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Microstructure in the incommensurate and the commensurate charge-density-wave states of $2H$-$TaSe_2$: A direct observation by electron microscopy

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We have obtained images of the microstructure in the incommensurate and the commensurate charge-density-wave states of $2H$-$TaSe_2$ with the use of superlattice dark-field electron microscopy. Large orthorhombic domains are observed in the commensurate phase. With warming to higher temperatures the incommensurate stripe phase appears. The incommensurate phase on a cooling cycle, however, is found to be more complicated. Instead of the hexagonal symmetry indicated by early x-ray diffraction results, we find that the charge-density waves actually adopt orthorhombic symmetry on a microscopic scale. The thermal evolution and detailed configuration of domains and discommensurations in these phases are studied in detail. It is found that charge-density-wave dislocations play the most prominent role in various charge-density states of $2H$-$TaSe_2$.

I. INTRODUCTION

Among the many polytypes of the transition-metal-dichalcogenide layer crystals which exhibit charge-density-wave (CDW) phase transitions, the $2H$ polytype $TaSe_2$ has been studied most thoroughly both experimentally and theoretically. This is due to the many fascinating CDW states exhibited by this remarkable material. Furthermore, $2H$-$TaSe_2$ exhibits a large thermal hysteresis effect[1]: The commensurate-incommensurate (CI) transition temperature occurs at 84 K on cooling and 92 K on warming. Between 92 and 112 K on warming a stripe incommensurate phase occurs. Regions of the stripe phase are demarcated by one of the three CDW wave vectors which remains commensurate. The other two CDW wave vectors, however, become incommensurate. Within a given region, parallel commensurate stripes separated by narrow discommensurations (DC's) are expected. This picture of the stripe phase has recently been confirmed most directly by the authors[2] using dark-field electron microscopy in which images are obtained from the superlattice reflections produced by the CDW phase transition.

On cooling, x-ray diffraction studies show that the CDW, although incommensurate, retains hexagonal symmetry and it is generally believed that a honeycomb array of DC's can best describe this incommensurate phase.[3,4] It has been pointed out[5] that for the same density of parallel DC lines, DC's are twice as far apart in the honeycomb structure leading to a much weaker repulsive interaction between them. However, it is necessary to introduce crossing points in this case. If the crossing energy is negative, the honeycomb structure is always favored and the incommensurate-commensurate (IC) transition is first order. If the crossing energy is positive, the stripe structure is favored and the transition to the commensurate phase is continuous. A numerical study by Nakanishi and Shiba[6] using a Landau expansion with real coefficients indicates that the honeycomb array of DC's is favored. High resolution x-ray diffraction results, however, reveal a continuous CI phase transition. More recently Fung *et al.*[7] have shown by convergent-beam electron diffraction that the CDW in the commensurate phase does not have hexagonal symmetry but locally adopts an orthorhombic symmetry instead. The appearance of the orthorhombic commensurate phase even further complicates the issue.

In this paper, which represents an extension of our earlier work,[2] we present direct observations of the domains and DC's microstructures in the commensurate and the incommensurate CDW states of $2H$-$TaSe_2$. Observations are made for both the warming and the cooling cycles. Our observations substantiate the results obtained by Fung *et al.*[7] Moreover, we have examined the microstructures and the thermal evolution of all the different CDW phases in considerably more detail. In the commensurate phase, large orthorhombic domains are observed. On warming through the commensurate-incommensurate stripe phase transition at ~ 92 K, these large orthorhombic domains are seen to break up into a set of stripes through the nucleation of CDW dislocations. On cooling, the incommensurate phase is found to have orthorhombic symmetry on a microscopic scale although hexagonal symmetry is retained on a larger scale.

This paper is organized as follows: Experimental details are described in Sec. II. The domain and DC structures in the commensurate phase are discussed in Sec. III. In Sec. IV details of the stripe phase and its evolution from the commensurate phase are presented. The question of domain and DC's structures and the symmetry of the incommensurate phase on cooling can be found in Sec. V. Finally, conclusions and some remarks are made in Sec. VI.

II. EXPERIMENTAL DETAILS

Thin-film samples ($\lesssim 1000$-Å thick) were prepared for transmission electron microscopy (TEM) by cleavage of single-crystalline $2H$-$TaSe_2$ and were examined in a JEOL 200-kV electron microscope equipped with a single-tilt liquid-helium cold stage. The stage provides temperature control in the range 16–400 K with a stability ~ 0.1 K over a period of ~ 5 min. The actual temperature of the electron-beam-irradiated area is found to be no more than 3 K above the stage reading, as judged by the appearance and disappearance of the several different CDW phase transitions known from earlier x-ray studies.[1] The spatial resolution of the cold stage is better than 50 Å, being limited mainly by mechanical vibration transmitted through the coupling between the He transfer tube and the electron microscope. Dark-field images were formed with the superlattice reflections produced by the CDW phase transitions. Images of lattice distortions associated with the three CDW wave vectors were obtained by placing apertures around the superlattice spots in the desired direction, which we shall refer to as the "imaging direction." It should be noted that images shown in this paper can only be obtained from the CDW superlattice reflections and therefore they are conclusively associated with the CDW phase transitions.

III. COMMENSURATE PHASE

Electron micrographs taken from any CDW superlattice reflection in the commensurate phase reveal many large (~ 1 μm in size) dark domains separated by sharp boundaries. Imaging along the other two remaining CDW q directions shows that the dark domains of one type or another cover the entire area. This is shown in Fig. 1. It is noted from Fig. 1 that each dark domain appears dark for only one particular q and appears bright for the other two q's. If we assume the origin of the contrast seen in Fig. 1 is a result of local variation in diffracted amplitude (i.e., diffraction contrast), then Fig. 1 is indicative of broken hexagonal symmetry in the commensurate phase. Fung *et al.*,[7] using convergent-beam electron diffraction, have shown that the dark domains appear to have orthorhombic symmetry instead of the hexagonal symmetry previously suggested by the x-ray diffraction studies. In detail they found the following: For a given domain the convergent-beam pattern indicates that the $\{\frac{4}{3}00\}$ superlattice reflection along one CDW q direction (i.e., the orthorhombic distortion direction) is weaker than the same order reflections along the other two CDW q directions. This observation would explain why a particular dark domain appears dark for only one imaging direction.

The convergent-beam electron diffraction results, however, raise a serious problem that is difficult to understand. Since only $\{\frac{4}{3}00\}$ CDW reflections show the intensity asymmetry we might expect that the orthorhombic domains would be visible only if $\{\frac{4}{3}00\}$ CDW reflections were used for imaging and no contrast would be expected from other CDW reflections. In fact, the same domain pattern can be obtained with many different CDW reflections such as $\{n/3\,k\,0\}$ with n and k which are integers (as in Fig. 1). This observation appears to be at odds with the convergent-beam electron diffraction results. The reason why only $\{\frac{4}{3}00\}$ and not all $\{n/3\,0\,0\}$ CDW reflections are asymmetric in intensity in the convergent-beam pattern is not understood at present. Since the diffraction condition in the convergent-beam case is highly dynamical, detailed calculations by dynamical diffraction theory would be of great value to the understanding of the convergent-beam electron diffraction results.

Another unusual phenomenon which we observed sometimes is the contrast reversal of the orthorhombic domain patterns with the same imaging direction. An example of this is shown in Fig. 1(d) which is obtained from a different CDW reflection spot [as compared to Fig. 1(a)] although the imaging direction remains the same. It is clear

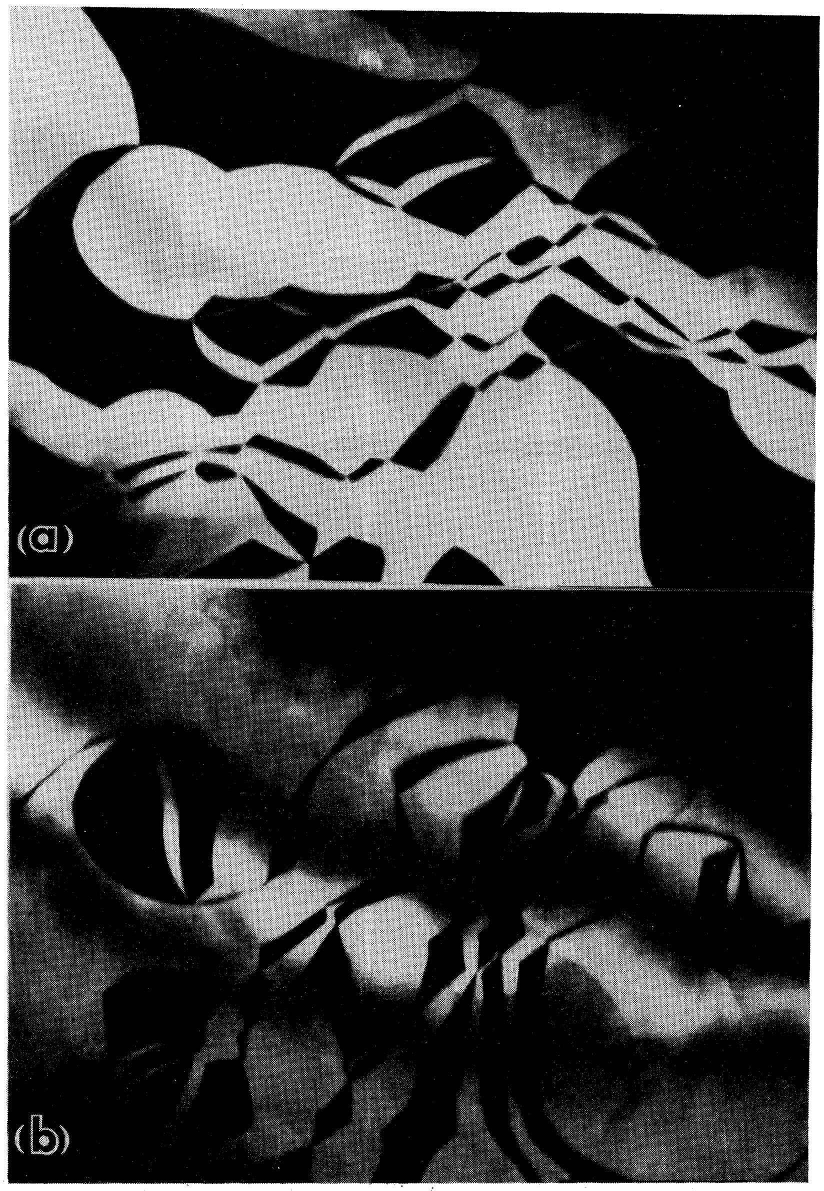

FIG. 1. (a)—(c) Images taken at 33 K in the commensurate phase along the three direction of the CDW wave vectors q_1, q_2, and q_3; (d) shows the image of the same areas as (a)—(c) taken with different superlattice reflection spot although the imaging direction remains the same as (a). The contrast is reversed in this case as compared to (a). (e) Line diagram showing the combined domain patterns of (a)—(c).

from Figs. 1(a) and 1(d) that the contrast is simply reversed. Contrast reversal can also be made to occur using the same CDW q spot under some circumstances by a slight tilt of the sample ($\sim 0.2°$). Whether this is an intrinsic effect of the domain contrast or is an extrinsic effect due to multiple scattering of electrons is not clear at the moment, although it seems somewhat unlikely that multiple scattering would give rise to the level of contrast seen in Fig. 1(d).

The appearance of orthorhombic symmetry rather than hexagonal symmetry in the commensurate phase has been considered recently in a number of theoretical studies.[8–10] It is found that orthorhombic symmetry occurs if the origin of the CDW, i.e., the position around which the CDW states have trigonal point symmetry within a layer, is at a Se site (or even on the line joining Se sites)

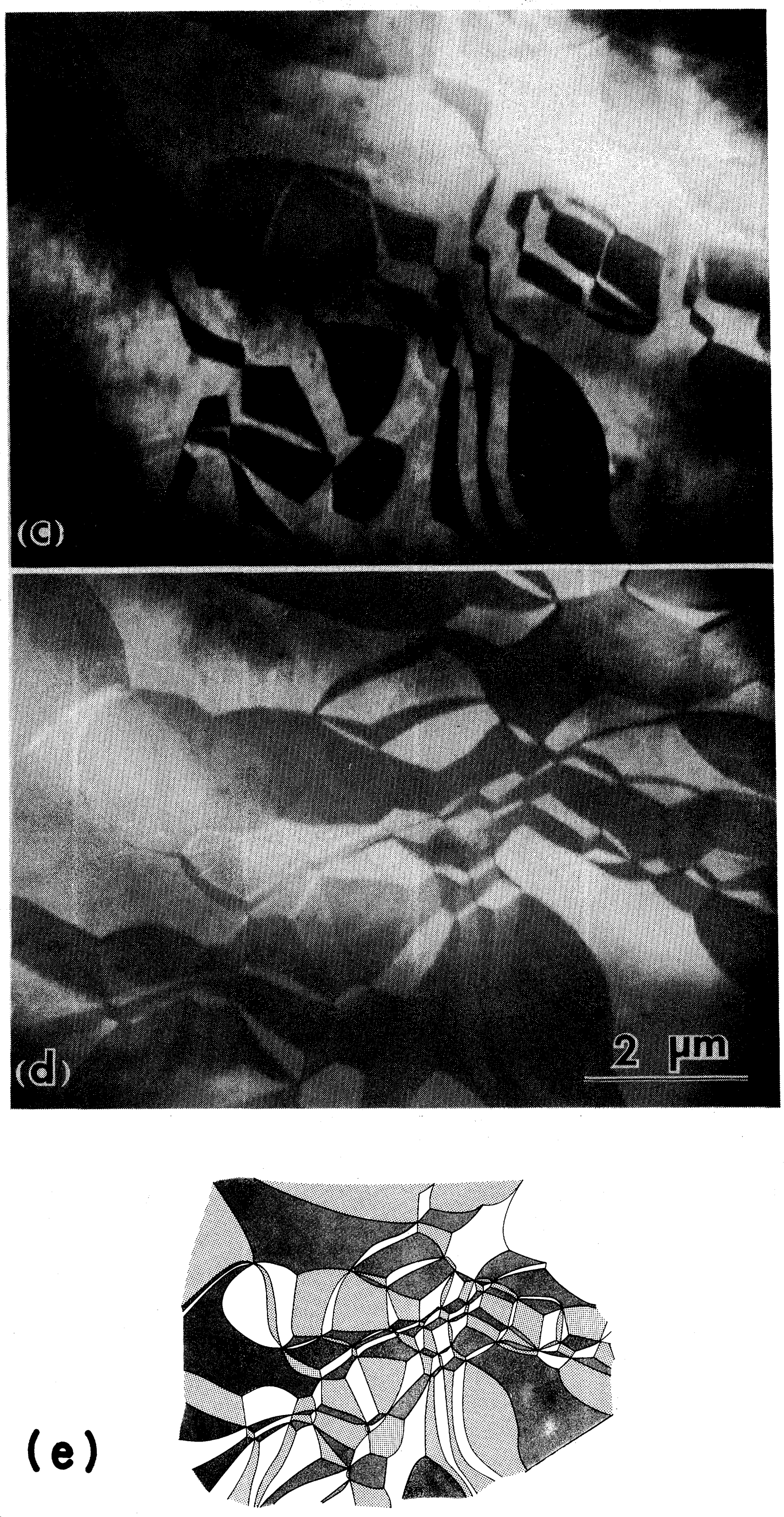

FIG. 1. (*Continued.*)

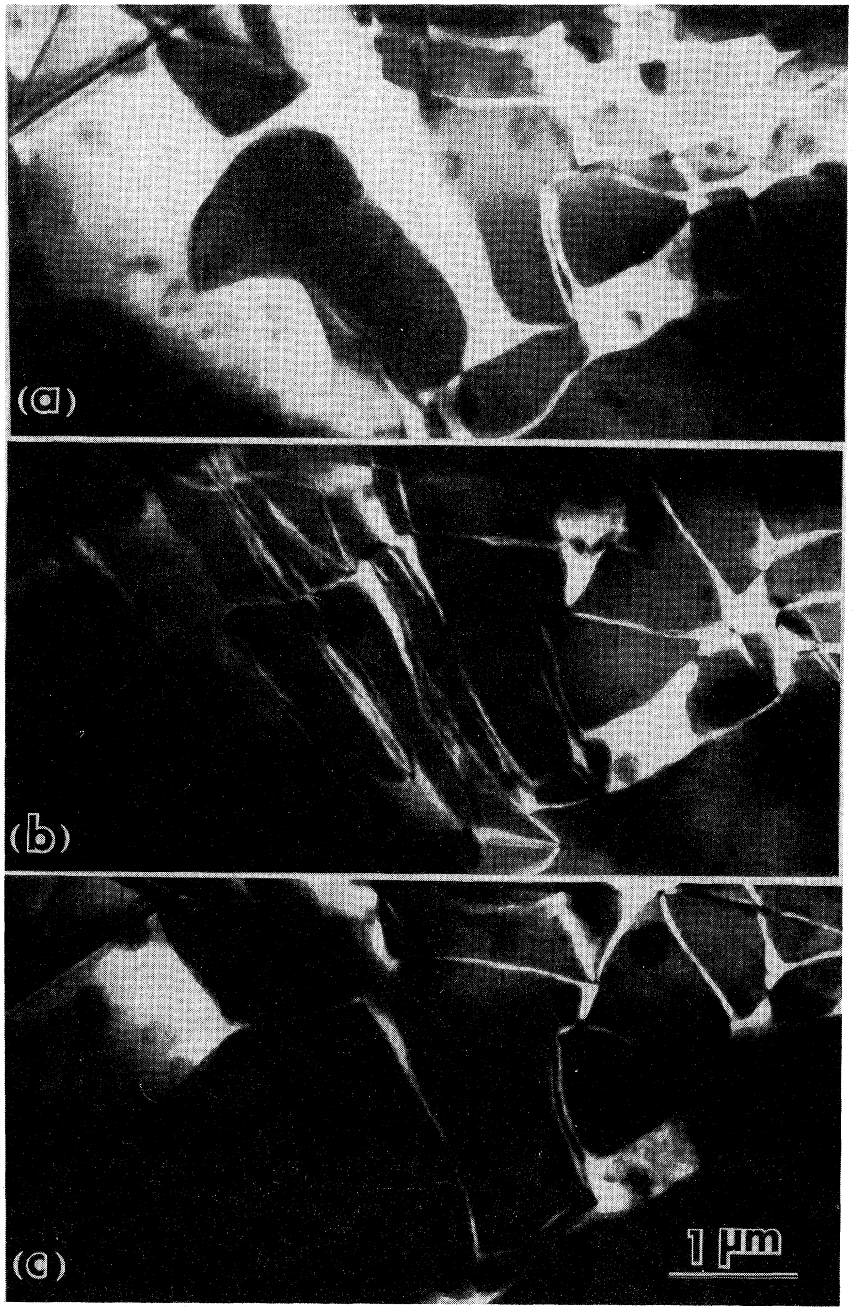

FIG. 2. Indication of the weak pinning nature of the domains in the commensurate phase. (a) shows a domain pattern obtained at 80 K on warming from 30 K. (b) shows the same area after being heated up to ~ 100 K and then cooled down to the same temperature of 80 K. (c) is obtained from (b) after being cooled down to 50 K and then warmed up to 80 K.

rather than at a Ta site which would have given an hexagonal symmetry. The orthorhombic distortion is favored when there is a competition between the terms in the Landau free energy arising from the overlap of the three CDW's and from the commensurability force.

