

Charge Density Wave States and Structural Transition in Layered Chalcogenide $\text{TaSe}_{2-x}\text{Te}_x$ *

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The structural features and three-dimensional nature of the charge density wave (CDW) state of the layered chalcogenide $1\text{T-TaSe}_{2-x}\text{Te}_x$ ($0 \leq x \leq 2.0$) are characterized by Cs-corrected transmission electron microscopy measurements. Notable changes of both average structure and the CDW state arising from Te substitution for Se are clearly demonstrated in samples with $x > 0.3$. The commensurate CDW state characterized by the known star-of-David clustering in the 1T-TaSe_2 crystal becomes visibly unstable with Te substitution and vanishes when $x = 0.3$. The $1\text{T-TaSe}_{2-x}\text{Te}_x$ ($0.3 \leq x \leq 1.3$) samples generally adopt a remarkable incommensurate CDW state with monoclinic distortion, which could be fundamentally in correlation with the strong q -dependent electron-phonon coupling-induced period-lattice-distortion as identified in TaTe_2 . Systematic analysis demonstrates that the occurrence of superconductivity is related to the suppression of the commensurate CDW phase and the presence of discommensuration is an evident structural feature observed in the superconducting samples.

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Low-dimensional electron systems have attracted increasing attention for applications in electronics, photonics and optoelectronics due to their unusual electrical and optical properties; interplay among various collective electronic states such as CDW, electronic phase separation and superconductivity is of tremendous significance in these kinds of materials. Though the fundamental structural features of CDW can be well understood in terms of Fermi-surface nesting, owing to electron-phonon coupling in the framework of the Peierls mechanism, on the other hand, there often exists simultaneously strong electron-electron interaction in some low-dimensional materials, giving rise to the coexistence and competition, among the multiple ordered states.^[1–4] The transition metal dichalcogenide TaX_2 (where $X=\text{Se, S and Te}$) can serve as an ideal platform for investigating the intricate interplay among multi-degrees of freedom.^[5–7] The CDW phases in TaX_2 are diverse, and the 1T-TaS_2 and 1T-TaSe_2 both go through the ICCDW (incommensurate CDW) to CCDW (commensurate CDW) phase via lowering temperature.^[8] It is well accepted that the CCDW phase of 1T-TaSe_2 originates from the strong electron-phonon and electron-electron interactions, and the commensurate modulation is well identified by a 13-atom star-of-David cluster supercell.^[9,10] Moreover, the importance of the complexity of the layer stacking textures and their impact on physical property has been recently investi-

gated in 1T-TaS_2 .^[11] The TaTe_2 is a typical quasi-two-dimensional (2D) transition metal dichalcogenide (TMD) of monoclinic distorted-1T structure accompanied with ribbon chain type clustering, for which the CDW distortion has been considered as strong q -dependent electron-phonon coupling-induced period-lattice distortion (PLD) with a single wave vector of $q = 1/3a^*$.^[12,13] The stabilization of charge density waves in 1T-TaS_2 , 1T-TaSe_2 and the hypothetical 1T-TaTe_2 has been analyzed using the density functional theory (DFT),^[13] and the rise of ribbon-chain type clustering would be attributed to the valence electron concentration at the Ta atoms exceeding 1, due to a higher charge transfer from Te to Ta.^[14,15]

Superconductivity in TMDs has inspired great interest in the study of coexistence, competition, or collaboration of multiple orderings near the CDW orders. The superconductivity in TMDs could be tuned by chemical doping or external stimulations,^[16–19] for example, superconductivity has been induced by high pressure,^[16,20] disordering and Fe and/or Se substitution in 1T-TaS_2 .^[5–7,21] Recent work reveals that an ordering of selenium and sulphur atoms surrounding tantalum within star-of-David clusters can boost superconductivity in layered chalcogenide $1\text{T-TaS}_{2-x}\text{Se}_x$ ($0 \leq x \leq 2.0$), which undergoes a superconducting transition in the nearly commensurate charge density wave phase.^[6,22] Recently, the superconducting properties of $1\text{T-TaSe}_{2-x}\text{Te}_x$ ($0 \leq x \leq$

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2.0) have been reported by two research groups.^[23,24] However, how CDW and superconductivity are correlated, and to what level the atomistic structure can play a role in understanding the origin of superconducting nature in 1T-TaSe_{2-x}Te_x ($0 \leq x \leq 2.0$) are still unknown.

