PHYSICAL REVIEW B VOLUME 27, NUMBER 7 1 APRIL 1983

Time-dependent strandlike domains in the charge-density-wave states of $NbSe_3$: An effect not induced by electric field

C. H. Chen, R. M. Fleming, and P. M. Petroff
Bell Laboratories, Murray Hill, New Jersey 07974
(Received 28 October 1982)

We have made observations of the strandlike domains associated with the charge-density-wave phase transitions in $NbSe_3$ with electric fields applied along the *b* axis of the crystal. No electric-field—induced changes of the strandlike domains were observed suggesting that the time-dependent images observed in $NbSe_3$ by dark-field electron microscopy [K. K. Fung and J. W. Steeds, Phys. Rev. Lett. 45, 1696 (1980)] do not originate from the depinning of charge-density waves by electric fields. We note that the time-dependent images are found only in a minority of the samples that we have examined. The origin of the strandlike domains and its time-dependent effect in $NbSe_3$ remains obscure at present despite our thorough understanding of the domain structures of incommensurate charge-density waves in other systems such as 2*H*-$TaSe_2$.

Recently, an electron microscopy study of $NbSe_3$ using a dark-field technique[1] revealed many fascinating microstructures related to the charge-density-wave (CDW) states. The study showed that strands approximately 200 Å in width and 2 μm in length were arranged parallel to the conducting *b* axis. The size of the strands was found to be relatively constant as a function of temperature. The most interesting feature of this initial electron microscope study was the observation of time-dependent "twinkling" of the strands at low temperatures. Sometimes individual strands would light up, branch, or vanish in fractions of a second. This twinkling frequency was found to increase as the temperature was lowered below ~ 59 K. It was noted that the twinkling effect was not something that always occurs on all the samples all the time. Although the twinkling is definitely associated with the CDW satellite reflections, the conditions which produce twinkling are not known. X-ray diffraction measurements show that the two CDW's in $NbSe_3$ are incommensurate.[2] The CDW's are presumably pinned to the lattice by impurities at low electric fields, but above a threshold field (on the order of 10 mV/cm) a nonlinear response thought to be associated with a depinning of the CDW occurs.[3] It has been speculated that the twinkling of the strandlike structure is perhaps a phenomenon that appears as a result of the depinning of CDW's by an electric field. Although no electric field was deliberately applied in the experiment of Ref. 1, the charging fields due to the secondary electron emission from the irradiated areas are always present.

In this paper we wish to report electron microscope observations of the strandlike domains with applied electric fields along the conducting *b* axis of $NbSe_3$ crystals. We have varied the strength of the electric field through the threshold depinning field and found that the electric field has no effect on the strandlike domain structure and does not induce twinkling of the strands. We find that the twinkling effect is sample dependent—some samples twinkle and some do not.

The crystals of $NbSe_3$ grow as ribbon-shaped whiskers of monoclinic structure[4] with the whisker axis along $\vec{b}$ and the plane of the ribbon parallel to $\vec{c}$. Very thin whiskers are chosen for the present purpose since they are usually thin enough for transmission electron microscopy (TEM) and no further cleavage of the crystals is required. For the application of electric fields along the *b* axis, the whiskers are mounted in parallel across a narrow slit of mica with the use of silver paint. Electrical continuity of each thin whisker is checked inside the electron microscope by passing current through the two electrical leads of the sample and observing the motion of the bend contours which occurs as a result of heating of the whisker. For those whiskers that are not electrically continuous, no changes of the bend contours are observed. In the vicinity of the whiskers thin metal foil shieldings were used to minimize the charging effect of the sample.

A JEOL 200-kV electron microscope equipped with a single-tilt liquid-helium cold stage was used. The stage provides electrical feedthrough to the sample and temperature control in the range 16 to 400 K with a stability ~ 0.1 K over a period of 5 min. The spatial resolution of the cold stage is estimated to be better than 50 Å. Dark-field images were formed with the superlattice reflections produced by the two CDW phase transitions. Our electric field measurements were made while observing dark-field images associated with the higher-temperature CDW transition (~ 144 K). We chose the higher-temperature CDW satellites primarily because the satellite intensities and consequently the dark-field images were stronger. There are no essential differences in the dark-field images[1] or the electrical response[3] between the two CDW phase transitions.

