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## Structural parameters determining the transition temperature of tetragonal $\text{KH}_2\text{PO}_4$ -type crystals

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A systematic study of the structural parameters determining the ferroelectric phase transition temperature  $T_c$  in tetragonal  $\text{KH}_2\text{PO}_4$  (KDP)-type crystals  $\text{MH}_2\text{XO}_4$  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  $\text{XO}_4$  (via O-X-O angle  $\alpha_1$ ) and the packing of M and  $\text{XO}_4$  along the  $c$  axis (via the rotation angle  $\theta$  around the  $c$  axis);  $\alpha_1$  reflects the dipole moment of  $\text{XO}_4$  and  $\theta$  may influence the amplitude of optical vibration of M and  $\text{XO}_4$ . 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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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  $\text{KH}_2\text{PO}_4$  (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  $\text{O}\cdots\text{O}$  hydrogen-bond distance  $R$  for the tetragonal KDP family.<sup>1</sup> Inclusion of our recent results for  $\text{KH}_2\text{AsO}_4$  (KDA) and  $\text{KD}_2\text{AsO}_4$  (DKDA), however, show a considerable deviation from this linear relation.<sup>2</sup> 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  $\text{MH}_2\text{XO}_4$  (space group  $I\bar{4}2d$ ) consist of alkali metals M and  $\text{XO}_4$  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*).<sup>3</sup> The proton tunneling model has been developed<sup>4</sup> and further extended to the proton-lattice coupling model.<sup>5</sup> The theoretical interpretation along these lines was accepted during the 1960s and 1970s.<sup>6,7</sup> 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.<sup>8,9</sup> 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.<sup>1</sup> 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  $\text{KH}_2\text{AsO}_4$  and  $\text{KD}_2\text{AsO}_4$  (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

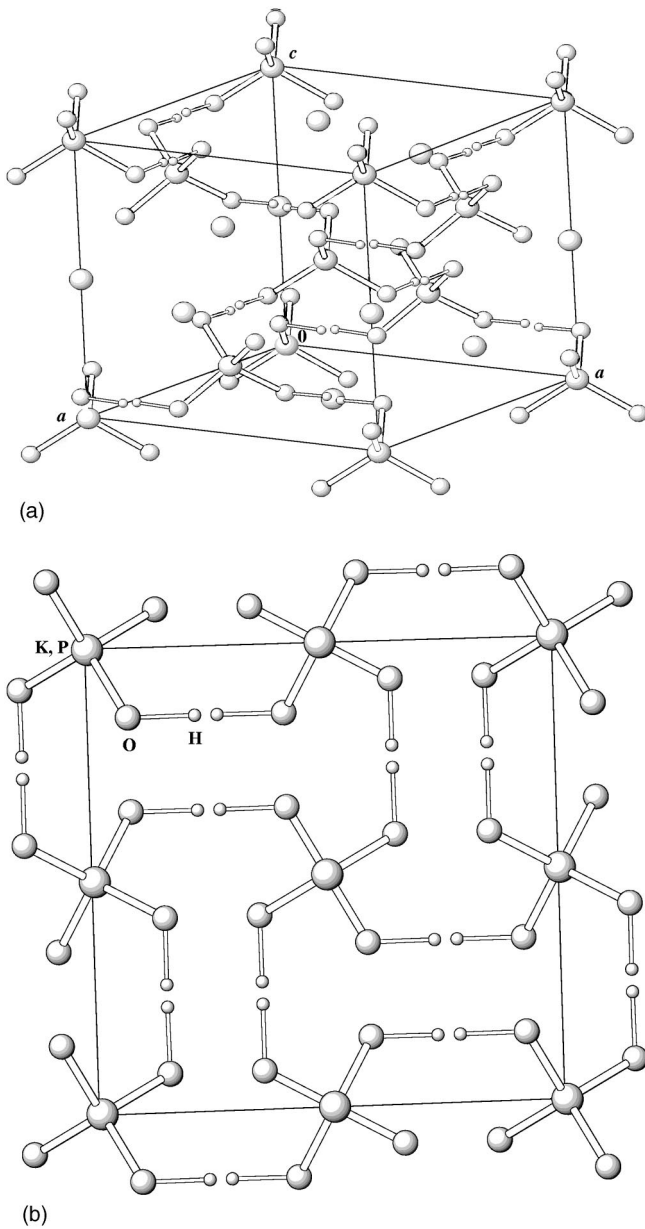


FIG. 1. Structure of tetragonal  $\text{KH}_2\text{PO}_4$  (KDP). (a) Perspective view and (b) projection along the  $c$  axis.

one of two O-X-O angles,  $\alpha_1$  (see Fig. 4) which characterizes the distortion of the  $\text{XO}_4$  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  $\text{PO}_4$  is systematically larger than that of  $\text{AsO}_4$  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  $\text{XO}_4$  around the  $c$  axis. Finally,  $T_c$  could be ex-

