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Lattice-induced modulation of a charge-density wave far from commensurability

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Using x-ray diffraction we have investigated whether the charge-density wave (CDW) is purely sinusoidal in the incommensurate (I) phase of $1T$-TaS_2. The second-order CDW satellite reflection is significantly more intense than a purely sinusoidal CDW model would predict. Our data suggest that the CDW is phase and amplitude modulated by the CDW-lattice interaction, despite the CDW system being far from commensurability.

The charge-density wave (CDW) wavelength is determined by the nesting properties of the Fermi surface and is not determined by the lattice periodicity alone. In a CDW system where the CDW is almost commensurate with the underlying atomic lattice, the influence of the CDW-lattice interaction on the CDW has been extensively studied theoretically and experimentally.[1-8] Close to commensurability, McMillan[1] theoretically examined the issue for the one-dimensional case and found that an additional periodic phase modulation of the CDW into commensurate domains should result. An interesting question is the extent to which the CDW-lattice interaction may induce a modulation of the CDW in a system where the CDW wave vectors are far from commensurability.

The incommensurate (I) CDW phase of $1T$-TaS_2 provides an excellent system for studying the CDW-lattice interaction in a CDW that is far from commensurability. Through x-ray diffraction, we have investigated whether the CDW periodic lattice distortion (PLD) is purely sinusoidal, rather than phase and/or amplitude modulated. We find second-order CDW satellite intensity in excess of that which can be explained by a purely sinusoidal PLD. The excess intensity is consistent with a phase and amplitude modulation of the CDW induced by the CDW-lattice interaction.

By x-ray diffraction we have measured the positions and integrated intensities of the (100) Bragg reflection, one of its first-order CDW satellites, and a second-order CDW satellite referred to the (201) Bragg reflection for a $1T$-TaS_2 crystal in the I phase at $T=363$ K (Fig. 1). The crystal (dimensions $0.4\times0.4\times0.01$ mm^3) was grown by a standard vapor transport technique.[9] We used a diffractometer with a "point and shoot" technique in which counts were sampled for a fixed time interval at points scanned through each peak parallel to each reciprocal axis. To each line profile a Gaussian function was fitted to extract peak coordinates, widths, and intensities. From the fitted widths and peak intensities of the line profiles, we obtained the integrated intensity.[10]

The measured first-order CDW satellite position is consistent with previous x-ray diffraction studies of the I phase.[11,12] For the first-order CDW satellite position we find

$$\mathbf{q}_{\mathrm{CDW1}}=1.282\mathbf{a}^*+0.002\mathbf{b}^*+0.333\mathbf{c}^* \; ; \tag{1}$$

uncertainties are ±0.002 for $\mathbf{a}^*$, $\mathbf{b}^*$, and $\mathbf{c}^*$ components.

In order to determine whether the CDW is purely sinusoidal we have investigated a second-order CDW satellite near the first-order satellite. For the second-order CDW satellite position we find

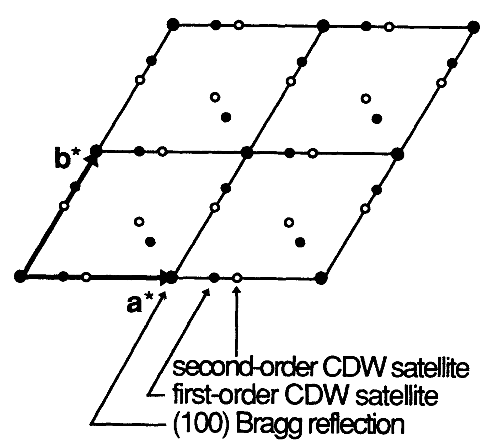

FIG. 1. Schematic of the reciprocal lattice projected onto the $\mathbf{a}^*$-$\mathbf{b}^*$ plane of $1T$-TaS_2 in the I phase. Large closed circles indicate Bragg reflections, small closed circles indicate first-order CDW satellites, and small open circles indicate second-order CDW satellites. Only CDW satellites on the $(h,k,\frac{1}{3})$ plane are shown. Light arrows point to the peaks measured in this study.

$$\mathbf{q}_{CDW2}=1.432\mathbf{a}^*+0.002\mathbf{b}^*+0.334\mathbf{c}^* \; ; \quad (2)$$

uncertainties are ±0.002 for **a***, **b***, and **c*** components. The observed second-order CDW satellite position is consistent with the measured CDW fundamental wave vectors found in this study. To the best of our knowledge, no intensity at the second-order satellite position in the *I* phase of $1T$-TaS_2 has ever been reported (or perhaps carefully investigated) before this study. The second-order satellite is much weaker than the first-order satellite and so it is more difficult to detect. A line scan profile through the second-order CDW satellite position along the **c*** axis in Fig. 2 shows an unmistakable peak.

