Phason velocities in TaS_2 by x-ray diffuse scattering

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(Received 22 March 1988)

The diffuse x-ray scattering surrounding satellite reflections caused by charge-density waves has been measured at two different temperatures and analyzed in terms of phason scattering. From this analysis, the phason velocity has been obtained for all directions of propagation.

While the lattice dynamics of ordinary crystals can be described in terms of phonons, it is not clear that the same ideas and methods can be applied to crystals with charge-density waves (CDW's). It was predicted a number of years ago by Overhauser[1] that special low-frequency excitations, associated with phase modulations, must exist in a CDW system. These excitations, called *phasons*, have indeed been observed experimentally,[2] and have led to the measurement of the phason temperature factor, e^{-CT}, which affects all first-order satellites equally unlike the ordinary Debye-Waller factor which depends on the scattering vector. Phasons are the normal modes of phase fluctuations of CDW's, and can be considered as coherent superpositions of phonon modes.[1] Their frequencies tend to zero in the neighborhood of satellites, therefore the diffuse scattering surrounding a CDW satellite arises mostly from phasons.

The experiment described in this article consists of absolute measurements of phason thermal-diffuse scattering (PTDS) in the neighborhood of two distinct first-order satellites, at two different temperatures, 363 and 423 K, from which the velocity of propagation of phasons in all directions can be obtained. (This is possible because there is only one phason mode for each wave vector.)

The studies reported in this work have all been done on the $1T_1$ polytype of TaS_2, for which the CDW system is incommensurate. The reason for this choice is that the physics of the incommensurate structure is well understood, in the sense that the sinusoidal model for CDW's is applicable, and the atomic displacements are reasonably well known.[2,3]

The spectrometer used is a standard four circle diffractometer on beam line X-18A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory (Upton, NY). The wavelength was 0.71 Å, and the monochromator was a double flat (unfocused) Si(111), without mirror. The divergence of the beam was about 15″ in the diffraction plane (vertical), and 30″ in the perpendicular plane (horizontal). A standard scintillation counter was used in all measurements. Care was taken to make sure that the counter aperture could accept only light from the irradiated crystal region, in order to avoid spurious contributions of scattering from air, mylar windows, etc. The beam size was about 1×1 mm^2, and the crystal was the same used in earlier experiments.[2,3] Care had to be taken in order to find a region, in the crystal, giving sharp unsplit diffraction peaks. The crystal was enclosed in a small homemade furnace with mylar windows. No problem was found with the third harmonic, which could be easily discriminated against electronically, due to the weak nature of the scattering.

The diffuse scattering was measured at equally spaced points within two prismatic little "boxes," centered around the same first-order satellite, called $\mathbf{Q}^3$ in Refs. 2 and 3, one close to (010) and the other close to (030). The shape of each box, in the ($\mathbf{a}^*$,$\mathbf{b}^*$) and ($\mathbf{b}^*$,$\mathbf{c}^*$) plane, is presented in Fig. 2. The projection of $\mathbf{Q}^3$ on the $hk0$ plane is located on $\mathbf{G}_{010}$ and $\mathbf{G}_{030}$, respectively. Since we were primarily interested in phason scattering, we scanned small regions in $\mathbf{K}$ space (surrounding the satellites), where the phonon scattering is less important. The linear scans parallel to $\mathbf{b}^*$ covered a region $\Delta k = 0.273$ and $b^* = 0.585$ Å^{-1}, h was kept constant during each scan between the extreme values $+0.128a^*$ and $-0.142a^*$ ($+0.261$ and -0.339 Å^{-1}), and the scan parallel to $\mathbf{c}^*$ spanned a length $\Delta l = 0.333c^* = 0.351$ Å^{-1}. The diffuse scattering was measured at about 1200 points within each box.

