# X-ray Studies of Phonon Softening in $TiSe_2$

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## Introduction

The charge-density-wave transition in $TiSe_2$ which results in a commensurate (2 x 2 x 2) superlattice at temperatures below ~200K presumably involves softening of a zone-boundary phonon mode. For the first time, this phonon-softening behavior has been observed over a wide temperature range by synchrotron x-ray thermal diffuse scattering.

## Methods and Materials

Our experiment was performed at the undulator beamline of Sector 33, operated by the University, Industry, and National Laboratory Collaborative Access Team, at the Advanced Photon Source, Argonne National Laboratory. A single crystal of $TiSe_2$ was prepared following standard methods[1] and attached to the copper cold finger of a closed-cycle helium refrigerator by thermally conductive grease. The sample assembly was enclosed in a vacuum shroud equipped with a hemispherical Be dome for the x-ray measurements. Incident x-ray radiation was set at 8.1 keV, and the quasielastically scattered radiation was collected using a four-circle diffractometer setup.

## Results

Figure 1 shows typical scans along an *A-L-A* line in *k* space at various temperatures. The momentum transfer $\mathbf{q} \int (q_1, q_2, q_3)$ for each scan is constrained such that $q_1 = 1$, $q_2$ varies linearly between −0.55 and −0.35, and $q_3 = 7/2$. The observed intensity variation is derived from thermal diffuse scattering (scattering by thermally populated phonons).

$$I(\mathbf{q}) \propto \sum_{j=1}^{9} \frac{\left| F_j(\mathbf{q}) \right|^2}{\omega_j(\mathbf{q})} \coth\left( \frac{\hbar \omega_j(\mathbf{q})}{2 k_B T} \right) \qquad (1)$$

where the phonon structure factor $F$ is given by

$$F_j(\mathbf{q}) = \sum_{n=1}^{3} f_n(\mathbf{q}) \exp[-M_n(\mathbf{q}) - i\mathbf{q}\cdot\hat{\mathbf{o}}_n] \frac{\mathbf{q}\cdot\hat{\mathbf{e}}_{n,j}(\mathbf{q})}{\sqrt{\mu_n}} \qquad (2)$$

In the above equations, $n$ is an atomic index in a basis consisting of one Ti atom and two Se atoms, $j$ is an index for the nine phonon branches, and $f$, $M$, $\tau$, $\mu$, $\omega$, and $\hat{e}$ stand for the atomic scattering factor, the Debye-Waller factor, the atomic position vector in the basis, the atomic mass, the phonon frequency, and the phonon polarization vector, respectively.

In Fig. 1, one can clearly see a peak at $q_2 = -1/2$, which corresponds to the $L$ point in the Brillouin zone. This thermal diffuse peak is weak and broad near room temperature. It narrows and intensifies as the temperature decreases. The inset shows additional scans with a reduced intensity scale. As $T$ decreases below $T_c$ = 189 K, a resolution-limited Bragg peak emerges with an intensity increasing as $1 - (T/T_c)^2$ in accordance with the prediction of a Landau theory for a normal-to-lock-in phase transition.

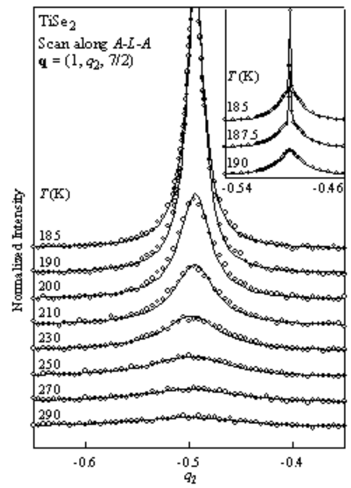


*FIG. 1. Linear scans of x-ray thermal diffuse scattering along an* A-L-A *line in reciprocal space;* q2 *= −1/2 corresponds to an L point. The sample temperature is indicated for each scan.*

The intensity variations as a function of $T$ and momentum transfer $q_2$, shown in Fig. 1, are analyzed using Eqs. (1) and (2) and a force constant model for the lattice dynamics. All force constants have been determined previously from a fit to the available neutron data at room temperature.[2] One of the force constants can be related to the softening, and this is employed as a fitting parameter for scans at various temperatures. The force constant resulting from the fit yields the phonon dispersion curves shown in the left panel of Fig. 2. The upper eight phonon branches are independent of temperature, while the lowest branch softens near the $L$ point as $T$ decreases towards $T_c$. At $T_c$, the $L_1^-$ frequency becomes zero, and a static lattice distortion sets in to form a (2 x 2 x 2) superlattice. This static distortion increases in amplitude as $T$ decreases, giving rise to an increasingly more intense Bragg peak as seen in Fig. 1. Figure 3 shows the frequency of the $L_1^-$ mode derived from our analysis. The solid circles represent data points above $T_c$, while the open circles are results obtained from the same analysis of the thermal diffuse peak with the Bragg peak ignored. The cusp in the curve allows us to pinpoint the transition temperature, which is in perfect agreement with the observed first appearance of a Bragg peak.

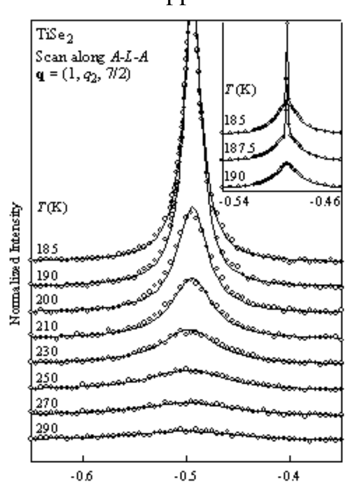


*FIG. 2. Phonon dispersion curves of $TiSe_2$ as a function of temperature. The lowest phonon branch softens under cooling towards $T_c$.*

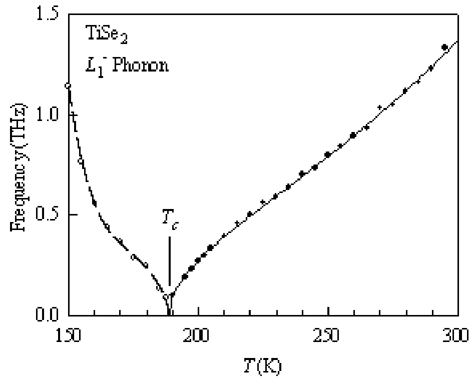


*FIG. 3. The filled circles represent experimentally deduced frequency of the* $L_1^-$ *phonon mode as a function of temperature. The open circles are results from the same analysis with the Bragg peak ignored. The curves are fits to the data.*

## Discussion

As mentioned in the introduction, the soft-mode concept is central to many theories of structural phase transitions. For $TiSe_2$, this predicted soft-mode behavior has never been observed directly by neutron scattering because of the lack of signal strength. With the advent of third-generation synchrotron radiation sources, phonon studies under conditions unfavorable to traditional neutron-scattering measurements become accessible.

## Acknowledgments

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## References

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