Strong magnetoelastic coupling in CrOCl

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The compounds *M*OX (*M* = Ti, V, Cr; X = Cl, Br) are isostructural and crystallize in the orthorhombic FeOCl structure-type with space group $Pmmn$. TiOCl and TiOBr have recently attracted interest, because of their properties related to the presence of quasi-one-dimensional (1D) $S = 1/2$ magnetic chains of Ti atoms [1, 2]. Upon cooling, TiOCl undergoes two phase transitions. Below T_{c2} = 90 K the crystal structure is incommensurately modulated [3, 4]; below T_{c1} = 67 K a twofold superstructure exists, which has been interpreted as a spin-Peierls state [1, 5]. Both transitions are accompanied by anomalies in the magnetic susceptibility, which indicate the development of magnetic order at low temperatures. TiOBr exhibits a similar series of phase transitions [6].

VOCl (S = 1) undergoes one phase transition at $T_{\rm N} = 80.5\,(5)$ K towards a state of antiferromagnetic (AF) order at low temperatures [7]. Employing synchrotron radiation at beamline D3 of Hasylab, we have recently found that the magnetic transition is accompanied by a monoclinic lattice distortion [2, 8]. This finding indicates a strong magnetoelastic coupling in VOCl, and it has profound consequences for the interpretation of the twofold magnetic superstructure [8, 9].

CrOCl ($S = 3/2$) undergoes one phase transition towards an AF state with a fourfold magnetic supercell [10]. In previous work the orthorhombic lattice symmetry was assumed to persists down into the magnetically ordered state [10]. We have measured temperature-dependent X-ray diffraction with synchrotron radiation at beamline D3 of Hasylab, which has revealed the development of a monoclinic lattice distortion at the first-order magnetic transition at $T_{\rm N}$ = 13.5 K.

Single-crystal X-ray diffraction with synchrotron radiation has been performed between room temperature and T = 8 K on the four-circle Huber diffractometer at beamline D3 of Hasylab. So-called ω–2θ maps have been measured at selected temperatures for the reflections $(0\bar{2}5)$, (204) and $(2\bar{2}0)$. Narrow detector slits of 6×0.02 mm^2, corresponding to an acceptance angle of of 0.0031° into the direction of 2θ, thus allow the accurate measurement of very narrow profiles of Bragg reflections. All three reflections appear as single maxima in the ω–2θ maps down to T = 15 K, indicative for orthorhombic lattice symmetry. A splitting in 2θ of any of the chosen reflections would indicate the presence of a twinned monoclinic crystal with a monoclinic angle of α, β or γ, respectively. We have found that $(0\ \bar{2}\ 5)$ is split below $T_{\rm N}$ = 13.5 K in both 2θ and ω (Fig. 1). This shows that the lattice is monoclinic with a unique **a**-axis in the magnetically ordered state. The magnitude of α has been derived from the splitting of the $(0\ \bar{2}\ 5)$ reflection. Its temperature dependence clearly shows the magneto-elastic phase transition to be of first order (Fig. 2).

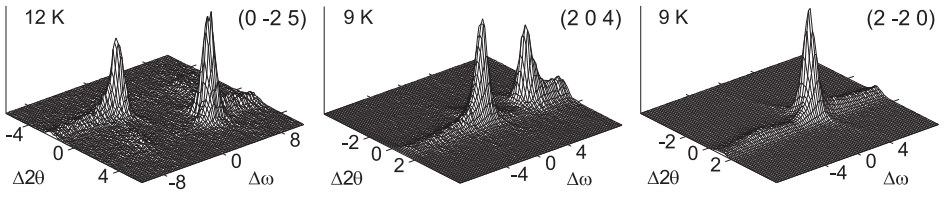

Figure 1: Diffracted intensity as a function of the scattering angle 2θ and the crystal orientation ω for selected reflections. $\Delta 2\theta$ and $\Delta\omega$ indicate the deviation from the center of the scan in units of 0.01°. Figure taken from [11].

While a splitting in 2θ might have been obtained by powder diffraction experiments, any splitting in ω can only be observed in single-crystal diffraction. At $T = 9$ K we have found that $(2\ 0\ 4)$ is

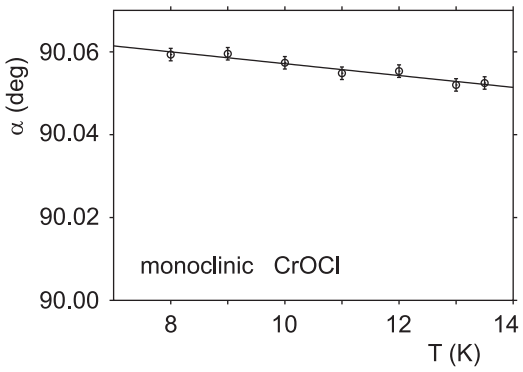

Figure 2: Temperature dependence of the monoclinic angle α as calculated from the observed splitting in 2θ of the reflection $(0\,\bar{2}\,5)$ (see Fig. 1). $\alpha = 0^\circ$ for $T > T_\mathrm{N} = 13.5$ K. Figure taken from [11].

split in ω, while $(2\,\bar{2}\,0)$ remains sharp (Fig. 1). These results show that the monoclinic distortion is achieved through a rotation of the $\mathbf{b}$-axis as opposed to a rotation of the $\mathbf{c}$-axis. The single-crystal X-ray diffraction experiments at beamline D3 thus have shown that the monoclinic lattice distortion is achieved by distortions of each single layer, which is the required mode of distortion for lifting the frustration for AF order on the orthorhombic lattice. This is strong evidence that shows that the monoclinic distortion is driven by the magnetic order [11].

In a second experiment, q-scans along $\mathbf{b}^*$ have been performed for selected reflections. Superlattice reflections indicate a nuclear modulation for $T < T_\mathrm{N}$ with a wavevector of $\mathbf{q}_X = (0, 1/2, 0)$ that is two times the wavevector of the magnetic superstructure. Again, this can be understood as a structural distortion driven by the AF magnetic order. Based on the results of experiments at beamline D3 of Hasylab on TiOCl, VOCl and CrOCl a model has been developed that explains the different behaviors of these isostructural compounds in terms of different orbital order [11].

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