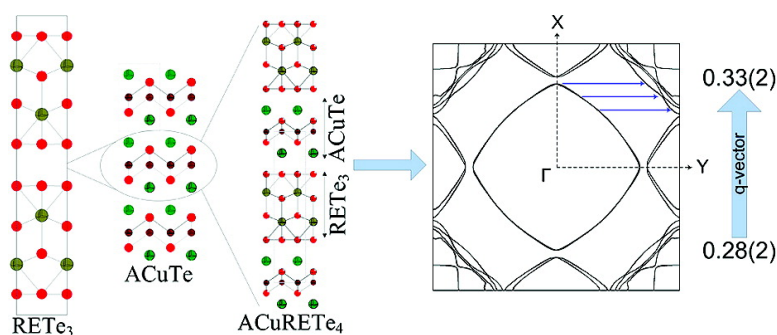


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Charge Density Waves in the Square Nets of Tellurium of $AMRETe_4$ ($A = K, Na; M = Cu, Ag; RE = La, Ce$)

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Charge density waves (CDWs) are cooperative states that arise from the coupling of phonons and free electrons in quasi-one- and two-dimensional metals. The modulation of the electron density due to this coupling creates a new broken symmetry ground state with a lower total free energy through a Peierls distortion. CDW formation is believed to be driven by Fermi surface instabilities mainly caused by nesting effects in the electronic band structure. Sometimes instabilities on the Fermi surface favor another cooperative state, i.e., superconductivity.¹ Understanding the mechanism of CDW destabilization and the competition between CDW states and superconductivity is of fundamental importance.

Several chemical tuning parameters can be employed to manipulate the CDW state. For example, it is of significant interest to be able to suppress a CDW and access a superconducting state. Theoretically, the CDW modulation is a function of the Fermi level and the nesting properties of the Fermi surface.² Doping (Ta and Ti doped NbSe₃),³ intercalation of atoms (In_xNb₃Se₄),⁴ and amine molecules (1T-TaS₂EDA_{0.25})⁵ have been widely used. This type of tuning involves electron transfer and alters the electron count on the CDW, which changes the modulation because it changes the energy of the Fermi level. This does not allow the study of the CDW state in a situation where structural changes are decoupled from changes in electron count. To observe such a decoupling, isoelectronic tuning is needed to change the character of Fermi surface nesting but not the electron count of the CDW. The family of $AMRETe_4$ ($A = K, Na; M = Cu, Ag; RE = La, Ce$) compounds⁶ may represent such a case.

The structure of $AMRETe_4$ can be seen as an intergrowth of electronically neutral $RETe_3$ ⁷ and $ACuTe$ ⁸ slabs in 1:1 ratio. The layered structure of $RETe_3$ is essentially intercalated with slabs of $ACuTe$. Because of this, the $RETe_3$ layers in $AMRETe_4$ are significantly separated compared to those in $RETe_3$, as shown in Figure 1. As the $RETe_3$ phases have CDWs,⁹ $AMRETe_4$ too has CDWs. Because the alternating layers are neutral, no electron transfer between them is necessary, and the $ACuTe$ layer does not alter the electron count in the adjacent layers of $RETe_3$. The insertion of the $ACuTe$ layer does, however, disrupt the van der Waals interactions that are present in the structure of the binaries $RETe_3$. Here, we report the details of the CDW in $AMRETe_4$ and compare them to those of the parent $RETe_3$ compounds.

We find that the CDW in $AMRETe_4$, which originates from a distortion of the Te nets in the $RETe_3$ slab in these compounds, is still present but, surprisingly, the modulation q -vectors are significantly different from the ones found in the $RETe_3$ series.¹⁰ The q -vector changes from $\sim 2/7$ in the binary phases to $\sim 1/3$ in the quaternary modifying the character of the CDW. If the CDW

