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Dynamics of isolated twin boundary in $(TMTSF)_2PF_6$

Control of its mobility

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Abstract. Intermittent and irregular motion of isolated twin boundary (kink) in organic crystal $(TMTSF)_2PF_6$ was studied at room temperature. Both the local velocity and the time of intermission are determined not only by external stress and temperature but also by the time (t_w) elapsed after the backward passage and before the following forward one. When the kink moves after longer t_w, its velocity becomes smaller and the time of intermission longer. Both tend to saturate for t_w longer than 10^2 s. This result indicates that some disorder is induced in the lattice by the backward motion and it is relaxed during t_w. We also found that the effect of the backward motion of one kink on its following motion is equivalent quantitatively to that of the forward motion of the pair-created counterpart.

PACS. 61.72.Mm Grain and twin boundaries – 61.66.Hq Organic compounds – 83.50.By Transient deformation and flow; time-dependent properties: start-up, stress relaxation, creep, recovery, etc.

1 Introduction

Schwenk *et al.* first observed that twin deformation occurs easily in single crystals of $(TMTSF)_2X$ salts (TMTSF is tetramethyltetraselenafulvalene, X = PF_6, ClO_4, AsF_6 and NO_3), a family of charge-transfer complexes [1,2]. Single crystals of $(TMTSF)_2X$ are of needle shape and the needle axis is parallel to the triclinic [100] direction. Planar TMTSF molecules are stacked face to face along [100] parallel to each other. When shearing force is applied in a suitable manner, the crystal is not broken but twin deformation occurs in a part of the crystal. The twin boundary between the deformed (D-) and the not-deformed (U-) parts is called "kink" throughout this paper.

Ishiguro *et al.* determined the orientational relation between D- and U-parts by the X-ray precession method [3,4]. The kink is on the (210) plane; D- and U-parts are in mirror symmetry with respect to (210). Twinned crystal is bent sharply at the kink, and the measured angle between D- and U-parts is consistent with the above relation found by Ishiguro *et al.* When a D-part appears between U-parts, a pair of parallel twin boundaries is created. When one is called "kink", the other is called "antikink" hereafter.

Schwenk *et al.* also found that the kink easily moves along the needle axis under weak shearing force and that the angle between D- and U-parts does not change after forced motion. In some areas of some crystals, kinks move spontaneously without external force.

In our previous work, the fine morphology near kinks in $(TMTSF)_2PF_6$ was examined by scanning electron microscopy and atomic force microscopy [5]. The line of a kink plane appearing on the crystal surface is microscopically straight and the kink width is less than 40 nm. As far as observed by optical microscopy, no change in the shape of the kink during motion was found [6]. From these observations, the kink is expected as a planar rigid plane.

We observed how an isolated kink moves repeatedly under constant stress within the same area of the crystal and measured time dependent position of a kink [5–8]. Contrary to the above expectation, it was found that the kink motion is unusual as follows. The velocity $v(x)$ depends strongly on its position x. The kink moves intermittently; it stops at some positions and moves again after intermission ranging over tens of seconds even under constant external stress. The positions where the kink shows intermission are fixed in the crystal and independent of the magnitude of applied shearing force and also of its direction. Based on these results we have argued that the intermission occurs at some strong pinning center like defects and/or impurities but the movement is retrieved by some unknown mechanism [5].

Both the local velocity $v(x)$ and the time during intermission t_{int} were observed to vary from run to run with a large scatter of factor 10 even though the motions were repeated within the same area under the same external force. However, these $v(x)$ curves in the area without intermission coincide with each other when they are normalized by each average velocity [7]. Further, the velocities before and after intermission and t_{int} itself in a run are correlated with each other; when the kink begins to move with a large velocity, t_{int} are short and it moves again rapidly.

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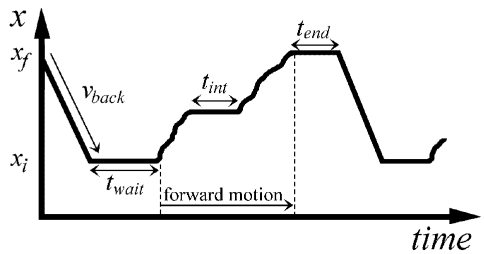

Fig. 1. Schematic time sequence of kink motion. The kink was forced to stay at x_f for t_{end}, to move backward to x_i with the velocity v_{back}, and to stay at x_i for t_{wait} before the following forward motion. The forward motion under constant applied force from x_i to x_f was recorded and analyzed.

