Ferroelectricity by Bose–Einstein condensation in a quantum magnet

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The Bose–Einstein condensation is a fascinating phenomenon, which results from quantum statistics for identical particles with an integer spin. Surprising properties, such as superfluidity, vortex quantization or Josephson effect, appear owing to the macroscopic quantum coherence, which spontaneously develops in Bose–Einstein condensates. Realization of Bose–Einstein condensation is not restricted in fluids like liquid helium, a superconducting phase of paired electrons in a metal and laser-cooled dilute alkali atoms. Bosonic quasi-particles like exciton-polariton and magnon in solids-state systems can also undergo Bose–Einstein condensation in certain conditions. Here, we report that the quantum coherence in Bose–Einstein condensate of the magnon quasi particles yields spontaneous electric polarization in the quantum magnet TICuCl₃, leading to remarkable magnetoelectric effect. Very soft ferroelectricity is realized as a consequence of the O(2) symmetry breaking by magnon Bose–Einstein condensation. The finding of this ferroelectricity will open a new window to explore multi-functionality of quantum magnets.

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\(T\)ICuCl\(_3\) is the first material whose field-induced quantum phase transition was classified as a realization of Bose–Einstein condensation (BEC) in the quantum magnets\(^1\). In this material, antiferromagnetic spin dimers, composed of a pair of Cu\(^{2+}\) ions with spin \(S = 1/2\), are three-dimensionally coupled by interdimer Heisenberg exchange interactions, which are weaker than the intradimer one\(^2-3\). This coupled dimer lattice provides an ideal playground for BEC of magnon quasiparticles. The ground state of the system is approximated to be direct product of the spin singlet states on the dimer bonds. Thus, TICuCl\(_3\) remains to be a quantum paramagnet down to the lowest temperature, while the excited triplet on a dimer, propagating through the lattice via the interdimer exchange interactions, can be regarded as a Bosonic particle with \(S\) elements of around the external magnetic field. Because of the finite matrix phase, which reflects the rotational symmetry of the system, the spin chirality between its spin singlet and triplet states. This microscopic coherence is developed throughout the dimer lattice by magnon BEC, the phase \(\phi\) is settled and thereby the electric dipole moment with a fixed direction emerges on a dimer. Therefore, if a sum of this electric dipole on each dimer over whole lattice has a finite value, a macroscopic spontaneous electric polarization will appear in the system.

Here, we demonstrate ferroelectricity, caused by magnon BEC, by the dielectric constant and the pyroelectric current measurements of TICuCl\(_3\). It is revealed that the spontaneous electric polarization proportional to an absolute value of the vector spin chirality in the ground state develops above \(H_c\). The observation of this ferroelectricity indicates that quantum magnets can be significant playgrounds for magnetoelectric coupling.

**Results**

**Ferroelectricity in TICuCl\(_3\).** To observe the ferroelectricity by magnon BEC, we have measured the dielectric constant (\(\epsilon\)) and the spontaneous electric polarization (\(P\)) in TICuCl\(_3\). Figure 1a shows the temperature dependence of the dielectric constant of TICuCl\(_3\) perpendicular to (102) plane in magnetic fields \((H)\) for \(H // [010]\). While no anomaly is found in the dielectric constant observed below 5 T, a peak appears at low temperature in magnetic fields above 6 T. As the magnetic field is increased, the peak becomes sharper and shifts towards higher temperature. The positions of the observed peaks are plotted in the temperature-field phase diagram shown in Fig. 1b. The vertical field axis of Fig. 1b is normalized by the \(g\)-value \(g = 2.06\) determined by the electron spin resonance (ESR) measurement\(^10\). The peak positions agree with the critical points of the magnon BEC, determined by the previous neutron diffraction measurements in TICuCl\(_3\) (ref. 13). This agreement indicates that the magnon BEC is accompanied by a sharp anomaly of the dielectric property, implying that the BEC phase in TICuCl\(_3\) is a multiferroic state with both ferroelectric and antiferromagnetic ordering. The appearance of the spontaneous electric polarization by the magnon BEC can be confirmed by the pyroelectric current measurements. Figure 1c shows the temperature dependence of the spontaneous electric polarization perpendicular to the (102) plane and in the magnetic field for \(H // [010]\), obtained by integrating the pyroelectric current. As expected, the electric polarization appears below the critical temperature in magnetic fields above 6 T. As the magnetic field is increased, the saturation value of the electric polarization at the lowest temperature increases.