Throughout this paper we will state the integrated intensities of CDW satellites relative to the integrated intensity of the (100) Bragg reflection. The experimentally determined first-order CDW satellite-integrated intensity $I(\mathbf{q}_{CDW1})_{expt}=3.06\times10^{-2}$, and the second-order CDW satellite-integrated intensity $I(\mathbf{q}_{CDW2})_{expt}=2.75\times10^{-4}$. The uncertainties in intensity are ±10%. The observed satellite intensities are included in Table I under "Expt. intensity."

In order to determine whether these relative intensities are consistent with a purely sinusoidal PLD, one must compare them to the relative intensities calculated from the structure factor. For a polyatomic lattice with three equivalent purely sinusoidal CDW's, Chapman and Colella[12] have obtained the following form for the structure factor:

$$S(\mathbf{q})=\sum_i f_i(\mathbf{q})\exp[i(\tau_i\cdot\mathbf{G}+n_1\phi_{i1}+n_2\phi_{i2}+n_3\phi_{i3})]$$
$$\times J_{n_1}(\mathbf{q}\cdot\mathbf{A}_{i1})J_{n_2}(\mathbf{q}\cdot\mathbf{A}_{i2})J_{n_3}(\mathbf{q}\cdot\mathbf{A}_{i3})$$
$$\times\exp[-C(n_1^2+n_2^2+n_3^2)T] \; , \quad (3)$$

where $S(\mathbf{q})$ is the structure factor, **q** is the scattering vector for a given CDW satellite with Miller indices n_1, n_2, n_3, $f_i(\mathbf{q})$ is the form factor of the *i*th atom, τ_i is the basis vector of the *i*th atom, **G** is the reciprocal lattice vector of the CDW satellite's parent Bragg reflection, ϕ_{ij} is the phase of the *j*th CDW acting on the *i*th atom, J_{n_i} are integer order Bessel functions, and $\mathbf{A}_{ij}$ is the atomic displacement amplitude of the *j*th CDW acting on the *i*th atom. The second exponential factor is the phason temperature factor (PTF).[13] The PTF is the phason analog of the Debye-Waller factor. It accounts for the diminishment of CDW satellite intensity due to thermally excited CDW phase fluctuations. In the PTF, *T* is temperature and *C* is an experimentally determined parameter.

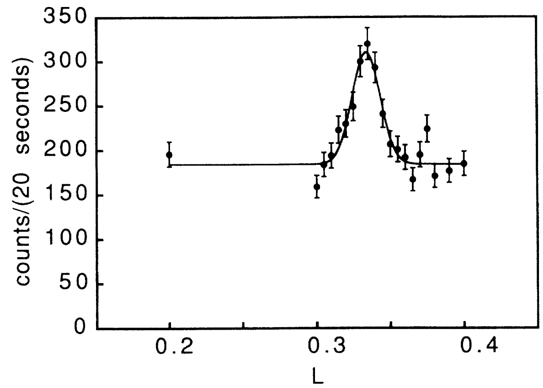

FIG. 2. Line scan profile though the second-order CDW satellite parallel to the **c*** axis obtained from x-ray diffraction at $T=363$ K in the *I* phase of $1T$-TaS_2.

We use Eq. (3), along with the values determined by Chapman and Colella[13] for ϕ_{ij}, $\mathbf{A}_{ij}$, and *C* from their x-ray diffraction study of $1T$-TaS_2 in the *I* phase, to calculate the relative intensities of the first- and second-order CDW satellites that we have measured. We obtain atomic form factors and anomalous dispersion corrections from standard tables.[14,15] In Eq. (3), for the first-order satellite, $\mathbf{G}=\mathbf{a}^*$, $n_1=1$, and $n_2=n_3=0$, and for the second-order satellite, $\mathbf{G}=2\mathbf{a}^*+\mathbf{c}^*$, $n_1=-2$, and $n_2=n_3=0$.

The calculated first-order CDW satellite intensity, $I(\mathbf{q}_{CDW1})_{calc}=2.84\times10^{-2}$, and the calculated second-order CDW satellite intensity $I(\mathbf{q}_{CDW2})_{calc}=7.83\times10^{-6}$. For the first-order satellite the experimental to calculated intensity ratio $I(\mathbf{q}_{CDW1})_{expt}/I(\mathbf{q}_{CDW1})_{calc}=1.08$ which is within our stated 10% uncertainty of the expected value of unity for the ratio. Thus for the first-order CDW satellite our results are in excellent agreement with the results of Chapman and Colella. However, for the second-order satellite the experimental to calculated intensity ratio $I(\mathbf{q}_{CDW2})_{expt}/I(\mathbf{q}_{CDW2})_{calc}=35.1$ which is dramatically different from the expected value of unity for the ratio. These results are summarized in Table I under "Calculated with PTF alone." We observe intensity at the second-order CDW satellite position in excess of that which can be explained by Eq. (3) in combination with previously determined parameters ϕ_{ij}, $\mathbf{A}_{ij}$, and *C*.

The PTF, though experimentally verified by Chapman and Colella between 363 and 423 K, provides an incomplete description of the effect of thermal fluctuations on

TABLE I. Comparison of the integrated intensities of a first- and second-order CDW satellite relative to the (100) Bragg peak as measured by x-ray diffraction with the results of our structure factor calculation for $1T$-TaS_2 in the *I* phase.