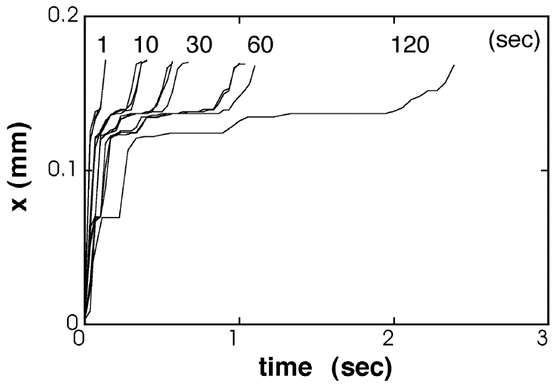

Fig. 2. Time dependent position $x(t)$ for various t_{wait}. Applied stress and v_{back} were 1.6×10^3 Pa and 0.13 mm/s, respectively.

We have argued that each crystal has its own relative $v(x)$ curve and also relative magnitude of t_{int} and that some predetermined factor, which controls the value of average velocity and t_{int}, exists besides the external force and its variety causes their scatter [8].

We observed the spontaneous kink motion reported by Schwenk *et al.* [2]; in some crystals kink can move without external force in restricted areas. The spontaneous motion is also intermittent and that both $v(x)$ and t_{int} scatter from run to run [6]. Thus it is ruled out that the large scatter of $v(x)$ and of t_{int} is caused by insufficiently controlled external force. The spontaneous motion always occurs so as to shrink the D-part; when the antikink is allowed to move in such an area, it tends to move spontaneously in the opposite direction [7]. Therefore, it is implied that the D-part is relatively unstable due to, *e.g.*, residual internal stress.

In this work we controlled all the relevant predetermining factors and measured isolated kink motion repeatedly in $(TMTSF)_2PF_6$ and then found what factor controls the kink mobility.

2 Experimental techniques

We used single crystals of $(TMTSF)_2PF_6$ with the typical dimensions $1 \times 0.2 \times 0.1$ mm^3. Motion of an isolated kink was observed at room temperature. One end of a twinned crystal was fixed and constant external force generated by bending a fine quartz tube applied to the other end. After arriving at a position x_f, the kink was pushed back to the initial position x_i, and then the observation was carried out in the area $x_i < x < x_f$ of the crystal. Details of our experimental apparatus have been published previously [5].

In this study, conditions before the set-in of motion, as well as during motion, were controlled. Using a computer controlled piezoelectric actuator, the time t_{end} of staying at x_f, the velocity v_{back} to push back the kink from x_f to x_i and the time t_{wait} of staying at x_i before the forward motion were determined. Figure 1 illustrates the time sequence of motion in the repeated measurements.

3 Results and discussion

3.1 Identification of the predetermining factors controlling the kink mobility

The motion was repeatedly observed with controlled t_{end}, t_{wait} and v_{back} under the same external force within the same area of the sample. The motion in the direction to shrink the D-part was analyzed. The observed $x(t)$ curves were quite reproducible; it was found that the very poor reproducibility of both the kink velocity $v(x)$ and t_{int} in our previous works [5–8] was caused because the above parameters were not controlled sufficiently.

With changing t_{end}, t_{wait} and v_{back} systematically, motion was observed repeatedly in order to find what determines the kink mobility. To find if the kink motion is affected by t_{end}, $x(t)$ curves with different t_{end} were compared, while t_{wait} and v_{back} were fixed to 10 s and 0.13 mm/s, respectively. No difference was found between $t_{end} = 10$ s and 60 s; neither $v(x)$ nor t_{int} is determined by t_{end} and their scatter observed in our previous studies is not due to that of t_{end}. It is clear that the preceding forward motion does not influence the next run.

