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Ammonium dihydrogen phosphate and potassium dihydrogen arsenate impurity effects on the dielectric behavior of potassium dihydrogen phosphate crystals

Y. Kim, S.-I. Kwun,* S. Park, B. Oh, and D. Lee
Department of Physics, Seoul National University, Seoul 151, Korea

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The dielectric constants of two types of mixed potassium dihydrogen phosphate crystals, one with ammonium dihydrogen phosphate (ADP) impurities and the other with potassium dihydrogen arsenate (KDA) impurities, have been measured at various impurity concentrations. The change of transition temperature and the dielectric behavior of the mixed crystals obtained from the dielectric-constant measurements are related to the role of impurities in the phase transition of the crystals. The transition temperatures of both mixed crystals decrease linearly as the impurity concentration increases, but the rate of decrease is strongly dependent on the type of impurity. The change of transition temperature in the mixed crystals is more sensitive to the concentration of ADP impurities than of KDA impurities. Domain-wall mobility in the region below the transition temperature remains high for crystals with ADP impurities, but becomes low for crystals with KDA impurities. A modified proton-lattice coupled model introduced here has proved to be a good theoretical model for explaining our experimental results and the roles of impurities in the crystals.

I. INTRODUCTION

The KH_2PO_4 (KDP) crystal is a well-known ferroelectric material in both theoretical and experimental aspects, and there are some other crystals with the same properties and structure as the KDP crystal. These KDP-type crystals separate into two groups below their transition temperature (T_c): one group with a ferroelectric phase (KH_2PO_4, RbH_2PO_4, KH_2AsO_4, etc.) and the other with an antiferroelectric phase ($NH_4H_2PO_4$, $NH_4H_2AsO_4$, etc.). All the KDP-type crystals show a large isotope effect. When the protons in these crystals, whose hydrogen bonds link the four nearest-neighbor $PO_4{}^{3-}$ radicals, are substituted with deuterons, the transition temperatures of the crystals rise greatly.

The phase transition of KDP-type crystals has been explained through several theoretical models. The first theoretical model which was suggested by Slater[1] failed to explain the isotope effect on KDP-type crystals. Blinc[2] was the first one who could explain the isotope effect. Even though Blinc's transverse Ising model explained the phase-transition mechanism qualitatively, it was impossible with this model to explain clearly the appearance of the spontaneous polarizations whose directions are nearly perpendicular to that of the hydrogen bonds.[3] This difficulty was solved by the proton-lattice coupled model (or modified tunneling model) suggested by Kobayashi.[4] In his model the hydrogen bonds are strongly coupled with an optical-phonon mode of the crystal. The ordering of the hydrogen bonds triggers the freezing of the optical-phonon mode so that cooperative displacements of heavy K^+ and $PO_4{}^{3-}$ ions occur. This causes spontaneous polarization to appear below transition temperature. Many experimental results from Raman scattering[5] and neutron diffraction[3,6] have supported the Kobayashi model but the effects of fluctuation and local ordering of polarizations have been neglected in the model.

These effects can be explained more easily by considering mixed crystals with impurities. Recent EPR and ESR experiments[7] have shown the occurrence of local ordering of small polarization clusters around impurities. Samara[8] has shown that partial deuteration is a valuable tool for investigating the mechanism of ferroelectricity in KDP-type crystals. Strong changes in the low-temperature Raman spectra of mixed KH_2PO_4-KD_2PO_4 crystals on deuteration and under hydrostatic pressure have been observed experimentally.[9]

Very recently Courtens[10] first investigated the phase transition of crystals of ferroelectric RbH_2PO_4 (RDP) mixed with antiferroelectric $NH_4H_2PO_4$ (ADP) molecules. This may have been the beginning of the study of KDP-type crystals mixed with different KDP-type impurities in comparison with many theoretical[11] and experimental[12] studies of partially deuterated KDP crystals.

The purpose of this paper is to report on the experimental results for KDP crystals mixed with antiferroelectric ADP impurities and KDP crystals mixed with ferroelectric KH_2AsO_4 (KDA) impurities. We have measured the effect of impurities on the dielectric constants of these mixed crystals. The transition temperatures of the mixed crystals and the domain-wall mobility in the ferroelectric phase are discussed. The results are explained on the basis of a modified proton-lattice coupling model. The different roles of ADP and potassium dihydrogen arsenate (KDA) impurities in the crystals are explained in detail.