In the following, combining the selected area electron diffraction patterns (SADPs), Cs-corrected high-angle annular dark-field (HAADF) and scanning transmission electron microscopy (STEM) measurements, we provide evidence that remarkable changes in CDW states are clearly observed in 1T-TaSe_{2-x}Te_x ($0 \leq x \leq 2.0$), associated with the transformation from commensurate phase (C phase) of star-of-David clustering modulation into an incommensurate phase (IC phase) with monoclinic distortion, via Te substitution. Our systematical measurements of atomic displacement in STEM analysis reveal that the IC-CDW states in 1T-TaSe_{2-x}Te_x ($0 \leq x \leq 2.0$) could be fundamentally in correlation with the strong q -dependent electron-phonon coupling-induced period-lattice-distortion (PLD) as identified in the TaTe₂. The three-dimensional character of the CDW states and the correlation between microstructure features and superconductivity have also been discussed for this layered system.

High-quality single crystals of 1T-TaSe_{2-x}Te_x ($0 \leq x \leq 2.0$) used in the present study were grown by the chemical vapor transport technique and have been well characterized, as reported in Ref. [24]. TEM and STEM observations were performed in the JEOL ARM200F equipped with double aberration correctors and operated at 200 kV.

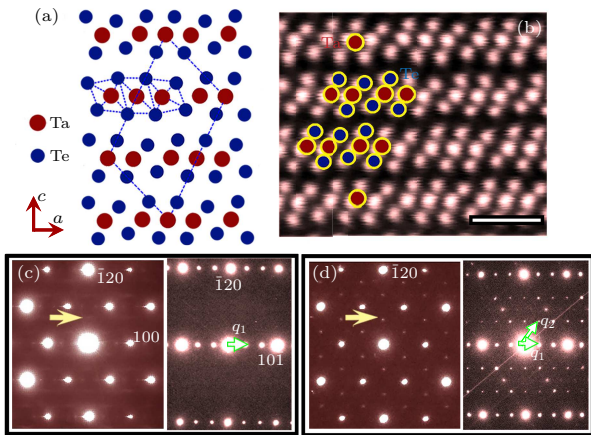


Fig. 1. (a) Structural model of monoclinic TaTe₂ with layered structure. (b) High-resolution STEM image of CDW modulation taken along [010] zone-axis in TaTe₂. SADPs taken along [001] and [212] zone-axis directions at 300 K (c) and 100 K (d). The scale bar is 1 nm.

We firstly focus on the structural features of CDW modulation and low-temperature (LT) phase transitions in TaTe₂. Figure 1(a) shows a structural model as reported in Ref. [25], illustrating the TaTe₂ crystal of a monoclinic average structure at room temperature, with two distinct Ta sites located in the center of

