Single-Particle and Collective Mode Couplings Associated with 1- and 2-Directional Electronic Ordering in Metallic $R\mathrm{Te}_3$ (R = Ho, Dy, Tb)

R. V. Yusupov,[1,*] T. Mertelj,[1] J.-H. Chu,[2] I. R. Fisher,[2] and D. Mihailovic[1]

[1]*Complex Matter Department, Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia*

[2]*Geballe Laboratory for Advanced Materials and Department of Applied Physics, Stanford University, Stanford, California 94305, USA*

(Received 30 June 2008; published 11 December 2008)

The coupling of phonons with collective modes and single-particle gap excitations associated with one- (1d) and two-directional (2d) electronically driven charge-density wave (CDW) ordering in metallic $R\mathrm{Te}_3$ is investigated as a function of rare-earth ion chemical pressure (R = Tb, Dy, Ho) using femtosecond pump-probe spectroscopy. From the T dependence of the CDW gap Δ_{CDW} and the amplitude mode, we find that while the transition to a 1d-CDW ordered state at T_{c1} initially proceeds in an exemplary mean-field-like fashion, below T_{c1}, Δ_{CDW} is depressed and departs from the mean-field behavior. The effect is apparently triggered by resonant mode mixing of the amplitude mode with a totally symmetric phonon at 1.75 THz. At low temperatures, when the state evolves into a 2d-CDW ordered state at T_{c2} in the $DyTe_3$ and $HoTe_3$, additional much weaker mode mixing is evident but no soft mode is observed.

DOI: 10.1103/PhysRevLett.101.246402 PACS numbers: 71.45.Lr, 72.15.Nj, 78.47.J−

Ordered electronic states in condensed matter physics are of fundamental importance as models for investigating the competition between different ground states and the collective behavior of quantum systems. They are also of a practical interest because electronic ordering gives rise to phenomena such as superconductivity and colossal magnetoresistance which are all macroscopic manifestations of underlying quantum phenomena. One class of systems which has received renewed attention recently are two-dimensional (2D) layered metals with electronically driven charge-density-wave (CDW) instabilities, partly because of the possible role that electronic ordering may play in high-temperature superconductivity in layered cuprates and (more recently) iron pnictides [1]. In weakly interacting systems, the instability is predominantly driven by a Fermi surface (FS) nesting, where a single wave vector q_N connects multiple points along the FS, giving rise to an enhanced generalized susceptibility at this wave vector, which in turn leads to the formation of an electronic ordered CDW state which reduces the energy of the system. How this behavior evolves in strongly coupled systems such as cuprates is still the subject of intense investigations and is not clear.

Layered rare-earth tritelluride compounds ($R\mathrm{Te}_3$, where R is a rare-earth ion) shown schematically in Fig. 1(a) are interesting newly discovered examples of very weakly coupled electronically driven [2] CDW systems whose properties can be tuned by changing the size of the R ion which changes the unit cell size along the crystallographic a axis, effectively exerting a chemical pressure. Initial electron diffraction [2] and subsequent high resolution x-ray diffraction (XRD) [3–5] studies have revealed the ubiquitous presence of a weak lattice modulation at a primary modulation vector q_{CDW}, where FS nesting leads to the formation of a one-directional (1d) incommensurate CDW. More recently, angle-resolved photoemission spectroscopy (ARPES) confirmed the existence of imperfect FS nesting and revealed that as a result of the CDW, a gap forms in the Fermi surface in the Γ-Z direction [6,7] of the Brillouin zone. Quantum oscillations from the reconstructed FS have been observed in $LaTe_3$ [8]. Recent theoretical work suggests that there may be a competition between 1d ''stripe order'' and 2d ''checkerboard order,'' which is finely tuned by the strength of the electron-phonon coupling λ. Indeed, x-ray diffraction [5] and STM data [9] on the heavier rare-earth members of the series confirm the presence of a ''rectangular'' 2d-ordered CDW state at low temperatures (at $T_{c2} \simeq 126$ K in $HoTe_3$ and 49 K in $DyTe_3$). In $TbTe_3$ there are also indications of possible 2d ordering from scanning-tunneling microscope studies at 6 K [9], but no long range ordering was seen by x-ray diffraction. In some layered chalcogenides, notably in $NbSe_2$, pressure leads to suppression of the CDW and emergence of superconductivity. Studies as a function of chemical pressure in tritellurides have shown that the 1d-CDW transition temperature T_{c1} decreases with decreasing R radius, but at the same time, another, coexisting 2d-ordered state appears in the heavier R members of the series, whose critical transition temperature T_{c2} increases with increasing pressure [see Fig. 1(b)]. So far, no superconductivity was discovered, but all compounds show metallic resistivity down to the lowest temperatures, in spite of CDW gaps on the FS.

