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# Infrared and Raman investigation of the charge–density-wave state in rare-earth tri-telluride compounds

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ABSTRACT

We summarize our recent efforts in investigating the charge–density-wave (CDW) state of the rare-earth tri-tellurides $RTe_3$ by means of infrared and Raman techniques. We identify the CDW gap, as order parameter of the broken-symmetry ground state, as well as the collective mode of the CDW condensate.



## 1. Introduction

The charge–density-wave (CDW), first predicted by Peierls for one-dimensional interacting electron gas systems [1], is a prototype example of collective state, which, similarly to superconductivity, belongs to the class of broken-symmetry ground state. The paradigm of CDW forming materials are the quasi one-dimensional compounds [1], the properties of which are nicely summarized in Ref. [2]. But electronically driven CDW states were also found and thoroughly investigated in novel two-dimensional (2D) layered compounds [3–7], an effort motivated in part by the fact that high temperature superconductivity in the copper-oxide systems may indeed emerge from a peculiar charge-ordering through the tuning of relevant parameters [6,8].

Two prominent energy scales generally characterize the CDW electrodynamic response: the collective amplitude/phason mode, associated with the oscillations of the amplitude/phase of the CDW condensate, respectively, and the single-particle gap ($2\Delta$) excitation, acting as order parameter of the transition [2]. It is worth mentioning that the amplitude mode is Raman while the phason is infrared active. Determining these energy scales is of great relevance in order to characterize the CDW quantum ground state.

Over the past few years we undertook a thorough spectroscopic investigation of the rare-earth tri-tellurides ($RTe_3$) [9], which may be considered as prototype quasi-two-dimensional (layered) materials and got lately a revival of interest. They host an *unidirectional*, incommensurate CDW already well above room temperature for all R elements lighter than Dy [10,11], while in the heavy rare-earth tri-tellurides (i.e., R=Tm, Er, Ho, Dy) the corresponding transition temperature, $T_{CDW1}$, lies below $\sim 300$ K and decreases with increasing R mass. In the latter systems, a further transition to a *bidirectional* CDW state occurs at $T_{CDW2}$, ranging from 180 K for $TmTe_3$ to 50 K for $DyTe_3$ [10,11]. The drastic change in transition temperatures with the size of the R ion or externally applied pressure on a given material [12] is accompanied by a similarly large change in the properties of the CDW itself. In particular, the CDW gap of $RTe_3$ progressively collapses when the lattice constant is reduced, which, in turn, induces a transfer of spectral weight into the metallic component of the excitation spectrum [13–15], the latter resulting from the fact that the Fermi surface in these materials is only partially gapped by the formation of the CDW.

This conference proceeding is devoted to briefly summarize our most recent comprehensive efforts to identify order parameter and collective mode(s) of $RTe_3$ by means of infrared and Raman spectroscopy. A full account of our data and their analysis can be found in the already quoted references. This report is specifically based on our work appeared in Refs. [16,17]. We also invite the reader to consult these references for technical details about the experimental setups.

## 2. Results and discussion

Fig. 1 highlights $\sigma_1(\omega)$ in the infrared energy interval for $ErTe_3$, a heavy rare-earth member of the tri-tellurides family with CDW phase transitions at $T_{CDW1}=265$ K and $T_{CDW2}=157$ K [10,11]. Upon lowering the temperature we first observe a narrowing of the zero-energy resonance, ascribed to the effective metallic (Drude) contribution to the absorption spectrum. Contrary to the 1D materials, where the CDW phase transition leads to an insulating state [2], the

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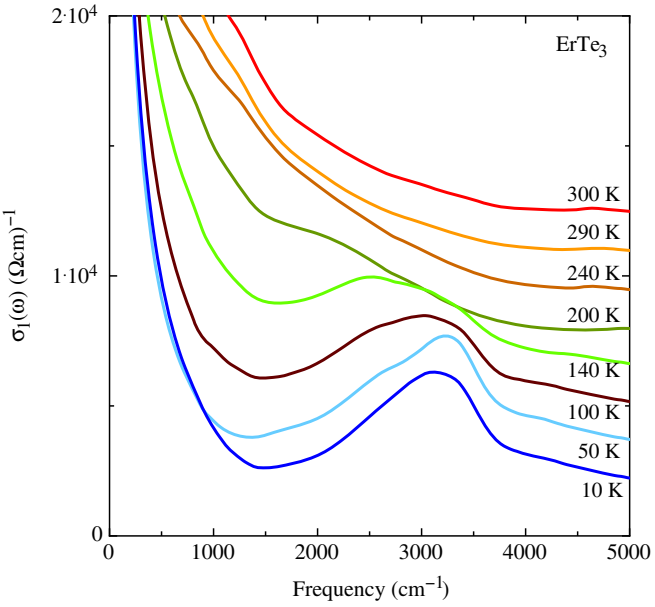


**Fig. 1.** Temperature dependence of $\sigma_1(\omega)$ in the infrared energy interval for $ErTe_3$. All spectra have been shifted for clarity by a constant value of $1.5 \times 10^3\ \Omega\ cm^{-1}$ [16].

