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A microscopic model for the concentration dependence of the antiferrodistortive phase transition in mixed betaine phosphate/phosphite crystals

H Braeter, J Totz and D Michel

Universität Leipzig, Fakultät für Physik und Geowissenschaften, Linnéstraße 5, D-04103 Leipzig, Germany

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Abstract. The concentration dependence of the high temperature antiferrodistortive (afd) phase transition temperature T_C in single crystals of the mixed crystal system betaine phosphate and betaine phosphite ($\text{BP}_{1-x}\text{BPI}_x$) is studied. New experimental data obtained by ^2H nuclear magnetic resonance (NMR) spectroscopy on deuterated single crystals of this system confirm the nonlinear behaviour of $T_C(x)$, in particular the maximum at intermediate concentrations. A microscopic model is proposed which in extension of the treatment of a small defect concentration makes use of the virtual crystal approximation (VCA) to be applicable to the mixed crystal system $\text{DBP}_{1-x}\text{DBPI}_x$ with finite concentrations x . By this means the experimentally observed behaviour of the afd phase transition temperature as a function of x is elucidated and the nonlinear behaviour of $T_C(x)$ is explained in agreement with the afd character of the transition.

1. Introduction

The influence of defects on the static and dynamic behaviour in a crystal undergoing a structural phase transition has been experimentally and theoretically investigated in the past two decades [1–4] for fundamental reasons, e.g. phase behaviour and transition temperatures. Many ferroelectrics which are then subject of those investigations, due to their interesting electrical and elastic properties, have been studied with respect to defect influences as well. A group of these ferroelectrics, the components of which are connected by hydrogen bonds and to which also a number of betaine compounds belong, is of general interest. In this framework recently the mixed crystal system of betaine phosphate and betaine phosphite was investigated for different finite concentrations x [5]. This mixed crystal system can be considered as being derived from the pure substances by introducing small or finite defect concentrations of the respective other compound.

The properties of betaine phosphate (BP), $(\text{CH}_3)_3\text{NCH}_2\text{COOH}_3\text{PO}_4$, betaine phosphite (BPI), $(\text{CH}_3)_3\text{NCH}_2\text{COOH}_3\text{PO}_3$ and the respective deuterated compounds (DBP and DBPI), as well as the mixed crystal system $\text{DBP}_{1-x}\text{DBPI}_x$, have been studied extensively during recent years using x-ray, dielectric [6–13] and magnetic resonance techniques [14–17]. Together with other ferroelectrics which also contain hydrogen bonds, these crystals are considered to be model substances for the study of the phase behaviour and of structural phase transitions. Detailed knowledge of the structure (unit cell parameters, space groups etc) is available [6]. For our purpose the specification of the local deuterium lattice sites for $\text{DBP}_{1-x}\text{DBPI}_x$ is shown for a sequence of one DBP and two DBPI molecules in figure 1. The betaine molecules

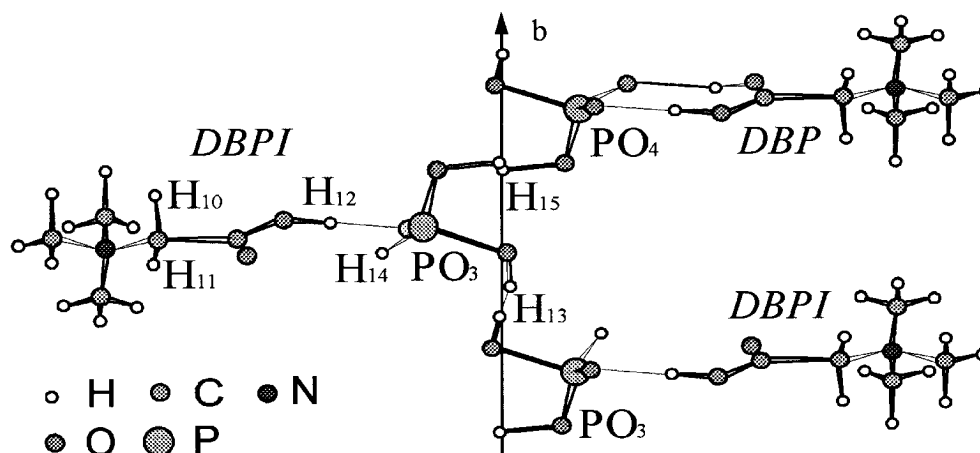


Figure 1. Structure of $\text{DBP}_{1-x}\text{DBPI}_x$ in the antiferrodistortive phase. A sequence of one DBP and two DBPI molecules is shown. The deuterated lattice sites are indicated for one formula unit according to [6].