Femtosecond pump-probe spectroscopy (FPPS) has recently been shown to be eminently suitable to the study of quasiparticle (QP) and collective excitations of electronically ordered systems [10–13]. It allows the measurement of low-frequency modes with very high resolution which are inaccessible to Raman spectroscopy, as well as a direct measurement of the QP recombination kinetics across the

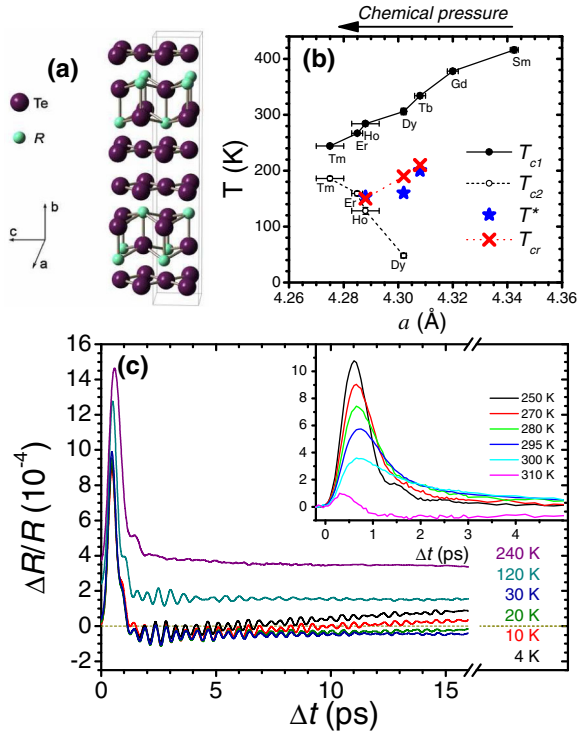

FIG. 1 (color online). (a) The structure of $R\mathrm{Te}_3$. (b) The phase diagram of $R\mathrm{Te}_3$ showing the critical temperatures T_{c1} and T_{c2} for the 1d and 2d transitions, respectively, as a function of lattice constant a. Chemical pressure increases with decreasing R and a. (c) The raw data of the reflectivity $\Delta R/R$ as a function of time delay Δt of DyTe_3 at different temperatures. The oscillations are the coherently excited phonons and amplitude mode. The transient observed at short times is the single-particle response. The data for the other members of the series are qualitatively the same.

CDW or superconducting gap. In this Letter, we use FPPS to investigate the evolution of the CDW gap and the coupling of the amplitude mode and single-particle excitations with phonons in the 1d- and 2d-ordered states of three tritellurides for the first time: HoTe_3 and DyTe_3, which exhibit two CDW transitions, and TbTe_3, for which there is only one transition.