II. EXPERIMENTAL

A. Sample preparation and characterization

The mixed crystals with impurities were grown by slow evaporation of aqueous KDP solutions with 5, 10, 15, and 20 mole % of impurity powder with respect to the KDP power before evaporation. The impurity concentrations of

TABLE I. The concentrations of impurity molecules in the mixed crystals.

Impurity (mole %)	Concentration (x) $K_{1-x}(NH_4)_xH_2PO_4$	$KH_2P_{1-x}As_xO_4$
0	below 1.8×10^{-5}	below 1.8×10^{-5}
5	7.2×10^{-3}	3.5×10^{-2}
10	1.4×10^{-2}	7.6×10^{-2}
15	2.2×10^{-2}	10.7×10^{-2}
20	3.4×10^{-2}	12.6×10^{-2}

the mixed crystals were analyzed by the titration method and are shown in Table I.

The relative ratios of the impurities in the crystals to those in the sample solutions are quite different for different impurities as shown in Table I. The ratio is 0.14 for ADP, but it is 0.72 for KDA. The ratio seems to depend mainly on the structural similarity between the KDP and the impurities. The ratio of the lattice constant for the *c* axis to that for the *a* axis at room temperature is 0.936 for KDP, 1.007 for ADP, and 0.938 for KDA.[13] The room-temperature unit-cell volume of KDP differs from that of KDA by only 7.6% but from that of ADP by 9.8%. As the amount of the impurity in the solutions increases the mixed crystals become less transparent.

B. Dielectric-constant measurements

The dielectric constants of the sample crystals were measured with a capacitance meter (model: Sanwa MI-318) at 100 kHz. The samples were *c*-cut plates. The samples placed in a sample cell were cooled with liquid nitrogen and their temperature was controlled from 80 K to room temperature with a temperature controller. A thermocouple was used to measure the temperature of the sample.

Particular attention was paid to accurate measurement of the difference in the transition temperature between the mixed crystal and the pure KDP crystal. Two samples, a pure KDP sample and an impurity mixed sample, were placed together in the same sample cell in order to give the same conditions. The dielectric constants of the two samples were measured simultaneously, and then the difference in the transition temperatures of the crystals was obtained.

III. EXPERIMENTAL RESULTS

The pure KDP crystal and the pure KDA crystal was known to show phase changes at temperatures of 123 and 96 K, respectively.[14] They have isomorphic tetragonal (orthorhombic) structure above (below) their transition temperatures. The pure ADP crystal, on the other hand, has an orthorhombic structure whose space group is different from that of the KDP crystal below its transition temperature of 148 K.

The dielectric constants measured along the *c* axis of the pure and mixed KDP crystals with ADP impurities are shown in Fig. 1 as a function of temperature for different concentration of impurities. The equivalent experimental results for the pure and mixed KDP crystals with KDA impurities are shown in Fig. 2.

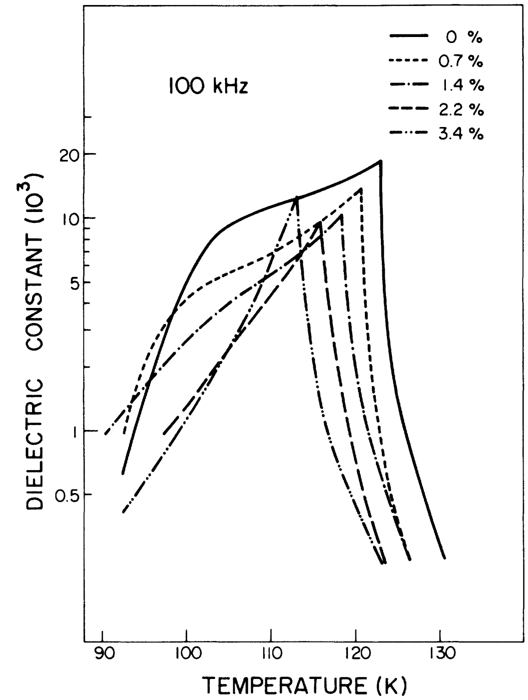

FIG. 1. Dielectric constant along the *c* axis of mixed KDP crystals with ADP impurities as a function of temperature for various impurity concentrations.

