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Hexagonal domainlike structure in $1T$-TaS_2

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X-ray analysis of the nearly commensurate phase of $1T$-TaS_2 confirms a domainlike structure predicted by a phenomenological charge-density-wave theory. The amplitudes of the atomic displacement waves induced by triple charge-density waves are analogous to those of an ideal domainlike structure consisting of 13 hexagonal domains. In each domain surrounded by discommensurations, 13 Ta atoms construct a star-shaped cluster and the clusters repeat regularly with the period of the $\sqrt{13}a$ structure.

$1T$-TaS_2 has the fundamental CdI_2-type structure with the hexagonal unit cell of $a_0 = 3.3650(2)$, $c_0 = 5.8967(4)$ Å, which consists of the stacking of two sulfur layers perpendicular to the c axis and one Ta layer between them. This material has two incommensurate charge-density-wave (CDW) phases above 200 K, one of which (appearing in the temperature range of 200–350 K) is called the nearly commensurate (NC) phase. Theoretical studies of CDW states of $1T$-TaS_2 were made by several people[1–3] and a domainlike structure stabilized by higher-order harmonics of CDW's was predicted in the NC phase.[3] This structure has been supported by x-ray photoelectron spectroscopy.[4,5] However, direct evidence has not yet been obtained. The domainlike CDW state induces atomic displacement waves which include higher-order harmonics, causing higer-order satellite reflections in diffraction patterns. Their x-ray intensities are exceptionally strong in the NC phase of $1T$-TaS_2. Therefore, it is expected that the domainlike structure is directly observable by x-ray analysis of this phase, applying a method of modulated structure analysis based on the multidimensional description.[6–8] This paper reports the result of analysis of the NC phase at room temperature using x-ray data collected by Brouwer,[9] which shows hexagonal domains separated by discommensurations.

Nakanishi and Shiba[3] predicted theoretically the appearance of the domainlike CDW state with 13 hexagonal domains surrounded by narrow discommensurations in the NC phase. In this case, the CDW's consist of the fundamental waves with the incommensurate wave vectors $\vec{q}^{(i)}$ $(i=1,2,3)$, $-\vec{q}^{(i)}+\vec{q}^{(j)}$ $(i,j=1,2;2,3;3,1)$, and their higher-order harmonics. The higher-order harmonics have wave vectors close to those of the corresponding fundamental waves in the reduced zone: $\vec{q}^{(i)} \pm \vec{k}^{(l)}$, $-\vec{q}^{(i)} + \vec{q}^{(j)} \pm k^{(l)}$ $(l=1,2,3)$ (see Fig. 1). Here $\vec{k}^{(1)}$ is

$$3(\vec{q}^{(1)} - \vec{q}_0^{(1)}) - (\vec{q}^{(2)} - \vec{q}_0^{(2)}) \ ;$$

$[\vec{k}^{(i)}$ $(i=2,3)$ are defined by cyclic replacement of indices, and the unit cell with $a = a_0$, $b = b_0$, $c = 3c_0$ is employed because the CDW triples the c axis. The wave vector $\vec{q}^{(1)}$ in the present case, $0.2446\vec{a}^* + 0.0684\vec{b}^*$, is very close to the wave vector of the $\sqrt{13}a$ structure, $\vec{q}_0^{(1)} = (3\vec{a}^* + \vec{b}^*)/13$. $[\vec{q}^{(i)}$ and $\vec{q}_0^{(i)}$ $(i=2,3)$ are obtained from $\vec{q}^{(1)}$ and $\vec{q}_0^{(1)}$ by 120° and 240° rotations around the c^* axis.] In the domainlike structure, the relative magnitudes of the harmonics take definite values to construct the hex-

