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Collective Pinning Dynamics of Charge Density Waves in $1T$-TaS_2

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Using high-resolution x-ray scattering and x-ray photon correlation spectroscopy (XPCS), we have investigated the structure and dynamics of charge density wave (CDW) dynamics in pure and titanium-doped $1T$-TaS_2. Time-averaged scattering measurements of pure and doped samples reveal that $1T$-TaS_2 is a weakly pinned two-dimensional CDW system. Using XPCS, we find that after long anneals the CDW domain structure in the incommensurate phase (IC) is pinned and stable against spontaneous fluctuations thus rejecting phasons as spontaneous excitations in higher-dimensional CDW systems. By examining the dynamics of deeply-quenched samples upon heating, we find that meta-stable CDW configurations collectively re-arrange in a non-equilibrium manner. For nominally pure samples, we determine an energy barrier to relaxation of 4600 K that is considerably greater than that found for lower dimensional CDW's.

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Introduction

Materials with charge density waves (CDW's) serve as prototypical systems for correlated phenomenon. The collective effect of their electrons often leads to periodicities different from those of the underlying lattice resulting in incommensurate or superlattice structures and interesting physical behavior[1]. In CDW systems, the dimensionality and the spatial extent of correlations can be adjusted by varying the composition and defect and impurity doping levels. The spatial extent over which the phase of the CDW varies smoothly defines a correlation length and fluctuations about this smoothly varying state are called phasons[2]. Defects and dopants in CDW materials act as pinning sites and modify the phase correlation length. The effects of pinning are generally considered in two limits: weak or collective pinning and strong pinning.

The dynamical properties of such materials depend on the interaction of the CDW's with thermal and quenched disorder such as pinning sites[3]. These interactions affect the measured transport properties. From transport and specific-heat measurements, transient responses are seen to be history-dependent and glass-like[4–6]. Dimensionality, microscopic rearrangements and dynamical properties of the CDW state have been attributed to CDW rearrangement[7] but experimental work to date infers this mesoscopic dynamic behavior from macroscopic measurements. As such, it is highly desirable to have a direct structural measurement of the dynamic properties of specific CDW states with which one can hope to address the role of fluctuations. One such tool is x-ray photon correlation spectroscopy (XPCS). XPCS uses speckles produced by (partially) coherent x-rays illuminating a sample to characterize fluctuations at the nanoscale in a variety of materials. Coherent x-rays, speckle and XPCS have been used to characterize a variety of CDW materials; see, for example, Refs. 8–12.

In this paper we used XPCS to investigate the microscopic structure and dynamics of CDW's in nominally pure and Ti-doped $1T$-TaS_2. We find that collective pinning plays a key role in stabilizing the CDW phase structures against spontaneous phason fluctuations. We have also investigated the metastable states and the corresponding relaxation behavior of suitably-prepared (deeply quenched) pure and doped $1T$-TaS_2 samples upon annealing. Surprisingly, we find that the fluctuations in such systems mimic the relaxations observed in jammed soft matter[13]. As compared to other quasi one-dimensional CDW systems, we attribute the unusual relaxation behavior to the increased dimensionality of CDW's in $1T$-TaS_2.

Results and Discussion

We studied CDW's with Ti doping levels of nominally pure, 4, 8 and 12%. Samples were prepared in the standard manner[14] by heating mixtures of the corresponding elements with excess sulfur in quartz tubes. The tubes were heated to 1200 K for two weeks followed by a quench to room temperature to obtain the desired $1T$-polytype. The CDW's we studied were in the incommensurate (IC) phase. This phase develops inside the hexagonal lattice of $1T$-TaS_2 below a transition temperature of $\sim$ 540 K but above the transition temperature to the lower temperature nearly commensurate (NC) phase. Titanium doping changes the properties of the IC phase, including lowering the IC-NC phase boundary[14].

Time-resolved coherent x-ray-scattering measurements were performed at beamline 8-ID-E at the Advanced Photon Source. The x-ray energy was 7.35 keV and 10×10 μm^2 slits selected a coherent portion of the x-ray beam. The sample was contained in a small sample cell mounted directly on a four-circle diffractometer. The cell was designed for both stability at a particular temperature and to facilitate rapid temperature changes.

