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Elastic coupling and anelastic relaxation associated with multiple phase transitions in *para*-chloroanilinium tetrachlorocuprate, $[p\text{-}ClC_6H_4NH_3]_2CuCl_4$

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HIGHLIGHTS

- Use of elasticity measurements to probe structural phase transitions.
- Use of elasticity measurements to probe dynamic processes.
- Using elasticity measurements to probe molecular species.
- Evidence for magneto-elastic coupling as a probe for magnetic phase transitions.

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ABSTRACT

The perovskite-like salt $[p\text{-}ClC_6H_4NH_3]_2CuCl_4$ **1** exhibits a wealth of magnetic and structural phase transitions which have been probed by variable temperature single crystal X-ray diffraction, SQUID magnetometry, resonant ultrasound spectroscopy (RUS), EPR spectroscopy, DSC measurements and DFT calculations. Single crystal X-ray diffraction studies between room temperature and 3 K reveal a rich tapestry of structural changes; at 298 K the structure conforms to a monoclinic setting but undergoes a first order phase transition upon cooling below ~275 K to a higher symmetry orthorhombic cell. This is facilitated by a transition to an intermediate phase at ~277 K. Whilst the intermediate phase has a limited stability window (~2 K) and has not been structurally determined, the two discrete phase transitions at 275.5 K and 277 K have been clearly detected by differential scanning calorimetry, EPR spectroscopy and RUS studies. On further cooling a dynamic relaxation process is observed in RUS measurements, evidenced by a Debye-like peak in the dissipation at ~140 K. Residual electron density maps from single crystal X-ray diffraction studies reveal that this may be associated with a freezing out of the $NH_3\cdots Cl$ hydrogen-bonding between cation and anion frameworks upon cooling. The activation barrier for this order/disorder process was estimated to be at least 27 kJ mol^{-1} from the RUS data. Variable temperature dc SQUID data reveal that **1** is a 2D ferromagnet with antiferromagnetic interactions between layers below 9 K. Analysis of the temperature dependence of the magnetic susceptibility for $T > 40$ K reveals that **1** exhibits Curie–Weiss behaviour with $\theta = +22.8$ K indicative of dominant ferromagnetic interactions. Good agreement is observed between the strength of the ferromagnetic interaction extracted from the Weiss constant ($J/k = +22.8$ K) and that calculated by DFT ($J/k = +25$ to $+28$ K) and from EPR studies ($J/k = +17$ K). The presence of short range ferromagnetic interactions is reflected in a marked temperature dependence of the g-factors determined from EPR spectroscopy below 20 K and possibly a small elastic anomaly in the RUS data. RUS studies indicate a very small elastic anomaly associated with the transition to long range order, implying weak or no magnetoelastic effect. At fields above ~15 G a spin flip transition is induced and **1** displays metamagnetic behaviour, with a saturation magnetization of 0.96 μ_B.

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† Dedicated to Dr Andres Goeta (1965–2011) whose friendship and enthusiasm for science will be greatly missed.

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1. Introduction

The series of ammonium salts $[RNH_3]_2MCl_4$ adopt a two-dimensional layered, perovskite-like structure in which the metal is six-coordinate and generates a corner-sharing octahedral structure in which the organic cations are accommodated between the MCl_4 layers. Derivatives where M = Cu(II) offer a rich vein of chemistry compared to other compounds in this series. Willett showed that the relative orientations of the Jahn–Teller distortion on neighbouring ions lead to ferromagnetic interactions via the Cu–Cl–Cu bridge [1]. Bulk ferromagnetism in the series $[ArNH_3]_2CuCl_4$ was reported to occur in the region 7.5–11 K and has been ascribed to additional dipolar interactions between the layers [2]. In addition to magnetic ordering, some derivatives have been shown to be thermochromic [3] and this has been tentatively assigned to changes in hydrogen-bonding patterns. Despite the diversity of changes in physical response associated with this family of salts, detailed structural studies are still necessary to further elucidate the details of these changes.

Amongst the anilinium derivatives, $[p\text{-}ClC_6H_4NH_3]_2CuCl_4$ **1** has a particularly rich behaviour. A previous crystallographic study revealed a distorted perovskite-type structure at room temperature (monoclinic $P2_1/c$) [4] and several phase transitions have been identified without full structural characterization. Nuclear quadrupole resonance has been used to identify two transitions over a very small temperature range at 275.5 and 277 K [5,6], and thermochromic transitions have been reported at 294 K (yellow–orange) and 214 K (orange–green) respectively [3]. The thermochromic transition at 294 K has been associated with a discontinuity in the magnetism and was ascribed to a weakening of the NH···Cl hydrogen bond whereas the transition at 214 K is reflected in a subtle change in gradient of the magnetic susceptibility and was proposed to be associated with a transformation to near square-planar layers [3]. Previous studies into the magnetic properties have produced conflicting results and the compound has been assigned as being a ferromagnet or as an antiferromagnet with a metamagnetic ('spin-flip') transition around 15 Oe [3,4,7]. In the present study we have probed the structural and magnetic phase transitions through a combination of SQUID magnetometry, X-ray crystallography, resonance ultrasound spectroscopy (RUS), DSC measurements, DFT calculations and EPR spectroscopy. These have led us to reinterpret the previous observations about the nature of the phase transitions in this system and may provide some insight into the nature of likely phase transitions in other related perovskite structures within this family. In particular, elasticity and acoustic dissipation data from RUS measurements provide evidence for coupling of structural and magnetic changes with strain.