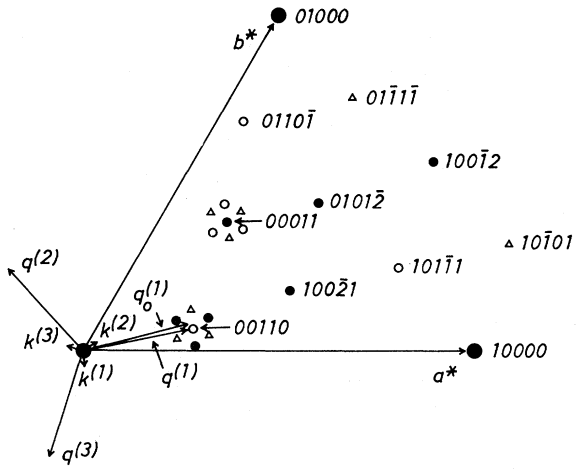

FIG. 1. Schematic view of the diffraction pattern in the nearly commensurate phase of $1T$-TaS_2. The large circles indicate the main reflections lying in a plane through $\vec{c}^* = 0$ and perpendicular to the c axis and small solid circles, the satellite reflections on the same plane and small open circles and triangles, the satellite reflections on planes through $\pm\vec{c}^*$. The main and fundamental satellite reflections are indexed. The 12 reflections around 00110 and 00011 satellites represent higher-order satellite reflections. The other higher-order satellites are abbreviated for simplicity. When the fundamental satellite at $\vec{Q}$ has the indices $h_1h_2h_3h_4h_5$, the higher-order satellites at $\vec{Q} \pm \vec{k}^{(i)}$ $(i=1,2,3)$ have indices $h_1 \mp 1, h_2, h_3 \mp 1, h_4 \pm 4, h_5 \mp 1$; $h_1 \pm 1, h_2 \mp 1, h_3 \mp 1$, $h_4 \mp 3, h_4 \pm 4$; $h_1, h_2 \pm 1, h_3 \mp 1, h_4 \mp 3, h_5 \mp 1$.

agonal domains. This CDW state will induce the displacement harmonics with the same relative magnitudes and definite directions. In the limit of $\vec{q}^{(i)} \to \vec{q}_0^{(i)}$ $(i=1,2,3)$ all the higher-order displacement harmonics have the amplitudes parallel to those of the corresponding fundamental waves. The relative magnitudes in this limiting case are listed in Table I, neglecting higher-order terms with small amplitudes, and the relative amplitudes of the displacement harmonics are shown in Fig. 2(b).

The x-ray diffraction experiments at room temperature[9] showed many strong satellite reflections at $\vec{K} \pm \vec{q}^{(i)}$ $(i=1,2,3)$, $\vec{K} \mp \vec{q}^{(i)} \pm \vec{q}^{(j)}$ $(i,j=1,2;2,3;3,1)$, which are called the fundamental satellite reflections for convenience, and weak higher-order satellites around them forming a two-dimensional sublattice spanned by the unit vectors of $\vec{k}^{(1)}$, $\vec{k}^{(2)}$, where $\vec{K}$ is a reciprocal lattice vector of the fundamental lattice with the unit vectors a, b, c. Almost all the observed higher-order satellite reflections were consistent with the result expected from the domainlike structure mentioned above: These relfections were explained by the strongest three harmonics in Table I and their counterparts forming the triple CDW's.

In order to confirm the domainlike structure, an x-ray analysis was performed based on the multidimensional description of modulated structures,[6-8] which is a unified method to analyze (commensurately or incommensurately) modulated structures.[8] In this method, five integers $h_1h_2h_3h_4h_5$ are assigned to a reflection with the diffraction vector $\vec{Q}$ by the use of

$$\vec{Q} = h_1\vec{a}^* + h_2\vec{b}^* + h_3\vec{c}^* + h_4\vec{q}^{(1)} - h_5\vec{q}^{(3)} \ .$$

Then the observed extinction rule for general reflections is given by $h_3 - h_4 + h_5 = 3n$. The other extinction rule due to the hyperscrew axis or hyperglide plane is not present. From the extinction rule and the fundamental structure, the five-dimensional space group $C_{1p6}^{P\bar{3}}(\alpha\beta 1/3)$ (Refs. 10 and 11) was deduced. The extinction rule is explained by the centering translation $(E10, 0, \frac{1}{3}, -\frac{1}{3}, \frac{1}{3})$ in this space group, where the translation vector in the five-dimensional space is written in unit vector components.[8] This space group allows only sine waves for the displacements of Ta atoms and both sine and cosine waves for S atoms.[8] The 63 Fourier amplitudes of the modulation waves for the displacements and the temperature factors with wave vectors shown in Table I were taken as variable parameters and were determined by use of the least-squares method which minimizes the squared weighted R factor. The least-squares program converged with a R factor of 0.10 for the 806 satellite reflections including 156 higher-order satellites.

