Organosuperelasticity

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Superelastic Shape Recovery of Mechanically Twinned 3,5-Difluorobenzoic Acid Crystals**

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Abstract: *Generally, superelastic behavior cannot be expected in mechanically twinned crystals because there is essentially no strain on the interface that is a driving force for spontaneous shape recovery. However, we found that single crystals of 3,5-difluorobenzoic acid are superelastic organic crystals under mechanical twinning. The unexpected shape recovery can be explained by molecular distortion on the twinning interface, which suggests a new mechanism for superelasticity in molecular materials.*

Superelasticity (transformation pseudoelasticity) is one of the specific characteristics of a solid accompanied by reversible deformation during the loading/unloading of mechanical shear stress with the generation/degeneration of a daughter phase from a mother phase through diffusionless transformation with specific lattice correspondences capable of connecting different lattices on the martensitic interface. Ti-Ni alloys have been known for several decades and are the most representative superelastic materials and are widely used for structural materials or devices, where different crystal phases are generated by a stress-induced phase transition.[1–3] Recently, we found superelasticity in terephthalamide (TPA) crystals for the first time in organic compounds involving a stress-induced phase transition.[4] Superelasticity in organic compounds (organosuperelasticity) would vary by a higher degree of structural freedom in the component molecules than that in atomic compounds such as metal alloys.

Recovery of deformation twinning from a deformed shape is thought to be impossible according to the general understanding developed for atomic solids because of the equivalency for crystal structures with mirror symmetry at the interface, there being no difference in thermal energy (chemical potential).[5] However, we considered the possibility of superelasticity in the twins of organic solids mediated by the high degree of structural freedom of molecular components, which can simultaneously contribute to the easy and fast diffusionless transformability with the structural regularity of components and their packing in the interface by depressing the undesired deformation by slip, dislocations, and so on, which can lower the energy of the structure at the interface. There are few reports of mechanical twinning in organic crystals, and superelasticity has not previously been reported.[6–10] Herein, we show the first example of superelastic shape recovery action in the mechanical twins of an organic single crystal of 3,5-difluorobenzoic acid (**1**), which is explained by dissymmetric molecular distortion on the twinning interface.

Single crystals of **1** were prepared by sublimation of 3,5-difluorobenzoic acid (TCI Co., Ltd.) at about 1 kPa and 50 °C, which gave colorless rod-like single crystals with typical lengths of 0.3–1.0 mm. The shear stress on the crystal surface of $(0\bar{1}\bar{1})$ bent the shapes of single crystals of **1** accompanying the generation of the daughter crystal domain (α_1) from the original mother crystal domain (α_0) with a sharp boundary transferring upon twinning deformation. The bending angle of the crystal specimen measured under an optical microscope was significantly large (27°; Figure 1 a). Surprisingly, the bent crystal spontaneously restored to its original straight shape when the shear stress was removed and the boundary transferred back by 2.5 mm s^{-1} at 298 K (Supporting Information, Movie S1). The interface is necessary to shape-recovery motion and one interface transfers to the crystal end by knocking out of another interface from one end of the crystal (Supporting Information, Movie S2).

As expected from the macroscopic crystal transformation, a loop in the stress–strain curve was obtained by the loading

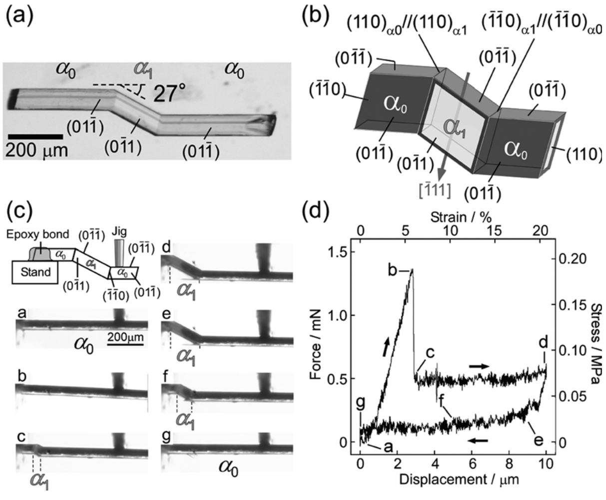

Figure 1. Properties of mechanical twinning of **1**. a) Photograph of a crystal ($0.95\times0.08\times0.08$ mm^3) and b) crystal face indexes of **1** bent along $[\bar{1}11]$. c) Snapshots of a bent crystal ($0.68\times0.13\times0.05$ mm^3; Supporting Information, Movie S3) and d) stress–strain curve of **1** under shear stress at 298 K.

