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On the issue of superstructure phase transitions in monoclinic RbD_2PO_4 crystal

Ya Shchur

Institute for Condensed Matter Physics, Svientsitskii Street 1, 79011, Lviv, Ukraine

E-mail: shchur@ph.icmp.lviv.ua

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Abstract

This paper presents the results of group-theory analysis, lattice dynamics simulation and phenomenological treatment in three temperature phases of the monoclinic RbD_2PO_4 . Combining the methods of group theory with the analysis of crystal structure peculiarities in different structural phases, it is shown that the lowest temperature phase should reveal a strict antiferroelectric state with $P2_1$ symmetry rather than the ferroelectric state reported repeatedly. Lattice dynamics simulation was performed in the quasi-phenomenological approach comprising the Coulomb, short-range, covalent, van der Waals and hydrogen-bonded interactions. The probable mechanisms of phase transitions are considered.

1. Introduction

The RbD_2PO_4 (DRDP) crystal belongs to the well known family of KDP type crystals. More than 40 years ago the crystals of this type found a wide technological application, especially in nonlinear optics, electro-optics, acousto-optics and optical data processing. Therefore, a proper understanding of the underlying physical processes in these compounds may be not only of basic theoretical interest, but appears to be important for technological application as well.

At an ambient pressure, DRDP undergoes two structural phase transitions with decreasing temperature at $T_1 = 377$ and $T_2 = 317$ K [1, 2]. The high temperature phase transition $P2_1/m$ ($Z = 2$; a_0, b_0, c_0) \rightarrow $P2_1/c$ ($Z = 4$; $a_0, b_0, 2c_0$) does not change the point group symmetry ($2/m$) and is accompanied by the appearance of superstructure along the c crystallographic axis [3]. Both the high (phase I) and the intermediate (phase II) temperature phases demonstrate no polar properties. The low temperature phase transition has been the subject of much debate. It was established that there was a unit cell multiplication along the a axis below T_2 ($Z = 8$; $2a_0, b_0, 2c_0$) [2]. However, there was reported contradictory information concerning the symmetry of the lowest temperature phase (phase III). X-ray diffraction data enabled the authors of paper [4] to refine the symmetry of phase III as acentric $P2_1$, whereas the relatively recent neutron scattering investigation [5] suggested the centric $P2_1/n$ space group for this phase. Recently the $P2_1$ space group was refined again for phase III by means of x-ray diffraction [6].

The detailed Raman scattering study of DRDP at the II–III phase transition [7] manifested a good consistency of spectroscopic data with the centric $2/m$ symmetry of phase III. The number of observed NMR lines at the temperature $T_2 - 4$ K was only half of that expected for the acentric $P2_1$ space group [8], thus indicating the centric type of crystal structure as well.

The polar nature of the lowest temperature phase III is also rather contradictory. Double hysteresis loops characteristic of the antiferroelectric state were detected below the T_2 point [2] in DRDP, whereas the triple hysteresis loops inherent in the ferroelectric state were observed for a mixed $\text{Rb}_{0.7}\text{C}_{0.3}\text{D}_2\text{PO}_4$ compound [9] in phase III. Based on the dielectric and pyroelectric measurements, the authors of paper [10] were unable to determine whether phase III was ferroelectric or antiferroelectric. Intensive dielectric [11–17], structural [18, 19], spectroscopic [20], resonance [21], acoustic [22, 23] and dilatometric [24] studies did not shed more light on the physical nature of the lowest temperature phase. Moreover, as was found in [13], the spontaneous polarization does not appear at T_2 but at $T_2 - 6$ K. This enabled the authors of paper [13] to suggest the existence of the fourth phase. According to this suggestion, the strictly antiferroelectric centric phase may exist within a narrow temperature range (between T_2 and $T_2 - 6$ K), whereas the acentric phase may appear below $T_2 - 6$ K. However, this assumption concerning the fourth structural phase of DRDP has not yet been directly corroborated by investigations of other types.