two different types of distorted TaTe₆ octahedral. The distorted TaTe₆ octahedral connect via common edges forming two-dimensional corrugated slabs and lead to the formation of Ta double zigzag chains (called ribbon chain).^[25] It should be noted that the undistorted 1T structure notation has been used to describe the TaTe₂ structure to facilitate a better comparison with 1T-TaSe₂ in the following. The atomic structure was further examined using Cs-corrected STEM as shown in Fig. 1(b), and the two types of the distorted TaTe₆ octahedral can be well identified. This feature is clearly illustrated in the structural model superimposed on the experimental image. Figure 1(c) shows typical SADPs taken along [001] and [212] zone-axis directions of TaTe₂ at room temperature. The main diffraction spots with relatively strong intensity can be well indexed by the known structure, and the series of weak diffraction spots appearing at around $1/3(100)$ positions can be explained by the short coherence length of the CDW states ($q_1=1/3(10\bar{1})$ for 1T structure notation) along the c -axis direction. On the other hand, the most striking structural phenomenon revealed in our TEM observations is the appearance of a series of new superstructure reflections showing as diffuse streaks along the a^* direction, which are indicated by the arrow. Since the low temperature phase transition in TaTe₂ at 170 K accompanied with an evident magnetic and electrical anomaly has been reported,^[25] this change could be correlated with the formation about a new modulation and a low-temperature clustering of Ta atoms due to alterations of electronic structure at the Fermi level as revealed by single crystal x-ray diffraction data and theoretical calculations.^[25] In this low temperature structure, a new three-fold superstructure is formed by varying distances in the double zigzag chains.^[25] Figure 1(d) shows the SADPs taken along [001] and [212] zone-axis directions at about 100 K. In comparison with room-temperature data shown in Fig. 1(c), the superstructure spots centered on $1/3(\bar{1}20)$ and became visibly stronger and sharper. Theoretical simulations for the above structural models can give rise to the diffraction patterns in good agreement with the experimental ones. Here we assign $q_2=1/3(02\bar{1})$ by using the additional superstructure modulation in the [212] zone axis diffraction pattern. Our low-temperature in-situ TEM observations clearly show that this structural transition yields complicated atomic changes in the three-dimensional crystal structure. Importantly, this LT structure modulation dominates the microstructure features of superconducting materials, which will be discussed in the following.

Although 1T-TaSe₂ has received extensive attention in recent years due to its quasi-2D incommensurate CDW states, superconductivity and phase separation, very limited studies have been carried out to understand the three-dimensional nature of the CDW states.^[11] The commensurate superstructure within the a - b plane in 1T-TaSe₂ can be well described by a supercell. Within each supercell, the six nearest and

six next-nearest Ta neighbors of the central Ta atom are displaced inward, forming a 13-atom star-of-David cluster as shown in Fig. 2(a). Figures 2(b)–2(d) show a series of SADPs taken along relevant zone-axis directions of 1T-TaSe₂ at room temperature. As reported in the previous publications, all the superstructure reflections in Fig. 2(b) can be indexed by the commensurate modulations $q_c = (4a^* - b^*)/13$ without considering the c^* components. The diffraction patterns taken along the [212] and [140] zone-axis directions display a clearly c^* component of the modulation wave vector and an evident long coherence length of the star-of-David clusters coupling along the c -direction (Figs. 2(c) and 2d)). Our result clearly reveals that the coupling of the CDW states among layers is evident despite the weak van der Waals bonding, and the CDW states can be written as $q_c = (4a^* - b^* + 2c^*)/13$.

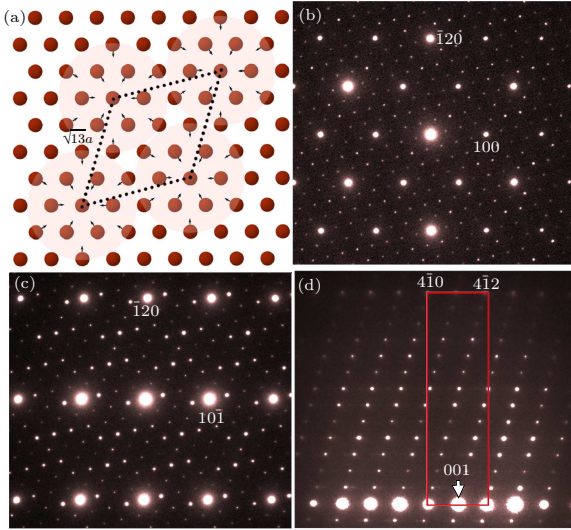


Fig. 2. (a) Schematic model of Ta atoms with star-of-David clustering CCDW superstructure. (b) SADPs taken along the [001] zone-axis direction showing the superstructure diffraction spots. [(c), (d)] SADPs taken along the [212] and [140] zone-axis directions, emphasizing the dimensionality of three for the CDW states.

