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3D long-range magnetic ordering in $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$ compound revealed by internal magnetic field from muon spin rotation and first principal calculation

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ABSTRACT

We report the results of muon spin rotation measurement that reveal a 3D long-range magnetic ordering in the inorganic CuCl_4 layers separated by $(\text{C}_2\text{H}_5\text{NH}_3)$ organic ligands. The measured temperature dependent internal magnetic field down to 300 mK shows the 3D long-range magnetic ordering with magnetic transition at the Néel temperature of $T_N = 10.06$ K and critical exponent of 0.31. The ground state internal dipole field is calculated by considering muon zero-point motion effect at the muon stop position determined by first principal DFT calculation, in combination with magnetization density calculated on the basis of a specific magnetic structure model. The calculated result is shown in good agreement with the measured value of internal field at the ground state temperature, thereby justifying the magnetic structure model adopted for this system and explaining the 3D nature of magnetic ordering. This model may therefore be applicable to the study of other magnetic materials.

1. Introduction

The measurement of muon spin rotation/relaxation (μSR) has been widely performed to provide useful information on the local internal magnetic field related to spin ordering or spin fluctuations in the material [1,2]. This information is deduced from the experimental data on the basis of interaction between the muon spin and surrounding internal magnetic field which is non-uniformly distributed, and hence the interaction crucially depends on the muon stopping site. In a more complex situation, the initially stopped muon might diffuse to its surrounding sites during the relaxation process. Therefore, the distribution of possible muon sites should be taking into account in the analysis. Failing to do that was shown to result in poor agreement with the experiment result [3,4]. However, even the ab-initio calculations taking into account the muon diffusion effect as performed previously [5], turned out to produce less than satisfactory agreement with experimental results. The discrepancy is supposed to have its origin in neglecting the effect of the local crystal structural change due to the arrival of the muon which is bound to affect the electronic structure as well [6–8]. In turn, the muon diffusion process may also be influenced by the corresponding modified local magnetic field. The relation between the calculated muon positions as a result of the diffusion process

and the magnetic structure in the magnetic ordered system has yet to be explored [9–11].

This study is aimed to investigate the magnetic ordering of organic-inorganic hybrid material by performing the zero-field muon spin rotation measurement and further comparing the ground state internal magnetic field calculated on the basis of DFT formalism with the experimental data. The hybrid material of interest in this study is a typical 2D magnetic system with a large interlayer spacing, and yet appears to indicate a 3D nature of the magnetic transition [12]. This compound is classified as an organic-inorganic hybrid material with the organic component of $(\text{C}_n\text{H}_{2n+1}\text{NH}_3)$ and the inorganic part of CuCl_4 . In the inorganic part, the Cu^{2+} ion is surrounded by the Cl^- ions forming an octahedral coordination with corner sharing of Cl^- between the 2D Cu layers of CuCl_4 octahedra. The present study is focused on $(\text{C}_2\text{H}_5\text{NH}_3)_2\text{CuCl}_4$ (EA-Cu) compound, with interlayers distance of about 1 nm, as shown in Fig. 1. Based on the magnetization study, de Jongh reported that the EA-Cu is an antiferromagnetic compound with ferromagnetic alignment in the Cu-layer [12]. The intralayer anisotropy field was estimated to be about 10^3 fold stronger than the interlayer field [13]. It is therefore desirable to provide experimental clarification for the 3D nature of the magnetic ordering in EA-Cu. Meanwhile the DFT calculation for EA-Cu has been performed to determine the

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Fig. 1. Crystal structure of EA-Cu in (a) *ac*-plane and (c) *ab*-plane. The buckling of the Cu-Cl octahedra is shown in panel (b).

possible muon stopping sites [14]. It is extended in this study for the determination of the internal magnetic field and its comparison with the measured data. This is carried out by performing the additional calculation employing the muon zero-point motion (ZPM) effect and magnetization density by adopting specific magnetic structure model.

2. Experiments

The zero-field (ZF) μ SR measurement was performed by means of the port-2 ARGUS spectrometer at the RIKEN-RAL Muon Facility, ISIS-UK. The single crystal was grown by a slow evaporation process from an aqueous solution containing stoichiometric quantities of $C_2H_5NH_2$, $CuCl_2 \cdot 2H_2O$, and concentrated HCl solution. The solution was heated in a water bath at 80 °C for an hour before the drying process taking place in open air. In order to insure that the muon will be stop inside the sample, the as-grown crystal is further compressed into a compacted pellet of 2 mm thickness and 20 mm diameter. The EA-Cu crystallizes in orthorhombic crystal structure of *Pbca* space-group with unit cell parameters of $a = 7.4789$ Å, $b = 7.1713$ Å, and $c = 21.2406$ Å, as shown in Fig. 1, where the *ab*-plane shows the buckling of octahedra structure. The magnetization of the sample was measured using MPMS Squid magnetometer having saturated moment of $1 \mu_B/f.u.$ similar to the result reported in Ref. [15].