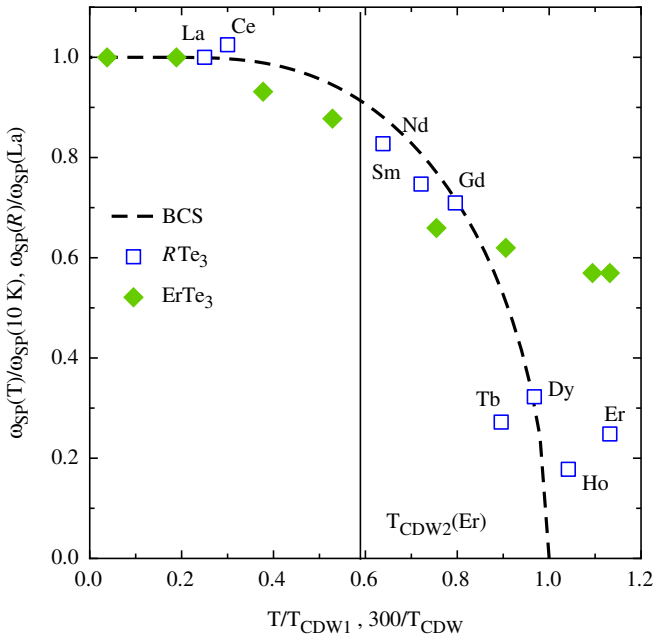


**Fig. 2.** Temperature and chemical pressure dependence of $\omega_{SP}$, normalized by the low temperature values of $ErTe_3$ or by the values of $LaTe_3$ in the $RTe_3$ series (i.e., chemical pressure). The temperature axis is normalized by the respective critical temperatures ($T_{CDW1}$, or $T_{CDW}$ for the $RTe_3$ series) [10,11]. The vertical thin dotted lines mark the critical temperature $T_{CDW2}$ for $ErTe_3$. The BCS prediction [20] for the order parameter is shown for comparison [16].

persisting metallic part in $\sigma_1(\omega)$ at low temperatures of 2D materials overcasts the collective mode (we return below about this issue). Hand in hand with the narrowing of the metallic component there is the appearance of a pronounced mid-infrared feature, peaked at about 3000 $cm^{-1}$ and which obviously pairs with the depletion seen in $R(\omega)$ at about the same energy (not shown here) [16]. The $\sigma_1(\omega)$ spectra as a function of temperature on $ErTe_3$ do share common features with our previous data upon lattice compression on the $RTe_3$ series [13–15].

The mid-infrared peak is ascribed to the charge excitation across the CDW gap into a single particle (SP) state. In the following we will refer to this feature as the SP peak at $\omega_{SP} = 2\Delta$ [13]. Upon increasing the temperature, the gap absorption progressively shifts into and is almost screened by the high-frequency tail of the metallic part in $\sigma_1(\omega)$ (Fig. 1). Close to and above $T_{CDW1}$, the gap feature is indeed at best a broad shoulder overlapped to the Drude component. The explicit temperature dependence of $\omega_{SP}$ in $ErTe_3$ is shown in Fig. 2. $\omega_{SP}(T)$ is here normalized by its value deep into the CDW ground state (i.e., $\omega_{SP}(10\ K)$), while the temperature axis is normalized by the respective $T_{CDW1}$. As expected, $\omega_{SP}$ monotonically increases with decreasing temperature below $T_{CDW1}$. It is worth noting that the optical estimation of the CDW gap for $ErTe_3$ at 10 K (i.e., $\omega_{SP} \sim 3000\ cm^{-1}$, Fig. 1) is nearly identical with the gap value extracted from ARPES experiment [18]. However, the temperature dependence of $\omega_{SP}$ does not display any clear-cut anomalies in coincidence with the second phase transition at $T_{CDW2}$. On the contrary, the ARPES investigation does give evidence for a smaller gap (i.e., of the order of 800 $cm^{-1}$) due to the second CDW [18]. Nevertheless, ARPES also establishes that the area of Fermi surface gapped by the first CDW transition is three times the area gapped by the second one [18]. Therefore, the excitation due to the smaller gap is most probably overcast by the effective metallic contribution in the absorption spectrum and could well merge into the high frequency tail of the Drude resonance. Moreover, with our optical method we only measure the average energy-excitation over the whole Brillouin zone, missing the k-space resolution of ARPES.

