Preliminary

Space Group of Highly Crystalline α Chitin in the Grasping Spines from Arrow Worms *(Sagitta spp.)*[*1]

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Chitin is a prominent structural polysaccharide of insects, crustaceans consisted of a linear polymer of β-1, 4 linked D-acetyl glucosamine having similar glycosidic linkages and conformation of two-fold screw axis identical to cellulose. Chitin has various polymeric forms such as α chitin (antiparallel structure), β chitin (parallel structure), and γ chitin (mixture of α chitin and β chitin). Transformation of β chitin to α chitin is irreversible and is analogous to that of cellulose I to II. The mechanism of the transformation of chitin should thus be indicative.

As to the space group of α chitin, by X-ray diffraction Minke & Blackwell analysed lobster tendon[1)] and proposed $P2_12_12_1$ unit cell including two chains located in an antiparallel manner. On the other hand, Atkins et al. observed forbidden reflections in electron diffraction of *Sagitta* α chitin[2)]. These reflections suggested that the space group of α chitin was not $P2_12_12_1$, and that the chain polarity of α chitin might be parallel. In this study, we thus examined carefully the forbidden reflections from several kind of *Sagitta spp.*

Examining the Sample Sagitta Grasping Spine

Bone et al. mentioned that surrounding organism store metals Zn or Si in the grasping spines of *Sagitta*[3)]. Furthermore they found that these metals are distributed in the tissue of grasping spines. Actually, grasping spines gave especially sharp diffraction patterns of electron diffraction which likely come from those of metallic crystalline. (Consequently *Sagitta* chitin appeared as a certain complex with metal.)

The specific gravity, 1.46 by solution-gravity method coincided with calculated value by

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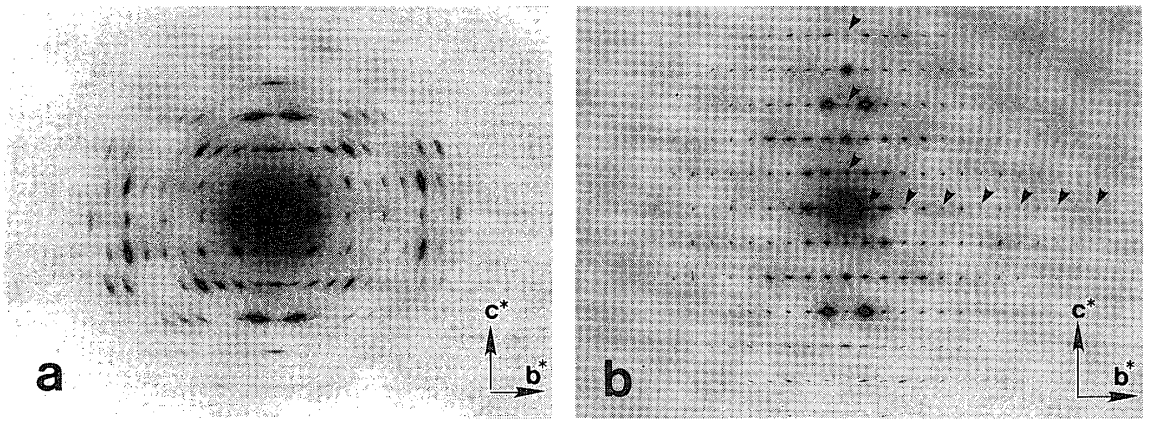

Fig. 1. Electron diffraction diagram of b*c* plane from *Sagitta* grasping spine; (a) symmetry agrees with $P2_12_12_1$, (b) rules out the symmetry of $P2_12_12_1$ with forbidden reflections (arrowheads).

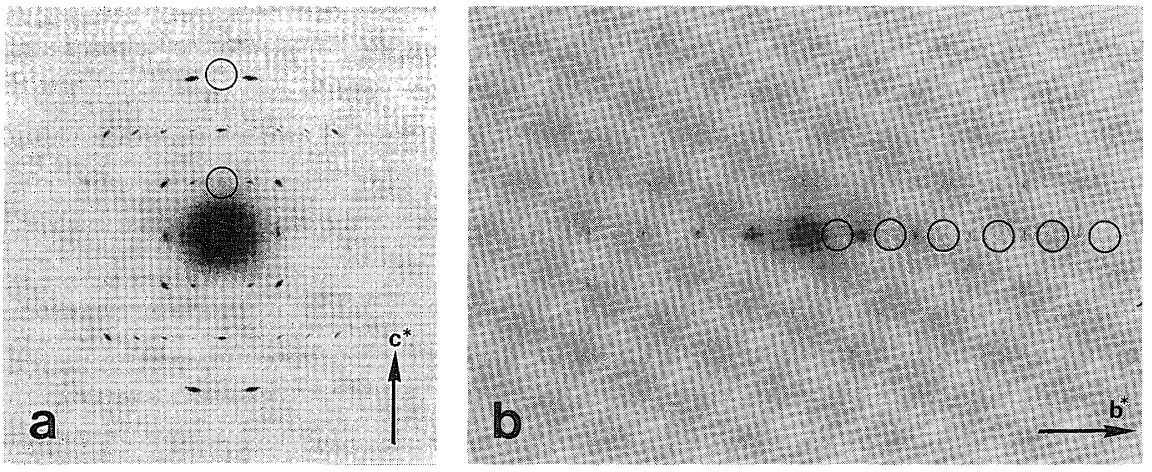

Fig. 2. Electron diffraction diagram,taken after rotating (a) 18° around the c* axis, (b) 11° around b* axis from the b*c* section as in Fig. 1a Forbidden reflections are disappeared (in circles).

Minke-Blackwell model. Furthermore EDS analysis showed there were no absorbance peaks of metals from the specimen which indicated sharp electron diffraction patterns with forbidden reflections. As the lattice image obtained by grasping spine indicated that the crystallite width was 100 nm at least, *Sagitta* is an appropriate sample of α chitin.

Examination of the Space Group

The X-ray diffraction patterns shows systematic absence of reflections satisfying of $P2_12_12_1$ symmetry. On the other hand, the electron diffraction patterns frequently ruled out the symmetry of $P2_12_12_1$. In these cases the patterns were prominent: all the lattice points were recorded in the observed area, and they were clearly isolated, which strongly

suggested that double diffraction (dynamical effect) is occurred.

To examine double diffraction effects, we recorded intensities of reflections while the sample was rotated around b* axis or c* axis. The forbidden reflections disappeared by elimination of possible reflections source of double diffraction. Also with successive electron radiation the forbidden reflections drastically became weak.

These investigation strongly indicated that double diffraction occurred because of unusual high crystallinity. Consequently we concluded that the space group of α chitin is $P2_12_12_1$, where chains are located in nature is of great importance in comparison with the cellulose system dominated by parallel structures.

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