Characterization of phonon softening in the $TiSe_2$ charge density wave transition via x-ray scattering

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Introduction

Titanium diselenide crystallizes into a semimetallic layered structure typical of transition-metal dichalcogenides, whose preparation and physical properties are summarized in an exhaustive review article by Yoffe [1]. Upon cooling below about 200 K, $TiSe_2$ undergoes a structural and electronic phase transition described by the formation of a commensurate real-space $2a \times 2b \times 2c$ superlattice with the resultant folding of reciprocal space [2, 3].

This electronic phase transition can be described in terms of the softening of a transverse zone boundary phonon at the *L* point (1/2,0,1/2) in the Brillouin zone [2–4]. The softening of this mode as a function of temperature through the phase transition is, as of yet, unobserved and should yield information as to the order and character of the charge density wave (CDW) phase transition, the location of the basis atoms participating in the soft mode, and the amount of charge transfer between basis atoms as it affects the bond strengths.

In this User Activity Report, we report a characterization of this phonon mode softening through analysis of thermal diffuse scattering of x-rays along various line scans in *k*-space. The softening is detected as an increase in thermal diffuse scattering about the *L* point. A least-squares analysis based on a lattice dynamics calculation yields the temperature dependence of this softening behavior. This method compares favorably with traditional neutron scattering techniques (which have so far been unsuccessful in detecting the detailed mode softening behavior) in required sample volume and experimental simplicity.

Methods and Materials

Our experiment was performed at the undulator beamline of sector 33 (UNI-CAT - University, Industry, and National Laboratory Collaborative Access Team) at the Advanced Photon Source (APS). A single crystal of $TiSe_2$ was prepared following standard methods [1] and was freshly cleaved before being placed under vacuum. The sample was cooled by a closed-cycle helium refrigerator. Incident radiation at 8.1 keV was introduced and collected in a standard four-circle diffractometer setup. Line scans and rocking curves were recorded over many zones at various temperatures.

Results and Discussion

Typical line scans through the *L* point are shown in Figure 1. One can see a room-temperature phonon hump intensifying as the sample temperature decreases. A resolution-limited Bragg peak appears below the transition temperature. The solid curves represent fits to the diffuse peak using Eq. (1) for the first-order thermal diffuse scattering plus a constant background.

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

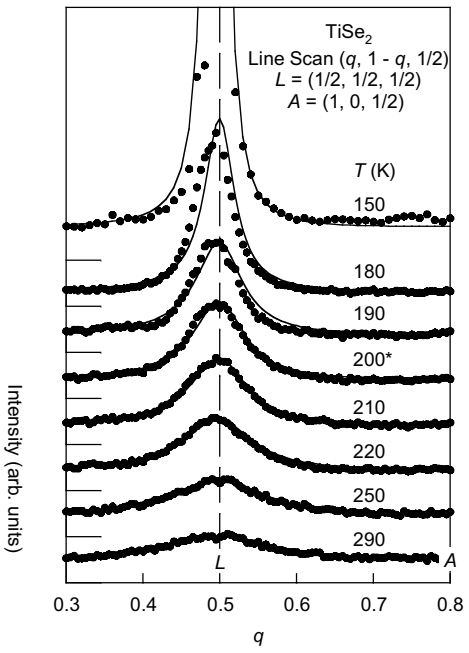

Figure 1: Typical line scans through the *L* point.

In Eq. (1) ω_j depends on **q** and are the phonon frequencies with associated polarization vectors $\hat{\mathbf{e}}_{n,j}$ for basis atom *n* in mode j = 1,...,9. In Eq. (2) f_n and M_n are the atomic scattering factor and the Debye-Waller factor, respectively, for basis atom *n* with mass μ_n.

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

The $1/\omega_j$ dependence of the cross section governs the intensity divergence for fully softened phonon modes. The polarization configuration in this experiment ensures the selection of the soft mode in the *A*-*L* direction. The fits shown in Figure 1 are based on a force constant model from Jaswal [5]. For the curves at different temperatures, the force constant *A* for the Ti-Se bond is allowed to vary as a function of *T*. Except for an overall normalization constant for all of the curves, there are no other fitting parameters in the model. Here one can see that the features of each line scan are successfully reproduced. The phonon dispersion at each temperature calculated from the force constants is shown in Figure 2.

Low-temperature phonon dynamics of $TiSe_2$ have been previously unattainable via traditional neutron scattering techniques. This work illustrates that x-ray scattering could be an important complementary tool. The fast data acquisition rate, simplicity of the experiment, and minimal requirement of sample volume make this method attractive for a wide range of applications in materials research.

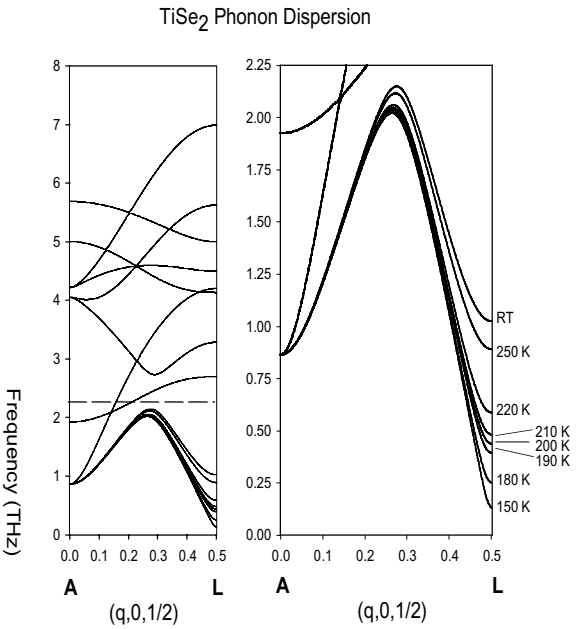

Figure 2: The phonon dispersion at each temperature calculated from the force constants.

Acknowledgements

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References

[1] J.A. Wilson and A.D. Yoffe, *Adv. Phys*. **18**, 193 (1969).

[2] F.J. Di Salvo, D.E. Moncton, and J.V. Waszczak, *Phys. Rev. B* **14**, 4321 (1976).

[3] N. Wakabayashi, H.G. Smith, K.C. Woo, and F.C. Brown, *Solid State Commun.* **28**, 923 (1978).

[4] K. Motizuki, N. Suzuki, Y. Yoshida, and Y. Takaoka, *Solid State Commun.* **40**, 995 (1981).

[5] S.S. Jaswal, *Phys. Rev. B* **20**, 5297 (1979).