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Twin Boundary in Bechgaard Salt: Structure and Unusual Dynamics

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PACS.61.72.Mm − Grain and twin boundaries
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Abstract. — Structure and dynamics of twin boundaries in (TMTSF)2PF6 were studied. From microscopic observations, they are planar in shape and their width is less than 20 nm. No change in their shape was found. Their movement and pair annihilation do not leave any trace in the crystal surface. Their motion under external force as well as spontaneous movement are intermittent and chaotic. Role of internal degree of freedom is essential.

1. Introduction

In this paper we report on the structure and dynamics, forced motion under external stress as well as spontaneous movement, of the twin boundary (referred to as "kink" hereafter) induced in single crystals of (TMTSF)2PF6. The crystal structures of (TMTSF)2X, so called Bechgaard salts, are triclinic. It is, therefore, possible to grow both right-handed and left-handed crystals as twins. Mechanical twinning can be also expected. Just after the synthesis of (TMTSF)2X Bechgaard was already aware that kinks can be introduced into the crystals and that they show a peculiar behavior under external force. Schwenk et al. [1, 2] were the first to report these interesting phenomena. They [1] report that kinks can be easily created and that they move under small lateral force. Later, they [2] observed that the crystals contain localized regions, through which a larger force is necessary for the kink to move, and that it moves freely in some crystals. Based on these observations, they argued that the range of deformation associated with the kink is macroscopically large. Ishiguro et al. [3, 4] found from analysis of X-ray precession photographic images, that the kinks are parallel to (210) and that the two sides separated by a kink are in mirror symmetry with respect to (210).

In our previous work [5], motion of a single kink under lateral force was studied, wherein we confirmed that a weak external force can drive the kink over a macroscopic distance. Its motion was found to be hysteretic even though constant force was continuously applied. In particular, the kink moves intermittently under constant force with rapid movement and intermission being repeated as it is displaced along the needle. We have verified that the intermittency is not attributable to any experimental setup and that the intermittent motion is reproducible.

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The positions at which the kink stops during intermission are well defined. These positions, though not regularly arranged, are independent of the magnitude of stress. Although they cannot be assigned by microscopic observation, strong potential barriers due to lattice defects are presumably distributed in such positions. Just before an intermission, the kink is often decelerated gradually and then it stops rather suddenly. After the velocity begins to decrease, the kink moves by $20 \sim 30 \mu m$, a distance that it is 3 orders of magnitude longer than the upper bound of kink width estimated in the next section of this paper. The kink motion is resumed after intermission, the intermission being shorter for larger stress. When the stress is large enough, the kink does not stop but shows temporal deceleration at these positions. Only under the smallest stress used in [5], can its motion be expressed phenomenologically by that of a massless body in a viscous medium.

2. Crystal Growth and Formation of Kink

Single crystals of (TMTSF)$_2$PF$_6$, which are needle-shaped were grown by the standard electrochemical method. As shown previously by Ishiguro et al. (Fig. 3 of Ref. [4]), natural crystal facets are clear in all crystals, of which Miller indices are (001), (011), (011), (011) and (011). We found two additional sets of planes, which were assigned as (010) and (010) from the angles between neighboring facets.

When a large couple of forces is carefully applied, kink-antikink pair is usually created. More kinks can be created simultaneously. The kink is in a form of sharp bend of crystal, which can be identified clearly even by naked eye. The angle of $\sim 20^\circ$, between the two sides separated by a kink, is consistent with the findings of Ishiguro et al. [3, 4] i.e. that they are in mirror symmetry with respect to (210).

We compared the X-ray oscillation photographic images from the two sides separated by a kink. Initially the a-axis of one side was adjusted parallel to the rotation axis. After recording the diffraction image from that region, the sample orientation was adjusted so that the a-axis of the other side was parallel to the rotation axis. Both images gave the same layer line spacing. On comparing the two diffraction patterns, it was found that the images from the two regions are in mirror symmetry with each other with respect to the 0-th layer line. It was confirmed that the crystal is twinned, one part being right-handed while the other is left-handed.

3. Static Structure

The structure of the kink in (TMTSF)$_2$PF$_6$ was studied at sub-micron scale to find out whether a kink at rest is localized or extended, and if any trace of kink movement and of pair annihilation remains within the crystal. Optical- and scanning electron-(SEM) microscopes as well as the atomic force microscope (AFM) were used at room temperature.

Figure 1 is the AFM height image of a set of three kinks, recorded by scanning in the direction perpendicular to the a-axis. The line of intersection of a kink with the surface is microscopically straight. The kink is rather flat, not wavy, even in areas where natural growth steps appear at the surface. Elastic interaction is expected between the kink as a mobile defect and other types of lattice imperfection. The kink plane may be distorted if it is constrained to an area where imperfections are concentrated, just like the surface of constant phase of the charge/spin density wave embedded in distributed impurities. However, no distortion of the kink at rest was observed by AFM observation. From a detailed examination of recorded CCD images presented in the next section, we found that moving kinks are flat within a resolution of 5 $\mu m$. Therefore, even if the kink plane is not flat, the distortion occurs over a smaller length scale.
From Figure 1, the height of the sample surface shows a sharp bend at the kink and no sign of finite width can be found. From the AFM image and SEM photographs at large magnification, it is estimated that the upper bound of the kink width is smaller than 20 nm. On the other hand, there is no a priori reason to expect that the crystal bends discontinuously, within a molecular distance, at the kink. The TMTSF molecular column bends at the kink with the molecules on the two sides that are not parallel to each other but make an angle ~ 20°, which requires energy. In addition the distance between anions is also changed. The kink width should depend on these factors.