are arranged approximately perpendicular to the chains and are connected to the phosphate and phosphite tetrahedra by two hydrogen bridges ($\text{O}_5\text{-H}_{14}\text{-O}_1$ and $\text{O}_2\text{-H}_{12}\text{-O}_3$) and one hydrogen bond ($\text{O}_2\text{-H}_{12}\text{-O}_3$), respectively [6]. In DBPI the fourth deuteron is directly bound to the phosphorus atom (P-H_{14}). Various details with respect to the different phases have been revealed in these previous works. For instance, in a study of the structural phase transition from a paraelastic high temperature phase (pe) to an antiferrodistortive phase (afd) at 365 K [7] and 355 K [8] for the pure DBP and DBPI components, respectively, it was found that the phase transition temperatures approximately did not change in case of deuteration. One aspect of recent ^2H NMR studies on the system $\text{DBP}_{1-x}\text{DBPI}_x$ was the investigation of this high-temperature afd phase transition. These studies [5] suggest a quite remarkable dependence of the afd phase transition temperature T_C on the concentration x , i.e. a nonlinear behaviour with a maximum of T_C at an intermediate concentration. For a first interpretation a simple microscopic model, based on the common model of coupled anharmonic oscillators [18, 19], was used successfully in order to arrive at a preliminary explanation of the dependence of T_C on x .

The aim of this paper consists at first in an experimental confirmation of the behaviour of $T_C(x)$ mentioned above by additional ^2H NMR measurements on deuterated single crystals of $\text{DBP}_{1-x}\text{DBPI}_x$. These studies were performed for more values of x , in particular at intermediate concentrations near the supposed maximum of T_C . In extension of the previous work we also suggest using a different model (spherical-like model) which not only allows us in principle to calculate the phase transition temperature in the perfect crystal from the lattice parameters, but which is also fully consistent with the antiferrodistortive character of this transition. In our proposed model except the virtual crystal approximation (VCA) [20] no other approximation has to be used for the explanation of the concentration behaviour of T_C . To demonstrate this procedure we point out first (section 2.1) the important steps in the application of our spherical-like model to the static and dynamic behaviour of the considered two-component solid solution. Then in section 2.2 we discuss the limiting case of a perfect crystal and generalize these results to the case of any mixed crystal $\text{DBP}_{1-x}\text{DBPI}_x$. To obtain the microscopic parameters for our system we again make use of the VCA. Following this line, in section 3 we shall study the correspondence of theory and experiment where the

main question will be whether a good agreement of the predictions of our model with the experimentally obtained nonlinear $T_C(x)$ behaviour can be achieved.

2. Theory

2.1. Model

To investigate the influence of a defect in a crystal with a structural phase transition, we propose the Hamiltonian of the spherical-like model (Beck *et al* [21]). Under all microscopic models investigated, only in the spherical-like model are the assumptions of the mean-field approximation satisfied. Since in our NMR experiments the concentration dependence of T_C is fairly weak, we cannot use another model (e.g. the Φ^4 model) to explain this dependence because then the influence of fluctuations near T_C cannot be adequately described within this small temperature range. As shown e.g. in [21], in the classical limit this model describes a phase transition with a one-component order parameter. We would like to mention that an analogous situation was encountered for the explanation of the quantum effects in structural phase transitions. Here the spherical-like model was both successfully used and theoretically investigated [21–24]. For our case of a two-component solid solution $BP_{1-x}BPI_x$ we use the following form:

$$H = \sum_j \left(\frac{P_j^2}{2m_j} - \frac{A_j}{2} Q_j^2 \right) + \frac{1}{4} \sum_{j,k} f_{jk} (Q_j - Q_k)^2 + \frac{B_j}{4N} \left(\sum_j (Q_j)^2 \right)^2 - \sum_j (F + \delta F_j(t)) Q_j \equiv H_0 - \sum_j \delta F_j(t) Q_j. \quad (1)$$

