Optical spectroscopy study on $CeTe_3$: Evidence for multiple charge-density-wave orders

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We performed optical spectroscopy measurement on a single crystal of $CeTe_3$, a rare-earth-element tri-telluride charge-density-wave (CDW) compound. The optical spectra are found to display very strong temperature dependence. In addition to a large and pronounced CDW energy gap that is already present at room temperature, as observed in earlier studies, the present measurement revealed the formation of another energy gap at a smaller energy scale at low temperature. The second CDW gap removes the electrons near E_F, which undergo stronger scattering. The study yields evidence for the presence of multiple CDW orders or strong fluctuations in the light rare-earth-element tri-telluride.

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I. INTRODUCTION

Collective quantum phenomena, such as charge density waves (CDW's) and spin density waves (SDW's), are among the most fascinating phenomena in solids and have been a subject of considerable interest in modern condensed matter physics. Most CDW or SDW states originate from the nesting topology of Fermi surfaces. This results in a divergence or strong anomaly in susceptibility at the nesting wave vector, leading to an instability of the electronic structure. The CDW or SDW states are stabilized via electron-phonon or electron-electron interactions by opening up energy gaps in the nested regions of the Fermi surfaces, which thus leads to a lowering of the electronic energies of the occupied states. The formation of an energy gap at the transition has been generally taken as a characteristic feature of CDW or SDW order.

Among various CDW materials, the rare-earth tri-telluride RTe_3 (R = Y, La, and rare-earth elements) has attracted much attention[1] due to their widely tunable properties by either chemical substitutions[2–5] or application of pressure.[5–8] RTe_3 has a layered structure[9,10] (inset of Fig. 1) consisting of the alternate stacking of insulating corrugated RTe slabs and two square Te layers along the b axis. The crystal lattice is weakly orthorhombic, which belongs to the space group *Cmcm* (No. 63).[9] Under much high pressure, the difference between the two short axes gradually disappears and the structure seems to undergo a transition from orthorhombic to tetragonal.[5] R in the compound is trivalent, donating three electrons to the system. They completely fill the Te p orbitals in the RTe slabs, but partially fill those Te p orbitals in the square Te layers.[10,11] Metallic conduction occurs in the Te layers, leading to highly anisotropic transport properties.[10,12]

Band-structure calculations indicate two very simple Fermi surfaces[4,13] that exhibit little dispersion along the b axis. It is revealed by angle-resolved photoemission spectroscopy (ARPES)[11,14] that the nesting of the Fermi surfaces drives the CDW instability. In the RTe_3 family, the incommensurate nesting wave vector is about the same, i.e., it is along the c^* in the base plane of the reciprocal space.[1,15] ARPES measurement demonstrated a nonuniform distribution of gap amplitude in the first Brillouin zone, which reaches the maximum in the optimal nested region at $k_x = 0$ and decreases to zero far from the a^* axis.[4] The maximum gap value decreases from a light to a heavy rare-earth element. For $CeTe_3$, a very large energy gap ($\approx$400 meV)[11] has been revealed by ARPES. It is expected from mean-field theory that the CDW transition should appear even above the melting temperature of the compound.[15] However, the CDW ordering temperatures are found to be substantially reduced from the light to heavier rare-earth elements.[3]

Optical spectroscopy is a powerful technique to probe the energy gap in the ordered state. It also yields fruitful information about conducting carrier response. Optical measurements on $CeTe_3$ at room temperature[2] and under pressure[6,7] have been reported, which provided clear evidence for the formation of the partial energy gap[11] in the CDW state and its evolution with pressure. Since the CDW transition temperature of this compound is extremely high,[3] the room temperature is believed to be already deeply into the CDW state, and it is claimed that no temperature dependence exists in the optical spectra below room temperature.[2] Here we present a temperature-dependent optical measurement on $CeTe_3$. In contrast to the early assertion, we observed a prominent temperature dependence of the optical spectra. Much more surprisingly, our measurements revealed a different gap structure developing below 300 K at the lower energy scale, evidencing the formation of another CDW order at low temperature.

