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Incommensurate structure of the spin-Peierls compound TiOCl in zero and finite magnetic fieldsA. Krimmel,^{1,*} J. Stremper,² B. Bohnenbuck,² B. Keimer,² M. Hoinkis,^{3,4} M. Klemm,³ S. Horn,³ A. Loidl,¹ M. Sing,⁴ R. Claessen,⁴ and M. v. Zimmermann⁵¹*Experimentalphysik V, Elektronische Korrelationen und Magnetismus, Universität Augsburg, D-86159 Augsburg, Germany*²*Max-Planck-Institut für Festkörperforschung, Heisenbergstrasse 1, D-70569 Stuttgart, Germany*³*Experimentalphysik II, Institut für Physik, Universität Augsburg, D-86159 Augsburg, Germany*⁴*Experimentelle Physik 4, Universität Würzburg, D-97074 Würzburg, Germany*⁵*Hamburger Synchrotronstrahlungslabor HASYLAB at Deutsches Elektronen-Synchrotron DESY, Notkestrasse 85, 22603 Hamburg, Germany*

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We report on a detailed single crystal x-ray diffraction study of the unconventional spin-Peierls compound TiOCl. The intermediate phase of TiOCl is characterized by an incommensurate modulation which is virtually identical to that recently found in the homologue compound TiOBr. The first order phase transition between the spin-Peierls ground state and the incommensurate phase reveals the same kind of thermal hysteresis in both its crystal structure and magnetic susceptibility. A weak, but significant magnetic field effect is found for this phase transition with a field induced shift of the transition temperature of $\Delta T_{c1} = -0.13$ K for an applied field of $B = 10$ T along the chain direction. The field induced changes of the incommensurate crystal structure are compatible with a scenario of competing intrachain and interchain interactions.

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I. INTRODUCTION

Strongly correlated low dimensional spin systems have attracted great interest due to a large variety of fascinating physical properties. The reduced dimensionality often allows for a description by exactly solvable theoretical models which may clarify fundamental quantum mechanical aspects of solids, including phenomena of significant technological potential like high- T_c superconductivity. Moreover, the complex interplay between the different microscopic degrees of freedom (charge, spin, orbital, and lattice degrees of freedom) is at the heart of numerous phase transitions leading to exotic ground states. Considering a one-dimensional (1D) antiferromagnetic (AFM) $S=1/2$ spin chain, a coupling to the lattice may result in a spin-Peierls transition with a non-magnetic, dimerized ground state. The first example of an inorganic spin-Peierls compound is CuGeO_3 .¹ More complex physics is obtained if the spins are additionally coupled to charge or orbital degrees of freedom, as manifested, i.e., in a metal-to-insulator transition (MIT) in $\text{Na}_{1/3}\text{V}_2\text{O}_5$.²

Recently, the titanium-based oxohalides TiOX ($X=\text{Cl}, \text{Br}$) have been discussed as new unconventional inorganic spin-Peierls systems.^{3–15} They crystallize in an orthorhombic structure with Ti-O bilayers within the ab plane well separated by Cl/Br ions.¹⁶ Quasi-1D $S=1/2$ spin chains along the crystallographic b axis are formed via orbital ordering giving rise to a strong direct exchange with an exchange constant of $J/k_B \approx 660$ K.³ For TiOCl, the low temperature spin-Peierls state is established by a steep decrease of the magnetic susceptibility below $T_{c1} = 67$ K,³ 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.¹⁰ Infrared⁶ and Raman spectroscopy,⁷ as well as electron spin resonance (ESR)⁵ and nuclear magnetic resonance (NMR) experiments⁴ corroborated these results and revealed a spin excitation gap

of $\Delta = 430$ K. However, a conventional spin-Peierls scenario is insufficient to account for the physical behavior of TiOCl. 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. Based on the temperature dependence of the g factors and linewidth in ESR experiments⁵ and, in particular, on phonon anomalies found in Raman and IR spectroscopy^{6,7} it has previously been proposed that orbital fluctuations play an essential role and may extend well above T_{c2} up to 130 K. This interpretation has been further supported by recent specific heat measurements⁸ and is also in agreement with electronic structure calculations.^{3,17} Moreover, the importance of correlation effects has been revealed by combined local density approximation (LDA)+DMFT studies.^{11,18}