Here Q_j and P_j are the local normal coordinate and the conjugate momentum of a particle with ‘effective mass’ m_j at a lattice site \vec{R}_j of a three-dimensional cubic lattice, respectively. These parameters approximately describe the critical vibrations in the crystal (see, e.g. the well-known book of Lines and Glass [18]). The quantity $A_j > 0$ is the parameter of the local harmonic single-site potential, B_j/N simulates an infinitely weak (for a number of particles $N \rightarrow \infty$), but infinite range of anharmonic interactions. Considering further the proposed model Hamiltonian, f_{jk} describes a harmonic interaction between the particles, which has to fulfill the condition $0 < \sum_{l \neq k} f_{lk} \equiv f_0 < \infty$. F and $\delta F_j(t)$ are the static and dynamic parts of some external force acting at the lattice site \vec{R}_j , denoted by the subscript j in the following considerations, respectively. The effective mass in each lattice point can be expressed in the following way:

$$m_j = m_1 \quad A_j = A_1 \text{ and } B_j = B_1 \quad \text{if site } j \text{ is occupied by BP unit cells} \quad (2a)$$

and

$$m_j = m_2 \quad A_j = \gamma A_1 \text{ and } B_j = \kappa B_1 \quad \text{if site } j \text{ is occupied by BPI unit cells.} \quad (2b)$$

All quantities f_{jk} are finite $0 \leq |f_{jk}| < \infty$ and have the following values:

$$\begin{aligned} f_{jk} &= f_{jk}^{(1,1)} && \text{if the sites } j \text{ and } k \text{ are occupied by BP unit cells} \\ f_{jk} &= f_{jk}^{(1,2)} = f_{jk}^{(2,1)} && \text{if the sites } j \text{ and } k \text{ are occupied by different unit cells} \\ f_{jk} &= f_{jk}^{(2,2)} && \text{if the sites } j \text{ and } k \text{ are occupied by BPI unit cells.} \end{aligned}$$

The static part \bar{Q}_j and the linear response part $\delta \bar{Q}_j(t)$ of the statistical mechanical average can be calculated exactly in the thermodynamic limit ($N \rightarrow \infty$) with the help of the response

function $\chi_{jk}(t - t')$ which is given by the Green function $\langle\langle Q_j(t), Q_k(t') \rangle\rangle$ (see e.g. [20])

$$\chi_{jk}(t - t') = \frac{1}{2\pi} \int_{-\infty}^{\infty} \chi_{jk}(\omega) e^{-i\omega(t-t')} d\omega = -\langle\langle Q_j(t) | Q_k(t') \rangle\rangle \quad (3)$$

where

$$\langle\langle Q_j(t), Q_k(t') \rangle\rangle = -\frac{1}{i\hbar} \theta(t - t') [Q_j(t), Q_k(t')]. \quad (4)$$

Here the average $\langle \dots \rangle$ is over an equilibrium position and θ is the unit step function. Indeed, from the lattice dynamics we determine the \bar{Q}_j by the requirement

$$\frac{d}{dt} \langle P_j \rangle = \frac{i}{\hbar} \langle [H_0, P_j] \rangle = 0 \quad (5)$$

and from the response theory [20] we find the Fourier transform of $\delta \bar{Q}_j(t)$

$$\delta \bar{Q}_j(\omega) = \sum_k \langle\langle Q_j | Q_k \rangle\rangle_{\omega} \delta F_k(\omega). \quad (6)$$

Here in equations (5) and (6) the exact expressions for \bar{Q}_j are given by the statistical relationship $\bar{Q}_j = -(\partial f_N / \partial F)$, where f_N is the free energy of the considered system (1). Consequently we obtain the following expression for an infinitesimal change, $d\bar{Q}_j$, of the static displacement in dependence on an infinitesimal change of the external field dF

$$d\bar{Q}_j = \frac{\Delta Q_j}{T} dF = \chi_{jj}(0) dF. \quad (7)$$

Here the fluctuations ΔQ_j are given according to the fluctuation–dissipation theorem by the relationship

$$\Delta Q_n = k_B T \text{Re} \chi_{nn}(\omega = 0) \geq 0. \quad (8)$$

Hence, the quantity $|dQ_j|$ increases with rising $|dF|$. \bar{Q}_j is a continuous function of F .