FPPS involves the measurement of the transient reflectivity response after excitation by ultrashort (50 fs) laser pulses [11,13]. The laser pulses excite electron-hole pairs which relax to states near the Fermi level in <50 fs by avalanche QP multiplication. When there is a gap for electronic excitations at low energy, such as a CDW or superconducting gap, a relaxation bottleneck may form and a nonequilibrium population of the QPs at the gap edge, which can be probed by excited state absorption with a probe laser pulse, thus effectively measuring QP density in real time. This QP density is usually assumed to be directly proportional to the transient change of reflectivity $\Delta R/R$ which allows us to directly observe the presence of a CDW gap, the QP relaxation time τ_{QP}, and their evolution with temperature. In addition to the QP excitations, with FPPS we also observe collective excitations such as phonons and the amplitude mode (AM) [11], typically with very high resolution and low noise. In our experiments the pump and probe wavelengths were 400 and 800 nm, respectively. The pump fluence was $\sim 20\ \mu\mathrm{J/cm}^2$, and laser heating was checked to be minimal. The crystals used in this study were prepared by slow cooling a binary melt, as described previously [14]. Clean surfaces oriented perpendicular to the b axis of the crystal were exposed by cleavage prior to the measurement.

The raw data on the transient reflectivity are shown in Fig. 1(c) for DyTe_3 (data on all three compounds are qualitatively similar). The QP response gives rise to the short transient, while the oscillations are from the coherently excited phonons and the AM. The QP data are analyzed in the following way: The maximum value of $\Delta R/R(t)$ was used as a measure of QP density (A_{QP}), while the lifetime was obtained by fitting the falling slope of the fast transient with $\Delta R/R(t) = A\exp[-t/\tau_{\mathrm{QP}}]$. The fast transient is then subtracted from the data to obtain the oscillatory responses, which are then analyzed separately.

The amplitude of the QP response A_{QP} and the lifetime τ_{QP} for all three compounds are shown in Fig. 2 as a function of T. Their temperature dependence is very similar near T_{c1}. The data are fit using a theoretical model for the photoinduced signal amplitude of gapped systems [11]:

$$A_{\mathrm{QP}} \propto \frac{[\Delta(T) + k_B T/2]^{-1}}{1 + \gamma\sqrt{\frac{2k_B T}{\pi\Delta(T)}}\exp[-\Delta(T)/k_B T]}, \qquad (1)$$

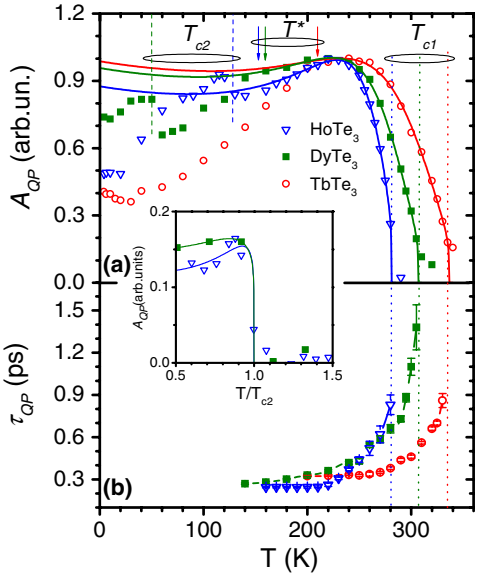

FIG. 2 (color online). (a) The amplitude of the QP response as a function of temperature for TbTe_3, DyTe_3, and HoTe_3. The solid lines are the fits to the data using the predicted single-particle response for a BCS-like gap function under bottleneck relaxation conditions given by Eq. (1). (b) The relaxation time of the single-particle response shows a divergence as T_{c1} is approached from below.

where $\Delta(T)$ is the gap with a BCS-like T dependence and γ is a parameter (see [11] or [12] for a description of γ). We see that the solid lines show remarkable agreement with the data near T_{c1}. The gap values for the Ho, Dy, and Tb tellurides obtained from the fit are $\Delta(0)_{1D} = 118(2)$, 123 (3), and 125(6) meV, respectively, in good agreement with previous optical measurements [15] and somewhat less than the maximum gap obtained in ARPES [7], which we attribute to the fact that optical measurements, in general, perform an average over $\vec{q}$. The values of γ were 20(5) for all traces. The relaxation time is theoretically related to the gap as $\tau_{QP} \propto 1/\Delta_{1d}(T)$ near T_c [10], so the divergence of τ_{QP} for all three compounds is further remarkable indication of mean-field (MF) behavior, where $\Delta_{1d}(T) \rightarrow 0$ as $T \rightarrow T_{c1}$.