The size and arrangement of the orthorhombic domains appear to be dependent upon the local strains in the sample. In areas which are highly strained we find domain size is usually smaller and there can be a preponderance of the domains with specific orthorhombic distortion.

Pinning of CDW's, which is of considerable interest, has been treated in numerous theoretical studies.[11–13] It is generally believed that impurities and crystalline defects are the pinning centers for the CDW's. In our study, pinning of the orthorhombic domains was found to be weak as shown in Fig. 2. Figure 2(a) shows a domain pattern taken at 80 K. (No significant changes of the domain pattern between 20–80 K can be seen on warming.) Figure 2(b) shows the same area after the sample has been heated up to 95 K (already in the stripe phase regime) and then cooled down again to 80 K. In Fig. 2(b) many stripes are still present. These stripes combine into bigger domains upon further cooling. Figure 2(c) is obtained after cooling from the condition as shown in Fig. 2(b) down to 50 K and then warming up again to 80 K. The domain patterns are clearly different indicating weak pinning of the CDW. This observation is, however, contradictory to the observation of Fung *et al.*[7] in which strong pinning was observed. This may be due to a difference in the impurity levels or strains in the samples.

Boundaries of the orthorhombic domains seem to be quite mobile in the temperature region around 80–90 K. Images obtained in this temperature range usually do not show very sharp domain boundaries due to the movement of the boundaries during the exposure of an image which typically takes $\lesssim 10$ sec.

IV. INCOMMENSURATE PHASE ON WARMING

A. Stripe phase (92 K $\leq T <$ 112 K)

1. Evaluation of the stripe phase

As we have already shown, the commensurate CDW states consists of many orthorhombic domains separated by sharp boundaries. The evolution of the incommensurate stripe phase from the commensurate orthorhombic phase is a very fascinating phenomenon. As the temperature approaches the commensurate stripe phase transition around 92 K, stripes are found to nucleate within the orthorhombic domains. A pictorial sequence depicting the evolution of the stripe phase is shown in Fig. 3. As we noted earlier, domain boundaries become mobile in the temperature range 80–90 K, thus the boundaries in Figs. 3(a) and 3(b) appear not as sharp as those shown in Fig. 1. It can be seen from Figs. 3(a) and 3(b) that when the stripes are nucleated within the orthorhombic domain, they always exhibit a characteristic contrast of dark (D) and bright (B) stripes as with nodes at which three dark stripes join together, $B \mid D \mid B \mid D \mid B$. Each dark or bright stripe is a couple of hundred Å in width. After the stripes are nucleated, the next obvious event is some movement of the nodes, which occurs within a few seconds of their nucleation. The node at which three black stripes join together is called a CDW dislocation.[2] The fact that it *always* requires three dark stripes to form such a CDW dislocation is evident from Fig. 3 and other micrographs which we will show in later sections. This suggests that the phase slip between each dark regions is $2\pi/3$. The phase relationship between a dark stripe and a white stripe will become clear later in the next section. As the temperature increases, the remaining unstriped orthorhombic regions become unstable with respect to further nucleation of stripes and the stripe density increases further, as shown in Figs. 3(c) and 3(d). The average spacing of the stripes is about ~450 Å at 95 K and ~350 Å at 100 K. This result agrees very well with the spacing L deduced from the x-ray diffraction measurement[1] of incommensurability δ ($L = 2\pi/3\delta$). The nucleation of stripes appears to be first order and visible crystal imperfections such as dislocations do not seem to be the origin of the nucleation process. There appears to be no visible reason why the nucleation process takes place at a particular point.

It is noted from Fig. 3 that orthorhombic domains with a given orthorhombic distortion direction can eventually give rise to two different regions with stripes running at an angle $\pi/3$ to the origin distortion direction and making an angle $2\pi/3$ between them. What is even more interesting is that domains with different orthorhombic distortion directions [i.e., the dark and the bright domains as shown in Fig. 3(a)] can nucleate stripes running in the same direction [Fig. 3(b)]. This implies that a particular orthorhombic distortion direction does not give rise to any preferred orientation for the stripes. However, we find that, in a given area, there is a preponderance of stripes running along a particular direction. We believe this is affected by the local strains in the sample.[14]

The width of the dark and the bright stripes appear to decrease somewhat at the higher temperatures [Figs. 3(c) and 3(d)]. It becomes obvious, after close examination of the microstructure of the stripes (e.g., by following a stripe from its beginning to its end or where it loses its trace) that the detailed configuration of the stripe is rather complex. For example, a stripe in one region can bend through an angle of $2\pi/3$ and end up in a neighboring region with different stripe orientation.

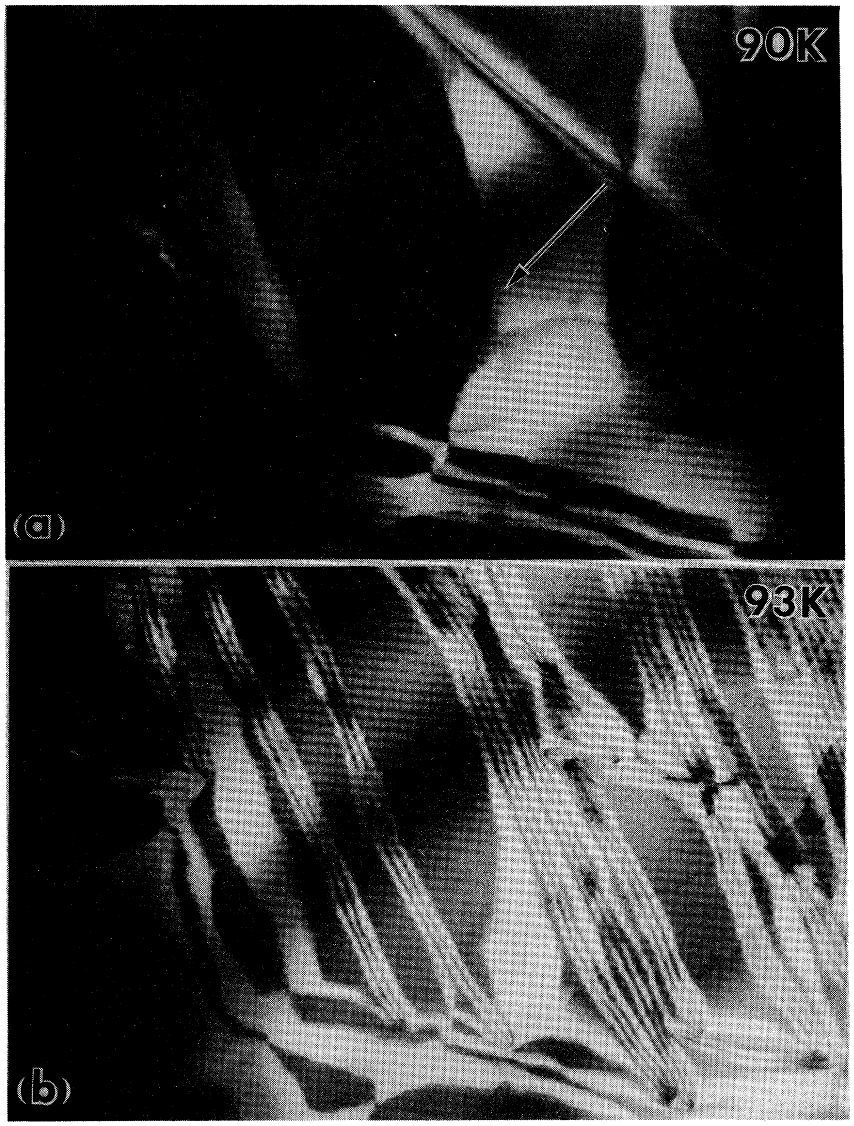

FIG. 3. Evolution of the stripe phase from the orthorhombic commensurate phase. Imaging direction is also indicated by the arrow.

In the following, we will discuss the nature and the characteristics of the stripes.

2. Properties and configuration of stripes

We have just described the nucleation and the evolution of the stripe phase from the commensurate orthorhombic phase. One question which remains to be addressed is the actual nature of the dark and bright stripes and why they appear as dark or bright. We have already explained why some orthorhombic domains appear dark and other domains appear bright with a particular imaging CDW q direction. Since the stripes evolve from the orthorhombic domains, it is natural to consider that the dark and the bright stripes in the stripe phase may also have orthorhombic symmetry (i.e., they are commensurate domains) with different orthorhombic distortion directions. If this is the case, boundaries between dark and the bright stripes, as opposed to the stripes themselves, would be the DC's as discussed in many theoretical papers.[15] This picture of the stripe phase was proposed by Fung *et al.*[7] In Fig. 4 we show that this indeed is the correct picture for the stripe phase. We have already demonstrated that each orthorhombic domain appears dark along only one particular CDW q-imaging direction. A reversal of contrast would then be expected when the imag-

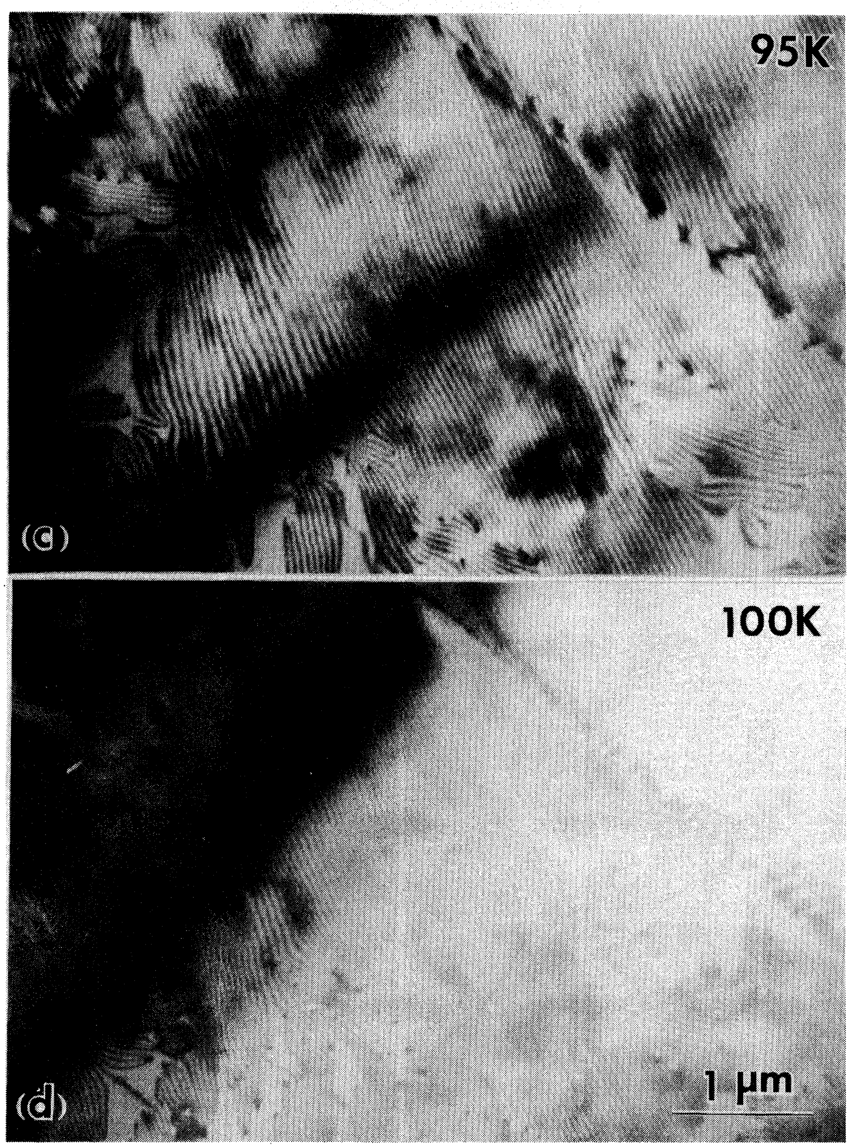

FIG. 3. (*Continued*.)

ing direction is changed from q_1 to (say) the q_2 direction if the dark and the bright stripes are orthorhombic domains. This contrast reversal is clearly seen in Figs. 4(a) and 4(b).

The experimental result that *all* the stripes have orthorhombic symmetry, and not alternate sequence of orthorhombic and hexagonal symmetry, is significant. Earlier theoretical considerations conceived the possibility of a single stripe consisting of a hexagonal domain between two orthorhombic domains.[10] This occurs when the CDW origin moves along the line joining the Ta sites. Our observations suggest instead that the CDW origin moves only along the line joining the Se sites. It has been shown[16] that this is possible if one allows the order parameters to vary slightly in the Landau theory. The energy difference between these two types of DC's is expected to be quite small.

The configuration of the CDW dislocations which are seen in every image of the stripe phase can now be understood as shown in Fig. 5. For the purpose of argument let us assume that the dark stripes have orthorhombic distortion along q_2 and the bright stripes have orthorhombic distortion along the q_3 direction. The sharp boundaries between the dark and the bright stripes are discommensurations of $q_2 \mid q_3$ type. It has been shown[8–10] that in dealing with the CDW's in $2H$-$TaSe_2$ one has to take into account the double-layer

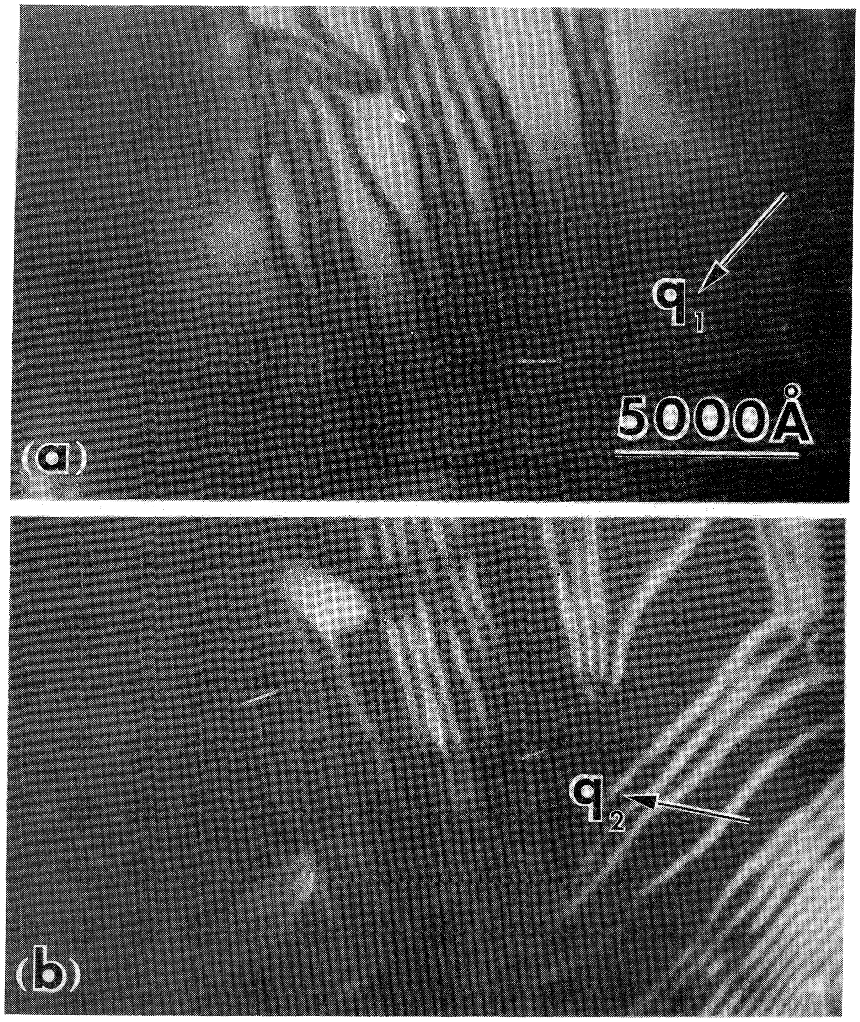

FIG. 4. Stripes images obtained at 94 K on warming when the imaging direction is changed from (a) q_1 to (b) q_2 direction. A reversed contrast for the $q_1 \mid q_2$ stripes running $\sim 20°$ to the vertical direction can be clearly seen.

crystal structure of $2H$-$TaSe_2$. If we denote the phases of the triple-q CDW in the even and the odd layer as $(\phi_1,\phi_2,\phi_3)_+$ and $(\phi'_1,\phi'_2,\phi'_3)_-$, respectively, the change of these phase angles across a CDW dislocation is that shown in Fig. 5.[16] It is noted that across a discommensuration only phases in the even layers change by $\pm 2\pi/3$ and phases in the odd layers remain unchanged, or vice versa. It

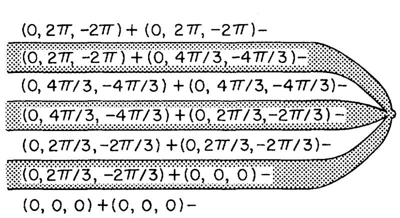

FIG. 5. Phase relationship of the stripes around a CDW dislocation.

is evident that three stripes of the same type and three pairs of DC's are always required to form a CDW dislocation such that the total phase change along any path around the dislocation is 2π. This arrangement of DC's is slightly more complicated than the one discussed by McMillan.[15] The dynamics of the CDW dislocation is perhaps the most fascinating aspect of the entire evolution process of various CDW phases. The appearance and disappearance of CDW dislocations seem to be first order. The configuration of dislocations is also quite interesting. Some of the patterns which we have observed frequently are shown in Fig. 6(a). Many of the dislocations depicted in Fig. 6(a) can be found in Fig. 6(b).

