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Divergence in the Behavior of the Charge Density Wave in *RE*Te$_3$ (*RE* = Rare-Earth Element) with Temperature and *RE* Element

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Incommensurability in modulated systems is often linked to high-transition-temperature superconductivity[1] and density wave materials.[2] Incommensurate (IC) to commensurate (C) or near-incommensurate (NIC) transitions may give rise to interesting and often unexplained anomalies in physical properties.[3] Charge density wave (CDW) states can be created through a Fermi surface nesting effect and the creation of a new ground state with broken translational symmetry. A band gap opens at the Fermi level, and an overall energy lowering is achieved compensating the potentially energetically unfavorable IC transition.

A wide variety of physical characterization techniques have been used to probe and study CDW transitions. Temperature-dependent transport and magnetic and thermal properties are some of the typical methods applied.[4] Since the CDW distortion affects the Fermi surfaces, angle-resolved photoemission spectroscopy (ARPES) has proven to be a useful characterization method for this class of materials.[5] A direct observation of the electronic band structure near the Fermi surface (obtained through ARPES) gives information of the nature of the CDW state. In some two-dimensional systems, however, this distortion leads only to a pseudogap keeping the *RE*Te$_3$ system in the metallic state.[6] Therefore, structural transitions correlated with these electron band changes can be difficult to examine.

Temperature-dependent X-ray scattering studies of incommensurate two-dimensional systems remain but a few[7] and include 2H−NbSe$_2$ and 2H−TaSe$_2$,[8] NbSe$_3$,[9] and 1T-TaS$_2$.[10] In all cases the systems tend to "lock-in" in a more thermodynamically stable commensurate state as the temperature decreases. In other words, incommensurability (δ), defined as the departure from the commensurate state, tends to zero with falling temperature.[11] A phenomenological Landau theory developed by McMillan[12] can describe the IC to C transitions and explain the instabilities in transport properties, etc.

Here we report the temperature dependence of the incommensurate CDW state of *RE*Te$_3$ (*RE* = La, Ce, Pr, Nd, Sm, Gd, Tb, Dy, Ho, Er, and Tm). The results are unexpected in that the CDW modulation dependence as a function of decreasing *RE* radius and decreasing temperature follows opposite trends, even though both factors cause a unit cell contraction. To the best of our knowledge this is unique behavior among all reported CDW systems and underscores the need to better understand the electronic factors responsible for these phenomena.

The CDW structures of *RE*Te$_3$ (*RE* = Ce, Pr, Nd) were solved at 300 K only recently using superspace crystallographic techniques.[13] The average structure of *RE*Te$_3$ adopts the space group *Cmcm*. It consists of puckered double layers of *RE*Te sandwiched by planar square nets of Te making *RE*Te$_3$ slabs which stack along the *b*-axis creating van der Waals (vdW) gaps, Figure 1A. The modulations originate from distortion in the ideal square Te net with a **q**-vector along the *c*-axis of the so-called subcell. Although the *RE*Te$_3$ exhibit Fermi surface nesting,[4,6] transport and magnetic properties in the range of 1.8−300 K show no indication of an IC to C transition. Temperature-dependent X-ray diffraction experiments on the isostructural LaSeTe$_2$, showed no temperature dependence of its **q**-vector.[14]

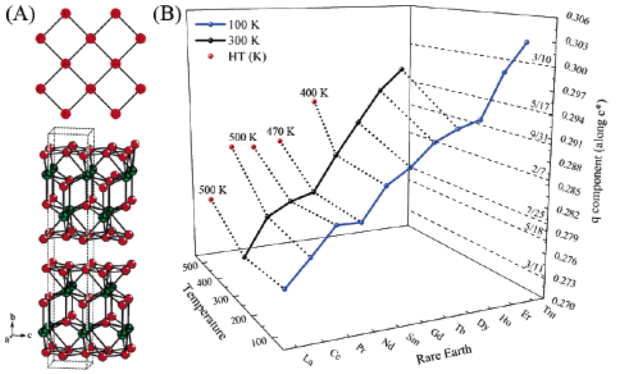

Figure 1. (A) Average undistorted structure of *RE*Te$_3$ (defined as the subcell) and ideal square Te net; (B) *q*-vector dependence as a function of *RE* element and temperature. Parallel dashed lines notate some possible low index commensurate approximants.

All crystallographic refinements at variable temperatures converged successfully by using the average structure of NdTe$_3$ as a starting model.[15] The *RE*Te$_3$ series adopts the *C*2*cm*(00γ)000 superspace group. A general characteristic is that the direction of the **q**-vector is always along the *c** axis.[16] The **q**-vector as a function of *RE* for a given temperature increases from La to Tm, Figure 1B. At 100 K, all analogues possess a CDW with **q** values varying from 0.2719(3) to 0.3028(4) for La and Tm, respectively. At 300 K, the CDW for the three heaviest *RE* (Ho, Er, and Tm) disappears judging from the vanishing of the **q**-vector. At 500 K, only La, Ce, and Pr still have a modulation **q**-vector. Nd has a **q**-vector of 0.2874(4) at 470 K, and for Sm it is 0.2936(4) at 400 K. Interestingly, evidence of a lock-in transition to a low index C state at low temperatures (100 K), according to McMillan,[12] was not observed as all **q**-vector values tend to stabilize to an IC state. For a given temperature the CDW state seems to fade with decreasing *RE* element radius. For example Ho, Er, and Tm do not exhibit a CDW state at all at room temperature. This CDW suppression can be attributed to "chemical pressure" where the Te net is squeezed by the decreasing unit cell size caused by the shrinking *RE* atoms. Indeed it is known that pressure can suppress the CDW state and in some cases can turn on a superconducting state.[17]

