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X-Ray Study of Charge Density Wave Structure in 1T-TaS_2

Satoshi TANDA, Takashi SAMBONGI,
Toshiro TANI†* and Shoji TANAKA†

Department of Physics, Hokkaido University, Sapporo 060
†Department of Applied Physics, University of Tokyo, Tokyo 113

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Positions of satellite reflections in charge density wave (CDW) phases of 1T-TaS_2 were measured by X-ray diffraction. In the commensurate (C-) phase, stacking of CDW layers is considerably disordered. On heating from the C-phase there appears a new incommensurate triclinic structure up to 280 K, where anomalies have been observed in various properties.

The charge density wave (CDW) phase transition and properties of the ordered phases of the layered transition-metal dichalcogenides continue to be of experimental and theoretical interest. In particular, recent discoveries, in 2H–$TaSe_2$, of striped discommensurate state[1] and orthorhombic symmetry[2] in the commensurate(C)-CDW phase, have motivated re-examination of the CDW structure of other layered compounds such as 1T–TaS_2. The crystal structure of 1T–TaS_2 has one layer per unit cell with trigonal symmetry, and Ta atoms are octahedrally coordinated. It has been believed that 1T–TaS_2 exhibits successive CDW phase transitions from the incommensurate-phase to the nearly-commensurate (NC)-phase ($200\ \mathrm{K} < T < 350\ \mathrm{K}$) and from NC-phase to C-phase ($T < 200$ K) as temperature is lowered. Scruby *et al.*[3] performed electron and X-ray diffraction studies of 1T–TaS_2 and reported that the in-layer wave vector ($\boldsymbol{Q}_{//}$) of C-phase is $(3/13)\boldsymbol{a}^* + (1/13)\boldsymbol{b}^*$; $\boldsymbol{a}^*$ and $\boldsymbol{b}^*$ are in-layer reciprocal lattice vectors. They proposed that C-CDW stacking in 1T–TaS_2 is specified by a vector $\boldsymbol{a}+\boldsymbol{c}$, that is, the C-CDW layers are stacked along the c-axis with the origin of each layer shifted successively by $\boldsymbol{a}+\boldsymbol{c}$ or the equivalent. Furthermore, they suggested that the stacking is somewhat disordered. Fung *et al.*[4] performed the convergent beam electron diffraction experiment in 1T–TaS_2 and proposed that the stacking of the layer becomes disordered without any clear c-repeat in the C-phase. Since the stacking order in the C-phase has not been established, we report in this paper the wave vector of C-CDW in 1T–TaS_2 determined by X-ray diffraction.

Recently, many workers have clarified the presence of anomalies, near 280 K and only on heating, in various properties such as the thermal expansion,[5] the Seebeck coefficient and the resistivity[6] and the ion channeling.[7] Fung *et al.*[4] proposed that there appears a new structure with the period of $7c$ up to 250 K. We found that a new incommensurate triclinic phase (denoted as T-phase) exists between NC- and C-phases. The anomalies at 280 K correspond to the transition from the T-phase to the NC-phase.

Preparation of single crystals of 1T–TaS_2 used in this work is described in ref. 8. Samples with $\rho_{//}(T=4.5\ \mathrm{K}) = (2.0-5.5)\times 10^{-2}\ \Omega\mathrm{cm}$ were used. Crystals prepared by Inada, Ohnuki and Tanuma[9] were also used to examine whether the CDW stacking is sample dependent. The results described below are independent of samples supplied from different sources. Instruments used in this work have been described in ref. 10. Lattice constants a and c were determined from the positions of two Bragg reflections (1, 1, 0) and (1, 1, 1). The line widths (the half width at the half maximum) of the Bragg reflections were $0.006c^*$ along the c^*-axis, while the in-plane

* Present address: Materials Division, Electrotechnical Laboratory, Ibaraki 305.

widths were somewhat narrower.