TABLE I. Relative magnitudes of displacement harmonics in the ideal domainlike structure. The first column shows the wave vectors of the fundamental waves and the second column represents magnitudes of the harmonics relative to those of fundamental waves in the $\sqrt{13}a$ structure.

	$\vec{q}$	$\vec{q}-\vec{k}^{(1)}$	$\vec{q}+\vec{k}^{(3)}$
$\vec{q}=\vec{q}^{(1)}$	0.866	0.291	
$\vec{q}=\vec{q}^{(1)}-\vec{q}^{(3)}$	0.634	0.293	0.534

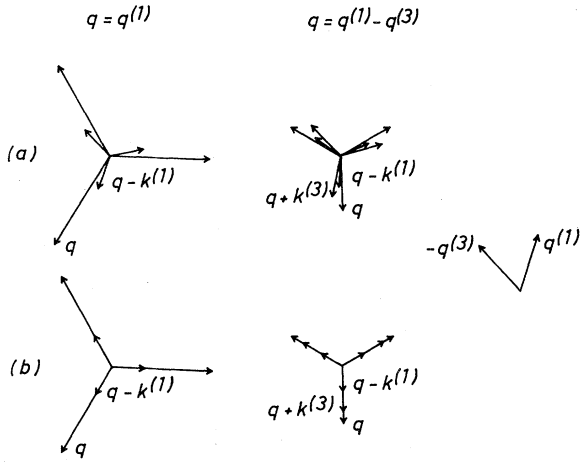

FIG. 2. Relative amplitudes of the displacement waves of Ta in the *ab* plane. (a) present work. (b) the ideal domainlike structure predicted by a phenomenological theory. The triple arrows with the same length making an angle of 120° with each other show the amplitudes of triple displacement waves with the wave vector indicated in the figure and its counterparts. The displacement of Ta at $\vec{x}$ is represented by $\sum_i \vec{u}_i \sin(\vec{Q}_i \cdot \vec{x})$, where $\vec{u}_i$ is the amplitude of the wave with the ith wave vector $\vec{Q}_i$ shown in the figure.

The result showed that the displacements of Ta atoms are larger than those of S atoms and lie in the *ab* plane. The relative amplitudes of the displacement waves are shown in Fig. 2(a), where the magnitude of the fundamental wave with the wave vector $\vec{q}^{(1)}$ is $0.0342a$. This shows that (i) the directions of the amplitudes of higher-order harmonics are nearly parallel to those of corresponding fundamental waves lying in the *ab* plane, (ii) the relative magnitudes between the fundamental waves and their higher-order harmonics are similar to those of the ideal domainlike structure predicted by the theory as is clear from the comparison with Fig. 2(b), and (iii) the amplitudes of the fundamental displacement waves with wave vector $\vec{q}$ are nearly antiparallel to $\vec{q}$, indicating that each wave is almost longitudinal as expected from the CDW state. Figure 3 shows the atomic arrangement in a Ta layer perpendicular to the

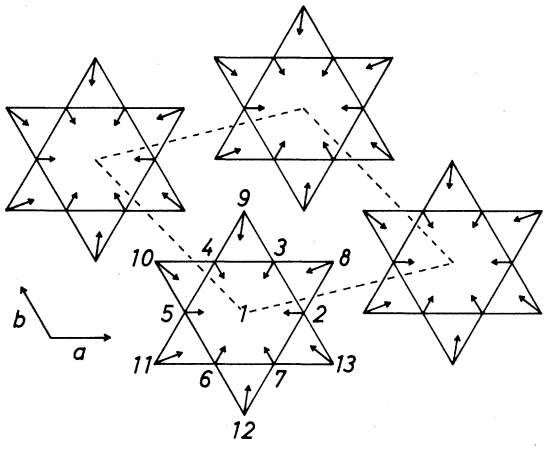

FIG. 3. Displacements of Ta atoms from their regular positions in a domain of the nearly commensurate phase. The arrows show the displacements of Ta atoms (×5) in the *ab* plane. Star-shaped clusters arranged with the period of the $\sqrt{13}a$ structure are linked by solid lines. The broken lines indicate the unit cell of the $\sqrt{13}a$ structure. The 13 atoms constructing a cluster are numbered.