Resonant ultrasound spectroscopy [8] has been used extensively to study elastic relaxations associated with phase transitions, including some recent examples of ferroelastic, ferroelectric and relaxor oxide perovskites (e.g. Walsh et al., 2008 [9], McKnight et al., 2009 [10], Thomson et al., 2010 [11], Carpenter et al., 2010 [12], 2012 [13], Farnsworth et al. [14]) but is not well known in the chemistry literature. The basic principle is that mechanical resonances are excited in a small sample with dimensions typically in the range 1–5 mm. The square of the frequencies of these scale with the elastic constants of the sample and the resonant peak widths provide a measure of acoustic dissipation (energy loss) due to defects such as ferroelastic twin walls. Since the fundamental property being investigated is elasticity, it follows that any change in structure which couples with strain will usually be detected. Elastic constants can change by tens of % for strains of only a fraction of % (e.g. Carpenter and Salje 1998) [15]. In systems where there is a paramagnetic-magnetically ordered phase transition then magneto-elastic coupling can lead to additional changes in RUS frequencies with temperature [16,17]. Also relevant in the present context is a study of the mineral lawsonite, $CaAl_2(Si_2O_7)(OH)_2\cdot H_2O$, in which it was found that changes in hydrogen bonding give rise to characteristic patterns of acoustic dissipation [18] which must also involve some coupling with strain. Thus there is scope for investigating the dynamics of bonding changes between the organic components of metal organic frameworks.

2. Experimental methods

2.1. Synthesis

Copper(II)chloride (0.134 g, 1 mmol) and *p*-chloroaniline (0.25 g, 2 mmol) were dissolved in ethanol (100 ml) and 10 drops of conc. hydrochloric acid were added. The solution was heated under reflux for 30 min and then left to cool to room temperature and finally cooled to 4 °C. The brown, plate-like crystals (0.24 mg, 52%) produced were isolated via gravity filtration. Larger crystals for the RUS studies were grown by slow evaporation of a saturated ethanol solution at room temperature.

2.2. RUS

A single crystal of irregular shape and mass 18 mg was used in the low temperature RUS experiments. The sample was placed between the two transducers across a pair of faces in a mount which was lowered vertically into a helium flow cryostat, as described by McKnight et al. [18]. A few mbars of helium were added to the sample chamber to allow heat exchange. Temperatures have been calibrated against the 106 K transition in $SrTiO_3$ [19] and are believed to be accurate to within ±1 K. Data were collected automatically in a cooling and heating cycle with a settle time of 15 min at each temperature to allow for thermal equilibration. The sample was cooled from 280 to 10 K in 30 K steps before further cooling to 4 K. Measurements were then taken up to 20 K in 1 K steps, from 20 to 130 K in 5 K steps, 130–150 K in 1 K steps, 150–265 K in 5 K steps, 265–285 K in 1 K steps and 285–315 K in 5 K steps. A second set of measurements on a different crystal of irregular shape and mass 14 mg was taken over the following temperature range: 265–273 K in 1 K steps, 273–279 K in 0.1 K steps, 279–284 K in 1 K steps, 284–279 K in 1 K steps, 279–273 K in 0.1 K steps 273–265 K in 1 K steps. All spectra were collected in the frequency range 100–1200 kHz with 50,000 data points per spectrum. Spectral analysis was undertaken using Igor Pro (Wavemetrics). Selected peaks were fit with an asymmetric Lorentzian function to obtain the peak frequency, f, and width at half maximum height, Δf. Elastic constants scale with f^2 and the inverse mechanical quality factor, Q^{-1}, was calculated as $\Delta f/f$ (large Q^{-1} implies high attenuation).

2.3. Magnetism

The magnetic susceptibility for **1** was measured on a Quantum Design MPMS SQUID magnetometer with a polycrystalline sample mounted in a gelatin capsule. Variable temperature (5–300 K) measurements were undertaken in applied fields of 100, 500, 1000 and 2500 G with the sample cooled to base temperature in zero field and measurements taken in the range 5–20 K in 1 K steps, 20–50 K in 2 K steps and 50–300 K in 5 K steps. Variable field measurements were undertaken at 5 K with measurements in the range 0–500 G in 50 G steps, 500–1000 G in 100 G steps and from 1000 to 20,000 G in 1000 G steps. Data were corrected for sample diamagnetism (Pascal's constants) and for the gelatin capsule.

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