In x-ray diffraction, the IC phase corresponds to well-defined, isolated peaks associated with the CDW wavevector $\mathbf{q}_{\rm CDW} = 0.283\,\mathbf{a}^* + \mathbf{c}^*/3$. Among all the diffraction maxima, a strong first-order satellite peak was measured around the (002)-Bragg reflection using a symmetric scattering geometry. The scattered intensity was recorded with a direct-detection CCD detector. The small illumination volume minimizes the dependence of the structure factor on the sample mosaic, as confirmed by our resolution-limited measurements of the (002)-Bragg peak. (The resolution-limited full-width-at-half-maximum of the (002) Bragg peak is 6×10^{-5} Å^{-1}. Our resolution is determined by the coherent beam size, namely $2\pi/D$, where $D \approx 10$ μm is the horizontal x-ray coherence length.) This Bragg peak was also used as a check of the stability of our setup.

To investigate the structure of the CDW, we conducted a detailed study of the satellite peak. With $\mathbf{c}^*$ specifying the conventional basal plane, we will refer to these scans as in-plane- and out-of-plane profiles, respectively. Representative in-plane **H**-direction (open circles; **K**-direction was found to be equivalent) and out-of-plane (open squares) line scans for nominally-pure $1T$-TaS_2 samples are plotted in Fig. 1(a). In both directions, substantial diffuse scattering is observed but the out-of-plane direction is considerably more disordered than the in-plane direction. The degree of disorder can be quantified by fitting the profiles to Lorentzian line shapes. Solid lines in Fig. 1(a) show the best-fit results. In-plane, we find a correlation length of $\xi_\parallel \approx 1000$ Å, while out-of-plane we see $\xi_\perp \approx 200$ Å. Like other canonical CDW systems such as blue bronze[15], the ratio $(\xi_\parallel/\xi_\perp) \sim 5$ displays considerable anisotropy meaning that, structurally, the CDW exhibits low-dimensional character. An important distinction, however, between our system and blue bronze or $NbSe_3$, for example, is that the correlation lengths, though anisotropic, are smaller than found in high-quality examples of the latter. The smaller correlation lengths produces diffuse scattering and speckles more amenable to time correlation analysis while the opposite is true for $NbSe_3$[8] and similar systems.

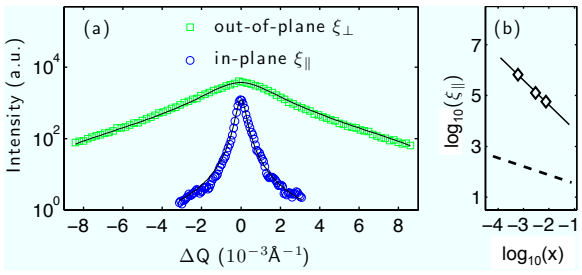

FIG. 1: (Color online) (a) Line profiles through the CDW satellite peak in $1T$-TaS_2 in the out-of-plane and in-plane directions. Solid lines are best fits to Lorentzian line shapes. (b) $\xi_\parallel$ versus doping (x) compared with strong- (dashed line) and weak-pinning (solid line) functional forms.

Defects and impurities within a CDW system act to pin the CDW phases in certain configurations (amplitude variations are not expected to be important well below the Peierls temperature[16,17]). Our data may be used to distinguish between 2 possible pinning states: i) strong pinning where the correlation length is proportional to the average separation between the impurities and results in a $\xi_\parallel \propto x^{-1/3}$ power-law-relationship, and ii) weak collective pinning where the correlation length far surpasses the mean impurity separation and results in a $\xi_\parallel \propto x^{-1}$ power-law-relationship[18]. In Fig 1(b), open diamonds are the measured in-plane correlation lengths versus doping level (x), the solid line is the power-law expected for weak collective pinning and the dashed line is that for strong pinning. Clearly, the CDW's in $1T$-TaS_2 are weakly pinned. Moreover, the combination of weak pinning and the Lorentzian line shape of the CDW indicate that the structure of the CDW can be ascribed to phase modulation and that the phase-phase correlation across domains vanishes exponentially with increasing distance[16]. Finally, the observed inverse power-law-relationship can be used to estimate the defect density in nominally pure $1T$-TaS_2 yielding an effective defect density of 0.39% [though the nature of these defects (vacancies or residual impurities, for exmaple) can not be determined from our measurements].

To summarize, we find that IC $1T$-TaS_2 is a weak, collectively-pinned phase-modulated CDW structure. In theory, one would expect to find low-energy spontaneous excitations (known as phasons) in such a system[3]. In fact, phasons have been observed in other CDW systems using neutron scattering[15] and in $1T$-TaS_2 via diffuse x-ray scattering measurements[19]. Accordingly, we performed XPCS measurements of the first order CDW peak in pure and doped IC $1T$-TaS_2.