Based on the comprehensive understanding of the CDW states and structural features of the two end members (TaTe₂ and 1T-TaSe₂), we further investigate the microstructure and the CDW modulation in the 1T-TaSe_{2-x}Te_x ($0 \leq x \leq 2.0$) system. Figure 3(a) shows the SADPs taken along the relevant [001] and [212] zone-axis directions for three typical samples, and careful analysis suggests that the better and clearer view of evolution about the CDW modulation in samples can be obtained along the [212] zone axis direction. The first structural alteration following the Te substitution for Se in 1T-TaSe₂ can be identified as the changes of CDW modulation, and it is recognizable that the star-of-David CDW structure disappears and the q_2 superstructure becomes evidently visible in the $x = 0.3$ sample as shown in Fig. 3(a). This superstructure modulation is quite different from the intrinsic modulation in 1T-TaSe₂. Moreover, our careful analysis demonstrates that the superstructures corre-

sponding to the star-of-David cluster modulation in 1T-TaSe₂ completely vanish in all the samples with Te concentration greater than 0.3. Though the resultant modulation shows up very similar features with that observed in TaTe₂ at low temperature (Fig. 3(b)), a clear incommensurability depending on the Te concentration can be observed in most samples. Furthermore, the systematic diffraction analysis shows that the modulation vectors q_2 change with Te substitution content and tend to lock into commensurate modulation when the Te substitution content reaches $x = 1.3$.

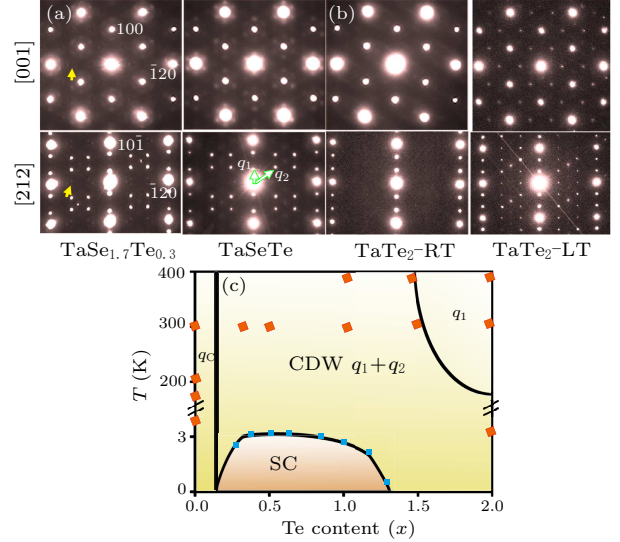


Fig. 3. (a) SADPs taken along two zone-axis directions, showing the evolution of the superstructure spots via Te substitution at 300 K. The clear incommensurability as indicated by arrow can be seen in TaSe_{1.7}Te_{0.3} samples. (b) SADPs of LT TaTe₂ obtained at 100 K. (c) A proposed simplified electronic phase and structure diagram of TaSe_{2-x}Te_x as functions of the temperature T and content x , derived from previous reported transport measurements^[24] and our structure characterization.

In the 1T-TaSe_{2-x}Te_x ($0 \leq x \leq 2.0$) samples, the signature of superconductivity emerges as $x > 0.3$ and finally disappears for $x > 1.3$, while the zero resistances are observed when $0.5 < x < 1.3$.^[24] The maximum of superconducting onset temperature of 2.5 K is found with $x = 0.6$. It is noted that all superconducting samples commonly contain two incommensurate CDW modulations of q_1 and q_2 , and q_1 is similar to the satellite spots observed in TaTe₂, while with a clear incommensurability. Based on the phase diagram in Ref. [24] and the TEM experimental measurements of physical properties and structural characterizations for 1T-TaSe_{2-x}Te_x ($0 \leq x \leq 2.0$) samples, we show a brief phase diagram focusing on the q modulations in Fig. 3(c), and the red square dots represent the experimental data obtained by TEM.

