

Time-domain evidence for an excitonic insulator

S. Hellmann¹, T. Rohwer¹, M. Kalläne¹, K. Hanff¹, A. Carr², M. M. Murnane², H. C. Kapteyn², L. Kipp¹, M. Bauer¹, and K. Rossnagel¹

¹Institute of Experimental and Applied Physics, University of Kiel, D-24098 Kiel, Germany

²JILA and Department of Physics, University of Colorado and NIST, Boulder, Colorado 80309-0440, USA

Abstract. Time- and angle-resolved photoemission spectroscopy with a high-harmonic-generation source is used to classify the potential excitonic insulator $1T$ -TiSe₂ and the reference Peierls-Mott insulator $1T$ -TaS₂ on the basis of the melting times of “spectroscopic order parameters”.

1 Introduction

Since the concept of the excitonic insulator was introduced about 50 years ago [1], the identification of a real excitonic insulator has remained elusive. The reason probably is that the excitonic insulator instability is mathematically and physically almost indistinguishable from the more familiar Peierls instability, which explains charge-density wave (CDW) formation in low-dimensional materials as a consequence of strong electron-lattice interaction. In its canonical form, the excitonic insulator model starts from an indirect semiconductor with a small band gap or from a semimetal with a small band overlap and considers the limit when the band gap or overlap goes to zero: at some point either the band gap becomes smaller than the exciton binding energy or the band overlap and number of free carriers become so small that screening turns negligible; in both cases the system will become unstable toward spontaneous exciton formation and a CDW instability. The essential and intriguing difference to the Peierls instability is that the excitonic insulator instability is purely electronically driven, the periodic lattice distortion concomitant with the CDW being only an accidental by-product.

A material that has repeatedly been claimed to be an excitonic insulator is $1T$ -TiSe₂ [2,3], a layered compound that indeed appears to exhibit the defining characteristics: at room temperature, $1T$ -TiSe₂ shows a small gap [4] or overlap [2] between the Se $4p$ valence band maximum at the center of the Brillouin zone ($\Gamma(A)$ point) and the Ti $3d$ conduction band minimum at the zone edge ($M(L)$ point); and below about 200 K, it adopts a commensurate ($2 \times 2 \times 2$) CDW superstructure that enables direct Se $4p$ -Ti $3d$ interaction resulting in a ~ 100 -meV wide energy gap. Yet, although the spectral signatures are clear, the ultimate origin of the transition is very hard to identify.

For example, the most salient and remarkable feature of the transition in angle-resolved photoemission spectroscopy (ARPES) is the appearance of strikingly intense folded Se $4p$ bands at the original $M(L)$ point. But the simple static view of this “spectroscopic order parameter” cannot be used to pin down the excitonic insulator because the large spectral weight carried by the folded bands can be explained neither by electron-lattice interaction nor by electron-electron interaction alone [3,5] and the relative contributions cannot be separated straightforwardly.

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Here we report time-resolved ARPES measurements on $1T$ -TiSe₂, which reveal the dominant interaction in the CDW state in the time domain. Exploiting the technique's unique combination of femtosecond time resolution and momentum selectivity [6] and using the well-known Peierls-Mott insulator $1T$ -TaS₂ as a reference [7-10], we establish a hierarchy of melting times for different types of electronic order in momentum space. We specifically demonstrate that the CDW state of $1T$ -TiSe₂ melts on a sub-vibrational, i.e., electronic, time scale. In our opinion, these results provide the most conclusive evidence for the existence of the excitonic insulator so far.

2 Experiment

Time-resolved pump-probe ARPES experiments were performed with 43-eV extreme ultraviolet probe pulses selected from a high-harmonic-generation source by a pair of multilayer mirrors. All measurements were done under identical excitation conditions. The $1T$ -TiSe₂ and $1T$ -TaS₂ samples were held at an equilibrium temperature of 110 K and excited with 30-fs (FWHM), 790-nm near-infrared pump pulses at two absorbed energy densities of 300 Jcm⁻³ and 600 Jcm⁻³. The effective time and resolutions were 32 fs and 400 meV, respectively.

3 Results

Figure 1 compares the dynamics of the (electronically caused) Mott gap at $\Gamma(A)$ and the (structurally caused) Peierls gap near $M(L)$ of the reference compound $1T$ -TaS₂ (top and bottom rows) to the dynamics of the superstructure Se $4p$ peak (the "exciton peak") at $M(L)$ of $1T$ -TiSe₂ (middle row). The first column displays energy-versus-momentum snapshots taken without pumping and at characteristic pump-probe delays (marked by arrows in the second column). The second column exposes the delay dependence of the ARPES spectra at or near the corresponding high-symmetry points for the lower excitation density. And the third and fourth columns show the electronic order parameter transients for both excitation densities, as determined from the time-dependent spectra by integrating the ARPES intensity over adequate energy intervals (centered slightly above or slightly below the Fermi energy).