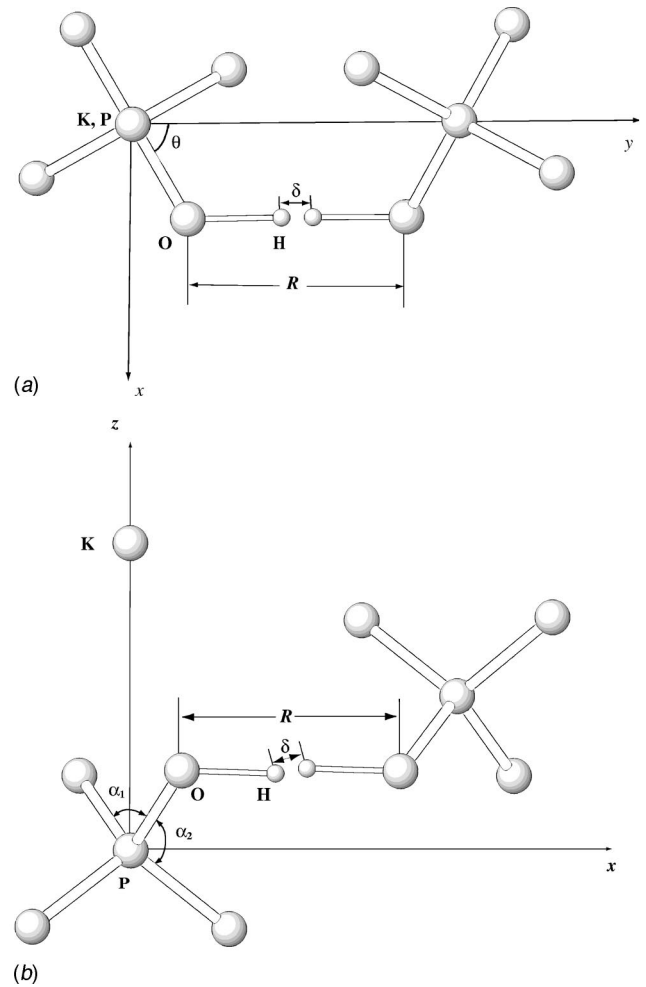


FIG. 2. Part of the structure of tetragonal  $\text{KH}_2\text{PO}_4$  (KDP) and some structural parameters. (a) View along the  $c$  axis and (b) view along the  $a$  axis.

pressed empirically by three structural parameters  $R$ ,  $\alpha_1$ , and  $\theta$  as

$$T_c = C_1 R + C_2 \alpha_1 + C_3 \theta + C_4. \quad (1)$$

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

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

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

$$R_e = \left( R + \frac{C_2}{C_1} \alpha_1 + \frac{C_3}{C_1} \theta \right) C_5, \quad (3)$$

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

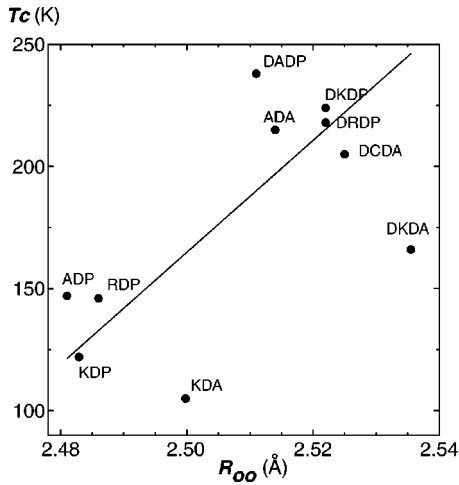


FIG. 3. Correlation between the transition temperature  $T_c$  and hydrogen-bond distance  $R$  in the tetragonal  $\text{KH}_2\text{PO}_4$  (KDP) family. KDP:  $\text{KH}_2\text{PO}_4$ ; DKDP:  $\text{KD}_2\text{PO}_4$ ; RDP:  $\text{RbH}_2\text{PO}_4$ ; DRDP:  $\text{RbD}_2\text{PO}_4$ ; KDA:  $\text{KH}_2\text{AsO}_4$ ; DKDA:  $\text{KD}_2\text{AsO}_4$ ; ADP:  $\text{NH}_4\text{H}_2\text{PO}_4$ ; DADP:  $\text{NH}_4\text{D}_2\text{PO}_4$ ; ADA:  $\text{NH}_4\text{H}_2\text{AsO}_4$ ; DCDA:  $\text{CsD}_2\text{AsO}_4$ .

