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X-ray-diffraction study of the periodic lattice distortion associated with a charge-density wave in $1T$-VSe$_2$

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The periodic lattice distortion associated with a charge-density wave in $1T$-VSe$_2$ was investigated by x-ray diffraction. The charge-density-wave transition was observed at 110 K. From the observation of the satellite reflections the wave vector of the periodic lattice distortion was determined to be $(0.250\pm0.003)a^* + (0.307\pm0.003)c^*$ below 85 K and $(0.250\pm0.003)a^* + (0.314\pm0.003)c^*$ above 85 K. The a^* component is temperature independent, while the c^* component shows an abrupt change in the vicinity of 85 K. Discussion is developed on the physical origin of the incommensurability of the c^* component.

INTRODUCTION

The charge-density-wave (CDW) phase transition in the layered transition-metal dichalcogenides MX_2 has been extensively studied,[1-3] where M is the group-Vb transition-metal and X is the chalcogen element. The crystal structure of MX_2 consists of the stacking of the layer in which the transition-metal atom sheet lies between the chalcogen atom sheets. In each sheet atoms are hexagonally close packed. The chemical bonding within the layer is covalent, while the bonding between layers is of a weak van der Waals type. In the layer the transition metal is surrounded by the chalcogen atoms in the octahedral or trigonal prismatic coordination. The layered transition-metal dichalcogenides can be prepared in a number of polytypes. These polytypes differ from each other in the stacking arrangement of the octahedral or trigonal prismatic coordination layer. The simplest polytype is the $1T$ structure which has one octahedral coordination layer per unit cell and trigonal symmetry. Designations such as $1T$ or $2H$ come from the number of the layers and from overall symmetry.

The study of the CDW phase transition in the $1T$ polytype has concentrated on the tantalum dichalcogenides such as $1T$-TaS$_2$ and $1T$-TaSe$_2$. The ($3d$) transition-metal dichalcogenide $1T$-VSe$_2$ has received less attention. This is due to the fact that preparation of the highly stoichiometric single crystal is very difficult. This material is always found to grow metal rich. The excess vanadium atoms are believed to exist in the van der Waals gap between the successive layers and to possess the localized magnetic moment which shows up as a Curie tail in the low-temperature magnetic susceptibility.[4-7] Therefore, the measurement of the magnetic susceptibility can be used to estimate the concentration of the excess vanadium atoms.

The CDW superlattice in $1T$-VSe$_2$ is very different from those observed in $1T$-TaS$_2$ and $1T$-TaSe$_2$ due to its resemblance to the superlattice observed in the $2H$ polytype. Williams first performed an electron diffraction measurement of the CDW superlattice in $1T$-VSe$_2$.[8] At 140 K he found the superlattice to be incommensurate along the a axis by about 2%, while it is commensurate along the c axis, $c'=3c$, and observed the superlattice which is $a'=4a$ and $c'=3c$ at 40 K. Tatlock also studied the CDW superlattice in $1T$-VSe$_2$ by electron diffraction.[9] His result showed that the superlattice is 6% incommensurate at 90 K and commensurate within the experimental accuracy at 72 K along the a axis. After Tatlock's study, van Landuyt *et al.* performed an electron diffraction study of the same material.[10] Their results are complicated and very different from those found by Williams and Tatlock. They observed that at least three phase transitions take place between room temperature and liquid-N$_2$ temperature.

Recently, a convergent-beam electron diffraction study[11] and two independent x-ray diffraction studies[12,13] were performed with the use of high-quality single crystals. These experiments revealed the very interesting fact that the CDW superlattice in $1T$-VSe$_2$ is commensurate within the layer, while it is incommensurate along the *c* axis, which is the direction perpendicular to the layer. In this paper we report the detailed results of our x-ray diffraction study and discuss the results, especially the physical origin of the incommensurate periodic lattice distortion (PLD) perpendicular to the layer.

EXPERIMENT

Single crystals of $1T$-VSe$_2$ were prepared by the chemical transport method with iodine as the transport agent. As the starting materials 99.95% pure vanadium wire and 99.999% selenium shot were used. Stoichiometric content was reacted in an evacuated quartz tube with excess selenium of 2 mg/cm^3. The growth temperature was 620 °C.

The temperature dependence of the electrical resistance was measured in a small piece cut out of the single crystal used in x-ray diffraction measurement with an ordinary dc four-probe method. The sharp kink corresponding to the CDW phase transition was observed at 110 K. The residual resistivity ratio was 18. By x-ray diffraction measurement at room temperature with a four-circle diffractmeter, the lattice constants were determined to be $a = 3.356$ Å and $c = 6.104$ Å.

