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Structural parameters determining the transition temperature of tetragonal KH$_2$PO$_4$-type crystals

M. Ichikawa*

Division of Physics, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

D. Amasaki[†]

Division of Physics, Graduate School of Science, Hokkaido University, Sapporo 060-0810, Japan

T. Gustafsson

Materials Chemistry, Ångström Laboratory, Uppsala University, Box 538, SE-751 21 Uppsala, Sweden

I. Olovsson

Materials Chemistry, Ångström Laboratory, Uppsala University, Box 538, SE-751 21 Uppsala, Sweden

A systematic study of the structural parameters determining the ferroelectric phase transition temperature T_c in tetragonal KH$_2$PO$_4$ (KDP)-type crystals MH$_2$XO$_4$ has been performed by searching the correlation between different structural parameters and T_c. It has been revealed that the transition temperature is determined not only by the hydrogen-bond distance R, as reported earlier, but also by the distortion of XO$_4$ (via O-X-O angle α_1) and the packing of M and XO$_4$ along the c axis (via the rotation angle θ around the c axis); α_1 reflects the dipole moment of XO$_4$ and θ may influence the amplitude of optical vibration of M and XO$_4$. The contribution of each structural part to the transition temperature T_c in the tetragonal KDP family has been revealed in a comprehensive way for ferroelectrics.

In ferroelectric crystals, all the nuclear charges, their positions and the electron distribution over the whole crystal contribute to the macroscopic polarization in a continuous way. This characteristic is different from ferromagnets with a discete unit of electron spin. It is then, in general, very difficult to specify which microscopic component constitutes the macroscopic polarization (or the closely related transition temperature T_c). The KH$_2$PO$_4$ (KDP) family is one of the typical hydrogen-bonded ferroelectric crystals which has been most extensively studied. The structural moiety consists of alkaline metal, tetrahedral ion, and a hydrogen bond to connect two tetrahedra. From a microscopic structural point of view, it was empirically revealed earlier that T_c correlates linearly with the O$\cdots$O hydrogen-bond distance R for the tetragonal KDP family.[1] Inclusion of our recent results for KH$_2$AsO$_4$ (KDA) and KD$_2$AsO$_4$ (DKDA), however, show a considerable deviation from this linear relation.[2] Stimulated by these facts, a further search of unknown correlations between T_c and structural parameters characterizing KDP-type crystals has been done. As a result it has been found that the distortion of the tetrahedral ion and the packing degree of alkaline metal and tetrahedra along the c axis also contribute to the transition temperature in addition to the hydrogen-bond distance. This study thus reveals how each basic structural unit contributes to the transition temperature in ferroelectrics.

Tetragonal KDP-type crystals MH$_2$XO$_4$ (space group $I\bar{4}2d$) consist of alkali metals M and XO$_4$ tetrahedra packed along the c axis (*lattice*) and OHO hydrogen bonds connecting two tetrahedra lying in the $a-b$ plane (*proton systems*) (Figs. 1 and 2). In order to explain the remarkable isotope effect of T_c (~ 100 K) known for this family, proton tunneling was invoked in 1960, mainly focusing on the hydrogen-bond system (*proton tunneling* model).[3] The proton tunneling model has been developed[4] and further extended to the proton-lattice coupling model.[5] The theoretical interpretation along these lines was accepted during the 1960s and 1970s.[6,7] An interpretation of the isotope effect in terms of the geometric isotope effect of the hydrogen-bond distance was proposed by one of the present authors.[8,9] As an extension of this line, it was reported that a positive linear relation between T_c and R appears to be valid for the tetragonal KDP family.[1] However, it was still not well understood why only the hydrogen-bond system would play the cruicial role on the phase transition temperature and whether the remaining structural parts also contribute to it. Recently we have made structural studies of KH$_2$AsO$_4$ and KD$_2$AsO$_4$ (the end members with respect to T_c) in order to get comprehensive information about the phase transition and isotope effect in the tetragonal KDP family. This study gave the unexpected result that R of KDA and DKDA are larger compared to those of KDP and DKDP, respectively, in spite of lower T_c of the former compounds. This seemed to indicate that there exist other factors influencing T_c. A systematic study was thus performed to search for other structural factors which correlate with T_c.