In view of the different orthorhombic distortion along the dark and bright lines within a region of parallel stripes, regions with three possible stripe

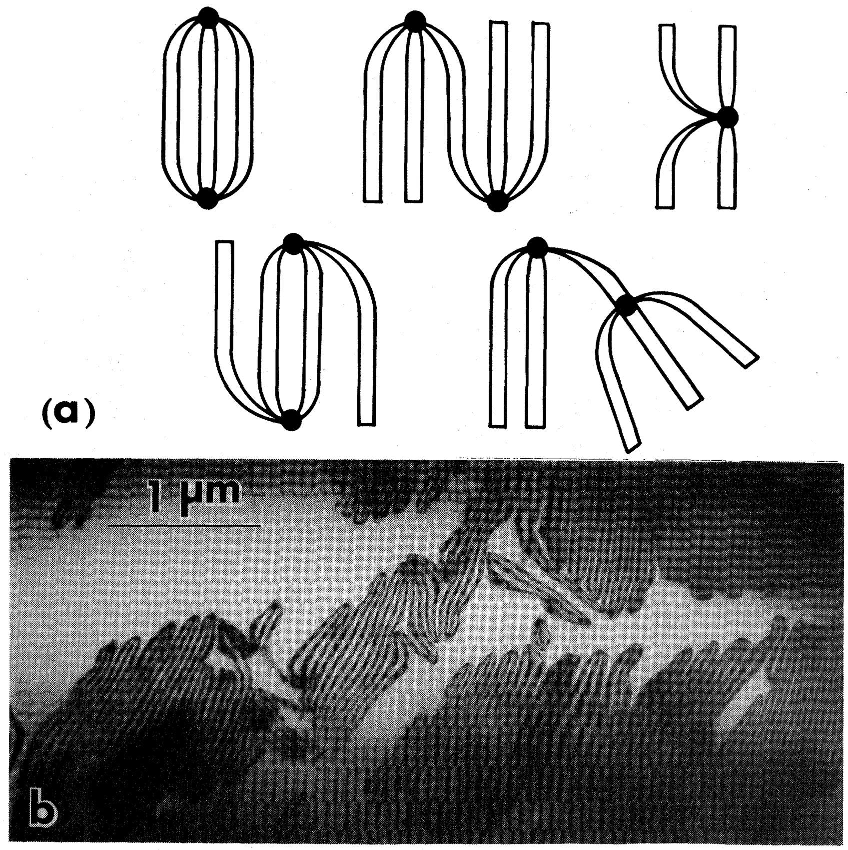

FIG. 6. (a) Line diagrams showing many configurations of CDW dislocations which can be seen in (b).

configurations are shown schematically in Fig. 7 in which possible orthorhombic distortion directions for each stripe are also indicated. It becomes clear that with a particular imaging CDW q direction, for example, q_1, only regions of stripes of $q_1 \mid q_2$ type and $q_1 \mid q_3$ type would be visible. Note again, that only stripes with q_1 distortion will appear

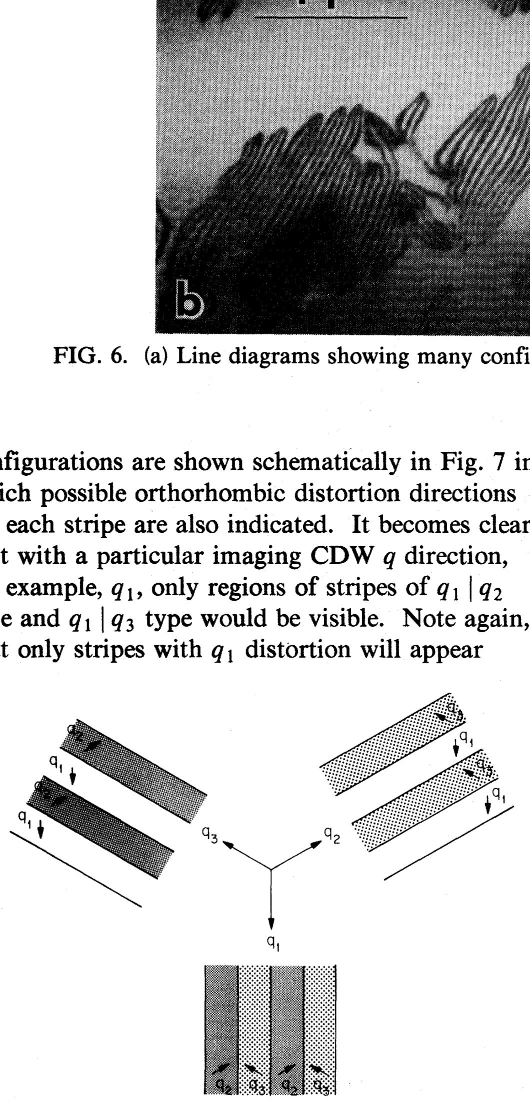

FIG. 7. Regions with three types of stripe configurations, i.e., $q_1 \mid q_2$, $q_2 \mid q_3$, and $q_3 \mid q_1$.

dark, and stripes with q_2 and q_3 distortion will appear to be bright. Regions with stripes parallel to the imaging q_1 direction would appear uniformly bright with no imaged stripes since the orthorhombic distortion of the stripes is of the $q_2 \mid q_3$ type. Following the same argument, each region should be visible twice if imaging is carried out along the three CDW q directions. In other words, regions of the $q_2 \mid q_3$—type distortion should be seen either with q_2 or q_3 as imaging direction, however, a reversal of contrast (i.e., dark stripe becomes bright and vice versa) would be expected. Figure 8 shows images of stripes at 94 K with three imaging q directions. The details of these images are entirely consistent with the model we have just described. We have noted that CDW dislocations usually exist at the boundaries between regions of different stripe orientation. Sometimes a dislocation at the boundary is composed of two dark stripes in one region and another dark stripe in a neighboring region. Occasionally, stripes in a particular region can bend through $2\pi/3$ and end up in a neighboring region. Also, sometimes when this happens a

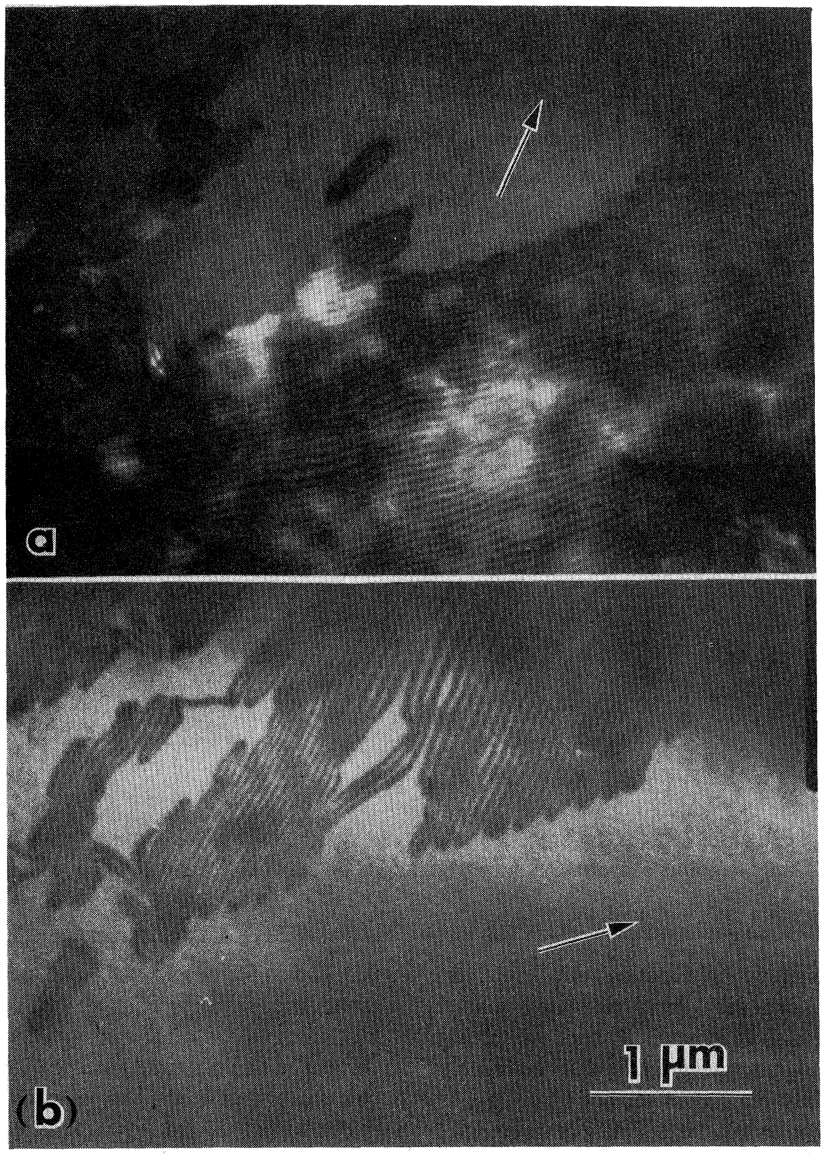

FIG. 8. (a)—(c) Images taken at 94 K in the stripe phase along the three CDW wave-vector directions as indicated. (d) is obtained after a small thermal cycle is compared with (a). Stripe patterns are clearly different.

"defect" structure in the stacking sequence of the orthorhombic distortion in the stripes can occur. A case of this kind of defect structure is shown in Fig. 9. Figure 9(a) shows stripe images obtained at 94 K with imaging direction, for example, q_1. Images for the same area but with imaging direction along the q_3 direction are shown in Fig. 9(b). The interesting feature of Fig. 9(b) is the appearance of two relatively wide bright stripes in which one or two dark stripes are missing. This would not be expected if the configuration of stripes was always like the one shown in Fig. 7. What happens in Fig. 9(b) is as follows. When some stripes with q_1 orthorhombic distortion in the region of type $q_1 \mid q_2$ bend over $2\pi/3$ and end up in a different region of type $q_1 \mid q_3$, they carry some of the q_2 stripes with them and the q_2 stripes have therefore ended up in a "wrong" region. As a result of this, the stacking sequence in this defect area would become $q_3 \mid q_1 \mid q_2 \mid q_1 \mid q_3$ or $q_3 \mid q_1 \mid q_2 \mid q_1 \mid q_2 \mid q_3 \cdots$, etc. A stacking fault of $q_1 \mid q_2$ or $q_2 \mid q_1 \mid q_2$ is created in this case. This defect area will appear to be bright if the imaging direction is chosen to be along the q_3 direction.

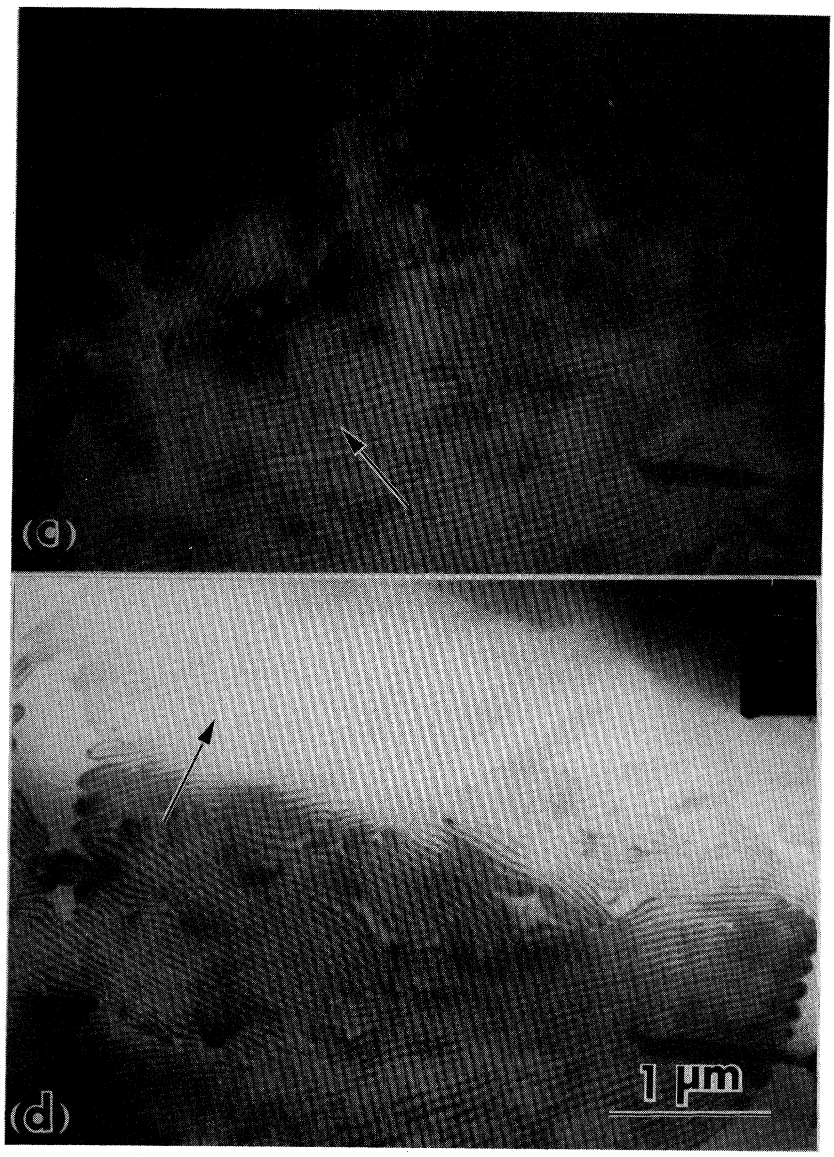

FIG. 8. (*Continued.*)

This is exactly what happens in the wide bright stripes as indicated in Fig. 9(b).

Under some occasions, a stripe region of the type, for example, $q_2 \mid q_3$ can have a stripe with orthorhombic direction q_1 running across it. When this happens a shift or a break of the $q_2 \mid q_3$ stripe across the q_1 stripe can occur, which is shown in Fig. 10. In this case, q_2 stripes are facing q_3 stripes (not q_2 stripes) across the intersecting q_1 stripe. This is probably due to the interaction of DC's. We will come back to discuss this interaction in Sec. V.

Crystalline defects such as dislocations or grain boundaries are often thought of as pinning centers of CDW's. Throughout our studies, we have never found that the visible crystalline defects play any significant role in the pinning of CDW's. Figure 11 shows an image in the stripe phase in which several crystalline dislocation lines are visible. These dislocation lines as indicated by arrows. No effect can be seen as the dislocation lines run through the stripes.

Again, as in the commensurate phase, we find the CDW in the stripe phase is not strongly pinned. This was shown in Fig. 8(d) in which images are taken from the same area as Fig. 8(a) at

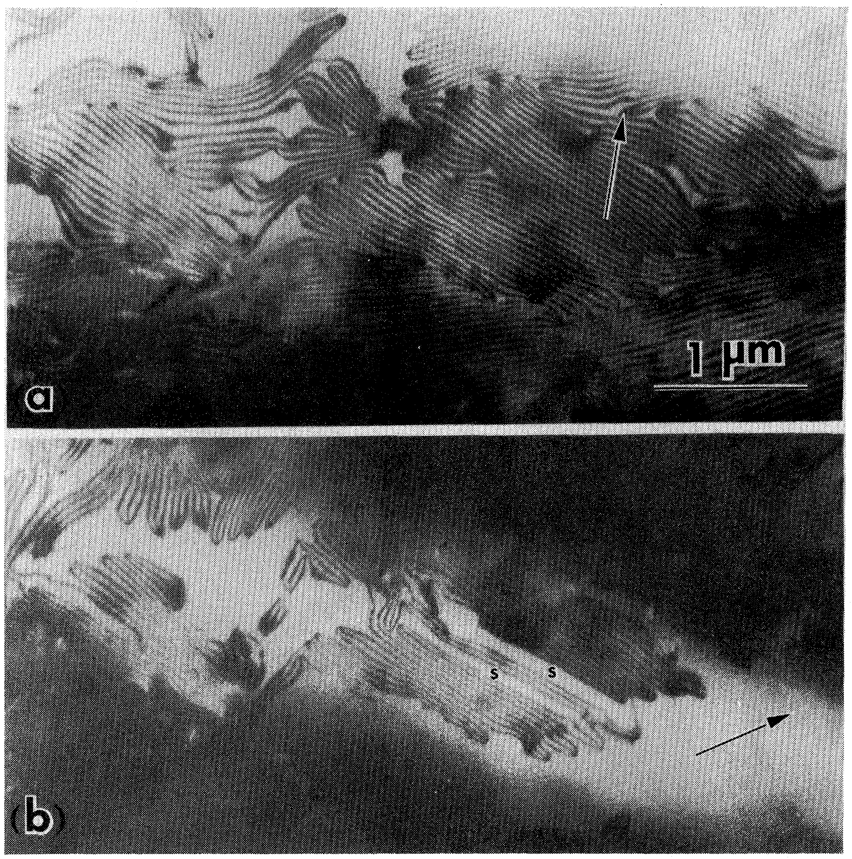

FIG. 9. Two relatively wide bright stripes marked by s in (b) are identified as a stacking fault in the stripe phase. The images are taken at 94 K.