3. Computational scheme

The DFT calculation of EA-Cu is performed by using the generalized gradient approximation (GGA) [16] as formulated by Perdew-Burke-Ernzerhof (PBE) [17] which is implemented in the Vienna ab-initio simulation package (VASP) [18,19]. To represent the valence and semi-core states of the system, the projector augmented wave (PAW) approach [20] is used with a cut-off energy of 400 eV in order to achieve fast convergence. The Brillouin zone integration is performed by $4 \times 4 \times 4$ Monkhorst-Pack k-point mesh [21] with a Gaussian smearing of 0.01 eV. The resulted ground state electronic structure is in a good agreement with previous reports [22,23]. Based on this result, the positions of minimum electronic potential have been determined as the possible muon stopping sites [14].

In the presence of muon and the interaction between muon and its surrounding ions in the crystal structure, the minimum potential sites will inevitably be modified arising from the disturbed local crystal structure. In order to take into account those effects, we place the muon at the global potential minimum as a starting condition for the

determination of the relaxed local structure in a $2 \times 2 \times 1$ supercell. In the next step, the calculation is repeated by putting the muon at the new global potential minimum. The stable local structure is obtained by iterating the above calculation in a self-consistent process until reaching a convergence marked by 0.01 Å difference between the minimum potential positions calculated from two successive iterations.

The muon stopping sites can then be determined by solving the Schrödinger equation given below [6]:

$$\left[-\frac{\hbar^2}{2m_\mu} \nabla^2 + V_\mu(r) \right] \psi_\mu(r) = E_\mu \psi_\mu(r), \quad (1)$$

where

$$V_\mu(\vec{r}) = q_\mu \sum_i \frac{\rho(\vec{r}_i)}{|\vec{r} - \vec{r}_i|} \quad (2)$$

is the muon potential. In Eq. (2), q_μ and $\rho(\vec{r}_i)$ are the muon charge and electron density at the relaxed ion positions $\vec{r}_i$, respectively. The above Schrödinger equation can be solved numerically by finite different method [24]. For that purpose, a cubic space around the muon position is discretized into $20 \times 20 \times 20$ meshes where each corner points is assigned with 3D kinetic energy and the muon potential energy satisfying the following equation:

$$-\frac{\hbar^2}{2m_\mu} \sum_{\alpha=x,y,z} \left(\frac{\psi_{i-1,j,k} - 2\psi_{i,j,k} + \psi_{i+1,j,k}}{\Delta_\alpha^2} \right) + V_{i,j,k} \psi_{i,j,k} = E_\mu \psi_{i,j,k}. \quad (3)$$

The notation $\psi_{i,j,k}$ in this equation represents the muon state in the (i, j, k) mesh, and Δ_α is the length along one side of the (i, j, k) cubic mesh in the $\alpha = x, y, z$ directions. The size of the cubic space is expanded to obtain the minimum ground state energy sufficiently deep to trap the muon, E_μ . In this calculation, within the cubic mesh side of 2 Å, the ground state energy of 500 meV is obtained with the convergence criterium of 0.1 meV. The probable spatial distribution of muon (muon density) in the cubic space is obtained from the $|\psi|^2$.

The total dipole field at the muon site, $H_{dip}(\vec{r})$, is calculated using the following equation:

$$H_{dip}(\vec{r}) = \sum_m \frac{1}{|\vec{r} - \vec{r}_m|^3} \left[3(\vec{\rho}_m^S \cdot (\vec{r} - \vec{r}_m)) \frac{(\vec{r} - \vec{r}_m)}{|\vec{r} - \vec{r}_m|^5} - \vec{\rho}_m^S \right], \quad (4)$$

where $|\vec{r} - \vec{r}_m|$ is the distance between muon stopping site and the position $\vec{r}_m$ of the magnetization density, $\vec{\rho}_m^S$. The magnetization density is obtained using a non-collinear magnetic structure implemented into ab-initio package software VASP [25]. In the present study, a magnetic structure assume for this calculation is characterized by ferromagnetic interaction in the Cu-plane and antiferromagnetic interaction between the Cu-planes [12]. In addition to that, the canted magnetic moment deduced from the tilted octahedral Cu-Cl structure is taking into account in the calculation. The resulted magnetization density is consistent with the result reported previously [23]. The total internal field probed by the muon is calculated by summing up all the dipole fields acting on the muon inside the Lorentz sphere around the muon. The resulted value will be compared with the experimental value obtained from the μ SR measurement.

