Relationship between ferroelectricity and magnetic structure of PbCuSO₄(OH)₂ with CuO₂ ribbon chains

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Abstract. Neutron diffraction, magnetization and dielectric constant have been measured for single-crystal samples of PbCuSO₄(OH)₂ with quasi one-dimensional spin-1/2 chains formed of edge-sharing CuO₄ square planes called CuO₂ ribbon chains. An antiferromagnetic transition with an incommensurate helical magnetic ordering and a ferroelectric transition have been found to appear simultaneously at $T_N \approx 2.8$ K. From the neutron diffraction studies, $0 \mathbf{k} \pm \delta \mathbf{l}/2$ ($k=$even, $l=$integer) superlattice magnetic reflections with incommensurate modulation $\delta \sim 0.189$ have been found below $T_N$. Based on the neutron diffraction and magnetization measurements, the magnetic structure and the relationship to the ferroelectricity are discussed.

1. Introduction

Systems having both ferroelectric and magnetic orderings are called multiferroics and various such examples have been found [1]. Although multiferroics with high transition temperature attract much attention from the viewpoint of technological applications [2], we have been searching and studying systems with CuO₂ ribbon chains to investigate effects inherent to their quantum nature.

The ribbon chains are formed of edge-sharing CuO₄ square planes have one-dimensional Cu²⁺ spin ($S=1/2$) chains. Within the next-nearest-neighbor exchange interaction $J_2$ through the Cu-O-Cu exchange paths is antiferromagnetic ($J_2 > 0$), and rather strong as compared with the nearest-neighbor exchange interaction $J_1$ through the Cu-O-Cu paths, because the Cu-O-Cu angle is close to 90°. In such system, the competition between $J_1$ and $J_2$ causes magnetic frustration, which induces a nontrivial magnetic structure in the magnetically ordered phase. Theoretically, a helical magnetic structure is expected for $|J_2/J_1| > 1/4$ within a classical spin model [3]. The $J_1$-$J_2$ quantum spin chains such as the CuO₂ ribbon chains can provide a good playground for exotic quantum phases driven by frustration. A spin nematic-(quadrupolar)-ordered phase is a prime example, where various phases are predicted as a function of external magnetic field $H$ and $J_1/J_2$ [4,5].

LiVCuO₄ [6-8] and LiCu₂O₂ [9] are known as model systems of the CuO₂ ribbon chains, and have multiferroic nature. The magnetic structures of both systems are helical with modulation vector $\mathbf{Q}$ along the chain direction [7-8,10-12], and they exhibit a ferroelectric transition with the spontaneous polarization $\mathbf{P}$ described by the relation $\mathbf{P} \propto \mathbf{Q} \times \mathbf{e}_3$ as theoretically predicted [13-15], where e₃ are the helical axis.

PbCuSO₄(OH)₂ is another example having CuO₂ ribbon chains. The structure is schematically shown in Fig. 1 (space group P2₁/m; monoclinic; $a=9.701$ Å; $b=5.650$ Å; $c=4.690$ Å; $\beta=102.65$°) [16].
Figure 1. Crystal structure of PbCuSO$_4$(OH)$_2$. The edge-sharing chains of CuO$_4$ square planes (called CuO$_2$ ribbon chains) are separated by the Pb$^{2+}$ ions and the SO$_4^{2-}$ tetrahedra. The $a'$- and $c'$-axes are defined to be suitable for the local structure of the CuO$_2$ ribbon chains.

The unit cell contains only one equivalent chain which is separated by the nonmagnetic Pb$^{2+}$ ions and SO$_4^{2-}$ tetrahedra. The $a'$- and $c'$-axes are chosen to be convenient to describe the local structure of CuO$_2$ ribbon chains (see Fig. 1). We have found that the system exhibits a ferroelectric transition induced by the antiferromagnetic ordering at the Néel temperature $T_N \sim 2.8$ K [17]. Here, in order to determine the magnetic structure of the system, magnetization measurements and neutron diffraction studies have been carried out on a single-crystal sample of PbCuSO$_4$(OH)$_2$, and on the basis of these results, a possible magnetic structure is proposed, and the relationship between the obtained magnetic structure and the ferroelectricity is discussed.

2. Experiments

Single crystals of a natural mineral PbCuSO$_4$(OH)$_2$ called linarite have been used in the present study. The crystal axes were determined by X-ray diffraction. The magnetic susceptibility $\chi$ and magnetization $M$ were measured using a SQUID magnetometer (Quantum Design) in the temperature range from 2 to 350 K. The dielectric constant $\varepsilon$ was measured using an ac capacitance bridge (Andeen Hagerling 2500A) at 1 kHz (typical sizes of $\sim 2 \times 1 \times 2$ mm$^3$) to which the electrodes were attached with silver paint.