Table 1. The irreducible multiplier representations of $P2_1/m$ (at the BZ points $k = 0, k = \frac{1}{2}b_3$), $P2_1/c$ ($k = \frac{1}{2}b_1$) and $P2_1/n$ ($k = 0$) space groups.

$P2_1/m$	$\{E 0\}$	$\{2 \frac{1}{2}b\}$	$\{m \frac{1}{2}b\}$	$\{I 0\}$
$P2_1/c$	$\{E 0\}$	$\{2 \frac{1}{2}b + \frac{1}{2}c\}$	$\{m \frac{1}{2}b + \frac{1}{2}c\}$	$\{I 0\}$
$P2_1/n$	$\{E 0\}$	$\{2 \frac{1}{2}a + \frac{1}{2}b + \frac{1}{2}c\}$	$\{m \frac{1}{2}a + \frac{1}{2}b + \frac{1}{2}c\}$	$\{I 0\}$
A_g	1	1	1	1
B_g	1	-1	-1	1
A_u	1	1	-1	-1
B_u	1	-1	1	-1

In order to review the problem of reliability of phase transitions in DRDP we have performed a symmetry consideration of the lattice transformations and lattice dynamics simulation in three temperature phases. The investigation of lattice dynamics peculiarities of DRDP may provide very interesting information since the superstructure phase transitions are associated apparently with the soft mode condensation at the Brillouin zone (BZ) boundary at the $k = \frac{1}{2}b_3$ (phase I \rightarrow phase II) and $k = \frac{1}{2}b_1$ (phase II \rightarrow phase III) points. The semi-phenomenological atomistic potential comprising the Coulomb, short-range, covalent, van der Waals and hydrogen-bonded interactions was utilized for simulation in the present paper.

2. Crystal structure and group-theory treatment

The peculiar crystallographic feature of DRDP, such as the CsD_2PO_4 (DCDP) crystal, is the presence of two kinds of hydrogen bonds. Owing to the various kinds of experiments [5, 8] it is well established that the D_1 deuterons are ordered near the particular oxygen atoms on the $O_1-D_1 \cdots O_2$ hydrogen bonds in all temperature phases, whereas the D_2 deuterons are disordered between the two possible sites on the $O_3-D_2 \cdots O_4$ bonds in phases I and II and become ordered in phase III. Note that the D_2 deuterons, being still disordered on the hydrogen bonds in phase II, become distinguished into the two kinds, D_2 and D_3 ones, which are chemically and physically nonequivalent [3]. In contrast to the DCDP case, there is no large difference of the length between the c -axis directed $O_1-D_2 \cdots O_2$ and b -axis running $O_3-D_2(D_3) \cdots O_4$ hydrogen bonds.

Since the number of formula units Z is two, four, and eight in phases I, II, and III, respectively, the phonon spectrum of DRDP consists of 48, 96, and 192 normal modes in these phases, respectively. There is the following classification of phonon modes into three temperature phases according to irreducible representations in the BZ centre (Γ) and along the main directions of the BZ (Δ, Λ):

$$\begin{aligned}
 &P2_1/m, Z = 2 \text{ (48 modes)} \\
 &\Gamma: 13A_g + 8B_g + 11A_u + 16B_u \\
 &\Delta((b_1, b_3)\text{plane}): 29\Delta_1 + 19\Delta_2 \\
 &\Lambda(b_2): 24\Lambda_1 + 24\Lambda_2 \\
 &P2_1/c, Z = 4 \text{ (96 modes)} \\
 &\Gamma: 21A_g + 21B_g + 27A_u + 27B_u \\
 &\Delta((b_1, b_3)\text{plane}): 48\Delta_1 + 48\Delta_2 \\
 &\Lambda(b_2): 48\Lambda_1 + 48\Lambda_2
 \end{aligned}$$

$$P2_1, Z = 8 \text{ (192 modes)}$$

$$\Gamma: 96A + 96B$$

$$\Delta((b_1, b_3)\text{plane}): 192\Delta$$

$$\Lambda(b_2): 96\Lambda_1 + 96\Lambda_2.$$

Let us investigate the reliability of various space groups G of different temperature phases in DRDP using the methods of group theory. According to the Birman–Worlock statement [25], the irreducible representation responsible for the phase transition $G^{\text{old}} \rightarrow G^{\text{new}}$ from the ‘old’ to the ‘new’ space group should satisfy the following condition:

