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# Phase transition in caesium dihydrogen phosphate crystal with thallium impurities

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**Abstract.** A mixed crystal between two one-dimensional hydrogen bonding crystals of caesium dihydrogen phosphate (CDP) and thallium dihydrogen phosphate (TDP),  $\text{CDP}_{1-x}\text{TDP}_x$ , was studied by dielectric constant measurements of phase transition characteristics. Dielectric constant dependence on temperature in the  $\text{CDP}_{1-x}\text{TDP}_x$  crystal was best fitted by a power-law equation of the form  $\epsilon' = C(T - T_0)^{-\gamma}$  with  $\gamma = 1.43$  for CDP, and  $\gamma = 1.39$  and  $\gamma = 1.34$  for  $\text{CDP}_{1-x}\text{TDP}_x$  mixed crystals of  $x = 0.003$  and  $x = 0.008$  respectively. A quasi-one-dimensional Ising model was employed to explain the experimental observations in terms of the decrease in the intrachain interaction constant,  $J_{\parallel}/k_B$ , and the increase in the interchain interaction constant,  $J_{\perp}/k_B$ , with increasing TDP impurity concentration  $x$ .

## 1. Introduction

Hydrogen bonded ferroelectrics have been a great concern of many research works studying the order–disorder phase transition. Proton ordering in hydrogen bonds is known to lead to ferroelectric transition in  $\text{KH}_2\text{PO}_4$  (KDP) crystals, where  $\text{PO}_4$  tetrahedrals are linked by the three-dimensional network of hydrogen bonds. On the other hand, monoclinic systems of caesium dihydrogen phosphate (CDP) and thallium dihydrogen phosphate (TDP) crystals have a two-dimensional network of hydrogen bonds, where the proton ordering of the phase transition becomes one dimensional [1, 2]. In the CDP crystal, undergoing the ferroelectric transition at  $T_c \simeq 154$  K, ferroelectric polarization is developed along the monoclinic  $b$ -axis [3]. The protons in the zigzag chains of hydrogen bonds connecting  $\text{PO}_4$  tetrahedra along the  $b$ -axis are ordering at the transition, while the protons in the asymmetric potential of hydrogen bonding along the  $c$ -axis are ordered already at room temperature. This strong anisotropy was also observed in the neutron scattering experiment near the transition temperature, where the correlation length along the chain direction of the  $b$ -axis was found to be much longer than the transverse interchain correlation length [1]. The TDP crystal exhibits a phase transition anomaly of dielectric constant [4] at  $T_c \simeq 230$  K which was identified as the antiferroelectric transition by the double hysteresis loop measurements of its deuterated analogue [5]. In the TDP crystal, the  $c$ -axis hydrogen bonds involved in the zigzag connection of  $\text{PO}_4$  tetrahedra are ordered in the phase transition, but the longer asymmetric hydrogen bonds along the  $b$ -axis of dielectric anomaly remain without any apparent change [2].

CDP and TDP crystals are also very similar in the room temperature crystal structure. The pseudo-orthorhombic cell of the CDP crystal can be defined with dimensions of about

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4.5 Å × 6.5 Å × 15 Å which closely matches the dimensions of a primitive unit cell in TDP crystal [6, 7]. The centrosymmetric hydrogen bonds connecting the PO<sub>4</sub> tetrahedra form zigzag chains in the direction of the 6.5 Å axis in both crystals, and the longer asymmetric hydrogen bonds connect the chains in the direction of the 4.5 Å axis. No other hydrogen bonds exist between the planar sheets of the above two kinds of hydrogen bonds. The hydrogen bonds which are active in the phase transition are those of the zigzag chains in the direction of the 6.5 Å axis. However, the two crystals belong to different space groups, and the ferroelectric polarization of the CDP crystal develops along the direction of the 6.5 Å axis whereas the antiferroelectric ordering of the TDP crystal develops along the direction of the 4.5 Å axis.

Although the similar crystal structures and the competing order parameters are expected to lead to the dipole glass formation in the mixed crystal between CDP and TDP, the dipole glass phase has not been observed yet in the mixed crystal [8]. It seems that the mixed crystal between two components of different space groups may not grow in homogeneous mixing.

We thus restrict ourselves to the case of a random mix of impurities where we expect to see the impurity effects of TDP in the phase transition of CDP crystal. CDP crystal is one of the one-dimensional hydrogen bond, order-disorder phase transition systems [9–15], where a quasi-one-dimensional Ising model can be applied.

