Thermodynamic and transport properties of YTe₃, LaTe₃, and CeTe₃

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Measurements of heat capacity, susceptibility, and electrical resistivity are presented for single crystals of the charge density wave compounds YTe₃, LaTe₃, and CeTe₃. The materials are metallic to low temperatures, but have a small density of states due to the charge density wave gapping large portions of the Fermi surface. CeTe₃ is found to be a weak Kondo lattice, with an antiferromagnetic ground state and \( T_N = 2.8 \) K. The electrical resistivity of all three compounds is highly anisotropic, confirming the weak dispersion perpendicular to Te planes predicted by band structure calculations.

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I. INTRODUCTION

The title materials belong to the family of quasi-two-dimensional charge density wave (CDW) compounds \( R \)Te₃, where \( R=Y, \ La-Sm, \ Gd-Tm \). The CDW was first observed for these materials by DiMasi and co-workers via transmission electron microscopy (TEM). They found superlattice peaks corresponding to a single incommensurate modulation wave vector, with a magnitude \( q_{\text{CDW}} \approx 2/7 \) \( (2\pi/\alpha) \), varying slightly with \( R \). The incommensurate superstructure was subsequently solved for \( R=\text{Ce, Pr, and Nd} \) by Malliakas et al. using a four-dimensional analysis. Angle resolved photo emission spectroscopy (ARPES) experiments on SmTe₃ (Ref. 4) and CeTe₃ (Refs. 5,6) have confirmed the description of the lattice modulation in terms of a CDW, graphically showing how the electronic structure is gapped for regions of the Fermi surface that are optimally nested. Consistent with the large size of the CDW gap [up to a maximum of 400 meV for CeTe₃ (Ref. 5)], the material appears to be deep in the CDW state even at room temperature, and no CDW transitions are observed in the resistivity up to 300 K.

The average (unmodulated) structure of \( R \)Te₃ is shown in Fig. 1. The lattice is weakly orthorhombic, belonging to space group \( \text{Cmcm}^9 \) (No. 63), and consists of two structural motifs: nominally square planar Te sheets and corrugated \( R \)Te slabs. Note that in the standard space group setting, the \( b \) axis is oriented along the long crystal axis, perpendicular to the Te planes. First principle band structure calculations by Laverock et al. reveal broad sheets of Fermi surface with very little \( b \)-axis dispersion, that principally derive from \( p_x \) and \( p_y \) orbitals of the planar Te sites. Seen along the \( b \) axis, the Fermi surface consists of inner and outer square sheets (both of which are doubled due to the effect of bilayer splitting), large regions of which are nested by a single incommensurate wave vector corresponding to the observed lattice modulation.

Given both the large size of the CDW gap and the simplicity of the electronic structure of this material, the \( R \)Te₃ family has attracted a growing amount of interest as a model set of compounds to study the effect of incommensurate modulation on electronic structure. However, remarkably little is known about the low-temperature thermodynamic and transport properties of these materials. In this paper we describe an alternative crystal growth technique for these compounds, and present results of heat capacity, susceptibility, and resistivity measurements for the two nonmagnetic members of the rare-earth series (YTe₃ and LaTe₃) and for CeTe₃ (specifically chosen since our first ARPES experiments were for this particular compound). We show that the materials have a very low density of states, caused by the CDW gapping a substantial portion of the Fermi surface. We also show that CeTe₃ exhibits weak Kondo behavior, implying that there will be some small 4f contribution to the Fermi surface at low temperatures for this compound.