$$\frac{1}{n} \sum_{g^{\text{new}} \in G^{\text{new}}/T^{\text{new}}} \chi_k^j(g^{\text{new}}) = \text{positive integer}, \quad (1)$$

where n is the order of the factor group G/T and $\chi_k^j(g)$ is the character of symmetry element g ($g = \{h|\alpha\}$, α is the non-primitive translation associated with the point symmetry operation h) of the j th irreducible representation in the k point of BZ. There is the following relation between $\chi_k^j(g^{\text{new}})$ and $\chi_k^j(g^{\text{old}})$ for the case of one-vector k -star (this case is relevant to both phase transitions in DRDP):

$$\chi_k^j(g^{\text{new}}) = \exp[-ik(t_0(h) + \alpha^{\text{old}})] \chi_k^j(g^{\text{old}}), \quad (2)$$

where $t_0(h) = \alpha^{\text{new}}(h) - \alpha^{\text{old}}(h) + s - hs$ is the displacement vector and s is a vector between the origin O' of G^{new} and O of G^{old} [25]. Note that α^{new} is written in terms of the basic translation vectors $\{a, b, c\}$ of the ‘old’ phase. Therefore, $t_0 + \alpha^{\text{old}} = \frac{1}{2}b + c$ for the point symmetry operations 2 and m of the $P2_1/c$ group and $t_0 + \alpha^{\text{old}} = a + \frac{1}{2}b + \frac{1}{2}c$ for the same symmetry operations 2 and m of the $P2_1/n$ group. Hence, the multiplication factor $\exp[-ik(t_0(h) + \alpha^{\text{old}})] = -1$ in (2) for operations 2 and m of both $P2_1/c$ ($k = \frac{1}{2}b_3$) and $P2_1/n$ ($k = \frac{1}{2}b_1$) groups. Using the irreducible representations of $P2_1/m$ ($k = \frac{1}{2}b_3$), $P2_1/c$ ($k = \frac{1}{2}b_1$) and $P2_1/n$ ($k = 0$) groups in corresponding points of the BZ (see table 1), and relations (1) and (2), we come to the conclusion that the same B_g irreducible representation is responsible for both $P2_1/m \rightarrow P2_1/c$ and $P2_1/c \rightarrow P2_1/n$ phase transitions.

Choosing the origin O' of $G^{\text{new}} = P2_1/c$ at the point $(0, 0, 1/4)$, one may show that the A_u representation may also be responsible for the $P2_1/m \rightarrow P2_1/c$ phase transition. The conclusion concerning the activity of the A_u (B_1^-) soft mode at the I–II phase transition was drawn in [19]. However, the activity of the A_u polar mode at the $P2_1/m \rightarrow P2_1/c$ transition should induce the polar (antiferroelectric) phase, which contradicts the experimental

observation [1, 13, 16]. In contrast, the statement regarding the activity of B_g representation adequately describes the physical nature of phase II and the structural changes occurring at the I–II phase transition. Since normal modes transforming in the $P2_1/m$ phase according to B_g symmetry are not dipole active, the softening of the B_g phonon at the BZ boundary at the $k = \frac{1}{2}b_3$ point induces the non-polar $P2_1/c$ structure in phase II with the unit cell doubled along the c axis. The analysis of experimentally observed changes between the $P2_1/m$ [18] and $P2_1/c$ [3] structures shows that they agree well with the B_g eigenvectors of the $P2_1/m$ group, namely