Since we have demonstrated the evolution of the CDW orders with the change of Te concentration in diffraction patterns, we now go on to discuss the atomic structural features and local structural alterations corresponding to the CDW modulation in 1T-TaSe_{2-x}Te_x ($0 \leq x \leq 2.0$). Our structural investiga-

tions have been performed on a few well-characterized samples, e.g., 1T-TaSe₂ (q_c phase), TaTe₂ (q_1 phase) and superconducting 1T-TaSeTe (incommensurate q_1 and q_2 phase), using aberration-corrected STEM images. Careful analysis suggests that the overlap of the main sites of Ta with Se/Te atoms can be avoided along the [010] axis direction, thus the atomic shifts for relevant atomic columns can be well addressed. Figure 4(a) presents the electron diffraction patterns with the q_1 modulations and typical HAADF-STEM images viewed along the [010] axis for these samples, in which the layered structural features and structural alteration associated with the q_1 CDW modulation have been well demonstrated. Based on the fundamental theory for HAADF images, the dot brightness in the image for a specific atomic column is proportional to Z^n ($1 < n < 2$, Z is the atomic number).^[26,27] Therefore, it is distinguishable that the large bright dots arranged in a square lattice are the projection of the Ta atomic columns, and the small dots are Te/Se atomic columns. The STEM image clearly shows the two types of the distorted TaTe₆ octahedral in TaTe₂, and the notable variation of the Ta-Ta column distance and the Ta-Te column distance. As was reported, the ordering of selenium and sulphur atoms surrounding tantalum within the star-of-David cluster can boost superconductivity in 1T-TaS_{2-x}Se_x ($0 \leq x \leq 2.0$).^[22] In the 1T-TaSeTe structure, it is evidently recognizable that there is no long range order of the Te atoms substitution in the sample. One of the most notable structural features revealed is that the average structure of 1T-TaSeTe superconductor contains a clear monoclinic distortion, and Te/Se shows a much smaller deviation in comparison with the TaTe₂ phase. This local structural change could not be distinguished from XRD characterization.^[23,24]

The distances between Ta-Ta columns of typical samples in Fig. 4(a) are measured by MATLAB software, as shown in Figs. 4(b) and 4(c), where atomic columns are fitted as two-dimensional Gaussian functions. It is noted that the atomic configuration in 1T-TaSeTe adopts a very similar clustering as observed in the TaTe₂ crystal, but the column distance variation is much smaller, e.g., the Ta-Ta column distance ranges from 3.27 Å to 4.46 Å for TaTe₂ and 3.37 Å to 3.8 Å for 1T-TaSeTe. Careful measurements also demonstrate that the Te/Se atoms deviation from the original 1T structure is much smaller, and this fact suggests that TaTe(Se)₆ octahedral is much less distorted in the superconducting samples. Analogous structural phenomena have been noted and discussed in Ref. [22], when the more electronegative Se atoms were doped into TaTe₂, the top portion of the chalcogen p -block bands would be lowered, and the extent of the p - d band overlap decreases, which results in less electrons transferring from chalcogen p -block bands to the metal d -block bands. The metal oxidation state of TaSe_{2-x}Te_x may have the less d -electron counts than that in TaTe₂.^[6,13-15,22] Therefore, it is reasonable that Se doping causes the reduced TaTe(Se)₆ octahe-

dral distortion in the 1T-TaSe_{2-x}Te_x systems.^[13-15] Another piece of structural information that can be evidently recognized in Fig. 4(c) is the presence of the discommensuration within a few atomic layer thicknesses. It is well known that strong electron-phonon coupling often leads to a discommensurate (DC) rather than uniformly incommensurate state in the 1D incommensurate CDW system.^[28] The discommensurations yield rapid phase change, which may be related to the appearance of superconductivity.^[16] The STEM observation along the [212] zone axis direction showing clear q_1 and q_2 structural modulations has also been carried out. Unfortunately, the detailed atomic displacement cannot be directly read out due to the overlap of the Ta atoms and Se/Te atoms.