A scatter plot between T_c and R is shown in Fig. 3. It can be clearly seen that KDA and DKDA data remarkably deviate from the T_c vs R linear and positive correlation. This seems to suggest that an unknown negative correlation with T_c is superposed on the positive correlation between R and T_c. A negative correlation was thus found between R and
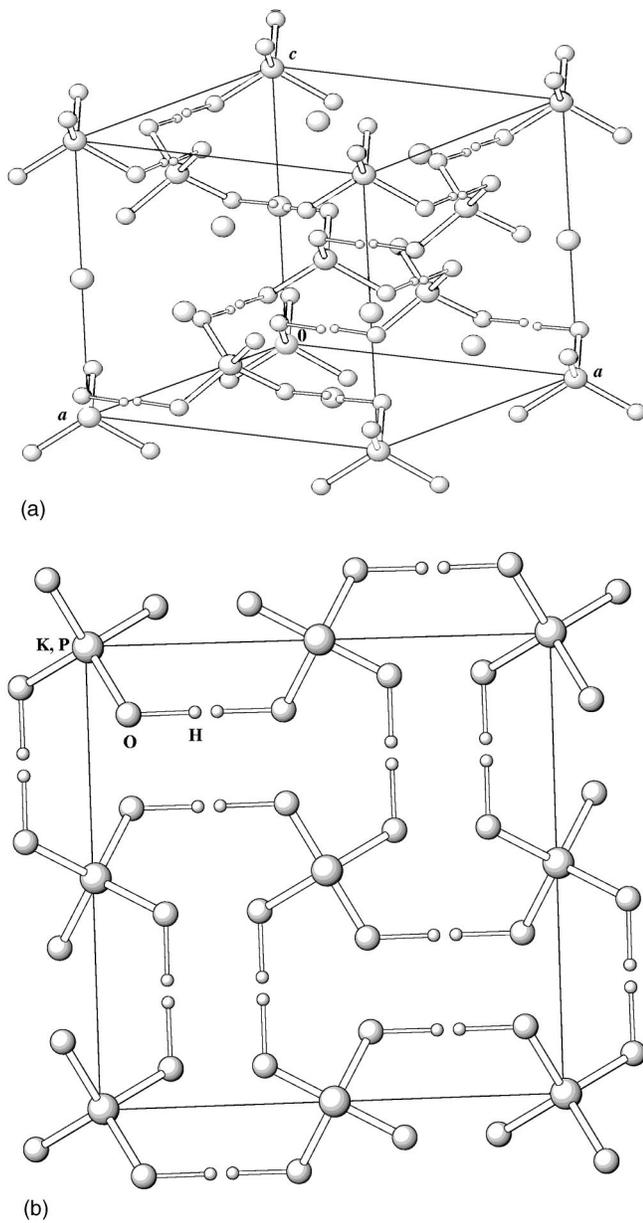
FIG. 1. Structure of tetragonal KH_2PO_4 (KDP). (a) Perspective view and (b) projection along the c axis.
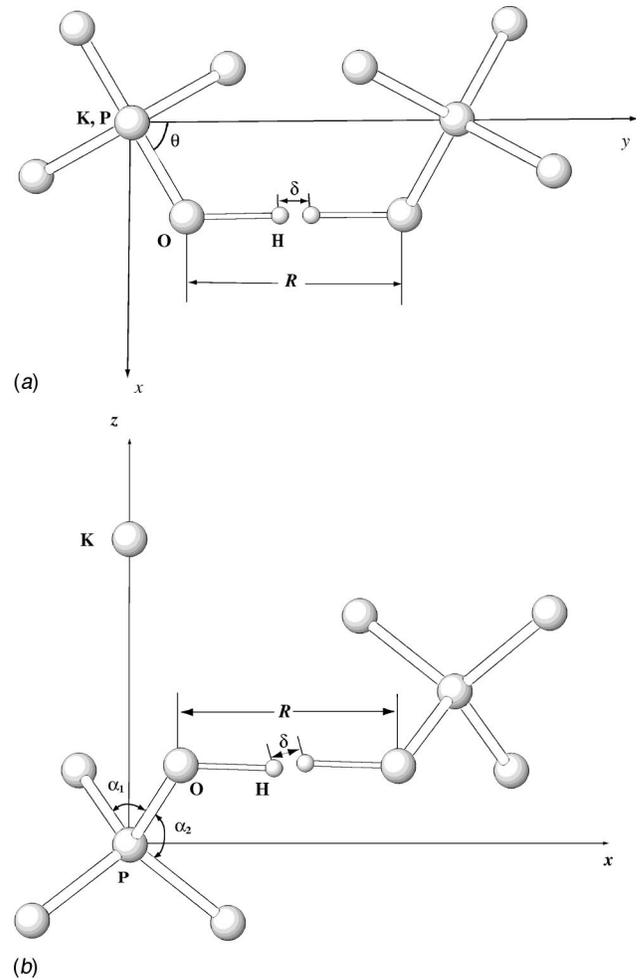

