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Multiferroic behavior in organo-metallics

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Abstract. The study of multiferroic (MF) and magnetoelectric (ME) materials seeks to understand and harness the coupling between electric and magnetic polarizations. To date, research into ME and MF bulk materials has largely focused on inorganic oxides and only a relatively small number of materials have been found with significant ME couplings. We explore organo-metallics where transition metal ions are incorporated into a flexible and designable organic lattice. We present recent results on ME and MF behavior in single crystals of the organo-metallic compounds $NiCl_2$-$4SC(NH_2)_2$ and $CuCl_2$-$2(CH_3)_2SO$.

1. Introduction

Magnetoelectrics (ME) are materials in which a magnetic field H can modify the electric polarization P and conversely, an electric field E can modify the magnetization M. ME multiferroics are a subset of ME in which both M and P involve long-range order and the resulting diverging susceptibilities at the transitions lead to potentially stronger magnetoelectric coupling [1–4]. Research in this field is motivated by the promise of devices with new functionality as well as improving the speed, energy-efficiency and size of existing circuits. Most ME and multiferroics are transition-metal oxides or fluorides where the magnetoelectric interactions are mediated via superexchange through the oxide and fluoride anions. Magnetoelectric interactions can also be expected in other materials such as organo-metallic solids and very recently a few examples have been reported [5–7], thereby opening a new field of materials to exploration of these effects. Organic materials tend to possess soft lattice structures that can be easily modified by magnetic forces, leading to large magnetic field-induced changes in P. 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. Ferroelectricity is known to occur in a number of organic molecules [8], and was most recently discovered above room temperature in croconic acid [9]. In this paper we present two examples of magnetic field-induced electric polarizations in organo-metallic materials. In the first, $NiCl_2$-$4SC(NH_2)_2$ (DTN), thiourea $(SC(NH_2)_2)$ is electrically polar and an H-induced P is likely due to magnetic forces distorting the lattice and thus the angles of these polar molecules. The second example, $CuCl_2 \cdot 2[(CH_3)_2SO$ (CDC), is a multiferroic material in which a non-collinear magnetic order occurs in magnetic fields that breaks spatial inversion symmetry (SIS),

thereby creating the necessary symmetry conditions for a net P to form that is closely coupled to the magnetic order and the magnetic field.
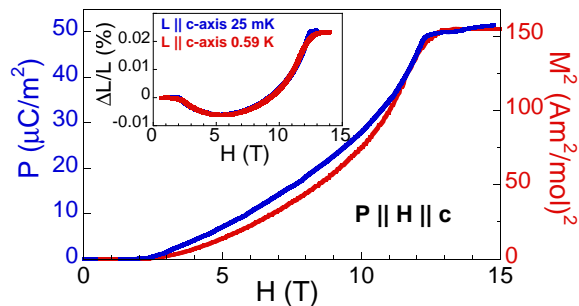
2. $NiCl_2$-$4SC(NH_2)_2$ (DTN)

Figure 1. DTN: Comparison of the electric polarization P [7] and the square of the magnetization M^2 vs magnetic field H [10] at 0.55 K. Inset: Percentage length change ΔL of the sample along the c-axis as a function of $H||c$ relative to its zero field value [11].
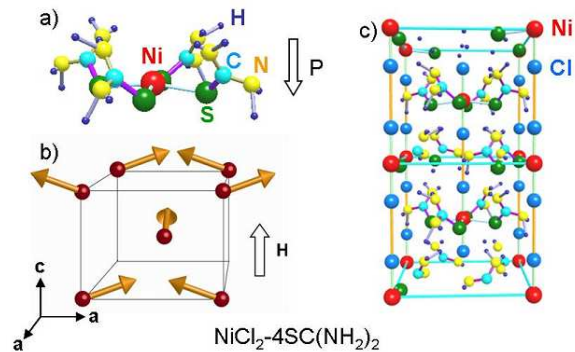

Figure 2. Crystal structure of DTN showing a) the thiourea coordination around the Ni ions and the likely direction of P, b) the Ni spins for $2 \leq H \leq 12$ T, and c) two unit cells of the crystal structure.

