Tunneling spectroscopy of $\text{RTe}_2$ ($\text{R}=\text{La, Ce}$) and possible coexistence between charge-density waves and magnetic order

M. H. Jung
Department of Quantum Matter, ADSM, Hiroshima University, Higashi-Hiroshima 739-8526, Japan

T. Ekin
Faculty of Integrated Arts and Sciences, Hiroshima University, Higashi-Hiroshima 739-8521, Japan

Y. S. Kwon
Department of Physics, Sung Kyun Kwan University, Suwon 440-746, South Korea

T. Takabatake
Department of Quantum Matter, ADSM, Hiroshima University, Higashi-Hiroshima 739-8526, Japan

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Tunneling spectra are measured on the charge-density wave (CDW) compound $\text{LaTe}_2$ and the isostructural antiferromagnet $\text{CeTe}_2$ with $T_N=4.3$ K by a break-junction method. In contrast to the well-developed CDW gap $2\Delta=0.9$ eV wide for $\text{LaTe}_2$, the spectrum of polycrystal $\text{CeTe}_2$ is V shaped with $2\Delta=1.2$ eV. These gap structures agree with the optical-conductivity spectra for both compounds. The V-shaped spectrum for $\text{CeTe}_2$ suggests that the CDW gap is modified by the presence of electronic states hybridized with the $4f$ electron states. A smaller gap $2\Delta^c=0.5$ eV was observed for the bulk tunneling current in the $c$ plane of single crystals of $\text{CeTe}_2$. On cooling below $T_C=6.1$ K, where a short-range ferromagnetic order sets in, $2\Delta^c$ exhibits a sharp minimum. Furthermore, subgap anomalies appear below $T_C$ and suddenly increase at $T_N$. The normalized zero-bias conductance shows a minimum at $T_C$ and a sudden increase below $T_N$. These facts suggest possible interplay of CDW’s and magnetic order in $\text{CeTe}_2$.

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Charge-density waves (CDW’s) occur in numbers of low-dimensional materials, of which the electronic instabilities lead to their structural modulations. The CDW instability driven by Fermi surface nesting has a tendency to lower the electronic energy by opening an energy gap at the Fermi level. Electron-tunneling spectroscopy provides direct observation of the energy gap because the tunneling conductance is proportional to the electronic density of states. The competition between CDW condensation and superconductivity was found in certain systems. The coexistence between CDW’s and magnetic order has recently been reported for rare-earth based compound $\text{Er}_4\text{Ir}_4\text{Si}_{10}$. To the best of our knowledge, however, no evidence for the interplay of CDW’s and magnetic order has recently been reported yet.

Layered compounds such as transition-metal dicalcogenides $\text{T}_n\text{X}_2$ ($\text{T}=\text{transition metal; X}=\text{S, Se, Te}$) and rare-earth polychalcogenides $\text{RX}_n$ ($\text{R}=\text{rare earth; n}=2, 2.5, 3$) are susceptible to the CDW formation due to the electronic instability. The compounds $\text{T}_n\text{X}_2$ with the layered tetragonal Cu$_2$Sb-type structure consist of rare-earth-chalcogen layers separated by a chalcogen square sheet. Commensurate CDW was observed in $\text{RSexo}_9$ ($\text{R}=\text{La, Ce, Pr}$), where Se dimmers and ordered vacancies lead to distorted Se sheet superstructure. On the other hand, incommensurate CDW in SmTe$_2$ was reported to be stable at room temperature. The strong anisotropy in the gap of $2\Delta=0.5$ eV was revealed by the angle-resolved photoemission spectroscopy.