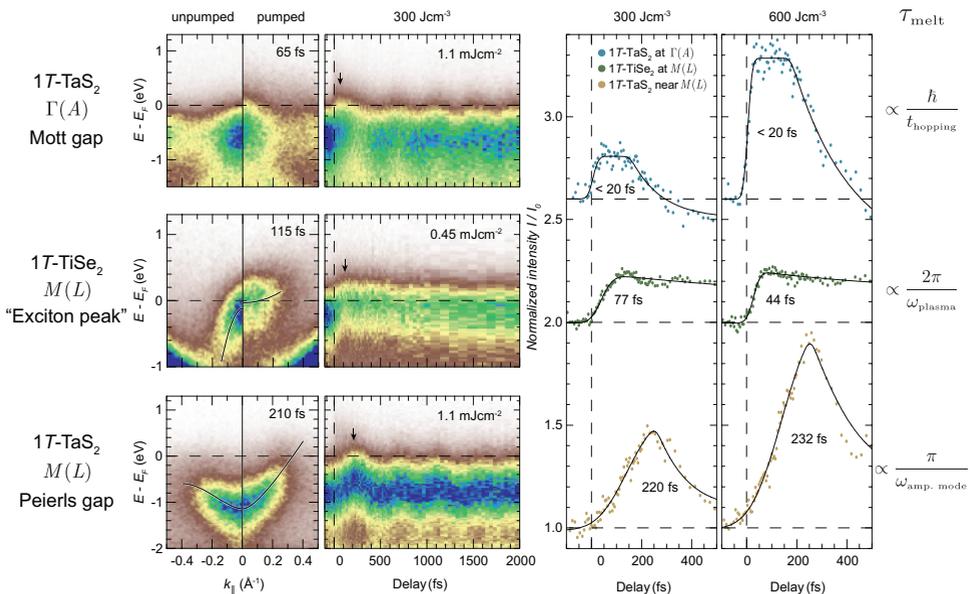


Fig. 1. Electronic structure dynamics of $1T$ -TaS₂ at the $\Gamma(A)$ point (top row) and near the $M(L)$ point (bottom row) and of $1T$ -TiSe₂ at the $M(L)$ point (middle row). For details see text.

Remarkably, the extracted melting times are consistent with distinct fundamental time scales related to the inverse hopping matrix element (Mott gap), the inverse plasma frequency (“exciton peak”), and the inverse CDW amplitude mode frequency (Peierls gap), respectively. However, the most important finding is that photo-excited $1T$ -TiSe₂ clearly responds on a sub-vibrational time scale, specifically on a time scale reflecting the characteristic time needed for the build-up of screening, which in turn is a key ingredient to the physics of the excitonic insulator. These results provide strong evidence for a predominantly electronic origin of the enigmatic CDW in $1T$ -TiSe₂.

4 Conclusion

In conclusion, time-resolved ARPES is used to settle the controversial nature of the CDW phase of $1T$ -TiSe₂: the dominant factor in the CDW state appears to be electron-electron interaction, which strongly suggests that $1T$ -TiSe₂ is indeed an excitonic insulator. The case study demonstrates how time-resolved ARPES can be applied to classify different types of electronic order, such as the ones occurring in Mott, Peierls, and excitonic insulators, in the time domain.

References

1. N. F. Mott, *Phil. Mag.* **6**, 287 (1961)
2. H. Cercellier, C. Monney, F. Clerc, C. Battaglia, L. Despont, M. G. Garnier, H. Beck, P. Aebi, L. Patthey, H. Berger, and L. Forró, *Phys. Rev. Lett.* **99**, 146403 (2007)
3. C. Monney, C. Battaglia, H. Cercellier, P. Aebi, and H. Beck, *Phys. Rev. Lett.* **106**, 106404 (2011)
4. J. C. E. Rasch, T. Stemmler, B. Müller, L. Dudy, and R. Manzke, *Phys. Rev. Lett.* **101**, 237602 (2008)
5. K. Rossnagel, *J. Phys.: Condens. Matter* **23**, 213001 (2011)
6. T. Rohwer, S. Hellmann, M. Wiesenmayer, C. Sohr, A. Stange, B. Slomski, A. Carr, Y. Liu, L. Miaja Avila, M. Källäne, S. Mathias, L. Kipp, K. Rossnagel, and M. Bauer, *Nature* **471**, 490 (2011)
7. L. Perfetti, P. A. Loukakos, M. Lisowski, U. Bovensiepen, H. Berger, S. Biermann, P. S. Cornaglia, A. Georges, and M. Wolf, *Phys. Rev. Lett.* **97**, 067402 (2006)
8. S. Hellmann, M. Beye, C. Sohr, T. Rohwer, F. Sorgenfrei, H. Redlin, M. Källäne, M. Marczynski-Bühlow, F. Hennies, M. Bauer, A. Föhlisch, L. Kipp, W. Wurth, and K. Rossnagel, *Phys. Rev. Lett.* **105**, 187401 (2010)
9. M. Eichberger, H. Schäfer, M. Krumova, M. Beyer, J. Demsar, H. Berger, G. Morienna, G. Sciaini, and R. J. D. Miller, *Nature* **468**, 799 (2010)
10. J. C. Petersen, S. Kaiser, N. Dean, A. Simoncig, H. Y. Liu, A. L. Cavalieri, C. Cacho, I. C. E. Turcu, E. Springate, F. Frassetto, L. Poletto, S. S. Dhesi, H. Berger, and A. Cavalleri, *Phys. Rev. Lett.* **107**, 177402 (2011)