Topologically linked crystals

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Abstract

We discovered a new class of topological crystals, namely linked rings of crystals. Two rings of tantalum triselenide (TaSe$_3$) single crystals were linked to each other while crystal growing. The topology of the crystal form is called a “Hopf link”, which is the simplest link involving just two component unknots linked together exactly once. The feature of the crystals is not covered by the conventional crystallography.

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1. Introduction

Exotic topological crystals, such as ring-shaped crystals, Möbius strips of crystals, and figure-of-eight (2\pi-twisted strip) crystals, have been successfully created in niobium (Nb) and selenium (Se) compounds (NbSe$_3$) \cite{1,2}, despite their inherent crystal rigidity. These crystals have topological forms consisting of closed strips with one component \cite{3}. And they have opened new field of investigation related to topological effects in quantum mechanics and nanotechnology \cite{4–11}.

Furthermore, we discovered new topological crystals in tantalum (Ta) and selenium (Se) compounds (TaSe$_3$), which are two ring-shaped crystals linked to each other exactly at once. Due to the link the two rings cannot be separated without cutting of chemical bonding. The linked rings of crystals are categorized in a higher class of topological crystals because the topology involves two components. This topology is called a “Hopf link”, which is the simplest link involving just two component unknots \cite{3}. Hopf links are realized in soft materials such as molecules \cite{12} and DNA \cite{13}, which are known as “catenanes.” However, it is very surprising that rigid crystals have these topological forms. The discovery of Hopf link of crystals introduces the concept of framed knots \cite{2} in crystallography. In this paper, we report the growing condition of the crystals and propose a model of formation mechanism of links.

2. Crystal features

Ring-shaped crystals of TaSe$_3$ have been discovered in 1999 \cite{14}, following the discovery in NbSe$_3$. TaSe$_3$ crystals are known to be a one-dimensional inorganic conductor that exhibits superconductivity below 2 K \cite{15,16}. TaSe$_3$ belongs to the same crystalline family as NbSe$_3$. These crystals are needle-like crystals called whiskers, since they grow extremely faster along $b$-axis than along $a$- and $c$-axis due to their one-dimensional crystal structures. Therefore,
they can be bent or twisted more easily than three-
dimensional crystals, resulting in the coexistence of local
crystal structures and global topological forms [1]. As a
result, these crystals possess similar characteristics to soft
materials.

Fig. 1 shows a scanning microscope image of linked
crystal rings with diameters of 54 and 46 μm. Both rings are
single crystals of TaSe₃. The red and blue ring-shaped
crystals are linked exactly once. The linked rings of crystals
have unusual properties associated with framed knots. By
several approaches such as X-ray diffraction, electron-
beam diffraction, and electric transport measurement, it
was confirmed that the  \( b \)-axis of ring-shaped crystals of TaSe₃
and NbSe₃ head along their circumference direction [17].
Therefore, the linking number of the crystals can be defined
by the trajectories of the \( b \)-axis. In the case of the Hopf link
of crystals, the linking number is 1. Since the number is a
topological invariant, uncontinuous transformation, such
as cutting of chemical bond, is necessary to separate the
two rings. Furthermore, if their thickness grows anyhow
the two rings cannot unite into one ring-shaped crystal.

3. Experimental procedure

The linked rings of crystals have been synthesized by
chemical vapor transportation (CVT) method [18,19]. The
synthesis techniques are the same as those used in previous
experiments [1,2] except that they employ an optimized
non-equilibrium condition involving the circulation and
supersaturation of selenium gas in a furnace.