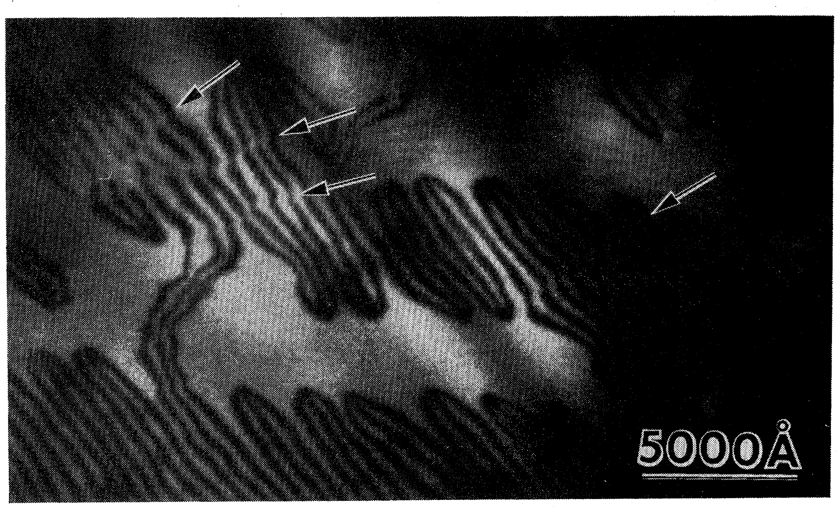

FIG. 10. Intersection of stripe regions of the type, for example, $q_2 \mid q_3$ with type-q_1 stripes. A shift or a break of the $q_2 \mid q_3$ stripes can be seen at the points of intersection as indicated by the arrows.

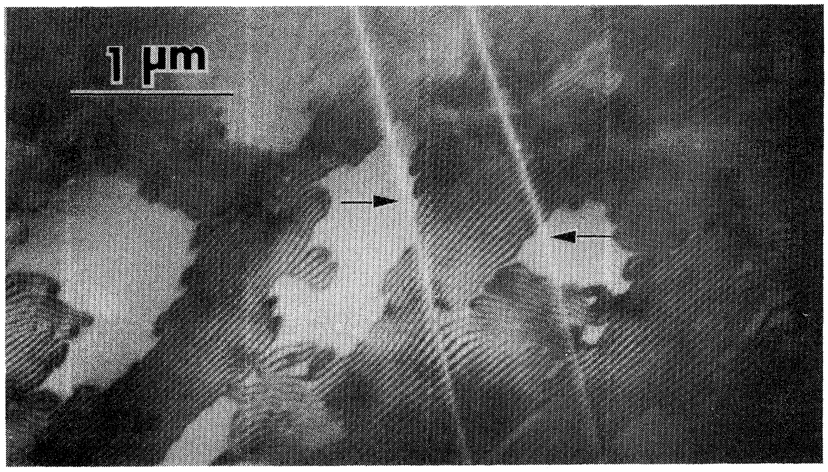

FIG. 11. Image taken at 97 K in the stripe phase showing a pair of crystalline dislocation lines (indicated by the arrows) running across the stripes. No significant effect can be seen at the points where they intersect.

the same temperature but after warming to ~ 110 K and then cooling down to 94 K. The detailed arrangement of the stripes is clearly not the same after this small thermal cycle. The "waviness" of the stripes is also indicative of weak pinning of discommensurations as described by Rice *et al.*[13]

B. Stripe phase to "hexagonal" phase transition ($T \gtrsim 112$ K)

X-ray studies[1] have shown that at $T \sim 112$ K a first-order phase transition takes place and the incommensurate CDW transforms from the stripe phase to a phase having hexagonal symmetry. Again, due to the orthorhombic symmetry of the stripes, it is questionable whether the CDW has hexagonal symmetry on a microscopic scale. In this section we shall discuss the nature of this transition and show how it takes place in real space. Figure 12 is a sequence of images taken with imaging direction as indicated at temperatures varying through this stripe to hexagonal transition. Close to the transition temperature, it is found that new stripes oriented roughly perpendicular to the original stripes are nucleated. The original stripes are distorted and become jagged whenever they are cut through by the new stripes. As a result of this distortion, a new set of stripes appear and traverse in a direction perpendicular to the imaging q direction (i.e., 30° with respect to the old stripe). As more and more new stripes are nucleated at higher temperatures, the old stripes become elusive and only stripes perpendicular to the imaging direction can be seen [Fig. 12(e)]. Images obtained from the three CDW q directions show, indeed, that we have three intersecting sets of fringes running at an angle $2\pi/3$ with each other (Fig. 13). The presence of three intersecting sets of fringes gives rise to the hexagonal symmetry on a macroscopic scale as obtained by x-ray diffraction. This image is similar to that observed in the incommensurate "hexagonal" phase on cooling. We will therefore leave the discussion of its details to Sec. V. Although the x-ray diffraction result suggests that the stripe to "hexagonal" phase transition is first order, our observation, however, does not show that this transition is strongly first order. New stripes have already started to nucleate at temperatures $\lesssim 105$ K which is below the 112 K indicated by the x-ray result.

V. INCOMMENSURATE AND COMMENSURATE PHASES ON COOLING

As we noted earlier, x-ray diffraction studies show that the CDW retains hexagonal symmetry all the way on cooling. This observation warrants reconsideration in the light of the presence of orthorhombic symmetry in the commensurate phase. In this section we present the change of domain and DC's microstructure seen as a function of temperature as temperature decreases. It is truly very interesting to *see* how the incommensurate phases transforms into the orthorhombic commensurate phase as the temperature approaches the IC phase transition. We shall also show that the

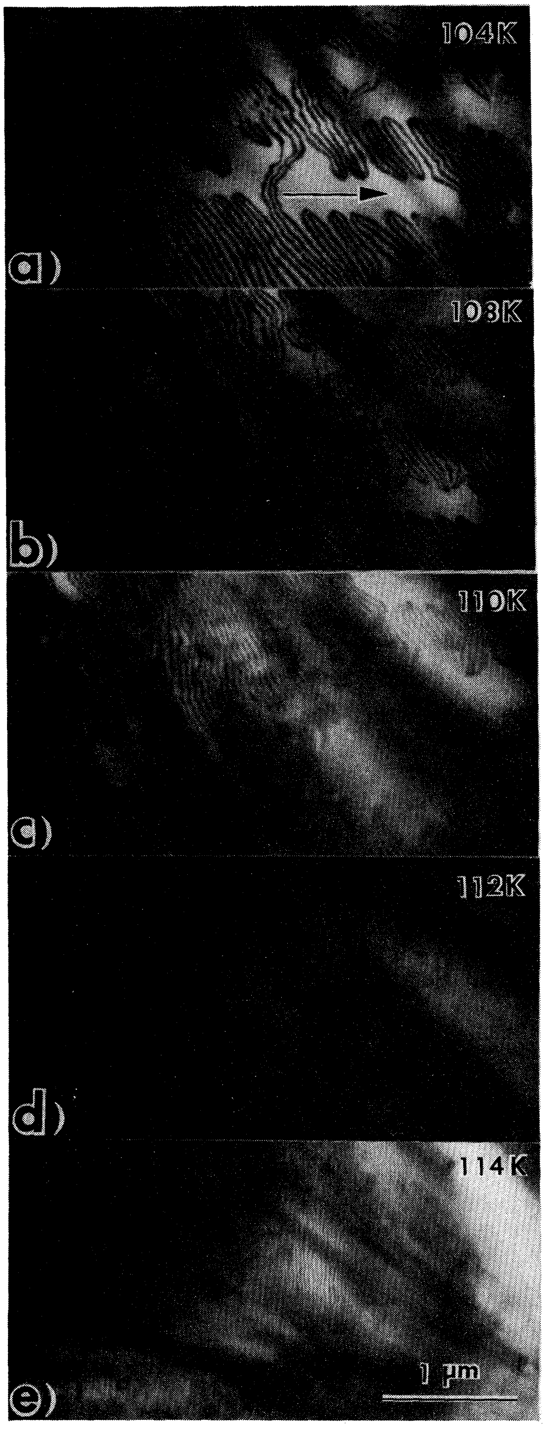

FIG. 12. (a)–(e) Images showing the transition from the stripe phase to the "hexagonal" phase on warming. At temperatures below the transition ∼112 K stripes are traversing at an angle 120° (or 60°) to the imaging direction as indicated in (a). At 114 K the stripes have rotated by 30° and become perpendicular to the imaging direction (e).

generally accepted honeycomb array of domain and DC's in the incommensurate phase is inconsistent with our observations. It seems that on the microscopic scale, orthorhombic symmetry is predominant over most of the temperature range in the incommensurate CDW state. Only at temperatures greater than ∼115 K is the existence of the hexagonal symmetry state of incommensurate CDW possible.

Figure 14 shows the evolution of the orthorhombic commensurate phases from a temperature ∼115 K. At 115 K parallel stripes ∼200 Å apart are seen at an angle $\pi/2$ to the imaging q direction. At 110 K another set of stripes at an angle $2\pi/3$ to the original set begins to show up, although the original stripes remain predominant. As a result of the intersection of the two set of stripes, the image of the stripes becomes fragmentary and less smoothed. As the temperature decreases further, the stripes becomes wavier and jagged domains begin to appear. At 85 K the jagged diamond-shape domains have become quite prominent. At 80 K some of the jagged domains combine into large domains similar to the orthorhombic domains in the commensurate phase. Further combinations of domains occur at lower temperature (∼75 K) and no changes of the domain structure are seen below 65 K. It is clear that through the course of the evolution of the orthorhombic commensurate phase, no hexagonal honeycomb array of domain and DC structure has been observed. We have already shown that in the orthorhombic phase we can image the entire area by triple-q imaging, and each domain will appear dark only once for one specific q. Similar image properties would be expected in the incommensurate phase prior to lock-in transition if these jagged domains have orthorhombic distortions. It becomes rather difficult to do triple-q imaging at higher temperature when the spacing between the stripes is small ($\lesssim$300 Å). Even when it is possible to do so at these temperature, overlaying three images on top of each other is very difficult due to the lack of sharp ($\lesssim$200 Å) reference points or objects. We have, therefore, picked a temperature in which domain sizes are large enough to distinguish and the difficulty of overlapping the triple-q images has been minimized. An example of this is shown in Fig. 15. It clearly shows that each dark domain appears dark only once for one q, characteristic of the domains with orthorhombic distortion. We note that domains are always joined at the corners, not along the edges, and the corners

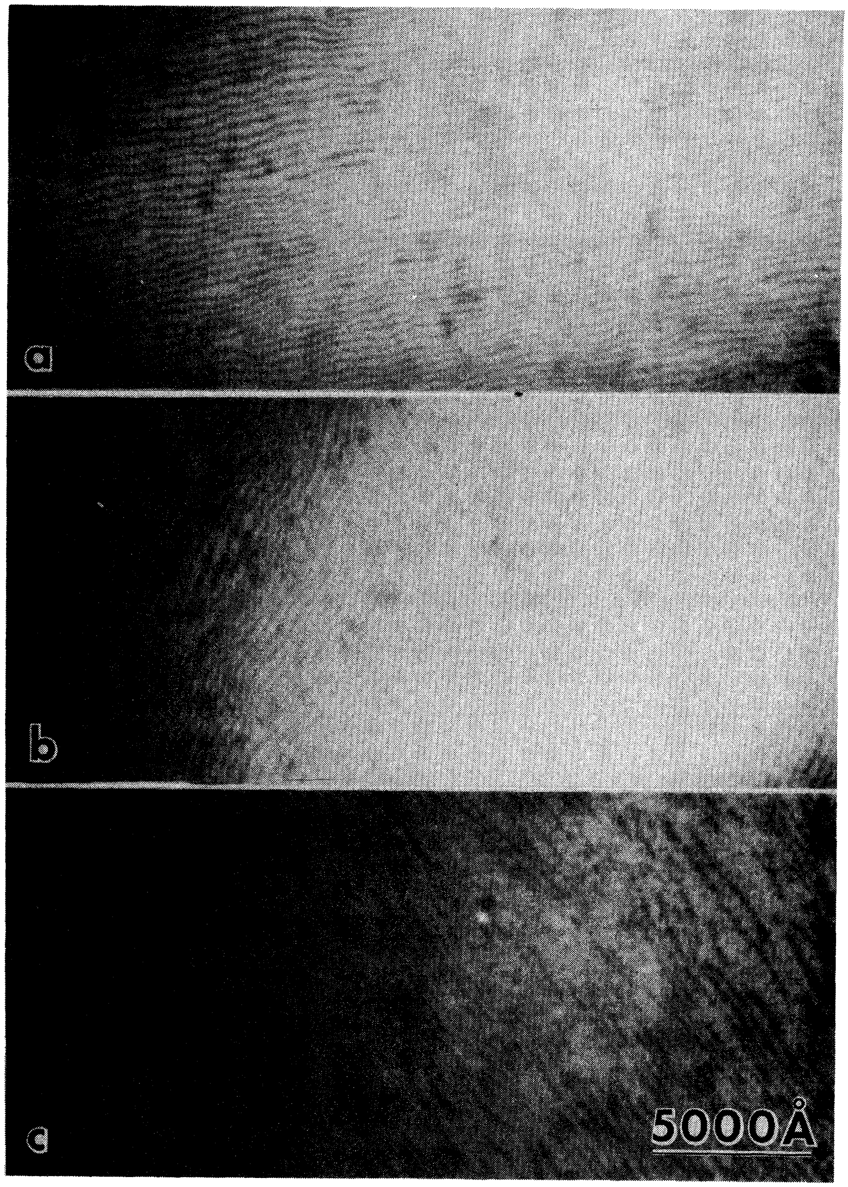

FIG. 13. (a)—(c) Triple-q imaging in the "hexagonal" phase on warming showing the existence of three sets of intersecting fringes in a given area.

adjoining the adjacent domain appear to be quite sharp ($\lesssim$200 Å) as can be seen in Figs. 14 and 15. The indication of this observation is that the interactions between DC's are rather weak. Also note that the CDW dislocations we described in the stripe phase are now formed with three somewhat irregular jagged chains consisting of quite large interconnecting orthorhombic domains. The size of the domains is quite nonuniform and can change from a few hundred angstroms to 1 or 2 μm (e.g., see Fig. 14).

We mentioned earlier that above $\sim$115 K the fringes are so closely packed with a spacing less than 200 Å that it is difficult to tell the precise domain and DC structure although the fringes appear to be quite continuous. Since we have already shown that at lower temperature the CDW's have orthorhombic symmetry on the microscopic scale, the question now is do the CDW's adopt hexagonal or orthorhombic symmetry at higher temperature? This is a difficult question to answer. On one hand we know that if the real image width is

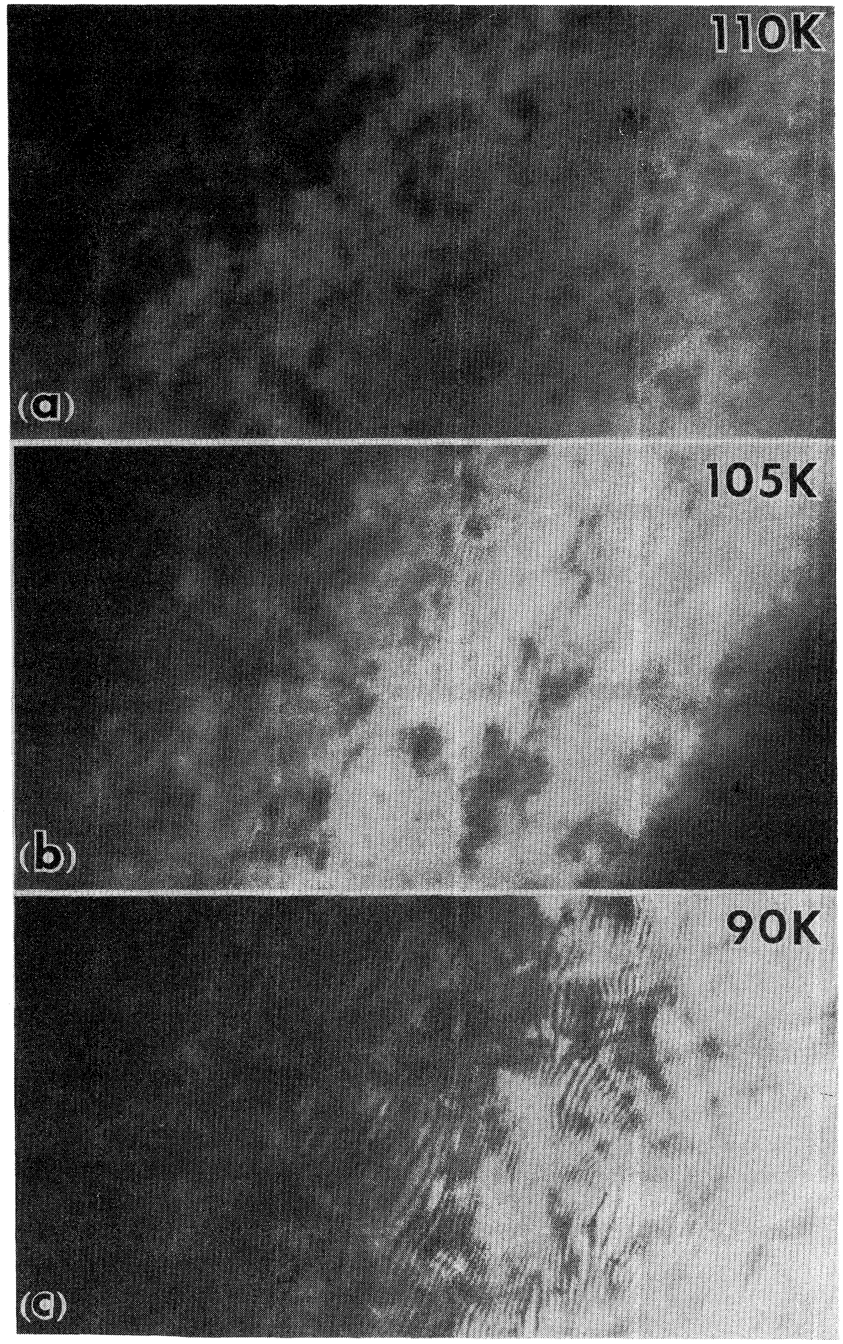

FIG. 14. (a)—(f) Evolution of the commensurate orthorhombic phase from the incommensurate "hexagonal" phase on cooling. Very fine fringes are seen at high temperatures and the fringes become jagged as temperature decreases. Combination of the jagged fringes into chains of large diamond-shaped domains occurs at temperatures near the IC transition ($\sim$82 K). Note that the diamond-shaped domains are connected through the corners of the domains.