Neutron scattering measurements were carried out using the triple axis spectrometer HQR (T1-1) of the thermal guide installed at JRR-3 of JA EA in Tokai. The horizontal collimations were 12°(effective)-40°-60°-60° and the neutron wavelength was 2.4595 Å. The 002 reflection of Pyrolytic graphite (PG) was used as the monochromator. A PG filter was placed after the second collimator to suppress the higher-order contamination. The crystal was oriented with the [010] and [001] axes in the scattering plane. The crystal was set in an Al-can filled with exchange gas, and the can was mounted in a liquid $^4$He cryostat.

3. Results and discussion

Figure 2 shows the temperature dependence of the magnetic susceptibility $\chi$ of PbCuSO$_4$(OH)$_2$ taken with the external field $H=1$ T along the three directions represented in the figure. All the $\chi$-$T$ curves take maxima at 4–5 K, which is attributed to the growth of the short-range spin correlation with decreasing $T$. They show abrupt drop at an antiferromagnetic transition temperature $T_N \sim 2.8$ K, which is consistent with the previously reported data of refs. [18] and [19]. We can see the anisotropy in the $\chi$-$T$ curves; $\chi$’s for $H \parallel a'$ and for $H \parallel b$ decrease below $T_N$ more remarkably than $\chi$ for $H \parallel c'$. Since the $a'$- and $b$-axes are (nearly) parallel to the CuO$_2$-planes, which have buckling, in the strict sense, as shown in Fig. 1, the ordered spin components in the antiferromagnetic phase are (nearly) parallel to...
Figure 2. Temperature dependence of the magnetic susceptibility $\chi$ of PbCuSO$_4$(OH)$_2$. The magnetic field of $H=1$ T is applied along the three directions shown in the figure. The inset shows magnetization curves taken at $T=2$ K under various magnetic field directions.

Figure 3. Temperature dependence of the dielectric constant $\varepsilon$ of PbCuSO$_4$(OH)$_2$. The electric field $E$ is applied along the three directions shown in the figure.

the CuO$_2$-plane ($a'b'$-plane). From analyzing the $\chi$-$T$ curves using the high temperature expansion up to the fourth orders in the temperature region of 50 K<$T$<350 K, the exchange interactions are evaluated to be $J_1=-13\pm3$ K (ferromagnetic) and $J_2=21\pm5$ K (antiferromagnetic), which are consistent with those reported in ref. [20]. The values of $|J_1|$ and $|J_2|$ are smaller than those of LiVCuO$_4$ and LiCu$_2$O$_2$ ($J_1=19$ K and $J_2=49$ K for LiVCuO$_4$ [21] and $J_1=-81$ K and $J_2=44$ K for LiCu$_2$O$_2$ [22]). Thus, the present system is worth exploring the exotic quantum phases in experimentally achievable static fields. The inset of Fig. 2 shows $M$-$H$ curves of PbCuSO$_4$(OH)$_2$ at $T=2$ K ($<T_N$) along various
magnetic field directions. The curves exhibit significant nonlinearity at around $H_c \sim 2.5$ T for $H // a'$ and $H // b$, whereas the magnetization for $H // c'$ is almost linear in $H$. Since the magnetic anisotropy of $S=1/2$ spins is expected to be small, the anomaly of $M-H$ curves at $H_c$ can be ascribed to the spin-flop transition. A similar spin-flop transition has also been confirmed by neutron diffraction measurements in LiVCuO$_4$ [7].

Figure 3 shows the temperature dependence of the dielectric constant $\varepsilon$ for single-crystal samples of PbCuSO$_4$(OH)$_2$ taken in the electric fields $E$ along the three directions represented in the figure. We have not found any anomaly of $\varepsilon$ for $E // b$ and $E // c'$. Only for $E // a'$, an anomaly is seen at $T_N \sim 2.8$ K. We have also observed that the electric polarization $P$ appears around $T_N$, and that its sign is reversed when the cooling electric field is reversed (not shown) [17]. These results indicate that the ferroelectric transition takes place simultaneously with the magnetic transition at $T_N$ and $P$ appears along the $a'$ axis.