Using the results obtained in the thermodynamic limit by Schneider *et al* [21, 22] one can write the solutions of equations (5) and (6) in the following form [26]. Here we have used the exact relationship $X = \lim_{\omega \rightarrow 0} \chi(\omega)$ between the static (X) and dynamic ($\chi(\omega)$) part of the susceptibility [21] for the spherical-like model:

$$\sum_k (\chi^{-1}(0))_{j,k} \bar{Q}_k = F_j \quad (9)$$

and

$$\sum_k (\chi^{-1}(\omega))_{j,k} \delta \bar{Q}_k(\omega) = \delta F_j(\omega). \quad (10)$$

Here the inverse susceptibilities $(\chi^{-1}(\omega))_{jk}$ are determined by the relationship

$$(\chi^{-1}(\omega))_{jk} = \frac{B_j}{N} \sum_n (\bar{Q}_n^2 + \Delta Q_n) - A_j + f_0 - f_{\bar{q}} - \omega^2. \quad (11)$$

A structural phase transition occurs if for a vanishing static external field ($F \rightarrow 0$) equation (9) has solutions $\bar{Q}_k \neq 0$ below the phase transition temperature T_C .

In carrying out the calculations below, reduced units will be used, in which as starting point the energy of our system (1) is measured in units of the depth of the single-site double-minimum potential $(A_1)^2/B_1$ in the BP unit cells (see e.g. [27, 28]).

2.2. Phase transition temperature of the antiferrodistortive structural phase transition

2.2.1. *Perfect crystal.* To solve equations (9) to (11) in the perfect crystal for $F \rightarrow 0$ let us assume at the beginning that they have an antiferrodistortive solution ($\bar{Q}_j^{(p)} = -\bar{Q}_{j+\bar{a}} = \bar{Q}_{j+2\bar{a}}^{(p)}$) and then prove it. (The index (p) indicates a perfect lattice.) In this case the square of the averaged static displacements, the fluctuations, the coupling constants and the dynamic single-site susceptibilities are invariant with respect to translations, $2\bar{a}$ ($\bar{Q}_n^2 = \bar{Q}^2$, $\Delta Q_n = \Delta Q$, $f_{jk} = f_{|j-k|}$ and $(\chi^{-1}(\omega))_{lk} = (\chi^{-1}(\omega))_{|l-k|}$). Consequently, we obtain from equation (11):

$$\chi_{jk}^{(p)}(\omega) = \frac{1}{N} \sum_{\bar{q}} \frac{\exp(i\bar{q}(\bar{R}_j - \bar{R}_k))}{\bar{Q}^2 + \Delta Q - 1 - f_0 - f_{\bar{q}} - \omega^2} = \frac{1}{N} \sum_{\bar{q}} \chi_{\bar{q}}(\omega) \exp(i\bar{q}(\bar{R}_j - \bar{R}_k)) \quad (12)$$

where

$$f_{\bar{q}} = \sum_{k \neq j} f_{jk} e^{i\bar{q}(\bar{R}_j - \bar{R}_k)}. \quad (13)$$

To include the effects of damping, we introduce a phenomenological damping Γ [21], caused by random time-dependent forces, and obtain then for the dynamic susceptibility the following expression:

$$\chi_{\bar{q}}^{(p)}(\omega) = \frac{1}{\omega_{\bar{q}}^2 - \omega^2 - i\Gamma\omega} = \frac{\omega_{\bar{q}}^2 - \omega^2}{(\omega_{\bar{q}}^2 - \omega^2)^2 + \Gamma^2\omega^2} + i \frac{\Gamma\omega}{(\omega_{\bar{q}}^2 - \omega^2)^2 - \Gamma^2\omega^2} \quad (14)$$

where according to equation (12)

$$\omega_{\bar{q}}^2 = \bar{Q}^2 + \Delta Q - 1 + f_0 - f_{\bar{q}}. \quad (15)$$

Taking into account that in the perfect lattice $(1/N) \sum_n (\bar{Q}_n^2 + \Delta Q) \equiv \bar{Q} + \Delta Q$ equation (15) shows that the frequency of each oscillator in the considered model depends on all anharmonic interactions.

As can be shown in a straightforward manner, the real part of the dynamic susceptibility (equation (14)) has no extreme as a function of \bar{q} and T . On the other hand, the imaginary part of it (equation (14)) passes a minimum at T for any \bar{q} , if

$$\omega^2 = \omega_{\bar{q}=\bar{q}_{cr}}^2 \equiv \bar{Q}^2 + \Delta Q - 1 = T \frac{1}{N} \sum_{\bar{q}} \frac{1}{\bar{Q}^2 + \Delta Q + f_0 - f_{\bar{q}}} - 1 = 0. \quad (16)$$