A signature of the gap feature is already present at 300 K, close to but yet above the first high temperature CDW phase transition at $T_{CDW1}$ (Fig. 2). We remark that this is a rather common situation in prototype CDW materials [19]. The persistence of the gap above the phase transition temperature can be considered as a fingerprint of precursor effects of the CDW formation and has been widely invoked as a manifestation of the fluctuation regime [19]. Therefore, CDW fluctuations seem to play an important role in $RTe_3$ as well, despite their two-dimensionality. The presence of substantial fluctuations is also confirmed by the observation of superlattice peaks with rapidly increasing width and decreasing correlation length well above $T_{CDW1}$ [11].

It is now instructive to compare the relevant parameter $\omega_{SP}$ achieved with our optical experiments when varying the temperature [16] and upon lattice compression [13]. For the purpose of clarity, we limit our comparison to the chemical series, having already showed that both chemical and applied pressure are equivalent [13–15]. Fig. 2 additionally displays the gap ratio for the chemical series (open squares) [13]. We took the $\omega_{SP}$ values measured at 300 K, normalized with the gap of $LaTe_3$, assumed to be the largest one for $RTe_3$. Instead of the normalized temperature, we consider here the ratio $300\ K/T_{CDW}$ as the effective temperature axis for the chemical series [16]. Within the CDW state, we evince a general common trend in the development of the gap for the $RTe_3$ compounds, when changing R, as well as for $ErTe_3$, when varying the temperature. As comparison, we reproduce the BCS temperature dependence of the order parameter [20], which overall mimics the experimental findings for $T < T_{CDW}$.

We now address the collective mode of the CDW condensate [17]. The response in $\sigma_1(\omega)$ of the residual metallic component (Fig. 1) completely screens all optically active modes (including the collective CDW phase excitation) and makes their observation by infrared absorption methods impossible. This is why we turned to Raman scattering in order to shed light on the collective mode, specifically on the amplitude one. A detailed view of the Raman scattering spectra and their temperature dependence in $DyTe_3$ ($T_{CDW1} = 307$ K and $T_{CDW2} = 49$ K [11]) is shown in Fig. 3. For $\omega \leq 80\ cm^{-1}$ and at low temperatures there is a weak peak close

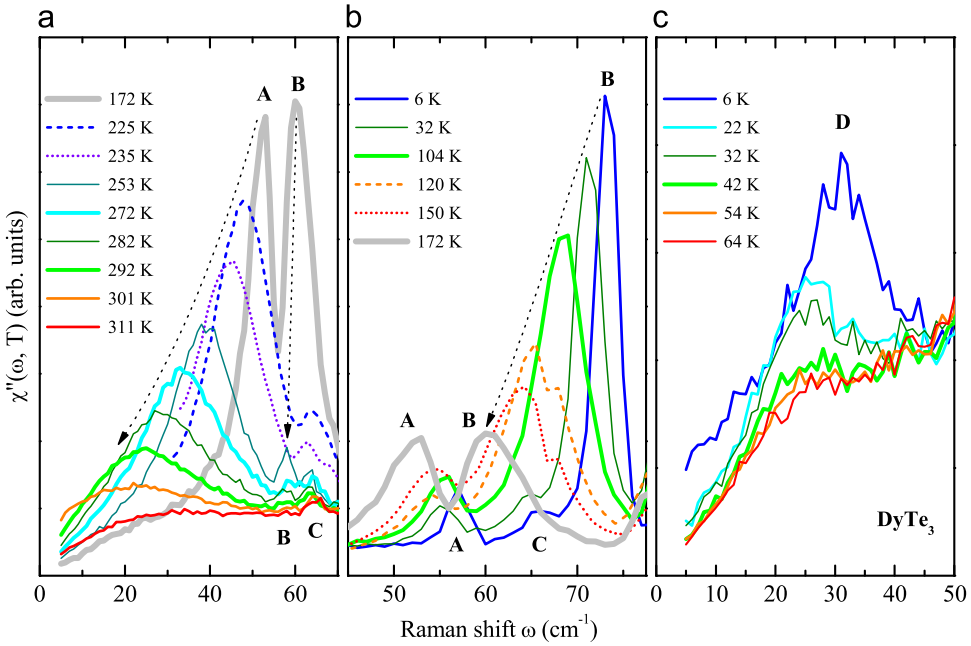


**Fig. 3.** Detailed view of the temperature dependence of the A, B and C modes of $DyTe_3$ above (a) and below (b) $T_{tr}$. The arrows highlight the trend of modes A and B with increasing temperature. (c) Low frequency interval characterized by mode D for temperatures close to and below $T_{CDW2}$. The relative intensity ratio among panels (a–c) is 2:8:1 [17].

