Evidence of phonon-charge-density-waves coupling in ErTe₃

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The vibrational properties of ErTe₃ were investigated using Raman spectroscopy and analyzed on the basis of peculiarities of the RTe₃ crystal structure. Four Raman active modes for the undistorted structure, predicted by factor-group analysis, are experimentally observed and assigned according to dipheriodic symmetry of the ErTe₃ layer. By analyzing temperature dependence of the Raman mode energy and intensity we have provided the clear evidence that all Raman modes, active in the normal phase, are coupled to the charge density waves. In addition, new modes have been observed in the distorted state.

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I. INTRODUCTION

Low-dimensional systems with highly anisotropic electronic structure often exhibit electronic instabilities that can lead to the superconductivity or charge-density waves (CDW). CDW can be created through a Fermi surface (FS) nesting effect. If the FS can be nested with one q-vector of a particular phonon mode, the ground state energy can be reduced by electron-phonon coupling resulting in gaps opening at the FS and the creation of a new ground state with broken symmetry. FS for an ideal (FS) nesting effect. If the FS can be nested with one dimensional (1D) system consists of two points, so new ground state with broken symmetry. FS for an ideal one dimensional (1D) system consists of two points, so it exhibits perfect nesting at q = 2k. In real systems, a good nesting is reduced only to some parts of the FS. In this cases CDW gap is expected to open only on the best nested FS parts and the system can remain metallic in its new ground state.

In the recent years the high-temperature CDW family of rare-earth tritellurides (RTe₃) attracted a lot of attention. A wide range of tunable parameters in the RTe₃ offers unique opportunity for the study of the CDW formation. For the layered quasi-2D material with tetragonal symmetry, the CDW ground state can either be bidirectional (checkerboards) or unidirectional (stripes) with a reduced symmetry. The high resolution x-ray diffraction angle resolved photoemission spectroscopy and femtosecond pump-probe spectroscopy showed that lighter rare-earth tritellurides (i.e. R=La-Tb) host unidirectional incommensurate CDW well above room temperature. For the heavy rare-earth tritellurides (i.e. R=Dy-Tm) transition temperature T_{CDW} (T_{CDW} = 265 K for ErTe₃) resides below the room temperature with another transition to a bidirectional CDW state at T_{CDW} (T_{CDW} = 158 K for ErTe₃).

The Raman scattering measurements of RTe₃ were analyzed, to the best of our knowledge, only in Refs. and reported the Raman scattering spectra of RTe₃ (R=La, Ce, Pr, Nd, Sm, Gd, Dy) at ambient pressure and high pressure Raman spectra of LaTe₃ and CeTe₃. In the case of the room temperature Raman spectra of LaTe₃, they observed five modes at about 72 cm⁻¹, 88 cm⁻¹, 98 cm⁻¹, 109 cm⁻¹ and 136 cm⁻¹ and labeled them as P1-P5. Polarization dependent measurements showed that the P4 peak at about 109 cm⁻¹ has 90° intensity change periodicity. They concluded that this mode can not be assigned within the undistorted structure and consequently assigned it as the B₁ symmetry mode of the distorted structure. In Ref. amplitudon modes are observed and analyzed for DyTe₃ and LaTe₃.

In this work we have measured Raman scattering spectra of ErTe₃ in normal and in CDW state. Our polarization dependent Raman scattering measurements above T_{CDW₁} showed that P4 mode, at about 120 cm⁻¹, persist in the normal state of ErTe₃. Appearance of this mode in the normal state and its B₁ symmetry leads us to a conclusion that the orthorhombic symmetry of the crystal does not play dominant role in the phonon properties of RTe₃. We have found that factor group analysis of the layer symmetry predicts 3A₁+2B₁+2B₂ modes to be observed in Raman scattering experiment from (010) plane of ErTe₃, in complete agreement with experimental findings. Temperature dependence of Raman mode energies and intensities have shown strong coupling of phonons with the CDW gaps.

II. EXPERIMENT

Single crystals of ErTe₃ were grown using flux method. The Raman scattering measurements were performed using Jobin Yvon T64000 Raman system in micro-Raman configuration. The 514.5 nm line of an Ar⁺/Kr⁺ mixed gas laser was used as an excitation source. All Raman scattering measurements presented in this work were performed from the (010) plane of ErTe₃ single crystals. Low temperature measurements
were performed using KONTI CryoVac continuous Helium flow cryostat with 0.5 mm thick window. Focusing of the laser beam was realized with a long distance microscope objective (magnification 50×). We have found that laser power level of 0.01 mW on the sample is sufficient to obtain Raman signal and, except signal to noise ratio, no changes of the spectra were observed as a consequence of laser heating by further lowering laser power. The corresponding excitation power density was less than 0.05 kW/cm².