smaller than the extinction distance of the imaging diffraction spot, the image can be distorted drastically and all sharp corners will be smoothed out.[17] Therefore, one can argue that at high temperature ($\gtrsim$115 K), the observed smooth moiré-like fringes are in fact arrays of saw-tooth DC's of hexagonal honeycomb structure. On the other hand, if we recall that the origin of the contrast as discussed in this paper arises from the orthorhombic distortion, then it seems that the CDW's might have

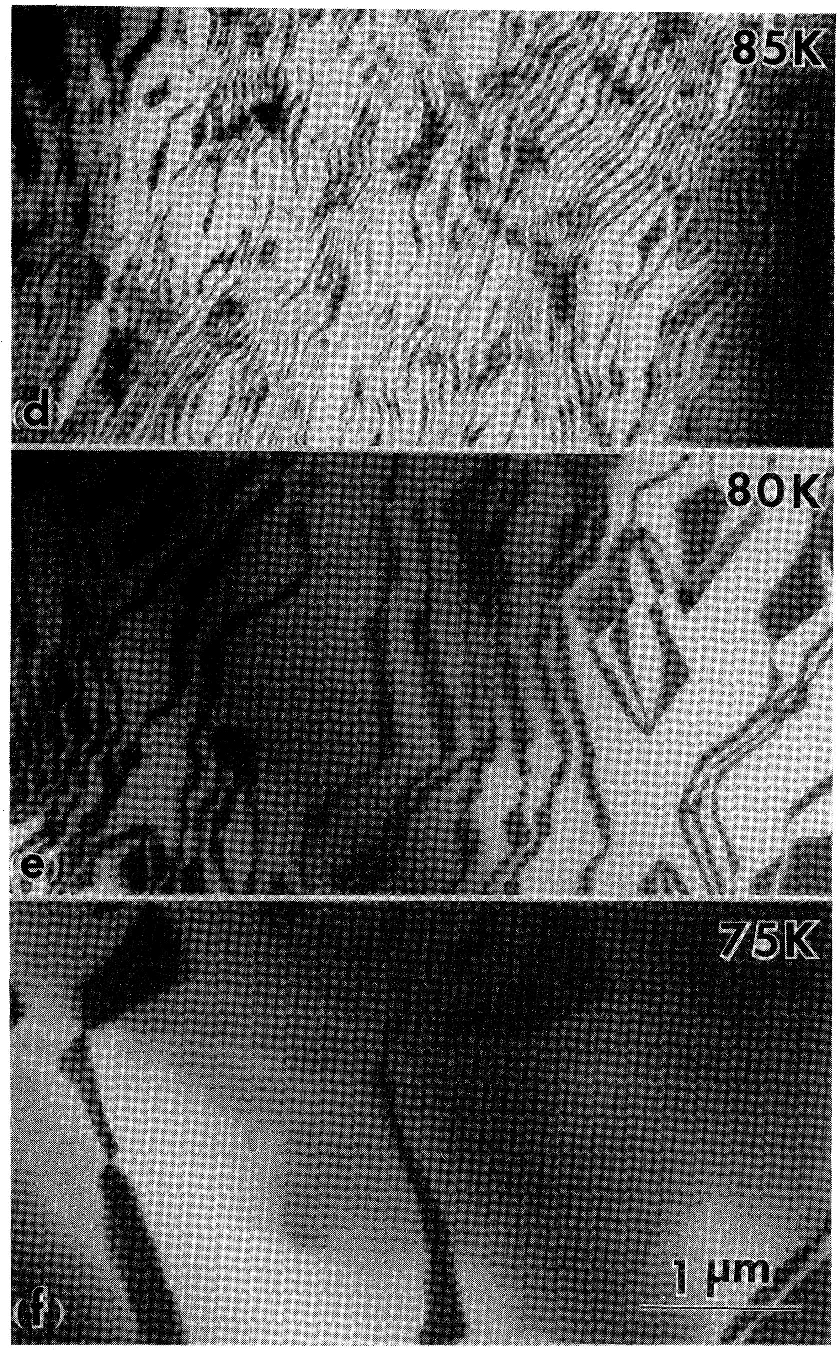

FIG. 14. (*Continued.*)

orthorhombic symmetry since domains with hexagonal symmetry should appear to be contrastless. From theoretical considerations it is thought[10] a hexagonal phase should exist if the temperature is high enough. The transition temperature from hexagonal to orthorhombic phase is not clearly known at the moment. Direct imaging of the fringes near the normal-incommensurate CDW transition is becoming harder as this temperature is approached due to the lack of intensity of the CDW reflections. We think the highest temperature at which good imaging is possible is around ~ 117 K. So the hexagonal to orthorhombic transition temperature must lie between 122 and 117 K.

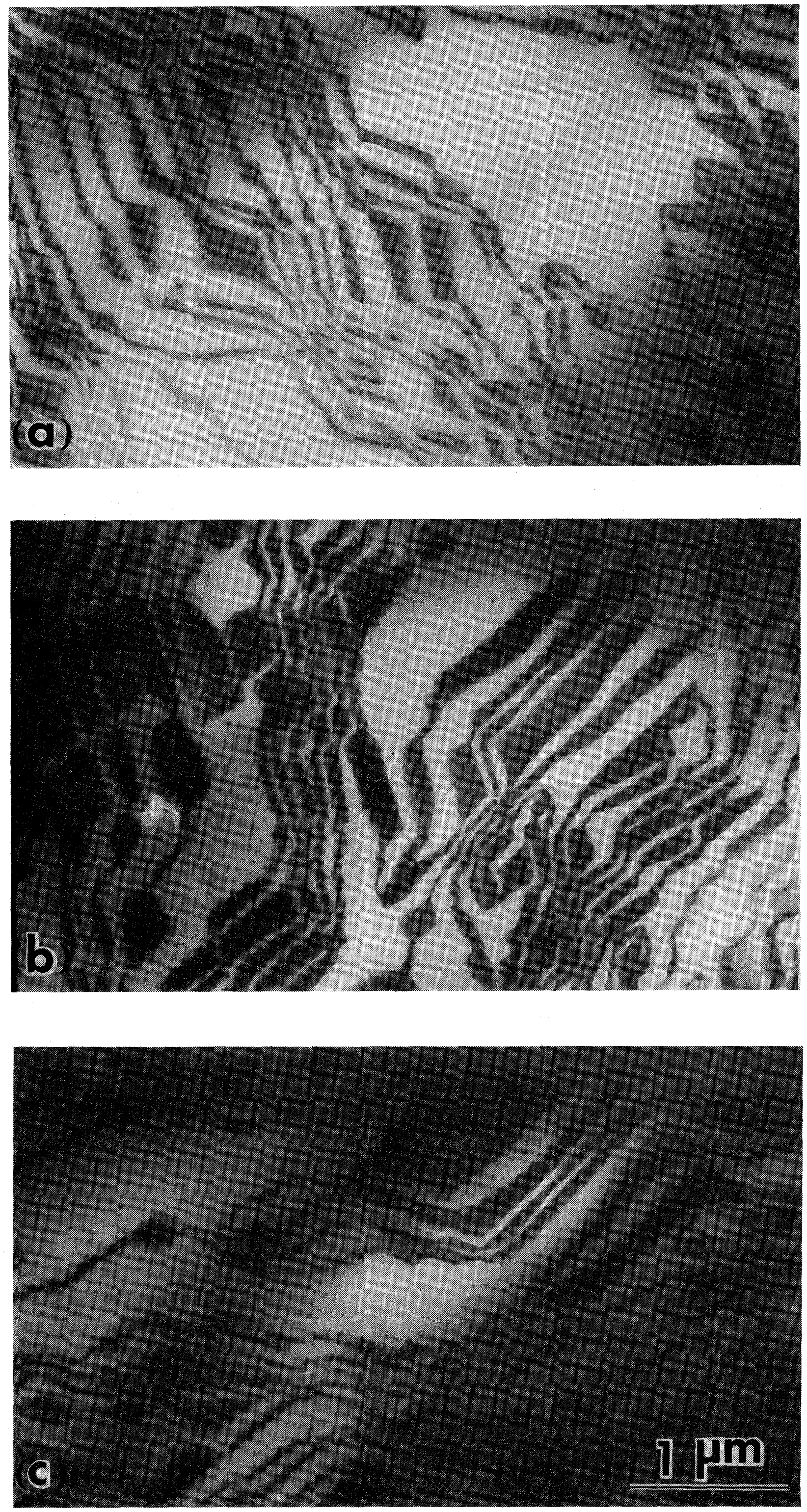

FIG. 15. (a)–(c) Triple-q imaging at 86 K in the "hexagonal" phase on cooling. Image characteristics are similar to the orthorhombic domains in the commensurate phase (Fig. 1); i.e., a domain appears dark for only one particular imaging direction and appears bright for the other two imaging directions.

Very recently, theoretical studies of Littlewood and Rice[10] within the frame work of Landau theory showed that a DC in the hexagonal incommensurate phase can split into two hexagonal-orthorhombic interfaces with a orthorhombic domain in between. The size of the orthorhombic domains increases as the temperature decreases. Our observation of the evolution of the domain and DC structure on cooling seems to be understandable in a qualitative fashion within this model. Schematics showing the growth of the diamondlike orthorhombic domains from the DC's in the hexagonal phase is shown in Fig. 16. DC's along the q_1 direction split and form orthorhombic domains with distortion along the q_1 direction; the same thing happens for DC's along the q_2 and q_3 directions. As a result of the growth of DC's along q_1, q_2, and q_3 directions, chains of diamond-shaped orthorhombic domains joining at their corners would be expected in the images with imaging direction along any CDW wave vector, and the domain boundary pattern would have either threefold or sixfold junctions. Such domain contrast and the topological arrangement of the domain boundaries are consistent with our observations [see Fig. 1(e)]. Note that at points where

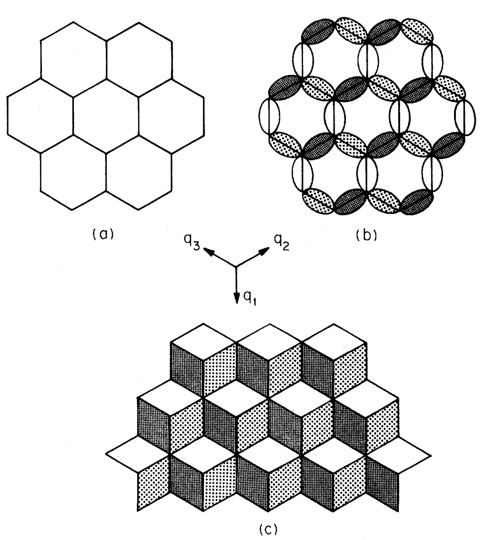

FIG. 16. (a) Honeycomb array of DC's in the hexagonal incommensurate phase. (b) Formation of orthorhombic domains with two hexagonal-orthorhombic interfaces by splitting of the DC's in (a). (c) Final domain pattern as a result of splitting of DC's in the ideal situation. It is clear that the domain boundary pattern has either threefold or sixfold junctions.

three domains with the same orthorhombic distortion join together, i.e., a CDW dislocation, the domain boundary pattern will no longer have threefold or sixfold junctions. Figure 16(c), of course, is an idealized case in which all the domains have exactly the same size and diamond shape. This does not occur in the real case as is evident from the images we have shown. However, the qualitative feature and the general trend of the evolution of the orthorhombic phase is consistent with the DC splitting model proposed by Littlewood and Rice.[10] Note that the CDW's have hexagonal symmetry on a macroscopic scale due to the existence of microscopic domains with orthorhombic distortion along the three principal hexagonal symmetry directions, i.e., q_1, q_2, and q_3.

In view of the understanding we now have for the domain and DC structure on cooling, we can examine more closely the change of domain and DC structure when the CDW's go through the stripe to hexagonal transition at 112 K on warming. In Sec. IV we noted the evolution from the striped to the macroscopic "hexagonal" phase through the evolution of other type of stripes running perpendicular to the original stripes. We find that the only possible configuration of domain and DC with intersecting stripes is the one shown in Fig. 16(c) if we insist that all the DC's orient in the way they are expected, i.e., $q_2 \mid q_3$ DC's are parallel to q_1, $q_1 \mid q_2$ DC's are parallel to q_3, etc. In other words, it is not possible to have intersecting stripes without reorientation of some of the DC's. Evidently misorientation of a DC is energetically unfavorable and is unstable against rearrangement of domain and DC's. As a result of this rearrangement, a stripe originally, for example, with orthorhombic distortion along q_1, can break up into small orthorhombic domain with distortion direction along q_1, q_2, and q_3 [see Fig. 16(c)]. Sharp corners of the domain and DC structure as shown in Fig. 16(c) can only be seen clearly at lower temperatures ($\lesssim 95$ K). At higher temperatures the spacings between the chains are small and the chains appear to be less jagged. This could be due to imaging effects mentioned earlier or the weak interaction among DC's which will smooth out the sharp corners where DC's intersect.

In Sec. IV B we mentioned that in the stripe phase a stripe domain, for example, of $q_1 \mid q_3$ type, can be intersected by a single stripe of q_2 type and as a result kinks or breaks are developed in the stripes of the $q_1 \mid q_3$ domain at the points where they intersect the q_2 stripe. Most often a shift of

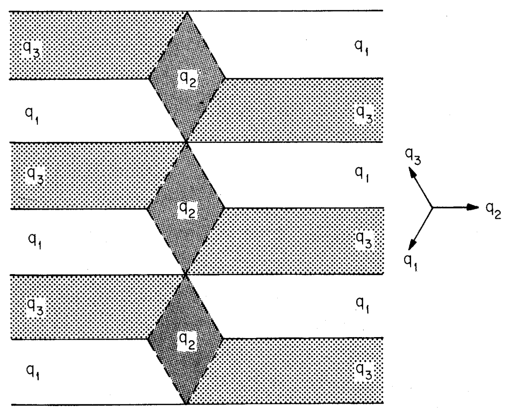

FIG. 17. Line diagram showing the stripe and DC arrangement when a q_2 stripe intersects a stripe region of type $q_1 \mid q_3$.

stripes, i.e., dark stripes are facing bright stripes across the intersecting q_2 stripe and vice versa, appears. Furthermore, we have also noticed that when this kind of intersection occurs, q_2 is often running roughly perpendicular to the $q_1 \mid q_3$ stripes. We can consider this case as a special case of Fig. 16(c). A schematic diagram for this simple case is shown in Fig. 17. Again, no misorientation of DC's are assumed. It is expected from Fig. 17 that images of $q_1 \mid q_3$ stripes will show breaks or shift along the stripes and image of the q_2-type stripe will show chains containing jagged diamond-shape domains. This is indeed observed frequently (see Fig. 10). At higher temperatures due to the small size of a single stripe it is naturally very difficult to expect the real image to be exactly identical to the conceptual picture of Fig. 17. However, the resemblance of the gross features to the images is quite remarkable.

VI. CONCLUSIONS AND REMARKS

$2H$-$TaSe_2$ is the most fascinating transition-metal-dichalcogenide layer compound found so far in respect to the phenomena of CDW's. In this paper we have presented direct observations of the change of domain and DC structure when the CDW's go through various phase transitions. It is found that the emergence of the orthorhombic distortion from the hexagonal symmetry has the most prevailing influence in all these phase transitions. One of the most exciting observations is the microstructures down to $\lesssim$ 100 Å in various CDW states. The capability of studying the microstructures through various phase transitions is a great step forward in the advancement of research in this field. It should be noted that the domain and DC structures we have discussed in the present work extend throughout the thickness of the sample. The images we have shown are, therefore, two-dimensional projections of these structures. Although the images can be understood qualitatively, detailed theoretical understanding is still lacking. For example, it is not totally clear from the theoretical point of view why CDW dislocations can be nucleated so easily as observed experimentally. The abundance of CDW dislocations can be seen in most of the images shown in this paper. Stacking faults and misorientation of DC's as described in the paper clearly are energetically unfavorable and are not seen quite so often. Theoretical understanding of these types of defects would be very valuable.

From the experimental point of view, there are still a few things that need further investigation. For example, the contrast reversal we discussed in Sec. III is not completely understood. Whether this is a real effect or an artifact due to multiple scattering can not yet be said with complete certainty. Another topic concerns the microstructure of a DC which has not been addressed. Since DC's appeared to be very sharp with a width smaller than our resolution ($\sim$50 Å), high-resolution images (down to few Å scale) would be needed to reveal the microstructure of DC's on an atomic scale. Work in this area is now in progress.

ACKNOWLEDGMENTS

We would like to thank P. B. Littlewood, T. M. Rice, D. M. Moncton, D. B. McWhan, and F. J. DiSalvo for many invaluable discussions, and J. W. Steeds and J. A. Wilson for sending us a copy of their unpublished paper.