## 2. Experiment

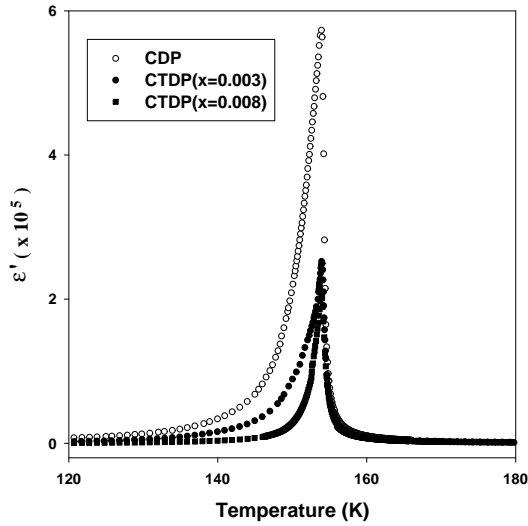
After the solution growth of CDP and TDP crystals from the mixed aqueous solution of Cs<sub>2</sub>CO<sub>3</sub>, Tl<sub>2</sub>CO<sub>3</sub> and H<sub>3</sub>PO<sub>4</sub>, we mixed TDP crystallites with CDP crystals in the mole percentage ratio of 1% and 10% to make the aqueous mixed solutions. The mixed solutions were used to grow (CDP)<sub>1-x</sub>(TDP)<sub>x</sub>, (CTDP-*x*), mixed crystals by slow evaporation at constant temperatures. The grown CTDP-*x* crystals are observed to have the same morphology as CDP and also the same x-ray diffraction patterns of CDP crystal, which suggest that thallium ions are replacing the caesium ions. The TDP concentrations in the grown crystals of CTDP-*x* were found to be 0.3% and 0.8%, instead of the original mole percentage ratios of 1% and 10% in the starting mixed solutions, as obtained from the spectroscopic chemical analysis.

Samples of *b*-cut plates were aluminium coated in a vacuum for electrodes of dielectric constant measurements. Dielectric measurements were made at the probe frequency of 10 kHz and with a field amplitude of 1 V cm<sup>-1</sup>, by the use of the impedance analyser (HP-4192A). A closed cycle helium refrigerator (APD-Displex) and a personal computer interfaced to a temperature controller (Lakeshore-330) with silicon diode sensors were employed for low temperature thermostatic controls. From room temperature to 20 K, the sample was cooled at the cooling rate of 1 K 4 min<sup>-1</sup>, but slower rates of 1 K 20 min<sup>-1</sup> to 1 K 40 min<sup>-1</sup> were used in the vicinity of phase transition.

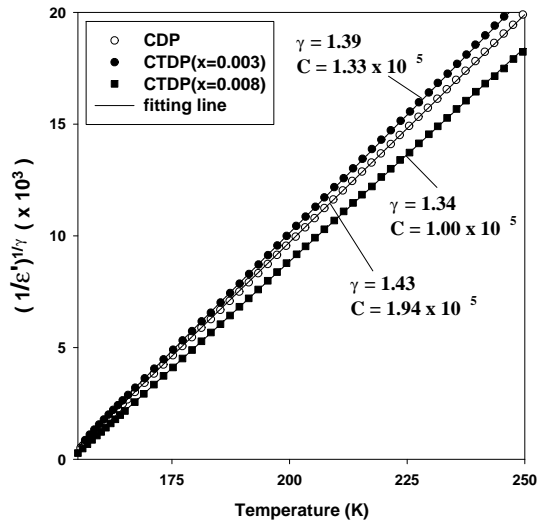
## 3. Results

We have shown the real parts of dielectric constants as a function of temperature for CDP and CTDP-*x* mixed crystals in figure 1. The phase transition temperature shift was within  $\Delta T_c \sim 0.2$  K from  $T_c \sim 154$  K of CDP crystal with a TDP-*x* doping concentration of  $x = 0.003$  and  $0.008$ . CDP crystal, differing from other KDP-family crystals, does not follow the Curie–Weiss law but has a different relation of dielectric constant dependence on temperature [9],

$$\epsilon' = C/(T - T_o)^\gamma \quad (1)$$



**Figure 1.** Dielectric constant dependence on temperature in CDP and CTDP- $x$  crystals.



**Figure 2.** Best fit results for dielectric data of figure 1 by use of equation (1). Note the slopes of the fit depending on both values of  $\gamma$  and Curie constant  $C$ .

where they observed  $\gamma = 1.31 \pm 0.1$  for  $3 \text{ K} \leq T - T_c \leq 90 \text{ K}$  but a crossover to  $\gamma = 1$  for  $0 \text{ K} \leq T - T_c \leq 3 \text{ K}$ . In figure 2 we have shown our best fit results of experimental data by use of equation (1) and, in table 1, the corresponding best fit values of parameters.