In Table II the transition temperature (T_c) obtained from Figs. 1 and 2 for the two types of mixed crystals are listed. These are also shown in Fig. 3 as a function of

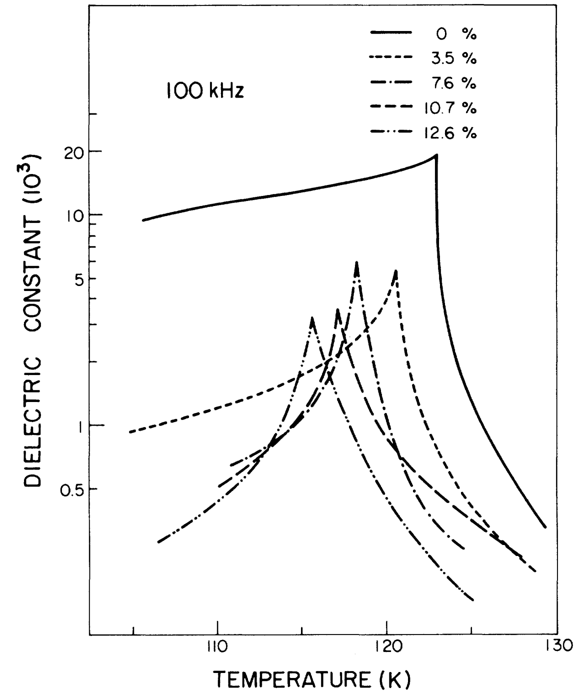

FIG. 2. Dielectric constant along the *c* axis of mixed KDP crystals with KDA impurities as a function of temperature for various impurity concentrations.

TABLE II. The transition temperatures of the mixed crystals with ADP and KDA impurities.

$K_{1-x}(NH_4)_xH_2PO_4$		$KH_2P_{1-x}As_xO_4$	
Concentration (x)	Transition temperature (K)	Concentration (x)	Transition temperature (K)
pure	123.0	pure	123.0
0.007	120.6	0.035	120.5
0.014	117.9	0.076	118.2
0.022	115.7	0.107	117.1
0.034	112.8	0.126	115.6

concentration of impurities in the crystals. The transition temperatures of the mixed crystals decrease proportionally with increase of impurity concentration, though the rate of decrease of T_c is dependent on the type of impurity in the crystal.

Figure 1 shows clearly the typical dielectric behavior of the KDP-type pure crystals in the ferroelectric phase: the presence of the plateau region where the dielectric constant remains very large. This plateau region disappears at about 100 K. Figure 2 shows that the plateau regions vanish as the ferroelectric KDA impurities increase, whereas Fig. 1 shows essentially no change in the plateau region in spite of an increase in the antiferroelectric ADP impurities. This fact is shown more clearly in Figs. 4 and 5.

Figures 4 and 5 show the inverse dielectric constants of the mixed crystal with ADP and KDA impurities. They show that the Curie-Weiss law is well satisfied for the pure and mixed crystals. The measured Curie constants for the mixed crystals below the transition temperature are listed in Table III. Because of the presence of the plateau region, the pure KDP crystal and the mixed crystals with ADP impurities have very high Curie constants. But the Curie constants below the transition temperature of the mixed crystals with KDA impurities approach the value predicted by the mean-field theory as the concentration of KDA impurity increases. Thermal hysteresis was not found during the dielectric-constant measurements and a sharp but continuous phase transition took place at the transition temperature for all mixed crystals.

IV. DISCUSSION

A. Modified proton-lattice coupled model

Blinc *et al.*[11(b)] discussed the dynamics of isotopically disordered ferroelectric crystals of the $K(H_{1-x}D_x)_2PO_4$ type on the basis of the coupled proton-deuteron tunneling-lattice optic-mode model. This model can be modified to describe the phase transition of mixed crystals with randomly distributed impurities.