Next it was examined if the kink motion is affected by t_{wait}. We recorded the repeated kink motions with different t_{wait} while the external force, t_{end} and v_{back} were kept constant. Figure 2 shows $x(t)$ with different t_{wait} ranging from 1 s to 120 s. From the figure, clear and strong correlation is found between t_{wait} and the mobility; the velocity becomes lower and t_{int} longer as t_{wait} is longer. When t_{wait} was controlled, values of both the local velocity and t_{int} were reproduced within 5%. Both $v(x)$ and t_{int} change by a factor of ten, when t_{wait} is changed from 1 s to 120 s. It can be concluded unambiguously that t_{wait} has an essentially important effect on the kink mobility. The same conclusion was obtained when the motion in the opposite direction was analyzed.

The following experiments were carried out to find whether t_{wait} corresponds to the time elapsed before the kink passes forward through a position after the backward passage (denoted as t_w) or to the period of staying at x_i

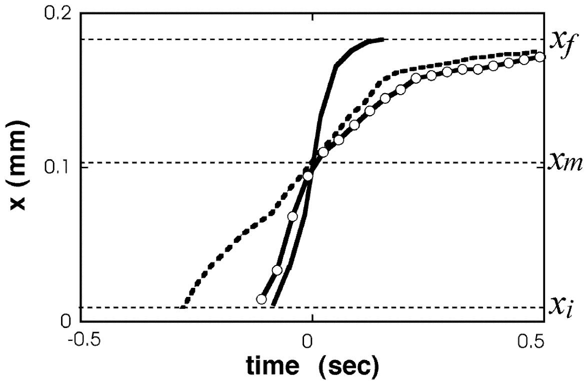

Fig. 3. Time dependent position $x(t)$ after backward movement interrupted at x_m (open circles), compared with $t_{wait} = 1$ s (solid line) and 30 s (dotted line) without interruption during backward motion. The time axis of $x(t)$ curves is shifted so that the times when the kink passed through x_m fall into the same point. Applied stress and v_{back} were 1.6×10^3 Pa and 0.13 mm/s, respectively.

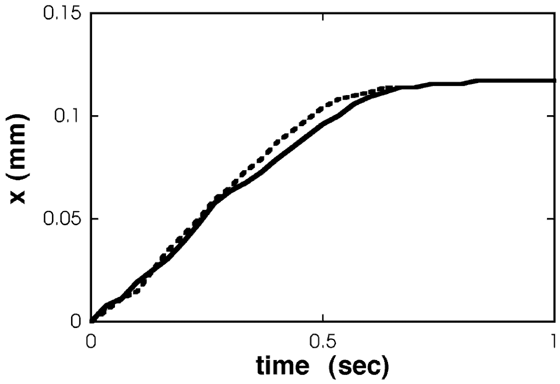

Fig. 4. Time dependent position $x(t)$ when v_{back} was 0.13 mm/s (solid line) and 0.07 mm/s (dotted line). Applied stress and t_{wait} were 1.5×10^3 Pa and 10 s, respectively.

(denoted as t'_w). The former is dependent on position as long as v_{back} is finite. During the backward motion, the kink was stopped at a point x_m ($x_i < x_m < x_f$). After staying at x_m for 30 s, the kink was brought to x_i and forced forward motion was started after t_{wait} of 1 s. In Figure 3 the result is compared with two $x(t)$ curves with $t_{wait} = 1$ s and 30 s. In the latter two curves the preceding backward movement had not been interrupted. In this figure the time axis is shifted so that the times when the kink passes through x_m coincide with each other. It can be found from the figure that the trajectory after interrupted backward motion fits to that of $t_{wait} = 1$ s in the area $x_i < x < x_m$ but to that of $t_{wait} = 30$ s in $x_m < x < x_f$. Thus it can be concluded that the length of the time after the backward passage, t_w, influences the mobility in the following forward motion. The same conclusion was obtained when the motion in the opposite direction was analyzed.

Based on the finding that t_w but not t'_w is the predetermining factor of the kink mobility, the change which occurs during t_w is in the lattice but not in the kink as far as changes in the kink and in the lattice are separable; some disorder is induced in the lattice by the forced backward motion and it is relaxed during t_w. In this respect, it might be that the lattice becomes less and less ordered when the kink is pushed backward with larger v_{back}. While no obvious difference was found between $x(t)$ with $v_{back} = 0.13$ mm/s and 0.07 mm/s as shown in Figure 4, we cannot rule out the possibility that the kink motion is influenced by much larger v_{back} than used in this study. It should be remarked that the exact value of t_w varies with the position. However, it is approximated by t_{wait} hereafter as far as t_{wait} is long, because the time during backward motion is constant and short.