However, a continuously increasing amount of experimental evidence is excluding orbital degeneracy. ARPES measurements could not detect any evidence for phonon assisted orbital fluctuations,¹¹ in agreement with a very recent ESR study also ruling out orbital excitations.¹⁹ Moreover, recent polarization dependent optical measurements in combination with cluster calculations provide evidence that the orbital degrees of freedom are actually quenched.¹² Alternatively, it has been proposed that interchain interactions within the bilayers lead to an incommensurate spin-Peierls state below T_{c2} that locks in in a conventional commensurate dimerized phase below T_{c1} .¹²

In fact, such a behavior has been observed in the homologue compound TiOBr.¹⁵ TiOBr and TiOCl have the same electron configuration and crystal structure and exhibit similar physical properties. Like TiOCl, TiOBr shows two phase transitions at $T_{c1} = 27$ K and $T_{c2} = 47$ K. The low temperature

phase of TiOBr also shows a twofold superstructure along the b axis in agreement with a spin-Peierls ground state.^{15,20} Recently, a single crystal x-ray diffraction study on TiOBr revealed an incommensurate modulated structure for the intermediate phase,¹⁵ in accordance with optical data and cluster calculations.

Here we report on 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 (Ref. 21) and CuGeO₃ (Ref. 22).

II. EXPERIMENTAL RESULTS

Single crystals of TiOCl were prepared by chemical vapor transport¹⁶ from the starting materials TiCl₃ and TiO₂. The samples were characterized by magnetization measurements employing a SQUID magnetometer and the magnetic properties were found in excellent agreement with published results. Magnetic field dependent single crystal x-ray diffraction measurements employing synchrotron radiation have been performed at the beamline BW5 of HASYLAB (DESY, Hamburg). An incident photon energy of 100 keV was used. 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. A Cernox sensor calibrated in a field of $B=8$ T at 77 K was used as thermometer. The corresponding accuracy of the temperature values is approximately 0.02 K. The sample with a size of $1 \times 1 \times 0.01$ mm³ was oriented with the bc plane in the horizontal scattering plane. The magnetic field was oriented along the scattering vector in the chain direction. This geometry was possible due to the small scattering angles at high photon energies. 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 $(0, 1.5, 0)$.

Figure 1 shows the temperature dependence of the intensity of the $(0, 1.5, 0)$ reflection around the first phase transition at $T_{c1}=67.5$ K in a zero field and in an external field of $B=10$ T. As evident from Fig. 1, the intensity remains virtually constant at low temperatures, and starts to steeply decrease at 66.5 K and vanishes at 67.5 K. Within the experimental accuracy, no differences between the measurements in the zero field and $B=10$ T are observed with a marginal possible error of the temperature below 0.02 K.

Figure 2 shows the evolution of the low temperature $(0, 1.5, 0)$ reflection for increasing temperatures, covering essentially the temperature range of the second, intermediate phase $67.5 \text{ K} = T_{c1} \leq T \leq T_{c2} = 92.5$ K. At T_{c1} the $(0, 1.5, 0)$ reflection splits into two incommensurate satellites which also show an additional incommensurate component along k . Previous studies did not observe such incommensurate satellites.^{10,15} The improved and almost perfect crystalline quality of our present sample combined with the knowledge of the results of the bromide¹⁵ enabled us to determine such

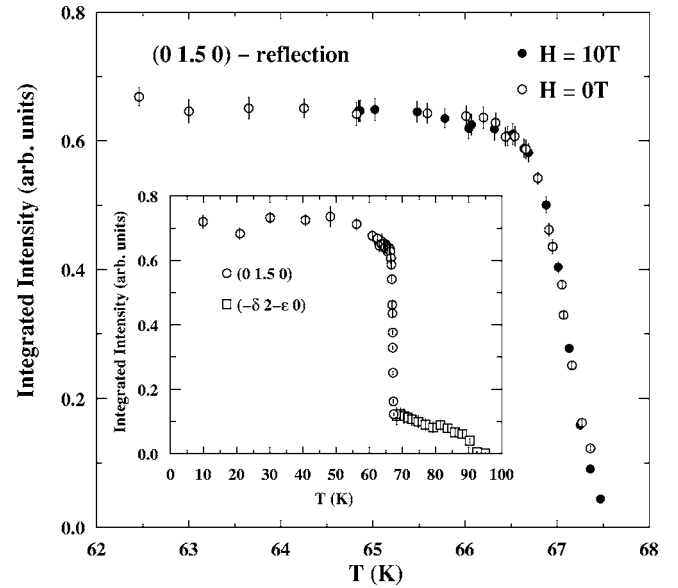


FIG. 1. Temperature dependence of the intensity of the $(0, 1.5, 0)$ superlattice reflection of TiOCl in the vicinity of the first phase transition around $T_{c1}=67$ K. Shown are measurements in a zero field (open circles) and in an external field of $B=10$ T (full circles), respectively. The inset shows intensities of both commensurate and incommensurate reflections over the whole temperature range.