DTN is a magnetic field-induced antiferromagnet in which superexchange coupling between Ni spins creates long-range order in a dome-shaped region of $T - H$ space between $2 \leq H||c \leq 12$ T with a maximum T_N of 1.2 K at about 5 T [12]. Uniaxial anisotropy along the c-axis creates a zero-field spin gap of ~ 10 K between the Ni $S_z = 0$ and $S_z = 1$ states, which is closed with applied H. At 2 T, the Ni spins form an XY antiferromagnetic (AFM) structure with the spins lying perpendicular to c, and gradually cant with increasing field until they saturate at 12 T. As shown in Fig. 1, P along the c-axis is also induced above 2 T and roughly follows the square of the magnetization M^2 [7], increasing until 12 T and then saturating. The ME effect is bilinear, such that P always points along the same direction regardless of the sign of H. Empirically, we find that M^2 most closely tracks P both in its H-dependence and the fact that it is also bilinear in H. We suspect that the origin of P is the highly polar sulfur-carbon double bond in the thiourea molecules, which all tilt in the same direction along the c-axis (see the crystal structure in Fig. 2). Since the crystal is relatively soft, the magnetic forces between Ni spins can distort the lattice and we would expect the angles of the thiourea molecules to change as well. The relative change in length $\Delta L/L$ of the c and a-axis as a function of H is shown in the inset to Fig. 1. It was shown [11] that when the Ni spins are anti-aligned along the c-axis (the direction of strongest AFM coupling) the AFM bonds are satisfied and the Ni spins can reduce their energy by attracting each other, increasing the AFM coupling. This occurs between 2 and 5.5 T. However, as the Ni spins cant along the c-axis, they become increasingly aligned and thus start to repel each other, leading to a change in sign of $\Delta L/L||c$ at 5.5 T. The angles of the thiourea molecules, whose axes are tilted between c and a may not be a strict function of the c-axis magnetostriction effect. No hysteresis is observed in $P(E)$ or $P(H)$, nor do we see signatures of the 2 and 12 T transitions in the dielectric constants. Thus we conclude that only M and not P in DTN result from long-range order, thus DTN is a magneto-electric, not a multiferroic.
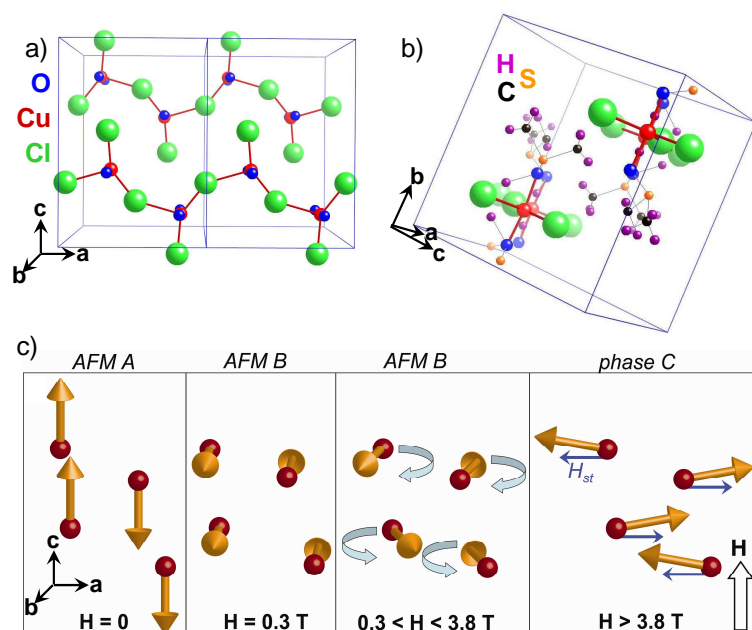
Figure 3. Crystal structure of CDC showing zig-zag Cu-Cl chains. b) Structure showing the organic molecules that mediate AFM exchange along the b-axis. c) Effect of applied H on the Cu $S = 1/2$ spins (shown as arrows) for one unit cell. The effective field-induced staggered magnetic fields H_{st} from spin-orbit couplings are indicated in the final panel [6].
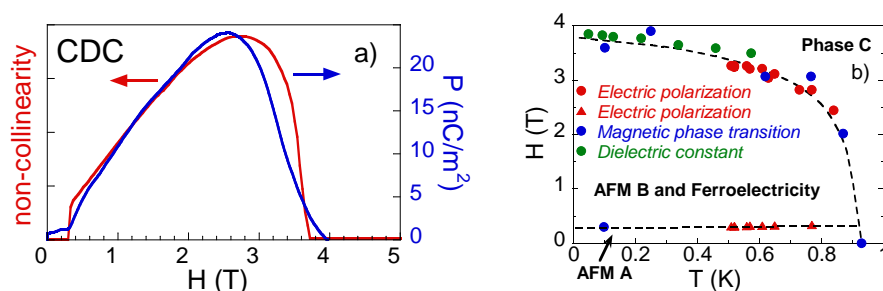