III. RESULTS AND DISCUSSION

ErTe₃ crystallizes in the Cmcm (D₁₇h) space group orthorhombic structure with unit cell parameters a = 4.31 Å, b = 24.45 Å, c = 4.31 Å and Z = 4. All ions are in the c Wyckoff position (C₂ᵥ site symmetry). The unit cell of ErTe₃ crystal structure (Fig. 1) is built up of corrugated double layers of Te sandwiched by planar square nets of Te making ErTe₃ slabs stacked along the b-axis. These slabs are mutually connected only by van der Waals forces.

Factor group analysis (FGA) for the crystal symmetry gives the normal-mode distribution, Γ = 4A₉ + 4B₃g + 4B₃u + B₁u + B₂u + B₃u. Based on the corresponding Raman tensors and the selection rules (see Table 1), we found that only A₉ symmetry modes can be observed for our experimental configuration, in which both incident and scattered light are polarized parallel to the (ac) crystal plane.

Fig. 2 (a) shows room temperature Raman scattering spectra of ErTe₃ (normal state) measured in parallel polarization for different orientations of the sample. By changing an angle between incident light polarization and the crystal axes (by rotating the sample) one can find the position at which the Raman mode at about 120 cm⁻¹ disappears. The disappearance of this mode is shown to
Layered crystals can be properly treated as molecular crystals in which the molecular unit is a sheet extended infinitely in two dimensions. Considering the vibrational properties of the individual layers, we break the periodicity in the direction perpendicular to the layer. Because the crystal structure of RTe$_3$ consists of two RTe$_3$ layers mutually connected by weak van der Waals forces, it is natural to expect that layer symmetry dominates in vibration properties of RTe$_3$.

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The structure of the ErTe$_3$ slab is shown in Fig. 1. The diperiodic symmetry group which fully describes symmetry of the ErTe$_3$ layer is DG 64, with two formula units per unit cell. Two R and two Te atoms are in c (C$_{4v}$ site symmetry) and four Te atoms are in f (C$_{2v}$ site symmetry) Wyckoff positions. FGA for the ErTe$_3$ slab gives, $\Gamma = 3A_{1g} + B_{1g} + 3A_{2u} + B_{2u} + 4E_u + 4E_u$. There are four Raman active modes ($3A_{1g} + B_{1g}$) to be observed in (010) plane. Correlation diagram between crystal (orthorhombic) and layer (tetragonal) symmetries is presented in the Table. According to the Raman tensors for tetragonal symmetry (Table I), the B$_{1g}$ symmetry mode has intensity change periodicity of 90°. From the selection rules, we have found that the B$_{1g}$ symmetry mode is Raman active (in parallel polarization configuration) for all orientations of the sample except $a'a'$ and $c'c'$. This is in agreement with our experimental findings. In this way we can assign P4 mode of ErTe$_3$ (peak around 120 cm$^{-1}$) as the B$_{1g}$ symmetry mode of the ErTe$_3$ slab. This means that 90° periodicity change of P4 mode intensity is not related with CDW state, as proposed in Ref. 18. It is a consequence of the dominant role of ErTe$_3$ layers in the optical properties of the crystal. The peaks at 132 cm$^{-1}$, 92 cm$^{-1}$ and 80 cm$^{-1}$ can be assigned as the A$_{1g}$ symmetry modes of the ErTe$_3$ slab.

We cannot exclude the twinning effect as a cause of tetragonal symmetry dominance in Raman spectra of ErTe$_3$. Namely, due to the weak inter-layer van der Waals bonding, b-axis stacking faults can appear, resulting in twin formation. Such single crystals often can have regions for which the a and c axes are exchanged and sample exhibits an average 4-fold symmetry, even though it really comprises a superposition of two orthogonal orthorhombic symmetries.

ErTe$_3$ exhibits two successive second order phase transitions upon cooling at $T_{CDW_1}=265$ K and $T_{CDW_2}=158$ K, followed by the modulation of electronic charges and unidirectional and bidirectional ground state formation. According to the Landau’s theory of second order phase transitions, for each second order phase transition a characteristic order parameter can be introduced. In the case of CDW formation, order parameter is the CDW gap. Temperature dependence of the CDW gap can be written as $\Delta(T)/\Delta(0) \sim (1 - T/T_{CDW})^\beta$, where $\beta$ is the critical exponent.

Temperature dependances of the energy of the 92 cm$^{-1}$ (A$_{1g}$) and 120 cm$^{-1}$ (B$_{1g}$) modes of ErTe$_3$ are shown in Fig. 3. The temperature-induced anharmonicity
The vibrational properties of ErTe$_3$ were investigated using Raman spectroscopy and analyzed on the basis of
the RTe$_3$ crystal structure. We have concluded that vibrations of the RTe$_3$ layers play dominant role in the optical properties of the crystal. Four Raman active phonons predicted by FGA of the layer symmetry were observed and assigned. Temperature dependence of the energies and intensities of the modes, Raman active for the undistorted structure, have clearly shown coupling of phonons to the CDWs. Theoretical calculations perfectly map experimental data for the critical exponent $\beta = 0.3$. In the distorted state of ErTe$_3$ additional Raman modes have been observed.

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