Research Article

The Origin and Coupling Mechanism of the Magnetoelectric Effect in $TM\text{Cl}_2$-4SC$(\text{NH}_2)_2$ (TM = Ni and Co)

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Most research on multiferroics and magnetoelectric effects to date has focused on inorganic oxides. Molecule-based materials are a relatively new field in which to search for magnetoelectric multiferroics and to explore new coupling mechanisms between electric and magnetic order. We present magnetoelectric behavior in NiCl_2-4SC$(\text{NH}_2)_2$ (DTN) and CoCl_2-4SC$(\text{NH}_2)_2$ (DTC). These compounds form tetragonal structures where the transition metal ion (Ni or Co) is surrounded by four electrically polar thiourea molecules [SC$(\text{NH}_2)_2$]. By tracking the magnetic and electric properties of these compounds as a function of magnetic field, we gain insights into the coupling mechanism by observing that, in DTN, the electric polarization tracks the magnetic ordering, whereas in DTC it does not. For DTN, all electrically polar thiourea molecules tilt in the same direction along the **c**-axis, breaking spatial-inversion symmetry, whereas, for DTC, two thiourea molecules tilt up and two tilt down with respect to **c**-axis, perfectly canceling the net electrical polarization. Thus, the magnetoelectric coupling mechanism in DTN is likely a magnetostrictive adjustment of the thiourea molecule orientation in response to magnetic order.

1. Introduction

In magnetoelectric multiferroics, magnetic and electric order coexist and are coupled to each other. For example, if a magnetic field can modify ferroelectricity or an electric field can modify magnetic order, new functionalities can be envisioned with applications to electric devices and sensors [1–3]. A great effort has been dedicated to finding new classes of multiferroic materials and understanding magnetoelectric coupling mechanisms [4]. Molecule-based magnets are a promising class of materials in which to couple magnetic and electric order. Here, magnetism can derive from magnetic metal ions and ferroelectricity from electrically polar organic molecule fragments [5–7].

NiCl_2-4SC$(\text{NH}_2)_2$, dichloro-tetrakis-thiourea-nickel (DTN) [8–11], has been extensively studied for its quantum magnetism. It possesses a field-induced quantum phase transition that has been analyzed in terms of Bose-Einstein condensation of the spin degrees of freedom [12]. Recently it was also found to show magnetostriction consistent with exchange striction in the antiferromagnetic state [7]. DTN is a molecule-based magnet in which NiCl_2-4SC$(\text{NH}_2)_2$ molecules pack in a body-centered tetragonal structure, with Ni–Cl–Cl–Ni bonding along the **c**-axis and hydrogen bonding between thiourea molecules in the **ab**-plane. The four thiourea molecules surrounding each Ni ion are electrically polar. The components of the thiourea electric polarization in the **ab**-plane cancel each other; however,
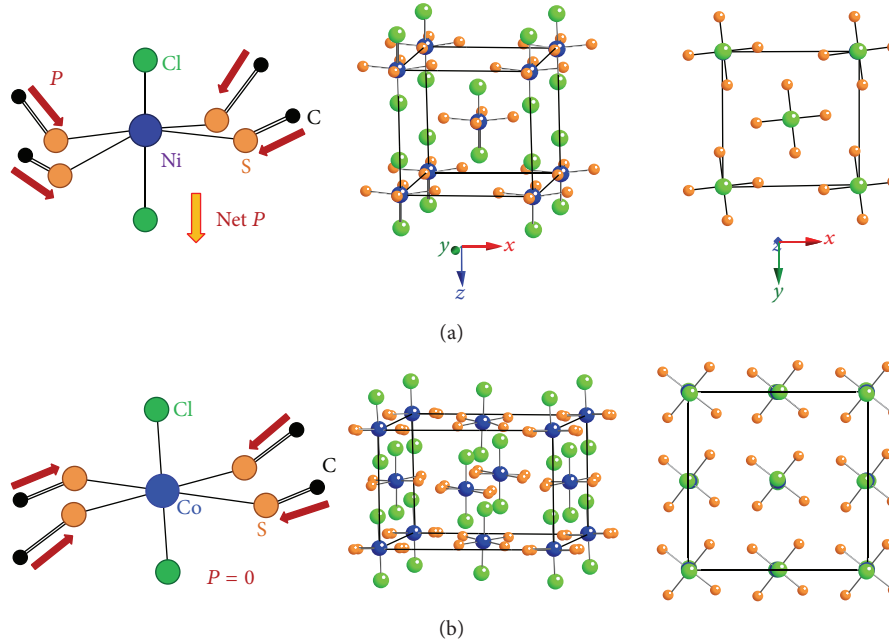
(a)