For $\text{LaTe}_2$, a periodic lattice distortion was observed through transmission electron microscopy. It was shown that the CDW’s with the superlattice wave vector $q=a^*/2$ are stable even at room temperature. Band calculations of $\text{LaTe}_2$ suggested that the CDW states arise from the nesting between the electron and hole Fermi surfaces of the Te square sheet. However, no direct evidence of the CDW gap in $\text{LaTe}_2$ has been given to date. Recently, we have grown high-quality single-crystalline samples of $\text{CeTe}_{2–\delta}$ ($\delta=0.15$). This value of $\delta$ is common to $\text{SmTe}_2$ and $\text{DySe}_2$, which was ascribed to the defective Te layers built isolated Te. This vacancy stabilizes the dimerization of Te ions and the structural modulation, resulting in semiconducting behavior of the electrical resistivity. The electronic band structure of $\text{CeTe}_2$ is in nature analogous to that of $\text{LaTe}_2$ except the existence of the $4f$ state, which is believed to deform the gap because of the hybridization between the Ce $4f$ state and the Te $5p$ hole band in the Te sheet. Recently, the possible presence of CDW’s has been suggested in $\text{CeTe}_2$ from the electrical resistivity measurements. The $c$-axis resistivity $\rho_{||c}$ exhibits a semiconducting temperature dependence of the order of a few tens of $\Omega\text{cm}$, while the $c$-plane resistivity $\rho_{\perp c}$ shows a broad maximum at 100 K and then decreases on cooling, resulting in the resistivity ratio $\rho_{\perp c}/\rho_{||c} \sim 150$ at 1.5 K. At low temperatures, $\text{CeTe}_2$ undergoes two characteristic transitions. The electrical resistivity exhibits a sharp peak at $T_C=6.1$ K, below which a two-dimensional ferromagnetic order develops in the $\text{CeTe}_2$ layer. Below $T_N=4.3$ K, a three-dimensional antiferromagnetic order occurs among the ferromagnetic $\text{CeTe}$ layers in the spin sequence up-down-up-down-up along the $c$ axis. It should be interesting if the magnetic orders in $\text{CeTe}_2$ have significant effect on the CDW gap.
In this paper, we report electron-tunneling experiments on LaTe$_2$ and CeTe$_2$. The results give the evidence for the CDW gap in these compounds. We have used an in situ break-junction method, which prevents Ce-based compounds from serious surface oxidation. A platelet sample with its cross section $0.1 \times 2 \text{ mm}^2$ was mounted on a flexible substrate and cracked at 4.2 K by applying an adjustable bending force. In this way, we were able to make stable tunneling junctions with a clean interface. The tunneling conductance $dI/dV$ was measured by an ac-modulation technique with a four-probe method. If a few junctions coexist at the interface, then the observed conductance is a superposition of contributions from each junction, where the tunneling current may strongly depend on the surface state and geometry with respect to the crystallographic axis.

In order to study the possible interplay between the magnetic order and CDW in CeTe$_2$, we have measured the temperature and magnetic-field dependence of the tunneling spectra in the vicinity of $T_C$ and $T_N$, using single-crystalline samples. We confirmed that the stoichiometry, electrical resistivity, and magnetic susceptibility of the present samples agree with previous results.

Figure 1 shows representative data of $dI/dV$ for polycrystalline samples of LaTe$_2$ and CeTe$_2$. The gap features are reproducible for several samples and different junctions with various resistance values over a wide range, 30–5000 $\Omega$, which is much larger than the estimated sample resistance 0.1–1 $\Omega$. In the top frame, the typical $dI/dV$ curve for LaTe$_2$ at 60 K exhibits well-defined symmetric peaks at $V=0.85 \text{ V}$ with respect to the zero bias. The gap width of 1.70 eV is unchanged at least over the measured temperatures up to 120 K. In the middle frame, the curve 2 exhibits double-gap structures with the bias separations of 1.70 and 0.86 V. Here it is noteworthy that the former is twice the latter. This double structure may come from two junctions coexisting at the broken interface, as mentioned above; the former corresponds to $4\Delta/e$ of SIS (S is the semiconducting state with CDW, I is the insulating barrier) junction and the latter corresponds to $2\Delta/e$ of SIN (N is the normal state without CDW) junction, where $\Delta$ is half the energy gap. It is likely that the SIS junction is formed at a cleaved surface between layers in a grain, whereas the SIN junction is formed at a grain boundary. Also in CeTe$_2$ two gap values are observed, $4\Delta=2.4 \text{ eV}$ in the curve 4 and $2\Delta=1.2 \text{ eV}$ in the curve 3, respectively. Because the gap value is comparable to that for LaTe$_2$, we attribute this gap to the CDW gap in CeTe$_2$. If the empirical relation $2\Delta/k_BT_{\text{CDW}}=12–14$ is used, then $\Delta\sim 1 \text{ eV}$ yields $T_{\text{CDW}}\approx 1000 \text{ K}$. Therefore, no change of the gap value against temperatures up to 120 K is reasonable. However, there is a significant difference in the gap structure between polycrystalline samples of LaTe$_2$ and CeTe$_2$ at various temperatures. The gap features are reproducible for several samples and different junctions with various resistance values over a wide range, 30–5000 $\Omega$, which is much larger than the estimated sample resistance 0.1–1 $\Omega$. In the top frame, the typical $dI/dV$ curve for LaTe$_2$ at 60 K exhibits well-defined symmetric peaks at $V=0.85 \text{ V}$ with respect to the zero bias. The gap width of 1.70 eV is unchanged at least over the measured temperatures up to 120 K. In the middle frame, the curve 2 exhibits double-gap structures with the bias separations of 1.70 and 0.86 V. Here it is noteworthy that the former is twice the latter. 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the two compounds. In contrast to the U-shaped spectra for LaTe$_2$, the spectra of CeTe$_2$ is V shaped with electronic density-of-states within the gap. This in-gap state may originate from the hybridization of Ce 4$f$ states with conduction-electron states. We will discuss this point later by the comparison with the data of optical conductivity.