FIG. 1. (Color online) Schematic diagram showing the average crystal structure of \( R \)Te₃ (\( R=Y, \ La-Sm, \ Gd-Tm \)). Dashed lines show the unit cell.
II. SAMPLE PREPARATION AND EXPERIMENTAL METHODS

Single crystals were grown via a self-flux technique, similar to our previous report for the related single-layer compounds LaTe2 and CeTe2. We favor this technique over the alkali halide flux technique that has been previously used because it does not introduce other elements to the melt, and produces large crystals with a high degree of structural order. Elements in the molar ratio \(R_xTe_{1-x}\), \(x=0.015-0.030\), were put into alumina crucibles and vacuum sealed in quartz tubes. The mixtures were heated to 800–900 °C and slowly cooled over a period of 4 days to end temperatures in the range of 500–600 °C. The remaining melt was decanted in a centrifuge. Resulting gold-colored crystals were malleable, micaceous plates with dimensions of up to \(5 \times 0.4 \times 5\) mm, and oriented with the long \(b\) axis perpendicular to the plane of the crystal plates. The material is somewhat air sensitive, and crystals must be stored in an oxygen and moisture-free environment. High residual resistance ratios of the crystal plates. The material is somewhat air sensitive, and crystals must be stored in an oxygen and moisture-free environment. High residual resistance ratios (up to 120) confirm the crystal quality.

The heat capacity of the single-crystal samples was measured using a relaxation time technique in a Quantum Design Physical Property Measurement System (PPMS). Crystals with a mass of approximately 10 mg and flat surfaces were selected for good thermal contact with the sample platform. Data were taken in zero applied field from 1.8 to 300 K.

Magnetization measurements were made using a commercial (Quantum Design MPMS5) SQUID magnetometer. Applied fields of 1000 and 5000 Oe were used to measure the temperature dependence of the low field dc susceptibility \((M/H)\) from 1.8 to 300 K. Data were taken for fields oriented in an arbitrary direction in the \(ac\)-plane (i.e., in the plane of the Te sheets).

The electrical resistivity was measured using geometric bars cut and cleaved from the larger as-grown crystals. Electrical contact was initially made using Dupot 4929 silver epoxy directly on to the crystal surface, with typical contact resistances of 10–15 \(\Omega\). Subsequent experiments used evaporated gold pads, with improved contact resistances of 2–3 \(\Omega\). Resistivity measurements were made using an LR-700 ac resistance bridge operating at 16 Hz. In-plane measurements were made for arbitrary current directions in the \(ac\)-plane, using a standard four point contact geometry. The \(b\)-axis resistivity was measured using a modified Montgomery geometry, with one current and one voltage contact on the top face of the platelike crystal, and the other voltage and current contacts on the bottom face. Several measurements were made for each compound.

III. RESULTS

Heat capacity data for the two nonmagnetic members of the \(R\)Te3 series (\(R=\)Y and La) are shown in Fig. 2. Linear fits to \(C_p/T\) vs \(T^2\) were performed from 2.1 to 3.7 K for YTe3 and 1.9 to 3.7 K for LaTe3, avoiding the slight deviation from linearity below 2 K which is presumably associated with a nuclear Schottky anomaly. The resulting estimate for the low-T \(T^3\) coefficient gives Debye temperatures \(\Theta_D\) of 183.8±0.5 and 180.4±0.5 K for YTe3 and LaTe3, respectively, the small difference due to the different atomic weights of Y and La. The y intercept of the linear fit gives the electronic contribution to the heat capacity, with \(\gamma=0.8\) and 1.1±0.1 mJ/mol K2 for YTe3 and LaTe3, respectively. Within a free-electron model, these values correspond to densities of states of 0.33 and 0.48 states/eV/f.u., respectively, for the two compounds.

The susceptibility of YTe3 and LaTe3, shown in the lower inset to Fig. 2, is diamagnetic and largely temperature independent. Rough estimates of the Pauli susceptibility give values for the density of states that agree with those found from heat capacity measurements. A weak contribution from magnetic impurities is observed at low temperatures, consistent with the starting purities of the rare-earth elements (99.5%). The small feature at 50 K corresponds to trapped oxygen.