In order to clarify the magnetic structure, we have carried out neutron diffraction studies on a single crystal of PbCuSO$_4$(OH)$_2$. The neutron scattering intensities were measured at $q=(0, k, l)$ in the reciprocal space at $T=1.7$ K ($<T_N$) and $7.0$ K ($>T_N$). At 1.7 K, we observed magnetic superlattice reflections at $q=(0, k, l)$ with $k=\text{even}$, $l=\text{integer}$ and $\delta \sim 0.189$. Profiles of $\omega$-scan (sample-angle scan) for $0 \delta 1/2$ and $0 \delta 3/2$ reflections are shown in Figs. 4(a) and 4(b), respectively. Figure 5 shows the temperature dependence of the peak intensities for $0 \delta 1/2$ reflection obtained by subtracting the background intensity from the raw data. From the figure, we find that the magnetic ordering grows with decreasing $T$ below $T_N$. The determination of the magnetic structure of the present system is difficult by only the present neutron diffraction data, because the number of the observed magnetic reflections is insufficient to determine many parameters to describe the modulated magnetic structure. Therefore, the magnetic structure of the present system is discussed from the combined studies of neutron diffraction and detailed magnetization measurements in the following paragraph.

The behavior of the $\chi-T$ and $M-H$ curves has following features. (i) The evaluated $|J_2/J_1|$ is $\sim 0.62$, which is theoretically expected to favor a helical type magnetic structure. (ii) The magnetic susceptibility $\chi$ below $T_N$ indicates that the ordered spin components are (nearly) parallel to the CuO$_2$-plane ($a'b$-plane). (iii) The spin-flop transition at $H_c \sim 2.5$ T for $H // a'$ and $H // b$ also indicates that the ordered spin components in the antiferromagnetic phase lie in the CuO$_2$-plane ($a'b$-plane). The observed magnetic reflections at $q=(0, k, l/2)$ ($k=\text{even}$, $l=\text{integer}$) have the following features. (iv) The $\delta$ value of $\sim 0.189$ indicates that the magnetic ordering is characterized by the incommensurate

![Figure 4](image-url)
modulation vector $Q$, corresponding to the periodicity of $\approx 5.29b$ (pitch angle $\Delta \phi \approx 34^\circ$) along the Cu-chain direction. (v) The period of spin modulation along the $c$-axis is $2c$, and spins at Cu$^{2+}$ sites shifted by $(0,0,1)$ are anti-parallel to those at the original sites. Considering the above results, the magnetic structure of PbCuSO$_4$(OH)$_2$ is found to be the helical type with the ordered spin components parallel (or nearly parallel) to the CuO$_2$-plane and the helical axis $e_3$ parallel (or nearly parallel) to the $c'$ axis (see the inset of Fig. 5). From the analyses of the neutron diffraction data, this structure is consistent with the observed intensities of the magnetic reflections, and the ordered moment at $T=1.7$ K is evaluated to be $\approx 0.5 \mu_B$ by comparing the magnetic scattering intensities with nuclear ones.

Here, we discuss the relationship between observed magnetic structure and ferroelectricity of PbCuSO$_4$(OH)$_2$. The magnetic structure is the helical with $a'b$-plane, where the incommensurate modulation vector $Q$ is parallel to the $b^*$ axis and the helical axis $e_3$ is (nearly) parallel to the $c'$ axis as shown in the inset of Fig. 5. The ferroelectric polarization $P$ is observed along $a'$. Then, these properties indicate that the equation $P \propto Q \times e_3$ holds, as was proposed by microscopic theoretically [13 15], where the ferroelectricity is originated from the helical type magnetic structure through the spin-orbit interaction. From the obtained data, the multiferroic nature of the present system is found to be basically similar to that of LiVCuO$_4$. We think that the characteristics of the PbCuSO$_4$(OH)$_2$ are small values of $|J_1|$ and $|J_2|$ and simple crystal structure containing one equivalent chain in a unit cell [17].

4. Conclusion
We have shown the experimental results of neutron magnetic reflection, magnetic susceptibility, magnetization, and dielectric constant for single-crystal samples of PbCuSO$_4$(OH)$_2$. The ferroelectric transition takes place simultaneously with the magnetic transition at $T_N$, and the ferroelectric polarization $P$ appears along the $a'$ axis. The 0 $k\delta l/2$ ($k=$even, $l=$integer) magnetic reflections ($\delta \approx 0.189$) have been observed below $T_N$. We have found that Cu$^{2+}$ spins are ordered to the helical structure parallel to the $a'b$-plane, and the incommensurate modulation vector $Q$ is along the Cu-chain, where the relation $P \propto Q \times e_3$ is valid.
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