Raman scattering evidence for a cascade evolution of the charge-density-wave collective amplitude mode

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The two-dimensional rare-earth tritellurides undergo a unidirectional charge-density-wave (CDW) transition at high temperature and, for the heaviest members of the series, a bidirectional one at low temperature. Raman scattering experiments as a function of temperature on DyTe$_3$ and on LaTe$_3$ at 6 GPa 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.

PACS number(s): 71.45.Lr, 62.50.−p, 78.30.−j

Electronic instabilities are at the origin of phenomena as diverse as the formation of spin-density wave (SDW) and charge-density wave (CDW) or superconductivity, the interplay of which is among the most intriguing open questions of modern solid-state physics. Besides determining the ground state of the quantum system in which they occur, electronic instabilities also fundamentally affect its excitation spectrum. In the CDW state, on which we focus here, a gap opens up in the single-particle spectrum, and two new collective modes, associated with the oscillations of the amplitude and of the phase of the CDW, respectively, appear.[1] The paradigm of CDW forming materials are the quasi-one-dimensional compounds,[2] the properties of which are nicely summarized in Ref. [1]. 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]

A family of layered compounds which have attracted a lot of attention recently are the rare-earth (R) tritellurides RTe$_3$, first studied by DiMasi *et al.*[9] They host a *unidirectional* incommensurate CDW already well above room temperature for all R elements lighter than Dy,[10,11] while in the heavy rare-earth tritellurides (i.e., R=Tm, Er, Ho, Dy) the corresponding transition temperature, T_{CDW1}, lies below ∼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. The response of this residual metallic component 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 our recent study of the lighter rare-earth tritellurides.[16] By combining experimental observations and numerical simulations, 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 $c^* = \frac{2\pi}{c}$.[16] The existence of *two* soft modes directly follows from the crystal structure of the rare-earth tritellurides, characterized by two adjacent Te planes per unit cell, a feature that has been ignored in all theoretical models for CDWs in these systems until now.

While an unambiguous identification of the amplitude mode in RTe$_3$ by Raman scattering has been elusive so far, femtosecond pump-probe (FSPP) experiments, both in time- and angle-resolved photoemission on TbTe$_3$ (Ref. [17]) and in optical spectroscopy on RTe$_3$ (R=Tb, Dy, and Ho)[18] have provided rather convincing evidence for its existence in the unidirectional CDW phase. Although these latter experiments were performed down to temperatures well below T_{CDW2}, the amplitude mode associated with the bidirectional CDW was not observed.

Here, we present Raman scattering investigations as a function of temperature on DyTe$_3$ at ambient pressure [T_{CDW1}=307 K and T_{CDW2}=49 K (Ref. [11])] and on LaTe$_3$ at 6 GPa, with a lattice constant between that of DyTe$_3$ and HoTe$_3$, and T_{CDW1} ∼ 260 K.[10,12] The covered spectral range extends from 5 to 200 cm^{-1}, i.e., well beyond the previous low-frequency limit of about 65 cm^{-1},[16] thus giving access
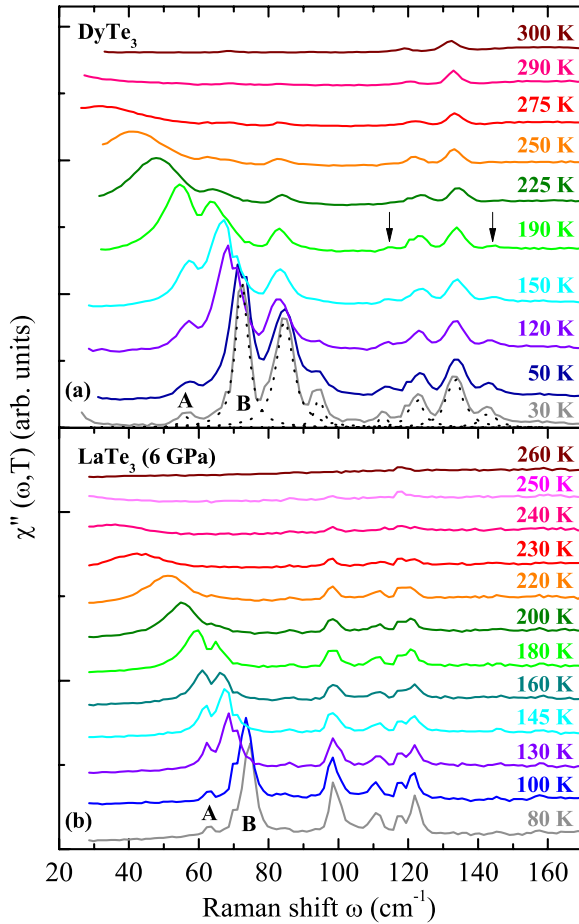
FIG. 1. (Color online) Temperature dependence of the Raman scattering spectra (a) of DyTe$_3$ at ambient pressure and (b) of LaTe$_3$ at 6 GPa. The spectra have been shifted for clarity. In panel (a) the oscillators employed for the data fits are shown for the measurement at 30 K (dotted lines) and the arrows mark the weak features at 113 and 143 cm^{-1}. The labels A and B denote the weak mode at ~60 cm^{-1} and the sharp one at ~70 cm^{-1} at low temperatures, respectively.

