

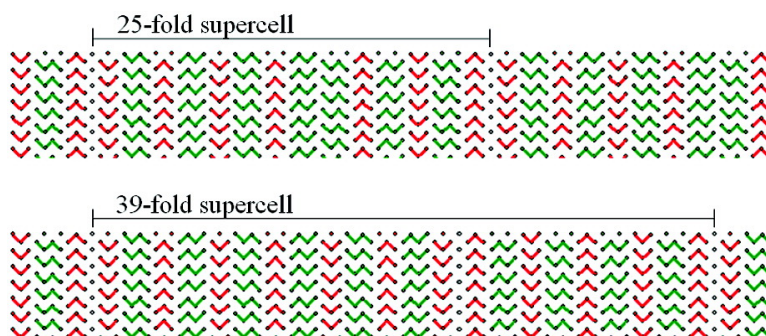
Communication

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Square Nets of Tellurium: Rare-Earth Dependent Variation in the Charge-Density Wave of RETe_3 (RE = Rare-Earth Element)

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Charge-density waves (CDWs) are broken symmetry states of mostly strongly anisotropic quasi-one-dimensional metals.¹ As a result of a Peierls instability, their ground state is a coherent superposition of electron–hole pairs which results in a periodic spatial modulation of the charge density. The study of CDWs is important because a successful description of the coupled electronic lattice instability reflects on the broader issue of the electronic aspects of structural stability, which is linked to several interesting phenomena, including superconductivity. The CDW state has not received the same level of attention as superconductivity, although the phenomenon is potentially equally important. Recently, even devices based on CDW materials have been proposed.² The vast majority of CDW studies focused on quasi-one-dimensional systems partly because two-dimensional counterparts are scarce.

The tritellurides, RETe_3 (RE = rare-earth element),^{3,4} were originally reported to crystallize in the layered so-called NdTe_3 structure type; however recently, they were recognized to be two-dimensional CDW materials. A salient feature of this structure is monolayers of Te atoms that appear to define “perfect” square nets. All Te–Te distances in the net are ~ 3.1 Å, too long to be normal bonds, yet too short to be ignored as nonbonding. Because of the novel bonding implications of a square net, it would be rather exciting if ideal square nets of Te actually existed. This picture, however, is incorrect and deceptive as it masks completely the true underlying structure.⁵ Square net arrangements of atoms are predicted theoretically⁶ to be unstable and prone to charge-density waves (CDW), and therefore, systems which feature them, such as RETe_3 , are of great interest. Electron diffraction studies on several RETe_3 compounds revealed evidence for the presence of long-range ordering.⁷ This casts doubt on the perfect square net picture and raises the possibility of lattice distortions of the charge-density wave (CDW) type in RETe_3 .⁸ Electrical conductivity measurements on RETe_3 systems indicate metallic behavior and absence of a band gap in these materials.⁹ Therefore, detailed knowledge of the long-range modulations is necessary to correctly understand the properties of RETe_3 . Modulations in Te nets have been found in more complex multinary compounds such as KBaAgTe_2 ⁵ and LaTe_2Se ¹⁰ which show oligomerization within the net to Te_x^{2-} fragments, where x varies depending on electrons per Te atom. Complicating further the structural issue is that the distortions can be incommensurate with the underlying sublattice, which historically has frustrated attempts at a complete crystallographic analysis.

The details of the modulated structures of the binary RETe_3 compounds have not yet been reported, although reasonable models have been proposed.⁷ In this work, we have succeeded in solving the incommensurate superstructures of CeTe_3 , PrTe_3 , and NdTe_3 using four-dimensional superspace crystallographic techniques.¹¹ The results are surprising in that the observed modulation does not give rise to a valence precise or localized bond definition and

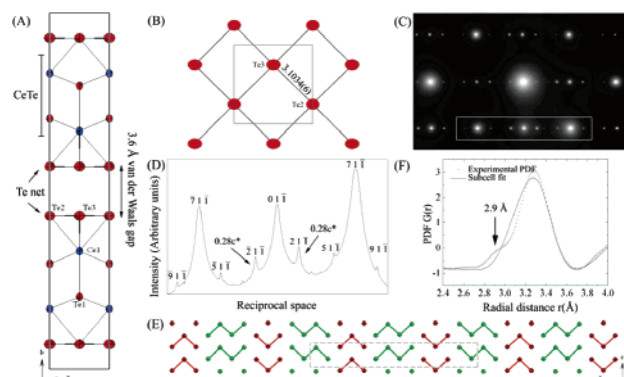


Figure 1. (A) Structure of CeTe_3 . The vdW gap is indicated (B) the ideal square net of Te atoms in CeTe_3 . (C) Selected area electron diffraction (SAED) pattern for CeTe_3 of the $(h0l)$ family showing the “7c” superlattice. (D) Intensity scan along the c^* -axis of the SAED pattern and approximate indexing based on supercell. The q -vector is also indicated. (E) Te net for all RETe_3 compounds based on an approximate 7-fold supercell crystallographic analysis. (F) PDF for CeTe_3 out to 4 Å. The peak at 3.3 Å is due mainly to RE–Te distances. The solid line represents the model from the undistorted $Cmcm$ substructure. The arrow indicates the Te–Te vector at ~ 2.9 Å in the modulated structure and highlights its discrepancy with the substructure.