an incommensurate structure also for the intermediate phase of TiOCl.

The observed incommensurate reflections are $(\pm\delta, \epsilon, 0)$, $(\pm\delta, 2-\epsilon, 0)$ and $(\pm\delta, 2+\epsilon, 0)$ consistent with space group $Pmmn$. 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 orthorhom-

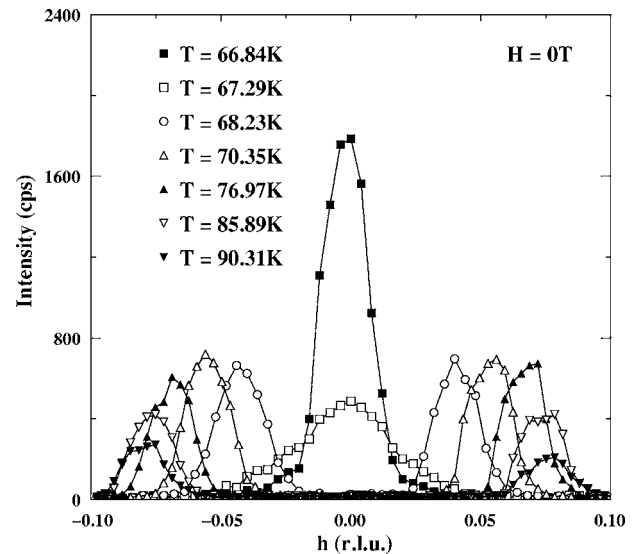


FIG. 2. Evolution of the $(0, 1.5, 0)$ superlattice reflection of TiOCl for various temperatures on passing through the first phase transition from the dimerized spin-Peierls ground state into the intermediate phase in zero field. The peak splitting indicates an incommensurate modulation of the intermediate phase.

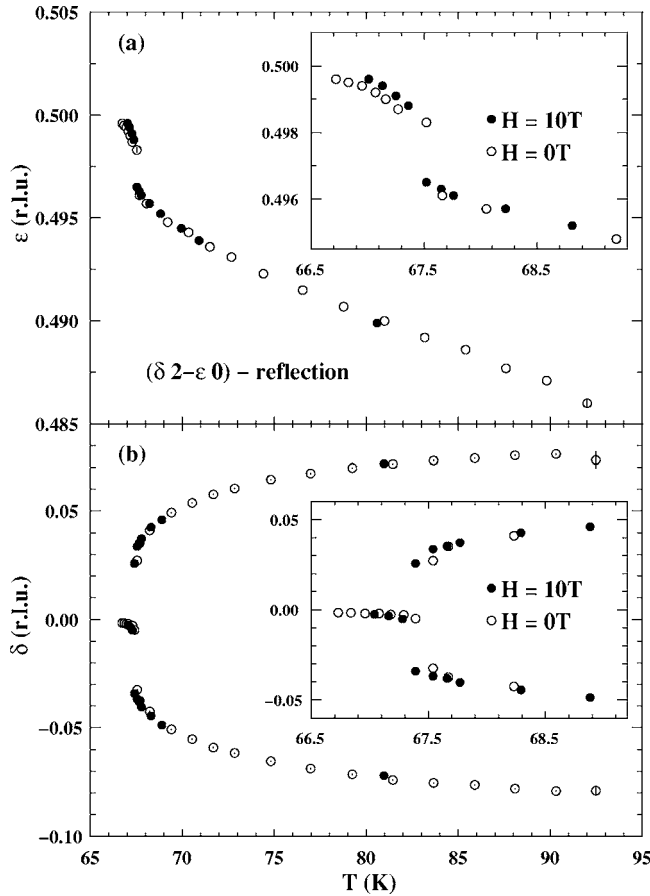


FIG. 3. Temperature dependence of the incommensurate components ϵ (a) and δ (b) of the $(\pm\delta, 2-\epsilon, 0)$ reflection of TiOCl in the intermediate phase in zero field (open circles) and in an external field of $B=10$ T (full circles). The insets show the incommensurate positions δ and ϵ in more detail around T_{c1} .

bic 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. 3. Figure 3(a), shows the k -component ϵ and Fig. 3(b), the h -component δ of the incommensurate satellite for the 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, the intensities of the satellite reflections exhibit slight changes also thus confirming a small field induced modification of the incommensurate crystal structure.

