# Accurate Structure Factors from Synchrotron Powder Diffraction Data at SPring-8

The distribution of electron density in materials determines their properties and functions. Many experimental and theoretical studies in materials science such as those using diffraction analysis, spectroscopy and density functional calculations (DFT) have been performed to reveal electron density distributions. An X-ray is a good probe of electrons. The structure factors from X-ray diffraction give information on total electron density distribution including both core and valence electrons. Accurate structure factors are always required in materials science fields, since the structure factors can be used not only for experimental charge density studies but also for evaluating different theoretical calculations.

Recent progress in synchrotron powder X-ray diffraction techniques including the third generation synchrotron X-ray source, detector, measurement system and analytical methods enable us to accurately determine structure factors for charge density studies. Powder diffraction data with high intensity and high angular resolution has now become available. A large Debye-Scherrer camera for studying charge density in detail has been installed at beamline **BL02B2**. The precise charge densities of several kinds of material such as $PbTiO_3$ [1] have been determined from powder diffraction data using the camera. For a proper understanding of the charge densities determined by SPring-8 powder data, quantitative estimation of accuracy of the data is essential. The evaluation of the quantitative accuracy of diffraction data is not an easy task. Benchmark tests need accurate data from both experimental and theoretical sides.

There are accurate structure factors of silicon and diamond that have been measured by various experimental methods, such as the Pendellösung method [2,3]. These data have been widely used for experimental charge density studies. Furthermore, the data have been, widely used for evaluating of the accuracy of theoretical calculations. In this study, we measured accurate powder diffraction data for both silicon and diamond at BL02B2 [4]. The accuracy of the data was estimated by comparing them with both the Pendellösung data and the results of several theoretical calculations.

The synchrotron powder diffraction experiments were carried out at beamline BL02B2. High-energy X-rays, 0.40122(1) Å, were used for reducing the effect of absorption. The higher-angle reflections in powder data have the disadvantage of collecting high counting statistics data because of factors such as the Lorentz factor. To improve the counting statistics of higher-angle-range data, we measured two data sets for one sample at one temperature. To extract accurate structure factors from two powder data sets, the simultaneous analysis of two data sets is most suitable. We developed Rietveld refinement software, which is suited for an accurate structural analysis of multi-powder data. It allows the simultaneous refinement of two different types of statistics for powder diffraction data. The R-factors based on weighted profile, $R_{wp}$, and the Bragg intensities, $R_I$, of Rietveld refinements were as small as 2.70% and 1.75% for silicon and 2.93% and 3.74% for diamond. We determined the observed structure factors on the basis of the Rietveld refinements.

The differences between the present structure factors and the previous structure factors determined by Pendellösung method [2,3] were within the standard uncertainty values of the present data. To evaluate the level of agreement between the present powder data and the Pendellösung data, we calculated inter-data-set agreement factors, which are expressed as $\Sigma|| F_{powder}| - | F_{Pendellösung}|| / \Sigma | F_{powder}|$. They are 0.5% for silicon and 0.2% for diamond. Considering that these values were obtained by totally different experimental methods, the level of agreement is excellent.

The structure factors of silicon and diamond have been extensively calculated using theoretical calculations. The structure factors are reported as atomic form factors, $f(h\,k\,l)$. The conversion of atomic form factors to structure factors and *vice versa* is very straightforward as long as the thermal parameters are known. To evaluate the level of agreement between the present powder data and the theoretical values obtained by Pere *et al.* [5], we calculated inter-data-set agreement factors, which are expressed as $\Sigma|| f_{powder}| - | f_{Theory}|| / \Sigma | f_{powder}|$. The values are within 0.53% for silicon and within 1.6% for diamond.