In contrast to the behavior near T_{c1}, below ≈ 200 K we see a systematic departure from the predicted MF behavior in all three compounds. The order parameter in $TbTe_3$ observed by x-ray diffraction shows a similar departure from MF behavior in the same temperature range [5]. In our case, two effects are visible: a drop in the amplitude below the MF prediction and a small but systematic gaplike feature which coincides with T_{c2} in $DyTe_3$ and $HoTe_3$. The inset in Fig. 2 shows that the gaplike anomaly at T_{c2} can be fit to the appearance of an additional CDW gap opening for both Ho and Dy tellurides. The fit gives values of the gap at $\Delta(0)_{2D} = 40(4)$ meV and $\Delta(0)_{2D} = 13.5(1.5)$ meV for $HoTe_3$ and $DyTe_3$, respectively, with $\gamma = 3$. No such gap opening is unambiguously seen in $TbTe_3$, where the existence of a second transition is uncertain [5]. Turning to the departure from MF behavior, we have plotted the point where the amplitude A_{QP} deviates from the MF prediction on the phase diagram in Fig. 1. The deviation is systematic in all three compounds and occurs in the temperature range 140 K $< T^* <$ 200 K.

Next, let us turn our attention to the AM and the phonons. To minimize problems with fast Fourier transform (FFT) artifacts in the data analysis, we fit the coherent phonon oscillations in two stages. First, we use a set of three oscillators which are fit in time domain, subtract them from the data, and then the residual time trace containing weak oscillations is analyzed separately. As a typical example, the raw time-domain data and FFTs of the fitted time trace and residual time trace are shown in Fig. 3 for $DyTe_3$ at $T = 3.8$ K. In Fig. 4, we show the evolution of the observed modes as a function of temperature. Following the mode assignments of Lavagnini *et al.* [16], in the distorted phase there are 56 A_1- and 28 B_1-symmetry modes, all of which we can observe in principle. However, similarly as in Raman, many may be overlapping and we observe only a few. Many of the phonon modes are observed to shift in frequency at low temperatures. The color map (Fig. 4) shows also the linewidths and intensities of the most intense modes. At low T, the modes are very sharp and quite intense, but near T_{c1}, all modes virtually disappear. A mode at 2.2 THz—which we attribute to the AM of the CDW—is seen to soften significantly on approaching T_{c1} from below. Resonant coupling of the AM with the mode at 1.75 THz is clearly seen in all three compounds. In addition, the mode near 2.6 THz is observed to show a frequency renormalization, which may be associated with the transition to bidirectional order at T_{c2} in Ho and Dy tellurides. In $TbTe_3$ we see no further effect at low T, consistent with the absence of low-temperature CDW ordering in this compound.

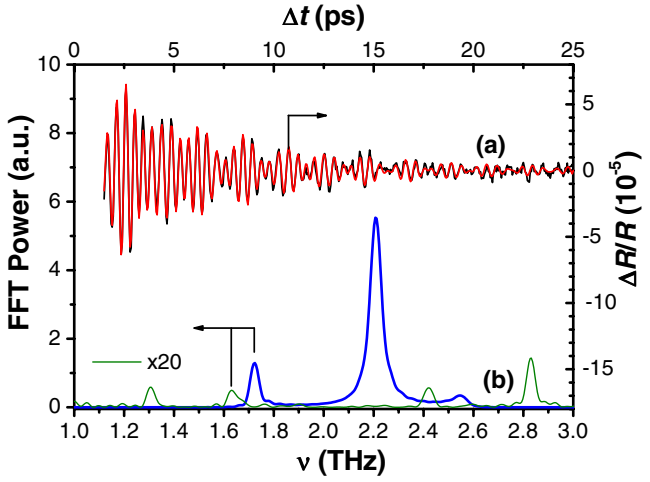

FIG. 3 (color online). (a) The oscillatory response in $DyTe_3$ at 3.8 K (black line) with a fit using three damped oscillators (red line). (The relaxation component is subtracted.) (b) The fast Fourier transform of the fitted trace shown in (a) (thick line) and the FFT of the remaining modes (thin line).

