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*Note: The content of the table is in Japanese.*
Structural parameters determining the transition temperature of tetragonal KH$_2$PO$_4$-type crystals

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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 $\alpha_x$) and the packing of M and XO$_4$ along the $c$ axis (via the rotation angle $\theta$ around the $c$ axis); $\alpha_x$ reflects the dipole moment of XO$_4$ and $\theta$ 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 discrete 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···O hydrogen-bond distance $R$ for the tetragonal KDP family. 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. 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 $I4_2d$) 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 $T_c$ ($\sim 100$ K) known for this family, proton tunneling was invoked in 1960, mainly focusing on the hydrogen-bond system (proton tunneling model). The proton tunneling model has been developed and further extended to the proton-lattice coupling model. The theoretical interpretation along these lines was accepted during the 1960s and 1970s. 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. 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. However, it was still not well understood why only the hydrogen-bond system would play the crucial 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 Tc) 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 $T_c$. The results indicate that the structural characterizing KDP-type crystals 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.

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one of two O-X-O angles, $\alpha_1$ (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 ($\alpha_1$). 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 $\alpha_1$ 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 $\alpha_1$ 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 $\theta$ of XO$_4$ around the $c$ axis. Finally, $T_c$ could be expressed empirically by three structural parameters $R$, $\alpha_1$, and $\theta$ as

$$T_c = C_1 R + C_2 \alpha_1 + C_3 \theta + C_4.$$  \hfill (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

$$R = -2R_{XO} \cos \theta \sin^2 \frac{\alpha_1}{2} + \frac{a}{2},$$  \hfill (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 $\alpha_1$ and $\theta$ in Fig. 5. $R_e$ is defined by

$$R_e = \left(R + \frac{C_2}{C_1} \alpha_1 + \frac{C_3}{C_1} \theta \right) C_5,$$  \hfill (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

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FIG. 1. Structure of tetragonal KH$_2$PO$_4$ (KDP). (a) Perspective view and (b) projection along the $c$ axis.

FIG. 2. Part of the structure of tetragonal KH$_2$PO$_4$ (KDP) and some structural parameters. (a) View along the $c$ axis and (b) view along the $a$ axis.
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 \( R, \alpha_1, \) and \( \theta \).

Let us discuss the implication of the present results. As for the rotation angle \( \theta \) around the \( c \) axis, it is still unclear what role it plays in the structure. It was found, however, that \( \theta \) 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

\[
s = \frac{c}{2} R_{XO} \cos \frac{\alpha_1}{2} - r_i, \tag{4}
\]

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

tetragonality \( c/a \) is determined by the ionic radius \( r_i \) of the \( M \) atom in the ferroelectric KDP family. 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. 3](image-url) 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: \( CsD_2AsO_4 \).

![Fig. 4](image-url) Correlation between the \( O-X-O \) angle \( \alpha_1 \) in the \( XO_4 \) ion and the hydrogen-bond distance \( R \) (cf. Fig. 3 for the abbreviation of the compound names).

![Fig. 5](image-url) Correlation between the transition temperature \( T_c \) and effective hydrogen-bond distance \( R_e \) (cf. Fig. 3 for the abbreviation of the compound names).

![Fig. 6](image-url) Correlation between the rotation angle \( \theta \) around the \( c \) axis and unfilled spacing \( s \). (cf. Fig. 3 for the abbreviation of the compound names).
nuclear density in KDP were resolved by high-resolution neutron diffraction. 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. 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, apart from the controversial point in the proton system, i.e., proton tunneling or order-disorder. Katrusiak recently referred to the coupling of displacive and order-disorder transformation in hydrogen-bonded ferroelectrics. Furthermore, quite recently, Bussmann-Holder and Michel proposed a new model for hydrogen-bonded ferroelectrics. 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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**FIG. 7.** Correlation between the tetragonality \(c/a\) and ionic radii \(r_i\) (cf. Fig. 3 for the abbreviation of the compound names).