[1]R. M. Fleming, D. E. Moncton, D. B. McWhan, and F. J. DiSalvo, Phys. Rev. Lett. 45, 576 (1980).
[2]C. H. Chen, J. M. Gibson, and R. M. Fleming, Phys. Rev. Lett. 47, 723 (1981).
[3]T. M. Rice, in *Feskörperprobleme: Advances in Solid State Physics,* edited by J. Treusch (Vieweg, Branschweig, 1980), Vol. XX, p. 393.
[4]P. Bak, Rep. Prog. Phys. (in press).
[5]P. Bak, D. Mukamel, J. Villain, and K. Wentowska, Phys. Rev. B 19, 1610 (1979).
[6]K. Nakanish and H. Shiba, J. Phys. Soc. Jpn. 44, 1465 (1978).
[7]K. K. Fung, S. McKernan, J. W. Steeds, and J. A. Wilson J. Phys. C 14, 5417 (1981).
[8]M. E. Walker and A. E. Jacobs, Phys. Rev. B 24, 6770 (1981).
[9]W. L. McMillan (unpublished).
[10]P. Littlewood and T. M. Rice, Phys. Rev. Lett. 48, 27 (1982).
[11]P. A. Lee and T. M. Rice, Phys. Rev. B 19, 3970 (1979).
[12]H. Fukuyama and P. A. Lee, Phys. Rev. B 17, 535 (1978).
[13]T. M. Rice, S. Whitehouse, and P. Littlewood, Phys. Rev. B 24, 2751 (1981).
[14]D. B. McWhan and R. M. Fleming, Proceedings of International Symposium of the Physics of Solids Under High Pressure, Bad Honnef, Germany, 1981 (unpublished).
[15]W. L. McMillan, Phys. Rev. B 12, 1187 (1975), 14, 1496 (1976).
[16]P. B. Littlewood and T. M. Rice (unpublished).
[17]P. B. Hirsh, A. Howie, R. B. Nicholson, D. W. Pashley, and M. J. Whelan, *Electron Microscopy of Thin Crystals* (Butterworths, London, 1967).

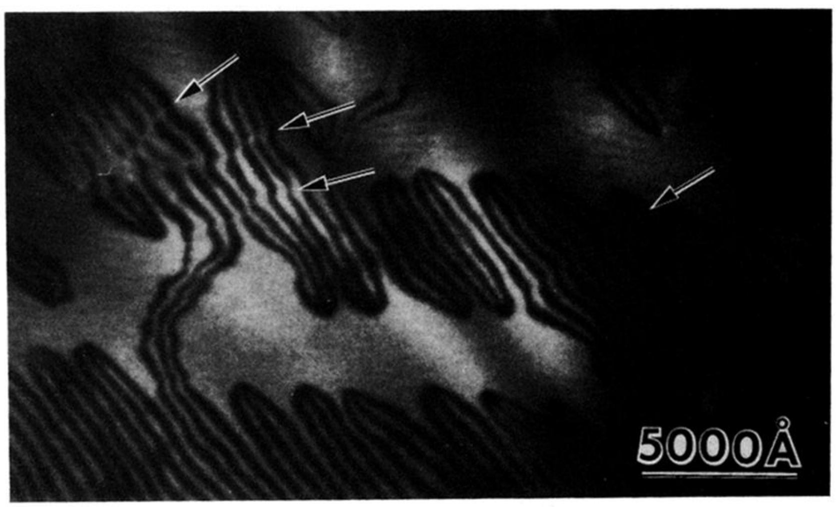

FIG. 10. Intersection of stripe regions of the type, for example, $q_2 | q_3$ with type-q_1 stripes. A shift or a break of the $q_2 | q_3$ stripes can be seen at the points of intersection as indicated by the arrows.

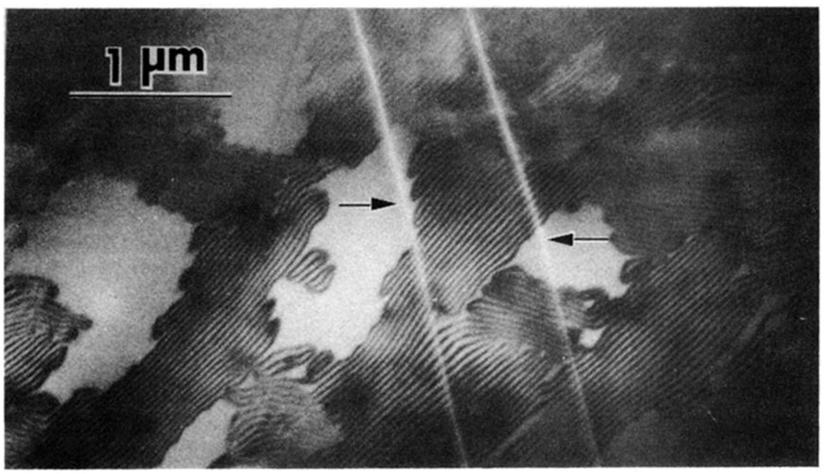

FIG. 11. Image taken at 97 K in the stripe phase showing a pair of crystalline dislocation lines (indicated by the arrows) running across the stripes. No significant effect can be seen at the points where they intersect.

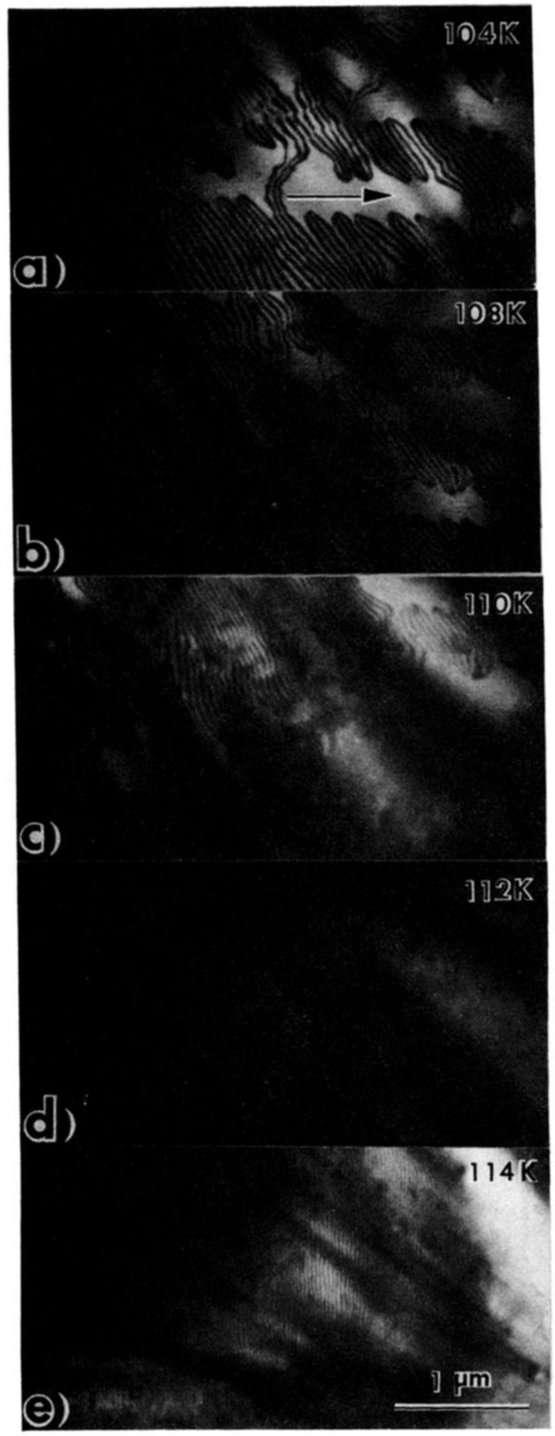

FIG. 12. (a)—(e) Images showing the transition from the stripe phase to the "hexagonal" phase on warming. At temperatures below the transition ~112 K stripes are traversing at an angle 120° (or 60°) to the imaging direction as indicated in (a). At 114 K the stripes have rotated by 30° and become perpendicular to the imaging direction (e).

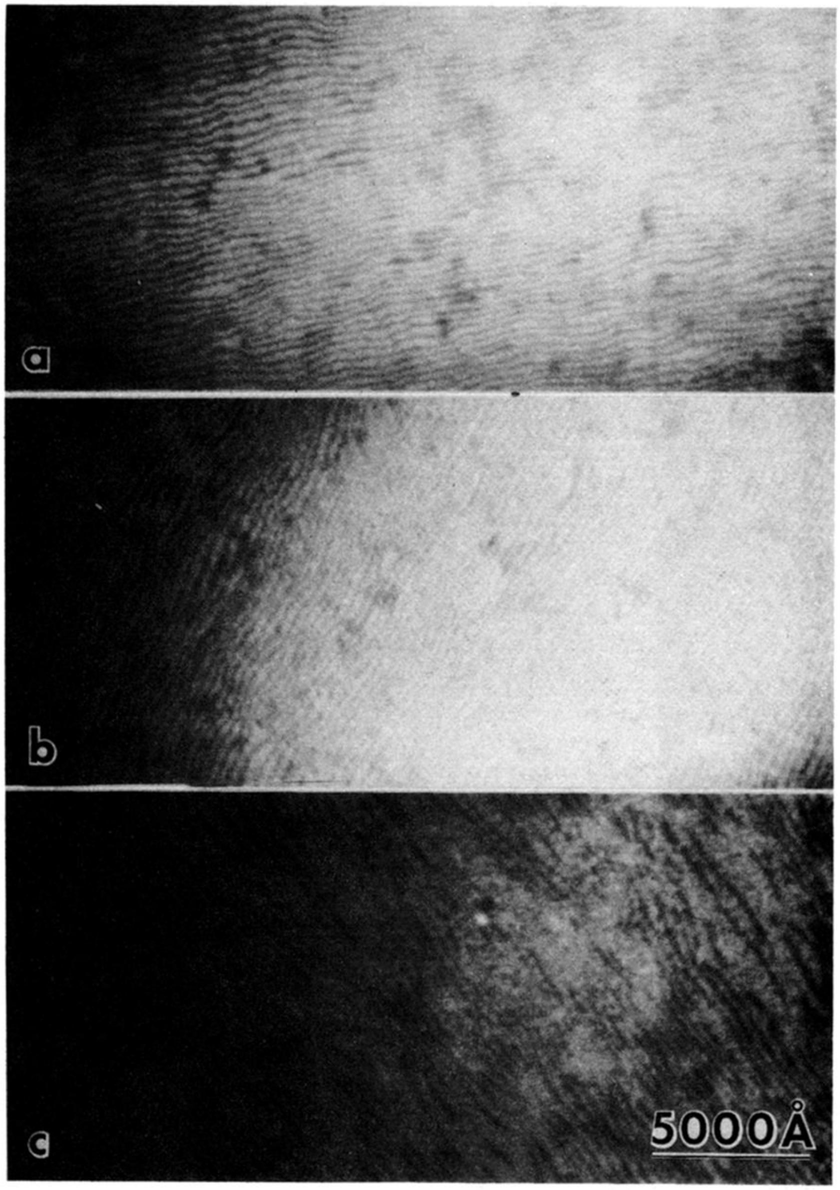

FIG. 13. (a)—(c) Triple-q imaging in the "hexagonal" phase on warming showing the existence of three sets of intersecting fringes in a given area.

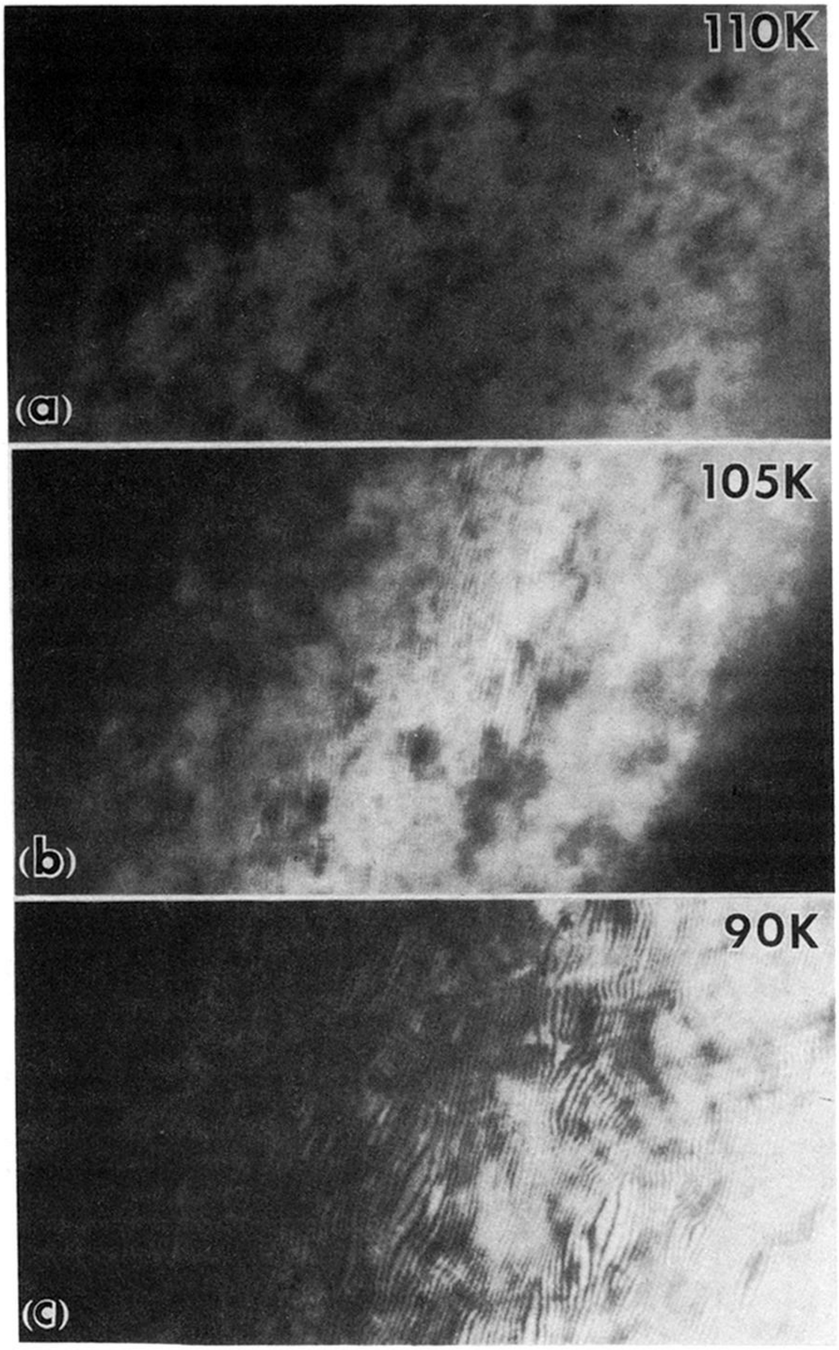

FIG. 14. (a)—(f) Evolution of the commensurate orthorhombic phase from the incommensurate "hexagonal" phase on cooling. Very fine fringes are seen at high temperatures and the fringes become jagged as temperature decreases. Combination of the jagged fringes into chains of large diamond-shaped domains occurs at temperatures near the IC transition ($\sim$82 K). Note that the diamond-shaped domains are connected through the corners of the domains.

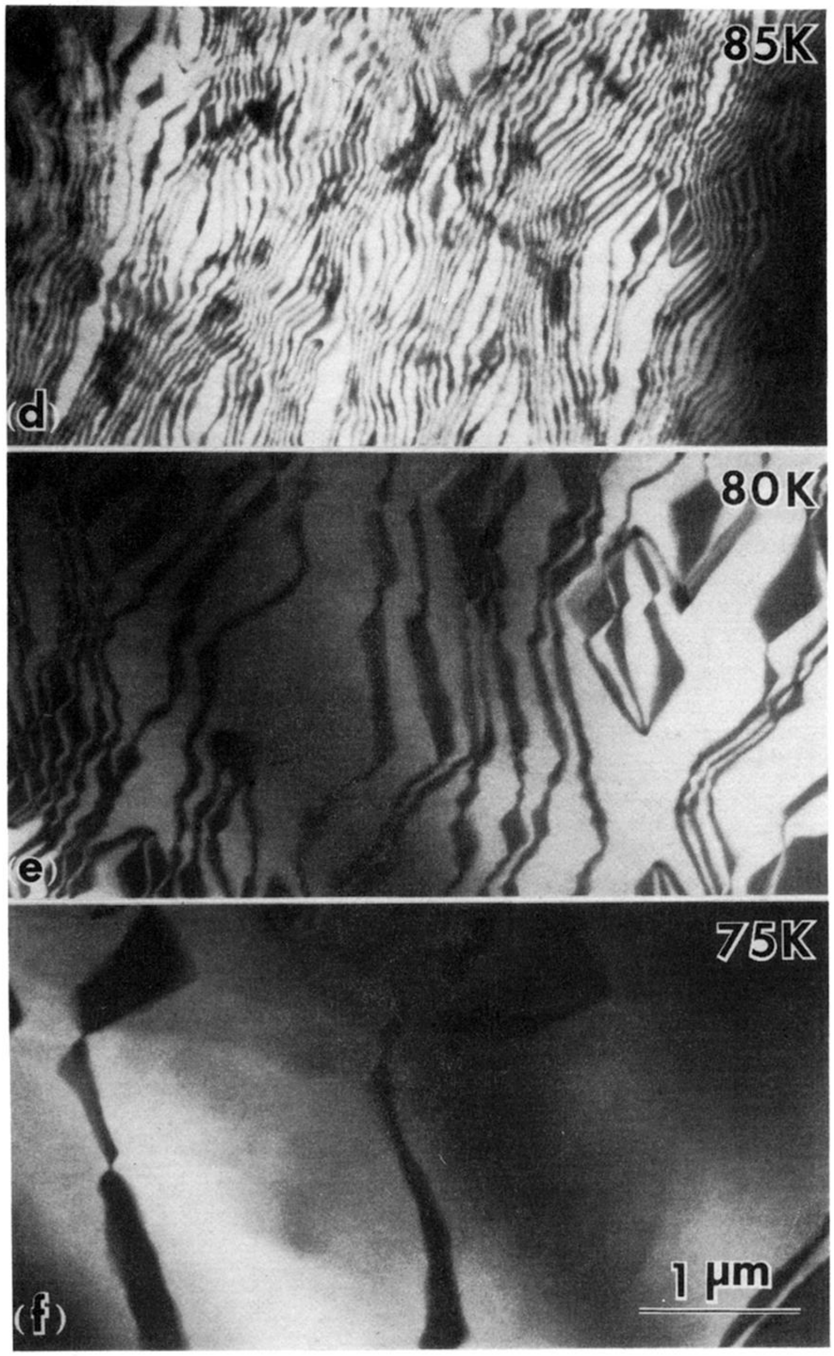

FIG. 14. (*Continued*.)