The modified proton-lattice coupled model to be used here is based on the following Hamiltonian which is written in the usual pseudospin formalism.[14] The Hamiltonian consists of three parts:

$$\mathscr{H}=\mathscr{H}_{\text{pro}}+\mathscr{H}_{\text{pro-lat}}+\mathscr{H}_{\text{lat}}\ . \tag{1}$$

$\mathscr{H}_{\text{pro}}$ describes the tunneling motion of protons in the O—H—O bonds of the crystal. The proton part of the Hamiltonian has the explicit form

$$\begin{aligned}\mathscr{H}_{\text{pro}}=&-\Omega_K\sum_i(1-C_i)S_i^x(K)-\Omega_I\sum_i C_iS_i^x(I)\\&-\tfrac{1}{2}\sum_{i,j}[(1-C_i)(1-C_j)J_{ij}^{KK}S_i^z(K)S_j^z(K)+C_i(1-C_j)J_{ij}^{KI}S_i^z(I)S_j^z(K)\\&\qquad+(1-C_i)C_jJ_{ij}^{KI}S_i^z(K)S_j^z(I)+C_iC_jJ_{ij}^{II}S_i^z(I)S_j^z(I)]-\sum_i(1-C_i)\mu_KS_i^z(K)E-\sum_i C_i\mu_IS_i^z(I)E\ .\end{aligned} \tag{2}$$

Here S_i^z (K or I) is the pseudospin along the c axis of the crystal of the KDP or impurity molecule at the ith site. C_i is 0 if a KDP molecule is at the ith site and 1 if an impurity molecule is at the ith site. Ω and J_{ij} are the tunneling frequency of the protons in the molecules and interaction energy between two nearest-neighbor pseudospins on the c axis at the ith and jth sites, respectively. The superscripts for J_{ij} show what kind of molecules interact; thus KK means that two KDP molecules interact. μ represents the electrical dipole moment of the molecules along the c axis and E represents the applied electric field along the c axis.

The proton-phonon interaction term, $\mathscr{H}_{\text{pro-lat}}$, has the following expression:

$$\begin{aligned}\mathscr{H}_{\text{pro-lat}}=&-\sum_{\vec{q},i}F_{\vec{q}}^K(1-C_i)Q_{\vec{q}}(K)S_i^z(K)e^{i\vec{q}\cdot\vec{r}_i}\\&-\sum_{\vec{q},i}F_{\vec{q}}^I\,C_iQ_{\vec{q}}(I)S_i^z(I)e^{i\vec{q}\cdot\vec{r}_i}\ .\end{aligned} \tag{3}$$

Here $F_{\vec{q}}$ is the spin-phonon interaction and $Q_{\vec{q}}$ is the displacement along the c axis of the relevant ions (K^+, $PO_4{}^{3-}$) for KDP molecules, (K^+, $AsO_4{}^{3-}$) for KDA molecules, or ($NH_4{}^+$, $PO_4{}^{3-}$) for ADP molecules. The polarization density is then associated with $Q_{\vec{q}}$.

The last term, $\mathscr{H}_{\text{lat}}$, is the Hamiltonian of the lattice vibration. The lattice vibration of the disordered system has

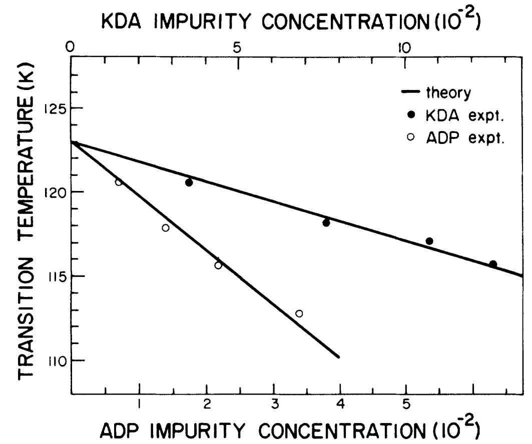

FIG. 3. Transition temperature of mixed crystals as a function of impurity concentration. The theoretical curves are calculated using the modified proton-lattice coupled model of Sec. III.

