

# Deformation mechanisms in polymer crystals

## Part 1 *The geometry of the stress-induced phase change of polymeric sulphur nitride (SN)<sub>x</sub>*

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Polymeric sulphur nitride (SN)<sub>x</sub> has been recently found to undergo a stress-induced martensitic transformation from the normal monoclinic phase to a new orthorhombic phase. The theories of shear-induced transformations in crystalline solids developed by Bevis, Crocker and co-workers have been used to predict the shear modes between the two forms of (SN)<sub>x</sub>. A comparison has been made between the theoretically predicted and experimentally measured modes for (SN)<sub>x</sub> and the transformation has been compared with a similar one that is observed in polyethylene.

### 1. Introduction

The metallic and superconductive properties of polymeric sulphur nitride [1-3] have stimulated considerable research interest in this polymer. (SN)<sub>x</sub> is produced by the solid-state polymerization of crystals of the cyclic dimer S<sub>2</sub>N<sub>2</sub> [4, 5]. Because the solid-state reaction and associated recrystallization processes are non-unique, molecular scale disorder and twinning is introduced during the dimer-to-polymer transformation [6, 7]. Despite these defects, certain polydiacetylenes are the only linear organic polymers presently obtainable as large dimension crystals with higher perfection than polymeric sulphur nitride [9-12].

It has been recently shown that the monoclinic phase of (SN)<sub>x</sub> that is produced by solid state polymerization can be transformed into a new phase which has orthorhombic symmetry by means of a shear-induced martensitic transformation [13]. The packing of the chains is substantially different in the new phase and it is expected that the electronic properties of the new phase will reflect this difference. Measurement of these properties has been impeded by present inability to produce fully transformed single crystals of the new phase.

The lattice parameters of the two phases and the orientation relationship between these phases have been measured by Baughman *et al.* [13]. Bevis and coworkers [14-16] have developed a theory which can be used to predict the transformation modes between two crystal structures that are related by a shear-induced transformation. They have used this theory to predict the transformation modes for the martensitic transformation between the orthorhombic and monoclinic forms of polyethylene (PE) [16]. The observed shear modes in polyethylene [17, 18] are found to be close to those predicted by Bevis and Crellin [16], with the modes involving the smallest shear displacements being favoured.

It is the purpose of this present paper to show that the martensitic transformation in (SN)<sub>x</sub> can be treated in a similar way to that in polyethylene. The only differences are that the particular phases have different lattice parameters and that in polyethylene the transformation is normally from an orthorhombic cell to a monoclinic one whereas in (SN)<sub>x</sub> the observed transformation is from a monoclinic cell to an orthorhombic cell. However, the direction of the transformation does not affect

the geometry, which depends only upon the lattice parameters of the two phases [14–16].

## 2. Previous investigations

### 2.1. The martensitic transformation in $(\text{SN})_x$

The crystal structure of the normal (phase I) monoclinic form of  $(\text{SN})_x$  has been determined by Mikulski *et al.* [3] as  $a_{\text{I}} = 7.637 \text{ \AA}$ ,  $b_{\text{I}} = 4.153 \text{ \AA}$ ,  $c_{\text{I}} = 4.439 \text{ \AA}$  and  $\gamma_{\text{I}} = 109.7^\circ$  with space group  $\text{P}2_1/\bar{a}$ . The unit-cell has been re-indexed by the authors so that  $c_{\text{I}}$  is parallel to the direction of the molecular chains as is conventional for polymer crystals [12]. This simplifies comparison of the unit cells and transformation modes in PE with those in  $(\text{SN})_x$ . Baughman *et al.* [13] have shown that the new phase in  $(\text{SN})_x$  is obtained by mechanical deformation of phase I  $(\text{SN})_x$  via the application of compressive stresses normal to the chain direction. The new phase (II) has been found to be orthorhombic with probable space group  $\text{P}2_12_12_1$  and  $a_{\text{II}} = 6.251 \text{ \AA}$ ,  $b_{\text{II}} = 4.807 \text{ \AA}$  and  $c_{\text{II}} = 4.429 \text{ \AA}$ . However, there is a complication in that after deformation the lattice parameters of the parent monoclinic phase I which is untransformed to phase II are changed. This second type of phase I will be called phase I\* and the lattice parameters are  $a_{\text{I}^*} = 7.849 \text{ \AA}$ ,  $b_{\text{I}^*} = 4.040 \text{ \AA}$ ,  $c_{\text{I}^*} = 4.429 \text{ \AA}$  and  $\gamma_{\text{I}^*} = 109.3^\circ$  [13].