Although our best fit results are limited to the temperature range of  $10 \text{ K} \leq T - T_c \leq 130 \text{ K}$ , the best fit value of  $\gamma$  was found to remain well above  $\gamma = 1$  without the crossover [9] to the three-dimensional characteristics of  $\gamma = 1$  in the vicinity of  $T_c$ , which is in better agreement with Deguchi *et al* [16]. Our  $\gamma$  values were found to be 1.43 for CDP crystal, 1.39 for CTDP- $x$  ( $x = 0.003$ ), and 1.34 for CTDP- $x$  ( $x = 0.008$ ) crystal. This slight decrease of  $\gamma$  values with

**Table 1.** Best fit parameters of dielectric constant data as fitted by equation (1).

	CDP		CTDP- $x$	
	Present work	Bline <i>et al</i> [9]	$x = 0.003$	$x = 0.008$
$\gamma$	$1.43 \pm 0.01$	$1.31 \pm 0.1$	$1.39 \pm 0.01$	$1.34 \pm 0.01$
$T_o$ (K)	152.4	150 ~ 152	152.0	153.7
$C$ ( $\times 10^5$ )	1.94	~ 1.0	1.33	1.00

increasing TDP concentration may be understood in terms of the quasi-one-dimensional Ising model [11, 17],

$$H_o = -J_{\parallel} \sum_{i=1}^N S_i S_{i+1} - \mu E_o \sum_{i=1}^N S_i \quad (2)$$

where  $N$  represents the number of hydrogen bonds in the chain,  $E_o$  represents the external field,  $S_i = \pm 1$  corresponds to the pseudo-spin position of the protons in the double well potential of the hydrogen bond, and  $\mu$  corresponds to the effective dipole moment of the hydrogen bond in the chain. Since the system is essentially a one-dimensional Ising chain, we must incorporate a mean-field long-range weak interaction between the chains to ensure the thermodynamic singularities of the phase transition. This model then gives rise to the following result,

$$\epsilon = \frac{A}{T \exp(-a/T) - B} \quad T > T_c \quad (3)$$

where  $A = 4\pi n\mu^2/k_B$ ,  $B = J_{\perp}/k_B$ ,  $a = 2J_{\parallel}/k_B$ ,  $n$  is the number density of dipoles,  $k_B$  is the Boltzmann constant and  $J_{\perp}$  and  $J_{\parallel}$  are long-range interchain and short-range intrachain interaction constants, respectively. The ordering transition temperature,  $T_c$ , is given by

$$\exp(-2J_{\parallel}/k_B T_c) = J_{\perp}/k_B T_c. \quad (4)$$

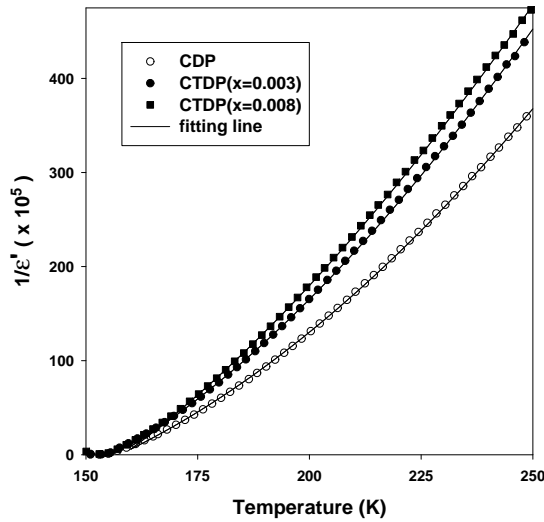
In table 2 we have collected previous data of best fit values of the quasi-one-dimensional Ising model as applied to several hydrogen bonding systems of one-dimensional characteristics. From this table, we can see that the interaction constants vary a great deal between different systems and the one-dimensional anisotropy is enhanced by deuteration. In the case of betaine phosphate (BP) crystal [13] and betaine phosphate-arsenate ( $x$ ) mixed crystal [15], we obtain a negative interchain interaction constant and a positive intrachain interaction constant, which explains the ferroelectric ordering in the chain, but we obtain a weaker antiferroelectric ordering between the neighbouring chains. This model of mean-field approximation can thus be applied to the antiferroelectric system as well as the ferroelectric system of the one-dimensional hydrogen bond chains.

**Table 2.** Best fit parameters of dielectric constant data as fitted by the quasi-one-dimensional model (equation (3)).