Equation (9) with equation (12) can be solved by the Fourier transformation in the real space. Using for this purpose together with equation (12) the relation

$$\bar{Q}_l = \frac{1}{\sqrt{N}} \sum_{\bar{q}} \exp(i\bar{q}\bar{R}_l) \quad (17)$$

we obtain that a solution $\bar{Q}_j^{(p)} = -\bar{Q}_{j+\bar{a}}^{(p)} = \bar{Q}_{j+2\bar{a}}^{(p)} \equiv \bar{Q} \neq 0$ with $\Delta Q_j^{(p)} = \Delta Q_{j+\bar{a}}^{(p)} = \Delta Q_{j+2\bar{a}}^{(p)} \equiv \Delta Q$ exists at $(\bar{a}\bar{q}_{cr}) = 1$, if here the mode softens: $f_{\bar{q}_{cr}} = f_0$. Explicitly one can write

$$\bar{Q} \equiv \sum_k \chi_{jk}^{(p)}(0) F = \frac{F}{\bar{Q}^2 + \Delta Q - 1} \quad (18)$$

where according to equations (10) and (15)

$$\Delta Q = T \frac{1}{N} \sum_{\bar{q}} \frac{1}{\Delta Q - 1 + f_0 - f_{\bar{q}}}. \quad (19)$$

Consequently, with this finding our assumption proposed at the beginning of this section is proved.

If $(\Delta Q - 1) < 0$, then for all $|F| > 0$ equation (17) has only one real root, the absolute value of which continuously increases with increasing $|F|$ according to equation (7). The sign of this root depends on the sign of F . For $|F| \rightarrow 0$ this distortion approaches a finite value. In the case $(\Delta Q - q) > 0$ also one real root of equation (18) exists with the same properties with respect to the change of F . This solution vanishes if $|F| \rightarrow 0$. For a vanishing static external field equation (18) provides a non-vanishing value \bar{Q} only, if the expression in the denominator goes to zero, and therefore we obtain, from equation (18) with equation (19), finally the result

$$\bar{Q} = \sqrt{1 - T \frac{1}{N} \sum_{\bar{q}} \frac{1}{f_0 - f_{\bar{q}}}} \quad (20)$$

for the averaged static displacements. This equation gives us the possibility to determine the phase transition temperature (for $\bar{Q} = 0$) to be $T_C = ((1/N) \sum_{\bar{q}} [1/(f_0 - f_{\bar{q}})])^{-1}$. This derivation of the temperature dependence of the order parameter (averaged static displacement \bar{Q}) on a microscopic level (equation (20)) will be discussed again in section 3.2.

2.2.2. *The two-component solid solution in the virtual crystal approximation.* The Dyson equation for the two-component solid solution can be written in the form

$$\begin{aligned} \chi_{jk}(\omega) &= \chi_{jk}^{(p)}(\omega) + \sum_{nn'} \chi_{jn}^{(p)}(\omega) V_{nn'}(\omega) \chi_{n'k}^{(p)}(\omega) \\ &+ \sum_{nn'} \sum_{mm'} \chi_{jn}^{(p)}(\omega) V_{nn'}(\omega) \chi_{n'm}^{(p)}(\omega) V_{mm'}(\omega) \chi_{m'k}^{(p)}(\omega) + \dots \end{aligned} \quad (21)$$

with

$$V_{nn'}(\omega) = (\chi^{-1}(\omega))_{nn''} - ((\chi^{(p)}(\omega))^{-1})_{nn'}. \quad (22)$$

To carry out the configuration-averaged dynamic susceptibility $\overline{\chi(\omega)_{jk}^{conf}}$ in the VCA (see e.g. Elliott *et al* [20]) it is assumed that the perturbation terms $V_{nn'}(\omega)$ in the power series (equation (21)) are configuration averaged independent of each other. This approximation is applicable if the inequality $V_{nn'}(\omega) \ll 1$ holds. After this average the considered series (equation (21)) are translationally invariant and we obtain:

$$\overline{\chi(\omega)_{\bar{q}}^{conf(VCA)}} = \frac{1}{(\bar{Q}^{VCA})^2 + \Delta \bar{Q}^{VCA} - A^{VCA}/B^{VCA} + f_0^{VCA} - f_{\bar{q}}^{VCA} - \omega^2 A^{VCA}/m^{VCA}}. \quad (23)$$