The possibility that phase I\* is another crystallographic phase is not excluded. However, the X-ray diffraction data are consistent with identical unit cell symmetry and quite similar unit cell parameters for phase I and phase I\*. These similarities and the similar X-ray diffraction intensities suggest that phase I\* has basically the phase I structure. The less than three percent difference in unit cell parameters of phase I and phase I\* may be due to the internal strain fields of structural defects introduced by plastic deformation. High stacking fault concentrations involving phase II type of packing arise in phase I as a consequence of reaction non-uniqueness. These defects are evident in the electron density maps for phase I crystals as disordered sites. Similarly, stacking faults involving phase I type of packing are expected in phase II. These defects can lower the symmetry of phase II to monoclinic by producing about one percent difference in axial lengths which are equivalent in defect-free phase II.

The degree of phase I to phase II conversion increases with increasing temperature for the

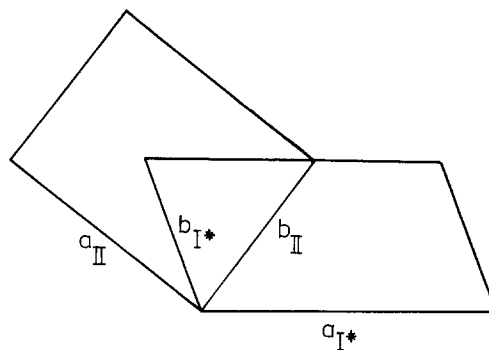


Figure 1 The orientation relationship between the deformed monoclinic phase (I\*) and the orthorhombic phase (II) of  $(\text{SN})_x$  [13].

mechanical shear process. The conversion of phase I to phase II and whether the untransformed polymer consists largely of phase I or phase I\* appears to depend upon crystal orientation in the stress field. Because of the small crystal sizes and the high strains employed, as well as the fact that brittle fracture occurs during deformation, these aspects have been difficult to quantify. For polymer fibres with low phase II component, phase I parameters have been observed for the untransformed polymer. On the other hand, for polymer fibres having high phase II component, phase I\* parameters have been observed for the untransformed polymer.

The orientation relationship between phases I\* and II has been determined by Baughman *et al.* [13] and it is illustrated schematically in Fig. 1. The orientation relationship is

$$\begin{aligned}(010)_{\text{I}^*} \angle (110)_{\text{II}} &= 0.2 \pm 1.1^\circ \\ (100)_{\text{I}^*} \angle (1\bar{1}0)_{\text{II}} &= -4.2 \pm 1.1^\circ \\ [001]_{\text{I}^*} &\text{ is parallel to } [001]_{\text{II}}\end{aligned}$$

A similar orientation relationship is observed for a sheared fibre consisting of a mixture of phase I and II.

$$\begin{aligned}(010)_{\text{I}} \angle (110)_{\text{II}} &= -0.4 \pm 2.0^\circ \\ (100)_{\text{I}} \angle (1\bar{1}0)_{\text{II}} &= -5.2 \pm 2.0^\circ \\ [001]_{\text{I}} &\text{ is parallel to } [001]_{\text{II}}\end{aligned}$$

### 2.2. The geometry of the martensitic transformation in PE

Bevis and Crellin [16] have calculated the possible orientation relationships between the orthorhombic and monoclinic forms of PE using the theories of shear-induced transformations in crystalline solids

developed by Bevis, Crocker and co-workers [14, 15]. They determined the shear modes of the transformation and listed them in order of increasing shear strain. In PE the problem can be solved in two dimensions since the repeat distance of the lattice in the chain direction is identical in the two crystal structures. The transformations take place by means of a simple shear of the parent lattice in the plane perpendicular to the molecular chains.