II. EXPERIMENT AND RESULTS

The single crystals of $CeTe_3$ were grown by a self-flux method.[12] Ce and Te elements with the molar ratio of 1 : 40 were mixed, then put into an alumina crucible and sealed in a quartz tube under vacuum. The mixture was heated to 860°C and remained at that temperature for 10 h, then slowly cooled to 560°C at a rate of 3°C/h. At the final temperature, the rest flux Te was still in liquid and separated from the crystals in a centrifuge. Platelike single crystals with a dimension of 3 × 3 mm^2 were obtained after breaking the crucible. The samples were stored in a glove-box in an argon atmosphere since the compound is somewhat air- and moisture-sensitive. The crystals were characterized by x-ray diffraction (XRD) and scanning electron microscopy (SEM) measurements. Figure 1 shows the $(0k0)$ XRD patterns for the single-crystal samples of $CeTe_3$ with Cu $K\alpha$ radiation. The XRD patterns indicate that the samples have good crystallization along the b axis. The

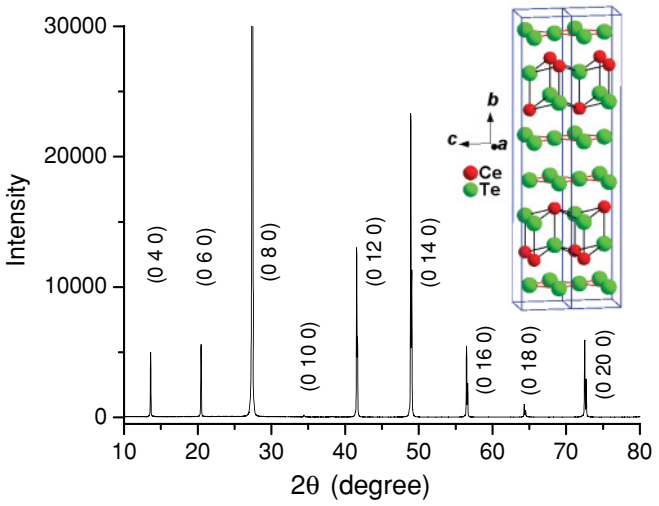

FIG. 1. (Color online) The (0k0) x-ray diffraction pattern of single-crystal $CeTe_3$. The strongest peak (intensity up to near 10^5) is only partially displayed in order to show other peaks clearly. The inset shows the crystal structure.

obtained b-axis lattice parameter is $b = 26.0348$ Å, which is consistent with the reported lattice parameter in the literature.[5] The energy-dispersive spectroscopy (EDS) analysis equipped with SEM indicates the correct Ce : Te = 1 : 3 ratio.

The temperature-dependent in-plane (ac-plane) resistivity was obtained with the four contact technique in a quantum design physical properties measurement system (PPMS) and plotted in Fig. 2. The resistivity shows good metallic behavior below room temperature. In agreement with previous studies,[12] a sharp drop near 3 K is observed, which could be attributed to the antiferromagnetic ordering of the spins from the localized $4f$ electrons of Ce.[8,12,16] The above characterizations indicate the good quality of the single crystal.

The near-normal incident reflectance spectra were measured by Bruker IFS 113 and 66 v/s spectrometers in the frequency range from 40 to 25 000 cm^{-1}. An *in situ* gold and aluminum overcoating technique was used to get the reflectivity $R(\omega)$. The real part of the conductivity $\sigma_1(\omega)$ is obtained by the Kramers-Kronig transformation of $R(\omega)$. A Hagen-Rubens relation was used for low-frequency extrapolation. A constant value was used for high-frequency extrapolation up to 100 000/cm^{-1}, above which an ω^{-4} dependence is employed.

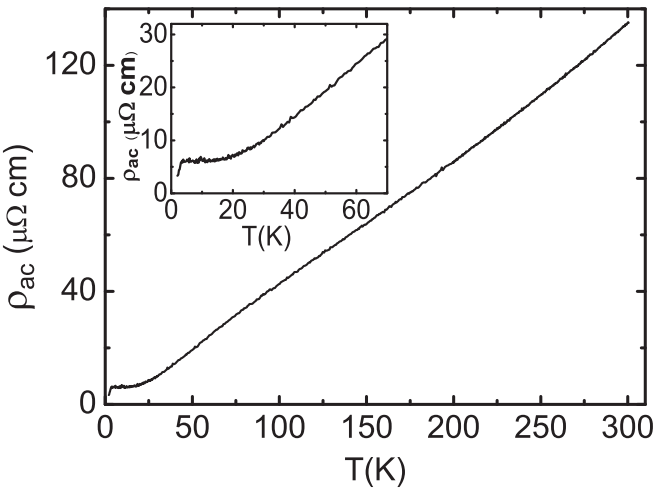

FIG. 2. The temperature-dependent in-plane (ac-plane) resistivity of single-crystal $CeTe_3$. Inset: the expanded plot of $\rho(T)$ in the low-temperature range.