When a lateral force is applied to a kink-antikink pair, the kink and antikink are displaced in opposite directions. The pair is stable even when the mutual separation is reduced to < 40 nm indicating that the interaction between a kink and an antikink should be of short range. It was observed that they annihilate on further reduction of the separation, though the limiting distance could not be determined.

We recorded the AFM image of an area where a kink had passed through and compared it with the image of the same before passage. No trace of kink movement was detected in these images implying that the passage of kinks does not leave any permanent deformation or damage within the crystal. The area where a kink-antikink pair had been annihilated was also examined. No indication of pair annihilation was detected from AFM images within resolution of ~ 10 nm.

4. Dynamics

The displacement of isolated kinks under constant external force was measured at room temperature by an optical microscope equipped with a CCD camera. Images were recorded with a commercial video-recorder. The time resolution was 1/30 s. A force perpendicular to the needle was applied by bending a thin quartz tube in contact with the sample. It was kept constant within 1% during kink motion. Details of our experimental technique have been published previously [5]. Figure 2 shows the position of an isolated kink as a function of time
Fig. 2. — Position of a kink as the function of time elapsed after the set-in of motion. (a) in one direction and (b) in the other direction. Shear stress, 0.84 g·weight/mm², was calculated from the applied force divided by the sample cross-sectional area, 2 × 10⁻² mm². Different symbols denote different runs.

after motion has set in under constant force. The observed area is far from the tips of the sample and also far from the positions where a strong force was applied during kink creation. As the reference of position, we used characteristic positions of the sample, e.g., irregularity of its shape. Attention was paid throughout this work not to drive the kink to these reference positions.

Intermittency of its motion is apparent. While we argued in the previous paper [5] that it is not attributable to any experimental setup, more decisive evidence for intrinsic nature of this intermittency was obtained by observation of spontaneous intermittent motion. Schwenk et al. [2] already noted that there are local regions in which the kink moves by itself without any applied stress. We observed that, after a kink moved freely and stopped at a position, movement in the same direction was resumed after an intermission shorter than one second. In our experiment, the orientation of samples was adjusted so that the kink moves in a horizontal plane and any effect of gravity is excluded.

The locations where the kink stops or is decelerated under larger stress are independent of the magnitude of stress. From comparison of Figure 2a with 2b in which the same kink moves in the opposite direction, the positions of intermission are independent of the direction of motion. While some defects localized in these positions presumably work as the barrier for the kink motion, it is not likely that these defects are simple lattice imperfections such as point defects and dislocations because we have shown previously [5] that the kink is decelerated when it passes through a region of 10 ~ 20 μm before stopping. The stress field of these simple imperfections is not extended to control the kink motion over a millimeter-micron distance. Surface irregularities might be equally effective. However, we observed that the kink continues to move where the surface does not look so smooth.

Figure 3 shows repeated records of the position of a kink moving in one direction under the same conditions. To record the motion of a kink repeatedly, we used the following procedure: after a run, the kink was pushed up to the initial position by another force in the opposite direction while the measuring force was kept applied. Just after the second force was released the next run was initiated in the same direction. While the positions of intermission are clearly displayed in the figure, the kink is decelerated temporarily at several other positions. The time
Fig. 3. — Position of a kink under the external stress of 0.79 gr-weight/mm². Different symbols denote different runs.

Fig. 4. — a) Relations between the average velocities $V_1$ (filled circles) before intermission at $x = 0.13$ mm and $V_2$ (open diamonds) after and the time of intermission $\tau_1$. b) Relation between $V_1$ and $V_2$. Applied stress was 0.84 gr-weight/mm².

of intermission and the velocity between successive intermissions are widely distributed. As measurements were repeated, rapid and slow motion was observed in random sequence without any systematic variation of the overall velocity; no permanent effect of repeated runs on the lattice or on the kink itself was found.

The possibility of a correlation between the time of intermission and the average velocities between successive intermissions was examined. Figure 4 shows the mutual relations between the time of intermission $\tau_1$ (at $x = 0.130$ mm in Fig. 3), the average velocities $V_1$ (in the area between $x = 0.075$ mm and 0.130 mm) and $V_2$ (between $x = 0.130$ mm and 0.200 mm). Clear correlation is found between them; when the kink moves with high velocity, the time of intermission is short and it moves again with high velocity. From Figure 4b, the velocities in the two areas are approximately the same; $V_1 \approx V_2$. This result shows that the kink or
the barrier has the internal structure or internal degree of freedom by which the capability
to memorize the kink velocity prior to intermission is provided. Though not revealed in the
surface observations presented in the previous section, finite width as well as some curvature
should be carefully examined in future works.

