Incommensurate structure of the spin-Peierls compound 
TiOCl in zero and finite magnetic fields

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Recently, the titanium-based oxohalides TiOX (X=Cl, Br) have been discussed as new unconventional inorganic spin-Peierls systems [1]. They crystallize in an orthorhombic structure with Ti-O bilayers within the ab-plane well separated by Cl/Br ions. Quasi-1D S=1/2 spin chains along the crystallographic b-axis are formed via orbital ordering giving rise to strong direct exchange with an exchange constant of \( J/k_B \approx 660 \) K [1]. For TiOCl, the low temperature spin-Peierls state is established by a step decrease of the magnetic susceptibility below \( T_{c1} = 67 \) K [1], accompanied by a simultaneous lattice dimerization of the Ti\(^{3+}\) ions, as evidenced by corresponding superlattice reflections showing a doubling of the unit cell along the b-axis [2]. A wealth of experimental results have established a first order phase transition from the spin-Peierls ground state into a second, intermediate phase at \( T_{c1} = 67 \) K, which extends up to \( T_{c2} = 91 \) K where a second order phase transition separates the intermediate phase from the normal paramagnetic state at high temperatures. The nature of the intermediate phase of TiOCl has not yet been clarified. We performed a detailed x-ray diffraction study on single crystalline TiOCl to elucidate the nature of the intermediate phase and to investigate any magnetic field effect of the phase transitions. This is motivated by a large magnetic field dependence of the incommensurate structure observed above a threshold magnetic field in other spin-Peierls compounds such as TTF-CuBDT [5] and CuGeO\(_2\) [6].

Magnetic field dependent single crystal x-ray diffraction measurements have been performed at the beamline BW5 of HASYLAB using an incident photon energy of 100 keV. The sample was mounted in a cryomagnet allowing for temperatures \( 1.6 \leq T \leq 300 \) K in horizontal fields up to \( B = 10 \) T. The sample with a size of 1x1x0.01 mm\(^3\) was oriented with the bc-plane in the horizontal scattering plane. The magnetic field was oriented along the scattering vector in the chain direction. By tilting the cryomagnet, also small values in \( h \) were accessible. At low temperatures \( T = 10 \) K, a number of superlattice reflections along the chain direction \((0, k+0.5, 0), k = 0, 1, 2\) have been recorded. The strongest intensity was found for \((0, 1.5, 0)\). Monitoring this reflection upon temperature clearly confirmed a first order phase transition at 67.5 K. Within the experimental accuracy, the intensities of the \((0, 1.5, 0)\) reflection in zero field and in an external magnetic field of 10 T were identical. At \( T_{c1} \) for \((0, 1.5, 0)\) reflection splits into two incommensurate satellites which also show an additional incommensurate component along \( h \). The observed incommensurate reflections are \((\pm \delta, \epsilon, 0), (\pm \delta, 2 - \epsilon, 0)\) and \((\pm \delta, 2 + \epsilon, 0)\) consistent with space group \( Pnmn \). The incommensurately modulated intermediate phase can be described by a propagation vector \( \mathbf{q} = (\pm \delta, 0.5 + \epsilon, 0) \) with \( 0 \leq \delta \leq 0.078 \) and \( 0.4857 \leq \epsilon \leq 0.5 \). The satellites can be monitored up to \( T = 92.5 \) K where the undistorted orthorhombic structure of the paramagnetic phase is recovered. The temperature dependence of the two incommensurate components of the reflection \((\pm \delta, 2 - \epsilon, 0)\) is shown in Fig. 1. Fig. 1a, shows the \( k \)-component \( \epsilon \) and Fig. 1b, the \( h \)-component \( \delta \) of the incommensurate satellite for zero field and in an applied field of \( B = 10 \) T. An expanded view around \( T_{c1} \) is given in the corresponding insets. For both components, a small, but significant shift \( \Delta T_{c1} = -0.13 \) K of the phase transition temperature is observed in the external field of 10 T along the chain direction. Remarkably, the transition temperatures for the modulations along the \( h \)- and \( k \)-direction appear to be slightly different. A scan along \( k \) at \( T = 67.52 \) K shows a single peak at \( k = 1.5015 \) whereas a scan along \( h \) shows a peak splitting with \( \delta = \pm 0.03 \) at \( T = 67.54 \) K. Moreover, also the intensities of the satellite reflections exhibit slight changes thus confirming a small field induced modification
of the incommensurate crystal structure. The absolute values and the temperature dependence of the modulation vector in TiOCl are almost identical to those observed for TiOBr [4]. We therefore conclude that both, TiOCl and TiOBr exhibit the same kind of incommensurate modulation in their intermediate phase. Due to the large energy scale in TiOCl with an exchange constant of $J/k_B \approx 660$ K no significant magnetic field effects are expected within the accessible field range of conventional laboratory magnets. Our measurements in an external field of $B = 10$ T could not observe any significant change of the principal superlattice reflections of type $(0, k + 0.5, 0)$ characterizing the dimerized spin-Peierls ground state. However, a weak but significant field effect is found for the phase transition into the incommensurate phase with a field induced shift of the transition temperature of $\Delta T_{c1} = -0.13$ K for $B = 10$ T. The negative temperature shift indicates a stabilization of the incommensurate structure and a suppression of the antiferromagnetic spin singlet formation of the spin-Peierls ground state by the external field. These observations may be accounted for within the scenario of frustrated inter-chain interactions that give rise to a second, incommensurate phase [3]. The small magnetic field effect on the incommensurability confirms that the incommensurate modulation is of fundamentally different origin as the field-induced modulation observed in classical spin-Peierls systems [5, 6].

![Figure 1: Temperature dependence of the incommensurate components $\epsilon$ (a) and $\delta$ (b) of the $(\pm \delta, 2 - \epsilon, 0)$ reflection of TiOCl in the intermediate phase in zero field (open circles) and in an external field of $B = 10$ T (full circles). The insets show the incommensurate positions $\delta$ and $\epsilon$ in more detail around $T_{c1}$.](image)

References