FIG. 2. Part of the structure of tetragonal KH_2PO_4 (KDP) and some structural parameters. (a) View along the c axis and (b) view along the a axis.

one of two O-X-O angles, α_1 (see Fig. 4) which characterizes the distortion of the XO_4 ions (cf. Ref. 2); in short, this suggests a positive correlation between T_c and the distortion (α_1). These facts imply that the decrease in T_c due to decreased distortion as R increases is superposed on the opposite (positive) correlation between T_c and R. It is also recognized that the α_1 value of PO_4 is systematically larger than that of AsO_4 when the corresponding compounds are compared.

In spite of the addition of the contribution of α_1 to the T_c dependence, a systematic deviation between observed and estimated T_c was still noticed. After further investigation, it became clear that this deviation correlates with the rotation angle θ of XO_4 around the c axis. Finally, T_c could be ex-

pressed empirically by three structural parameters R, α_1, and θ as

$$T_c = C_1 R + C_2 \alpha_1 + C_3 \theta + C_4. \tag{1}$$

The best fit to all the available data at atmospheric pressure gave the values: $C_1 = 2850$, $C_2 = 69.50$, $C_3 = -15.36$, $C_4 = -13\,720$. The three parameters are interrelated through the relation

$$R = -2R_{XO} \cos \theta \sin \frac{\alpha_1}{2} + \frac{a}{2}, \tag{2}$$

where R_{XO} denotes the X-O length (see Fig. 2).

T_c has been plotted against an effective hydrogen-bond distance R_e incorporating the effect of α_1 and θ in Fig. 5. R_e is defined by

$$R_e = \left(R + \frac{C2}{C1} \alpha_1 + \frac{C3}{C1} \theta \right) C_5, \tag{3}$$

