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Magnetic structures of $[Co_3(pyz)(HPO_4)_2F_2]$, a fluorinated cobalt phosphate with a pillared layer structutre

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Abstract

The magnetic structure of $[Co_3(pyz)(HPO_4)_2F_2]$ compound was characterized by neutron diffraction. The crystal structure of the compound consists of two-dimensional neutral sheets of $[Co_3(HPO_4)_2F_2]$, which are pillared through pyrazine ligand. Magnetic unit cell size perpendicular to the sheet plane is twice the interplane distance, indicating an antiferromagnetic arrangement.

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Keywords: Layered structure; Antiferromagnetic arrangement; Neutron diffraction

1. Main text

Pure phase of $[Co_3(pyz)(HPO_4)_2F_2]$ compound was reported to be synthesized by hydrothermal methods [1,2]. Synthesis of organic–inorganic hybrid compounds has drawn lots of attention. Combining the robustness of inorganic frameworks with the versatility and chemical flexibility of organic ligands creates interesting effects [3]. The synthesis of magnetic hybrid materials provides the possibility of new magnetic materials by selection of appropriate bridging ligands. The structure of the titled compound was determined by single-crystal X-ray diffraction to consist of neutral sheets of $[Co_3(HPO_4)_2F_2]$, which were pillared through pyrazine ligand to form 3D frameworks [1]. The magnetic properties were revealed by zero-field-cooled susceptibility measured at 10 Oe, which showed a sharp peak at 20 K. Below this magnetic transition temperature, magnetic hysteresis loops showed interesting steps [1,2], which left the magnetic structures at low-temperature illusive.

We have performed neutron diffraction studies on the titled compound at the National Institute of Standard and Technology (NIST) triple-axis neutron spectrometer BT-9. The temperatures were chosen to be between 1.5 and 35 K, and no external magnetic field applied.

The neutron diffraction spectrum measured at 35 K is shown in Fig. 1. The plus sign is the experimental data, solid line is the fitting result. Short bars below the spectrum are the expected peak positions. The difference between experimental data and the fitting result is also shown at the bottom. The χ^2 value is 2.389, indicating a good fitting result. The structure for the compound was determined to be monoclinic with space group C2/c (no. 15), and lattice constants $a = 22.048(12)$ Å, $b = 7.571(6)$ Å, $c = 7.500(25)$ Å, $\beta = 104.62(6)^o$. This is roughly in agreement with the single-crystal X-ray result at room temperature to 1.5%. Whether the discrepancy is due to different batch of samples is under investigation.

When the sample is cooled below magnetic transition temperature, more diffraction peaks revealed. The intensity difference is shown in Fig. 2. The circles are data points with error bars indicated. Gray line is the expected difference from our model with $\{h\,k\,l\}$ for magnetic diffraction index indicated. The detail analysis of the

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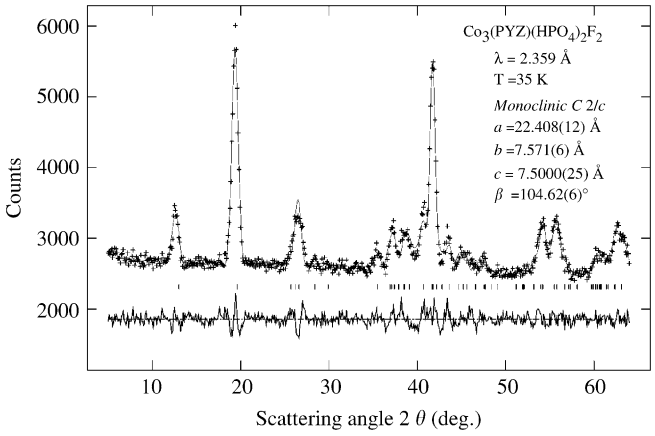

Fig. 1. Neutron spectrum at 35 K.