to the energy region in which the collective modes are expected to appear. In the temperature interval between T_{CDW1} and ~50 K, we observe that, in both systems, the amplitude mode in the unidirectional CDW phase exhibits a transition to a higher frequency around T_{tr} ~ 170 K, which manifests itself in the form of a transfer of spectral weight between two peaks, whose positions as a function of temperature are well described by a BCS model[1] for two condensate densities with different critical temperatures. These consecutive unidirectional CDW transitions can be clearly resolved in our experiment and represent a genuine experimental breakthrough, highlighting the importance of bilayer effects. Furthermore, a feature below ~50 K appears in DyTe$_3$. From its temperature dependence, it can be unambiguously identified with the amplitude mode associated with the bidirectional CDW phase.

The single crystalline samples of RTe$_3$ were grown by slow cooling of a binary melt.[10,11] Raman spectra were collected on cleaved [010] surfaces in backscattering geometry. The Ar$^+$ and Kr$^+$ laser lines at 514 and 531 nm, respectively,
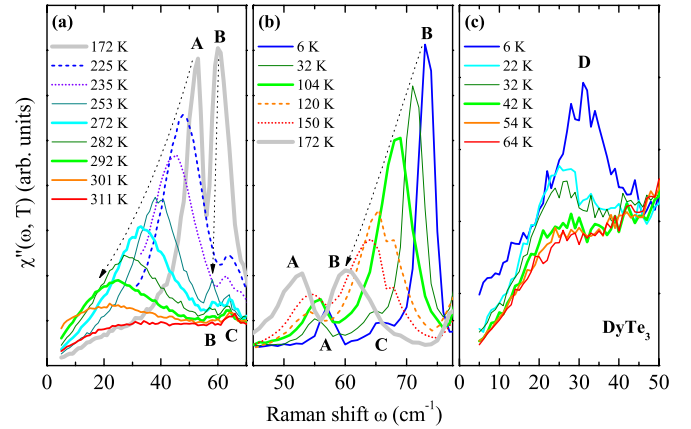

FIG. 2. (Color online) Detailed view of the temperature dependence of the A, B [see Fig. 1(a)], and C modes of DyTe$_3$ (a) above and (b) below T_{tr}. The arrows highlight the trend of modes A and B with increasing temperature. (c) Low-frequency interval characterized by mode D for temperatures close to and below T_{CDW2}. The relative intensity ratio among panels (a)–(c) is 2:8:1.

were used for excitation. The heating in the 30-μm-wide spot was kept below 5 K. Depending on the experimental requirements the scattered light was analyzed with a triple Jobin-Yvon T64000 and a double Jarrell-Ash 25–100 monochromator. The polarizations of the incident and scattered photons were parallel to each other and aligned with the *a* or *c* axis. High pressure was generated by means of a home-made diamond-anvil cell (DAC) with nitrogen as a pressure-transmitting medium. The pressure was determined by a standard ruby fluorescence technique.[19]

Figure 1 displays the imaginary part $\chi''(\omega,T)$ of the Raman response obtained by dividing the measured spectra by the thermal Bose factor. The general trend in temperature for both sets of data is quite similar, suggesting that by hydrostatically compressing the lattice (as for LaTe$_3$ at 6 GPa) one can recover the properties and responses of chemically compressed RTe$_3$ (i.e., through substitution of the R element). This confirms our earlier findings at 300 K as a function of pressure[16] and is further supported by our data collected on HoTe$_3$ as a function of temperature, which will be presented elsewhere.

