PS09.01.24 CHARGE DENSITY OF KDP(KH_2PO_4) BY THE MAXIMUM ENTROPY METHOD.
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In order to investigate the nature of hydrogen bond in KDP(KH_2PO_4), the charge density distribution of KDP is obtained at room temperature by the Maximum Entropy Method (MEM) from X-ray powder diffraction data. It is well known that KDP is the prototype of hydrogen-bonded ferroelectrics in which the hydrogen atoms are considered to play an important role in the phase transition and that the phase transition temperature is increased about 100K when hydrogen atoms in KDP are substituted by deuterium atoms. In order to understand such a large isotope effect, there have been performed many studies on the hydrogen bond both theoretically and experimentally. In this study, the nature of hydrogen bond of KDP is described through the charge density distribution. Considering much less scattering power of hydrogen for X-ray than the rest of atoms, it is not an easy task to detect the precise charge density distribution of hydrogen bond by MEM. So far, only one example is known which is ice(I_h) (Sakata, Takata, Oshizumi, Goto and Hondoh (Physics and Chemistry of Ice, 1992, 62-68)). In this case, only oxygen atoms are involved other than hydrogen atoms.

The data set used in the analyses are collected by powder X-ray diffraction experiments at Photon Factory, Tsukuba. The wave length of incident X-ray photons is 1.3Å and all the data up to 125 degree in 2-theta which correspond 0.74Å resolution. One of the results is shown in Fig. 1, in which not only fairly strong PO_4 covalent bond but also hydrogen bond between O – O

Fig.1 Charge density distribution of KDP projected c-axis. Contour lines are drawn between 5.2-35.2 with 1.2 [a.u.] step

atoms are recognized. It seems that the nature of hydrogen bond is weak covalent bond rather than ionic between fairly long distant two oxygen atoms. It is also found that the charge density at the mid point of O – O in KDP is higher than that in ice(I_h), which must be the reflection of strength of hydrogen bond in these materials. Indeed, O – O bond length in KDP is shorter than that in ice(I_h).
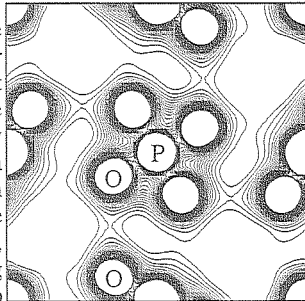
PS09.01.25 NUCLEAR DENSITY DISTRIBUTION OF KDP(KH_2PO_4) OBTAINED BY THE MAXIMUM ENTROPY ANALYSIS.
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The nuclear density distribution of KDP(KH_2PO_4) at room temperature is obtained by the Maximum Entropy Method (MEM) from neutron powder diffraction data. It is not common to carry out neutron powder diffraction experiment without replacing hydrogen to deuterium, because of large incoherent scattering cross section of hydrogen. One of the long term aims of the present study is to clarify the structural difference of KDP and DKDP, which shows huge isotope effects. Therefore it is absolutely necessary to have the nuclear density distribution of KDP. Since Slater proposed the order-disorder type phase transition model of KDP, many structural studies were carried out. By these study, it is confirmed that the hydrogen atom is located on local equilibrium position at room temperature which is paraelectric phase and the occupancy of the hydrogen atom describes the order parameter of phase transition.

The neutron powder diffraction experiment is carried out by HRPD (High Resolution Powder Diffractometer) at JAERI-3M. The powder pattern is recorded at the wave length 1.823Å and 78 reflections up to 2θmax=150 deg. are collected. This corresponds to 0.476Å resolution. The MEM calculation is done by computer program MEND, which can deal with negative scattering length of hydrogen atom. In the obtained density map of (00z) plane, the hydrogen atom is clearly recognized. They are elongated to the direction of the oxygen atom. But the twin local maxima of hydrogen bond are not seen due to the limited resolution of this study. It is highly desirable to perform the same experiment with much higher resolution (approximately 0.3Å resolution). The distribution of oxygen atom shows substantial skewness, which should be attributed to anharmonic thermal vibrations related to hydrogen bond.

PS09.01.26 ELECTRON DENSITY DISTRIBUTION OF SUPERCONDUCTOR Sr_2RuO_4 BY THE MAXIMUM ENTROPY METHOD.
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The electron density distribution in Sr_2RuO_4, which is a K_2NiF_4 structure type superconductor, was determined by the combination of powder X-ray diffraction data and maximum entropy method. The high-Tc superconductors commonly have a layered perovskite structure containing CuO_2 planes, in which the electronic structure is characterized by large hybridization between Cu d and O p states. On the other hand, Sr_2RuO_4 is a recently discovered superconductor which contains RuO_2 planes instead of CuO_2 planes. Theoretical calculation showed that there also exists the large hybridization between Ru d and O p states in Sr_2RuO_4. (T. Oguchi, *Phys. Rev.* B, 1995, **51**, 1385-1388) However, no direct observation of hybridized Ru d and O p states has been done. Therefore, it is important to examine the electron density distribution of Sr_2RuO_4 and to compare the theoretical results.

The Sr_2RuO_4 powder used in the present work was prepared by heating the mixed powder of ruthenium and strontium carbonate in air at 1200°C for 24 hours. Powder pattern was measured at room temperature by θ-2θ step scanning using the CuKα radiation. Whole powder pattern fitting was applied in order to obtain integrated intensities for each reflection. The integrated intensities were converted into the structure factors by the ordinary least-squares refinement. Consequently, 60 structure factors were obtained. Based on these data, the electron density distribution was calculated by the maximum entropy method. The resultant density map shows the strong covalent bondings between Ru and octahedrally coordinated O atoms. The RuO_6 octahedron is small tetragonally distorted, so Ru-O bondings are divided into two types, i.e., the equatorial bond (Ru-O1, ~1.93Å) and apical one (Ru-O2, ~2.06Å). Nevertheless the atomic distance of Ru-O2 is longer than that of Ru-O1, the electron density at middle point of Ru-O2 was much higher than that of Ru-O1.