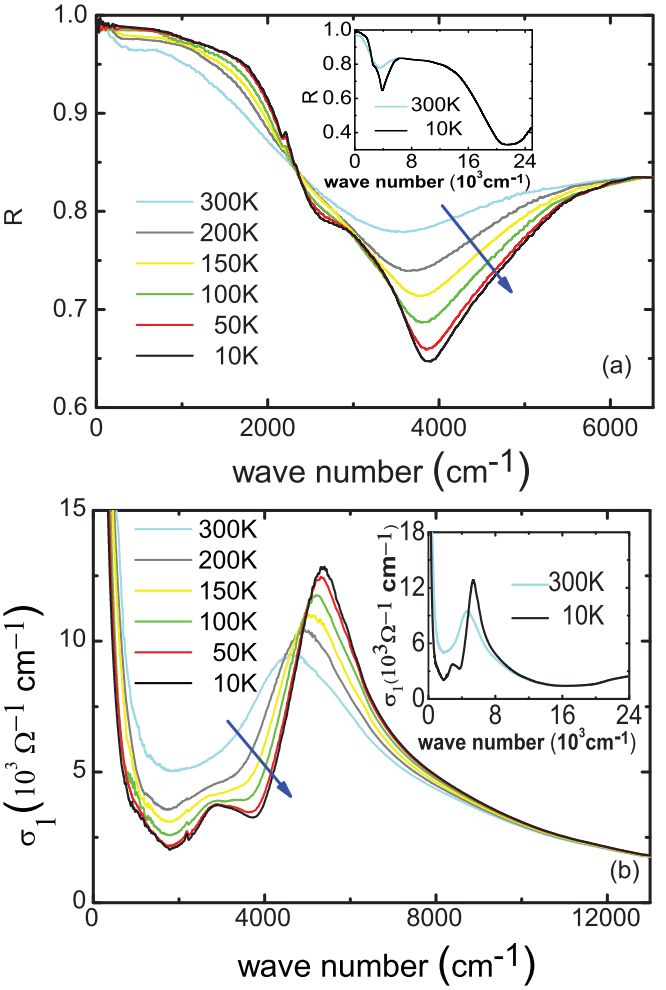

FIG. 3. (Color online) (a) The temperature-dependent reflectivity of $CeTe_3$ in the range from 40 to 6500 cm^{-1}. Inset shows the $R(\omega)$ at two representative temperatures over a broad frequency range from 40 to 25 000 cm^{-1}. (b) The frequency dependence of the real part of the optical conductivity at different temperatures. The arrow points to low temperatures. The inset shows the $\sigma_1(\omega)$ at 10 and 300 K over a broad energy range. The arrow indicates the temperature decreasing direction.

Figure 3(a) shows the $R(\omega)$ spectra up to 6500 cm^{-1} with its inset revealing the expanded range up to 25 000 cm^{-1}. Meanwhile, the real part of the conductivity $\sigma_1(\omega)$ is displayed in Fig. 3(b). At room temperature, the reflectance $R(\omega)$ shows rather high values at low frequency, but decreases rapidly with increasing frequency. A pronounced dip is seen near 3500 cm^{-1}. This leads to a strong peak in the conductivity $\sigma_1(\omega)$, roughly near 4600 cm^{-1}. The spectra provide optical evidence for the presence of an energy gap at room temperature.[3] The room-temperature data are consistent with those reported in earlier studies.[2] In addition to this peak in the midinfrared region, there exists a very sharp Drude component centered at zero frequency. The spectra demonstrate that the compound

remains metallic even if it is in the CDW state. This is also clearly illustrated in the above resistivity measurement.[12] Obviously, the Fermi surfaces are only partially gapped in the CDW state.[4,11,14]