We could not estimate the amount of the excess vanadium atoms existing in the van der Waals gap of our crystals because we could not measure magnetic susceptibility. However, DiSalvo and Waszczak investigated the relation between the CDW transition temperature and the excess vanadium-atom concentration in their study of magnetic susceptibility.[7] They showed that the CDW transition temperature decreases from 111 ± 1 K at a rate of 13 ± 3 K/at.% and that the excess vanadium-atom concentration of the crystal that shows the highest CDW transition temperature is 0.019%. From their results and the CDW transition temperature of our crystals, we concluded that the amount of the excess vanadium atom in our crystals is less than 0.2% in the worst case, and in the best case, it is the same as that of the best crystal prepared by DiSalvo and Waszczak.

Before the measurement at low temperature the a^* axis of the crystal was determined with the use of a four-circle diffractmeter, and then the crystal was attached to the sample holder. The crystal was rotated about the vertical axis and tilted about two horizontal axes.[14] The sample temperature was measured by a silicon diode thermometer inserted into the sample holder. The temperature of the measurement ranged from 10 to 140 K, and the temperature stability was maintained within ± 0.1 K.

The studied reciprocal-lattice region was a square represented by $(\xi,0,\zeta)$ with $1.5 < \xi < 2.5$ and $0.0 < \zeta < 1.0$, where ξ is the coordinate along the a^* axis and ζ is the coordinate along the c^* axis. We measured the wave-vector components of the PLD in the following way. By finding two Bragg reflections (200) and (201), the a^*c^* plane was made to coincide with the reflection plane. Then the crystal was rotated about the vertical axis to find the satellite reflections. The values of the wave-vector components were calculated from the rotation angle of the sample and from the diffraction angle. In the peak searching of the satellite reflection the crystal was rotated step by step by 0.01°. The profiles of the satellite reflection along the a^* and c^* axes were measured by rotating the crystal step by step by 0.05°.

Two single crystals in the same group were studied. The larger one was examined in detail. The size of this crystal is about $5 \times 5 \times 0.05$ mm^3. In the reciprocal-lattice region mentioned above two satellite reflections were observed. One is in the vicinity of the point (1.75,0,0.30) and the other is in the vicinity of the point (2.25,0,0.70). No satellite reflection was observed around the points (1.75,0,0.70) and (2.25,0,0.30). Temperature dependence of the wave-vector components and the halfwidth at half maximum (HWHM) were measured only on a satellite reflection observed in the vicinity of the point (2.25,0,0.70).

RESULTS

Figures 1(a) and 1(b) show the profiles of a satellite reflection measured at 13 K along the a^* axis and c^* axis, respectively. Figure 2 shows the temperature dependence of the a^* and c^* components of the reduced wave vector of PLD, where the halfwidth at half maximum was adopted as the error limit. The a^* component is temperature independent and its value is $0.250a^*$, that is, it is commensurate. This result is consistent with the results of the convergent-beam electron diffraction study by Fung *et al.*[11] and with the x-ray diffraction study by Moncton *et al.*[12] The c^* component is incommensurate over the measured temperature range. This result is the same as the above-mentioned previous studies. However, we discovered an abrupt change in the c^* component in

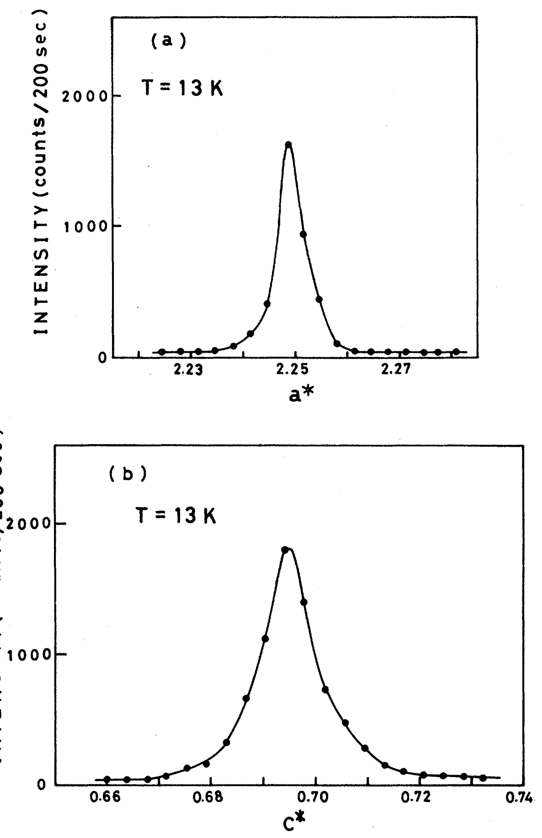

FIG. 1. Profiles of a satellite reflection (a) along the a^* axis and (b) along the c^* axis.

the vicinity of 85 K. Figures 3(a) and 3(b) represent the temperature dependence of HWHM of a satellite reflection along the a^* and c^* axes, respectively, where the dashed line is the HWHM of the (201) Bragg reflection. The HWHM along the a^* axis is nearly equal to that of the Bragg reflection. This result means that a long-range order over the whole crystal occurs within the layer. On the other hand, the correlation length along the c^* axis is shorter than that within the layer. With a Lorentzian resolution correction, the inverse of HWHM yields a correlation length of less than 400 Å along the c^* aixs. No detectable change in HWHM was observed in the vicinity of 85 K.