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of shear stress on a portion of the crystal surface $(0\bar{1}\bar{1})_{\alpha 0}$, which is nearly parallel to the shear-twinning direction of $[\bar{1}11]$ (Figure 1 b). After one end of a single crystal was fixed with epoxy bond, a metal blade (25 μm wide) was pushed across the crystal surface of $(0\bar{1}\bar{1})_{\alpha 0}$ at a constant speed of 500 μm min^{-1} (Supporting Information, Movie S3). As shown in Figure 1 d, stress was detected at (a) after the blade reached the crystal surface and a linear increase in the loading force began (a–b). At the point where the stress had increased up to 0.189 MPa (1.37 mN) at (b–c), an abrupt decrease of stress was observed after passing (c) with the generation of the α_1 domain from the fixed side of the specimen. The stress then remained in a plateau state during the growth and propagation of the α_1 domain (c–d). Soon after the point for switching the unloading process (pulling the blade back), the stress decreased to 0.03 MPa at (e), and a reversible transformation to α_0 from α_1 progressed while the plateau state remained with the width of the α_1 domain (f) contracting. After a slight decrease in stress, the stress and the α_1 domain disappeared at (g). The critical shear stress required for transformation ($\sigma_{\text{f-trans}}$) is about 0.07 MPa and that for reverse transformation ($\sigma_{\text{r-trans}}$) is in the range of 0.01–0.03 MPa. The estimated energy storage density (E) and energy storage efficiency (η) were calculated as 11.9 kJ m^{-3} and 0.178, respectively. The values of $\sigma_{\text{f-trans}}$, E, and η in **1** were one-seventh to one-fifth of the values of TPA ($\sigma_{\text{f-trans}}$: 0.496 MPa, E: 62 kJ m^{-3}, and η: 0.925).[4]

Although **1** exhibited superelastic behavior, a single crystal X-ray structural analysis of the bent crystal of **1** resulted in the mechanical twinning state with an interface of $(110)_{\alpha 0}//(110)_{\alpha 1}$ (or $(\bar{1}\bar{1}0)_{\alpha 1}//(\bar{1}\bar{1}0)_{\alpha 0}$), which is formed by connecting the identical lattices at the interface which is relatively rotated 180° around the direction of shear stress $[\bar{1}11]$ (type II twinning; Supporting Information, Figure S2).[11] The crystal structures of both crystal domains are the same, which does not produce the so-called Bain strain on the interface (Supporting Information, Table S1, Figure S2). In the crystals, 3,5-difluorobenzoic acid molecules formed dimers by double O−H···O=C hydrogen bonds of carboxylic acid (O···O distance: 2.625 Å) along the long axis of the each molecule with a dihedral angle of 9.48° between the carboxylic acid and the phenyl plane (Figure 2 a). The dimers associated to form a polymer sheet bound by the weak hydrogen bond as C−H···O=C (C···O distance: 3.378 Å) between the carbon atom of the phenyl ring and the oxygen atom of the neighboring molecule. The dimers stacked upon each other by π–π interaction with distances of 3.397 Å (C−C) and 3.218 Å (C−O) (Figure 2 b).

Considering the crystal connection in the twinning, the estimated bending angle is 27.8° from the projection directions of $[0\bar{1}1]_{\alpha 0}$ and $[01\bar{1}]_{\alpha 1}$ (Figure 2 c), which agrees with the macroscopic bending angle (27°) measured under a microscope. The proportion in the displacement of the shear position on the $(0\bar{1}\bar{1})_{\alpha 0}$ surface and the moving (far) side of the α_1/α_0 interface was 1:2.02, which also agrees with the expected value of 1:1.96 using the X-ray crystal data. Therefore, the harmonious support of the macro- and microscopic structural changes demonstrates deformation twinning of **1**. The movable range of the superelastic shear strain of **1** is expected to be 52.7 % by crystal structure, which is larger than that of TPA (11.34 %; bending angle of 6.47°), because the plane of the polymer sheets in **1** are more sharply oriented against the bending crystal surface of $(0\bar{1}\bar{1})$ than that of TPA, which is a key factor in determining the degree of bending at the interface.[4] Owing to the twinning deformation of **1**, another explanation for the origin of the recovery stress is required.

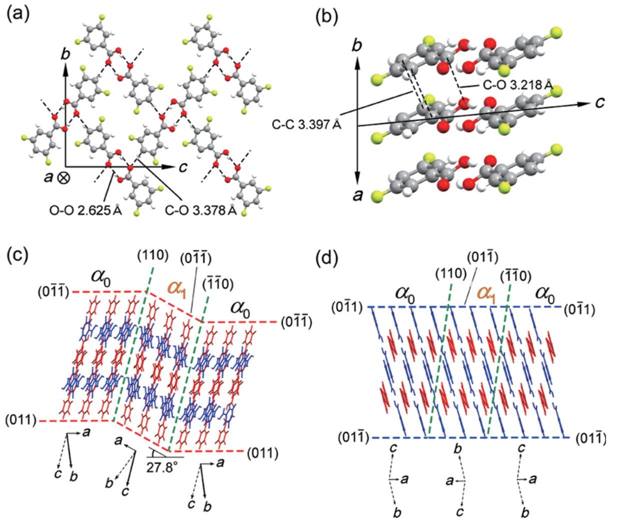

Figure 2. Crystal structure of **1**. a), b) Intermolecular interactions of **1** obtained by single crystal X-ray structural analysis (90 K). C gray, H white, O red, F light green. c), d) Connection between crystal packing on twinning interfaces. The dimers nearly along $[\bar{1}11]$ and $[11\bar{1}]$ are indicated in red and blue, respectively.