Given the small size of the scanned region in K space, it is clear that the high resolution of a synchrotron beam was an indispensable ingredient for success in this experiment. Since the mosaic spread of the crystal region chosen for the experiment was around 1–2 arcminutes, we felt that adequate resolution could be achieved without need for an analyzing crystal, which would have reduced the intensity considerably. The average counting rate at each point was in the range of 10–60 counts/sec, and a typical dwelling time on each point was 15 sec. All measurements were put on an absolute basis. This was done by measuring the intensity scattered by an amorphous sample (fused silica) at $2\theta \cong 90°$.[4] In this way the primary intensity I_0 could be measured, multiplied by a constant which includes the area of the counter aperture and the crystal to counter distance. The intensity data points were then expressed in electron units, and the Compton scattering was subtracted.[5] The assumption was made, at this point, that the isodiffusion contours of phason scattering around a satellite were ellipsoids.[1] Since the lattice dynamics of $1T_1$-TaS_2 is not known, phonon scattering was subtracted using a phenomenological expression with two adjustable parameters. The following formula with eight adjustable parameters was used to fit the experimental data:

$$I_{eu}(\mathbf{q}) = \left[\sum_{i,j} A_{ij} q_i q_j\right]^{-1} + (B_1 + B_2 \mathbf{q}\cdot\mathbf{u})^{-2} \quad (1)$$

where $I_{eu}(\mathbf{q})$ is the experimental intensity, in electron units, $\mathbf{q}$ is the phason scattering vector, $\mathbf{u}$ is the unit vector parallel to $\mathbf{Q}^3$, q_i are components of $\mathbf{q}$ relative to an orthogonal set of axes centered at $\mathbf{G}_{hkl}+\mathbf{Q}^3$, A_{ij} are the six independent parameters of the ellipsoids ($A_{ij}=A_{ji}$). The last term in Eq. (1) is designed to describe phonon scattering. The q^{-2} dependence of the first term in Eq. (1) follows from the linear proportionality between frequency and wave vector for phasons, valid when dispersion is ignored, which is certainly true for small q's. All data points could be fitted by Eq. (1) with an R factor[6] $\approx 10\%$. Figure 1 shows the quality of the fit along five parallel straight lines in reciprocal space. A strong indication for the soundness of the fitting procedure is that the phonon scattering contribution turns out to be proportional to temperature (as expected from the equipartition principle). Another favorable feature of the fitting is the fact that, when the constraint of keeping the ellipsoids centered at $\mathbf{G}_{hkl}+\mathbf{Q}^3$ was relaxed, they turned out to be still centered at $\mathbf{G}_{hkl}+\mathbf{Q}^3$, with the largest axis parallel to $\mathbf{c}^*$, and the smallest one parallel to $\mathbf{b}^*$, as expected from symmetry considerations.[7] Figure 2 shows two sections of isodiffusion contours in reciprocal space. They correspond to an intermediate intensity value, as explained in more detail in the caption to Fig. 2. The ratios of the three major axes of the ellipsoid are 2.5:1.8:1.

In order to establish a correspondence between PTDS and frequencies of the associated phasons, we need to know the theory of PTDS. This is done in a separate paper.[8] The final formula will be reported here. In $1T_1$-TaS_2 we can assume that we have three identical CDW's:

$$\mathbf{u}_\kappa^i(\mathbf{L}_\kappa) = \mathbf{A}_\kappa^i \sin(\mathbf{Q}^i\cdot\mathbf{L}_\kappa + \phi_\kappa) \quad (2)$$

where $\mathbf{u}_\kappa^i$ is the CDW displacement of the κth atom, due to the ith CDW, $\mathbf{L}_\kappa$ is the position vector for the same atom in the Lth crystal cell, $\mathbf{Q}^i$ is the ith CDW wave vector, and ϕ_κ is the associated phase. If ϕ_κ fluctuates in space and time, we can write

$$\phi_\kappa = \sum_{\mathbf{q}} \phi_{\kappa\mathbf{q}} \sin(\mathbf{q}\cdot\mathbf{L}_\kappa - \omega_{\mathbf{q}} t) \quad (3)$$