Figure 1 shows a strandlike domain structure from a thin whisker that does not twinkle and has no applied electric field. These strandlike images are similar to those reported in Ref. 1. From Fig. 1 we see strands ~300 Å wide that run parallel to the *b* axis. In contrast with samples which show twinkling, no fringes along the strands are observed. We have observed the strandlike images as shown in Fig. 1 in all samples. Recent electron microscopy studies[5-7] of the CDW microstructure of $2H$-$TaSe_2$ in the incommensurate phase have confirmed a long-standing theoretical prediction stating that the incommensurate phase is composed of small commensurate domains separated by narrow domain walls or discommensurations. In view of this observation, it is difficult to understand why the strandlike domains appear to be parallel to the *b* axis in $NbSe_3$ since the CDW wave vector is commensurate in both a^* and c^* directions and incommensurate only in the b^* direction.[2] If the strandlike domains are commensurate domains, which are formed because of the incommensurability, then we would expect the strands to run perpendicular to the *b* axis. Furthermore, unlike CDW's in $2H$-$TaSe_2$ in which the domain sizes vary with temperature in the incommensurate phase, the strand dimensions in $NbSe_3$ remain relatively insensitive to temperature changes. X-ray measurements of incommensurability as a function of temperature also reveal a flat response.[2,8]

In $NbSe_3$ the model of electric field depinning of CDW's[9] has provided a framework for the qualitative understanding of many transport properties. We hoped that with the application of electric field we might be able to obtain important information about the strandlike structures and the twinkling effect. By varying the electric field slowly from zero to ~0.5 V/cm (well over the threshold depinning field), we find that the electric field neither changes the strandlike structure nor causes the strands to twinkle. In other words, the images obtained with an applied electric field are identical to the image shown in Fig. 1 without an electric field. This is very surprising since one would expect the lattice distortions to follow the motion of the CDW's once they are depinned by the electric field. This leaves us with two fundamental questions: What are the strandlike structures (are they really associated with CDW's) and what makes them twinkle under the yet unknown conditions? Our observations indicate that the twinkling effect is sample dependent and it does not occur very often among the samples we have examined. Our statistics reveal that from all the thin whiskers we have examined (over 50) less than 20% of the whiskers show twinkling, indicating twinkling is a somewhat rare phenomenon among the $NbSe_3$ whiskers. No apparent differences (such as crystal structure, defect, strains, etc.) between whiskers that twinkle and those that do not can be seen by standard transmission electron microscopy, although subtle differences in chemical compositions cannot be ruled out. A couple of different types of microstructure, as shown in Fig. 2, have been observed for whiskers that show the twinkling effect. Figure 2(a), which is similar to that reported in Ref. 1, contains regular fringes (~1000 Å apart) running along the strands. The appearance of the fringes was interpreted as Moiré effect due to slight differences (both in direction and magnitude) of the CDW wave vectors in the adjoining strands. Figure 2(b), lacking the well-defined fringes, however, shows only the irregular arrangement of broken segments of the strands. The physical significance of the differences in the microstructure is not understood at present.

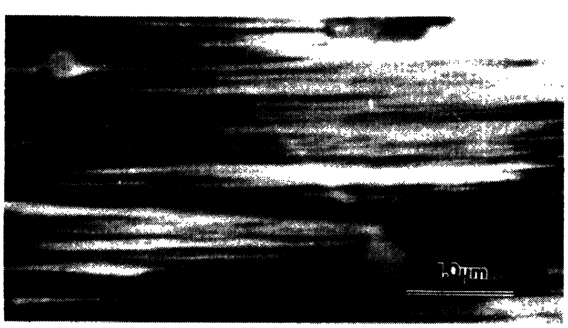

FIG. 1. Strandlike domain structure obtained by dark-field imaging using a CDW superlattice reflection. No electron field has been applied along the whisker axis of the crystal. The image remains unchanged after turning on the electric field above the depinning threshold.

Our studies also reveal that the thermal history of the samples appears to bear no direct correlation to the occurrence of the twinkling effect, although on many occasions twinkling is observed after the whiskers have been warmed up to temperatures ~170 K and then cooled down again. We conclude that although the twinkling effect does not depend on an applied electric field its origin remains a mystery. The fact that only a minority of the samples show the effect is particularly perplexing.

Let us now turn to the first question: What are the strandlike structures? Are they really induced by CDW phase transitions? It is natural to ask these questions since, as we have mentioned earlier, the existence of the strandlike structures is difficult to understand with the current understanding of incommensurate CDW's in other systems such as $2H$-$TaSe_2$, etc. In the case of $2H$-$TaSe_2$, dark-field domain contrast in the incommensurate phases arises from orthorhombic distortions of the hexagonal sym-

