Behavior of Thermal Parameters and the Phase Transition in DKDP

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It has been considered that the tunneling character of proton is coupled with other heavy atoms to induce ferroelectricity below 123 K in KDP (KH_2PO_4). If protons are replaced by deuterons, the transition temperature elevates up to T_c = 213 K in DKDP. There remains a question whether heavy atoms are in disordered or displacive within anharmonic potentials above T_c. In order to elucidate this point, we have performed detailed structure analyses of DKDP above and below T_c.

Single crystals were grown by evaporation method from a heavy water solution of DKDP powder provided commercially. A rectangular prism of $2.8 \times 2.6 \times 2.5$ mm^3 was cut from a transparent block of the crystal. Aluminum electrodes were attached on the *c*-planes to apply an electric field so that the crystal was single domain below T_c. Neutron diffractmeter FONDER was employed to collect diffracted intensity data. Measured temperatures were 10, 70, 120, 160, 190, 210, 223, 250 and 303 K. Every profiles of the reflection peaks were checked and programs DABEX and RADIEL were used to correct absorption and extinction effects. Crystal structures were refined by using the least squared-calculation program, SHELXL-97. Split atom method was employed to represent disordered character of deuteron above T_c. All data sets were successfully analyzed; the *R* factors were about 4 % with anisotropic thermal parameters.

The positional parameters are almost steady below T_c. Figure 1 (a) displays the temperature dependence of the dipole moment of the unit cell estimated by assigning simple ionic point charges to each atom. The values are almost in good agreement with the reported spontaneous polarization (Samara 1973). All the Debye-Waller factors (mean-squared displacement) U_{33} decrease monotonically with decreasing temperature as shown in Fig. 1 (b). They do not vanish even at 0 K, representing quantum zero-point vibration, whose magnitude is lower than the expected value from the room temperature phase (Nelmes *et al*. 1982).

Below T_c, the ordering of deuteron induces a distortion of PO_4^{3-} tetrahedron and a displacement of K^+ ion. The magnitudes of the thermal vibration of K and P changes little at T_c. If they are disordered units in the paraelectric phase, they should have greater thermal parameters. So it is hard to image a disordered P or K above T_c. The thermal parameter indicates that D is almost in the ground state below 100K. A comparison with KDP will be presented elsewhere.

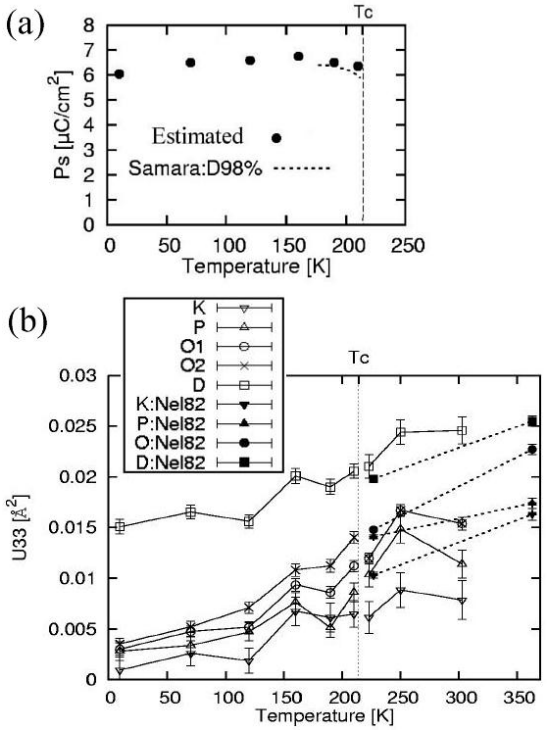

Fig. 1. Temperature dependence of (a) the estimated polarization with K^+, D^+, P^{5+} and O^{2-}, and (b) the Debye-Waller factor U_{33}.