In PE there is an added complication. Although the transformations can be determined by shearing one lattice into the other, there are molecules not on lattice points in both the orthorhombic and monoclinic forms. This means that certain modes do not shear all the molecules to the correct positions and there are also modes which shear all the molecules to the correct positions but do not restore the lattice. The molecules away from lattice points in PE are related to those at the lattice points by means of a twist about the molecular axis and/or a translation of  $c/2$ . Because of this, Bevis and Crellin had to also consider the transformation modes between pseudo-lattices where the molecules had been replaced by points. Bevis and Crellin assumed that after such a transformation the crystal structures would be restored by twists and/or translations of some of the molecules.

Good agreement has been found between the predicted and observed transformations by Bevis and co-workers [16–18] in PE single crystals and in oriented bulk PE by Young and Bowden [19, 20]. In general it is found that transformations involving the lowest shear strains are favoured.

### 3. Calculation of the shear modes for the martensitic transformation of $(\text{SN})_x$

The shear modes which transform the monoclinic (I) form of  $(\text{SN})_x$  into the orthorhombic (II) form have been calculated using the equations derived by Bevis and Crellin [16]. So that the equations are completely analogous to those for PE, the calculations have been performed by assuming that the transformation takes place by going from an orthorhombic to a monoclinic cell. Since the analysis only considers the geometry of the transformations the direction of the shear transformation does not matter and the transformation can be considered geometrically to be completely reversible even though this may not be the case in the material. The observation of unit cell volumes and chain axis dimensions which are identical,

within experimental error, for phase I, phase I\* and phase II considerably simplifies the problem and permits a two-dimensional solution. The parent two-dimensional lattice  $C$  has been taken as the orthorhombic (phase II) form of  $(\text{SN})_x$ . This has vectors  $c_1 (=a_{\text{II}})$  and  $c_2 (=b_{\text{II}})$  and included angle  $\alpha (=90^\circ)$ . The calculations were performed for the transformation of  $C$  into two slightly different product lattices  $P$  defined by  $P_1 (=a_{\text{I}} \text{ or } a_{\text{I}^*})$ ,  $P_2 (=b_{\text{I}} \text{ or } b_{\text{I}^*})$  and included angle  $\beta (= \gamma_{\text{I}} \text{ or } \gamma_{\text{I}^*})$  and  $U = (u_{ij})$ , which is the shear matrix of the particular transformation. The calculations have been performed for shearing the orthorhombic form of  $(\text{SN})_x$  into both monoclinic forms. It is not known whether or not the normal (I) monoclinic form is transformed directly to the orthorhombic form (II) or initially goes to the deformed monoclinic form (I\*).

The details of the calculations have been given by Bevis and Crellin. Only a brief outline will be given here. The components of  $U$  are

$$u_{ij} = \begin{pmatrix} u_{11} & u_{12} \\ u_{21} & u_{22} \end{pmatrix}$$

It can be shown that all such two dimensional matrices can shear one two dimensional lattice into another [16] and care must be taken to try sufficient ones so that none are overlooked. However, in practice it is found that only those with  $u_{11}$  etc. of the order of 0, 1 or 2 give rise to modes which have low shears associated with them.

The value of the shear strain associated with the shear process ( $s$ ) is given by Equation 3 of Bevis and Crellin [16]. The particular modes are defined by a shear plane  $K_1$  and a shear direction  $\eta_1$ . The full elements of a shear transformation  $K_1, K_2, \eta_1$  and  $\eta_2$  can be determined from Equation 1 of Bevis and Crellin for a particular  $U$ .

Examination of the crystal structures of phase I and phase II of  $(\text{SN})_x$  showed that it was not necessary to calculate the shear modes for the transformation of an orthorhombic pseudo-space lattice to a monoclinic pseudo-space lattice as was done in the case of PE [16]. Half of the molecules are not on lattice points in both the monoclinic and orthorhombic forms of  $(\text{SN})_x$ , as is true for PE. However, for  $(\text{SN})_x$  it is not possible to bring these molecules into the same orientation as the molecules on the lattice points by simple translations or twists (i.e. shuffles, cf. PE). The molecules not on the lattice points are chemically

TABLE I Transformation modes between the monoclinic (I) phase and the orthorhombic (II) phase of (SN)<sub>x</sub>.  $K_1$  and  $K_2$  are given for the orthorhombic cell.