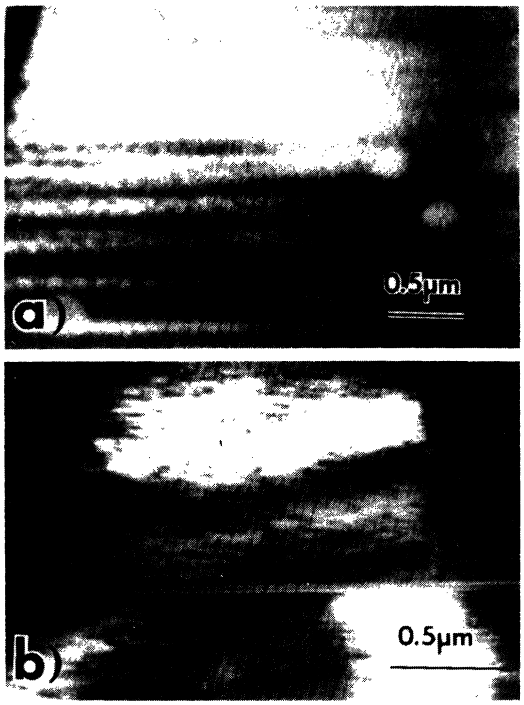

FIG. 2. Two types of CDW microstructures observed frequently in whiskers that show twinkling effect: (a) shows regular fringes (~ 1000 Å apart) running along the strands; (b) however, shows only the irregular broken segments of the strands.

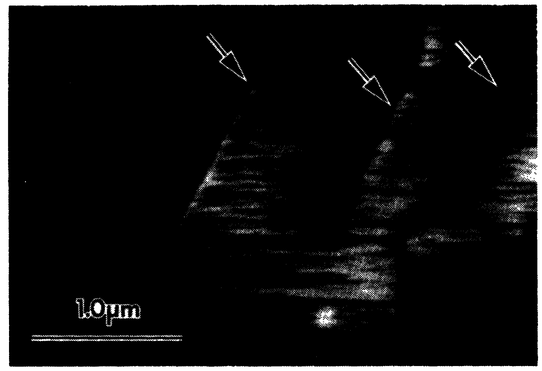

FIG. 3. Changes of strand contrast across dislocation lines. Dislocation lines are indicated by arrows.

metries along one of the three CDW wave vectors.[5,6] The origin of the contrast of the strandlike domain structures in $NbSe_3$ is, however, not so clear. We have done a number of observations toward this end. First, we have recorded and compared the strandlike domain structure after thermal cycles. We found that the detailed arrangement and the visibility of the strands are not the same. However, this may be due to the change of strains in the sample between thermal cycles. We have also recorded images of the same area using different-order CDW superlattice reflections in order to see if the contrast might change. In $2H$-$TaSe_2$ it was shown[5,6] that the domain contrast remains unchanged for different-order CDW superlattice reflections as long as the imaging direction remains the same. In $NbSe_3$, unlike the $2H$-$TaSe_2$, we find that contrast of strandlike domains varies with different-order CDW reflections. Furthermore, crystalline dislocations which do not affect the CDW domain microstructure in $2H$-$TaSe_2$ seem to have a significant effect in $NbSe_3$. Strands on each side of a dislocation line do not seem to have the same contrast indicating the extreme sensitivity of strand contrast to the strain fields. This is shown in Fig. 3. We also note that the strand contrast remains essentially unchanged as the sample thickness changes. We have observed strand structure in an area where thickness changes in steps and strands are found to run across the steps without any significant changes in contrast.

In conclusion we still have difficulties, however, in understanding the strand domain structure and its twinkling effect in $NbSe_3$ despite what we have learned about their properties. Possible explanations include Moiré fringes[1] and CDW discommensurations. Both of these effects would have to be associated with the CDW lattice only since no strandlike contrast can be seen in images using the main $NbSe_3$ lattice reflections. Either of these explanations would require the CDW to be incommensurate in a direction perpendicular to b^*. Scattering experiments done thus far have not had sufficient resolution to investigate this possibility. It should be noted that $NbSe_3$ is not the first and only crystal that has been observed to show the twinkling effect. In fact, it was found[10] a number of years ago that dark-field images obtained from using the ω-phase superlattice reflections in Nb-Zr alloys also showed the twinkling effect. The effect in this case was interpreted as due to fluctuations between the metastable ω phase and the β b.c.c. phase.

Finally, we note that similar strandlike structure and twinkling effect are also observed in orthorhombic TaS_3 in which the CDW's have been shown to be commensurate[11,12] in all three directions. This indicates that the strand domain structure and the twinkling effect may be common to this class of materials and may not have anything to do with the incommensurability of the CDW's. However, high-resolution scattering experiments are also required in this case in order to be sure that the CDW's in the directions perpendicular to the whisker axis are truly commensurate. The experimental result of TaS_3 will be published elsewhere.

[1]K. K. Fung and J. W. Steeds, Phys. Rev. Lett. 45, 1696 (1980).