III. DISCUSSION AND CONCLUSION

We have performed a detailed single crystal x-ray diffraction study of the spin-Peierls compound TiOCl. However, it

should be noted that the present investigation does not represent a complete crystal structure determination. Due to geometric restrictions by use of a large cryomagnet, only reflections of type $(0, k, 0)$ were explored in detail for their temperature dependence and possible field effects. Therefore, the focus was on the phase transitions in order to elucidate the nature of the intermediate phase of TiOCl and its relation to the unconventional spin-Peierls transition.

The temperature dependence of the $(0, 1.5, 0)$ reflection is characteristic for a doubling of the unit cell along the b axis due to the dimerized spin-Peierls ground state.¹⁰ A sudden decrease of the intensity is observed at $T_{c1}=67.5$ K which confirms that the transition is of first order. Moreover, a corresponding thermal hysteresis of the intensity of this superlattice reflection is observed. In combination with the same type of hysteresis found in the magnetic susceptibility, it is concluded that the nonmagnetic, dimerized ground state of TiOCl is realized via a first order spin-Peierls transition.

Recently, the unconventional properties of TiOX ($X = \text{Cl, Br}$) have been interpreted in terms of frustrated inter-chain interactions within the bilayers.¹² Within this scenario, the spin-Peierls mechanism would give rise to an intermediate phase characterized by an incommensurate order with a subsequent lock-in transition into the commensurate dimerized ground state.¹² In fact, such an incommensurate modulated structure has recently been observed in TiOBr.¹⁵ The intermediate phase of TiOCl is also characterized by such an incommensurate structural modulation with a propagation vector $\mathbf{q}=(\pm\delta, 0.5+\epsilon, 0)$ with $0 \leq \delta \leq 0.078$ and $0.4857 \leq \epsilon \leq 0.5$, as evidenced by a corresponding peak splitting. The intermediate phase of TiOCl exhibits a two dimensional (2D) modulation within the Ti-O bilayers. The absolute values and the temperature dependence of the modulation vector in TiOCl are almost identical to those observed for TiOBr (for TiOBr, the published temperature dependence of the modulation vector is restricted to the x component or δ).¹⁵ We therefore conclude that both, TiOCl and TiOBr exhibit the same kind of incommensurate modulation in their intermediate phase. Apart from the incommensurability, this modulation is characterized by rather large displacements along the b axis (chain direction) and comparable small amplitudes along the a axis.¹⁵ The intermediate phase can be interpreted as either due to frustrated spin-Peierls interactions¹² or, alternatively, as a phase with competing 1D spin-Peierls interactions and 2D magnetic interactions which are coupled to the lattice modulation.¹⁵

A crucial test to identify a spin-Peierls state is its generic B - T -phase diagram.²³ 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 doubling of the b axis due to the commensurately 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 indi-

cates 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 interchain interactions that give rise to a second, incommensurate phase.¹² In TiOCl, the formation of spin chains along the b axis with a strong antiferromagnetic exchange results from orbital ordering of the xy orbitals^{3,17} with a corresponding strong magnetoelastic coupling. The orbital ordering further gives rise to interchain π bonding with a predominantly ferromagnetic exchange. Based on band structure calculations,¹⁷ the interchain exchange can be estimated to be one order of magnitude weaker than the principal exchange along the chains. The competition between these different exchange interactions leads to frustration and an incommensurately modulated crystal structure.¹² The application of an external magnetic field then slightly shifts the

equilibrium position of these competing interactions. 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.^{21,22} To conclude, we have determined the incommensurate modulation of the intermediate phase of TiOCl and find some small, but significant changes upon the application of an external field of $B = 10$ T along the chain direction. These results are compatible with a frustrated spin-Peierls scenario.

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