Magnetoelectric effects in an organo-metallic quantum magnet

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We observe a bilinear magnetic field-induced electric polarization of $50 \ \mu C/m^2$ in single crystals of NiCl$_2$-4SC(NH$_2$)$_2$ (DTN). DTN forms a tetragonal structure that breaks inversion symmetry, with the highly polar thiourea molecules all tilted in the same direction along the $c$-axis. Application of a magnetic field between 2 and 12 T induces canted antiferromagnetism of the Ni spins and the resulting magnetization closely tracks the electric polarization. We speculate that the Ni magnetic forces acting on the soft organic lattice can create significant distortions and modify the angles of the thiourea molecules, thereby creating a magnetoelectric effect. This is an example of how magnetoelectric effects can be constructed in organo-metallic single crystals by combining magnetic ions with electrically polar organic elements.

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Magnetoelectrics are compounds in which the magnetic and electric susceptibilities are coupled, with magnetic fields inducing electric polarization and electric fields inducing magnetic polarization [1]. Research in this field is motivated by the promise of new devices as well as improving the speed, energy-efficiency and size of existing circuits [2–4]. The magnetoelectric effect can be particularly large when either the magnetic or electric subsystem is ordered, leading to diverging magnetic or electric susceptibilities. In particular, multiferroic behavior is a current hot topic that attempts to exploit the large effects that can result when both the magnetic and electric polarizations in electric insulators exhibit long-range order [2,5–12]. However, there is currently a dearth of materials exhibiting strong magnetoelectric coupling or multiferroic behavior and most research to date in these fields, particularly in multiferroics, has focused on transition-metal oxides. Thus the idea of using organic ferroelectrics as a starting point for building multiferroic or magnetoelectric materials has the potential to greatly expand the available number of compounds [13,14]. Ferroelectricity is known to occur in a number of organic molecules [15], and was most recently discovered above room temperature in croconic acid [16]. Organic materials tend to possess soft lattice structures that can be easily modified by magnetic forces, leading to large magnetic field-induced changes in the electric polarization. In addition, the flexibility for design of organic molecules and availability of electrically polar building blocks could allow us to construct a variety of new magnetoelectrics by design. A recent review of ferroelectricity in organic materials [15] has identified the electrically polar molecule thiourea, SC(NH$_2$)$_2$, as a strong candidate for organic ferroelectricity. In its crystalline form it is a ferroelectric with a $T_c$ of 169 K and an electric polarization of 3,200 $\mu C/m^2$ [17]. The origin of the electric polarization is primarily the polar double bond between carbon and the highly electronegative sulfur atom. This bond is only partially compensated by the remainder of the molecule. In pure thiourea, the individual thiourea molecules nearly but not quite anti-align, and an applied electric field can tilt the relative orientations, resulting in a ferroelectric response.

Here we present data on the compound NiCl$_2$-4SC(NH$_2$)$_2$ (DTN) in which the thiourea molecules all tilt in the same direction along the tetragonal $c$-axis, thereby breaking spatial inversion symmetry (see fig. [1]). The Ni magnetic spins occupy a tetragonal body-centered structure with antiferromagnetic interactions between nearest neighbors. Frustration between the two interpenetrating tetragonal sublattices of Ni spins causes the spins of the sublattices orient orthogonal to

![FIG. 1: Crystal structure of NiCl$_2$-4SC(NH$_2$)$_2$ (DTN) showing a) the thiourea coordination around the Ni ions and the likely direction of the electric polarization $P$, b) the canted frustrated antiferromagnetic structure of the Ni spins at intermediate fields between 2 and 12 T, and c) two unit cells of the full crystal structure.](image-url)
Sound spectroscopy is the a-axis. The bulk modulus measured using resonant ultrasonic spectroscopy is \( E_{33} = 7.5 \pm 0.7 \) GPa extrapolated to zero K \([21]\), which is an order of magnitude smaller than typical inorganic metals and oxides.

Single crystals of DTN were grown from aqueous solutions of thiourea and nickel chloride. Two sets of samples were measured, one grown in an electric field of 500 V/cm along the c-axis and the other in zero electric field. Comparable electric polarizations were observed to within 25% and data on the E-field grown samples are presented. The electric polarization as a function of magnetic field was measured at temperatures down to 0.55 K with the samples immersed in pumped \(^3\)He. Pulsed magnetic fields were employed at the National High Magnetic Field Laboratory (NHMFL) at Los Alamos National Laboratory. A relatively slow mid-pulse magnet (\( \sim 2000 \) T/s peak, 500 T/s average) was used to avoid heating and cooling from eddy currents and magnetoelastic effects. Capacitor plates were constructed by applying Dupont silver paint to the faces of the single crystals perpendicular to the c-axis, and the electric polarization along the c-axis for the DTN at various temperatures. c) Percentage change in length \( L \) of the sample as a function of magnetic field relative to its zero field value for \( H || c \), measured along the crystallographic a and c axes \([21]\).