already been studied extensively.[15] Here we assume that the bare frequency $\omega_{\vec{q}}$, associated with the motion of the relevant ions in the absence of any coupling to the proton system, is the same for KDP and impurities. This is very probable because a low-energy optic-phonon mode does not show strong local vibrations near impurities.[16] Therefore $\mathscr{H}_{\text{lat}}$ is written as

$$\mathscr{H}_{\text{lat}}=\tfrac{1}{2}\sum_{\vec{q}}(P_{\vec{q}}P_{-\vec{q}}+\omega_{\vec{q}}^2Q_{\vec{q}}Q_{-\vec{q}}) \;. \tag{4}$$

With the mean-field approximation (MFA) we get

$$\langle Q_{\vec{q}=0}(K)\rangle=\frac{NF_0^K}{\omega_0^2}\langle S^z(K)\rangle \;, \tag{5}$$

$$\langle Q_{\vec{q}=0}(I)\rangle=\frac{NF_0^I}{\omega_0^2}\langle S^z(I)\rangle \;, \tag{6}$$

where N is the total number of unit cells. After Eqs. (5) and (6) are inserted into the Hamiltonians of Eqs. (3) and (4), the proton-lattice coupled model is transformed into the usual proton-tunneling model with renormalized pseudospin interaction energy J_{ij} (Ref. 14), where

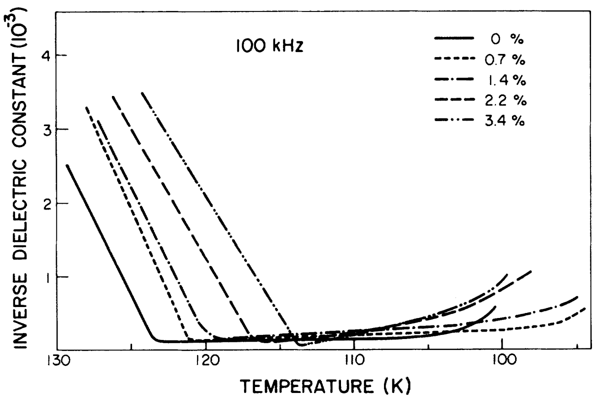

FIG. 4. Inverse dielectric constant of mixed KDP crystals with ADP impurities for various impurity concentrations.

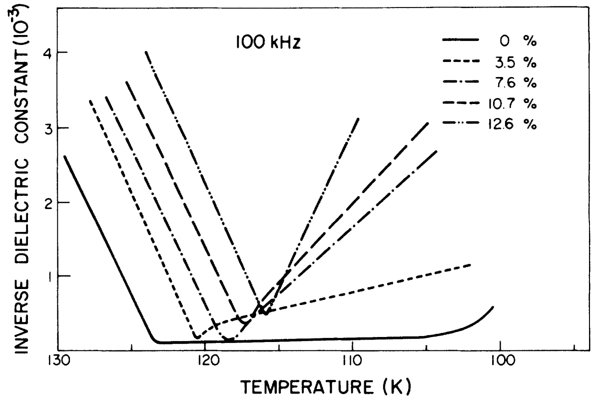

FIG. 5. Inverse dielectric constant of mixed KDP crystals with KDA impurities for various impurity concentrations.

$$\begin{aligned}
&\tilde{J}_{ij}^{KK}(\omega)=J_{ij}^{KK}+\sum_{\vec{q}}\exp[i\vec{q}\cdot(\vec{r}_i-\vec{r}_j)]\,|F_{\vec{q}}^K|^2/(\omega_{\vec{q}}^2-\omega^2) \;,\\
&\tilde{J}_{ij}^{II}(\omega)=J_{ij}^{II}+\sum_{\vec{q}}\exp[i\vec{q}\cdot(\vec{r}_i-\vec{r}_j)]\,|F_{\vec{q}}^I|^2/(\omega_{\vec{q}}^2-\omega^2) \;,\\
&\tilde{J}_{ij}^{KI}=J_{ij}^{KI} \;.
\end{aligned} \tag{7}$$