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  $R$ ,  $\alpha_1$ , 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  $\text{XO}_4$  along the  $c$  axis. We define unfilled spacing  $s$  as a measure of the spacing unoccupied by M and  $\text{XO}_4$  ions in the  $c$  axis length as

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

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

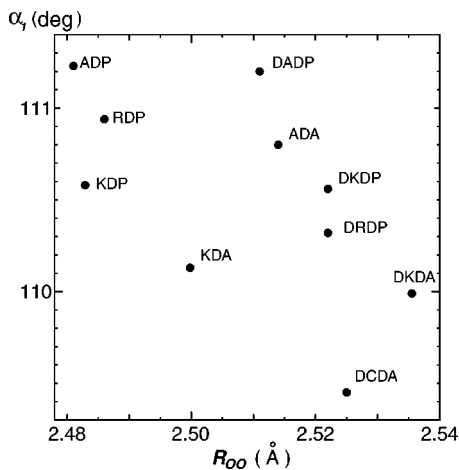


FIG. 4. Correlation between the O-X-O angle  $\alpha_1$  in the  $\text{XO}_4$  ion and the hydrogen-bond distance  $R$  (cf. Fig. 3 for the abbreviation of the compound names).

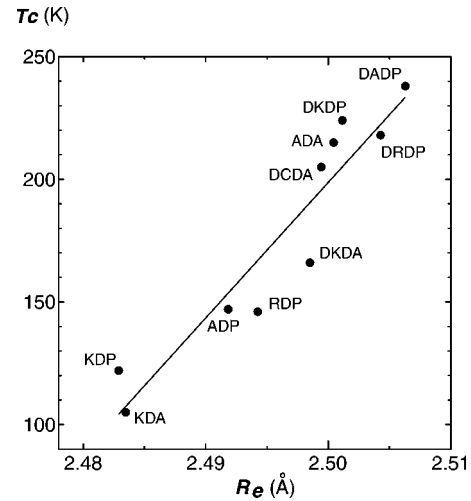


FIG. 5. Correlation between the transition temperature  $T_c$  and effective hydrogen-bond distance  $R_e$  (cf. Fig. 3 for the abbreviation of the compound names).

tetragonality  $c/a$  is determined by the ionic radius  $r_i$  of the M atom in the ferroelectric KDP family.<sup>11</sup> 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  $\text{XO}_4$  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  $\text{XO}_4$  ions: The larger the dipole moment of the  $\text{XO}_4$  ions, the higher the  $T_c$ . Thirdly, with respect to the M- $\text{XO}_4$  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- $\text{XO}_4$  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

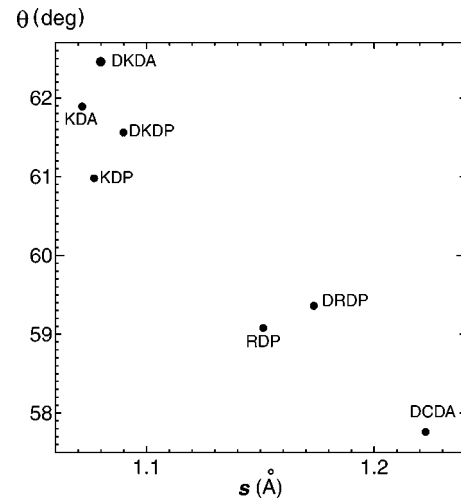


FIG. 6. Correlation between the rotation angle  $\theta$  around the  $c$  axis and unfilled spacing  $s$ . (cf. Fig. 3 for the abbreviation of the compound names).

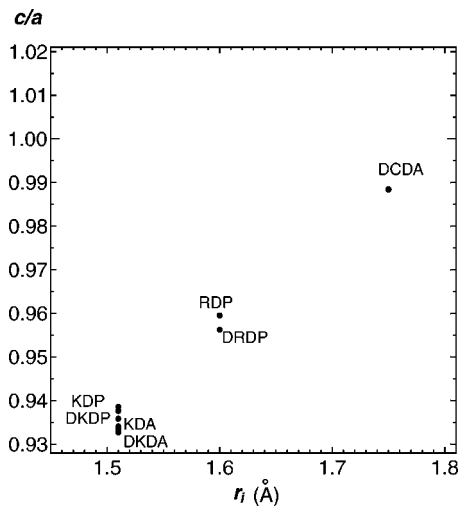


FIG. 7. Correlation between the tetragonality  $c/a$  and ionic radii  $r_i$  (cf. Fig. 3 for the abbreviation of the compound names).

nuclear density in KDP were resolved by high-resolution neutron diffraction.<sup>10</sup> 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.<sup>12</sup> 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,<sup>5</sup> apart from the controversial point in the proton system, i.e., proton tunneling or order-disorder. Katrusiak<sup>13</sup> recently referred to the coupling of displacive and order-disorder transformation in hydrogen-bonded ferroelectrics. Furthermore, quite recently, Bussmann-Holder and Michel<sup>14</sup> 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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