**Magnetic field dependence of electric polarization in TICuCl\(_3\).** Figure 1d shows the field dependence of the electric polarization, observed at 2.0 K in the same configuration for the temperature dependence measurements described above. Continuous increase of the electric polarization with increasing the magnetic field is observed above \(H_c\). We compare the field evolution of the electric polarization to the expectation value of the vector spin chirality \(S_S = S_S \times S_S\) of a coupled dimer system in the condensed ground state, calculated in terms of a bond operator formulation. As described in refs 2-3, the bond operator formulation can quantitatively explain the magnetic field dependence of both longitudinal and transverse spin components, observed in

\[
\langle \Psi | S_x S_z | \Psi \rangle = \frac{1}{\sqrt{8}} \sin 2\theta (\sin \phi, \cos \phi, 0),
\]

where \(S_x\) and \(S_z\) are the spins, composing a dimer. From this fact, we anticipate the appearance of the electric dipole moment in this superposed state. When the macroscopic coherence is developed throughout the dimer lattice by magnon BEC, the phase \(\phi\) is settled and thereby the electric dipole moment with a fixed direction emerges on a dimer. Therefore, if a sum of this electric dipole on each dimer over whole lattice has a finite value, a macroscopic spontaneous electric polarization will appear in the system.
The light blue shading area turns out to be a multiferroic state with both antiferromagnetic and ferroelectric orders. The magnetic field is normalized by $P$ shows the peak position of the dielectric constant. Open squares are the critical points, determined by the previous neutron diffraction measurements. The magnetic field is normalized by $P$ shows the field dependence of the vector spin chirality $<S_1 \times S_2>$, indicated that the electric polarization in TlCuCl$_3$ is greatest for [010] direction, indicates that the electric polarization $P \perp$ (102). The calculation is carried out in terms of the bond operator theory. Inset shows the field dependence of the bond operator theory. Inset shows the field dependence of the vector spin chirality $<S_1 \times S_2>$ and the longitudinal spin component $<S_z>$, calculated up to 100 T.

**Discussion**

Let us discuss the relation between the direction of the electric polarization and the symmetry of the field-induced BEC phase in TlCuCl$_3$. Inset of Fig. 1d shows the field dependence of $P \perp$ (102), the magnetic order, which is characterized by wave vector $Q$, breaks the space inversion and the twofold helical symmetries of the crystal lattice. Only a remaining element of the symmetry in the BEC phase is a glide plane parallel to (010). Therefore, the electric polarization, induced by external magnetic fields for $H$//[010], should lie in (010) plane. Figure 2 exhibits the temperature dependences of the electric polarizations perpendicular to (102) plane and parallel to [010] axis in magnetic fields for $H$//[010]. The experimental result that almost no electric polarization appears for [010] direction, indicates that the electric polarization points along (010) plane as expected from the symmetry of the BEC phase.