[C-phase] Superlattice reflections along the lines $L_1=(10/13, 12/13, \zeta)$ and $L_2=(18/13, 19/13, \zeta)$ were scanned at 150 K. They correspond to the primary and the secondary satellites in the incommensurate phases, respectively. From the measured values of the rotation angle of the sample and the diffraction angle (2θ), the position of the superlattice reflection was determined. To check the reliability of instruments used, the in-plane wave vector $\boldsymbol{Q}_{//}$ in the C-phase was measured. Assuming $\varphi=13.90°$, where φ is the angle between $\boldsymbol{Q}=(3/13, 1/13, 0)$ and $\boldsymbol{a}^*$, the magnitude of $\boldsymbol{Q}_{//}$ was determined as $(0.277\pm 0.001)a^*$. This value should be compared with $0.27735a^*$ which satisfies the commensurability condition. Figure 1(a) shows the profiles of the superlattice reflections nearest to the Bragg reflections (1, 1, 0) and (1, 1, 1) along the line L_1 at 150 K. Two broad peaks (the half width at the half maximum of $0.1c^*$) centered at $(0.310\pm 0.003)c^*$ and $(0.825\pm 0.003)c^*$ were found. The peak intensity of the latter is several times larger than that of the former. Figure 2(a) shows the profile of the

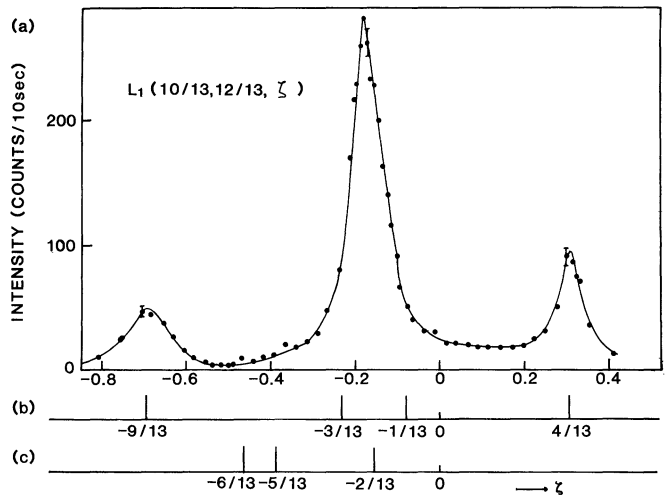

Fig. 1. (a) Scan along the line L_1 (10/13, 12/13, ζ) at 150 K. The peak at $\zeta\simeq -9/13$ is equivalent to that at $\zeta\simeq 4/13$. (b) Expected positions of the superlattice reflection of the ordered $a+c$ stacking. (c) ordered $2a+c$.

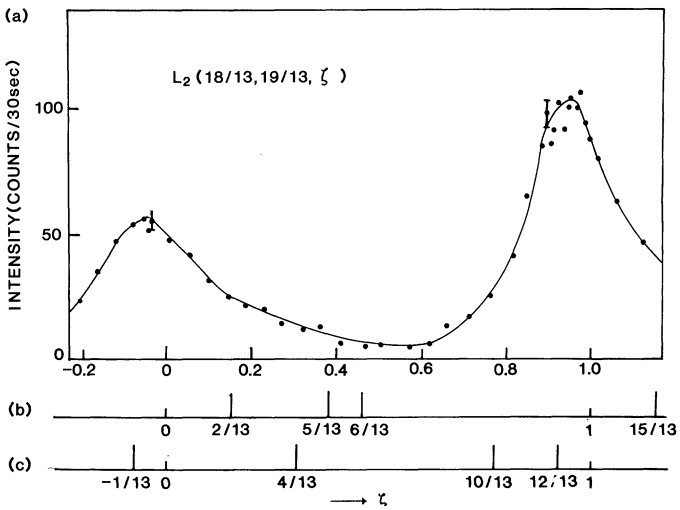

Fig. 2. (a) Scan along the line L_2 (18/13, 19/13, ζ) at 150 K. (b) ordered $a+c$ stacking. (c) $2a+c$ stacking.

