Chemical Reaction

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1. Introduction

The spectrum of flux of SPring-8 shifts toward higher energy compared to the second generation SR spectrum, which is favorable for accurate structure factor measurement. The brilliant SR enables the accurate measurement even of high-order reflections from very small crystals. The short path-length and wavelengths of X-rays reduced absorption and extinction effect significantly. The well-collimated parallel beams of SR are expected to afford wider reciprocal space free from multiple diffraction(MD), though the intensity perturbation due to MD will be enhanced very much when it happened. Therefore intensity measurement for crystals with very heavy atoms are expected to be done more accurately at least than that for organic crystals measured with laboratory X-ray sources.

The subgroup "Chemical Reaction" was set up by small-molecule crystallographers belonging mainly to the field of chemistry. The researches we will do in Spring-8 are the ones based on the accurate structure factor measurement employing the single-crystal diffractometry. Our researches are thus divided into the four kinds of categories,

a. Excited-state crystallography,
b. Electron density measurement,
c. Solid state chemical reactions,
d. Small crystallite structure determination.

The researches **a**, **c** and **d** require accurate measurement of structure factors as well as the research **b**, because of feebleness of the diffracted X-rays due to short time of X-ray illumination (research **c**), due to small crystal size (research **d**), and because of the subtle difference of the diffracted intensities from crystals in the ground and excited states (research **a**).

Bending magnet beamline BL02B1 (Crystal Structure Analysis) was assigned to four subgroups including our group . The four groups designed six-circle diffractometer to fulfill the requirement of the groups and it will be installed by the end of this fiscal year. Details of the beamline and the diffractometer are described in Spring-8 Information. In the present report the research objectives of our group are described in conjunction with the vacuum camera installed at beamline BL02B1. The vacuum camera is an evacuated cylindrical camera with an imaging plate(IP) attached inside. It enables to measure structure factors under vacuum, that is, extremely low noise and can be used for crystallite structure analysis(**d**) and electron density measurement(b) .

2. Research Objectives for BL02B1

Many of crystalline compounds synthesized in chemistry, biology, material science and mineralogy are tend to be tiny needles and thin plates. The crystal structure of these compounds were left unsolved. The number of these crystallites is expected to be far larger than that of the solved ones. The structure of these crystals are analyzed with the powder diffraction method. However the complicated crystal structure are generally difficult to solve by the method. The beamline BL02B1 will make possible the structure factor measurement of crystallites with diameters less than 10 μm. The structure analysis of the unstable compounds is another problem to solve. It often happens that an unstable compound has much more interesting property and to solve the crystal structure is a key to understand the whole chemical process. The crystals of these compounds cannot always be handled under normal conditions. For example a crystal with melting point below room temperature are grown in capillary by slow cooling. They are mounted on a diffractometer as an assembly of small crystallites. Rocks are composed of several kinds of crystallites distributed among amorphous materials. The distribution of the crystallites in the rock and the gradual change of the composition of elements , which occupy special sites in the unit cell gives a lots of information on the rock-formation and the earth. If the narrowly collimated X-ray beam could be irradiated on a crystallite, there will be a lot of progress in these fields. Thus lots of users from various fields are expected to use our beamline to determine the crystallite structures.

Since SR decays with time, rapid measurement of structure factors with two dimensional detectors is very effective for electron density measurements (research **b**). Structure factors of a $KNiF_3$ crystal with a diameter 50μm were measured preliminary with the vacuum camera employing conventional tube X-rays. Reflections up to $2\theta=150^\circ$ were recorded within 3 and a half hours. Similar measurement can be done at BL02B1 in 10 minutes. Therefore the intensity decay of SR with time is not a serious problem. As described in the foregoing section well-collimated parallel beams of SR makes the reciprocal space free from MD wider, though the intensity perturbation due to MD is enhanced very much when it happened. Whether the vacuum camera can be used as a good tool for accurate structure factor measurement will be tested at BL02B1 .

3. Future Research Objectives

For the researches **a** and **c**, construction of an undulator beamline is proposed by our group. Electronic states of molecules in excited states have been extensively studied by spectroscopy. However structures and electron density of excited molecules have not been measured directly but estimated from the evidences obtained by spectroscopy. These information on molecules can in principle be obtained by diffraction. However diffraction has been developed as the method to measure information of stable molecules in the ground state. Since the measurement by diffraction usually takes more than an hour, diffraction could not measure these information of excited molecules, which have very short lifetime ranging from msec to nsec. Photo-excited molecules often exhibit fluorescence and phosphorescence corresponding to the transition between singlet states, and triplet to siglet transition, respectively. Since the lifetime is short and the number of excited molecules is small, highly accurate structure factor measurement is necessary. And since the lifetime of excited molecules generally becomes longer and temperature shift of the sample due to heat load induced by laser becomes smaller as temperature decreases, low temperature measurement is essentially necessary for the research. The aim of the research a is to measure structures and electron densities of photo-excited molecules by diffraction utilizing intense and well-collimated X-rays from SPring-8 undulator beamline.

For research **a** and **c** two-dimensional charged-particle detector, MSGC(Multi Strip Gas Chamber) is now being developed by Profs. Tanimori and Ohashi of Tokyo Institute of Technology, one of the members of our group. This permits us real-time measurement of structure factors with higher accuracy than the present two-dimensional detectors. For excited molecules with ultra-short lifetimes use of the single-bunch mode operation of SPring-8 will be made.