Here we have introduced the following notations:

$$\begin{aligned} \bar{Q}^{VCA} &= (1-x)\bar{Q}_1 + x\bar{Q}_2 \\ \Delta Q^{VCA} &= T \text{Re} \overline{\chi(\omega \rightarrow 0)_{jj}^{conf(VCA)}} \\ A^{VCA} &= \frac{(1-x)A_1 + xA_2}{A_1} = (1-x) + x\gamma \\ B^{VCA} &= \frac{(1-x)B_1 + xB_2}{B_1} = (1-x) + x\kappa \\ f_{jk}^{VCA} &= (1-x)^2 f_{jk}^{(1,1)} + 2x(1-x) f_{jk}^{(1,2)} + x^2 f_{jk}^{(2,2)} \\ m^{VCA} &= \frac{(1-x)m_1 + xm_2}{m_1} \end{aligned} \quad (24)$$

where x is the configuration-average of the occupation number of the elementary cell of BPI, i.e. its concentration. According to equation (23) we get for the considered solid solution at $T_C(\bar{Q}^{VCA} = +0, 1 - \Delta Q^{VCA} = +0)$:

$$T_C(x) = \frac{(1-x) + x\gamma}{(1-x) + x\kappa} \left(\frac{1}{N} \sum_{\bar{q}} \frac{1}{f_0^{VCA} - f_{\bar{q}}^{VCA}} \right)^{-1}. \quad (25)$$

For a Debye type dispersion law equation (25) provides:

$$T_C = \frac{(1-x) + x\gamma}{(1-x) + \kappa x} \frac{2\pi^2}{(6\pi^2)^{1/3}} f_0^{VCA} = \frac{(1-x) + \gamma x}{(1-x) + \kappa x} \frac{f_0^{VCA}}{f_0^{(1,1)}} T_C(x=1). \quad (26)$$

Let us emphasize that the exact expression for the determination of T_C within the perfect spherical-like model in the thermodynamic limit (equation (25)) is equivalent to the corresponding expression approximately obtained by Bruce and Cowley [19] within the framework of the model of coupled anharmonic oscillators (see e.g. [18, 19]). Indeed, taking into account that the inverse sum of equation (25) is in the Debye approximation proportional to f_0 , we obtain the same result $T_C(x=0) = f_0$ in our units. In contrast to these authors, however, in our model the equilibrium equation (5) can be solved exactly.

The phase transition temperature is proportional to the product of the width of the single-particle double-minimum potential and the characteristic f_0 of coupling constants (equation (13)): $T_C \propto f_0$ (in our notation). It should be stressed as well that in the latter model this result is closely connected with the so-called independent-site approximation in the order-disorder case ($f_0 \ll 1$) or with the independent-mode approximation in the displacive situation ($f_0 \gg 1$), which both fail near T_C as clearly demonstrated by the same authors.

3. Correspondence of theory and experiment

3.1. NMR experiments at the high temperature phase transition in $DBP_{1-x}DBPI_x$

After we have tuned the spherical-like model to our system under study we shall, prior to its application, demonstrate the new experimental results on the high temperature antiferrodistortive (afd) phase transition in $DBP_{1-x}DBPI_x$, derived from our ^2H NMR studies. In a recent paper [5] this phase transition temperature from the afd to the paraelectric phase (pe) was determined by means of temperature dependent ^2H NMR measurements on single crystals of different representatives of the system $DBP_{1-x}DBPI_x$. Only a preliminary dependence of the high temperature phase transition on the phosphite concentration x could be obtained in this way in which the available $T_C(x)$ data pointed towards a nonlinear dependence, with T_C exhibiting a maximum at or near the middle of the mixed crystal row. However, due to the lack of crystals with concentration values of $0.15 < x < 0.6$ the results remained insufficient and the supposed maximum at $x = 0.5$ could not be checked.

This drawback is now overcome by means of additional measurements on recently grown crystals with $x = 0.3$ and $x = 0.5$, allowing us to obtain a more reliable phase diagram in the above sense. Furthermore, the temperature for the phase transition could now be calibrated more exactly by means of comparison to ultrasonic measurements on DBPI [29], which allow a precise determination of T_C . For each crystal the phase transition temperature $T_C(x)$ was determined from a set of ^2H NMR spectra which were measured in dependence on the temperature in the same manner as described in [5]. Therefore, T_C could be determined with an error of less than 0.2 K. The new $T_C(x)$ dependence, which allows more precise conclusions on the nonlinearity, is shown in figure 2. First, it is evident that the nonlinear behaviour with a single maximum is clearly confirmed. It follows furthermore, that the difference in T_C