Surprising results were observed at low temperatures. Roughly above but near 200 K, we can identify the development of a shoulder near 2700 cm^{-1} in $R(\omega)$ and it becomes more and more dramatic as the temperature decreases. Furthermore, the dip near 3500 cm^{-1} shifts to higher frequency and becomes much more pronounced than the high-temperature data. Then, in the $\sigma_1(\omega)$ spectra, an additional peak develops near 2800 cm^{-1} ($\sim$ 350 meV). Meanwhile, the spectral weight in the midinfrared region near this area is strongly suppressed and transferred to the very strong peak near 5000 cm^{-1}, causing a sizable shift of the original CDW gap toward higher energy. As we shall explain below, the peak that developed near 200 K is an indication of a new energy gap structure, which could be ascribed to the formation of a new CDW order. The change of the spectral weight at higher energies suggests that the band structure is substantially reconstructed with the formation of the new order.[11] Additionally, the free-carrier behaviors also change in response to the formation of the new CDW gap. The reflectance edge near 2500 cm^{-1} becomes sharper than the edge at high temperatures, reflecting a reduction of the free-carrier scattering rate.

It is also worth noting that a small peak feature near 2200 cm^{-1} in $R(\omega)$ develops along with the appearance of the above-mentioned shoulder while temperature decreases, which also leads to a peak in the $\sigma_1(\omega)$ spectra roughly at the same frequency. Different from the notable shift of the two broad peaks corresponding with the two CDW orders, the small peak position changes little at varied temperatures. We noticed that it could not be ascribed to the phonon mode[17] because it is located at such a high-energy scale, which is not expected based on the atomic mass of both Ce and Te. The origin of the peak has yet to be explored.

III. DISCUSSION

We shall first elaborate on the change of the conducting electrons with the development of the new energy gap. To estimate in a quantitative way, we decompose the conductivity spectra into Drude and Lorentz components at two representative temperatures: 300 K, the room temperature, and 10 K, the lowest measurement temperature:

$$\epsilon(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega/\tau_D} + \sum_{i=1}^{N} \frac{S_i^2}{\omega_i^2 - \omega^2 - i\omega/\tau_i}. \quad (1)$$

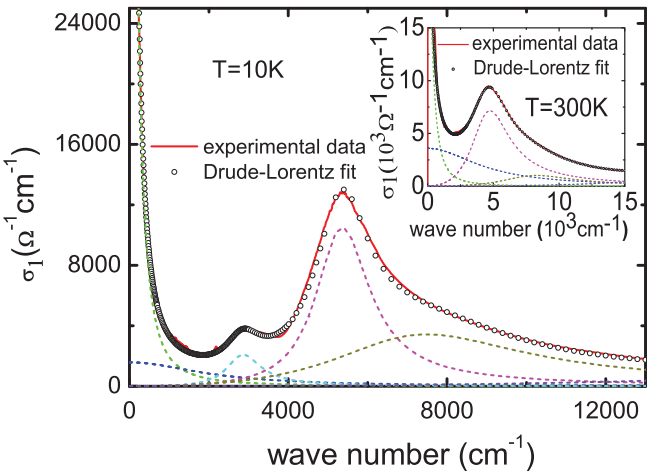

FIG. 4. (Color online) The experimental data of the $\sigma_1(\omega)$ spectrum at 10 K and the Drude-Lorentz fit result. Each term by displayed in the dashed line at the bottom. The inset shows the result at 300 K.

