

Anomalous coherent phonon oscillations in the commensurate phase of the quasi-two-dimensional 1T-TaS₂ compound

Y. Toda,^{1,2} K. Tateishi,¹ and S. Tanda¹¹*Department of Applied Physics, Hokkaido University, Kita 13 Nishi 8 Kita-ku, Sapporo 060-8628, Japan*²*PRESTO Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan*

(Received 24 March 2004; published 30 July 2004)

We have investigated the coherent dynamics of the collective motions of phonons in the commensurate phase of quasi-two-dimensional 1T-TaS₂ using femtosecond laser pulses. One of the coherent phonons increased in intensity as a function of time, this behavior being strongly correlated with the decay of charge-density-wave oscillations as well as the slow decay component in single-particle relaxation.

DOI: 10.1103/PhysRevB.70.033106

PACS number(s): 78.47.+p, 63.22.+m, 71.45.Lr

Coherent phonon motion excited by ultrashort laser pulses sometimes shows time anomalies, which are deeply connected with electronic/structural instabilities and are eventually responsible for transient phenomena in materials systems.¹⁻⁴ For example, coherent phonons in Bi under high-density excitation show time-developed frequency changes, which is a precursor phenomenon to photoinduced phase transitions and laser ablation.¹ Recently, coherently excited charge-density waves (CDW's) in low-dimensional compounds have been realized and extensively studied from various viewpoints.⁵⁻⁸ Since the formation of CDW ordering is accompanied by ionic displacements, instantaneously excited electrons change their equilibrium positions and result in collective motion. This occurs in the same manner as displacive excitation of coherent phonons (DECP) as predicted in various materials.⁹⁻¹¹ Unlike bulk materials, however, low-dimensional systems have an underlying instability that plays an important role in generating coherent motion even in low-density excitations.

The material used in the present study is a layered quasi-two-dimensional (2D) compound 1T-TaS₂, which was the first material for which CDW's were experimentally observed¹² and is now a typical example used for showing coherent CDW motion in time-domain measurements.^{6,7} Two phase transitions, incommensurate to nearly commensurate (NC) and NC to commensurate (C), take place at 350 K and ~200 K, respectively. Below ~200 K (T_{C-NC}), the CDW undergoes the first lock-in transition with a periodic lattice distortion (PLD). The excitation of CDW's has been studied extensively by electron, x-ray, and neutron diffraction measurements. Despite its simple lattice structure, the electronic properties, including the dynamics, are not fully understood. Below T_{C-NC} , where the Fermi surface (FS) nesting is important for CDW formation, the residual density of states (DOS) at the Fermi level has been observed by angle-resolved photoemission spectroscopy (ARPES).¹³ Such pseudogap (PG) behavior in 2D materials is important because of the similarity with high-temperature superconducting cuprates (HTSC) for which the evolution of a PG is characteristic of high-temperature superconductivity.

Here we report the first observation of a temporal anomaly of coherent phonon motion in the C phase 1T-TaS₂. Transient pump-probe reflectivity changes show

several phonon oscillations including an efficient CDW amplitude motion (AM) below T_{C-NC} . In high-resolution experiments at 3.3 K, time-dependent spectra clearly indicate that one of the E_g phonons exhibits a unique delay for its generation, which depends on the decay of the AM mode. The slow decay component of the single-particle (SP) response, which is attributable to the relaxation in a gap state in the C CDW, is also identical to the decay of the AM, and therefore also accounts for the increase of E_g . These results suggest that the observed time anomaly is closely associated with the SP dynamics in the C-phase 1T-TaS₂.

Time-domain reflectivity data for phonon motion as well as SP relaxations are measured with a standard pump-probe setup. For the excitation source we use a mode-locked Ti:sapphire laser with a full-width at half maximum (FWHM) of 130 fs centered at an energy of 1.55 eV with a repetition rate of 76 MHz. The pump and probe pulses were orthogonally polarized and focused by an objective lens onto a single crystallite with a domain size of ~100 μm . The spot size of the pulses was estimated to be about 10 μm in diameter. To reduce heating effects in the sample, the average power was set to 0.1 nJ/pulse. The pump pulse was chopped at a frequency of 2 kHz and the reflectivity change of the probe was detected at the chopping frequency by a lock-in amplifier.