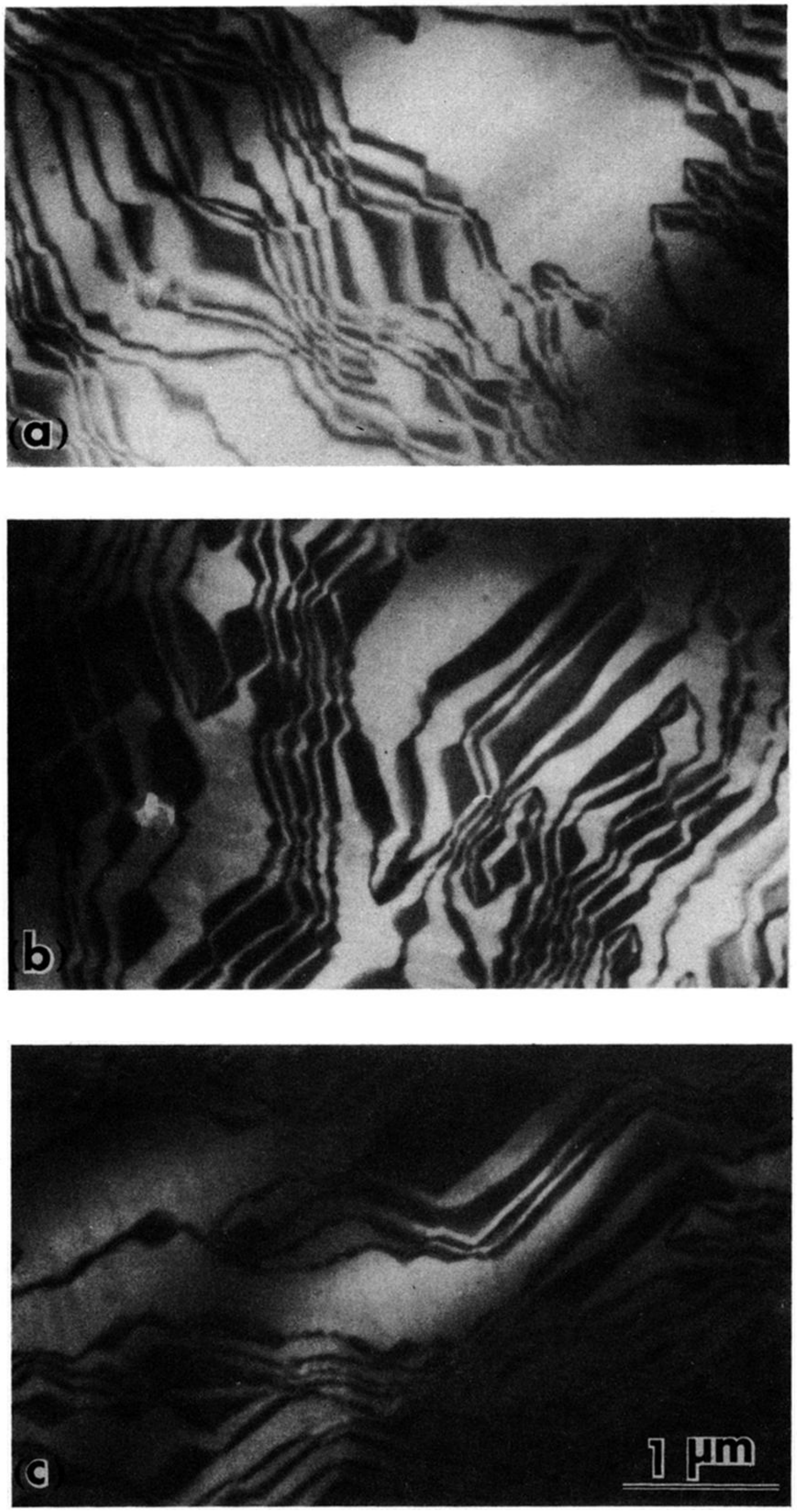

FIG. 15. (a)—(c) Triple-q imaging at 86 K in the "hexagonal" phase on cooling. Image characteristics are similar to the orthorhombic domains in the commensurate phase (Fig. 1); i.e., a domain appears dark for only one particular imaging direction and appears bright for the other two imaging directions.

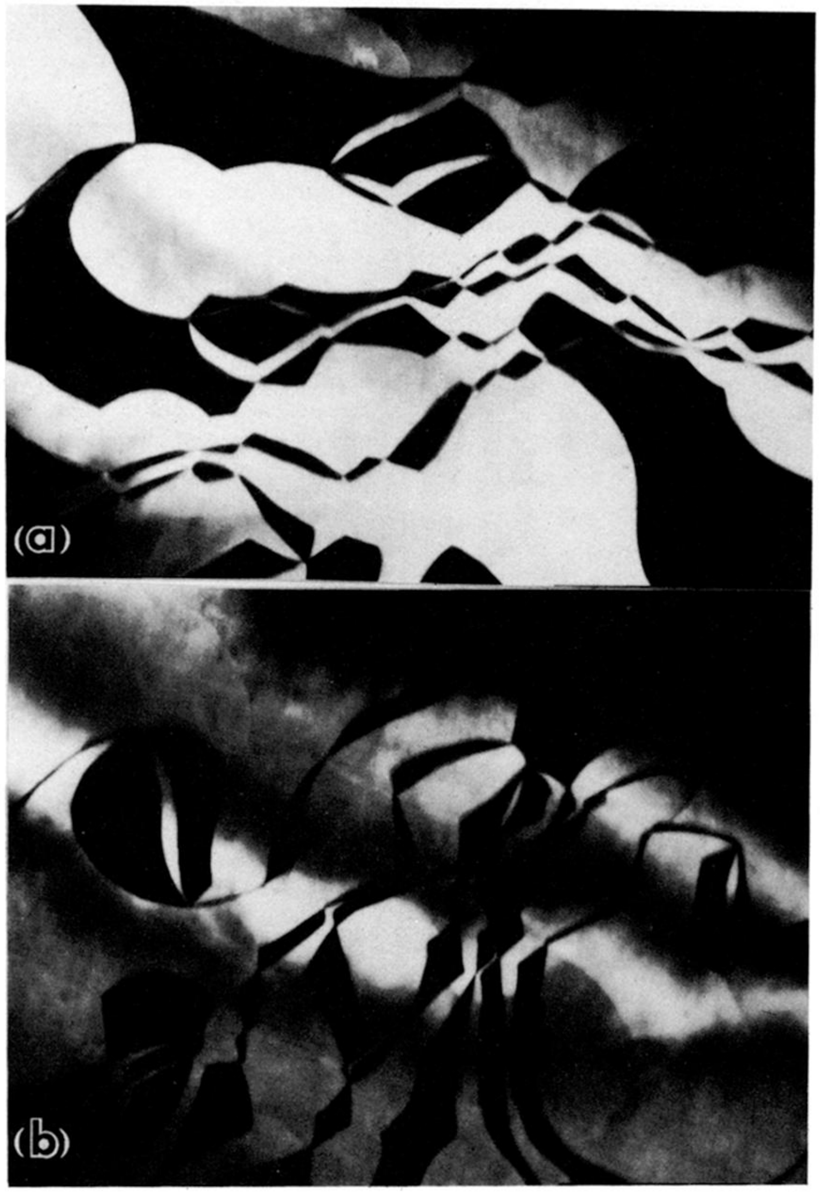

FIG. 1. (a)–(c) Images taken at 33 K in the commensurate phase along the three direction of the CDW wave vectors q_1, q_2, and q_3; (d) shows the image of the same areas as (a)–(c) taken with different superlattice reflection spot although the imaging direction remains the same as (a). The contrast is reversed in this case as compared to (a). (e) Line diagram showing the combined domain patterns of (a)–(c).

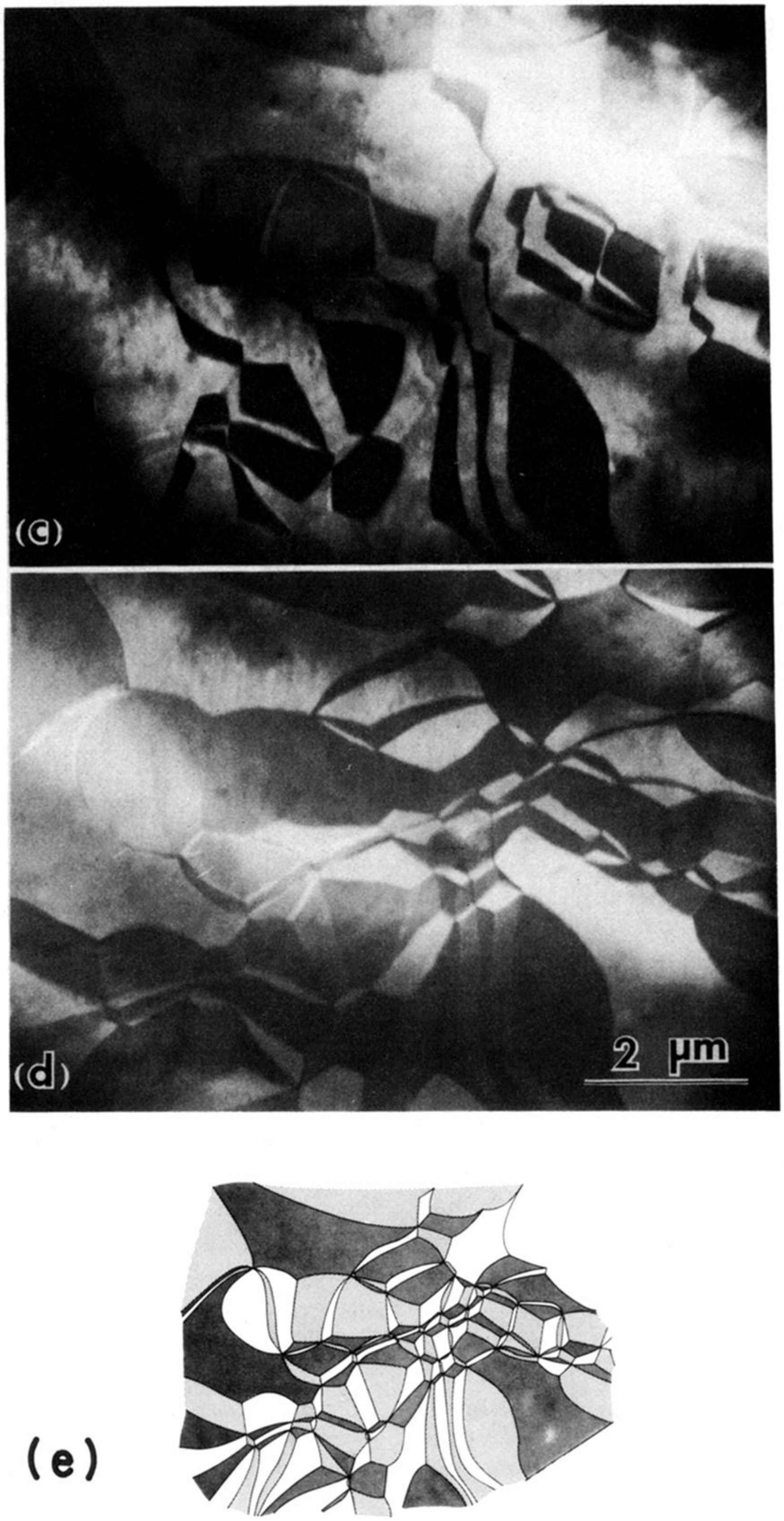

FIG. 1. (*Continued.*)

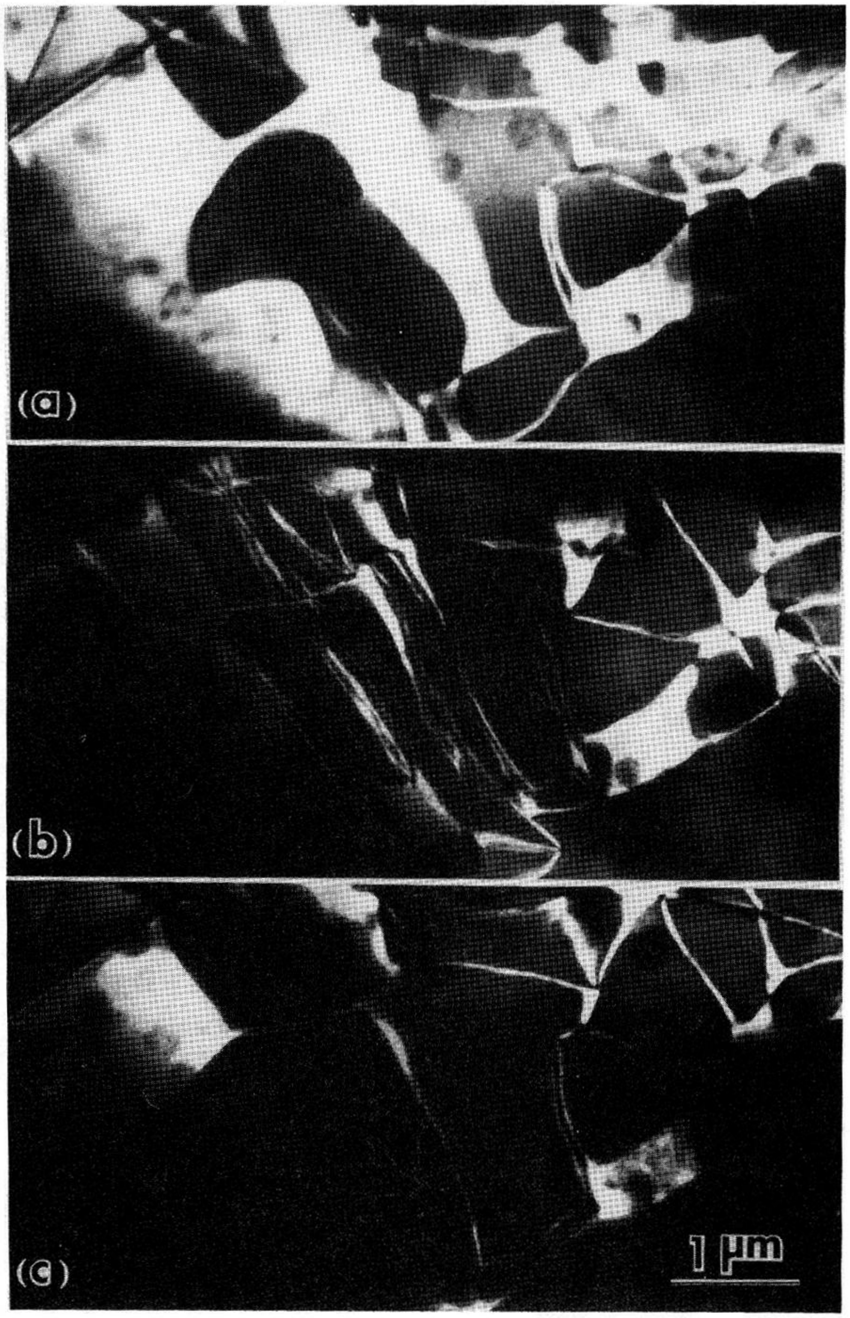

FIG. 2. Indication of the weak pinning nature of the domains in the commensurate phase. (a) shows a domain pattern obtained at 80 K on warming from 30 K. (b) shows the same area after being heated up to ~100 K and then cooled down to the same temperature of 80 K. (c) is obtained from (b) after being cooled down to 50 K and then warmed up to 80 K.

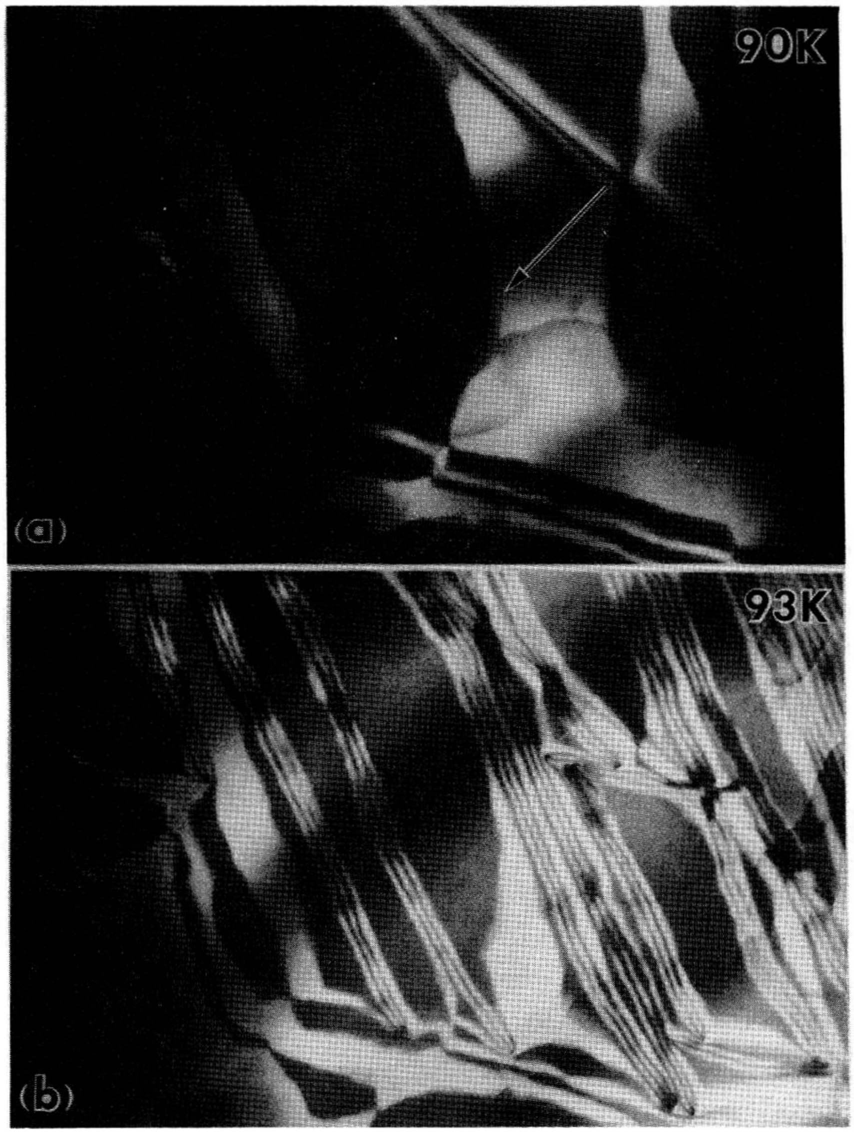

FIG. 3. Evolution of the stripe phase from the orthorhombic commensurate phase. Imaging direction is also indicated by the arrow.