(b)

FIGURE 1: Crystal structure of (a) $NiCl_2$-$4SC(NH_2)_2$ (DTN) and (b) $CoCl_2$-$4SC(NH_2)_2$ (DTC) with some atoms omitted for clarity. The cartoons on the left show the direction of the electric polarization produced by the S=C bonds.
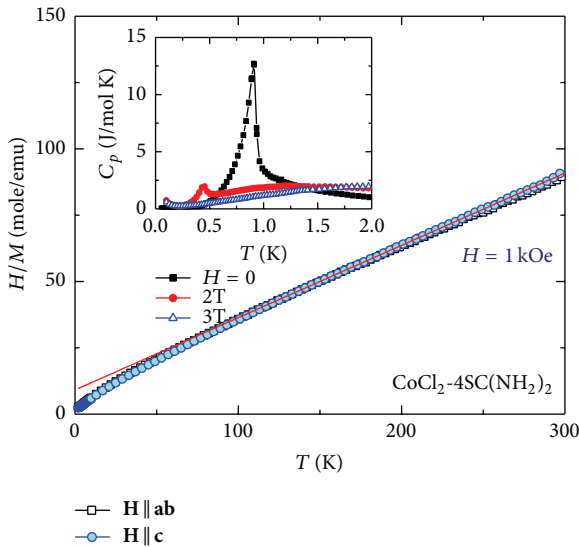

FIGURE 2: Inverse magnetic susceptibility, $H/M(T)$, of $CoCl_2$-$4SC(NH_2)_2$ as a function of temperature for magnetic fields **H** of 1 kOe applied ∥ **ab** and ∥ **c**. Solid lines represent a Curie-Weiss fit. Inset shows specific heat data at selected magnetic fields for **H** ∥ **c**.

the **c**-axis components are added to create a net electric polarization along **c**, which could be responsible for the magnetic field-modified ferroelectricity in this material. The Ni^{2+} **S** = 1 spins are gapped at zero field due to single ion anisotropy, with an $S_z = 0$ ground state and an $S_z = \pm 1$ excited state [9]. Application of a magnetic field along the **c**-axis lowers the $S_z = 1$ state until it becomes degenerate

with the $S_z = 0$ ground state. The two levels are degenerate between 2 and 12 T since the levels are broadened (dispersed) by antiferromagnetic coupling. At 2 T, where the ground state and $S_z = 0$ state first become degenerate, antiferromagnetic order results with the spins in the **ab**-plane, perpendicular to the applied field. Above 2 T the spins increasingly "cant" as the magnetic field is increased, until they saturate at 12 T. For magnetic fields in the **ab**-plane, the different S_z levels mix together, the spin gap never closes, and no magnetic ordering occurs for any field. For **H** ∥ **c** it has been observed that the electric polarization also shows a strong magnetic-field dependence between 2 and 12 T [7] similar to the magnetization. We have suggested [7] that the thiourea molecules could be responsible for the electric polarization, and their angles with respect to the crystalline axes are changed when magnetostriction acts on the Ni spins and distorts the shape of the unit cell. Thus, we proposed that an indirect magnetostrictive mechanism is responsible for magnetoelectric coupling in DTN. Here we present new results on $CoCl_2$-$4SC(NH_2)_2$ (DTC), which shows magnetism but no electric polarization, confirming our assumption.