Here, ϵ_∞ is the dielectric constant at high energy, and the middle and last terms are the Drude and Lorentz components, respectively. The results are shown in Fig. 4. At room temperature, the $\sigma_1(\omega)$ spectrum could be well reproduced by two Drude components and two Lorentz terms. The two Drude components, one with very narrow peak width and one with a much broader peak width, describe the conducting carrier responses arising from different bands or Fermi surfaces. The Lorentz peak structure near 4800 cm^{-1} reflects the CDW gap. At 10 K, one more Lorentz component near 2800 cm^{-1} is added to reproduce the new CDW gap feature. However, the broader Drude component becomes intensively suppressed while the narrow Drude component displays a relatively smaller change. The fit parameters for the Drude-Lorentz model are listed in Table I. In general, we found that both the ω_p and $1/\tau$ decrease at lower temperature. This result could be easily interpreted: the formation of the new CDW gap further removes those electrons near E_F that experience stronger scattering, leading to a reduction of conducting carrier density; meanwhile, the scattering rate is reduced due to the reduction of scattering channels. It is noted that in the dc resistivity $\rho(T)$ of $CeTe_3$, no obvious anomaly below 300 K was observed.[3] This is also understandable. From the semiclassical Boltzmann transport theory, the resistivity is determined by the complex function of Fermi velocity, the scattering rate, and their weighted integral over the whole Fermi surface. Whether $\rho(T)$ shows an anomaly depends on the balance of those quantities, which could experience substantial changes across the transition.

TABLE I. Temperature dependance of the plasma frequency ω_p and scattering rate $\gamma_D = 1/\tau_D$ of the Drude term, the resonance frequency ω_i, the width $\gamma_i = 1/\tau_i$, and the square root of the oscillator strength S_i of the Lorentz component (all entries in 10^3 cm^{-1}). Two Drude terms and two other low-energy Lorentz terms are displayed at room temperature. One more Lorentz mode is added at 10 K.

	ω_{p1}	γ_{D1}	ω_{p2}	γ_{D2}	ω_1	γ_1	S_1	ω_2	γ_2	S_2	ω_3	γ_3	S_3
300 K	27	0.42	31	4.5				4.7	3.5	39	8.3	6.6	20
10 K	27	0.17	14	2.1	2.8	1.1	11	5.4	1.6	32	7.5	5.9	35

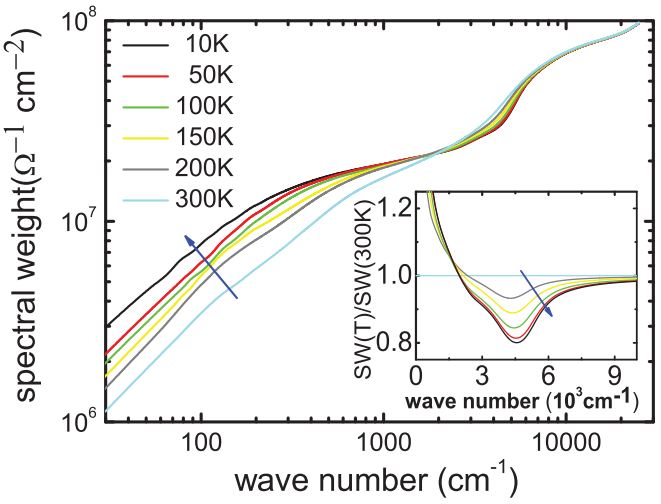

FIG. 5. (Color online) The spectral weight in logarithmic scale up to 25 000 cm^{-1} at each temperature. Inset: The normalized spectral weight SW(T)/SW(300 K) up to 10 000 cm^{-1}. The arrow points to low temperatures.

The central issue of the present paper is the observation of the new gap feature at about 2800 cm^{-1} (~350 meV) near 200 K. As the gap formation is a characteristic feature for a density wave instability, the structure could naturally be ascribed to a new CDW order at low temperature. From the analysis of the free-carrier response, we found that the new CDW order occurs mainly in the bands or Fermi surfaces responsible for the broader Drude component. Those states were gapped away from the Fermi level E_F. As we already pointed out, not only were those states affected by the new order, but the bands far away from the E_F were also influenced, because the gap corresponding to the first CDW at high temperature was shifted to higher energy.