Fig. 2(a) shows a 2-D coherent x-ray-scattering pattern of the CDW satellite peak of 4% Ti-doped $1T$-TaS_2 measured at 353 K. The dashed line represents a linear slice through the center of the pattern and is plotted in Fig. 2(b). The data correspond to an integrated collection time of 1000 s. The grainy features or speckle in the scattering patterns are consistent with coherent scattering from static disordered systems. The fact that persistent speckles are observed over extended times shows that the CDW is static on time scales of at least 1000 seconds. Based on this and similar results for other samples and different temperatures and quantitative time autocorrelation analysis[20] (not shown), we conclude that the IC phase is stable against spontaneous phase fluctuations. This result can be understood in the context of the phase pinning discussed above which dominates even in

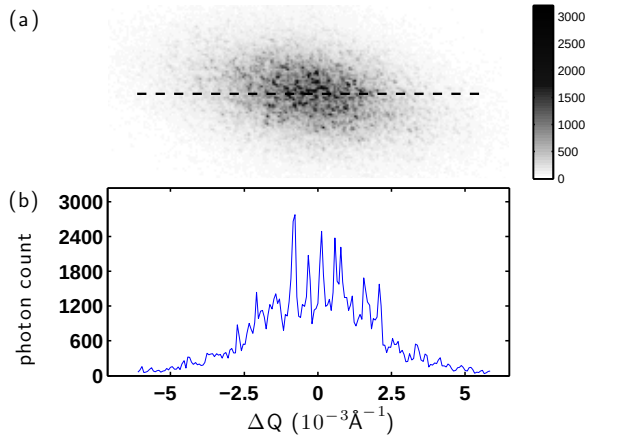

FIG. 2: (Color online) (a) Time-integrated 2-D intensity profile of the first order CDW satellite of 4% Ti-doped 1T-TaS_2 in the IC phase. The dashed line is a slice through the center of mass and is plotted in (b). The rapid intensity variations are speckle.

nominally pure 1T-TaS_2. While this nicely demonstrates the stability of the equipment, it is in contrast to previously reported diffuse x-ray scattering measurements[19] that were interpreted as evidence for spontaneous phase fluctuations. The origin of this discrepancy is not fully understood. We point out, however, that sample preparation results in a quenched CDW system in metastable equilibrium and the subsequent slow relaxation upon annealing to a new metastable or stable equilibrium generates microscopic fluctuations that would mimic such spontaneous thermal fluctuations. In fact, an analysis of annealing behavior and the corresponding fluctuations and relaxation behavior are the principle topics of the remainder of this paper.

Thermodynamically, the static phase domain structures we have observed correspond to either a ground state or a long-lived metastable state. To investigate the nature of these states, we have used XPCS, which directly probes the domain dynamics, to examine the response of the sample to thermal impulses with $\Delta T \sim \pm 10$ K. To our surprise, we observed that in freshly prepared deeply quenched, samples, slow microscopic re-arrangements of the CDW phase structure could be initiated by positive temperature jumps to a new annealing temperature within the IC phase. Conversely, if a crystal had been annealed at an elevated temperature for a sufficiently long period, subsequent positive or negative temperature jumps that stayed below this annealing temperature did not result in any observable dynamics in the phase structures. In both cases, the time averaged structure of the CDW peak was unchanged. Given such asymmetric behavior, we infer that the slow response is a sluggish relaxation process related to annealing a strongly out-of-equilibrium (quenched) CDW system. To better understand the observed dynamics in deeply quenched samples undergoing fresh anneals, we developed two schemes to heat 1T-TaS_2 crystals: Scheme 1 was one-step heating in which a temperature change was made and then the relaxation was allowed to evolve indefinitely and Scheme 2 was multi-step heating in which the sample was heated to successively elevated temperature plateaus via fixed temperature step sizes and dwell times. All measurements are made isothermally.

To characterize the microscopic response after a thermal impulse, we use the two-time correlation function

$$C(\overline{\mathbf{q}}, t_1, t_2) = \left\langle \left(\frac{I_{t_1} - \langle I_{t_1} \rangle \text{ens}}{\langle I_{t_1} \rangle \text{ens}} \right) \left(\frac{I_{t_2} - \langle I_{t_2} \rangle \text{ens}}{\langle I_{t_2} \rangle \text{ens}} \right) \right\rangle_{\mathbf{q}} \quad (1)$$