superlattice reflection along the line L_2 at 150 K. A broad peak (width of $0.28c^*$) centered at $(0.020\pm0.003)c^*$ was found. Along both lines of L_1 and L_2, the observed intensity is larger than the background everywhere; there was no point where the intensity is effectively zero. These findings are quite reproducible; repeated measurements with different crystals gave essentially the same results. The broadness is neither due to the instrumental resolution nor to the crystal quality. We observed that the primary satellite in the NC-phase has the width of $0.006c^*$ centered at $(1/3)c^*$, which is the same of the widths of Bragg reflections and is slightly larger than the instrumental resolution of $0.001c^*$. The correlation length $\xi_\perp$ perpendicular to the layer is longer than 330 Å or about 56 layers ($c=5.93$ Å). Therefore the stacking in the NC-phase is well ordered with a $3c$ repeating period. Moreover, we found that the widths of the superlattice reflections in the C-phase were independent of the cooling rate. The superlattice reflection is intrinsically broad in the C-phase. A rough estimate of the correlation length in the C-phase along the line L_1, on the assumption that the superlattice reflection is Lorentzian-shaped, gives $\xi_\perp=20$ Å or about 3 layers. On the other hand, the in-layer correlation length remains long; widths of peaks on the line L_1 are slightly larger than the instrumental resolution, and are of the same order as that in the NC-phase. These results show that the stacking of the C-CDW in 1T–TaS_2 is disordered, while the superlattice is well ordered within the layer.

If the C-CDW layers are stacked successively with the origin shifted by $n\boldsymbol{a}+\boldsymbol{c}$ ($n=1, 2$) or the equivalent, three kinds of domains are expected to appear corresponding to the different direction of "$\boldsymbol{a}$", 120° apart from each other. Furthermore, there are two different kinds of domains; left-hand (α) and right-hand (β) ones. Reflections from α and β domains are easily distinguished. On the other hand, reflections from three 120° domains are observed by X-ray on the same lines L_1 and L_2. First, if the C-CDW stacking is ordered with the vector $\boldsymbol{a}+\boldsymbol{c}$, as proposed by Scruby *et al.*,[3] three spots should appear on the line L_1, at $\zeta=-1/13$, $-3/13$ and $-9/13$ (Fig. 1(b), and on the line L_2 at 2/13, 5/13, and 6/13 (Fig. 2(b)). Second, if the stacking is ordered with $2\boldsymbol{a}+\boldsymbol{c}$ as in 1T–$TaSe_2$, c^*-components of the superlattice reflections on the line L_1 are $-2/13$, $-5/13$, and $-6/13$ (Fig. 1(c)) and $-1/13$, $-3/13$, and 4/13 on the line L_2 (Fig. 2(c)). Third, if the stacking is specified by $\boldsymbol{c}$, c^*-components of all reflections must be zero. However, the present results cannot be explained by either stacking sequence. As the stacking under the commensurabilty condition has only three choices of $2\boldsymbol{a}+\boldsymbol{c}$, $\boldsymbol{a}+\boldsymbol{c}$ and $\boldsymbol{c}$, our experimental results show that the stacking in the C-CDW phase is not ordered $n\boldsymbol{a}+\boldsymbol{c}$ ($n=0, 1, 2$). Moreover if the stacking is $2\boldsymbol{a}+\boldsymbol{c}$ or $\boldsymbol{a}+\boldsymbol{c}$ but the direction of the shift "$n\boldsymbol{a}$" is not ordered, a broad (width of approximately $0.1c^*$) superlattice reflection at $(1/3)c^*$ should appear on the line L_1, as was observed by Moncton *et al.*[11] in 1T–$Ta_{1-x}Zr_xSe_2$.