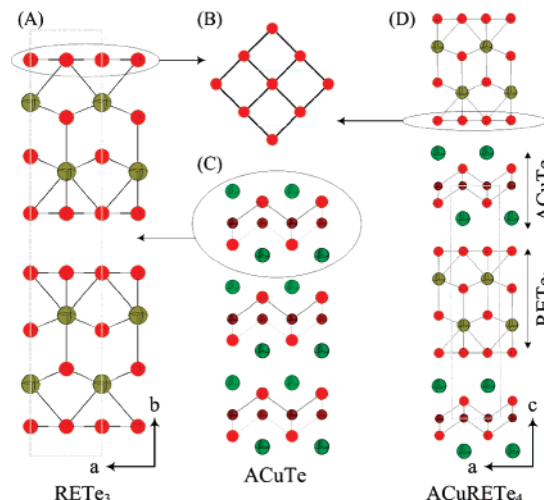


Figure 1. (A) The layered structure of $RETe_3$ ($NdTe_3$ -type). The van der Waals gap is indicated by the arrow. (B) The undistorted square net of Te atoms in $RETe_3$ and $AMRETe_4$. (C) The electronically neutral $ACuTe$ layer which when inserted in the structure of $RETe_3$ gives $AMRETe_4$. (D) The structure of $AMRETe_4$ ($A = K, Na; M = Cu, Ag; RE = La, Ce$). Green atoms are A; Red atoms are Te.

q -vector were strictly governed by the electronic structure of the $RETe_3$ itself, no significant changes would be expected by separating the $RETe_3$ slabs.

The insertion of the $ACuTe$ layers into the van der Waals gaps of the $RETe_3$ structure separates the $RETe_3$ slabs, Figure 1. The inter-slab interactions in $RETe_3$ should be diminished so that a quasi three-dimensional system becomes more two-dimensional in character. This opens the possibility that the changes in the CDW of $AMRETe_4$ arise from the enhanced two-dimensionality of the $RETe_3$ layer.¹¹ This would imply that the van der Waals interface between adjacent Te square nets in $RETe_3$ is important in affecting the Fermi surface nesting. The $AMRETe_4$ compound could present a rare example that illustrates the effect of dimensionality on the CDW distortion without changing the electron count.

The $AMRETe_4$ ($A=K, Na; M = Cu, Ag; RE = La, Ce$)¹² adopts a layered structure composed of two types of layers, the semiconductive $[NaCuTe]$ and metallic $[RETe_3]$, Figure 1. Each component is known to exist as an independent compound.^{7,8} The $[RETe_3]$ layer adopts the $NdTe_3$ structure type and has an anti-PbO type $[RETe]^{+}$ sublayer sandwiched between two square Te nets. The $[CuTe]^{-}$ layer can be described as an ideal anti-PbO structure type, made up of ribbon tetrahedral $[CuTe_4]$ units that share edges in two dimensions. The neutral $[NaCuTe]$ and $[RETe_3]$ slabs alternate in a 1:1 ratio and stack along the c -axis separated by van der Waals gaps to build the structure. Because both slabs have no net charge, the average electron count in the Te atoms of the net of the $[RETe_3]$

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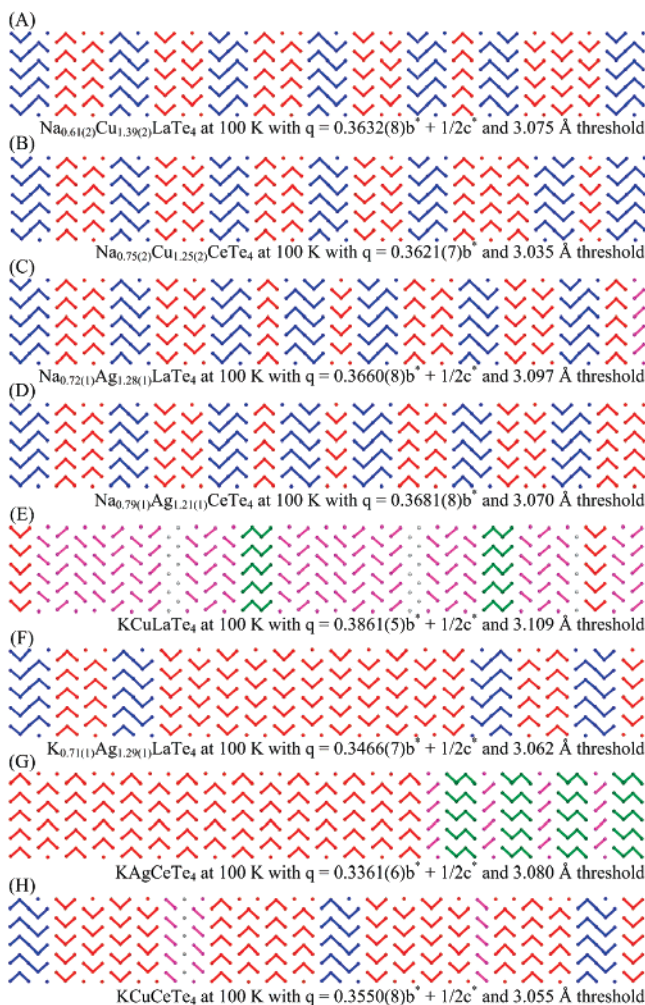