4. Results and discussions

Fig. 2 shows the temperature dependent time spectra of the EA-Cu. The internal field obtained from the Fourier transforms of the time spectra is presented in Fig. 3. The best fit to the critical behaviour of temperature dependent magnetic field $B = B_0(1 - T/T_N)^\beta$ is achieved over the temperature range all the way down to 300 mK, yielding $B_0 = 248.35$ G and T_N of 10.06 K with $\beta = 0.31$. The Néel temperature is consistent with the value obtained from the magnetization measurement [12,15]. The existence of the critical exponent β shows that the magnetic system can be regarded as the Heisenberg type of magnetic system [26]. The muon spin rotation data have thus clearly shown

Fig. 2. The typical zero-field muon time spectra of EA-Cu measured (a) from 0.3 K to 3.0 K and (b) from 9.75 K to 10.05 K.

Fig. 3. The internal field extracted from the Fourier transform of the muon time spectra. The solid line is the best fit of the expression $B = B_0(1 - T/T_N)^\beta$.

the presence of 3D long-range ordering in the EA-Cu hybrid, even with 1 nm interlayer distance.

The determination of muon stopping site relies on the value of an internal magnetic field in the material, especially the value at a very low temperature in order to utilize the ab-initio calculation for the groundstate internal magnetic field. In this work, the experimental value is extrapolated from temperature dependent internal magnetic field as described earlier. Fig. 4a describes the possible muon stopping sites which are located near the apical Cl^- ions of CuCl_4 as reported previously [14]. It is reproduced here as easy reference for the following discussion. As mentioned earlier, the internal magnetic field sensed by the muon is modified by the change of local ion distribution caused by the presence of the muon. As a consequence of this local

structural change, the sites of minimum electrical potential will also be displaced accordingly as illustrated in Fig. 4b. However, the resulted internal field calculated at $T = 0$ K on the basis of the modified potential energy shows a considerably larger value of 281 G compared to the extrapolated experimental value of 248.35 G at the ground state temperature. This implies the need of considering the effect of muon diffusion which will lead to distributed muon sites around its initial stopping site. For that propose, the muon zero point motion calculation is invoked to improve the result.

Fig. 5 show the contour probability of muon positions around the minimum potential obtained from the ZPM calculation. The contour plot is drawn from the interpolated values of the probabilities $|\psi_\mu|^2$ in the meshes within the cubic space around the global minimum of the modified potential. It should be noted that the distribution of the muon position is not isotropic, and the highest probability of the muon position is found when the muon is located near the Cl^- ion, consistent with the expected tendency between the negative ion and the positive muon. The internal magnetic field probed by the muon in the ZPM volume is calculated using the data of Eq. (4). The total dipole field calculated over the volume of Lorentz sphere taking into account the magnetization density is shown to yield internal field of 247.63 G. In this calculation, the radius of the Lorentz volume is taken as 100 Å to achieved a fast convergence of the computation. The internal field obtained by this procedure is very close to the experimental value as denoted by 0.3% fractional difference. This result may therefore serve to justify the use of the ZPM method in combination with the magnetic structure model proposed in this study.

5. Conclusion

We have presented in this report the temperature dependent internal magnetic field measured from EA-Cu hybrid single crystal by muon spin rotation/relaxation. The result reveals the experimental evidence of 3D long-range magnetic ordering with the transition

Fig. 4. (a) Possible muon stopping sites near the apical Cl^- of CuCl_4 . The distances between the muon sites are indicated by r . (b) The electrostatic potentials obtained from the DFT calculation without and with muon located at the global minimum (A1 site) obtained iteratively by placing the muon at A1 site and relaxing the crystal structure.

Fig. 5. The contours of the possible muon positions in (a) ab -plane, (b) ac -plane, (c) bc -plane and the associated probabilities.

temperature $T_N = 10.06$ K and critical exponent of 0.31. It is further shown that the experimental data of the ground state internal magnetic field can be explained by the dipole field calculation result using the muon ZPM scheme on the basis DFT determined muon stopping sites, in combination with the magnetic structure model involving the local canted magnetic moments deduced from the local crystal structure. The 3D nature of the magnetic ordering may thus be related with the proposed magnetic structure which may also be applicable to the analysis of magnetic properties of other materials.

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