The scatter of the overall velocity is not attributed to that of the external force. We have
observed repeated records of the same kink in the same area under different magnitudes of
force and found wide scatter of the velocity in all data. Nevertheless, the center of distribution
of the overall velocity is located at a larger value under a larger force. If the scatter shown
in Figures 3 and 4 is a result of insufficient control of force, the uncertainty of the magnitude
of force should be as large as 10% or more. Prior to the set-in of motion the external force
itself was adjusted with an accuracy much better than 1%. Even if some friction is present
between the sample and quartz actuator, it is not plausible that the frictional force is the origin
of the wide distribution of both the local velocities and the time of intermission. If friction is
significan, systematic increase or decrease of the overall velocity with repeated runs should
be expected as the result of smoothing or roughening of the contact area. While an effect
of friction may not always be neglected, such a systematic change of the kink velocity was
observed. Elastic relaxation of the quartz actuator does not play any significant role in our
experiment. If a kink moves rapidly while the quartz tube remains bent, the force on the kink
might decrease or the contact with the tube might even be lost. As a result the kink might
stop before the contact is recovered. However, we have observed that the bending deformation
of the quartz tube is relaxed without any observable residual in a time scale short enough to
trace the kink motion. In addition, if the force is reduced by the rapid motion the reduction of
the force should be more significant when the kink velocity is larger. As a result, a longer time
of intermission is expected after rapid movement; a large velocity should be correlated with
long intermission. The experimental result shown in Figure 4 is the opposite; large velocity is
correlated with short intermission.

In our experiment, the initial kink position was not adjusted precisely. As a result, the initial
position in Figure 3 is rather scattered. If a potential energy is associated with the barrier,
the sliding velocity at a position would be determined by the initial position. Figure 5a shows
the times of intermissions (τ2 is the intermission time at x = 0.22 mm in Fig. 3) and Figure 5b
the local velocities V1 and V2. Neither the times of intermissions nor the average velocities
show any systematic correlation to the initial position x1. Prior to the onset of motion, the
driving stress was kept applied while the kink was brought into the initial position. Therefore,
no impulse was given to the kink at the onset. From these considerations, it is clear that the
scatter of the overall velocity is not due to uncontrolled initial conditions.

Spontaneous movement is usually completed without retrieval; the kink was at the final
position for at least 1 ~ 3 minutes. Figure 6 shows the displacement without external force
across a region located between two barriers. Free movement was observed only in one direction.
Because the sample orientation was adjusted in our experiment so that the kink moves
horizontally, the spontaneous movement is not due to gravity. The kink moves with high intial
velocity and then is decelerated before stopping. The most significant fact is that the overall
velocity depends on how the kink has been brought to the initial position near one barrier.
When force is applied after the preceding run to push it back to the initial position and then
the force is released (denoted as U-mode), it moves with high velocity and stops at a point.
Even when the kink is brought to the initial position from the opposite side of the barrier after
being driven backward across the freely running area (J-mode), the kink continues to move
without force and stops at the same position. In the latter case, however, the overall velocity
is much smaller and the characteristic time scale is several times larger. This feature was
observed in several samples. Even if some initial velocity is given in the J-mode while crossing
Fig. 5. — a) Times of intermission $\tau$ plotted against the initial position $x_i$. $\tau_1$ is at $x = 0.13$ mm and $\tau_2$ at 0.22 mm in Figure 3. b) Local velocities $V_1$ (in the region $0.075 \text{ mm} < x < 0.130 \text{ mm}$ in Fig. 3) and $V_2$ ($0.130 \text{ mm} < x < 0.200 \text{ mm}$) plotted against $x_i$.

Fig. 6. — Displacement of a kink in the freely running area. Three rapid records are in the U-mode, the other three slow ones are in the J-mode. See text.

the barrier, it is not the origin of the above difference because the overall velocity is smaller in the J-mode than in the U-mode. Presumably, the frictional force acting on the moving kink or the potential provided by barriers is modified by the way in which the kink is brought to the initial position.

In conclusion, the motion of the twin boundary or kink is quite complicated. Even under controlled conditions both the local velocity and the time of intermission vary from run to run; we cannot predict the velocity at a position. Though the positions of intermission are reproducible, we cannot know how long the kink staves at these positions before resuming its motion. In this sense, the kink motion is chaotic. The kink should not be regarded as a simple rigid planar object; presumably it has some hidden internal degree of freedom, e.g.,
local variation of the intermolecular angle, to which the motion resumed after intermission is related. Higher order interaction between kink and barriers should be considered also.

In this work the time resolution of the kink motion was limited by the use of a commercial video-recorder. Kinks more than half in number showed a motion too rapid to be recorded. Hopefully, more information on the kink dynamics can be gained from the observation of rapid transient motion.

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