Determination of the magnetic structure of the multiferroic substance $Cu_3Mo_2O_9$

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We study magnetic and dielectric properties of the multiferroic substance $Cu_3Mo_2O_9$. Cu^{2+} ions have spin 1/2. There are three crystallographic Cu^{2+} sites (Cu1, Cu2, and Cu3) in the orthorhombic structure (*Pnma*). The J_4 exchange interaction forms antiferromagnetic (AF) chains of Cu1 spins. The J_3 exchange interaction forms AF dimers of Cu2 and Cu3 spins. The J_1 and J_2 exchange interactions connect the chain and dimers. The four interactions generate magnetic frustration. $Cu_3Mo_2O_9$ exhibits both AF order and ferroelectricity below the transition temperature $T_N = 7.9$ K. A ferromagnetic component appears in finite weak magnetic fields parallel to the a or c axis. Several phase transitions and 2/3 magnetization plateau appear in magnetic fields. It is important to determine the magnetic structure of $Cu_3Mo_2O_9$ to understand these results.

We found five very weak reflections that were forbidden in *Pnma* in high statistics x-ray powder diffraction patterns at 290 K. In maximal subgroups of *Pnma*, only monoclinic $P2_1/m$ can have all the forbidden reflections. We observed no phase transition above T_N in the specific heat of $Cu_3Mo_2O_9$. Consequently, we tentatively suggest that the space group above T_N is $P2_1/m$. The *a*, *b*, and *c* axes in *Pnma* correspond to the *a*, *b*, and *c* axes in $P2_1/m$, respectively. The Cu1 (4*a*) position in *Pnma* is split into Cu11 (2*a*) and Cu12 (2*d*) positions in $P2_1/m$. The Cu2 and Cu3 (4*c*) positions are split into Cu21 and Cu22 (2*e*)-, and Cu31 and Cu32 (2*e*)-positions, respectively.

We measured neutron powder diffraction patterns at 1.6 and 12 K using the DMC diffractometer in PSI ($\lambda = 4.507$ Å). Several magnetic reflections are apparent at 1.6 K. All the reflections can be indexed in the chemical cell with the propagation vector $\mathbf{k} = \mathbf{0}$. There are four Shubnikov groups based on $P2_1/m$. The best-fit candidate is $P2_1/m'$, which corresponds to the irreducible representations (IR) $m\Gamma_1^-$. The *a* and *c* components of magnetic moments are allowed on the dimer sites (2*e*), whereas the magnetic moments on the chain sites (2*a* and 2*d*) are zero by symmetry of $m\Gamma_1^-$. There are two IRs even by inversion operator $m\Gamma_2^+$ and $m\Gamma_1^+$, that allow non-zero chain moments. We performed Rietveld refinements using $m\Gamma_1^-$ for dimer moments and $m\Gamma_2^+$ or $m\Gamma_1^+$ for chain moments. In both cases, the reliability indexes are smallest for the chain moments close to zero.

The magnetic structure is shown in Fig. 1. Magnetic moments on dimer sites are $\mathbf{M}_{21} = (0.57(2), 0, 0.04(3))\mu_B$ on Cu21 sites, $\mathbf{M}_{22} = (0.46(3), 0, -0.50(3))\mu_B$ on Cu22 sites, $\mathbf{M}_{31} = (0.27(4), 0, 0.69(3))\mu_B$ on Cu31 sites, and $\mathbf{M}_{32} = (0.04(4), 0, -0.50(3))\mu_B$ on Cu32 sites. The angle between two moments in Cu21-Cu32 and Cu22-Cu31 dimers are $90(8)^\circ$ and $116(6)^\circ$, respectively. The chain moments may exist but the magnitudes are very small, meaning that spins in chains are nearly disordered. The magnetic structure indicates that a partial disordered (PD) state is realized.

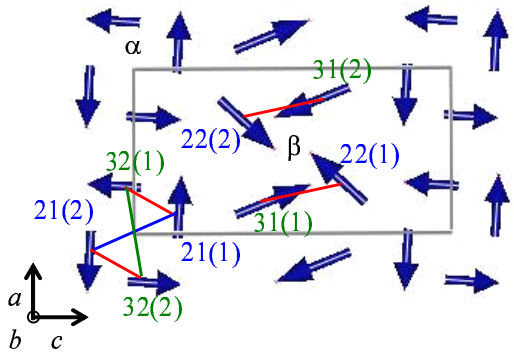

Fig. 1. The magnetic structure of $Cu_3Mo_2O_9$