to 60 $cm^{-1}$ and a sharp one around 70 $cm^{-1}$ (labels A and B) [21]. Upon destroying the CDW state with increasing temperature the sharp B mode first softens, gets progressively broader and loses spectral intensity in favor of the A feature (Fig. 3b). At $T_{tr}$ of about 170 K, the two modes roughly share the same amount of spectral intensity (Fig. 3(a) and (b)). Upon approaching $T_{CDW1}$ the energy of the B mode becomes constant, while its intensity drops above $T_{tr}$ and vanishes at $T_{CDW1}$, as does that of the A mode, whose resonance frequency saturates at 23 $cm^{-1}$ (Fig. 3a). In contrast mode C, which is only seen at high resolution (Fig. 3(a) and (b)), exists already above $T_{CDW1}$ and survives the transition, without displaying any temperature dependence. This latter mode is assigned to a lattice vibration, as evinced from the phonon dispersion calculation [22].

In the low temperature spectra of $DyTe_3$ an additional mode (D) in the range below 50 $cm^{-1}$ (Fig. 3c) is found, which disappears upon increasing the temperature above $T_{CDW2}$. Interestingly, its energy at $T_{CDW2}$ saturates at the same value (23 $cm^{-1}$) as the one of the A mode at $T_{CDW1}$, which we interpret as being due to an impurity scattering rate of this order of magnitude in our sample [23]. From the temperature dependence observed in Fig. 3c, we can safely conclude that this mode is the collective amplitude mode of the bidirectional CDW state.

By combining experimental observations and numerical simulations [22], we were able to demonstrate the tight coupling between the CDW gap and the lattice degrees of freedom and to make a robust prediction for the Kohn anomaly inducing the CDW phase transition. An *ab initio* calculation of the phonon dispersion relation for the orthorhombic pseudotetragonal ($a=c$) structure of $LaTe_3$ showed that two optical branches have an instability in the vicinity of the wave vector $q=(2/7)c^*$ with $c^*=2\pi/c$ [22]. The existence of *two* soft modes directly follows from the crystal structure of the rare-earth tri-tellurides, characterized by two adjacent Te-planes per unit cell, a feature that has been ignored in all theoretical models for CDW's in these systems until now.

At $T_{CDW1}$ the system undergoes a transition into one of the two predicted unidirectional CDW states. This transition results in a strong renormalization (from $\sim$120 $cm^{-1}$ to $\sim$60 $cm^{-1}$) of the frequency of the phonon at $q_{CDW1}$ of the second branch expected to soften according to the calculations of Ref. [22]. As the temperature is lowered, the minimum on the free energy surface corresponding to the first unidirectional CDW moves towards smaller values of $q$, until it reaches a (saddle-)point at a temperature close to $T_{tr}$ where it becomes more favorable for the system to settle into the second calculated soft mode. The minute change in $q$-vector involved in this step does not alter the size of the gapped area on the Fermi surface and consequently it should not be seen in the electrical resistivity [11]. What it does, however, is to interchange the original amplitude mode and renormalized phonon, so that feature A is an amplitude mode between $T_{CDW1}$ and $T_{tr}$ and a phonon below $T_{tr}$, while the opposite holds true for the B mode. This means that mode B is originally a renormalized phonon mode above $T_{tr}$ and takes over the role of the amplitude mode below $T_{tr}$ [17].

## 3. Conclusions

We collected optical data over a broad spectral range and as a function of temperature on $ErTe_3$. We observe the temperature dependence of both the Drude component, due to the itinerant charge carriers, and the single-particle peak, ascribed to the charge–density-wave gap excitation. The CDW gap progressively opens while the metallic component gets narrow with decreasing temperature. An important fraction of the whole Fermi surface seems to be affected by the CDW phase transitions. It turns out that the temperature [16] and the previously investigated pressure dependence [13,14] of the most relevant CDW parameters share several common features and behaviors. Particularly, the order parameter of the CDW state is in general agreement with the predictions of the BCS theory.

Raman scattering experiments [17] as a function of temperature on $DyTe_3$ provide a clear-cut evidence for the emergence of the respective collective CDW amplitude excitations. In the unidirectional CDW phase, we discover that the amplitude mode develops as a succession of two mean-field, BCS-like transitions with different critical temperatures, which we associate with the presence of two

adjacent Te planes in the structure. As future outlook, we shall mention our present effort in determining the selection rules for the amplitude modes and therefore their exact polarization dependence. This important issue will be addressed in a forthcoming paper.

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