$$\begin{aligned} \text{Rb}_I(b) - \text{Rb}_{II}(b) & \quad \text{O}_{3I}(a) - \text{O}_{4I}(a) + \text{O}_{3II}(a) - \text{O}_{4II}(a) \\ \text{P}_I(b) - \text{P}_{II}(b) & \quad \text{O}_{3I}(b) + \text{O}_{4I}(b) + \text{O}_{3II}(b) + \text{O}_{4II}(b), \\ \text{O}_{1I}(b) - \text{O}_{12}(b) & \quad \text{O}_{3I}(c) - \text{O}_{4I}(c) + \text{O}_{3II}(c) - \text{O}_{4II}(c) \\ \text{O}_{2I}(b) - \text{O}_{22}(b) & \quad \text{D}_{II}(b) - \text{D}_{III}(b) \end{aligned} \quad (3)$$

assuming their antiparallel type in the neighbouring sublattices of $P2_1/c$ phase. The set of eigenvectors (3) corresponds to the displacements of constituent atoms along the crystallographic axes. The Roman numerals refer to molecular units. Among these eigenvectors of B_g type in the $P2_1/m$ phase there is no eigenvector corresponding to the vibrations of D_2 deuterons tunnelling on the $\text{O}_3 - \text{D}_2 \cdots \text{O}_4$ hydrogen bonds. This means that the softening of the B_g phonon mode should not change the type of D_2 deuteron distribution, which corresponds to the experimental observation in phase II [3]. Note that the eigenvectors of A_u type contain the components of displacements of D_2 deuterons.

However, the $P2_1/c \rightarrow P2_1/n$ symmetry transformation induced by the softening of the B_g normal mode at the $k = \frac{1}{2}b_1$ point contradicts both the antiferroelectric and the ferroelectric type of phase III. First of all, the eventual B_g soft mode does not evoke the D_2 (D_3) deuteron ordering in the lowest temperature phase III, because no D_2 (D_3) eigenvector transforms according to the B_g irreducible representation in the $P2_1/c$ phase (the $P2_1/c$ symmetry of phase II has not been prejudiced in all structural works available [3, 5]). Secondly, the analysis of the experimental crystal structure changes appearing at the phase II \rightarrow phase III phase transition [3, 5] (assuming the multiplication of the unit cell along the a axis) manifests no correlation with the B_g eigenvectors of the $P2_1/c$ space group. This means that neither $P2_1/n$ nor any other centric space group may correspond to the symmetry of phase III of the DRDP crystal. Therefore, the symmetry of phase III may be only acentric. Regarding the structural analysis data [3–6], one may conclude that the $P2_1$ group reliably describes the structure of phase III.

There are two scenarios for the realization of the $P2_1/c \rightarrow P2_1$ phase transition. The first was earlier suggested on the basis of the phenomenological approach [26] and consists in the simultaneous condensation of two phonon modes of B_g and B_u symmetry at the BZ boundary at the $k = \frac{1}{2}b_1$ point. This scenario leads to the ferroelectric ordering of heavy Rb, P, and O atoms and to the uncompensated homogeneous polarization appearing in phase III. According to the B_u symmetry eigenvectors for D_2 and D_3 deuterons,

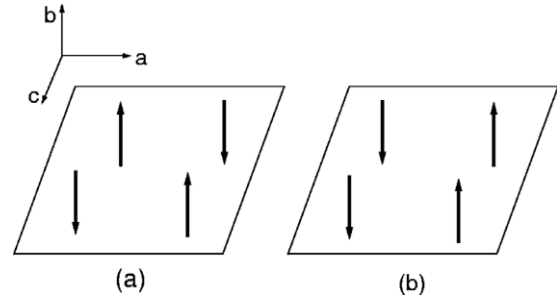


Figure 1. Schematic sketch of the deuteron ordering along the b -axis running deuterium chains in the low temperature $P2_1$ phase induced by the eventual softening of B_u (a) and A_u (b) modes at the BZ boundary at the $k = \frac{1}{2}b_1$ point.

softening of the B_u mode evokes the static shift of D_2 and D_3 atoms along the b -axis (in phase III) in such a way that the neighbouring b -chains of deuterons become oppositely directed along both a - and c -axes (antiparallel order; see figure 1(a)). Another eventual scenario of the $P2_1/c \rightarrow P2_1$ phase transition is the condensation of the A_u phonon mode at the $k = \frac{1}{2}b_1$ point. In this case, the strict antiferroelectric state will appear in phase III. The softening of the A_u phonon mode leads to the parallel order of b -chains of deuterons along the c -axis and to the antiparallel order along the a -axis (see figure 1(b)). The last type of deuteron order in phase III agrees well with the deuteron arrangement observed experimentally by neutron diffraction [5]. From this point of view, the reliability of the single A_u soft mode condensation seems higher than the two B_g and B_u mode softenings. This means that phase III should reveal a strict antiferroelectric order with the $P2_1$ symmetry, rather than the ferroelectric state reported repeatedly [1, 9, 13, 14].