Since molecules have their shapes and orientations regulated by crystal packing, an energy deviation based on mismatched molecular orientations and/or positions even on a twinning interface can be considered. With reference to structural deviation on the interface, each orientation and barycentric position of dimers adapts itself so as to maintain continuity of the intermolecular interactions (Figure 3 a). For the in-plane direction of the interface, slight shifts of molecules A (colored red in Figure 2, 3) can preserve π–π interactions on the interface because their phenyl planes are nearly parallel to the interface (Figure 3 b). For the out-of-plane direction of the interface, however, a conformational adjustment of molecules B (colored blue in Figure 2, 3) is additionally required because the C_2 symmetry should cleave the hydrogen bond at the center of the dimer (Figure 3 c, left). By considering the dissymmetric molecular distortion, the pseudorotation axis orthogonal to the C(phenyl)–C(carbonyl) bond axis of the molecules B avoids the cleavage of the double hydrogen bonds across the interface (Figure 3 c right). The slight molecular conformational change on the interface is a reasonable hypothesis for the origin of the recovery stress. The distortion energy (1.69×10^{-4} J m^{-2}, 4.9×10^{5} J m^{-3}, and 210 J mol^{-1} (the case for mere benzoic acid)[12]) gained from the dihedral twist between the carbonyl and phenyl planes from 8.3° to 12.7° is large enough to explain the energy required for the recovery stress in the transfer of the interface (6.5×10^{-6} J m^{-2}, 1.9×10^{4} J m^{-3}, and 8.0 J mol^{-1}), which was estimated by the stress-strain curve (Figure 3 d).

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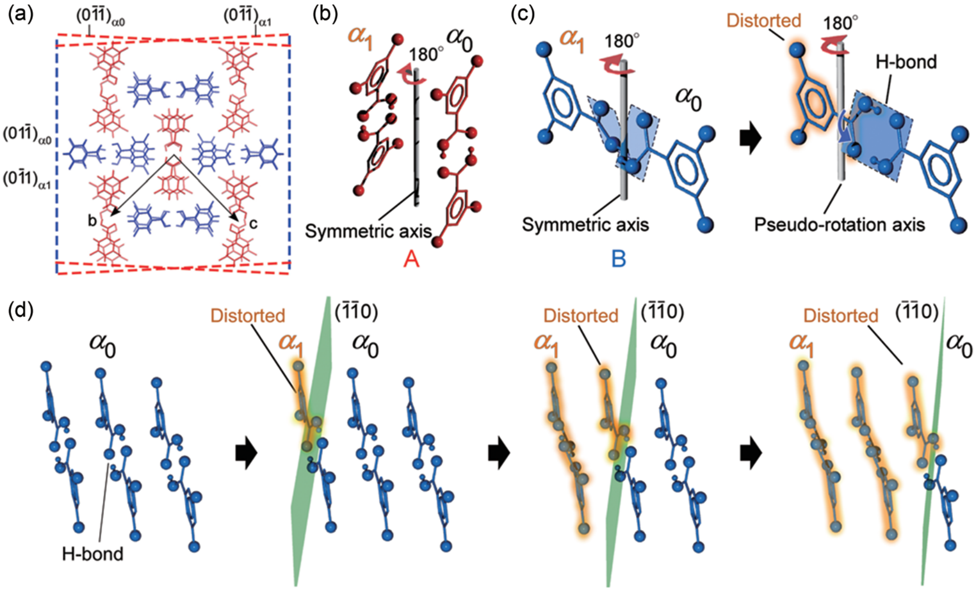

Figure 3. Origin of the recovery stress. a) Mismatches of molecular orientations and positions between α_0 and α_1 domains on the twinning interface. b), c) Comparison of molecular conformations in α_0 and α_1 domains around the symmetric axis (C_2 rotation axis) on the interface (red: molecule (A) oriented nearly along $[\bar{1}11]$, blue: molecule (B) oriented nearly along $[11\bar{1}]$). d) Moving of the distorted part (highlighted in yellow) following the moving interface (green plane) in the row of molecules (B).

In conclusion, we confirmed the spontaneous shape recovery of mechanically twinned 3,5-difluorobenzoic acid crystals with movable martensitic interface in generating a certain recovery stress. While the manner of the observed shape recovery satisfies the definition of superelasticity developed for metal alloys, the origin of recovery stress is rationally explained by the molecular distortion that occurs on the interface. Thus, molecular solids can exhibit superelasticity even for twinning deformation through the distortion of molecular components on the interface, which cannot be considered for atomic solids such as metal alloys.

Keywords: carboxylic acids · crystal engineering · mechanical properties · organosuperelasticity

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