where C_5 is a scaling factor, determined so that $R_e = R$ for KDP. It can be seen that the scatter of the points is considerably improved as compared to Fig. 3. From these empirical
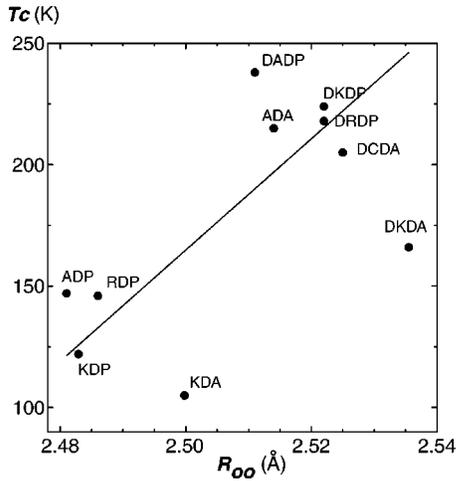
FIG. 3. Correlation between the transition temperature T_c and hydrogen-bond distance R in the tetragonal KH_2PO_4 (KDP) family. KDP: KH_2PO_4; DKDP: KD_2PO_4; RDP: RbH_2PO_4; DRDP: RbD_2PO_4; KDA: KH_2AsO_4; DKDA: KD_2AsO_4; ADP: $NH_4H_2PO_4$; DADP: $NH_4D_2PO_4$; ADA: $NH_4H_2AsO_4$; DCDA: CsD_2AsO_4.

facts it may be stated that the transition temperature T_c in the tetragonal KDP family can be expressed by a linear combination of three structural parameters R, α_1, and θ.

Let us discuss the implication of the present results. As for the rotation angle θ around the c axis, it is still unclear what role it plays in the structure. It was found, however, that θ correlates with the degree of packing of M and XO_4 along the c axis. We define unfilled spacing s as a measure of the spacing unoccupied by M and XO_4 ions in the c axis length as

$$ s \equiv \frac{c}{2} - R_{XO} \cos \frac{\alpha_1}{2} - r_i, \qquad (4) $$

where r_i denotes ionic radii of the alkaline metal [cf. Fig. 2(b)]. There is a negative correlation between s and θ, as shown in Fig. 6. It may be worthwhile to note here that the
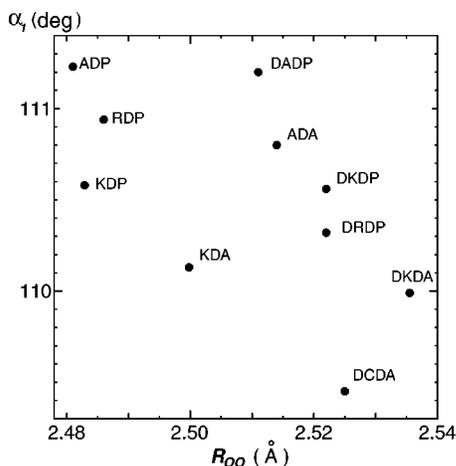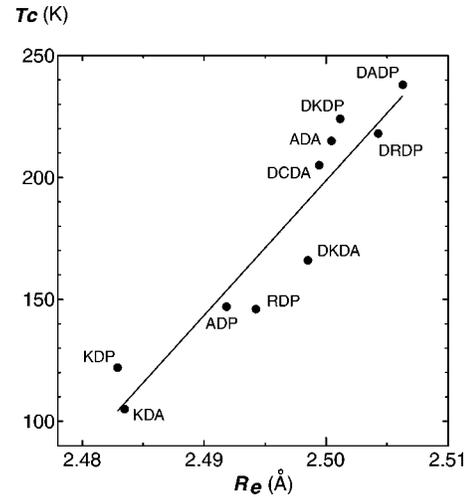

FIG. 5. Correlation between the transition temperature T_c and effective hydrogen-bond distance R_e (cf. Fig. 3 for the abbreviation of the compound names).

tetragonality c/a is determined by the ionic radius r_i of the M atom in the ferroelectric KDP family.[11] This is shown in Fig. 7.

Now the implication of all these results is clear. Each structural part contributes to T_c in the following way. Firstly, as for the hydrogen-bond part in the $a-b$ plane, the longer the hydrogen-bond distance R connecting XO_4 ions, the higher the transition temperature. In other words, the longer the separation between the two H(D) sites, the higher the transition temperature. Secondly, T_c depends on the distortion of the XO_4 ions: The larger the dipole moment of the XO_4 ions, the higher the T_c. Thirdly, with respect to the M-XO_4 part along the c axis, the larger the unfilled spacing s along the c axis, the higher the transition temperature. The unfilled spacing s may be related to the amplitude of the M-XO_4 optical vibration along the c axis.