We can greatly simplify the Hamiltonian using the virtual-crystal approximation (VCA) since the basic forces are long range. Then the Hamiltonian of the modified proton-lattice coupled model is expressed as

$$\begin{aligned}
\mathscr{H}=&-\Omega_K\sum_i S_i^x(K)-\sum_i H_i^z(K)S_i^z(K)\\
&-\Omega_I\sum_i S_i^x(I)-\sum_i H_i^z(I)S_i^z(I) \;,
\end{aligned} \tag{8}$$

where $H_i^z(K \text{ or } I)$ is the effective field felt by the KDP or impurity. The explicit forms of $H_i^z(K)$ and $H_i^z(I)$ are

$$\begin{aligned}
&H_i^z(K)=(1-x)\tilde{J}_0^{KK}\langle S_i^z(K)\rangle+x\tilde{J}_0^{KI}\langle S_i^z(I)\rangle+\mu_KE \;,\\
&H_i^z(I)=x\tilde{J}_0^{II}\langle S_i^z(I)\rangle+(1-x)\tilde{J}_0^{KI}\langle S_i^z(K)\rangle+\mu_IE \;,
\end{aligned} \tag{9}$$

where x is the concentration of impurities in the mixed crystal and

$$\tilde{J}_0^{KK}=J_0^{KK}+\frac{N\,|F_{\vec{q}=0}^K|^2}{\omega_{\vec{q}=0}^2} \;,$$

etc., where $\tilde{J}_0^{KK}=\sum_j\tilde{J}_{ij}^{KK}$ and $J_0^{KK}=\sum_j J_{ij}^{KK}$. The thermal expectation values of the the pseudospin operators are now determined from the following equations:

$$\begin{aligned}
&\langle S^z(K)\rangle=\frac{\mathrm{Tr}[S^z(K)e^{-\beta\mathscr{H}}]}{\mathrm{Tr}e^{-\beta\mathscr{H}}}=\frac{1}{2}\frac{H^z(K)}{H_K}\tanh(\tfrac{1}{2}\beta H_K) \;,\\
&\langle S^x(K)\rangle=\frac{\mathrm{Tr}[S^x(K)e^{-\beta\mathscr{H}}]}{\mathrm{Tr}e^{-\beta\mathscr{H}}}=\frac{1}{2}\frac{\Omega_K}{H_K}\tanh(\tfrac{1}{2}\beta H_K) \;,\\
&\langle S^z(I)\rangle=\frac{\mathrm{Tr}[S^z(I)e^{-\beta\mathscr{H}}]}{\mathrm{Tr}e^{-\beta\mathscr{H}}}=\frac{1}{2}\frac{H^z(I)}{H_I}\tanh(\tfrac{1}{2}\beta H_I) \;,\\
&\langle S^x(I)\rangle=\frac{\mathrm{Tr}[S^x(I)e^{-\beta\mathscr{H}}]}{\mathrm{Tr}e^{-\beta\mathscr{H}}}=\frac{1}{2}\frac{\Omega_I}{H_I}\tanh(\tfrac{1}{2}\beta H_I) \;,
\end{aligned} \tag{10}$$

TABLE III. Curie constants of the mixed crystals.

$K_{1-x}(NH_4)_xH_2PO_4$		$KH_2P_{1-x}As_xO_4$	
x	$T<T_c$ (K)	x	$T<T_c$ (K)
pure	225 000	pure	225 000
0.007	180 000	0.035	21 600
0.014	96 200	0.076	5240
0.022	35 100	0.107	4670
0.034	26 700	0.126	2370

where $\beta=1/k_BT$ and

$$(H_K)^2=\Omega_K^2+[H^z(K)]^2,\quad (H_I)^2=\Omega_I^2+[H^z(I)]^2 .$$

The transition temperature T_c can be determined by linearizing the equations for $\langle S^z(K)\rangle$ and $\langle S^z(I)\rangle$, so we obtain the following equation:

$$1-[\tilde{J}_0^{KK}\tanh(\tfrac{1}{2}\beta_c\Omega_K)/2\Omega_K](1-x)-[\tilde{J}_0^{II}\tanh(\tfrac{1}{2}\beta_c\Omega_I)/2\Omega_I]x$$
$$+[\tilde{J}_0^{KK}\tilde{J}_0^{II}-(\tilde{J}_0^{KI})^2]x(1-x)\tanh(\tfrac{1}{2}\beta_c\Omega_K)\tanh(\tfrac{1}{2}\beta_c\Omega_I)\frac{1}{4\Omega_K\Omega_I}=0 , \quad (11)$$

where $\beta_c=1/k_BT_c$.