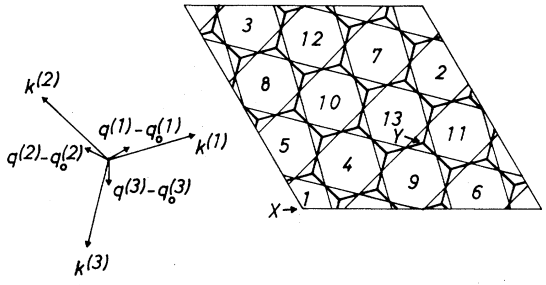

FIG. 4. Domainlike structure of the nearly commensurate phase. The hexagonal domain surrounded by thick lines corresponds to the Wigner-Seitz cell with the two-dimensional reciprocal lattice spanned by $\vec{k}^{(1)}$ and $\vec{k}^{(3)}$ and thin lines represent the place of the minimum amplitude of $\cos(\vec{k}^{(i)}\cdot\vec{x})$ $(i=1,2,3)$. In each hexagonal domain, 13 Ta atoms construct a star-shaped cluster and the clusters are arranged regularly with the period of $\sqrt{13}a$ structure as shown in Fig. 3. The 13 hexagonal domains in the figure have the same cluster arrangement but their cluster centers are located at different positions. The number shows the position of the cluster center, which means the cluster center is located at the position with the same number in Fig. 3.

c axis written by using the obtained amplitudes but assuming the commensurate waves vectors of the $\sqrt{13}a$ structure. This is quite similar to the result of Brouwer's analysis assuming the $\sqrt{13}a$ structure[9]: 13 Ta atoms construct a star-shaped cluster and the largest displacement occurs at the second-nearest Ta atoms of a cluster center. The difference between this $\sqrt{13}a$ structure and the real (incommensurate) structure is that the real structure consists of 13 domains. In the domainlike structure, when a domain has a structure shown in Fig. 3, the centers of the cluster in the remaining 12 domains are shifted to the 6 first-nearest neighbors and 6 second-nearest neighbors of the central Ta atoms as derived from the phases of the CDW's in 13 domains.[3] This is shown in Fig. 4, where the number in each domain represents that the center of the cluster is located at the Ta site with the same number in Fig. 3. The three-dimensional structure is constructed by stacking the same layer after shifting its origin by $\vec{r}_0$, where $\vec{r}_0$ is a lattice vector in the *ab* plane fulfilling

$$(\vec{q}^{(1)}-\vec{q}_0^{(1)})\cdot\vec{r}_0=4\pi/3\ ,$$

$$(\vec{q}^{(3)}-\vec{q}_0^{(3)})\cdot\vec{r}_0=4\pi/3(\mathrm{mod}2\pi)$$

(Ref. 3). (This is derived from the extinction rule.) This means that in the upper layer, the point X is shifted at the point Y in Fig. 4. The period $3c_0$ along the c axis results from this stacking. As shown above, the relative amplitudes between displacement harmonics are very close to those of the ideal domainlike structure. Therefore, we can consider that the NC phase consists of hexagonal domains surrounded by discommensurations and has star-shaped clusters of Ta atoms in each domain which are arranged regularly with the period of the $\sqrt{13}a$ structure. Rigorously speaking, the structure will deviate from that in Fig. 3 near the discommensuration. In the present case, the hexagonal domain is about 47 Å in a side, which includes about 44 clusters. Of these, about 23 clusters are located near the discommensurations: The domain boundary runs across these clusters. However, the detailed study near the discommensurations is out of the scope of the present study.

In conclusion, the domainlike structure with 13 hexagonal domains, which was predicted by the theory, is confirmed by the x-ray analysis based on the five-dimensional space group $C_{1p6}^{P\bar{3}}(\alpha\beta 1/3)$. The analysis suggests that the CDW's with the wave vectors $-\vec{q}^{(i)}+\vec{q}^{(j)}$ $(i,j=1,2;2,3;3,1)$ and their higher-order harmonics have large amplitudes and the nearly commensurate phase of 1T-TaS_2 largely deviates from the simple CDW state.

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