Figure 3 shows a $P$–$E$ hysteresis loop at 4.2 K for the electric polarization perpendicular to (102) plane, observed for $H$//[010] at 14 T. Step-like reversals of the electric polarization are observed around the electric coercive field $E_c = 0.03$ MV m$^{-1}$. To the BEC phase in the magnetic field parallel to [010] axis, determined by the previous neutron diffraction measurement. The crystal symmetry of TlCuCl$_3$ belongs to the P2$_1$/c space group. However, in magnetic fields for $H$//[010], the magnetic order, which is characterized by wave vector $Q$, breaks the space inversion and the twofold helical symmetries of the crystal lattice. Only a remaining element of the symmetry in the BEC phase is a glide plane parallel to (010). Therefore, the electric polarization, induced by external magnetic fields for $H$//[010], should lie in (010) plane. Figure 2 exhibits the temperature dependences of the electric polarizations perpendicular to (102) plane and parallel to [010] axis in magnetic fields for $H$//[010]. The experimental result that almost no electric polarization appears for [010] direction, indicates that the electric polarization points along (010) plane as expected from the symmetry of the BEC phase.
knowledge of the authors, this value of the electric coercive field is the smallest among the magnetically induced ferroelectrics. The electric polarization reversal requires a reversal of the vector spin chirality. Thus, it causes 180° rotation of the antiferromagnetic domain easily occurs in TlCuCl₃. The insets show that a local electric field would allow to control the vortices and might even affect the nature of the phase transition by the magnon BEC.

Figure 2 | Temperature dependence of the electric polarizations $P_{//[010]}$ and $P_{\perp[012]}$ for $H_{//[010]}$ at 18 T. Inset shows the spin structure in the field-induced phase of TlCuCl₃ for $H_{//[010]}$, determined by the previous neutron diffraction measurements. Grey shedding shows a unit cell of TlCuCl₃. Bold solid and dashed lines show the dimer bonds, which are connected each other by the two-fold helical $Z_1$ or the glide symmetry transformations of the $P_2_1/c$, which is the space group of TlCuCl₃. Arrows are spins of Cu²⁺ ion. The transverse components of the spins direct along the easy axis, which is inclined from [010] by 39° in the (010) plane. The spin ordering breaks the space inversion $I$ and the $Z_1$ symmetries, whereas the glide plane parallel to (010) remains. Therefore, the electric polarization, induced by the magnetic field for $H_{//[010]}$, should lie in (010) plane. The experimental result that almost no $P_{//[010]}$ is observed, agrees with the symmetry of the spin structure.

Figure 3 | $P$-$E$ hysteresis curve of $P_{\perp[012]}$ for $H_{//[010]}$. Small electric coercive field for reversal of $P$ indicates that 180° rotation of the antiferromagnetic domain easily occurs in TlCuCl₃. The insets show schematic pictures of the electric polarization on the dimer. The electric polarization reversal requires a reversal of the vector spin chirality $S_1 \times S_2$.

Methods

Measurements of dielectric constant. A single crystal TlCuCl₃, which was grown by the Bridgman method, was cut into thin plates with the widest plane parallel to cleavage (010) and (012) plane, and then silver paste were applied on faces of the crystal as electrodes. (010) and (012) planes are orthogonal each other. We measured the dielectric constant at 10 kHz by an LCR meter (Agilent E4980A).

Measurements of electric polarization. To obtain the temperature dependence of the spontaneous electric polarization, the pyroelectric current was measured after applying a poling electric field of 0.043 MV m⁻¹ from 20 to 2 K by using an electrometer (Keithley 6517B). The magnetic field dependence of the electric polarization was obtained by integration of the electric current observed in sweeping magnetic field at a constant ratio 0.984 T min⁻¹. The $P$-$E$ curve was obtained by measurements of electric current induced by sweeping electric field at a constant ratio 21.75 kV m⁻¹ s⁻¹. Both dielectric and pyroelectric current measurements were carried out by utilizing a 18 T superconducting magnet.

Data availability. The data that support the findings of this study are available from the corresponding author on request.

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Author contributions

S.K., K.K. and Y.S. performed the dielectric constant and the pyroelectric current measurements. K.W. and M.H. supervised the project. M.M. carried out the theoretical calculation. H.T. grew the single-crystal sample. S.K. wrote the paper. All authors discussed the results and the manuscript.

Additional information

Competing financial interests: The authors declare no competing financial interests.

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