$N$	$U$	$K_1$	$K_2$	$s$
$T1$	10 11	3.08, -1, 0	1, 1.19, 0	0.365
$T2$	10 01	1, -1.34, 0	4.41, 1, 0	0.489
$T3$	01 11	1.08, 1, 0	1, -1.53, 0	0.887
$T4$	10 21	9.01, -1, 0	1, 1.16, 0	0.954
$T5$	01 10	1, 1.85, 0	1.15, -1, 0	0.983

identical to those on the lattice points but can be brought into the same orientation by a  $180^\circ$  rotation normal to the chain axis direction [13]. To achieve this transformation from one chain-type to another in a physically reasonable fashion would require bond rotations *cis-to-trans* and *trans-to-cis* all along the chain length, such as by the propagation of a point defect. For kinetic reasons, this type of motion is unlikely to predominate. Using the notation of Bevis and Crellin [16] this means that only  $m = 1$  modes need to be considered.

The correspondence matrices, the indices of the planes  $K_1$  and  $K_2$  with respect to the parent  $C$  orthorhombic lattice and magnitude of the shears ( $s \leq 1$ ) for the transformation modes are listed in Table I for the transformation to the unsheared monoclinic cell and in Table II for the transformation to the sheared monoclinic cell.  $K_1$  is the shear plane, which is unrotated and undistorted during the transformation, and  $K_2$  is a second characteristic plane of the transformation, which is rotated but undistorted. The modes are listed in order of increasing shear strain.  $T$  indicates the

TABLE II Transformation modes between the deformed monoclinic (I\*) phase and orthorhombic (II) phase of (SN)<sub>x</sub>.  $K_1$  and  $K_2$  are given for the orthorhombic cell.

$N$	$U$	$K_1$	$K_2$	$s$
$T1$	10 11	2.70, -1, 0	1, 1.02, 0	0.405
$T2$	10 01	1, -1.18, 0	3.94, 1, 0	0.532
$T3$	01 11	1.01, 1, 0	1, -1.50, 0	0.940
$T4$	10 21	7.46, -1, 0	1, 1.10, 0	0.939
$T5$	01 10	1, 1.84, 0	1.09, -1, 0	1.041

transformation mode and numerals 1 to 2 represent the position of the shear mode in the table. The subscripts 1 or 2 indicate, respectively, the direct mode and the reciprocal mode where  $K_1$  and  $K_2$  are interchanged. It can be seen in Tables I and II that for a given correspondence matrix the shear planes are similar for the transformations to the different monoclinic cells. The shear strains ( $s$ ) are mainly larger for the transformation to the deformed monoclinic cell.

Using the data in Table II, the plane of shear plots are drawn in Fig. 2 for modes  $T1_{1,2}$  to  $T5_{1,2}$ . Examination of these modes shows that only the  $T1$  and  $T3$  modes shear the molecules as well as the lattice points to their correct positions. For modes  $T2$ ,  $T4$  and  $T5$  a body-centred monoclinic cell is produced and shuffled by half of the molecules are required to restore the molecular units to their correct position in the monoclinic cell.

#### 4. Discussion

Since the orientation relationship for the transformation between  $I^*$  and II is the one that is known most accurately it is the one that will be considered in detail. The observed orientation relationship between the monoclinic (phase  $I^*$ ) form of (SN)<sub>x</sub> and the orthorhombic (phase II) form is given in Section 2.1 and Fig. 1.  $(010)_{I^*}$  is approximately parallel to  $(110)_{II}$ . Examination of the calculated modes in Fig. 2 shows that the two modes where these two planes are closely parallel are  $T1_2$  and  $T3_1$ . However, closer examination reveals that the mode that is closest to the observed one is  $T3_1$ , since for this mode  $(100)_{I^*} \perp (110)_{II}$  is  $-5 \pm 1^\circ$ . At first sight therefore it seems that the problem is solved very simply. However, it is worthwhile looking into the transformation in more detail as several interesting points arise.