3. Model of lattice dynamics

Lattice dynamics simulation of DRDP was performed in the quasi-harmonic approximation utilizing an interatomic potential similar to the one used for lattice dynamics modelling of CDP and DCDP crystals [27, 28],

$$\begin{aligned} \Phi(r_{kk'}) &= \frac{e^2}{4\pi\epsilon_0} \frac{Z(k)Z(k')}{r_{kk'}} + Sa \exp\left(-\frac{br_{kk'}}{R(k) + R(k')}\right) \\ &+ D_j \exp\left(-\frac{n_j}{2} \frac{(r_{kk'} - r_{0j})^2}{r_{kk'}}\right) - \frac{w}{r_{kk'}^6}. \end{aligned} \quad (4)$$

The first term in (4) corresponds to Coulomb, the second to short-range Born–Mayer type, the third to covalent and the fourth to van der Waals contributions. $Z(k)$ and $R(k)$ are the effective radius and charge, respectively, of the k th kind of atom. $a = 1822$ eV and $b = 12.364$ are constants and $r_{kk'}$ is the distance between the atoms of k and k' types. S , D_j , n_j , r_{0j} and w are adjustable parameters. The third term in (4) was also used for the simulation of oxygen–deuterium interactions within hydrogen bonds.

We used the same values of model parameters both in the high temperature $P2_1/m$ and in the intermediate $P2_1/c$ phase of DRDP. These values were the same as those utilized

for lattice dynamics simulation of DCDP in the paraelectric phase [27, 28] with an exception of $R(\text{Rb})$ and those associated with hydrogen bond length (r_{02}, r_{03} and r_{04}). This seems obvious due to the different lengths of hydrogen bonds in DCDP and DRDP. Finally, we came to the following parameters: $Z(\text{Rb}) = 0.978$; $Z(\text{P}) = 1.94$; $Z(\text{O}_1) = -1.14$; $Z(\text{O}_2) = -0.91$; $Z(\text{O}_3) = Z(\text{O}_4) = -0.984$; $Z(\text{D}) = 0.55$; $R(\text{Rb}) = 2.278 \text{ \AA}$; $R(\text{O}_1) = 1.436 \text{ \AA}$; $R(\text{O}_2) = 1.166 \text{ \AA}$; $R(\text{O}_3) = R(\text{O}_4) = 1.378 \text{ \AA}$; PO_4 groups: $r_{01} = 1.616 \text{ \AA}$; $D_1 = 24.345 \text{ eV}$; $n_1 = 3.2 \text{ \AA}^{-1}$; hydrogen bonds: $D_2 = 11.69 \text{ eV}$; $n_2 = 1.93 \text{ \AA}^{-1}$; $r_{02} = 1.384 \text{ \AA}$ (for $\text{O}_3\text{-D}_2$ and $\text{O}_4\text{-D}_3$); $r_{03} = 1.608 \text{ \AA}$ (for $\text{O}_2\text{-D}_1$); $r_{04} = 0.993 \text{ \AA}$ (for $\text{O}_1\text{-D}_1$); $w = 59.0 \text{ eV \AA}^6$ and $S = 1.985$ only for simulation of the O–O interactions within the same PO_4 units while $S = 1$ for interactions of all other kinds of atoms.

