, E_f.

These results indicate the ferromagnetic state is the more stable state and that $CuCl_2$ chains of nanometer length could be ferromagnetic. Since macroscopic-sized copper chloride is not ferromagnetic, $E_p - E_f$ should eventually decrease to zero with increasing chain length.

The band gap at $K = 0$ has been calculated for the ferromagnetic chains. There are two gaps corresponding to the spin-up, Δ_α, and the spin-down, Δ_β, states. For the 9.07 nm chain Δ_α is calculated to be 10.71 eV, and Δ_β is 4.75 eV. The density of states at the valence band is 7.07 states/eV for the spin-up state and is 5.39 states/eV for the spin-down state. This difference in the density of states for the spin-up and spin-down states further confirms the possibility of ferromagnetism in the nano-length chains. The Δ_α gap does not show much variation with chain length. While the Δ_β gap does show variation. Figure 3 is a plot of the Δ_β energy gap versus chain length. It is particularly interesting that above 6 nm there is a significant decrease in the gap energy to where some of the chains could be semiconducting. There is much interest in the materials research community to develop magnetic semiconductors, and it is possible that nanosized $CuCl_2$ chains could be candidate materials. Combining storage and switching in one material could enhance computer speed.

In order to further investigate this possibility, the band gaps have been calculated versus K vector for the chains. The unit cell used to calculated the band gap is shown in the insert in Figure 4 where the ferromagnetic state is treated by having both copper ions with parallel spin meaning the unit cell is a triplet. Figure 4 shows the calculated energy of the highest occupied orbital and the lowest unoccupied orbital versus the

K vector for the Δ_β gap. It is seen that for the ferromagnetic state, the gap at all values of K is such that the chains would be semiconducting.

4. Conclusion

The electronic and magnetic properties of nanosized $CuCl_2$ have been approximated theoretically by calculating the properties of isolated chains of $CuCl_2$. It has been shown that ferromagnetic chains having nanometer lengths are more stable than chains with no magnetic order. Calculation of band gaps indicate that at some lengths the chains could be semiconducting. This opens the possibility that nanosized $CuCl_2$ could be a magnetic semiconductor.

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