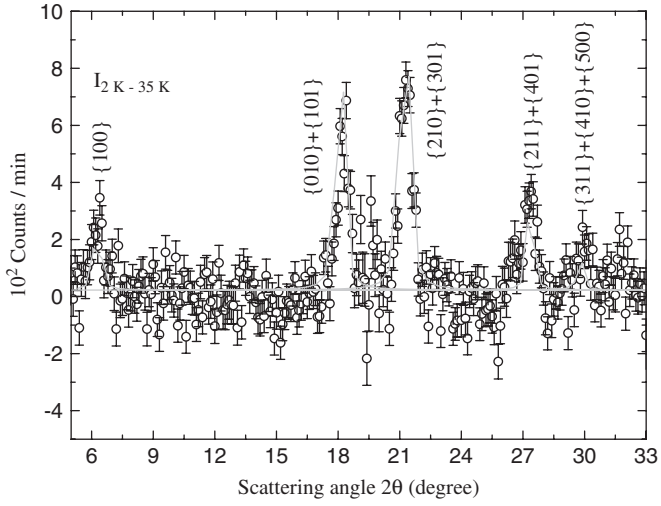

Fig. 2. The difference of intensities of neutron spectra between 1.5 and 35 K.

magnetic structures is too lengthy to be presented here. The most important feature we would like to emphasize is the diffraction peaks at the lowest 2θ values. The lowest peaks occurred at 6.15° and 12.36° in Figs. 2 and 1, respectively. This indicate that the magnetic structure repetition length along the *a*-axis, the longest axis, is twice as long as the structure one. The projections of the Co magnetic moments onto the *bc* plane are arranged antiferromagnetically. Other higher angle peaks indicated the moments are tilted out of the *bc* plane. The antiferromagnetic arrangement of the moments agrees with the magnetic hysteresis measurement [1,2], which had small magnetic moment values until the external field is strong enough to overcome the coupling. The magnetic moment then showed sharp steps.

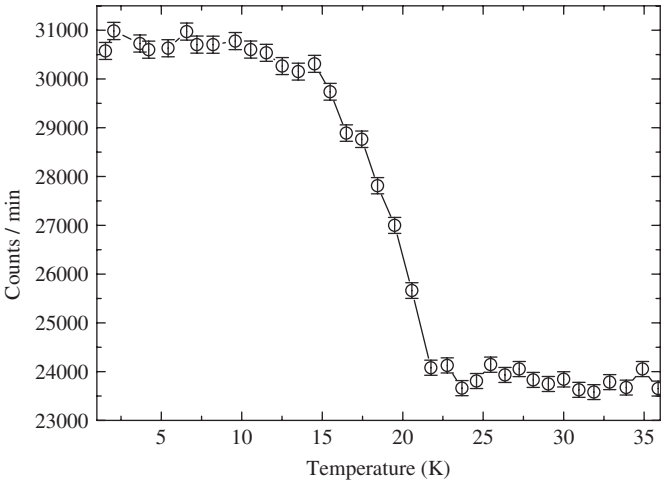

Fig. 3. Magnetic order parameter deduced from the peak at $2\theta = 21.3°$ at various temperature.

Temperature dependence of the magnetic ordering is performed by fixing the 2θ value at the strongest peak in Fig. 2, 21.29°. The variation of the order parameter (peak intensity) versus temperature is presented in Fig. 3. As the temperature is warmed from 1.5 K, the order parameter remains stable. At 10 K, it showed slight decrease followed by a large decrease from 15 to 21 K. Above 21 K, only fluctuation can be observed. This result agrees well with the magnetic susceptibility measurement, which showed sharp peak at 20 K [1].

To summarize, we have performed neutron diffraction experiment on the titled compound. Our results show agreement with the previous published single crystal X-ray structure determination and magnetic susceptibility, hysteresis measurements. The magnetic structure showed antiparallel arrangement along the *a*-axis, indicating an antiferromagnetic interplanar coupling.

Acknowledgments

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