We soaked a mixture of tantalum powder and selenium
granules of 1:3.15 molar ratio, which was put in one of the
ends of an evacuated quartz tube in an electric furnace that
has a horizontal temperature gradient of 1.5 °C/cm for 3 h.
The length of the tube was 20 cm and the inner diameter
was 17 mm. A total of 5% of excess selenium was added to
enhance the circulation and supersaturation of selenium
gas. The highest temperature region in furnace was set at
720 °C. The end of the tube with the mixture was placed at
the highest temperature region. The temperature gradient,
temperature near another end was around 700 °C, namely
the growth temperature of TaSe₃ crystals. Under this
condition, the selenium gas circulation carries tantalum to
lower temperature region and TaSe₃ crystals grow by vapor
phase epitaxy at an optimal temperature region. Further-
more, the selenium gas is condensed to liquid at the lower
temperature region because the gas is supersaturated.
Therefore, many selenium droplets of various diameters
are repeatedly created and annihilated at the lower
temperature region. It is a good condition for producing
topological crystals since the droplets are indispensable for
producing topological crystals [1,2].

A selenium droplet acts as a spool during crystal growth.
The spooling mechanism is a fundamental process of
crystals having topological forms. A whisker of TaSe₃
crystal grows on the surface of a selenium droplet by vapor
and liquid phase epitaxy and encircles it along a great circle
line (Fig. 2A) because of its one-dimensional crystal
growth. Finally its ends are connected (B), thus yielding a
ring once the droplet has evaporated (C). This scenario has
been verified by observation of the NbSe₃ crystals spooled
around selenium droplets [1,2]. Therefore, increase of
number of droplets derives increase of production prob-
ability of the ring-shaped crystals and other possible
topological forms in crystals.

By the optimization for producing topological crystals of
TaSe₃, we obtained many topological crystals more than
one thousand from one tube. The production ratio was
about 10 times larger than that of NbSe₃. Almost all were
ring-shaped crystals. We found the topologically linked
ring-shaped crystals in them.

4. Discussion

The spooling mechanism can explain the formation
mechanism of the one-component topological crystals such
as ring-shaped crystals, M"obius strip of crystals, and figure-of-eight crystals [1,2]; however, it cannot explain the mechanism of the link of crystals. To make a link, the whiskers on the selenium droplet must under-run another whisker at least once, or crystals must grow on a torus droplet. Nevertheless, these scenarios are physically unreasonable.

In addition to that, the Hopf link topology cannot be produced by splitting any one component topological crystals since the linked ring-shaped crystals were not twisted. For example, we obtain Hopf links by splitting the middle of 2π-twisted. However, this approach provides a link consisting of two 2π-twisted strips because the number of twists is conserved. Similarly, any nπ-twisted strips do not become the Hopf link of untwisted rings by splitting. Therefore, the Hopf link of crystals is categorized to new class of topological crystals.

A promising idea is that the linked rings of crystals are formed by a successive spooling mechanism. It seems likely that similar processes occur successively and produce linked rings of crystals. After a ring-shaped crystal is produced by the first spooling mechanism, a small selenium droplet is attached to the ring (Fig. 2D), and then a new ring grows on the second droplet (E). The second ring crystal is linked once when spooling around the second droplet. Finally, linked rings of crystals are yielded after the second droplet has evaporated (F). In fact, we often observed selenium droplets attached to rings (Fig. 3) under the optimized non-equilibrium conditions. This is strong evidence for our proposed mechanism. The small droplet might be the residue of the droplet on which the first ring grew, or it might have become attached to the first ring by chance. Our proposed mechanism provides a reasonable explanation for the different diameters of the two untwisted seamless rings of linked crystals.

5. Conclusion

We have developed our experimental set-up so that it is capable of forming many droplets in a controlled manner by using an optimized non-equilibrium condition that enhances the chance of encountering a target ring. It may be possible to grow a crystal chain with a desired number of links, as well as Borromean rings [20] with three components, with various topologies [3] and various similar materials [21,22] by controlling the configurations of the selenium droplets with the help of recently developed nanotechnology. Our crystals promote the expansion of the
ring topology concept called framed knots [3,24] and accelerate the reorganization of a framework of crystallography including topological molecules [20–23] unifying the notions of space group, homotopy, and embedding into curved surfaces [3].

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[17] Now preparing for publishing.