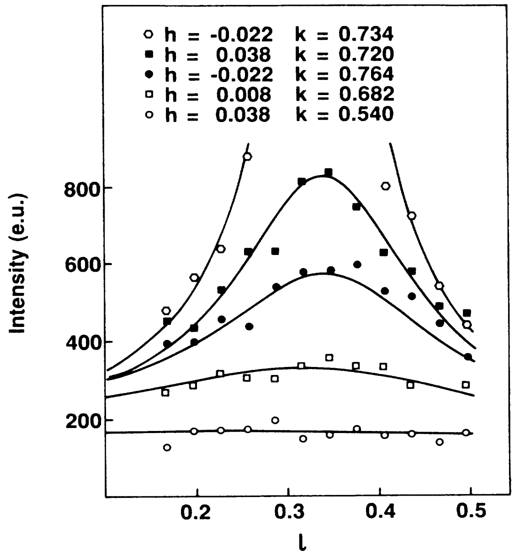

FIG. 1. Intensity data along different straight lines in $\mathbf{K}$ space all parallel to $\mathbf{c}^*$. The experimental points have been reduced to electron units (e.u.), by comparison with scattering from amorphous SiO_2, and then corrected by subtracting Compton scattering. The solid lines are fitted using Eq. (1). Data were taken at $T=363$ K.

where $\phi_{\kappa\mathbf{q}}$ and $\mathbf{q}$ are the phason amplitudes and wave vectors, respectively, and $\omega_{\mathbf{q}}$ the associated frequency.

We can then derive[8] the associated PTDS scattering amplitude at a particular position $\mathbf{K}$ in reciprocal space. We make the assumptions that (i) the phason amplitudes are the same for all atoms in the unit cell, (ii) the three CDW's are identical, and (iii) we only consider the phason mode associated with the nearest $\mathbf{Q}^3$ satellite reflection, so that

$$\mathbf{K} = \mathbf{G}_{hkl} + \mathbf{Q}^3 + \mathbf{q} \quad (4)$$

where hkl can be (010) or (030).

We find

$$I_{eu}(\mathbf{q}) = 2\left|\sum_\kappa f_\kappa(\mathbf{K}) \exp(i\tau_\kappa\cdot\mathbf{G}_{hkl}) J_0(\mathbf{K}\cdot\mathbf{A}_\kappa^1) J_0(\mathbf{K}\cdot\mathbf{A}_\kappa^2) J_1(\mathbf{K}\cdot\mathbf{A}_\kappa^3)\right|^2 e^{-2W} e^{-2M} \frac{k_B T}{(M_{Ta}A^2 + 2M_S C^2)\omega_{\mathbf{q}}^2} \quad (5)$$

where κ identifies the atomic species, τ_κ is the position vector within the unit cell, $\mathbf{G}_{hkl}$ is the nearest lattice vector to the $\mathbf{K}$ point, J_0 and J_1 are Bessel functions of integer order, $\mathbf{A}_\kappa^i$ is the CDW amplitude for the κth atom, due to the ith CDW, e^{-2W} and e^{-2M} are the phason temperature factor and Debye-Waller factor, respectively, both assumed to be the same for all atoms (as a rough approximation), k_B is the Boltzmann constant, T is the absolute temperature, A and C are CDW displacements for tantalum and sulfur atoms, respectively, derived in Ref. 2, M_{Ta} and M_S are the atomic masses, and $\omega_{\mathbf{q}}$ is the frequency of a phason with wave vector $\mathbf{q}$. The numerical values of e^{-2W} and e^{-2M} have been determined in separate experiments, described in Refs. 2 and 9, respectively.