$T3_1$  is a mode whereby the transformation shears both the molecules and lattice points to their correct positions. In (SN)<sub>x</sub> the two types of molecule in the unit cell differ in that they "point" in opposite directions [13]. However, in polyethylene there is some ambiguity because the two different types of molecules in this case differ only in a twist and/or a small translation along the  $c$ -axis. It is possible in this case that some molecules can shuffle and move to positions whereby the lattice is restored after a shear which does not restore the lattice [16]. In (SN)<sub>x</sub>, the ambiguity does not occur since the lattice cannot be restored by a

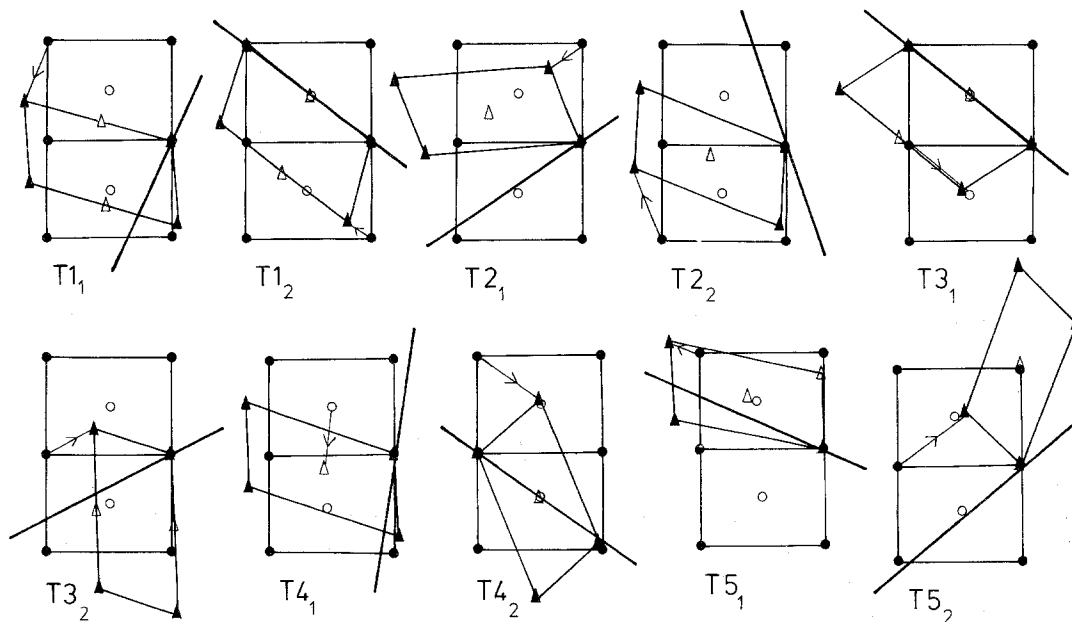


Figure 2 (001) plane of shear plots for the predicted transformation modes in  $(SN)_x$  and listed in Table II. Where the open triangle is in the centre of the monoclinic cell this is a  $m = 2$  mode [16] and shuffles are required to restore the lattice. In  $(SN)_x$  the transformation is from a monoclinic to an orthorhombic cell and so these particular shuffles would have to take place before the martensitic transformation.

translation of molecules along the chain direction. In modes where a body-centred monoclinic cell is produced (Fig. 2) shuffles perpendicular to the chain direction by half of the molecules will restore the correct monoclinic lattice. However, since it has been shown that only the  $T3_1$  mode is observed and this does not require any shuffles it appears that a mode which does not require shuffles may be preferred. The  $T2$  modes involve a lower shear strain and so may not be found because of the need for shuffles. The  $T4$  and  $T5$  modes involve about the same strains and do not occur. The need for shuffles in these modes is probably the reason why they are not found.

As well as the need for shuffles being a criterion for the activation of a particular mode the magnitude of the shear strain is known to be important [16]. Usually the modes with the lowest shear strain are favoured. There is a problem with  $(SN)_x$

in determining why the  $T3_1$  mode is favoured while the  $T1_2$  mode is not found. The  $T1_2$  mode involves a shear of 0.405 which is much less than the shear of 0.940 for  $T3_1$  and so ought to occur in preference to  $T3_1$ . The reason why  $T1_2$  does not occur could be due to several causes, one of which is illustrated in Fig. 3. If the  $T1_2$  mode operates, the stress required to activate this transformation could also cause the orthorhombic cell to twin on (110) as is found for polyethylene [19, 20]. This gives an orientation relationship between the orthorhombic and monoclinic cells which is very close to the one observed and  $T3_1$ . Twinning on the (110) plane of phase II is observed in some fibres of sheared  $(SN)_x$ . However, this twinning might merely be a consequence of the characteristic (010) twinning in the parent phase I  $(SN)_x$ . On the other hand, fibres of sheared  $(SN)_x$  have been observed in which there