		Calculated with PTF alone		Calculated with PTF and ATF	
CDW satellite	Expt. intensity	Calc. intensity	Ratio of expt. to calc.	Calc. intensity	Ratio of expt. to calc.
$\mathbf{q}_{CDW1}$	3.06×10^{-2}	2.84×10^{-2}	1.08	2.84×10^{-2}	1.08
$\mathbf{q}_{CDW2}$	2.75×10^{-4}	7.83×10^{-6}	35.1	1.49×10^{-5}	18.4

the intensity of CDW satellite reflections. In addition to thermally excited phasons, thermally excited amplitude fluctuations of the CDW may affect the CDW satellite intensity. Giuliani and Overhauser have proposed a complete CDW thermal fluctuation analysis[16] which includes an ampliton temperature factor (ATF) as well as a PTF. The ATF leads to enhancement of the higher-order CDW peak intensities. The ATF has not been experimentally verified, but its derivation parallels that of the PTF and requires no additional parameters.

In Giuliani and Overhauser's theory the square of the PTF may be written as

$$F_n^{\phi}(T)=\exp[-2n^2W_{\phi}(T)] \quad (4)$$

and the square of the ATF may be written as

$$F_n^{A}(T)=\exp[2|n|(|n|-1)W_A(T)]\ , \quad (5)$$

where n is the order of the CDW satellite. In the high-temperature limit ($T \gg \theta_{\phi}$ where θ_{ϕ} is the phason analog of the Debye temperature),

$$W_{\phi}(T)=CT \quad (6)$$

and

$$W_A(T)=0.2464CT\ . \quad (7)$$

The above expressions for $W_{\phi}(T)$ and $W_A(T)$ are calculated under the assumption of a linear phason dispersion relation. The parameter C in Eq. (6) has the same value as the parameter C in Eq. (3). In this more complete PTF and ATF theory, the second exponential factor in Eq. (3) is replaced by $[F_n^{\phi}(T)F_n^{A}(T)]^{1/2}$. For first-order CDW satellites ($n=1$), $F_n^A(T)=1$ so that the more complete theory gives the same result as the PTF alone, $I(\mathbf{q}_{\rm CDW1})_{\rm expt}/I(\mathbf{q}_{\rm CDW1})_{\rm calc}=1.08$. Upon including the ATF for the second-order satellite ($n=-2$), we find that $I(\mathbf{q}_{\rm CDW2})_{\rm calc}=1.49\times10^{-5}$ and $I(\mathbf{q}_{\rm CDW2})$expt/ $I(\mathbf{q}_{\rm CDW2})_{\rm calc}=18.4$ These results are summarized in Table I under "Calculated with PTF and ATF." After incorporating the complete PTF and ATF theory to calculate the expected second-order satellite relative intensity, we still find excess intensity.

The excess intensity of the second-order CDW satellite gives evidence that the I phase CDW in $1T$-TaS_2 is not purely sinusoidal but rather that the CDW-lattice interaction induces a phase and amplitude modulation of the CDW. We note that the CDW *is* phase and amplitude modulated into periodic domains in the nearly commensurate (NC) and triclinic (T) CDW phase[2,5,6,8,17] where the CDW is close to commensurability. In the NC and T phases the CDW-lattice interaction induces excess intensity in higher-order CDW satellites near first-order satellites. Thus $1T$-TaS_2 supports a CDW in which the CDW-lattice interaction is significant. However, if the CDW is modulated in the I phase as well, the frequency of the modulation, due to the second-order CDW harmonic, is $\mathbf{q}_{\rm CDW2}-\mathbf{q}_{\rm CDW1}=0.150\mathbf{a}^*=0.53(\mathbf{q}_{\rm CDW1}-\mathbf{a}^*)$. This means that the period of the modulation is only about twice the CDW period and so the modulation is not domainlike. We have searched for higher than second-order CDW satellites near the first-order satellite and found none. Since the second-order harmonic is the only harmonic which occurs with significant intensity in the neighborhood of a CDW fundamental, the resulting weak modulation of the CDW should be both phase and amplitude in character with the modulation wave vector parallel to the in-layer component of the CDW fundamental wave vector.

In conclusion, we have measured the intensities of the CDW first- and second-order satellites in the I phase of $1T$-TaS_2. We have shown that our measurements are inconsistent with the results of a structure factor calculation incorporating a purely sinusoidal PLD, the PTF, and the ATF. We propose that the observed excess intensity of the second-order CDW satellite is due to a periodic phase and amplitude modulation of the CDW. It should be recognized that this conclusion is based upon the PTF and ATF. If the assumption of a linear phason dispersion relation for the I phase of $1T$-TaS_2 is invalid, the PTF and ATF must be modified and our conclusion might be altered. However, diffuse x-ray scattering surrounding satellite reflections in $1T$-TaS_2 (Ref. 18) shows no evidence of a $q=0$ gap in the phason dispersion relation.

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