Figure 1(a) shows the typical transient reflectivity change measured at 3.3 K. Since the excitation photon energy of 1.55 eV can excite the carriers into continuum states far above a CDW gap, the general trend of the data can be attributed to a transient response of the photoexcited carriers, i.e., associated with SP transitions.⁵ As shown in the inset, the time evolution of the SP shows a large abrupt change within 1 ps and a subsequent slower decay. The signal returns almost to the initial level after 10 ps following the pump excitation. Subtracting the SP contributions, we can obtain a strong modulation signal as shown in Fig. 1(b). The corresponding Fourier transform (FT) spectrum clearly reveals several vibrational modes [Fig. 1(c)]. The dominant oscillation at 2.4 THz shows a good correspondence with a CDW AM mode observed in Raman data. Several transient properties of the AM oscillation including its temperature dependence have been reported by Demsar *et al.*⁶

Besides the AM mode, the FT spectrum also shows small peaks with frequencies at 1.5, 2.1, and 3.2 THz. Below

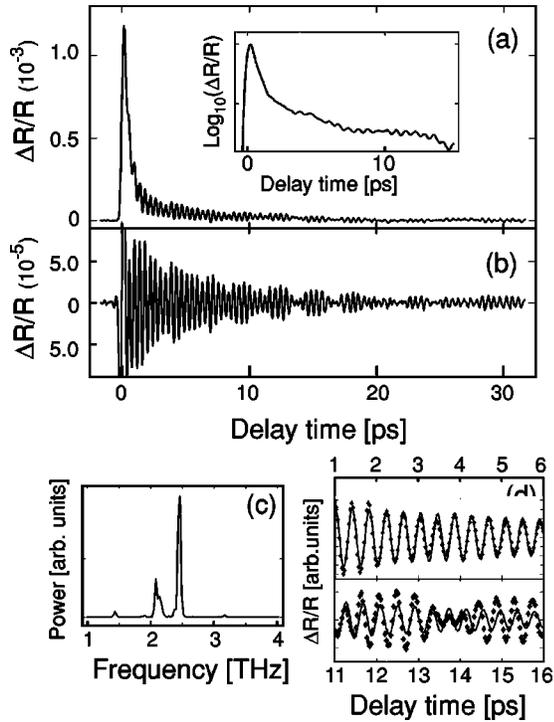


FIG. 1. (a) Time-resolved reflectivity change at 3.3 K. Inset: the nonoscillatory component for SP response. (b) Oscillatory component in (a), and (c) corresponding FT spectrum. (d) Expanded views of (b) with a different time range. Dashed line: a damped sinusoidal fit for the AM oscillation with the frequency of 2.43 THz and the decay of 6 ps.

T_{C-NC} , several Raman studies have also shown a number of phonon peaks and attributed them to folded-phonon features expected in C-phase 2D CDW due to the formation of PLD.¹⁴ The observed phonon frequencies and their temperature dependences also seem to be consistent with those of the Raman data while their relative intensities are quite different. The discrepancy with the relative peak intensities of the Raman spectra is consistent with the DECP process for coherent phonon generation.⁸ A feature of interest in the present study is the intense peak at 2.1 THz. On the basis of polarized Raman measurements, Sugai *et al.* attributed this peak to one of the folded phonons with E_g symmetry.¹⁴ Thus, we tentatively attribute the oscillation with the frequency of 2.1 THz to the E_g phonon.

To understand the time evolution of the coherent oscillations, we first tried to fit the modulation signal with a single exponentially damped sinusoidal function, in which the parameters are optimized for the AM mode. As shown in Fig. 1(d), the fitting function reproduces the experimental data quite well up to 10 ps. The oscillation in the initial time domain is found to be dominated by the AM mode. In contrast, the calculated AM oscillation does not match the data in the time range beyond 10 ps, suggesting contributions from other phonon motions.^{1,3}

In order to clarify the time dependences of the phonons spectra, we next employed a time-resolved FT (TRFT) analysis, where iterative FT was carried out by dividing the oscillation data into time windows with intervals of 10 ps

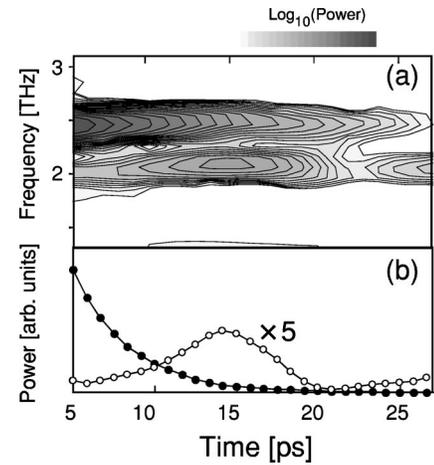


FIG. 2. (a) Gray-scale plots of TRFT spectra corresponding to the data in Fig. 1(b) as a function of delay time and frequency. (b) Cross-sectional view of the TRFT amplitudes. The solid and open circles correspond to the AM and E_g oscillations, respectively.