The isothermal electric susceptibility χ can be expressed by

$$\chi=(1-x)\frac{\partial P^K}{\partial E}+x\frac{\partial P^I}{\partial E}$$
$$=2N\left[(1-x)\mu_K\frac{\partial\langle S^z(K)\rangle}{\partial E}+x\mu_I\frac{\partial\langle S^z(I)\rangle}{\partial E}\right] , \quad (12)$$

where P^K and P^I are the electric polarizations of the KDP and impurity molecules, respectively. This goes to infinity as the temperature approaches T_c.

The modified proton-lattice coupled model mentioned above seems to be a good theoretical model for the $KH_2P_{1-x}As_xO_4$ crystal. KDP and KDA crystals have long-range orderings along the c axis so the change in the interactions between the c-axis components of the pseudospins of the KDP and KDA molecules seem to be a primary factor for the change of dielectric behavior in the mixed crystals. The modified model takes this fact into account. But the situation of the $K_{1-x}(NH_4)_xH_2PO_4$ crystal is different. The ordering of the protons in the ferroelectric phase of the KDP crystal is an "up-down" Slater configuration,[6] while the "lateral" ordering perpendicular to the c axis of the KDP crystal generates the antiferroelectric phase of ADP.[17]

The phase transition of the ADP crystal has been explained with two different theoretical models. The first model, proposed by Ishibashi *et al.*,[18] showed that the phase transition of ADP could be accounted for with the dipolar interaction and Slater configuration energy different from that of KDP. Havlin *et al.*[19] proposed the second model, which was very similar to the proton tunneling model. There, pseudospins in ADP experience the short-range ferroelectric interaction and the long-range antiferroelectric interaction only along the c axis. The proton tunneling is negligible compared with the proton-proton interaction. Recently the phase transition of mixed ferroelectric-antiferroelectric hydrogen-bonded systems has been explained[11(d)] with a theoretical model based on the model of Ishibashi. In our experiment the concentration of antiferroelectric ADP impurities was so small that the long-range antiferroelectric interaction between ADP impurities could be neglected when using the Havlin model to consider the effect of ADP impurities. Then our modified proton-lattice coupled model is also adequate to explain the phase transition of $K_{1-x}(NH_4)_xH_2PO_4$.

When impurities with a negligible proton-tunneling frequency Ω_I, such as ADP, are mixed into the KDP crystal and their concentration can be assumed to be very small, Eq. (11) gives the transition temperature

$$T_c=T_c^0\left[1-\left[\frac{(4k_BT_c^0/\tilde{J}_0^{KK})-(\tilde{J}_0^{KI}/\tilde{J}_0^{KK})^2}{1-(2\Omega_K/\tilde{J}_0^{KK})^2}\right]x\right] . \quad (13)$$

Here T_c^0 is the transition temperature of the pure KDP crystal.

B. Transition temperature

The dependence of T_c of the KDP crystal with antiferroelectric ADP impurities on impurity concentration is given by $T_c \simeq T_c^0(1-2.6x)$ at $x \lesssim 0.034$ as shown in Fig. 3. The decrease of T_c proportional to the impurity concentration is what can be expected from Eq. (13). The T_c of the KDP crystal with ferroelectric KDA impurities in Fig. 3 can be described by $T_c \cong T_c^0\,(1-0.50x)$ at $x \lesssim 0.126$. It is evident that the rate of decrease of T_c for mixed crystals with ferroelectric impurities is quite small compared with that for mixed crystals with antiferroelectric impurities.