At 4.2 K just below $T_N=4.3$ K, the $dI/dV$ curve of CeTe$_2$ reveals subgap anomalies at $V_1=\pm 0.1$ V and $V_2=\pm 0.2$ V, which are indicated by arrows in the bottom frame of Fig. 1. Since the anomalies are reproducible for various junctions, they appear to be inherent. The subgap anomalies in the curve 6 disappear upon heating to 10 K above $T_N$ to become the curve 5, whereas the main gap structure at $V=\pm 0.45$ V is unchanged. This disappearance should be only due to the thermal effect, because the junction is very stable and the main gap is reproduced. These two subgap anomalies found for polycrystalline samples are more clearly observed in single crystals, which is shown in Fig. 2. The bias separations are, respectively, denoted by $2V_1$ and $2V_2$. On heating, both $V_1$ and $V_2$ decrease suddenly at $T_N=4.3$ K and gradually decrease to vanish at $T_C=6.1$ K (see the right inset of Fig. 2). This temperature dependence is similar to that of the order parameter of a second-order phase transition. However, it is rather surprising that excitations of 0.1–0.2 eV (1000–2000 K) disappear only at 6.1 K. We have further examined the magnetic-field dependence of the subgap anomalies, which will be presented later.

The maximum at $V=\pm 0.24$ V ($2\Delta^*=0.48$ eV) was observed only in single crystals CeTe$_2$ for the bulk tunneling current in the c plane. The maximum possesses the strength of 40% of the background conductance, as seen in the left inset of Fig. 2. In order to trace the temperature dependence of $2\Delta^*$, the spectra are enlarged in Fig. 3. As the temperature is raised from $T_N=4.3$ K, $2\Delta^*$ initially decreases and turns to increases, then saturates to a value of 0.47 eV above $T_C=6.1$ K. For $T>T_C$, no temperature dependence in $2\Delta^*$ was observed as in $2\Delta$, but the magnitude of $2\Delta^*=0.47$ eV is nearly half of $2\Delta=0.9$ eV. The different values might be related to the shift in stoichiometry of the junctions and/or anisotropic nature of the gap in CeTe$_2$. However, the well-reproducible observations of $2\Delta^*$ for $I\perp c$ in several single crystals allow us to exclude the sample dependence. The large gap $2\Delta$ is then assumed to be the gap formed along the c axis, while the small one $2\Delta^*$ is in the c plane.

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Another remarkable feature of the $dI/dV$ curves in Fig. 2 is the hump at zero bias, which fades out above $T_C$. For such a zero-bias hump, two possible origins are recorded: (i) magnetic scattering across the tunneling barrier by the interaction...
of the carrier spins with the localized $4f$ moments, the so-called Kondo scattering, and (ii) Andreev-like reflection at the metallic contact accidentally formed at the interface. In any case, the zero-bias feature should be a consequence of the magnetic transition because it disappears on heating exactly at $T_C$. The normalized zero-bias conductance $\xi(B)\xi(0)$ at $0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1.5$, and $3$ $T$ from bottom to top. Magnetic-field dependence of the subgap $V_1(B)\xi(0)$ at $4.2$ $K$ is well scaled with the magnetization curve $M(B)$.