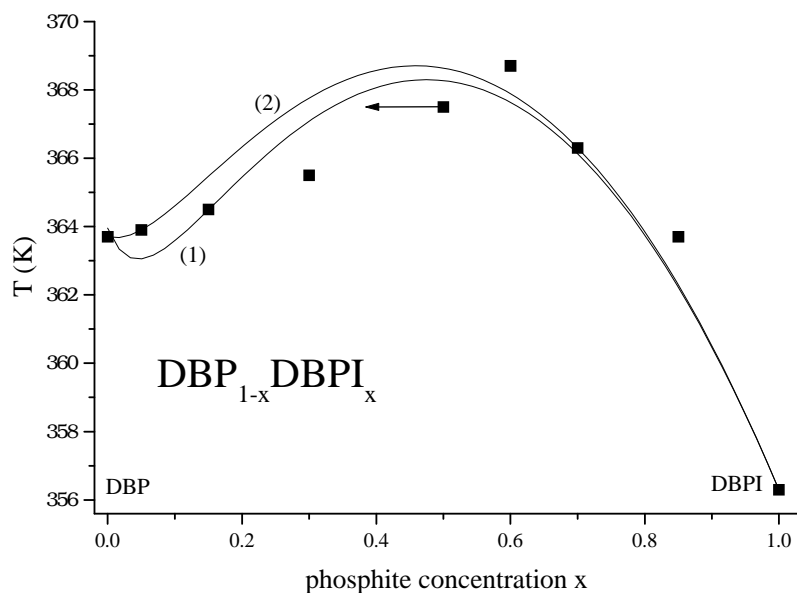


Figure 2. Phase transition temperature T_C as a function of the phosphite concentration x for different representatives of the system $\text{DBP}_{1-x}\text{DBPI}_x$. The temperature was calibrated on ultrasonic measurements on DBPI [29]. Experimental data (dots) are fitted by two parameter sets of our model.

between pure DBP and DBPI is indeed only ~ 7.5 K, indicating a slight deviation from the expected value of 10 K [7, 8]. From the detected maximum the phase transition temperature T_C decreases to 363.7 K (pure DBP) and 356.3 K (pure DBPI), with the decrease towards pure DBPI being steeper. Although we could very accurately determine both the temperature differences and the absolute temperature values, it still remains an uncertainty with respect to the concentrations x . The values x which we use throughout this work are the nominal ones, i.e. those values which are characteristic for the growing solution. It has been shown, however, that the real concentrations in the crystals are likely to be shifted towards lower values (lower DBPI concentration) [12]. Unfortunately, no quantitative correction is possible, but from the line width analysis of our ^2H NMR spectra we can clearly confirm this tendency, the effect of which is most prominent at intermediate concentrations. The necessary correction of the x values is indicated for $x = 0.5$ in figure 2, where the arrow only gives a qualitative impression. We shall mention as well that the qualitative $T_C(x)$ dependence was preliminarily confirmed by ultrasonic measurements on further crystals with different x values by the authors of [29].

3.2. Application of the model to the afd phase transition in $\text{DBP}_{1-x}\text{DBPI}_x$

The exact expression for the determination of T_C within the perfect spherical-like model in the thermodynamic limit (equation (25)) is applied to the $\text{DBP}_{1-x}\text{DBPI}_x$ mixed crystal system to elucidate the nonlinear behaviour of $T_C(x)$ under the assumption that the dynamics of our mixed crystals can be approximately considered as those of the spherical-like model with two sorts ($\alpha = 1, 2$) of lattice parameters as described at the beginning (equations (2a)–(2b)). To elucidate the concentration dependence of T_C we assume for simplicity that $f_{jk}^{(1,1)} = f_{jk}^{(2,2)}$

and obtain then with equation (26)

$$T_C(x) = T_C(x = 1) \frac{[(1-x)/\gamma] + x}{[(1-x)/\kappa] + x} [1 + 2x(1-x) \Delta f] \quad (27)$$

with $\Delta f = (f_0^{(1,2)} - f_0^{(1,1)})/f_0^{(1,1)}$ and x being the concentration of component 1 (DBPI in our case).