A good fit for T_c for the mixed crystal with ADP impurities is obtained as shown in Fig. 3 for a value of $|\tilde{J}_0^{KI}(\mathrm{ADP})|=0.38\tilde{J}_0^{KK}$ using the following values, derived by Havlin *et al.*[20]: $\tilde{J}_0^{KK}=816$ K and $\Omega_k=370$ K for a pure KDP crystal.[21] We can conjecture from the sharp decrease of T_c that $\tilde{J}_0^{KI}(\mathrm{ADP})$ is negative: $\tilde{J}_0^{KI}(\mathrm{ADP})=-0.38\tilde{J}_0^{KK}$. This indicates that there is competition between ferroelectric and antiferroelectric exchange interactions, and this frustration effect between pseudospins may lower the transition temperature. As the concentration of antiferroelectric impurities in the crystal increases, there is a possibility that there is no long-range order, so that no ferroelectric phase is present. The role of

ADP impurities in the mixed RDP crystals studied by Courtens[10] is considered to be the same in the mixed KDP crystals.

The theoretical curve shown in Fig. 3 for crystals with KDA impurities provides a value of $|\tilde{J}_0^{KI}(\text{KDA})| = 0.73\tilde{J}_0^{KK}$ using $\tilde{J}_0^{II} = 404$ K and $\Omega_I = 80$ K for Eq. (11) as values for the pure KDA crystal.[20] The slow decrease of T_c indicates that the ferroelectric impurities in the mixed crystal experience the ferroelectric exchange interactions with pseudospins of the KDP hosts. This $\tilde{J}_0^{KI}(\text{KDA})$ is conjectured to be positive. In that case the ferroelectric interactions between KDA impurities and KDP hosts maintain the ferroelectric phase in the low-temperature region at all impurity concentrations, as in the case of partially deuterated KDP crystals.

C. Domain-wall mobility

Another remarkable impurity effect in mixed crystals is the change in dielectric constants in the ferroelectric phase. Two types of impurities seem to affect the domain-wall mobility quite differently. The domain-wall mobility of the ferroelectric KDP crystal was sharply reduced at about 100 K. According to Fedosov and Sidorkin[22] this reduction shows that there is a sharp increase in the lattice energy barrier which must be overcome by a moving domain wall at that temperature. The reduction of mobility can explain the freezing of the domain structure and thus cause the decrease in dielectric constant, that is, the disappearance of the plateau region.

They also showed that the form of the domain walls between two domains, which have opposite orientations, may be of two different types: type I ($\uparrow\cdot\downarrow$) and type II ($\uparrow\downarrow$). Each arrow or dot corresponds to the amount of polarization along the ferroelectric axis. In the plateau region the type-I configuration has a lower energy and much higher mobility than the type-II configuration. The experimental results show that ferroelectric KDA impurities seem to strongly suppress the formation of domain walls of type I so that the plateau region is sharply reduced. On the other hand, antiferroelectric ADP impurities seem to have a minor effect on the domain-wall mobility so that the plateau region remains. Reduction in the mobility of the domain walls has also been noted in KDP-type crystals under γ-ray irradiation[23] and strong dc electric fields.[24] As shown in Table III, the Curie constants for the ferroelectric phase of KDA mixed crystals approach the mean-field value at high-KDA impurity concentrations. This seems to indicate that the fluctuations in polarization in the mixed crystals are reduced by adding impurities so that the mean-field approximation adequately describes the ferroelectric phase as well as the paraelectric phase. Experiments by using mixed crystals should give some clue in the study of fluctuation effects on phase transition.

V. CONCLUSIONS

Using dielectric-constant measurements on mixed crystals with ADP and KDA impurities we have showed the effect of impurities on the dielectric behavior of the system. A modified proton-lattice coupled model predicts the exchange interaction energy between an impurity and a host, $\tilde{J}_0^{KI}$ to be $-0.38\tilde{J}_0^{KK}$ for ADP and $0.73\tilde{J}_0^{KK}$ for KDA impurities. This indicates that the rapid decrease of T_c for antiferroelectric impurities is due to the frustration effect. The ferroelectric interaction between KDA impurities and KDP hosts seems to keep the rate of decrease of T_c low at the impurity concentrations we measured.

KDA impurities have a large influence on the dielectric constants in the ferroelectric phase. The disappearance of a plateau region suggests a change from high to low domain-wall mobility due to the KDA impurities. The behavior of the dielectric constant in the ferroelectric phase of the mixed crystals with ADP impurities is nearly the same as for the pure KDP crystals.

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*To whom correspondences should be addressed.

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