The anisotropic resistivity of LaTe3 is shown in Fig. 3.
The material is clearly metallic, due to the presence of significant ungapped portions of the Fermi surface, and the resistivity follows a temperature dependence which has only subtle differences from the Bloch-Grüneisen form. As has been previously noted for SmTe₃, the material has a large anisotropy, confirming the weak b-axis dispersion suggested by band structure calculations. For the crystals that were anisotropic, confirming the weak b-axis dispersion suggested by band structure calculations. For the crystals that were.

The density of states of YTe₃ and LaTe₃ estimated from our heat capacity measurements are significantly smaller than values calculated for the unmodulated crystal structure [0.8 states/eV/f.u. (Refs. 10,13)], confirming via a bulk measurement that substantial regions of the Fermi surface have been gapped by the CDW modulation. Ungapped portions of the original Fermi surface then contribute the observed metallic properties, with small differences in the measured density of states for the two compounds likely reflecting subtle differences in the nesting features of their respective Fermi surfaces.

In spite of their small density of states, the RTe₃ compounds are very good metals. The residual resistance of LaTe₃ is less than 0.5 Ω cm, and the residual resistance ratio is over 100. The layered crystal structure contributes towards a very anisotropic resistivity tensor, characterized by $\rho_{bc}/\rho_{ac} \approx 100$. Below 40 K this quantity rises still further, pre-

FIG. 4. The magnetic contribution to the heat capacity of CeTe₃ (left axis) and the magnetic entropy (right axis). Dashed lines show $R \ln(2J+1)$ and $R \ln 2$ (right axis).

FIG. 5. Representative resistivity data for CeTe₃ for currents flowing in the ac-plane (left axis) and along the b axis (right axis). Insets show (top) low-temperature behavior and (bottom) the Néel transition as seen in $d\rho/dT$ and $d\chi/T/dT$. Iyeiri and co-workers to account for their susceptibility data and commonly found for Ce in a low point symmetry.
sumably reflecting increased scattering for currents flowing in the $b$-axis direction relative to within the Te planes. Given the layered crystal structure, this effect is possibly associated with elastic scattering from stacking faults in the $b$-axis direction.

CeTe$_3$ is antiferromagnetic, with a Néel temperature $T_N=2.8\pm0.1$ K. Below 10 K the resistivity of CeTe$_3$ shows a mild upturn, suggestive of weak Kondo behavior. In this case, the broad maximum in the resistivity centered at approximately 6 K is associated with a coherence temperature of the Kondo lattice. ARPES data$^{6,14}$ show a nondispersing feature 0.3 eV below $E_F$ associated with the Ce 4$f$ levels, consistent with such a scenario. Given the low value of $T_N$ it is difficult to say whether there is any enhanced electronic contribution to the heat capacity at low temperatures, but the smallness of the resistivity anomaly suggests there will be minimal effect.

It is uncommon to find a Kondo lattice in an incommensurate CDW compound, and the interplay of these two physical effects raises some interesting questions. CDW formation not only reduces the number of electrons available to screen the Ce moment, but also results in a spatially varying local density of states (different for every Ce site for a truly incommensurate modulation), which would in principle be antagonistic to formation of coherence between local screening clouds. Nevertheless, the material is able to accommodate both physical effects, implying that the average density of states provides the screening, which must be extended over fairly large distances.

V. CONCLUSIONS

In summary, we have described an alternative technique to grow large, high-quality single crystals of the rare-earth tritellurides $R$Te$_3$. Our heat capacity and susceptibility measurements for the nonmagnetic members of this series ($R=$Y and La) indicate that the materials have a very low density of states associated with the small reconstructed Fermi surface in the CDW state. The Ce ion in CeTe$_3$ is trivalent at high temperatures, but the compound exhibits weak Kondo lattice behavior below approximately 10 K, before ordering to an antiferromagnetic ground state below $T_N=2.8$ K. These data imply that at low temperatures there will be a very small 4$f$ contribution to the DOS at the Fermi level for CeTe$_3$, but that this will not substantially affect the nesting features nor the CDW.

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13 S. B. Dugdale (private communication).

14 V. Brouet and Z.-X. Shen (private communication).