From the three parameters κ , γ and Δf of equation (27) the ratio $\gamma/\kappa = T_C(x = 0)/T_C(x = 1)$ is given by the experiment and equals 0.9796. Thus, for fitting this model to the measured T_C values two independent parameters remain. In fact, the fit can be executed in different ways. Two fit curves are given in figure 2 from which the correspondence of the experimental data to the model can be judged. Curve (1) was obtained by the best least mean squares fit of all three parameters to the experimental data points. Our experimental results are sufficiently well reproduced, although we observe the biggest deviations at intermediate concentrations. If we have in mind the concentration corrections towards lower x values, however, we may expect a better correspondence, since in particular the data points in the intermediate concentration region move towards the fit curve. A different possibility to apply our model is realized with curve 2. Here, the values for $x_1 = 0.7$ and $x_2 = 0.05$ were inserted in equation (27), and the resulting equation system was solved to determine the two remaining free parameters γ and Δf . The result of this procedure gives a good approximation of the experimental T_C values as well, although the same remarks with respect to the concentration values apply for this curve.

It is important to remark that for both cases the decisive common property is the qualitative description in that sense that from our approach necessarily follows that T_C must go through a maximum. Thus, in accordance with the experiment a nonlinear dependence of T_C on x with a maximum at or near the value $x = 0.5$ is described by our model. For a better understanding of the physical contents of this behaviour we consider equation (27). Although the $T_C(x)$ dependence cannot be explained in a straightforward manner according to the dependence on κ and γ , we may find an interpretation as follows. Taking now into account that $T_C(x = 0) \approx T_C(x = 1)(\kappa \approx \gamma)$, this relation points towards the importance of the occurrence of a long-range order. The latter depends, according to equation (27), on the value of the coupling constant, the value of which is maximal if the concentration is 0.5, as can be inferred from this equation. This implies the highest phase transition temperature at this concentration (at nominal $DPB_{0.4}DBPI_{0.6}$ for our available crystals).

Let us here still notice the following important fact: the heuristic criterion of the validity of the VCA stated above ($V_{nn'} \ll 1$) is fulfilled according to equations (27) and (25), respectively. Consequently, this approximation within the framework of the spherical-like model can be used for the description of the considered solid solution. Our proposed model guarantees the correct description of the experimentally observed afd character (doubling of the unit cell) of the transition and is also in agreement with the experimentally established order-disorder behaviour, where a soft mode does not exist below T_C .

This consistent description of the phase transition in our mixed crystal system tackles the situation from a more theoretical side as compared to previous NMR studies [17]. Since it describes the microscopic origin of the experimental behaviour shown by the betaine phosphate and betaine phosphite molecules, it suggests the following discussion for a deeper understanding of the system. In [17] the character of the phase transition was set into relation to the different occupation probabilities of two betaine molecule positions tilted in opposite directions with respect to the mirror plane. The most straightforward assumption claimed in the previous paper was that the statistically averaged difference of these probabilities, $p(T_C - T)$, is directly proportional to \bar{Q} , where the betaine units give the most important contribution to

the local normal co-ordinate. However, in this interpretation we have to note the apparent discrepancy with respect to the critical exponent β for the order parameter \bar{Q} ($\beta = 0.5$ in our case, see equation (20), in an arbitrary broad region below T_C) and the apparent critical exponent 0.25 ± 0.03 measured for the quantity $p(T_C - T)$ by means of NMR (in a region from 0.4 K up to 15 K below T_C). We explain the reason for this behaviour, that the probability $p(T_C - T)$ is not linearly related to the order parameter $\bar{Q}(T)$, but is rather given by the dependence $p(T_C - T) = f[\bar{Q}(T)]$. Therefore knowing the temperature dependence of \bar{Q} for the proposed microscopic model of the structural phase transition (equation (27)) we can find the temperature dependence of $p(T_C - T)$ from the relation above, i.e. the critical exponent β is one half in complete agreement with the exponent for specific heat [17]. However, the microscopic nature of the order parameter, which we previously suggested to be directly related to the order-disorder behaviour of the betaine units, is not identical with the average tilt angle proportional to the probability $p(T_C - T)$. It is also interesting to note again that in the paper [17] we also have tried to understand the apparent critical exponent close to 0.25 in terms of a tricritical behaviour according to the Landau theory [30]. In this case, in the Landau theory the expression for the free energy up to terms of sixth order has to be considered, which is in clear contrast to the results of the present theoretical treatment.

To conclude, we shall emphasize again that the concentration dependence of the high temperature phase transition temperature T_C in single crystals of the mixed crystal system $\text{BP}_{1-x}\text{BPI}_x$ can be theoretically explained by means of the microscopic spherical-like model in good consistence with the experiment.

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