The systematic change of **q**-vector with *RE* element can be naively explained by considering the broadening of frontier orbital bands near the Fermi level with decreasing unit cell volume (i.e., increased orbital overlap) resulting in a change in the nesting vector.[5] Because temperature variation causes similar changes in the cell volume, it is reasonable to expect the same trend in the change of **q**-vector as the one observed with *RE* variation. Surprisingly, our experiments show the **q**-vector for all *RE*Te$_3$ as

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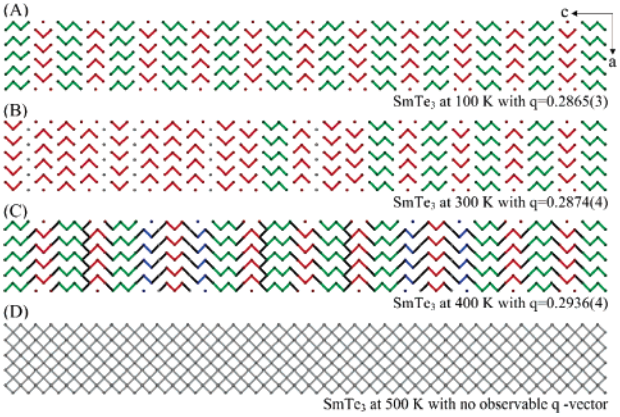

Figure 2. Evolution of the CDW in the Te net of $SmTe_3$ with temperature: (A) the Te net of $SmTe_3$ at 100 K. V- (red) and N-shaped (green) oligomers are shown using a bonding threshold of 3.002 Å; (B) Te net at 300 K at a threshold of 3.018 Å; (C) Te net at 400 K, minimum threshold of 3.042 Å (colored lines) and maximum at 3.063 Å (black lines). Intra- and interchain interactions begin to be more comparable. Dimers of Te are shown in blue. Panel D shows the perfect net due to vanishing of the CDW at 500 K at a threshold of 3.070.

a function of temperature follows the opposite trend, Figure 1B. For the lighter but larger *RE* elements (Ce−Sm) the change of **q**-vector from 100 to 300 K is negligible but it is significant between 300 and 500 K. Specifically, for $CeTe_3$ the **q**-vector drops from 0.2867(5) at 500 K to 0.2801(3) at 300 K and for $PrTe_3$ from 0.2864(4) to 0.2818(5). For Nd and Sm the **q**-vector vanishes at 500 K. The same irregular trend is more apparent from 300 to 100 K for the other *RE* (Gd, Tb, Dy, Ho, Er, and Tm) analogues. A possible reason for this behavior is that volume shrinkage associated with a temperature decrease induces a charge redistribution followed with a Te−Te bond length change owing to the flexibility of telluride to exhibit a wide range of Te−Te bonds. Although both parameters cause similar changes in the cell volume, the reason for the divergent trends observed for *RE* and temperature variation is not clear. This suggests that subtle changes in *RE*-Te bonding across the series play a key role that cannot be accounted for by cell volume changes alone.

Detailed examination of the distorted Te net in $SmTe_3$ at four different temperatures is shown in Figure 2. At 100 K the minimum Te−Te distance in the net is 2.9189(18) Å and the maximum 3.185(2) Å. By arbitrarily taking 3.002 Å to be the Te−Te bonding threshold, the net can be conveniently viewed as a sequence of trimers and tetramers, Figure 2A. At 300 K, the minimum and maximum Te−Te distance is 2.955(2) and 3.162(3) Å, and the Te pattern looks almost identical with the one at low temperature (see also Supporting Infofmation, Figure 5S) showing, to a large extent, the same sequence of trimers-to-tetramers at a threshold of 3.018 Å but up to a point, Figure 2B. The two Te nets begin to differ after a certain number of unit subcells (see from right to left). The distribution of Te−Te bonds has changed and the connectivity of the oligomers now results in a different sequence. Tetramers become trimers and single Te atoms resulting in more trimers in the net. With an increase in the temperature to 400 K, the contrast between minimum and maximum Te−Te distance becomes even smaller at 3.011(3) and 3.113(3) Å and more apparent changes are observed in the sequence of oligomers. Moreover, the difference between the Te−Te distances within and between the chains also diminishes, and interactions develop between chains, see Figure 2C. Bonding interactions between the oligomers are also verified by the observed metallic character of the system.[18] Finally, at 500 K the CDW vanishes to yield a perfect square net of Te atoms and the structure degenerates to the ideal subcell *Cmcm*, Figure 2D. Similar changes occur in the Te nets of all *RE*Te$_3$ members with increasing temperature (Supporting Information).

Furthermore, the electronic configuration of the *RE* atom appears to play a subtle but important role in the CDW of the *RE*Te$_3$ series, probably through varying involvement of f- and d-orbitals at different temperatures. Unfortunately, at this stage we have no theoretical explanation for this behavior since ab initio calculations cannot handle temperature variations, nor can they easily treat open f-shell systems. In addition, algorithms that can calculate band structures of "aperiodic" systems are not available. The combination of ab initio and modeling studies however can contribute to the understanding of the role of the f-electrons.

The experimental data reported here regarding the CDW distortions reveal unique behavior among CDW systems and underscores the incomplete level of current understanding of CDW physics.[19] The temperature dependence of the modulated structures of *RE*Te$_3$ compounds is anomalous. A change in cell volume with *RE* element has an opposite effect from comparable changes in volume caused by temperature. The evolution of CDW across the *RE*Te$_3$ series and with temperature is so subtle that no other characterization technique, such as ARPES, scanning probe, and transmission electron microscopy can probe them with the required precision. Only the excellent statistics of hundreds of satellite reflections provided by single-crystal scattering are able to determine these fine differences.

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Supporting Information Available: Details of structural analysis and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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