Crystal	$J_{\parallel}/k_B$ (K)	$J_{\perp}/k_B$ (K)	$J_{\perp}/J_{\parallel}$
CsD <sub>2</sub> PO <sub>4</sub> [9]	682.5	0.834	0.00122
RbD <sub>2</sub> PO <sub>4</sub> [10]	1200	0.168	0.00014
PbHPO <sub>4</sub> [11]	272.5	81.8	0.30
PbDPO <sub>4</sub> [11]	518.42	45.2	0.0872
BPI (N(CH <sub>4</sub> ) <sub>3</sub> CH <sub>2</sub> COOH <sub>3</sub> PO <sub>3</sub> ) [12]	~ 260	~ 20.5	~ 0.086
BP (N(CH <sub>4</sub> ) <sub>3</sub> CH <sub>2</sub> COOH <sub>3</sub> PO <sub>4</sub> ) [13]	84	-7.5	-0.079
(CH <sub>3</sub> ) <sub>2</sub> NH <sub>2</sub> H <sub>2</sub> As <sub>4</sub> [14]	195	66.2	0.338

Equation (3) of the model was applied for a best fit to the same experimental data of figure 2, and the results are shown in figure 3, where we can see deviations from the fit near to the transition temperatures, as reported in the previous works [16, 18]. We have thus restricted the range of fitting to  $T \geq T_c + 20$  K, and our results of fitting are shown in table 3 in comparison with other reported values [9, 16]. For the TDP doping in the CDP crystal by 0.8% molar concentration, the intrachain interaction constant,  $a/2$ , was reduced from 264 K to 210 K while the interchain interaction constant,  $B$ , was increased from 5.5 K to 11.1 K, and thus the ratio  $2B/a$  between the two interaction constants was increased from 0.02 to 0.05. In both CDP and TDP crystals, the dielectric anomalies of the phase transition are observed only in the respective direction of longitudinal ferroelectric or transverse antiferroelectric ordering. Therefore we expect the thallium impurities, which substitute caesium ions in CDP crystal, to become hard defects, and thus to reduce the longitudinal intrachain interaction strength with increasing interchain coupling strength of cross correlations between polarization fluctuations. This tendency of TDP impurity effects agrees with our observations that the deviation from the Curie–Weiss law tends to decrease with increasing TDP molar concentration, as can be seen from table 1.

This change of the interaction strength will certainly shift the phase transition temperature, as we can see in equation (4), where the transition temperature should decrease with decreasing



**Figure 3.** Best fit results for dielectric data of figure 1 by use of the quasi-one-dimensional Ising model (equation (3)).

**Table 3.** Best fit parameters of dielectric constant data as fitted by equation (3) for CDP and CTDP- $x$  crystals.

	CDP			CTDP- $x$	
	Present work	Blinc <i>et al</i> [9]	Deguchi <i>et al</i> [16]	$x=0.003$	$x=0.008$
$A$ (K)	6728	4650	6780	6728	6728
$B(J_{\perp}/k_B)$ (K)	5.5	3.6	6.0	7.0	11.1
$a/2(J_{\parallel}/k_B)$ (K)	264	305	265.5	245	210
$2B/a(J_{\perp}/J_{\parallel})$	0.020	0.012	0.022	0.028	0.052

$J_{\parallel}$  but increase with increasing  $J_{\perp}$ . Our three samples were observed to have nearly the same transition temperature at  $T_c \simeq 154$  K. The best fit parameters of the quasi-one-dimensional model are found to give, in equation (4), the transition temperatures of CDP, CTDP- $x$  (0.003) and CTDP- $x$  (0.008) crystals as 157.4 K, 157.4 K and 158.2 K respectively. This prediction of higher transition temperatures, inconsistent with the experimental value of  $T_c \simeq 154$  K, may be related to the large deviation of the model fitting near the transition temperatures. Although the model fails in the vicinity of the transition temperature, the qualitative nature of TDP impurity effects on the phase transition may be explained by the model. We can thus understand the negligible shift of the transition temperature in our CTDP- $x$  crystals as due to a cancellation between the two opposite effects of TDP doping on the transition temperature, both decreasing the intrachain interaction strength and increasing the interchain interaction strength.

#### 4. Conclusion

Dielectric constants of CDP $_{1-x}$ TDP $_x$  crystals are observed to deviate from the Curie–Weiss behaviour and to show the characteristics of the quasi-one-dimensional Ising model for a small mixing concentration of  $x \leq 0.008$ . TDP impurities in CDP crystals tend to reduce the intrachain interaction constant,  $J_{\parallel}/k_B$ , and to enhance the interchain interaction constant,  $J_{\perp}/k_B$ , so that the quasi-one-dimensional Ising model, with a weak transversal mean-field interaction, could explain the phase transition characteristics of CDP $_{1-x}$ TDP $_x$  crystals.

#### Acknowledgment

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