[2]R. M. Fleming, D. E. Moncton, and D. B. McWhan, Phys. Rev. B 18, 5560 (1978).

[3]R. M. Fleming and C. C. Grimes, Phys. Rev. Lett. 42, 1423 (1979); N. P. Ong and P. Monceau, Phys. Rev. B 16, 3443 (1977).

[4]J. L. Hodeau, M. Marezio, C. Roucau, R. Ayroles, A. Meerschaut, J. Rouxel, and P. Monceau, J. Phys. C 11, 4117 (1978).

[5]C. H. Chen, J. M. Gibson, and R. M. Fleming, Phys. Rev. Lett. 47, 723 (1981).

[6]K. K. Fung, S. McKernan, J. W. Steeds, and J. A. Wilson, J. Phys. C 14, 5417 (1981).

[7]C. H. Chen, J. M. Gibson, and R. M. Fleming, Phys. Rev. B 26, 184 (1982).

[8]R. M. Fleming, D. E. Moncton, and J. D. Axe (unpublished).

[9]P. A. Lee and T. M. Rice, Phys. Rev. B 19, 3970 (1979).

[10]A. L. J. Chang, W. Krakow, and S. L. Sass, Acta Metall. 24, 29 (1976).

[11]K. Tsutsumi, T. Sambongi, S. Kagoshima, and T. Ishiguro, J. Phys. Soc. Jpn. 44, 1735 (1978).

[12]C. Roucau, R. Ayroles, P. Monceau, L. Guemas, A. Meerschaut, and J. Rouxel, Phys. Status Solidi (a) 62, 483 (1980).

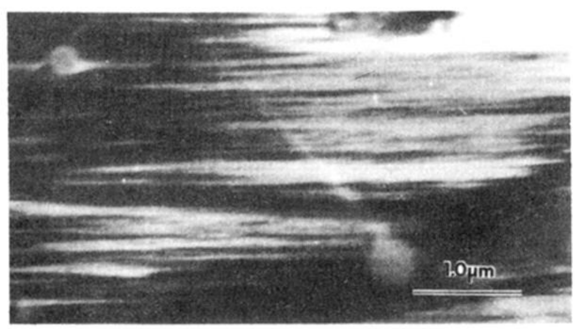

FIG. 1. Strandlike domain structure obtained by dark-field imaging using a CDW superlattice reflection. No electron field has been applied along the whisker axis of the crystal. The image remains unchanged after turning on the electric field above the depinning threshold.

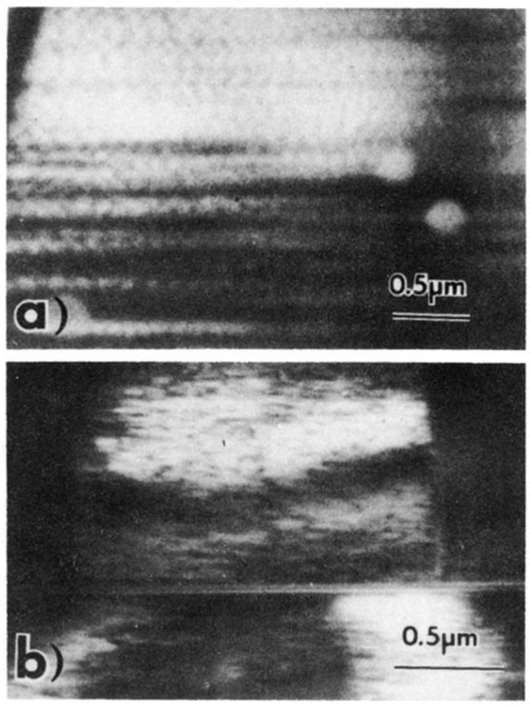

FIG. 2. Two types of CDW microstructures observed frequently in whiskers that show twinkling effect: (a) shows regular fringes (~1000 Å apart) running along the strands; (b) however, shows only the irregular broken segments of the strands.

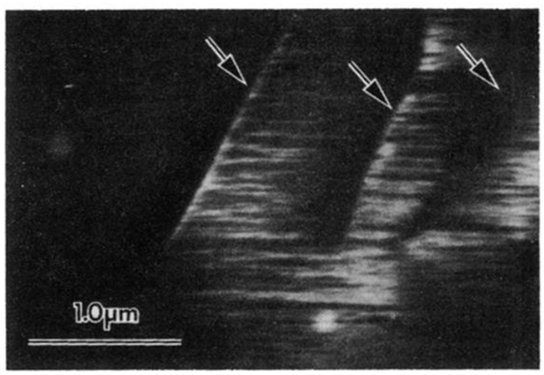

FIG. 3. Changes of strand contrast across dislocation lines. Dislocation lines are indicated by arrows.