FIG. 2: Temperature \( T \) - Magnetic field \( H \) phase diagram for \( H || c \) determined from specific heat and magnetocaloric effect (MCE) data, together with the result of Quantum Monte Carlo (QMC) simulations. The magnetization vs field measured at 16 mK and calculated from QMC is overlaid onto the phase diagram. The region of antiferromagnetism/Bose-Einstein Condensation (AFM/BEC) occurs under the red dome \([21]\).

FIG. 3: a) Comparison of the electric polarization \( P \) (this work) and the square of the magnetization \( M^2 \) vs \( H \) \([18]\) at 0.6 K. b) \( P(H) \) of DTN at various temperatures. c) Percentage change in length \( L \) of the sample as a function of magnetic field relative to its zero field value for \( H || c \), measured along the crystallographic a and c axes \([21]\).
ter cooling the sample in zero electric and magnetic field, e.g.
with no poling. The electric polarization and the square of the
magnetization show a similar magnetic field dependence, be-
ing roughly zero for fields up to $H_{c1} \sim 2$ T, and then increas-
ing strongly in the canted antiferromagnetic state until satu-
rization occurs above $H_{c2} \sim 12$ T. In Fig. 3b, $P(H)$ curves are
shown for different temperatures up to 10 K. The magnitude
of the jump in $P$ with $H$ remains roughly constant up to 1.6
K, even though this exceeds the maximum antiferromagnetic
ordering temperature and only becomes suppressed in the 10
K curve. This behavior is also similar to $M(H)$, as shown in
ref. [21], where the magnitude of $M(H)$ is primarily deter-
mined by the $\sim 10$ K energy scale of the largest antiferro-
magnetic interaction $J_c$. The signature of long-range ordering is
by contrast relatively small. In the $P(H)$ curves, a kink due
to antiferromagnetic ordering was also very small and could
only be distinguished for some of the curves.

The magnetostriction $(L(H) - L(0))/L(0)$ [21] is shown
in Fig. 3c, measured for magnetic fields along the c-axis, and
for length changes along both a and c. The magnetostriction
shows clear signatures of the magnetic behavior of the sys-
tem, particularly along c. However, the behavior is clearly
quite complicated with non-monotonic behavior along c and
monotonic behavior along a. The magnetostriction for $L/c$
curve at 25 mK was well fit by a 1-D theory in ref. [21],
which assumes that the Ni ions attract and repel each other
along the c-axis depending on their relative spin orientations,
and assuming that these forces are caused by a to first-order
linear dependence of $J_c$ on bond length acting in competi-
tion with the elastic energy of the lattice. We posit that the
thiourea molecules are the dominant source of electric polar-
ization in DTN, since these contain highly polar S=C bonds
that can cause electric polarizations up to $3.200 \mu$C/m$^2$ in
pure thiourea. The exact relationship between the angles of
these thiourea molecules and the overall length changes mea-
sured using magnetostriction is not easily calculated given the
available data, but is likely a function of both the nonmono-
tonic behavior along the c-axis and the monotonic behavior
along the a-axis.

In conclusion, we observe a magnetoelectric effect of 50
$\mu$C/m$^2$ in the organo-metallic compound NiCl$_2$-4SC(NH$_2$)$_2$
that is bilinear (e.g. even under reversal of the magnetic
field) and likely results from magnetic forces between Ni spins
distorting the soft organic lattice. We propose that the po-
lar thiourea molecules, in particular the double carbon-sulfur
bonds, are the likely origin of the electric polarization, and
their angles are modified due to magnetostrictive effects in this
compound. This compound is magnetoelectric – we do not see
any evidence of ferroelectric behavior that would render this
a multiferroic compound. However, the size of the magnetic
field-induced electric polarization, 50 $\mu$C/m$^2$ is only an order
of magnitude smaller than some commonly studied multifer-
roics, e.g. TbMnO$_3$ with $600 \mu$C/m$^2$ [13]. This is the first
example of the organic ferroelectric thiourea being used as a
building block to create magnetoelectric or multiferroic
behavior. Given the availability of thiourea and other organic
ferroelectrics with relatively large ferroelectric polarizations
and high ordering temperatures, coupled with the soft lattice
structures of organo-metallic compounds, we propose this hy-
brid approach as an interesting area for further growth.

Very recently multiferroic behavior has also been reported
in a few other organo-metallics materials including CuCl$_2$
$2[(CH$_3$_3)$_3$SO] [13] and TTF-BA [14]. The combination of
stronger magneto-electric couplings and higher temperatures
of the magnetic ordering are now a necessary step to further
develop this field.

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