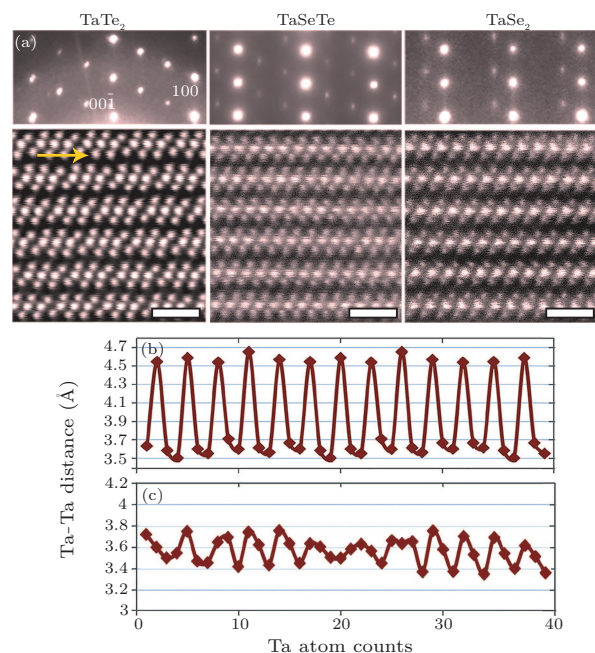


Fig. 4. (a) SADPs and atomic resolution HAADF-STEM image taken along the [010] zone axis direction of TaTe₂, TaSeTe and 1T-TaSe₂. [(b), (c)] The line profile of Ta-Ta column distance in TaTe₂ with $q_1=1/3(10\bar{1})$ and TaSeTe with $q_1=0.307(10\bar{1})$, respectively, illustrating the evident decrease of the local distortion and the presence of discommensuration and domain walls with a few atomic layer thicknesses. Yellow arrows indicate the line scan profile direction of the Ta-Ta distance. The scale bar is 1 nm.

In summary, we have directly observed the structural features of the layered chalcogenide 1T-TaSe_{2-x}Te_x ($0 \leq x \leq 2.0$) using the Cs-corrected STEM. The structural analysis evidently demonstrates that a remarkable change of CDW states from the star-of-David cluster C phase to monoclinic IC phase associated with the Te substitution is clearly observed. Noticeably, the incommensurate CDW states in 1T-TaSe_{2-x}Te_x ($0.3 \leq x \leq 1.3$) could be fundamentally in correlation with the strong q -dependent electron-phonon coupling induced period-lattice-distortion (PLD) as identified in the TaTe₂. Compared with the physical property measurement result, our experimental results demonstrate that the superconductivity in 1T-TaS_{2-x}Se_x ($0 \leq x \leq 2.0$)

is related to the structural instability caused by the strong q -dependent electron–phonon coupling-induced PLD, and has a significant correlation with the emergence of discommensurations in the CDW ordered states.