2. Results and Discussion

The literature shows that single crystals of DTN can be grown at room temperature from an aqueous solution [13], whereas single-phase samples of DTC require an ethanol solution [14–16]. In this work, $CoCl_2$ and $SC(NH_2)_2$ were dissolved in warm ethanol in separate glass beakers. After slowly mixing the solutions, the solvent was evaporated for a two-week period, and sub-mm dark blue plate-like crystals
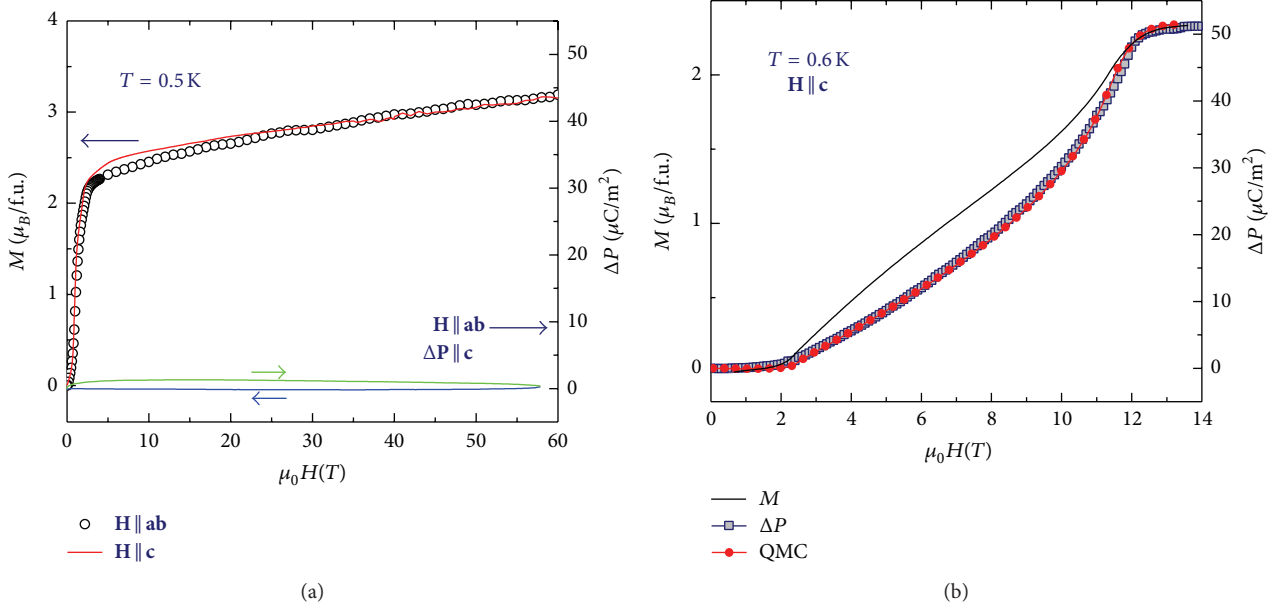
FIGURE 3: (a) $CoCl_2$-$4SC(NH_2)_2$. Left axis: magnetization isotherms $M(H)$ at $T = 0.5$ K for $\mathbf{H} \parallel \mathbf{ab}$ (open circles) and $\mathbf{H} \parallel \mathbf{c}$ (solid line). Right axis: electric polarization change $\Delta P(H)$ at $T = 0.5$ K for $\mathbf{H} \parallel \mathbf{ab}$ and $\Delta\mathbf{P} \parallel \mathbf{c}$. The horizontal small arrows indicate the up- and down-sweeps of the magnetic field. (b) $NiCl_2$-$4SC(NH_2)_2$. Left axis: $M(H)$ at $T = 0.6$ K for $\mathbf{H} \parallel \mathbf{c}$ (solid line). Right axis: $\Delta P(H)$ at $T = 0.6$ K for $\mathbf{H} \parallel \mathbf{c}$ (solid squares) and quantum Monte Carlo (QMC) calculations of the electric polarization (solid circles) [7].

with clear facets were obtained, with the $\mathbf{c}$-axis perpendicular to the plate surface. X-ray diffraction measurements at room temperature found a tetragonal structure with $P4_2/n$ and lattice parameters $a = 13.4571$ Å, $c = 9.0356$ Å [14–16]. The crystal structures of DTN and DTC are shown in Figure 1. In DTC, the Co ions pack in a face-centered arrangement, in contrast to DTN which is body centered. Each Co is surrounded by four thiourea molecules in the $\mathbf{ab}$-plane, and two Cl's along the $\mathbf{c}$-axis. The Co-Cl axes are tilted 4 deg with respect to the $\mathbf{c}$-axis, and the plane of the four Co-S bonds is tilted 8 deg from the $\mathbf{ab}$-plane with the tilt angle alternating from one nearest-neighbor Co to the next along a, b, and c (see Figure 1).