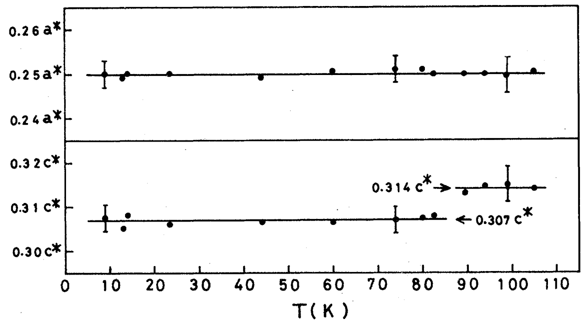

FIG. 2. Temperature dependence of the reduced wave vector of PLD. The upper part is the a^* component and the lower part the c^* component.

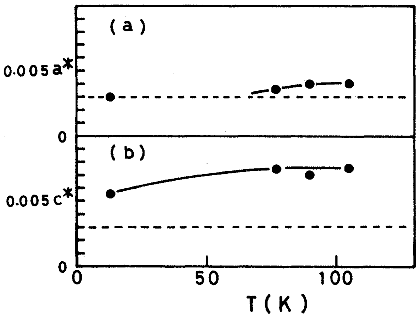

FIG. 3. Temperature dependence of the halfwidth at half maximum of a satellite reflection (a) along the a^* axis and (b) along the c^* axis. The dashed line is the halfwidth at half maximum of the (201) Bragg reflection.

DISCUSSION

The interlayer ordering of CDW in the layered transition-metal dichalcogenides[13] did not attract much attention. Wilson *et al.* explained the interlayer ordering in the incommensurate phase of 1*T*-TaSe$_2$ by the Coulomb interaction between CDW in the adjacent layers.[3] The triple-*q* CDW state forms the triangular charge-density lattice. The Coulomb interaction energy is minimized in Wilson's model. In a similar respect, Wilson predicted the commensurate $c'=4c$ for 1*T*-VSe$_2$.[15] However, this is not in agreement with what is observed in the recent diffraction studies.

Despite the understanding of the nesting wave vector of the Fermi surface in layered V*b* transition-metal dichalcogenides, the $k_z(c^*)$ dependence of the Fermi surface has been neglected. However, Woolley and Wexler showed that the variation of the Fermi surface along the k_z direction is essential for a proper understanding of the nesting wave vector in 1*T*-VSe$_2$.[16] The Fermi surface of 1*T*-VSe$_2$ constructed from their band calculation has a great curvature along the k_z direction, which may be one of the explanations of the incommensurate c^* component, namely, the nesting wave vector of 1*T*-VSe$_2$ has an incommensurate c^* component. Recently, Myron also calculated the band structure of $1T$-VSe_2 with the use of the augmented-plane-wave (APW) method.[17] The great curvature of the Fermi surface along the k_z direction is seen in his calculation too. The reduced wave vector of PLD observed in this paper is $0.250a^* + 0.314c^*$ above 85 K and $0.250a^* + 0.307c^*$ below 85 K. The nesting vector obtained from the band calculation by Woolley and Wexler is $0.30a^* + 0.33c^*$. The agreement between the theoretical and experimental results is not necessarily good. In order to verify that the incommensurate c^* component of PLD has the physical origin in the nesting vector of the Fermi surface having the great curvature along the k_z direction, the measurement of the wave vector of PLD associated with the CDW phase transition in the mixed crystal such as $1T$-$V_{1-x}Ti_xSe_2$ is necessary.

Wilson's model, mentioned above, takes into consideration only the Coulomb interaction between CDW in the adjacent layers. By taking into consideration the interaction between layers farther apart, the incommensurate c^* component may be explained.

Next, we consider the experimental result that the correlation length along the direction perpendicular to the layer is shorter than that within the layer. Our speculation is the following. The CDW state that is commensurate within the layer and incommensurate along the c^* axis loses the commensurability energy gain due to the matching between the peak of the charge density and the cation site. If the lattice distortion pattern in one layer maximizes the commensurability energy gain, no other layer can form the lattice distortion pattern with the maximum commensurability energy gain. Thus the correlation length along the c^* axis is shorter than that within the layer, because the short correlation length along the c^* axis reduces the loss of the commensurability energy gain.

The c^* component of the wave vector shows an abrupt change in the vicinity of 85 K. This change seems to correspond to the point-symmetry reduction found in the convergent-beam electron diffraction study. However, this change was not observed in the x-ray diffraction study by DiSalvo *et al.*[18] Their result is that the reduced wave vector of PLD is temperature independent and its value is $0.25a^* + 0.305c^*$. This descrepancy may depend on the difference in the sample quality.

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