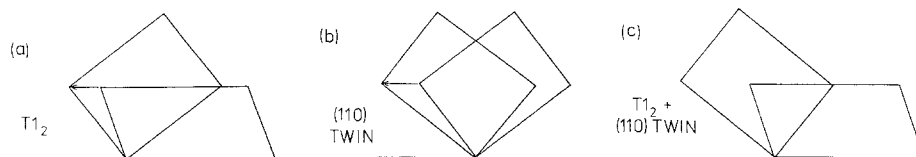


Figure 3 A proposed mechanism to produce the observed orientation relationship by means of the  $T1_2$  transformation and (110) orthorhombic twinning: (a)  $T1_2$  transformation, (b) (110) twinning, (c) Observed orientation relationship.

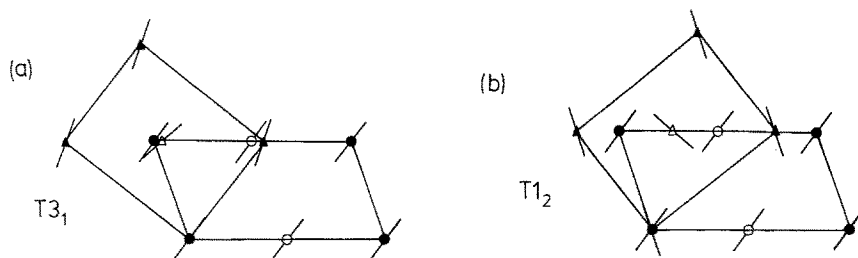


Figure 4 A schematic illustration of the change in the angles of the molecules in the unit cells for different transformations: (a)  $T3_1$ , (b)  $T1_2$ .

is no measurable (1 1 0) twinning in phase II (twin fraction is less than 0.03) [13].

An alternative explanation for the preference of  $T3_1$  over  $T1_2$  is illustrated schematically in Fig. 4. If the orientation of the molecules in the unit cell is taken into account, the rotation of the molecules about their long axes is much greater for the  $T1_2$  transformation than is required for  $T3_1$ . In the case of  $T3_1$ , the transformation can take place by rotations of less than  $15^\circ$  whereas rotations of up to  $90^\circ$  are required for the  $T1_2$  transformation.

At the moment it is not possible to decide which of the two explanations controls the choice of the  $T3_1$  transformations or if there are any other explanations which can account for this choice.

All the discussions so far has been concerned with the transformation between the deformed (phase I\*) monoclinic cell and the orthorhombic (phase II) cell. The arguments are identical for the transformations in Table I between the undeformed monoclinic (I) cell and the phase II structure. One interesting point is that the shear strains are smaller for the transformations between the undeformed monoclinic cell and the orthorhombic cell (Table I) than for the transformation between the deformed monoclinic cell and the orthorhombic one. Again more work must be done to determine at what stage of the deformation the original monoclinic (I) cell is transformed into the deformed monoclinic (I\*) cell. An X-ray investigation of the deformed material under load would be of interest here.

## 5. Conclusions

The transformation modes between the monoclinic and orthorhombic phases of the polymeric form of sulphur nitride  $(SN)_x$  have been calculated using the theory of shear induced transformation modes in crystals developed by Bevis, Crocker and

co-workers [14–16]. It has been shown that the theoretical mode with the third lowest shear strain ( $T3_1$ ) is the closest to the experimentally determined mode of Baughman and co-workers [13]. It is thought that this mode is preferred over ones involving lower shear strains because all the molecules are transformed to their correct positions and the rotations of the molecules during the transformation are small. However, an orientation relationship identical to the experimentally determined one can be derived from the mode involving the lowest shear strain ( $T1_2$ ) and (1 1 0) twinning of the newly formed orthorhombic cell. The transformation in  $(SN)_x$  is analogous to the stress-induced phase change in polyethylene. In single crystals of polyethylene it has been shown that the fold-plane exerts a strong influence on the operation of a particular transformation mode [18]. The single crystals of  $(SN)_x$  are macroscopic (typically  $0.5 \text{ mm} \times 0.5 \text{ mm} \times 0.05 \text{ mm}$ ) and the molecules are extended and so there are no fold plane constraints in this case.

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