

STRUCTURAL DETERMINATION OF TOPOLOGICAL CRYSTAL

To understand the physical, chemical and biological properties of novel functional materials, information on atomic arrangement in these materials has an indispensable role. The X-ray diffraction method is one of the most popular and powerful techniques in determining such atomic arrangement in a crystal cell. However, it has a limitation in structure determination. This is because X-ray diffraction is based on interference between waves scattered by atoms arranged coherently in space. For this reason, only crystals having a macroscopic translational symmetry can be analyzed by X-ray diffraction.

On the other hand, when the size of matter is reduced, its shape tends to bend and the macroscopic translational symmetry may be lost similar to carbon nanotubes and DNA wires. So our question is, “*Is it impossible to determine the atomic arrangement of a small matter with curved shape?*”

We attempt to answer the above question. Surprisingly, Tanda *et al.* produced entirely new crystals named “topological crystals” whose shapes are similar to a ring, a Möbius strip and a figure of eight [1]. Figure 1 shows the scanning electron microscopy images of NbSe₃ topological crystals [1]. Since *both ends of a crystal are bound and twisted*, these crystals are of an entirely different topological classes from ordinary crystals. Topological crystals can offer a chance of examining topological effects such as macroscopic interference in quantum mechanics.

From the crystallographic viewpoint, strains characteristic of each topological class will emerge in those crystals by joining two ends. In this report, we present the lattice parameter variation of topological crystals.

The difficulty in X-ray diffraction measurements of topological crystals lies in the nonuniformity of crystal orientation due to their curved shapes. If we divide or crush a topological crystal to obtain smaller crystalline powder with a macroscopic translational symmetry, we may lose important structural information originating from the topological shape. To overcome this difficulty, we decided to analyze the crystal structure without any sample treatment. To this end, we developed a two-axis sample rotator.

The sample rotator consists of two independent principal (P) and secondary (S) rotators crossing at an angle of 45 deg. The sample is mounted on the S axis (see inset of Fig. 2). With the rotation of S, one reciprocal lattice point traces a ring trajectory. With the distribution of reciprocal lattice points reflecting local crystal orientation originating from the curved shape, the assembly of ring trajectories nearly covers a part of a sphere in the reciprocal space. With the rotation of P, this part of the sphere intersects the Ewald sphere and the diffraction pattern will be similar to the Debye ring. Certainly, this is not the ideal Debye ring, which is found in powder crystals without a preferred orientation.

The effect of sample rotation on integrated reflection intensity (= Lorentz factor) should be taken into account. Since local crystal orientation varies continuously depending on the bent and the twist of a ‘topological crystal’, an accurate calculation of the Lorentz factor of a specific crystal is not realistic. Hence, we attempted to minimize the correction of the Lorentz factor by selecting the integration area in the imaging plate (IP) for estimating the diffraction intensity. Figure 2 shows the calculation of the

Lorentz factor for the new two-axis rotator. With the rotation of S, one reciprocal lattice point forms a ring trajectory. With an increase in angle between the point and S axis, the nearest distance between the ring trajectory and the Ewald sphere decreases, where the Lorentz factor originating from another P axis rotation tends to diverge. We removed the contribution from the nearest part by selecting

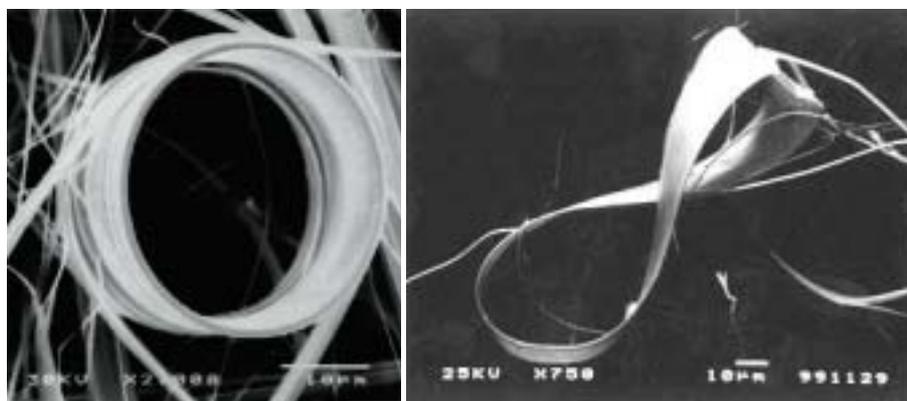


Fig. 1. Scanning electron microscopy images of topological NbSe₃ crystals, (a) ring crystal (no twist), (b) figure-of-eight crystal (2π twist).