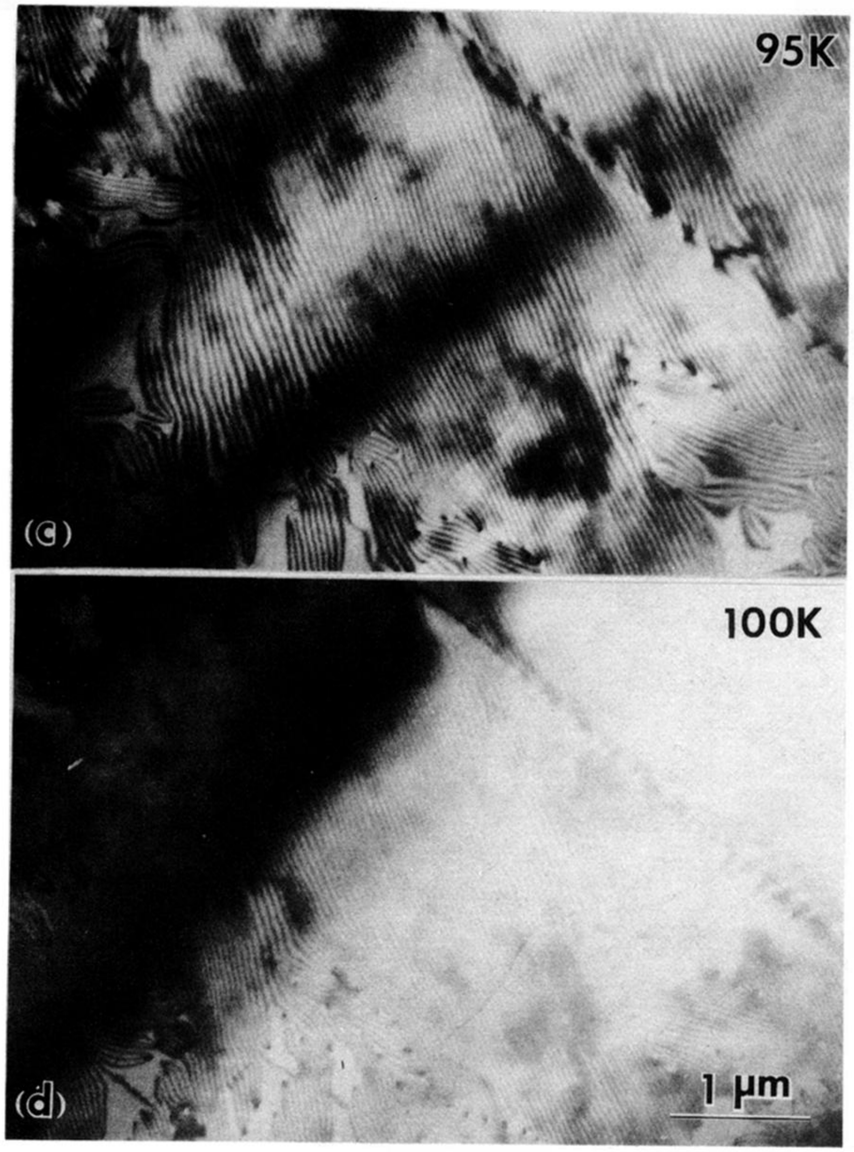

FIG. 3. (*Continued.*)

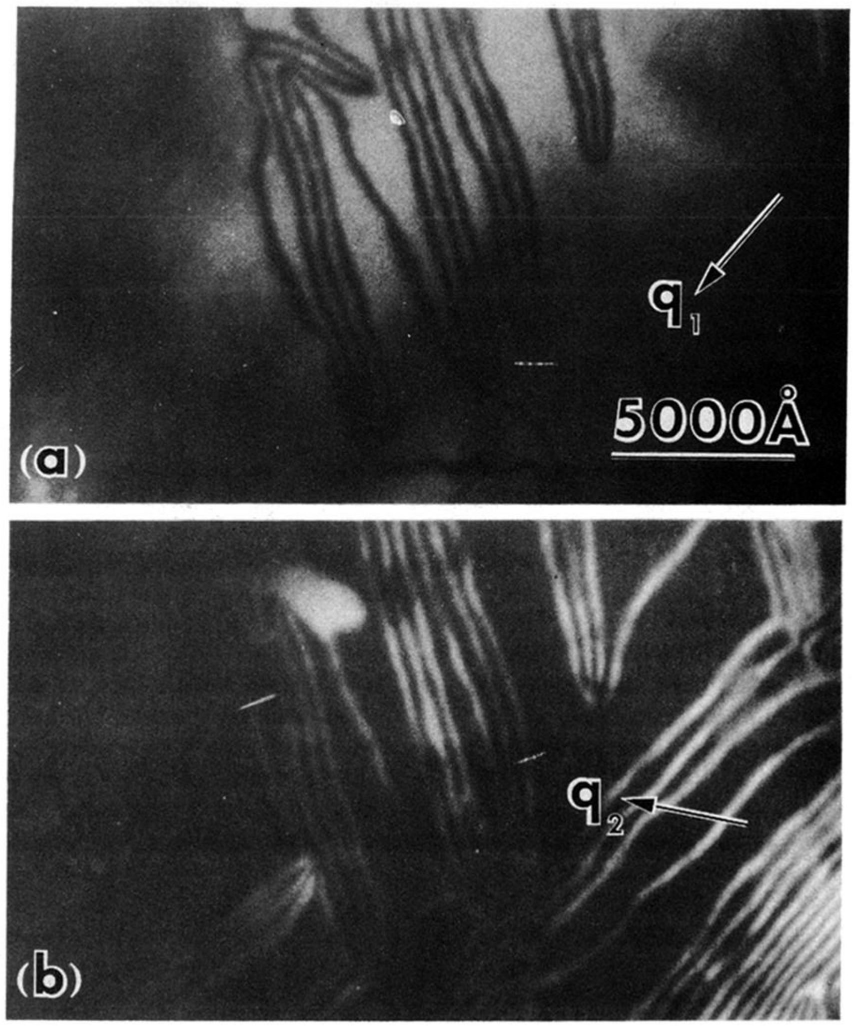

FIG. 4. Stripes images obtained at 94 K on warming when the imaging direction is changed from (a) q_1 to (b) q_2 direction. A reversed contrast for the $q_1 \mid q_2$ stripes running $\sim 20°$ to the vertical direction can be clearly seen.

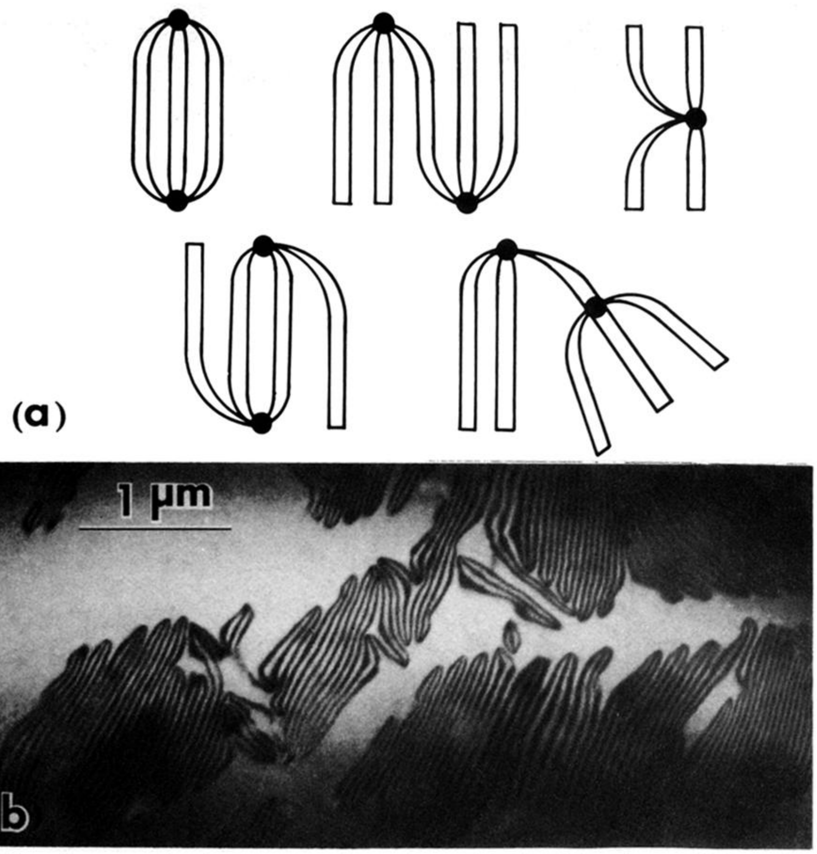

FIG. 6. (a) Line diagrams showing many configurations of CDW dislocations which can be seen in (b).

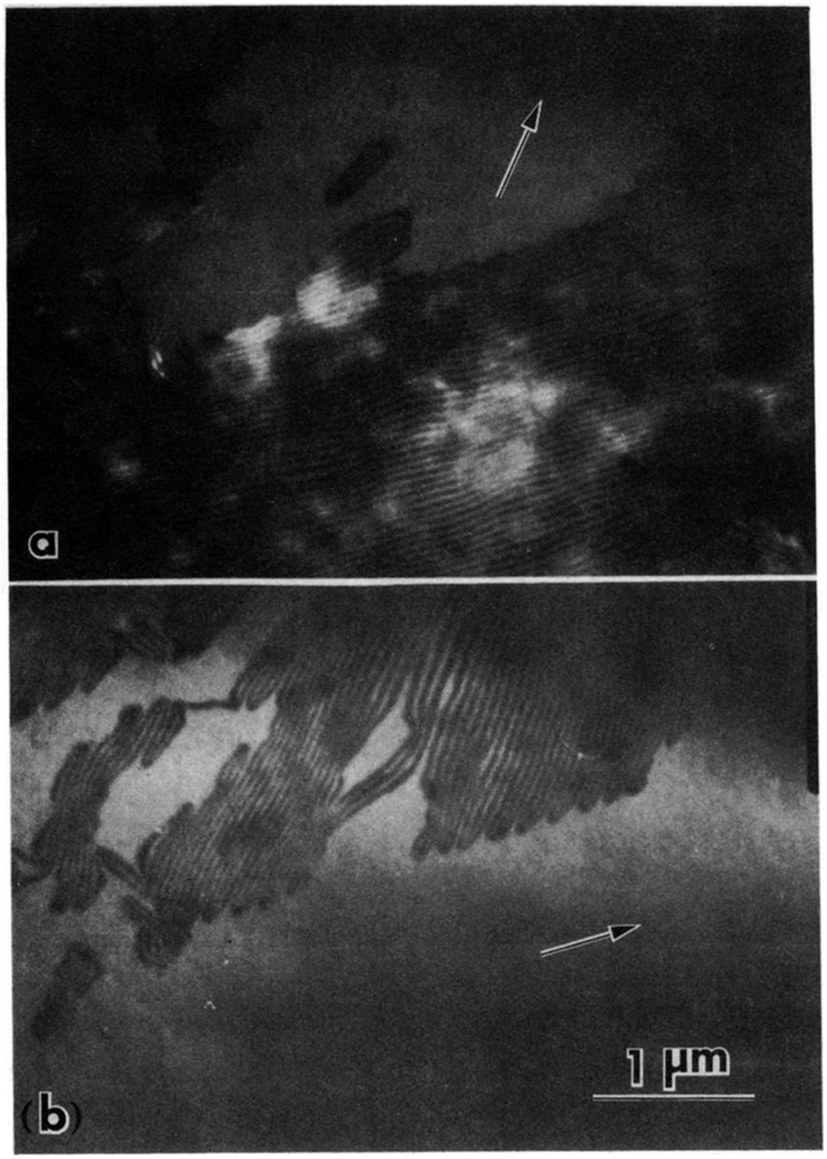

FIG. 8. (a)—(c) Images taken at 94 K in the stripe phase along the three CDW wave-vector directions as indicated. (d) is obtained after a small thermal cycle is compared with (a). Stripe patterns are clearly different.

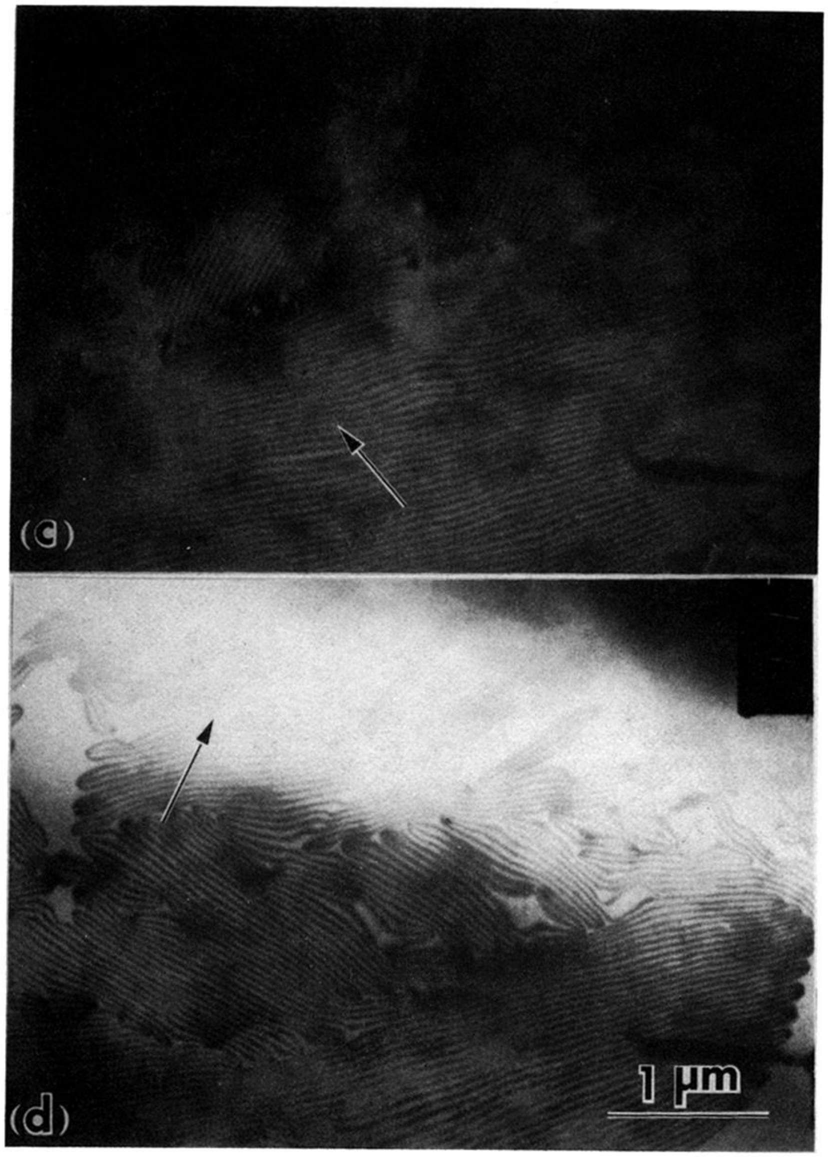

FIG. 8. (*Continued*.)

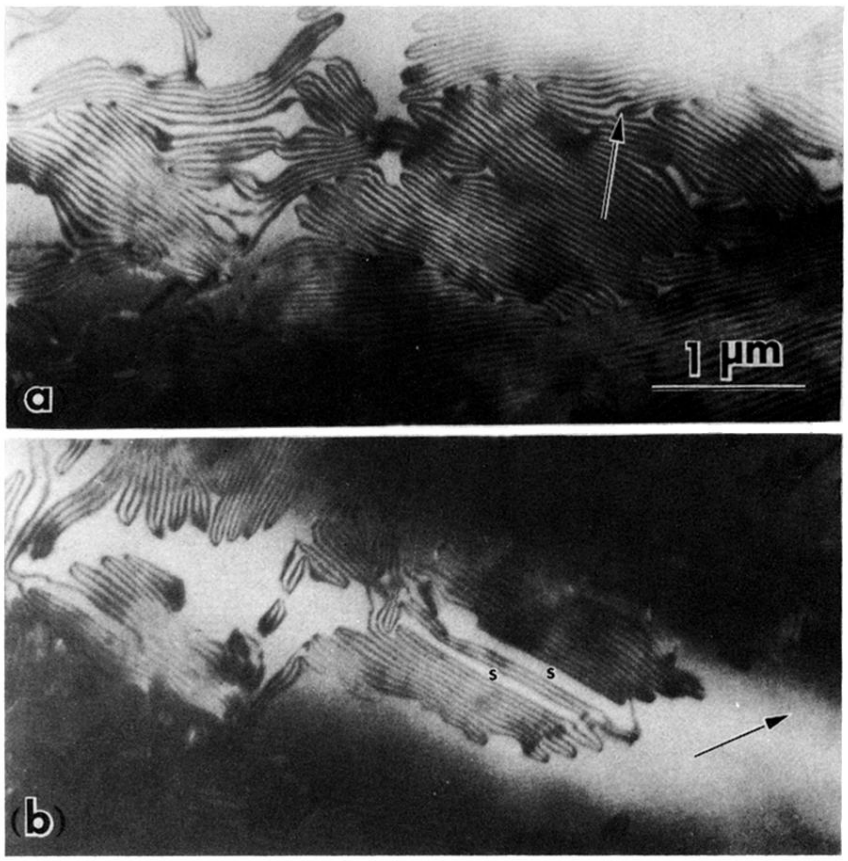

FIG. 9. Two relatively wide bright stripes marked by *s* in (b) are identified as a stacking fault in the stripe phase. The images are taken at 94 K.