In Fig. 4, we also show a model fit which describes the crossing of the AM with the 1.75 THz phonon. We use a simple model of two interacting vibrational modes, where the AM has a MF-like T dependence $\nu_{AM} = \nu_0 * (1 - T/T_c)^{\beta}$ and $\nu_p = 1.75$ THz, with an interaction term (off-diagonal matrix element) δ. The model is solved analytically, and the fits to the data in Fig. 4 give the same rather large value for the AM-phonon interaction in all three compounds: $\delta = 0.105 \pm 0.011$ THz (3.5 ± 0.5 cm^{-1}) and $\beta = 0.30(3)$.

Remarkably, the temperature T_{cr} at which the AM frequency crosses the 1.75 THz phonon is very close to T^* for all three tellurides (compare Figs. 2 and 4). Furthermore, we see that the 2.6 THz phonon for all three compounds appears just below T_{cr}. From this systematic behavior we conclude that the anomalies in the QP density are related to the strong mixing of the AM with the 1.75 THz phonon. In the absence of a phonon mode assignment for the 1.75 THz mode, we cannot analyze the ionic displacements quantitatively, but we can qualitatively understand the observed effect as follows. Since the 1.75 THz phonon is clearly coupled to the AM, by symmetry this mode is also directly coupled to the charge excitations of the charge-density wave. The strong mixing of the two modes will thus disturb the AM Te ion displacements by introducing other displacements corresponding to the 1.75 THz phonon, which

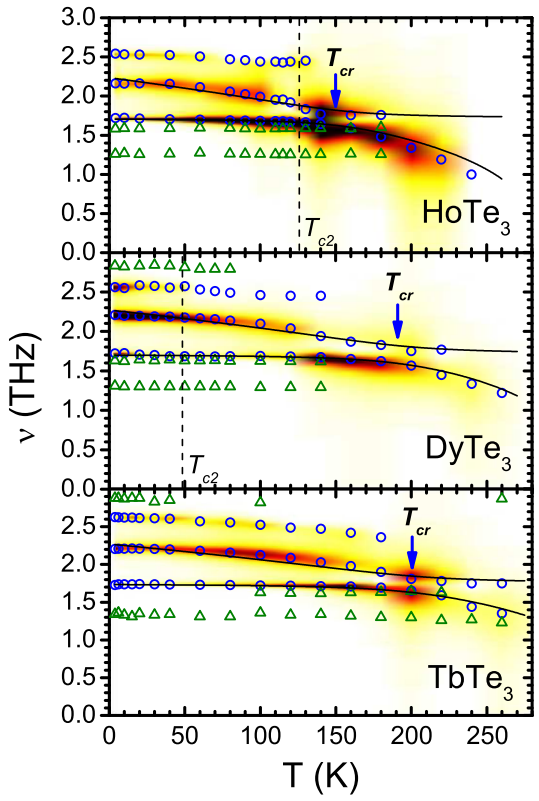

FIG. 4 (color online). A phonon intensity map as a function of T and ν for $HoTe_3$, $DyTe_3$ and $TbTe_3$ showing all of the observed oscillators. Mode mixing is evident between the AM (whose frequency is 2.2 THz at low T) and the 1.75 THz mode at intermediate temperatures and with the 2.6 THz phonon at low temperatures. The latter is particularly evident in $DyTe_3$. The lines are fits to the data using a simple level-crossing model calculation (see text).

will in turn have the effect of reducing the AM amplitude, and depress the CDW gap Δ_{CDW}. In other words, the CDW gap is renormalized by the 1.75 THz mode once it mixes with the AM. The appearance of the 2.6 THz phonon can then be understood to arise from symmetry breaking below T^*.