Figure 2. Distorted tellurium nets of $AMRETe_4$ at 100 K. A different sequence of trimers (red), tetramers (green), pentamers (blue) and some times dimers (purple) and monomers (gray) is observed for every analogue. (A) $Na_{0.61}Cu_{1.39}LaTe_4$ at a threshold of 3.075 Å. (B) $Na_{0.75}Cu_{1.25}CeTe_4$ at a threshold of 3.035 Å. (C) $Na_{0.72}Ag_{1.28}LaTe_4$ at a threshold of 3.097 Å. (D) $Na_{0.79}Ag_{1.21}CeTe_4$ at a threshold of 3.070 Å. (E) $KCuLaTe_4$ at a threshold of 3.109 Å. (F) $K_{0.71}Ag_{1.29}LaTe_4$ at a threshold of 3.062 Å. (G) $KAgCeTe_4$ at a threshold of 3.080 Å. (H) $KCuCeTe_4$ at a threshold of 3.055 Å. Its threshold value corresponds to the maximum value at which the trimers and tetramers, pentamers or dimers are not interconnected. A more extended region of the Te nets can be found in the Supporting Information.

sublayer remains $-0.5 e^-$. No electron transfer is necessary between the $[NaCuTe]$ and $[RETe_3]$ slabs. A more descriptive formula of the structure can be $Na^+[CuTe]^- [RETe]^+ [Te_2]^-$. The single-crystal structure refinement indicated that in some members of the family there is some interchange between the alkali atoms and monovalent M atoms in their crystallographic sites in the form $A_{1-x}M_{1+x}RETe_4$.¹³

The CDW in all $A_{1-x}M_{1+x}RETe_4$ analogs gives rise to modulated incommensurate superstructures. The application of superspace crystallographic techniques was necessary to solve their structure.¹⁴ Although the undistorted (no CDW) subcell structure has a tetragonal symmetry (Table 1S), the modulation q -vector is always along the b -axis, giving orthorhombic symmetry. The distortion is located in the planar Te nets of the $RETe_3$ slabs.¹⁵ Most of the $A_{1-x}M_{1+x}RETe_4$ ($A = K, Na; M = Cu, Ag; RE = La, Ce$) analogs adopt the $P2_12_12(0\beta/2)0s0$ superspace group, except for $NaMCETe_4$ ($M = Ag$ and Cu), which adopts $P2_12_12(0\beta/0)0s0$, and $KAgRETe_4$ ($RE = La$ and Ce), which adopts the lower symmetry $Pm(0\beta/2)0$ superspace group.

Table 1. Comparison of the Minimum and Maximum Distances of Te–Te within the Net (X-Ray Diffraction at 100 K) and RT Energy Gap Values of All $A_{1-x}M_{1+x}RETe_4$ ($A = K, Na; M = Cu, Ag; RE = La, Ce$) Quaternary Compounds with the Binary $RETe_3$ Analogs

compound	minimum distance (Å)	maximum distance (Å)	energy gap (eV)
$CeTe_3$	2.925(2)	3.255(3)	0.27(2)
$LaTe_3$	2.929(6)	3.272(7)	0.25(2)
$Na_{0.60(2)}Cu_{1.40(2)}LaTe_4$	2.999(4)	3.260(4)	0.25(2)
$Na_{0.78(1)}Cu_{1.22(1)}CeTe_4$	2.975(3)	3.241(2)	0.27(2)
$Na_{0.70(1)}Ag_{1.30(1)}LaTe_4$	3.037(4)	3.273(3)	0.27(2)
$Na_{0.78(1)}Ag_{1.22(1)}CeTe_4$	2.985(3)	3.264(3)	0.28(2)
$KCuCeTe_4$	2.972(2)	3.275(2)	0.33(2)
$KCuLaTe_4$	2.910(4)	3.392(4)	0.30(2)
$K_{0.71(2)}Ag_{1.29(2)}LaTe_4$	2.929(4)	3.447(4)	0.28(2)
$KAgCeTe_4$	2.896(9)	3.406(9)	0.30(2)