The temperature and magnetic-field dependence of the magnetization, $M(T, H)$, of DTC was measured in a Quantum Design (QD) Physical Property Measurement System (PPMS) with a vibrating sample magnetometer (VSM) option up to $\mu_0 H = 13$ T and down to $T = 2$ K. In addition, $M(H)$ measurements were extended up to $\mu_0 H = 60$ T and down to $T = 0.5$ K in pulsed magnetic fields (10 ms rise and 40 ms decay time) with an extraction magnetometer [17] at the National High Magnetic Field Laboratory (NHMFL) in Los Alamos National Laboratory. Specific heat, $C_p(T)$, was measured by the relaxation technique down to $T = 50$ mK in a QD PPMS with a dilution refrigerator option. The electric polarization change, $\Delta P(H)$, as a function of magnetic field was measured in pulsed magnetic fields for both $\Delta\mathbf{P}$ and $\mathbf{H}$ parallel and perpendicular to $\mathbf{c}$-axis [6, 7]. Platinum contacts were sputtered onto the samples to measure the induced magnetoelectric currents. The induced

magnetoelectric currents onto the electrode generated by the sample ΔP are recorded by using a Stanford Research 570 current-to-voltage amplifier.

The inverse magnetic susceptibility, H/M, as a function of temperature is linear above 120 K and no anisotropy between the $\mathbf{ab}$-plane and the $\mathbf{c}$-axis is observed as shown in Figure 2. A fit to the Curie-Weiss law above 120 K results in a paramagnetic Curie temperature $\theta_p \sim -35$ K and the effective moment $\mu_{eff} \sim 5.5\,\mu_B$, which is somewhat bigger than the expected free Co^{2+} ion value with spin $\mathbf{S} = 3/2$. The inset to Figure 2 shows the specific heat versus temperature at various magnetic fields. At zero field it shows a peak consistent with long-range magnetic ordering below $T_N = 0.94$ K, as shown in the inset of Figure 2, in agreement with the earlier results [14, 15]. We found that applying a magnetic field of ~ 3 T is sufficient to suppress T_N below the lowest measured temperature of 50 mK. Thus DTC does not require a magnetic field to close a spin gap and induce magnetic order, in contrast to DTN.

The magnetization isotherms, $M(H)$, for DTC were measured at $T = 0.5$ K up to 60 T (see Figure 3(a)). As the magnetic field increases, $M(H)$ rises rapidly until ~ 2 T. The $0 \leq H \leq 2$ T region also corresponds to the suppression of long-range order in the specific heat. For $\mu_0 H > 2$ T, $M(H)$ curves for both $\mathbf{ab}$-plane and $\mathbf{c}$-axis increase monotonically, reaching the value of $\approx 3.2\,\mu_B$/f.u. at $\mu_0 H = 60$ T. The effective moment and the saturated magnetization value are close to the expected $Co^{2+}\,\mathbf{S} = 3/2$ value, while no magnetic anisotropy can be resolved for DTC. The lack of anisotropy in an $S = 3/2$ ion implies that the three unpaired electrons in

Co^{2+} occupy the three t_{2g} levels, or else that splitting among t_{2g} and e_g levels is very small.

The electric polarization measurements indicate no observable signal up to 60 T as shown in Figure 3(a). Thus, for both the ordered and the paramagnetic region in DTC, no correlation between magnetism and electric polarization is observed. By contrast, Figure 3(b) shows results for DTN, where $\Delta P(H)$ and $M(H)$ are plotted at $T = 0.6$ K. Application of a magnetic field between 2 and 12 T induces canted antiferromagnetism of the Ni spins and the resulting magnetization tracks the electric polarization change [7].

3. Conclusions

In conclusion, DTN shows spatial-inversion-symmetry breaking and a magnetic field-modified electric polarization, whereas DTC is spatial-inversion symmetric and has no evidence of magnetic field-induced electric polarization changes. It is expected that the Ni magnetic forces create distortions and modify the angles of the thiourea molecules, in particular the double carbon-sulfur bonds, thereby creating a magnetic field-modified electric polarization. The observed electric polarization change as a function of magnetic field has been modified by the sum of exchange striction and crystal electric field striction [7]. By contrast, any magnetostriction in DTC does not break the centrosymmetric crystal structure and thus does not change the electric polarization.
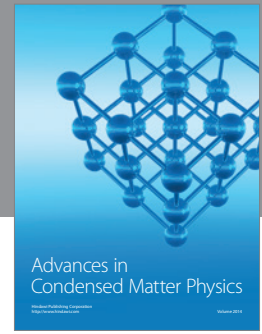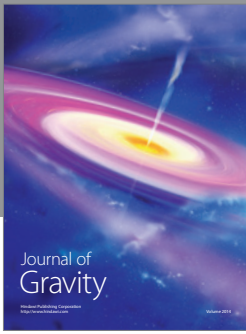
Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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