MEM analysis was carried out to investigate the usefulness of the structure factors determined in this study in revealing electron density distributions. The charge densities determined using theoretical calculations for silicon and diamond have been widely reported by many researchers. Most of charge the densities are reported as deformation maps. To compare the present MEM densities with other

theoretical deformation maps in detail, we have calculated deformation maps from MEM charge densities. MEM deformation maps of silicon and diamonds are shown in Figs. 1(a) and 1(b). The charge density at the bond midpoint for silicon and diamond are 0.22 and 0.42 eÅ$^{-3}$, respectively. The theoretical value of the valence density for silicon is 0.18 eÅ$^{-3}$ [6] and that for diamond is 0.45 eÅ$^{-3}$ [6]. The values determined in this study are almost identical to those determined using theoretical calculations and are within 0.04 eÅ$^{-3}$. The results can be regarded as showing that the present MEM charge densities are quantitatively reliable and that such densities can be used to discuss the physical properties of materials.

In this study, we accurately measured structure factors of silicon and diamond by synchrotron X-ray powder diffraction experiments. We evaluated the accuracy of the structure factors by comparing them with the Pendellösung data and the results of theoretical calculations. These results show that the powder diffraction data measured at BL02B2 is highly reliable. Since the data have sufficient accuracy, the present method can be widely used for various materials in powder form.

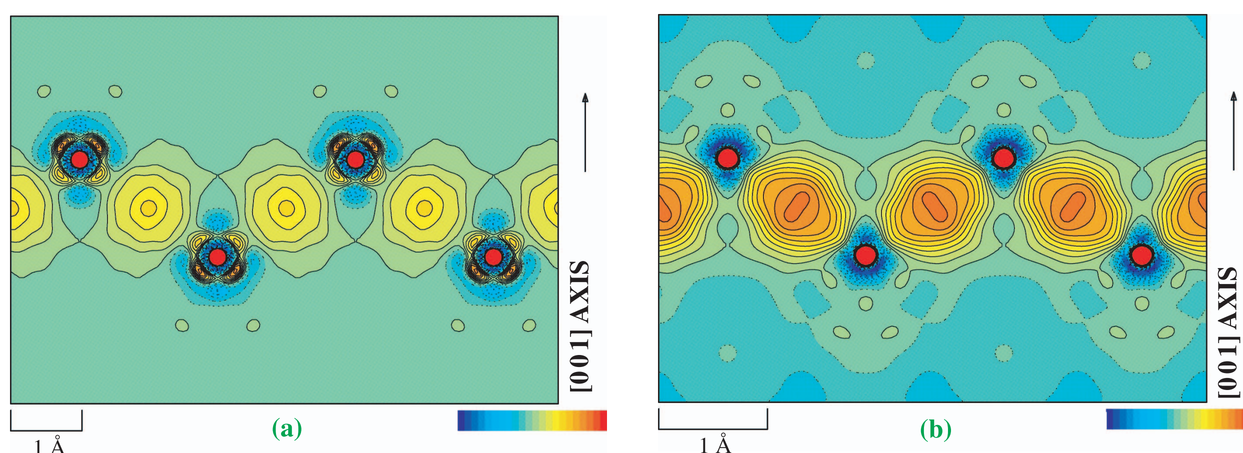


Fig. 1. The deformation charge densities of **(a)** silicon and **(b)** diamond for 110 plane based on MEM analysis. The contour lines are drawn from -0.55 to 0.55 with 0.05 eÅ$^{-3}$ step width for **(a)**, **(b)**.

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**References**

[1] Y. Kuroiwa *et al.*: Phys. Rev. Lett. **87** (2001) 217601.
[2] T. Saka and N. Kato: Acta Cryst. A **42** (1986) 469.
[3] T. Takama *et al.*: Acta Cryst. A **46** (1990) 514.
[4] *E. Nishibori, E. Sunaoshi, A. Yoshida, S. Aoyagi, K. Kato, M. Takata, and M. Sakata: Acta Cryst. A* ***63*** *(2007) 43.*
[5] J. Pere *et al.*: J. Phys. Cond. Matt. **11** (1999) 5827.
[6] Z.W. Lu *et al.*: Phys. Rev. B **47** (1993) 9385.