In the following experiments the effect of motion of the antikink was studied. Immediately after the kink was brought to x_i, the antikink was moved from $x'_f > x_f$ to a position x'_m ($x_i < x'_m < x_f$) and forced to stay there. Again after 30 s the forward kink motion was started. In this case, t_{wait} was equal to 60 s. In Figure 5 the result is compared with two $x(t)$ curves with $t_{wait} = 30$ s and 60 s. In the latter two curves, the antikink was not moved. It is clear from the figure that $x(t)$ after the antikink motion fits to that of $t_{wait} = 60$ s in the area $x_i < x < x'_m$ but to that of $t_{wait} = 30$ s in $x'_m < x < x_f$. Thus, the forward kink motion was influenced by its backward motion before 60 s in $x_i < x < x'_m$ but by the forward antikink motion before 30 s in $x'_m < x < x_f$. It can be concluded that the effect of backward kink motion and that of forward antikink motion on the forward kink motion are equivalent quantitatively.

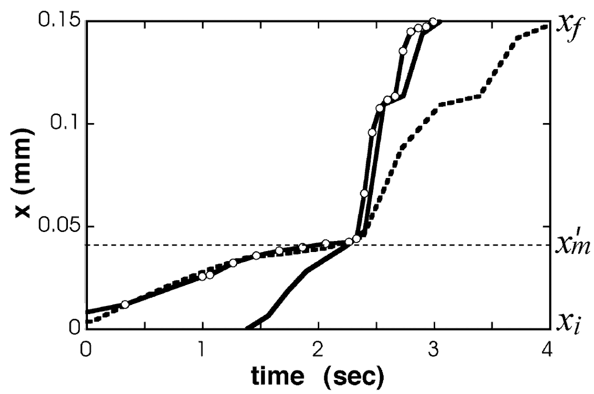

Fig. 5. Time dependent position $x(t)$ of a kink after the motion of the antikink in the same direction from x'_m(open circles), compared with those without motion of the antikink with $t_{wait} = 30$ s (solid line) and 60 s (dotted line). The time axis is shifted so that the times when the kink passed through x'_m coincide with each other. Applied stress and v_{back} were 1.6×10^3 Pa and 0.13 mm/s, respectively.

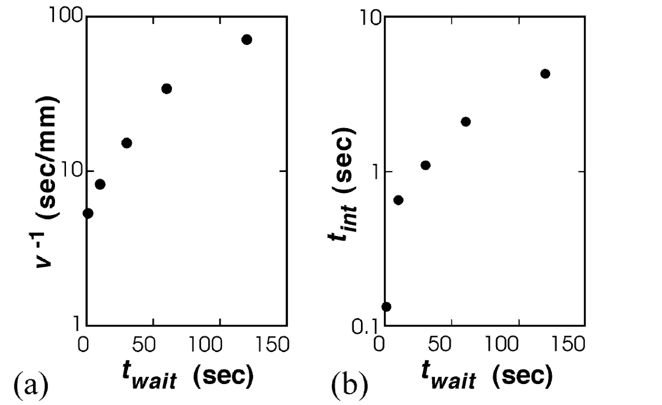

Fig. 6. Effect of t_{wait} on (a) v^{-1}, inverse of the average velocity in the area $0.14 < x < 0.17$ (mm) in Figure 2, and (b) t_{int}, the intermission time at $x = 0.14$ mm. Applied stress and v_{back} were 1.6×10^3 Pa and 0.13 mm/s, respectively.