At low temperatures and deep in the CDW state, we observe well distinct and rather sharp modes. Above 80 cm^{-1} the modes, previously ascribed to the Raman active phonons with A_{1g}, and A_1 and B_1 symmetry for the undistorted (pseudotetragonal) and distorted phase, respectively,[16] lose spectral weight with increasing temperature, while their width marginally changes as a function of temperature.

For $\omega \lesssim 80$ cm^{-1} and at low temperatures there is a weak peak close to 60 cm^{-1} and a sharp one around 70 cm^{-1} (labels A and B in Fig. 1), in agreement with the findings of Ref. 18. Their temperature dependence is specifically emphasized for DyTe$_3$ in Figs. 2(a) and 2(b). 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 [Figs. 1(a) and 2(b)]. At T_{tr} of about 170 (160) K for DyTe$_3$ (LaTe$_3$ at 6 GPa), the two modes roughly share the same amount of spectral intensity

[Figs. 1, 2(a), and 2(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. 2(a)]. In contrast mode C, which is only seen at high resolution [Figs. 2(a) and 2(b)], exists already above T_{CDW1} and survives the transition, without displaying any temperature dependence.

In the low-temperature spectra of DyTe$_3$ an additional mode (D) in the range below 50 cm^{-1} [Fig. 2(c)] 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.[20] As a consequence, a quantitative analysis of the low energy spectral range in terms of Lorentz oscillators is not possible. Yet, from the temperature dependence observed in Fig. 2(c), we can safely conclude that this mode is the collective amplitude mode of the bidirectional CDW state.[21]

A quantitative analysis is possible for the modes evolving with the unidirectional CDW below T_{CDW1}. To this end, we perform a fit of the response function χ'' with a series of damped harmonic oscillators,[22] after having subtracted a smooth background. A total of eight oscillators is employed for frequencies smaller than 170 cm^{-1} and a sample of all fit components is shown in Fig. 1(a). Figure 3 emphasizes the temperature dependence of the resonance frequencies and integrated intensities extracted from our fits for the two low-frequency modes A and B, for which we propose the following scenario.

At T_{CDW1} the system undergoes a transition into one of the two predicted unidirectional CDW states.[16] This transition results in a strong renormalization (from ~120 cm^{-1} to ~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. 16. As the temperature is lowered, the minimum on the free-energy surface corresponding to the first unidirectional CDW moves toward 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.[23] The minute change in q vector involved in this step does not alter the size of the gapped area on the Fermi surface (FS) and consequently it should not be seen in the electrical resistivity, especially in view of the relatively small effect induced by the drastic modification in FS topology occurring at T_{CDW1} and T_{CDW2}.[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. The higher limiting frequency at zero temperature of the amplitude mode developing below ~T_{tr} can be explained as follows. On the one hand, a smaller wave vector implies a higher frequency for the relevant phonon in the absence of CDW transition according to Fig. 3b of Ref. 16; on the other hand it is plausible that the electron-phonon coupling constant, taken to be q independent in conventional treatments,[1] slightly increases with decreasing wave vector when two close-by instabilities are involved. That the coupling increases below 200 K is
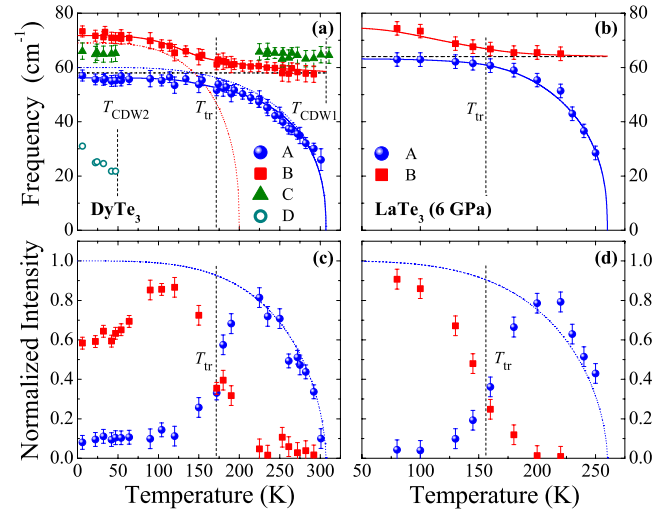