References

- [1] Di Salvo F J, Moncton D E, Wilson J A and Mahajan S 1976 *Phys. Rev. B* **14** 1543
- [2] Joe Y I, Chen X M, Ghaemi P, Finkelstein K D, De la Pena G A, Gan Y, Lee J C T, Yuan S, Geck J, MacDougall G J, Chiang T C, Cooper S L, Fradkin E and Abbamonte P 2014 *Nat. Phys.* **10** 421
- [3] Rossnagel K, Rotenberg E, Koh H, Smith N and Kipp L 2005 *Phys. Rev. B* **72** 121103
- [4] Grosse C, Atkins R, Kirmse H, Mogilatenko A, Neumann W and Johnson D C 2013 *J. Alloys Compd.* **579** 507
- [5] Liu Y, Ang R, Lu W J, Song W H, Li L J and Sun Y P 2013 *Appl. Phys. Lett.* **102** 192602
- [6] Ang R, Miyata Y, Ieki E, Nakayama K, Sato T, Liu Y, Lu W J, Sun Y P and Takahashi T 2013 *Phys. Rev. B* **88** 115145
- [7] Li L J, Lu W J, Zhu X D, Ling L S, Qu Z and Sun Y P 2012 *Europhys. Lett.* **97** 67005
- [8] Wilson J, Di Salvo F J and Mahajan S 1974 *Phys. Rev. Lett.* **32** 882
- [9] Eibschutz M 1992 *Phys. Rev. B* **45** 10914
- [10] Wilson J A, Di Salvo F J and Mahajan S 2001 *Adv. Phys.* **50** 1171
- [11] Ritschel T, Trinckauf J, Koepfner K, Büchner B, Zimmermann M v, Berger H, Joe Y I, Abbamonte P and Geck J 2015 *Nat. Phys.* **11** 328
- [12] Battaglia C, Cercellier H, Clerc F, Despont L, Garnier M G, Koitzsch C, Aebi P, Berger H, Forró L and Draxl C A 2005 *Phys. Rev. B* **72** 195114
- [13] Sharma S, Nordström L and Johansson B 2002 *Phys. Rev. B* **66** 195101
- [14] Doublet M L, Remy S and Lemoigno F 2000 *J. Chem. Phys.* **113** 5879
- [15] Vernes A, Ebert H, Bensch W, Heid W and Näther C 1998 *J. Phys.: Condens. Matter* **10** 761
- [16] Sipos B, Kusmartseva A F, Akrap A, Berger H, Forró L and Tutiš E 2008 *Nat. Mater.* **7** 960
- [17] Morosan E, Zandbergen H W, Dennis B S J, Bos W G, Onose Y, Klimczuk T, Ramirez A P, Ong N P and Cava R J 2006 *Nat. Phys.* **2** 544
- [18] Morosan E, Wagner K E, Zhao L L, Hor Y, Williams A J, Tao J, Zhu Y and Cava R J 2010 *Phys. Rev. B* **81** 094524
- [19] Di Salvo F J, Wilson J A, Bagley B G and Waszczak J V 1975 *Phys. Rev. B* **12** 2220
- [20] Ritschel T, Trinckauf J, Garbarino G, Hanfland M, Zimmermann M v, Berger H, Büchner B and Geck J 2013 *Phys. Rev. B* **87** 125135
- [21] Ang R, Tanaka Y, Ieki E, Nakayama K, Sato T, Li L J, Lu W J, Sun Y P and Takahashi T 2012 *Phys. Rev. Lett.* **109** 176403
- [22] Ang R, Wang Z C, Chen C L, Tang J, Liu N, Liu Y, Lu W J, Sun Y P, Mori T and Ikuhara Y 2015 *Nat. Commun.* **6** 6091
- [23] Luo H, Xie W, Tao J, Inoue H, Gyenis A, Krizan J W, Yazdani A, Zhu Y and Cava R J 2015 *Proc. Natl. Acad. Sci. USA* **112** 1174
- [24] Liu Y, Shao D F, Li L J, Lu W J, Zhu X D, Tong P, Xiao R C, Ling L S, Xi C Y, Pi L, Tian H F, Yang H X, Li J Q, Song W H, Zhu X B and Sun Y P 2016 *Phys. Rev. B* **94** 045131
- [25] Sörgel T, Nuss J, Wedig U, Kremer R K and Jansen M 2006 *Mater. Res. Bull.* **41** 987
- [26] Crewe A V, Wall J and Langmore J 1970 *Science* **168** 1338
- [27] Pennycook S J and Boatner L A 1988 *Nature* **336** 565
- [28] McMillan W 1976 *Phys. Rev. B* **14** 1496