and a resolution of 0.83 ps. Figure 2(a) shows a gray-scale plot of the modulus of the TRFT as a function of delay time and frequency. The vertical cross section of this plot corresponds to the FT spectrum in each time window. In the TRFT spectra, each phonon mode exhibits constant frequency, suggesting that laser-induced lattice heating was small. On the other hand, the time evolutions of amplitudes of each phonon mode are completely different from each other. Figure 2(b) shows horizontal cross sections of the AM and E_g peaks. In contrast to the abrupt appearance of the AM amplitude with a single exponential decay, the E_g mode does not initially contribute to the signal. Its contribution gradually increases until 15 ps, then decreases as a slow oscillation. This difference in the evolutions suggests that these two motions originate from different processes. Note that Demsar *et al.* has also observed phonon modes with nearly the same frequency as the E_g mode.⁷ However, because the amplitude of the E_g mode was so small during the observation time scale, they focused only on the AM motion in terms of transient properties of collective excitation. Indeed, the amplitude of the E_g mode in our data is also negligible under 10 ps. It is interesting to note that the E_g phonon motion remains around 30 ps after the pump excitation, which is much longer than the lifetime of the AM, as shown in Fig. 1(b). The long-lived coherence of the E_g phonon suggests the existence of homogeneously distributed PLD with long-range order.

It is surprising that there is little oscillation amplitude corresponding to the E_g phonon motion in the initial interval despite the relatively large oscillation in the time range above 10 ps. However, the absence of a signal does not mean the absence of coherent motion during that time. It is reasonable to consider that the coherent oscillation of the E_g phonon occurs during the optical excitation but cannot contribute to the reflectivity change. The observed long-lived coherence of the E_g phonon is a proof of such instantaneous excitation. The generation mechanism for the collective CDW motion is known to result from the instantaneous perturbation of the charge density. On the other hand, the PLD

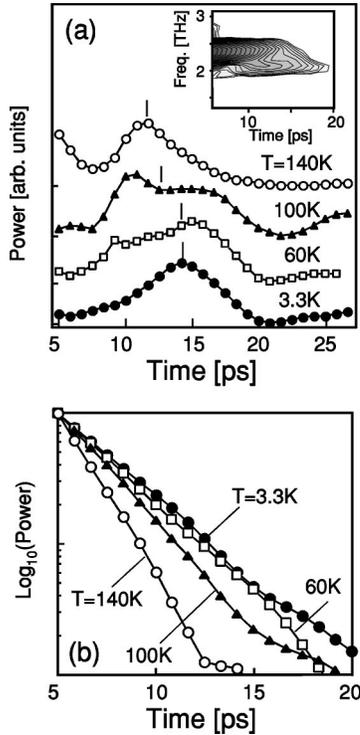


FIG. 3. (a) TRFT amplitude changes of E_g at various temperatures. The data are shifted vertically for clarity. The ticks indicate the estimated rise time. Inset: gray-scale plots of TRFT at 140 K. (b) TRFT amplitude changes of AM.

is formed at the expense of elastic energy of the lattice subsystem in the C phase. Therefore, the instantaneous modulation of the electronic system also induces a displacement of ion cores of the PLD, resulting in coherent folded-phonon motion as well as CDW AM motion.

Coherent phonons coupled with multiple electronic ground states is a plausible cause for the observed time anomaly. The superposition of phonon motions with slightly different energies results in a beat oscillation in their time evolutions. In this case, however, the superposition of phonon oscillations with a relative phase differing by π is needed to explain the absence of signal in the initial interval just after optical excitation. To our knowledge there is no generation mechanism that can account for such coherent phonon motion. In the present data it is difficult to infer a complete mechanism for the observed time anomaly of the E_g phonon. However, as discussed below, the SP dynamics in the C-phase $1T$ -TaS₂ is intimately associated with such time-dependent contributions of the phonon motion to the reflectivity changes.

In Fig. 3(a), we plot the TRFT amplitudes of the E_g mode as a function of time at different temperatures within the temperature range of the C phase. As observed at 3.3 K, a profound increase is measured for all temperatures except at 140 K where the E_g mode amplitude involves a contribution from the AM mode because these two frequencies are very close. A contour plot of TRFT at 140 K is shown in the inset, showing substantially the same time evolutions as shown in Fig. 2(a). Whereas the E_g shows a gradual increase at each temperature, its rise time shortens with increased tempera-

ture. In contrast, the AM exhibits an increasingly fast decay with increasing temperature, as shown in Fig. 3(b), which indicates that the AM decay is strongly correlated with the E_g increase.