for any pair of intensity profiles I_{t_1} and I_{t_2} collected at $\mathbf{q}$ and times t_1 and t_2, respectively[20]. The two-time correlation is a more general form of the time-independent correlation function of a system at equilibrium. In the equilibrium case, C is independent of t_1 and t_2 and depends only on the difference $\Delta t = |t_2 - t_1|$ and Eq. 1 reduces to the more familiar time autocorrelation function $g_2(\Delta t)$. For systems that are static within the limits of the time spacing of our measurements, the amplitude of C at small $|t_2 - t_1|$ is called the speckle contrast and depends on such experiment details as the size of the x-ray source, the size of the collimating pinhole and the scattering geometry among several other experiment-specific factors. Decays from this amplitude to 1 are indicative of dynamics while persistence of this amplitude, as described above in reference to the supposed spontaneous phase fluctuations, is indicative of stability. The instantaneous ensemble-averaged intensity $\langle I_t \rangle_{\text{ens}}$ is estimated by digital smoothing of each diffraction pattern[20,21]. Restricting the average over $\mathbf{q}$ to different regions of the peak, demonstrated that $C(\overline{\mathbf{q}}, t_1, t_2)$ is independent of wavevector. Thus we calculate two-time functions averaged over the whole peak. Whenever a system exhibits only static speckles, the two-time correlation function is a uniform value above zero. Figure 3 shows the measured two-time correlation functions plotted for pure and 8% doped 1T-TaS_2 after abrupt temperature changes from 383 to 393 K via Scheme 1. In both plots, time zero is defined to be the moment at which the temperature stabilized at the final temperature and we have normalized the time axes by the respective τ_0's, which are the initial time constants of $C(t_1, 0)$ (time constant of the first row of the two-time correlation).

First, we consider the response in the doped sample [Fig. 3(b)] after a temperature change. We observe similar correlation decays until $\approx 1.5\tau_0$ with $\tau_0 \approx 3000$ s for this doping level. Subsequently, the correlation function fans out and displays uniform constant contrast indicating that the system approaches static behavior. Nevertheless, upon further raising the temperature, the same early-time relaxation and later-time slowing down is observed. From these observations, we conclude that doped CDW's slowly evolve from one metastable state to another as they are annealed at progressively higher temperatures from a deeply quenched starting point. Similar

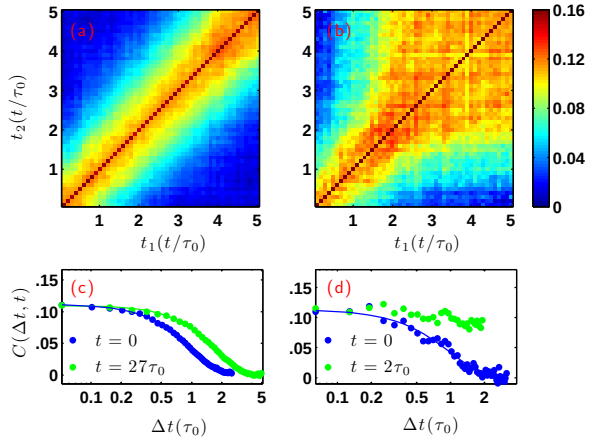

FIG. 3: (Color online) Measured two-time correlation functions of CDW relaxation after a temperature jump from 383 to 393 K. (a) Pure $1T$-TaS_2. (b) 8% doped sample. As functions of time difference, Δt, the corresponding decays measured at different age t's are plotted in (c) and (d), respectively. The horizontal white line in (b) show the cross-section used for plotting $t = 2 * \tau_0$ in Fig. (d).

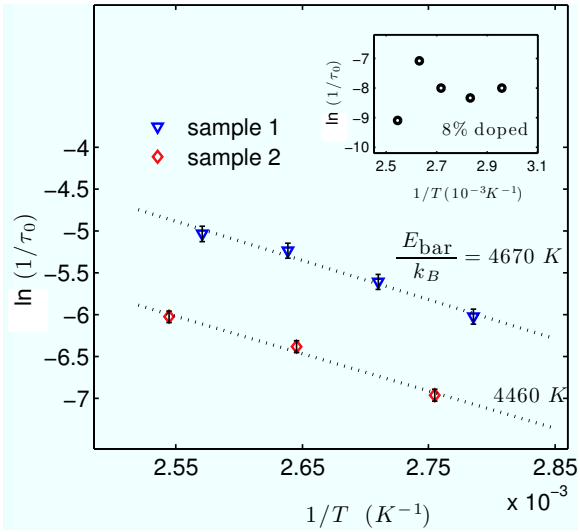

FIG. 4: (Color online) Arrhenius behavior of the CDW relaxations in pure $1T$-TaS_2 induced by successive thermal impulses (heating Scheme 2) of 10 K (triangles, sample 1) and 15 K (diamonds, sample 2). τ_0 is defined in the text. Inset: similar measurements on a 8%-doped system. No clear trend is found.

behavior was also observed in the 4% doped system while for the 12% system the relaxation was too slow be measured within the limits of our available time.