actually varies with RE element. Further, the modulation is more correctly described using a q -vector super-spacegroup approach rather than a conventional supercell analysis. The modulations we observe are different from those proposed earlier based on charge balancing arguments.⁶

The average structure of RETe_3 adopts the space group $Cmcm$. It consists of puckered double layers of (RETe) that are sandwiched by the planar nets of Te making a RETe_3 slab. The slabs then stack along the b -axis creating van der Waals (vdW) gaps. The formula can be more expressly written as $(\text{RETe})^+(\text{Te}_2)^-$ (Figure 1A). The RE atom is in a monocapped tetragonal antiprism of Te atoms. The apparent Te–Te distances in the square net are 3.1034(6) Å (for CeTe_3) (Figure 1B).

We performed electron diffraction studies on CeTe_3 , PrTe_3 , and NdTe_3 , and in every case, we clearly observed superstructure along the c -axis direction and on the plane of the Te net (Figure 1C). Although the superstructure can be approximated with a cell of $c_{\text{sup}} = 7c_{\text{sub}}$ based on the weak satellite reflections along the c^* direction, an intensity scan along the $(h1-1)$ row of reflections shows the satellite reflections of the main $(01-1)$ spot to be located at a distance of qc^* $q = 0.28$ (Figure 1D). This corresponds to an approximate supercell of $c = 7c_{\text{sub}}$. Single-crystal X-ray diffraction analysis of RETe_3 (RE = Ce, Pr, Nd) in space group $Ama2$ revealed an identical modulation on the Te net for all members (Figure 1E). Although this approach gave a much better view of the distortions in these compounds it is, however, still inadequate as it “glosses over” some important details of the structure. A more accurate description was obtained when the four-dimensional superspace

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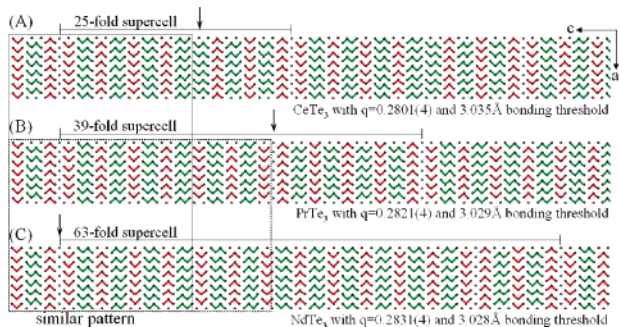


Figure 2. (A) Resolved structure of the Te net of CeTe₃ at a threshold of 3.035 Å showing V- and N-shaped oligomers. The arrow indicates the region of successive “tetramers”. (B) Te net of PrTe₃ at a threshold of 3.029 Å. The arrow indicates the presence of “single” Te atoms. (C) Te net of NdTe₃ at a threshold of 3.028 Å. Its threshold value corresponds to the maximum value at which the tetramers and trimers are not interconnected. The q -vectors correspond to a 25-fold, 39-fold, and 63-fold supercell, respectively. The boxed areas represent regions where identical domains are encountered between RETe₃ members. The changes in Te–Te bond distances are more subtle and gradual than what might be implied by the arbitrary (but reasonable) choice of the bonding cutoffs.

crystallographic approach was used to refine the structures based on the existence of a modulation q -vector.¹² X-ray diffraction gave accurate q values which, in fact, vary slightly but significantly with the RE element (i.e., $q = 0.2801(4)$, $0.2821(4)$, and $0.2831(4)$, respectively, for Ce, Pr, and Nd), and this has consequences on the observed distortion.

The superspace crystallographic analysis gave for CeTe₃ the minimum Te–Te distance in the net to be 2.9564(16) Å and the maximum 3.2407(18) Å. For PrTe₃, these distances are 2.956(3) and 3.214(3) Å, respectively, and for NdTe₃, 2.9454(14) and 3.2104(15) Å, respectively. By arbitrarily taking 3.035 Å to be the Te–Te bonding threshold, the square net of CeTe₃ can be easily viewed as a sequence of V-shaped “trimers” and N-shaped “tetramers” and, infrequently, even “single” Te atoms (Figure 2A). The Te–Te distances within the oligomers are shorter than the average 3.1034(6) Å found in the original *Cmcm* structure.