Summarizing the interplay between the different signatures of low-temperature ordering, we see that the onsets of 1d and 2d ordering are clearly seen in the QP response. Judging from the fits to the data, the increase in amplitude which coincides with T_{c2} is most likely associated with the opening of a second gap which accompanies the low-temperature transition to 2d ordering. High resolution XRD [5] and ARPES [17] in $ErTe_3$ indeed suggest the opening of an additional gap along the Γ-X direction. In contrast, in the phonon spectrum, an AM is associated only with the 1d transition at T_{c1}, and, in spite of high resolution and excellent signal to noise in our data, we do *not* observe any soft mode which can be associated with T_{c2}.

However, the QP response at low T in the three compounds investigated here cannot be simply attributed to just the opening of the gaps at T_{c1} and T_{c2}. The clear correlation among the temperature T^* where the QP response departs from MF behavior, the mode crossing temperature T_{cr}, and the appearance of the 2.6 THz phonon in all three compounds is an unambiguous indication of systematic disruption of 1d-CDW order resulting from coupling of a phonon at 1.75 THz to the CDW, and the drop of amplitude of the QP response well below T^* seen in Fig. 2 implies a renormalization of the gap. The increasing T^* (or T_{cr}) with decreasing rare-earth pressure is a direct consequence of the increasing T_{c1}, which shifts the crossing temperature T_{cr} of the AM with the 1.75 THz phonon. Finally, we note that the strong soft mode behavior of the AM is a clear indication that the transition at T_{c1} in $DyTe_3$ and $HoTe_3$ is of second order. From the fits to the T dependence of the QP response, it would appear that the low-temperature phase transition is also second order, but, since no soft mode is observed associated with this transition, this cannot be claimed with certainty. Nevertheless, none of the observed QP responses appear to show any temperature hysteresis associated with either T_{c1} or T_{c2}, apparently confirming this assignment. Absence of an additional AM developing below T_{c2} is surprising by itself as these excitations have been observed in all systems studied so far; the AM is totally symmetric and thus should be present in the coherent phonon spectra.

Studies at Jozef Stefan Institute are supported within the FP6, Project No. NMP4-CT-2005-517039 (CoMePhS). The work at Stanford University is supported by the DOE, Office of Basic Energy Sciences, under Contract No. DE-AC02-76SF00515.

*Permanent address: Kazan State University, Kremlevskaya 18, 420008 Kazan, Russia. Roman.Yusupov@ijs.si

[1] Y. Kamihara *et al.*, J. Am. Chem. Soc. **128**, 10 012 (2006).
[2] E. DiMasi, B. Foran, M. C. Aronson, and S. Lee, Chem. Mater. **6**, 1867 (1994).
[3] C. Malliakas, S. J. L. Billinge, H. J. Kim, and M. G. Kanatzidis, J. Am. Chem. Soc. **127**, 6510 (2005).
[4] C. Malliakas and M. G. Kanatzidis, J. Am. Chem. Soc. **128**, 12 612 (2006).
[5] N. Ru *et al.*, Phys. Rev. B **77**, 035114 (2008).
[6] G. Gweon *et al.*, Phys. Rev. Lett. **81**, 886 (1998).
[7] V. Brouet *et al.*, Phys. Rev. B **77**, 235104 (2008).
[8] N. Ru *et al.*, Phys. Rev. B **78**, 045123 (2008).
[9] A. Fang *et al.*, Phys. Rev. Lett. **99**, 046401 (2007).
[10] V. V. Kabanov *et al.*, Phys. Rev. B **59**, 1497 (1999).
[11] J. Demsar *et al.*, Phys. Rev. Lett. **83**, 800 (1999).
[12] P. Kusar *et al.*, Phys. Rev. B **72**, 014544 (2005).
[13] J. Demsar *et al.*, Phys. Rev. B **66**, 041101 (2002).
[14] N. Ru and I. R. Fisher, Phys. Rev. B **73**, 033101 (2006).
[15] A. Sacchetti *et al.*, Phys. Rev. B **74**, 125115 (2006).
[16] M. Lavagnini *et al.*, Phys. Rev. B **78**, 201101 (2008).
[17] R. Moore *et al.* (unpublished).