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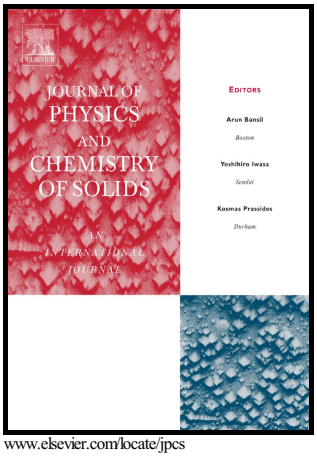

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Accurate measurement of the optical activity of alanine crystals and the determination of their absolute chirality

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Abstract:
Wavelength dependence measurements of the chiroptical properties in alanine crystals have so far been unsuccessful using conventional spectroscopic techniques. We describe our attempts to measure the wavelength dependence of the optical activity in L- and D-alanine crystals along each crystallographic axis, and to determine the absolute chirality of alanine crystals by correlating the absolute structure to the optical activity using an x-ray diffractometer and a generalized high accuracy universal polarimeter. We have succeeded in accurately measuring the optical rotatory dispersion in the <010> direction, which shows that the optical rotation of the D-alanine crystal is dextrorotatory and that of the L-alanine crystal is laevorotatory, thereby determining the absolute chirality. Furthermore, comparison with the optical activity in solution shows that the optical activity in alanine crystals is different not only in value, but also in the sign. These results have led us to conclude that the optical rotatory power in the crystalline state should not be simply the summation of molecular optical rotatory power values. We propose the necessity of a theory, which contains the contribution of molecular interactions within the crystal, in order to calculate the optical rotatory power of the crystalline state.

Keywords: Absolute structure, Optical activity, Linear birefringence, High accuracy universal polarimeter, Circular birefringence.

1. Introduction

Absolute structure is the structure of the spatial arrangement of the atoms in a noncentrosymmetric crystal, and is a concept that originated from studies on the X-ray diffraction technique and analyses proposed first by Knol *et al.*[1] and Bijvoet *et al.*[2] The determination of absolute structure contributes to the development of research into chirality, not only in physics and chemistry, but also in biology, pharmaceutics and related disciplines. However, it is often difficult to determine the absolute structure of crystals consisting only of light atoms.

The much-utilized concept of absolute structure was first proposed by Glazer *et al*.[3-5] In particular, absolute chirality has been defined as the relationship between absolute structure and chiroptical properties such as optical activity (OA) or optical rotatory power (ORP), which is more frequently used than circular birefringence (CB), and circular dichroism (CD). They have insisted that some previous reports on the absolute structures of uniaxial inorganic crystals needed to be corrected, and they succeeded in determining their absolute chirality. These works revealed that absolute chirality is a very useful term for use in chiral sciences and technologies, because once the absolute chirality of a crystal is correctly determined, X-ray crystal structure experiments and analyses for determining absolute structure become unnecessary. The absolute chirality is important for chiral crystals consist of achiral molecules such as glycine[6] because the chiroptical properties vanish in the solution.