It seems appropriate to point out that the proton system has an order-disorder character, since two peaks of proton
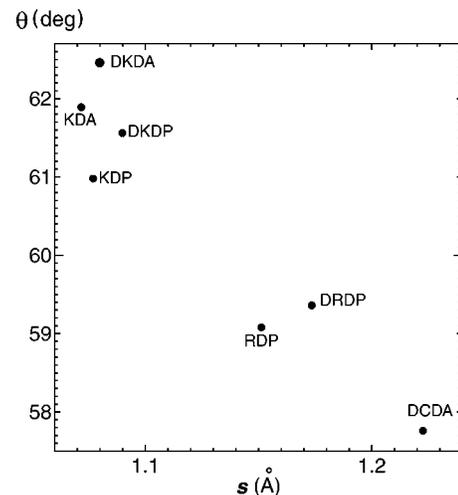

FIG. 4. Correlation between the O-X-O angle α_1 in the XO_4 ion and the hydrogen-bond distance R (cf. Fig. 3 for the abbreviation of the compound names).

FIG. 6. Correlation between the rotation angle θ around the c axis and unfilled spacing s. (cf. Fig. 3 for the abbreviation of the compound names).
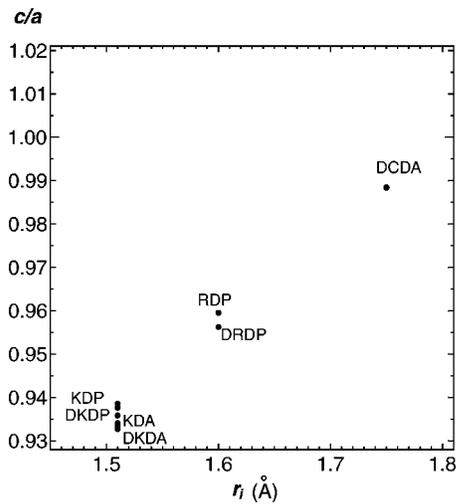
FIG. 7. Correlation between the tetragonality c/a and ionic radii r_i (cf. Fig. 3 for the abbreviation of the compound names).

nuclear density in KDP were resolved by high-resolution neutron diffraction.[10] The order-disorder proton movement in the $a-b$ plane couples with the reversal of the dipole moment of the XO_4 ions, which further couples with the M-XO_4 optical vibration along the c axis. These results thus give us a perspective as to how each structural moiety contributes to the transition. It may be noted here, however, that even if the proton exhibits an order-disorder character with a two proton-site separation more than 0.4 Å in the KDP case, the character of the M atom and the X and O atoms in the XO_4 group cannot be claimed as order-disorder. The shift of these atoms accompanying the proton movement is within the amplitude of thermal motion.[12] This means that the tetragonal KDP family is not a pure order-disorder-type ferroelectric in which each constituent atom in the crystal has a two-site character. In other words, the obtained results are compatible with the proton-lattice coupling model,[5] apart from the controversial point in the proton system, i.e., proton tunneling or order-disorder. Katrusiak[13] recently referred to the coupling of displacive and order-disorder transformation in hydrogen-bonded ferroeletrics. Furthermore, quite recently, Bussmann-Holder and Michel[14] proposed a new model for hydrogen-bonded ferroeletrics. The present results may contribute to the construction of a simple and realistic theoretical model for the phase transition and isotope effect in KDP-type crystals.

In summary, the present results provide a perspective as to how each structural unit contributes to the transition temperature in a ferroelectric. These results may provide a frame for constructing a theoretical model in a simpler and comprehensive way.

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*Corresponding author. FAX: +81-11-706-4926. Email address: ichikawa@phys.sci.hokudai.ac.jp

†Present address: Dents Hokkaido, Sapporo 060-8545, Japan.

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