To further illustrate the two CDW gap features, we present a spectral weight analysis here. In Fig. 5, the spectral weight $(\omega_c) = \int_0^{\omega_c} \sigma_1(\omega) d\omega$ is plotted as a function of cutoff frequency ω_c with its inset showing the normalized spectral weight SW(T)/SW(300 K). In the very low frequency range, the spectral weight increases upon cooling as a result of the Drude component narrowing, which is consistent with the dc resistivity behavior. However, the spectral weight becomes smaller at lower temperature in the frequency range roughly between 2000 and 4500 cm^{-1}; the normalized spectral weight at 10 K reaches a minimal value 80% at $\omega_{\min} \approx 4500$ cm^{-1}. This clearly indicates the development of energy gaps. Above the $\omega_{\min}$ frequency, the difference of the spectral weight at high and low temperatures gets smaller again, suggesting a spectral weight transfer from the frequencies below $\omega_{\min}$ to the higher-energy region above $\omega_{\min}$. The spectral weight is almost fully recovered near 10 000 cm^{-1}. Such a spectral weight transfer is due to the development of CDW orders upon cooling. In the inset of Fig. 5, an apparent shoulder near 2900 cm^{-1} is observed at low temperatures, which could be attributed to the spectral weight redistribution associated with the development of the new CDW order with a smaller energy scale.

It should be mentioned that, to the best of our knowledge, the new CDW order developed at low temperature in $CeTe_3$ as indicated by the present measurement was not identified before by other experimental techniques.[2,3,7,8,11,14,16,17] Since optical spectroscopy is a bulk probe technique, the data must be further examined carefully using other measurement techniques. It should be noted that the optical measurement itself is not adequate to determine the CDW transition temperature. This is because the pretransitional fluctuation effects are commonly present for CDW systems. For a quasi-one-dimensional (1D) system, the CDW phase-transition temperature expected from a mean-field or BCS-like theory (T_{MF} with relation $2\Delta \simeq 3.52 T_{MF}$) could be much higher than the real phase-transition temperature (T_p) of the system because the interchain coupling effect is not taken into account in the mean-field theory. Then, strong CDW fluctuations would exist in the temperature range between T_{MF} and T_p, and a CDW gap signature would be present.[18] Such effects were widely seen in quasi-1D materials, for example in blue and red bronzes.[18,19] For quasi-2D CDW systems, the fluctuation effect is reduced, but sizable differences between T_{MF} and T_p still exist. This has been seen for the rare-earth tri-telluride.

In fact, the two different CDW orders were observed in a number of heavy rare-earth-based RTe_3 compounds (where R = Dy, Ho, Er, and Tm). The second CDW transition was first observed by transport and high-resolution x-ray diffraction measurements.[3] On traversing the lanthanides series from lighter to heavier ones, the first CDW transition temperature T_{c1} decreases monotonically. In contrast, the second phase transition at lower temperature T_{c2} exhibits the opposite trend, increasing from 50 to 200 K. The wave vector of the second CDW order was found to be almost equal in magnitude to the first one, but oriented in the perpendicular direction: the first one along the c^* axis and the second oriented in the a^* direction.[3] Two CDW gaps were revealed by ARPES measurement on the heavier rare-earth-element-based compounds, for example $ErTe_3$: the first $\Delta_1 = 175$ meV along c^* and the second $\Delta_2 = 50$ meV along the a^* direction.[20] Furthermore, substantial fluctuation effects were revealed by different techniques, including the high-resolution x-ray diffraction[3] and optical[21] measurements showing the presence of superlattice peaks and a CDW gap feature well above the first transition temperature, respectively. Our measurement suggests that a similar second CDW transition is also present in the light rare-earth-element-based compound.[22] It is likely that the fluctuation effect becomes stronger in the light rare-earth-element-based compound. We believe that even if the static CDW is not formed, the very strong CDW fluctuations are already present.

IV. CONCLUSIONS

To conclude, we report an optical study of the single-crystal $CeTe_3$, a rare-earth element tri-telluride, which belongs to the layered quasi-two-dimensional charge-density-wave systems. We observed strongly temperature-dependent optical spectra, which is in sharp contrast to the earlier report. In addition to the large CDW gap feature, which already exists at room temperature, we also observed the development of another

CDW order near 200 K. The second CDW gap at low temperature removes the electrons near E_F that undergo large scattering. The Fermi surface is still partially gapped with good metallic behavior exhibited in the entire temperature range.

ACKNOWLEDGMENTS

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[22]Our recent optical measurement on $LaTe_3$ indicates that the compound behaves much the same as $CeTe_3$. With the exception of the large gap feature, which is already present at room temperature, a new peak at roughly 2900 cm^{-1}($\sim$ 360 meV) appears in the conductivity at low temperatures, indicating that a second CDW order also exists in $LaTe_3$.