The most surprising finding of the superspace analysis is that the three RETe₃ analogues do not have identical CDW distortions. A closer look at the pattern of the Te nets reveals substantial differences in the way the nets distort as the RE element changes (Figure 2). The net does not simply shrink to follow the lanthanide contraction. Instead, the long–short bond alternation among the Te atoms varies from Ce to Pr to Nd, forming different oligomeric patterns. Starting from the left of Figure 2, we can see that the net for the three compounds is identical up to a certain distance (shown by the boxed area). After that point, there is divergence; in CeTe₃, for example, Te atoms form two tetramers, thereby breaking the trimer-to-tetramer order (Figure 2A). In contrast, the order of oligomers in PrTe₃ and NdTe₃ continues to be identical until the appearance of single Te atoms in PrTe₃ (shown in the dotted boxed area) (Figure 2B,C). At this point, the patterns of PrTe₃ and NdTe₃ diverge.

To ensure that the observed modulations were representative of the bulk and not of isolated single-crystal domains sampled selectively by our electron or X-ray diffraction experiments, we sought a total scattering technique to check the entire sample. The PDF technique is a powerful and unique tool for the characterization and structure refinement of crystalline materials with intrinsic disorder.¹³ The technique has proven to be successful in determining the structure of crystalline materials exhibiting local deviations from the average structure arising from different degrees of disorder or

long-range modulations. The experimental PDF of all three RETe₃ systems presented here shows a pronounced shoulder on the first peak at ~ 2.9 Å, and it is due to the Te–Te bonds in the oligomers. The average *Cmcm* structure cannot account for this peak because it has no distance < 3.1 Å (Figure 1E). This proves that the distortion in the Te net is a bulk phenomenon of the RETe₃ systems.

The resolution of the modulated structures of RETe₃ compounds sheds light on the subtle details of their CDW distortion(s). Furthermore, it reveals for the first time that the nature of the CDW wave in these compounds varies subtly yet detectably with RE element. This result is surprising given that the substitution of one RE for the next is isoelectronic in nature and, therefore, should presage an identical distortion pattern.

Because of the fine differences found in CDW distortions across the RE series, the structural characterization of the remaining members of the RETe₃ family is now justified. It is necessary to apply the superspace group crystallographic approach in order to successfully decipher these subtle differences. The new information reported here regarding the CDW distortions opens fresh perspectives on how to think about these systems and provides new possibilities for more informed theoretical interpretations of their physical properties.

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

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- Crystal growth of all RETe₃ was accomplished with the flux technique described in ref 9.
- A STOE IPDS II diffractometer was used to collect intensity data (Mo K α radiation). An analytical absorption correction was performed, and all structures were refined with JANA2000 software (Petricek, V.; Dusek, M. Institute of Physics; Praha, Czech Republic, 2000). Crystal data: All RETe₃ structures adopt the *C2cm*(00 γ)000 (no. 40a) super-spacegroup with $Z = 4$. CeTe₃: $a = 4.3732(5)$ Å, $b = 25.9733(41)$ Å, $c = 4.3849(5)$ Å, $q = 0.2801(4)c^*$, $V = 498.1(2)$ Å³, 7356 reflections collected (2167 main + 5189 satellite), 2475 unique reflections (822 main + 1653 satellite) [$R_{\text{int}} = 0.029$], $R = 0.033$, $wR = 0.092$ for reflections having $I > 2\sigma(I)$, min/max residual electron density = $-2.69/2.23$ e Å⁻³. PrTe₃: $a = 4.3566(4)$ Å, $b = 25.8878(29)$ Å, $c = 4.3606(5)$ Å, $q = 0.2821(4)c^*$, $V = 491.8(2)$ Å³, 9783 reflections collected (3116 main + 6667 satellite), 3140 unique reflections (1094 main + 2046 satellite) [$R_{\text{int}} = 0.045$], $R = 0.051$, $wR = 0.142$, min/max residual electron density = $-3.50/4.01$ e Å⁻³. NdTe₃: $a = 4.3469(7)$ Å, $b = 25.8515(30)$ Å, $c = 4.3629(5)$ Å, $q = 0.2831(4)c^*$, $V = 490.2(2)$ Å³, 6554 reflections collected (1940 main + 4614 satellite), 1957 unique reflections (649 main + 1308 satellite) [$R_{\text{int}} = 0.032$], $R = 0.026$, $wR = 0.088$, min/max residual electron density = $-2.02/1.61$ e Å⁻³.
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