In the neighborhood of a CDW satellite there is an ad-

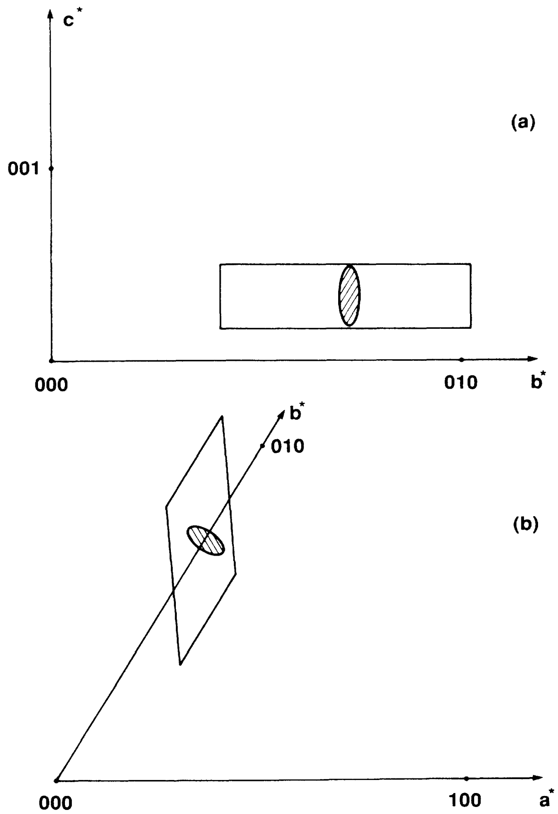

FIG. 2. Cross sections of one particular ellipsoid surface of constant phason scattering in **K** space, corresponding to $I_{eu}=350$. The parallelepipeds surrounding the ellipsoids are projections of the prismatic "boxes" in which phason scattering has been measured. A first-order satellite is located at the center of each box, $\mathbf{Q}^3$, close to (010). (a) is a planar section in the ($\mathbf{b}^*$,$\mathbf{c}^*$) plane. (b) is parallel to the ($\mathbf{a}^*$,$\mathbf{b}^*$) plane.

ditional contribution to scattering from an "image" of the acoustic-phonon spectrum emanating from each satellite. Such a contribution is negligible, as shown in Ref. 8.

Since we have assumed in the fitting formula [Eq. (1)] that no dispersion is present, we can obtain the velocity of propagation for phasons, V_ϕ, directly from the parameters of the ellipsoids by setting Eq. (1) equal to Eq. (5).

TABLE I. Phason velocities.

G (hkl)	T (K)	$V_\phi \| \mathbf{b}^*$	$V_\phi \perp \mathbf{b}^*$ (10^4 cm/s)	$V_\phi \| \mathbf{c}^*$
010	363	13.9	7.31	4.93
030	363	12.7	6.22	4.54
010	423	14.4	7.22	4.43
030	423	12.5	6.25	3.83

This has been done four times, at two different temperatures (363 and 423 K), and using data taken around (010) and (030). The latter two sets should give the same values of V_ϕ, and any possible discrepancy is a measure of the experimental uncertainties in our procedures. A value of V_ϕ can then be *calculated,* using the fitting parameters of Eq. (1), along *any* direction in **K** space. We report only three principal values, along $\mathbf{b}^*$, normal to $\mathbf{b}^*$, and along $\mathbf{c}^*$.

Table I shows the 12 values obtained for V_ϕ. It is gratifying to see that the values obtained from the (010) and (030) data, at any given temperature, are in reasonable agreement. The velocity along $\mathbf{c}^*$ is appreciably decreased at high temperature, unlike the velocity along $\mathbf{b}^*$ and that perpendicular to $\mathbf{b}^*$.

The numerical values of V_ϕ are of the same order of magnitude as the sound velocities, which was predicted.[1]

An attempt has been made to detect a $q=0$ gap, which might be due to pinning effects. This was done by adding a constant term A_0 to the denominator of the first term in Eq. (1). No evidence for the existence of such a gap was present in our fits.

In conclusion, we have shown how the experimentally measured phason thermal-diffuse scattering in $1T_1$-TaS_2 can be analyzed to provide values for velocities of propagation in all directions. Strong anisotropies are found, as expected in a layered compound.

This work was supported by the National Science Foundation Materials Research Laboratory (NSF-MRL) Program Grant No. DMR-84-18453, by NSF Grant No. DMR-84-02174, and by the U.S. Department of Energy Grant No. DE-FG02-85ER45183-A001). The authors are thankful to Professor A. W. Overhauser for having stimulated this research project, and for his many insights and invaluable suggestions.

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[6]The "reliability factor" (R factor) is defined as $\sum_i |I_i^o - I_i^c| / I_i^o$ where I_i^o and I_i^c are observed and calculated intensities, respectively.

[7]A plane through $\mathbf{b}^*$ and $\mathbf{c}^*$ is a mirror plane for the Bragg reflections *and* for the CDW satellites.

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