From these results we conclude that the C-CDW stacking in 1T–TaS_2 is specified by the complex of $2\boldsymbol{a}+\boldsymbol{c}$, $\boldsymbol{a}+\boldsymbol{c}$ or $\boldsymbol{c}$ with disorder. [T-phase] On heating from the C-phase, a new sets of satellite reflections appear at about 220 K. These T-satellites disappear at 280 K, where anomalies have been observed in various properties. It is single-phased; between 220 K and 280 K neither C-superlattice reflections nor NC-satellites are observed. Positions of the first and the second order satellite reflections in the T-phase were measured at 225 K, after keeping the sample at 150 K (C-phase) for three hours. A set of three satellites is observed in the neighborhood of the line L_1, each corresponding to the three 120° domains. The widths of these satellites are small and comparable with those of Bragg reflections. The second order satellites are observed near the line L_2. From the positions of (1, 1, 0), (1, 1, 1) and of the first and the second satellites, in-plane wave vectors $\boldsymbol{Q}_{//i}$ ($i=1, 2, 3$) are determined. (The observed second order satellites are specified by $\boldsymbol{Q}_i-\boldsymbol{Q}_{i+1}$.) The wave vectors best fit to the experimental data are, of the α domain, $\boldsymbol{Q}_1=(0.230, 0.090, 0.439)$, $\boldsymbol{Q}_2=(0.084, -0.332, 0.242)$ and $\boldsymbol{Q}_3=(-0.314, 0.242, 0.319)$ at T=225 K. (see Fig. 3) The sequence $\boldsymbol{Q}_1$, $\boldsymbol{Q}_2$ and $\boldsymbol{Q}_3$ is designated as clock-wise in the α domain. In the T-phase the

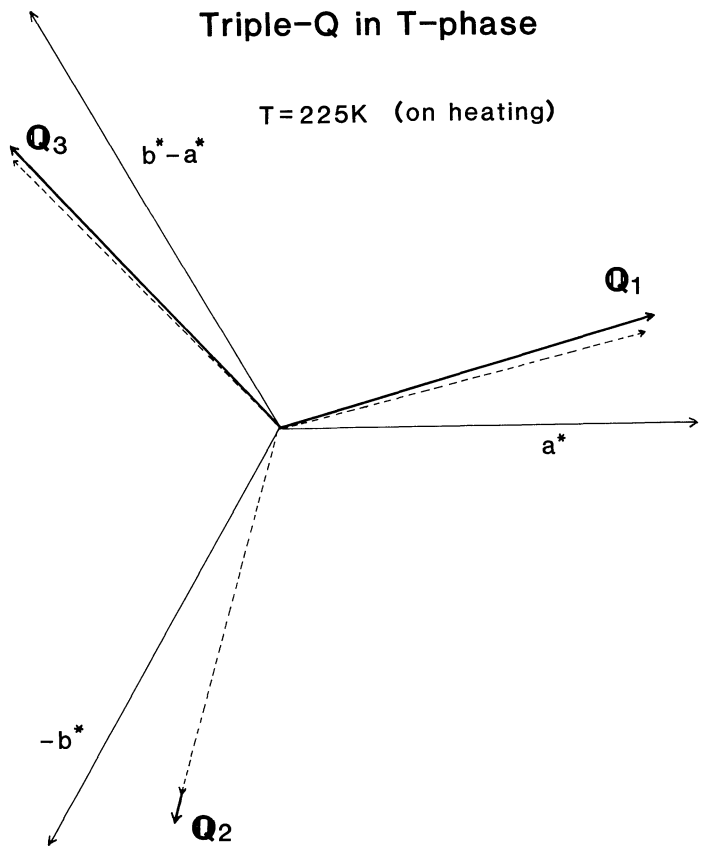

Fig. 3. Projection of the lattice modulation wave vectors in the new (T-) phase at 225 K. Broken lines; commensurate wave vectors.

trigonal symmetry is broken as in the striped phase of 2H–$TaSe_2$.[1] However, the T-phase is not striped, since $\delta_{//i}=Q_{//i}-Q_{//c}$ $(i=1, 2, 3)$ is not parallel to each other.

So far, it has been believed that T-phase can be observed only on heating. The foregoing data were obtained at 225 K on heating. However, we found that T-phase exists not only on heating but also on cooling; we observed T-satellites coexisting with NC-satellites between 250 K–200 K. Anomalies corresponding to the onset of the T-phase at 250 K, on cooling, have not been observed in transport and other properties as yet.

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