The inverse correlation between AM and E_g is also correlated with the decay of the slow component of the SP relaxation, as seen in the inset of Fig. 1(a). Note that the decay time of the SP shows a gradual decrease with increasing temperature, which is again in good correspondence with the temperature dependence of the phonon motion. A relaxation process was proposed to account for the SP dynamics in such 1D structures.⁵ The SP, excited above the band gap, can quickly relax by a number of possible scattering events, and then reach the band edge that arises from the FS nesting. Because the gap acts as a bottleneck for relaxation, the SP's around the band edge undergo a slow decay process. A similar bottleneck should be expected in the C-phase 2D CDW; however, the situation seems to be more complicated in $1T$ -TaS₂. At 140 K, i.e., even below T_{C-NC} , a small but finite DOS at Fermi level has been observed by ARPES.¹³ In our time-resolved data, the initial abrupt SP relaxation may be responsible for such a gapless feature wherein the instantaneously excited SP can relax very quickly to the ground state.¹⁵ However, SP relaxation also involves a slow decay, which implies that a gap still exists.¹⁶ Since our results are from measurements far below T_{C-NC} , that is, deep in the C-phase CDW, strongly localized electrons can produce a gap feature even in the presence of a remnant DOS. Indeed, a strong emission peak shifted well away from the Fermi level has also been observed in ARPES at 20 K.¹⁷ The slowly decaying SP signal thus reflects the partially existing gap states.

On the basis of this idea, the observed correspondence between SP and AM decay indicates that the AM motion contributes to the reflectivity change through the electrons in the gap state. This in turn explains the reflectivity change after the AM decay, which is determined by the SP response in the vicinity of the ground state. From the gradual increase of the E_g amplitude and its inverse correlation with the AM decay, we conclude that the E_g phonon motion cannot contribute to the signal in the presence of SP's in the gap state, but rather in the ground state. To date, little consideration has been given to the coherent phonon motion from PLD. However, their time evolutions show time anomalies, suggesting coherent phonon motions associated with different electronic states.

In summary, we have performed time-resolved spectroscopy of coherent phonon motions in C-phase $1T$ -TaS₂ and have observed an anomalous behavior in their time evolution. Time-resolved FT showed that one of the coherent phonons with E_g symmetry showed a gradual increase, in contrast to the AM motion which appeared instantaneously. Their temperature dependences indicated that the rise time of the E_g mode was strongly correlated to the decay of both AM and SP relaxation.

The authors acknowledge Dr. Oliver B. Wright for very useful discussions.

- ¹M. Hase, M. Kitajima, S. Nakashima, and K. Mizoguchi, Phys. Rev. Lett. **88**, 067401 (2002).
- ²C. Shank, R. Yen, and C. Hirlimann, Phys. Rev. Lett. **50**, 454 (1983).
- ³L. Huang, J. Callan, E. Glezer, and E. Mazur, Phys. Rev. Lett. **80**, 185 (1998).
- ⁴S. Hunsche, K. Wienecke, T. Dekorsy, and H. Kurz, Phys. Rev. Lett. **75**, 1815 (1995).
- ⁵J. Demsar, K. Biljakovic, and D. Mihailovic, Phys. Rev. Lett. **83**, 800 (1999).
- ⁶J. Demsar, L. Forro, H. Berger, and D. Mihailovic, Phys. Rev. B **66**, 041101 (2002).
- ⁷D. Mihailovic, D. Dvorsek, V. V. Kabanov, J. Demsar, L. Forro, and H. Berger, Appl. Phys. Lett. **80**, 871 (2002).
- ⁸K. Kenji, M. Hase, H. Harima, S. Nakashima, M. Tani, H. K. Sakai, Negishi and M. Inoue, Phys. Rev. B **58**, R7484 (1998).
- ⁹H. J. Zeiger, J. Vidal, T. K. Cheng, E. P. Ippen, G. Dresselhaus, and M. S. Dresselhaus, Phys. Rev. B **45**, 768 (1992).
- ¹⁰G. Garrett, T. Albrecht, J. Whitaker, and R. Merlin, Phys. Rev. Lett. **77**, 3661 (1996).
- ¹¹A. Lobad and A. Taylor, Phys. Rev. B **64**, 180301(R) (2001).
- ¹²J. Wilson, F. Di Salvo, and S. Mahajan, Adv. Phys. **24**, 117 (1975); Phys. Rev. Lett. **32**, 882 (1974).
- ¹³Th. Pillo, J. Hayoz, H. Berger, M. Grioni, L. Schlapbach, and P. Aebi, Phys. Rev. Lett. **83**, 3494 (1999); Phys. Rev. B **62**, 4277 (2000).
- ¹⁴S. Sugai, K. Murase, S. Uchida, and S. Tanaka, Physica B & C **105**, 405 (1981).
- ¹⁵Similar fast SP relaxation together with slow component has also been observed by Demsar *et al.* (Ref. 5).
- ¹⁶In Ref. 5, Demsar *et al.* pointed out that SP relaxations were well fitted by the stretched exponential decay as can be employed in HTSC's. The difference of temperature dependence from HTSC's may be due to the strong lock-in transition in 1T-TaS₂.
- ¹⁷Th. Pillo, J. Hayoz, D. Naumovic, H. Berger, L. Perfetti, L. Gavioli, A. Taleb-Ibrahimi, L. Schlapbach, and P. Aebi, Phys. Rev. B **66**, 245105 (2001).