The q -vector varies from 0.3361(6) in $KAgCeTe_4$ to 0.3861(5) in $KCuLaTe_4$, at 100 K. The difference in the cell constants along the plane of the Te net between these quaternary phases and the corresponding $RETe_3$ binaries is negligible ($\sim 2\%$). Surprisingly, however, the difference in q -vectors between quaternary (0.3550(8) for $KCuCeTe_4$) and binary (0.2790(3) for $CeTe_3$) compounds is large, $\sim 30\%$. A 2% change in the lattice constant cannot account for the large change in q -vector. A difference of $\sim 2\%$ in the cell parameters of the binary $RETe_3$ results in no more than 6% change in the q -vector.¹⁶ Given that the $RETe_3$ layers in the quaternary and binary compounds are isoelectronic, the large change in the CDW character could arise from the alteration occurring in interlayer coupling between adjacent Te nets of $RETe_3$ slabs upon insertion of the $AMTe$ layer.

The new CDW modulations found in the quaternary compounds features Te_x oligomers which are different from those observed in the $RETe_3$ ($RE = La$ and Ce) series. The majority of oligomers in the binary $RETe_3$ compounds are tetramers and trimers and occasionally single Te atoms and W-shaped pentamers.¹⁷ In contrast, every Te pattern within the $A_{1-x}M_{1+x}RETe_4$ series is unique with a different sequence of oligomers along the modulation direction. Interestingly, tetramers were not found in most of the quaternary phases. Instead, a sequence of trimers and pentamers with one linear Te atom and occasionally monomers and dimers is observed for the compounds that have a q -vector in the range of 0.36(1), Figure 2(A–D, F, H). For the two cases where the q -vector deviates significantly from this range, the Te patterns start to contain tetramers similar to those found in the binaries. Specifically, the majority of oligomers in the Te net of $KCuLaTe_4$ (q -vector of 0.3861(5)) consists of dimers and occasionally trimers, tetramers, and single Te atoms, Figure 2E. For $KAgCeTe_4$ (q -vector of 0.3361(6)), the net is mainly composed by trimers and a smaller fraction of dimers and tetramers, Figure 2G. The bond length distribution between Te atoms in the nets of $A_{1-x}M_{1+x}RETe_4$ is comparable with that in the $RETe_3$ binaries, Table 1.

The q -vector increases as the cell volume decreases, for example from 0.3361(6) in $KAgCeTe_4$ to 0.3861(5) in $KCuLaTe_4$, at 100 K. The same trend exists in the $RETe_3$ series.¹⁷ The temperature dependence of the q -vector between 100 K and 300 K seems negligible.

Electronic band structure calculations at the density functional theory (DFT) level¹⁸ performed on the undistorted structure of $KCuLaTe_4$ confirm that the Fermi surface topology favors the formation of a nesting vector (q -vector) along the b^* direction with a value of ~ 0.33 , Figure 3A.¹⁹ The Fermi surface topology is similar to the one for $LaTe_3$ that forms a nesting vector of 0.28(2). The difference is the presence of three extra bands, mainly Cu d and Te p in character from the $[KCuTe]$ layer, that are crossing the