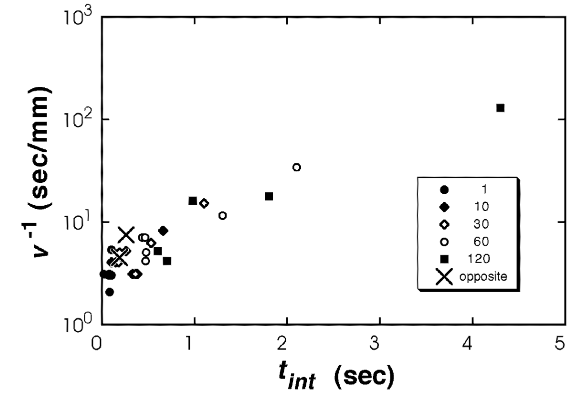

Fig. 7. Relation between t_{int} and inverse of the average velocity v^{-1} in the area $0.14 < x < 0.17$ (mm) in Figure 2 for various t_{wait} (s) and stress. Values of t_{wait} (s) are shown in the figure. Motions in the opposite direction (to expand the D-part) are denoted by the symbol (×) ($t_{wait} = 10$ s).

3.2 Dependence on t_{wait} of local velocity v(x) and the time of intermission t_{int} and their mutual correlation

Figure 6 shows the dependence of inverse of the average velocity v^{-1} and of t_{int} on t_{wait}. With increasing t_{wait}, v^{-1} and t_{int} increase monotonously. Both depend on t_{wait} strongly and non-linearly and tend to saturate for t_{wait} longer than 10^2 s. Details of the effect of much longer t_{wait} will be published separately.

Figure 7 shows the mutual relation between v^{-1} and t_{int} under various t_{wait} and applied stress. Clear correlation can be found between t_{int} and v^{-1}; when the kink moves with higher velocity, t_{int} is shorter. This relation is independent of t_{wait} and stress. The data obtained when the direction of the motion was reversed, *i.e.*, when the D-part was expanded, are also on the same curve, at least as long as t_{wait} is short. Therefore the effect of t_{wait} is equivalent to that of stress.

Deviation from the above correlation was found when the applied stress was lower than some limiting value. Study is in progress to find how the above correlation is modified when wider range of stress value is used.

4 Conclusion

One of the most important results of this study is that the kink mobility is heavily affected by its preceding backward motion. Ideally, D- and U-parts are energetically equivalent to each other. The barrier against the conversion between them should be associated with the configurational change of the constituent molecules and, therefore, should be symmetric. On the other hand, the present study has made it clear that the effective barrier is actually dependent on history. The D- (U-) part is rather unstable just when converted from the U- (D-) part. Presumably because it contains some kind of defects with a substantial concentration, the time rate of the following reversed conversion is high. The converted part of the crystal becomes more stable gradually during the time t_w. In the D- (U-) part just after the conversion, molecules whose orientation is the same as in the U- (D-) part may be distributed. These molecules change their orientation during t_w. The change during t_w does not contain any effect of previous forward motion. Because we could not find any correlation between kink velocity and t_{end}, only the last backward motion in the opposite direction is effective and any memory of the previous forward motion imprinted in the lattice is lost during the backward motion.

Another result is that the relaxation occurs with the characteristic time scale of hours at room temperature. While the orientational change in such molecules is naively expected to happen independently to each other, it would be difficult to explain why the relaxation is so slow unless these molecules are linked together by, *e.g.*, extended defects.

As mentioned in introduction, the kink in some crystals moves without external force only in the direction to expand the U-part. Even in crystals where spontaneous motion is not observed, larger force is necessary to widen the D-part than the U-part. Therefore, internal stress is distributed in the twinned crystal so as to widen the U-part. In other words, the D-part is relatively unstable compared with the U-part. But because the dependence of the kink mobility on t_{wait} is, at least qualitatively, independent of the direction of motion, the relaxation occurring during t_w is not related to the asymmetry between the relaxed D- and U-parts.

We reported that $v(x)$ in spontaneous motion depends on how the kink has been brought to the initial position x_i [6]. When force was applied after the preceding run to push it back to x_i and then force was released (denoted as U-mode in [6]), the kink moved with higher velocity. On the other hand, when the kink was brought to x_i from the opposite side of the high barrier area after driven backward across the freely running area (J-mode, in [6]), the kink continued to move spontaneously. In the latter mode, however, the average velocity was much lower and the characteristic time scale of the forward motion was several times larger than in U-mode. Such difference in the kink mobility between U- and J-modes can be also explained by the uncontrolled t_{wait}; in U-mode the kink stayed at x_i for very short time, while t_{wait} of several tens of seconds was necessary in J-mode.

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