FIG. 3. (Color online) Temperature dependence [(a) and (b)] of the resonance frequencies and [(c) and (d)] of the normalized integrated intensities of the A (blue dot) and B (red square) modes of DyTe$_3$ at ambient pressure and of LaTe$_3$ at 6 GPa. The dashed lines at about 59(63) cm^{-1} in panels (a) and (b) are the respective renormalized phonons which couple to the collective excitation. Panel (a) also reports the resonance frequencies of the C lattice mode (green triangle) and of the amplitude mode (D) for the bidirectional CDW of DyTe$_3$ [Fig. 2(c)]. The blue and red lines in panels (a) and (b) are the fits of the resonance frequencies for modes A and B (see text). The thin dotted lines in panels (a) and (c) and (d) are the BCS predictions for the resonance frequencies [$\omega \sim n_c(T)$] and for the order parameter [$I_A(T) \sim \Delta(T)$] (Refs. 1 and 27), respectively. The normalization factor in panels (c) and (d) corresponds to the total intensity of both modes.

also supported by the appearance of further two weak lines at 113 and 143 cm^{-1} [arrows in Fig. 1(a)]. The above situation can be quantitatively described by a model involving two temperature-dependent modes coupled to a phonon with a temperature-independent frequency. The results of Figs. 3(a) and 3(b) were obtained by assuming that the two modes have resonance frequencies proportional to the respective condensate densities [$n_c(T)$, thin dotted lines in panel a] and that they interact with the phonon at about 59(63) cm^{-1} for DyTe$_3$(LaTe$_3$) [dashed line in Figs. 3(a) and 3(b)] with a coupling constant of ~5(4) cm^{-1}.[26] In standard CDW systems, where only one phonon branch is unstable, the frequency of the amplitude mode is proportional to $\sqrt{n_c}$.[1] The dependence found here confirms that the two unstable phonon branches are intimately coupled and cannot be considered separately as far as their frequencies are concerned. Our description is similar to that previously used by Yusupov *et al.*,[18] based on the Ginzburg-Landau temperature dependence of the amplitude mode. This latter approach suffers from a few weaknesses: the resulting temperature dependence of the amplitude mode frequency is not consistent with the mean-field prediction and the model itself would be only valid at $T \sim T_{CDW1}$ and fails to reproduce our high-resolution data for $T \ll T_{CDW1}$.

In our model, the intensity of mode A first rises below T_{CDW1} with decreasing temperature. Around T_{tr}, domains characteristic of the second calculated distortion start to

form, leading to a transfer of spectral intensity to feature B at the cost of the high-temperature (A) one [Figs. 3(c) and 3(d)]. Close to T_{CDW1} there is a good agreement between the integrated intensity of feature A and the prediction for the BCS order parameter [i.e., $I_A(T) \sim \Delta(T)$].[27,28] Another peculiarity is the loss of spectral intensity of the B mode [Fig. 3(c)] at low temperatures ($T \lesssim 50$ K), which agrees with the increase in intensity observed below T_{CDW2} for the collective mode associated with the bidirectional CDW [Fig. 2(c)].

In summary, our careful analysis of the temperature dependence of the collective modes in RTe$_3$, as obtained by Raman scattering, has shown that the rare-earth tritellurides support not only one but *two* different unidirectional CDWs, a property that follows from the presence of two adjacent Te planes in the crystal structure. In addition, we have identified the collective mode associated with the low-temperature bidirectional CDW phase, recently observed by x-ray diffraction in the heavy RTe$_3$ compounds.[11]

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