Figure 4. a) $P(H)$ of CDC compared to the non-collinearity of the spins (see ref. [6]). b) H-T phase diagram showing regions of collinear and non-collinear antiferromagnetism (AFM A and B), ferroelectricity, and the spin-orbit-induced phase (phase C) that occurs at high fields for H along [001].

3. $CuCl_2 \cdot 2[(CH_3)_2SO]$ (CDC)

CDC is one of the first examples of an organo-metallic in which multiferroic behavior is clearly established [6]. In this compound, the Cu spins form a non-collinear magnetic structure in applied H that breaks SIS and allows a net P to occur. The crystal structure and orientation of the Cu $S = 1/2$ spins are shown in Fig. 3. The details of the spin arrangements, AFM couplings, and spin-orbit interactions were unraveled via inelastic neutron diffraction and specific heat measurements [13, 14]. The non-collinearity of the Cu spins results from a competition between an AFM superexchange interaction that favors one type of AFM order (labeled AFM A in Fig. 3c), and local staggered effective magnetic fields from spin-orbit couplings that favor a different AFM spin arrangement (phase C in Fig. 3c). Since the spin-orbit couplings are H-dependent, the relative strength of these two competing interactions can be tuned with applied magnetic field. The result is that after a spin-flop transition occurs at 0.3 T, the spins rotate from the b to the a-axis and become non-collinear in the process for fields between 0.3 and 3.8 T. In this magnetic field range, the SIS-breaking magnetic structure leads us to expect a net P and indeed this can be observed in Fig. 4a. Here $P(H)$ is plotted together with a measure of the

non-collinearity of the spins (actually the product of the two order parameters resulting from AFM superexchange and spin-orbit couplings) [6]. The phase diagram in Fig. 4b demonstrates that the observed region of non-collinear spins and net P exactly overlap. As described in ref. [6], this material is multiferroic since the P undergoes an actual phase transition, which can be observed asa peak in the dielectric constant at 3.8 T, and P is hysteretic and can be switched by a sequence of applied H pulses.

In summary, we show magnetoelectric and/or multiferroic behavior in two organo-metallic materials. In DTN, the polar nature of thiourea molecules is combined with Ni magnetism to create a net H-induced P of 50 $\mu C/m^2$. Thiourea itself is a potent ferroelectric with a P of 3000 $\mu C/m^2$ below 170 K. In a recent review of organic ferroelectrics [8], thiourea was identified as a promising candidates for ferroelectricity and thus for the construction of magnetoelectric materials in organic materials. In pure thiourea P is thought to originate from the slight misalignment of nearly oppositely aligned thiourea pairs. This work on DTN demonstrates that magnetism can indeed be incorporated into an organo-metallic lattice with thiourea, creating a net magnetoelectric effect.

In CDC, simultaneous phase transitions in the magnetization and electric polarization occur as a function of magnetic field, allowing a SIS-breaking structure to occur between 0.3 and 3.8 T. The H-induced suppression of both the magnetic and electric orders at 3.8 T results in a novel magnetoelectric quantum critical point. CDC is an example of using a complex non-collinear spin structure that breaks SIS to modify the lattice symmetry and allow a net P to occur. In this type of multiferroic, the non-collinear structure often result from competing or frustrating magnetic interactions (see e.g. [15] and references therein).

4. Acknowledgments

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