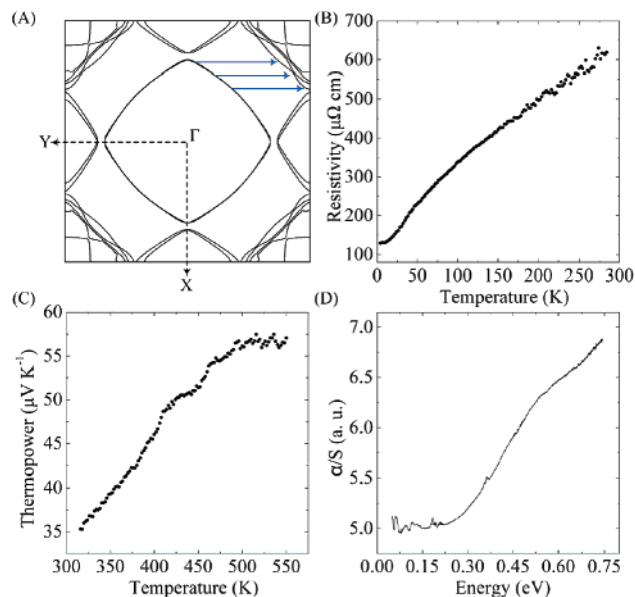


Figure 3. (A) Fermi surface topology of KCuLaTe₄. Possible nesting vectors (q -vectors) with an average length of 0.33(2) along the b^* axis (Y point) are drawn in blue arrows. (B) Temperature-dependent resistivity of KCuLaTe₄ single crystal. (C) Dependence of thermopower of KCuLaTe₄ single crystal. (D) Typical room temperature (RT) infrared absorption spectrum of Na_{0.78}Cu_{0.22}CeTe₄, showing a energy gap at around 0.27 eV.

Fermi surface and they are located outside the nesting region of the p bands of the Te net of [RETe₃] (see Figures 4S and 8S in the Supporting Information).

Generally, the formation of CDWs leads to the appearance of energy gaps at the Fermi level (E_f). In the case of RETe₃, however, near E_f there is an energy gap associated with the CDW distortion of the Te net but some electronic states still remain at E_f because of bands associated with other parts of the structure. Thus, the CDW distortions do not create a fully gapped Fermi surface.²⁰ This situation creates a poor metal character for RETe₃ and this is confirmed by electrical resistivity measurements.²¹ The situation in KCuLaTe₄ is similar as indicated by the temperature-dependent resistivity data shown in Figure 3B. The thermopower varies between +35 and +55 $\mu\text{V}/\text{K}$ in the range of 300–550 K. These are relatively small values and are consistent with metallic p -type character for the material, Figure 3C.

Despite the poor metal character of AMRETe₄, there are spectroscopically observed electronic transitions which can be assigned to the CDW energy gap of the Te-net. The energy values are between 0.25(2) eV for Na_{0.60}Cu_{1.40}LaTe₄ and 0.33(2) eV for KCuCeTe₄ at RT as measured by infrared diffuse reflectance spectroscopy, Table 1. A representative plot of the apparent energy gap is shown in Figure 3D.

The AMRETe₄ together with the RETe₃ are excellent model systems for fundamental studies of CDW distortions because their structures are simple and exhibit a wave modulation along a single axis direction. The results reported here suggest that interactions along the third, cross-plane dimension in the quasi-two-dimensional systems of AMRETe₄ and RETe₃ play an important role on defining the CDW modulations. The van der Waals gaps in RETe₃ influence band dispersion, which alters the Fermi surface nesting, thereby

changing the CDW character. In this regard, the van der Waals gaps in RETe₃ are not simple “innocent” spacers. Thus, we would expect the application of pressure to strongly influence these gaps and greatly affect and even suppress the CDW.

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

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- A_{1-x}M_{1+x}RETe₄ was synthesized from a mixture of A₂Te (A = K, Na; 0.500 mmol), M (M = Cu, Ag; 0.125 mmol), RE (RE = La, Ce; 0.125 mmol), and Te (2.0 mmol) that was sealed under vacuum in a quartz tube and heated to 700 °C for 5 days. The tube was then cooled to 300 °C at a rate of 4 °C/h, followed by quenching to RT at a rate of 10 °C/h. The excess A₂Te flux was washed off with *N,N*-dimethylformamide under nitrogen to reveal very thin red-brown plate-shaped crystals.
- In most of the quaternary series the alkali metal site is mixed-occupied with the coinage metal (except the K/Cu combination). The similar atomic radii and same square antiprismatic site environment of these atoms can facilitate such disorder.
- 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). Detailed crystal data reports can be found in the Supporting Information.
- The [CuTe]⁻ layer also contains a square Te net. However, it is not distorted as the formal charge on each Te atom in this layer is 2- and Te-Te interatomic distances greater than 4.4 Å.
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