We further studied the magnetic-field dependence of the subgaps at $4.2$ $K$ in fields up to $3$ $T$ applied parallel to the $c$ axis, the easy magnetization direction, using the same junction that was used for the temperature variation measurements in Fig. 2. The spectra in the inset of Fig. 5 show that the depth of the dips at $V_1 = \pm 0.1$ $V$ decreases but the separation $2V_1$ increases as the magnetic field is increased. In Fig. 5, we plot the magnetic-field dependence of $2V_1(B)$ and $2V_1(0)$ together with the magnetization curve $M(B)$ measured at $5$ $K$. The nonlinear increase of $2V_1(B)$ and $2V_1(0)$ is well scaled with $M(B)$. This fact indicates that the magnetic order of CeTe$_2$ gives rise to the subgap anomalies through the spin polarization of electronic states by the internal magnetic field. The spectra in Fig. 5 also show that the background conductance is raised with magnetic field. This change may be related to the field alignment of the Ce magnetic moments in parallel on both barrier sides. The increase of conduction driven by the alignment of magnetic moments is analogous to the field-induced spin-polarized tunneling in layered manganites (La, Sr)$_2$Mn$_2$O$_7$.  

Finally, we point out the close relation between the present tunneling spectra $dI/dV$ and optical-conductivity spectra $\sigma_{opt}$ obtained by optical-reflection measurements.

In conclusion, the energy gap of $2\Delta = 0.9$ and $1.2$ $eV$ was found for the layered compounds LaTe$_2$ and CeTe$_2$, respectively. Since the main gap $2\Delta$ in CeTe$_2$ is comparable to the CDW gap in LaTe$_2$ the gap in CeTe$_2$ is also ascribed to the CDW gap. The tunneling spectra of both systems, respectively, correspond well with the optical conductivity spectra. Further studies on the anisotropic gap structures are necessary by optical-reflection measurements on single-crystalline samples, together with photo-emission spectroscopic measurements that probe the quasi-particle density of states.

In Fig. 6, the data of $dI/dV$ for polycrystalline samples of LaTe$_2$ and CeTe$_2$ are, respectively, compared with symmetrized data of $\sigma_{opt}(E)$. It is remarkable that the overall spectral features of $dI/dV$ coincide with those of $\sigma_{opt}$. Namely, $\sigma_{opt}$ for LaTe$_2$ is nearly flat in a low-energy region below $0.3$ $eV$ and then increases rapidly with increasing photon energy, whereas $\sigma_{opt}$ for CeTe$_2$ is $V$ shaped. This quantitative agreement between the tunneling and optical spectra suggests that $2\Delta$ in $dI/dV$ and the energy gap $E_g$ in $\sigma_{opt}$ have the same origin. The main structure in $\sigma_{opt}$ is observed at $0.5$ $eV$ for both LaTe$_2$ and CeTe$_2$ which is essentially independent of temperature up to $300$ $K$. If the structures in $\sigma_{opt}$ reflect the direct transition across the band gap from the valence band to the conduction band, $E_g$ should equal to $2\Delta$. However, we find the relation $\Delta \approx E_g$ for both compounds. The reason of this twofold discrepancy is not clear at present, and we conjecture that the optical measurement does not probe the quasiparticle excitations, instead it sees the direct band gap of the conduction electrons.

In conclusion, the energy gap of $2\Delta = 0.9$ and $1.2$ $eV$ was found for the layered compounds LaTe$_2$ and CeTe$_2$, respectively. Since the main gap $2\Delta$ in CeTe$_2$ is comparable to the CDW gap in LaTe$_2$ the gap in CeTe$_2$ is also ascribed to the CDW gap. The tunneling spectra of both systems, respectively, correspond well with the optical conductivity spectra. A smaller gap $2\Delta^* = 0.5$ $eV$ was found for the bulk tunneling current in the $c$ plane of single crystals of CeTe$_2$. The important observation is that $2\Delta^*$ decreases when the Ce magnetic moments order ferromagnetically below $T_C$. This fact and the remarkable change in the zero-bias conductance at both $T_C$ and $T_N$ point to the significant interplay of the CDW’s and the magnetic orders in CeTe$_2$.  

FIG. 5. Inset: magnetic-field variations of $dI/dV$ spectra for a single crystal CeTe$_2$ taken in fields $B\parallel c$ at $0.05, 0.1, 0.2, 0.4, 0.6, 0.8, 1.5$, and $3$ $T$ from bottom to top. Magnetic-field dependence of the subgap $V_1(B)\xi(0)$ at $4.2$ $K$ is well scaled with the magnetization curve $M(B)\xi(c)$.
TUNNELING SPECTROSCOPY OF $\text{RTe}_2$ ($\text{R} = \text{La, Ce}$)...

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$^a$Present address: NHMFL, Pulse Field Facility, LANL, Los Alamos, NM 87545.