In the case of pure $1T$-TaS_2, where $\tau_0 \approx 500$ s, the results are very different. As shown in Fig. 3(a), the correlation decay times show a gradual increase with increased aging time after the temperature jump but the increase is much slower than for the doped samples. Although the relaxation eventually stops (based on extended anneals performed prior to our beamtime on other samples), the wait time could not be experimentally determined within the limits of our available beamtime. We can quantify the increase in correlation decay times in pure $1T$-TaS_2 by plotting cross-sections of the two-time correlation function at different aging times. Figure 3(c), shows such cross-sections, $C(t_1 > t_2, t_2 = t)$, plotted against the time difference $\Delta t \equiv |t_1 - t_2|$. A compressed exponential (solid line) of the form $C(\Delta t, t) = C_0 \exp\left[-2(\Delta t/\tau_t)^\beta\right]$, with C_0 the measured contrast in our experiment, τ_t the characteristic time of the decay, and $\beta = 1.5 \pm 0.1$ fits very well. We find that τ_t grows linearly to at least $30\tau_0$. The compressed exponential relaxation and our structural study provide insight into the nature of relaxation in the CDW system. The CDW satellite peak exhibits constant widths and intensities and is consistent with a weak collectively pinned CDW network. XPCS, on the other hand, reveals mesoscopic dynamics indicating that the CDW domains evolve to a new configuration. A picture therefore emerges of interacting domains moving under the influence of random pinning forces. In fact, this correlation function with $\beta = 1.5$ was developed for relaxtion of an elastic medium[22] and similar correlations have been observed for a variety of soft[13] and hard[11] condensed matter systems in which collective dynamics are significant and suggests that the deeply quenched CDW's in $1T$-TaS_2 relax through collective re-arrangements. We further explore this connection by examining results obtained for pure samples using heating Scheme 2.

Our Scheme 2 results for two different nominally pure samples are summarized in the Arrhenius plot of Fig. 4. Plotted in Fig. 4 are the inverse of the characteristic times, $\tau_0 \equiv \tau_{t=0}$, versus the inverse final temperatures. Triangles are data for sample 1 which was heated in successive +10 K steps while diamonds are data for sample 2 which was heated in successive +15 K steps. As the data show, increased final temperatures speed the relaxation process. In addition, by inspection, the data are consistent with Arrhenius behavior. Independent fits were performed as indicated by the dotted lines; both samples display a relaxation barrier of $E_{\rm bar} \sim 4600$ K or 0.40 eV. Compared with the thermal energy (~ 400 K) or the CDW gap (~ 870 K[23]), each of which roughly corresponds to the energy scale of other common CDW relaxations such as thermal creep[6] or phase slips[5], respectively, $E_{\rm bar}$ stands out as a considerable energy barrier. Based on the magnitude of the measured energy scale[3], the barrier acts on individual domains. Thus, $E_{\rm bar}$ is equal to the pinning energy per domain. Despite its importance to CDW phenomena, pinning in $1T$-TaS_2 is very difficult to characterize using conventional methods; our work provides a measurement of this energy scale.

Combining the observed relaxation plotted in Fig. 3(c) with the energy barrier observed in the Arrhenius plot, the following picture emerges for the behavior of CDW's in pure $1T$-TaS_2. In deeply quenched states, there exists considerable strain in the network of phase domain walls. Thermal impulses induce cascades of collective re-

arrangements to release excess stress (even in nominally pure samples). Strains (quench state) vary in different samples and the absolute time scale of the evolution may vary but, as demonstrated in Fig. 4, $E_{\rm bar}$ is a basic property of the CDW's in $1T$-TaS_2. In doped $1T$-TaS_2, as evidenced by the rapid cessation of dynamics after a temperature jump, the pinning effect is much stronger and rapidly damps any dynamics.

Conclusions

In conclusion, we have used coherent x-rays to investigate the microscopic nature of CDW's and CDW dynamics in nominally pure and Ti-doped $1T$-TaS_2. We find that weak collective pinning stabilizes the CDW phase structures against spontaneous phason fluctuations. We have also investigated the metastable states and corresponding relaxation behavior of deeply quenched samples upon annealing and find, surprisingly, that the fluctuations in such systems mimic the relaxations observed in jammed soft matter. As compared to other CDW systems, we attribute the unusual relaxation behavior to the increased dimensionality of CDW's in $1T$-TaS_2.

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