Materials Science : Structure

the integration area of IP (see inset figure), and suppressed the singularity in the Lorentz factor.

We measured three rings (a tube, a thick ring and a thin ring) and two figures of eight and one cut ring. Owing to the smallness of the sample crystal (e.g., $50 \times 10 \times 5 \mu\text{m}^3$), we used a low-temperature vacuum camera (LTVAC) at beamline **BL02B1** to diminish X-ray air scattering. To refine the unit cell parameter, we performed Rietveld analysis using RIETAN-2000 software.

The relationship between sample thickness and the ratio a/c are shown in Fig. 3. This change is caused by an increase in c length and a decrease in a . This unit cell deformation can be interpreted as a self-pressure effect in the thicker ring. The inner part of the thick ring can be pressurized from the outer part to maintain the sample shape. As compressibility along the one-dimensional b axis is nearly zero, the unit cell principally shrinks along the residual a axis (see Fig. 4). On the other hand, expansion in the c direction is reasonable because the direction is free from the above pressure effect. In the cut ring, the lattice parameter is not pressurized possibly owing to the relaxation caused by cutting. This success in the structure analysis of topological crystals encourages us to apply this developed method to other micro- or nanocrystals that do not have macroscopic translational symmetry.

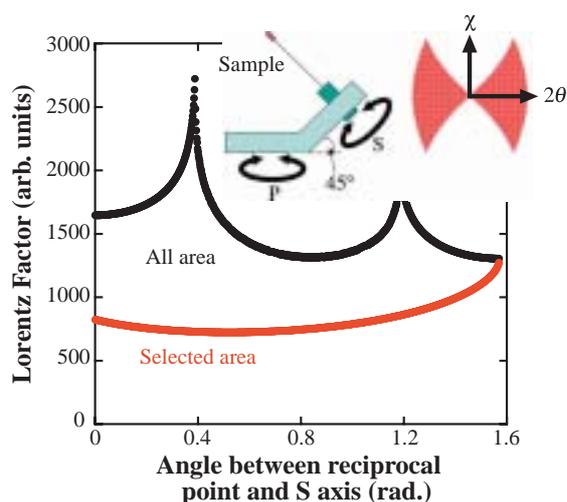


Fig. 2. Lorentz factor for the new two-axis rotator. Central inset: schematic view of two-axis rotator, right inset: selected integration area of IP.

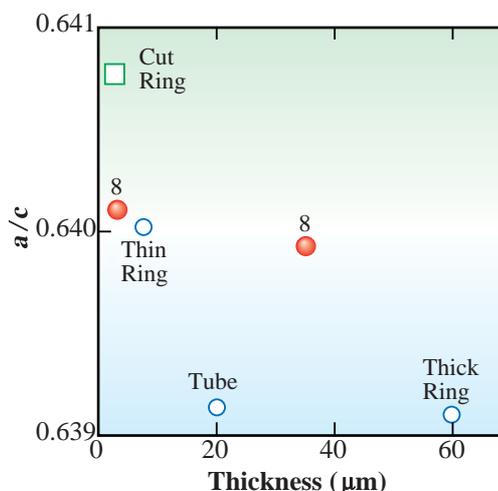


Fig. 3. Thickness dependence of a/c ratio.

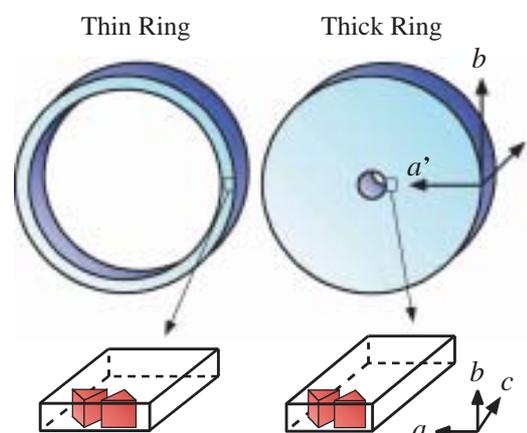


Fig. 4. Schematic view of unit cell deformation caused by self-pressure effect in the thick ring crystal.

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