Since above the T_2 phase transition point the D_2 and D_3 deuterons are in the tunnel motion between two possible sites on the $\text{O}_3\text{-D}_2(\text{D}_3) \cdots \text{O}_4$ hydrogen bonds, we treated them as located at the middle of the hydrogen bonds. This condition is indispensable for preserving both the $P2_1/m$ and $P2_1/c$ centric macroscopic symmetry. Therefore, modelling the $\text{O}_3\text{-D}_2$ and $\text{O}_4\text{-D}_3$ interactions in phases I and II we used the single r_{02} parameter instead of two r_{03} and r_{04} parameters utilized for the simulation of the $\text{O}_2\text{-D}_1$ and $\text{O}_1\text{-D}_1$ bondings, respectively. Due to the deuteron ordering on the shorter hydrogen bonds $\text{O}_3\text{-D}_2(\text{D}_3) \cdots \text{O}_4$ at the phase transition into the low temperature $P2_1$ phase there appears a charge redistribution around the oxygen atoms. This caused the need to modify some potential parameters in phase III to the following values:

$$\begin{aligned} Z(\text{O}_3) &= -1.058; & Z(\text{O}_4) &= -0.910; \\ R(\text{O}_3) &= 1.466; & R(\text{O}_4) &= 1.166 \text{ \AA}; \\ r_{02} &= 1.608 \text{ \AA} & & \text{(for } \text{O}_4\text{-D}_2\text{);} \\ r_{05} &= 1.24 \text{ \AA} & & \text{(for } \text{O}_3\text{-D}_2\text{).} \end{aligned}$$

Lattice dynamics simulation was done using the experimental crystal structure detected in phases I [18], II [3] and III [5], which had been relaxed to satisfy the lattice stability conditions. Note that the crystal structure of DRDP in phase III was refined in [5] as $P2_1/n$ and does not match our conclusion regarding the $P2_1$ symmetry of this phase, obtained above by means of group-theory analysis. However, we utilized the results of [5] since only this work presents the coordinates of deuterium atoms and, as was stated in [5], the coordinates of heavy atoms refined within $P2_1/n$ symmetry agree well with those obtained earlier by means of the x-ray technique [7] and attributed to the $P2_1$ structure.

4. Results of simulation and discussion

The comparison between the phonon frequencies calculated at the BZ centre and the experimental ones taken from spectroscopic data in two $P2_1/m$ and $P2_1/c$ phases was presented in our preliminary report [29]. In general, there

is a quite reasonable agreement between the theory and experiment. The overall disagreement between the calculated phonon frequencies and those measured experimentally amounts to 7.8, 8.6, and 4.8% for the modes of A_g , B_g , and A_u symmetry, respectively, in $P2_1/m$ phase ($T = 403 \text{ K}$) and 6.3, 6.1, and 1.1% for phonon modes of the same A_g , B_g , and A_u species, respectively, in $P2_1/c$ phase ($T = 332 \text{ K}$). The average disagreement between the experiment [7, 20] and the simulation for phonon frequencies of A symmetry calculated in the low temperature phase $P2_1$ (room temperature) is 3.9%. The comparison of the calculated modes of B_u ($P2_1/m$ and $P2_1/c$ phases) symmetry and the modes of B type ($P2_1$ phase) with experiment was not performed due to the inappropriate experimental method used in determining the mode parameters vibrating in the monoclinic (a, c) plane [7].

The low frequency dispersion relations of phonon modes of Δ_2 symmetry simulated along the b_3 direction of the BZ in the $P2_1/m$ phase ($T = 403 \text{ K}$) are depicted in figure 2(a). Note that our simulation was performed in the quasi-harmonic approximation assuming non-interacting normal phonon modes. However, accepting the possibility of mode interaction, one may suggest a crossing between the Δ_2 acoustic and the lowest Δ_2 optic phonon branch at a point near $k \approx 0.32b_3$ and the other crossing between the two lowest optic modes near the $k \approx 0.02b_3$ point. The eventual phonon mode interaction results in the clearly visible repulsion of these branches. If so, the lowest Δ_2 optic phonon branch reaches its smallest value at the $\frac{1}{2}b_3$ point of the BZ. Since the current simulation was performed at a temperature higher by 22 K than the phase transition point, one may expect that due to the nonlinear phonon interaction the lowest Δ_2 optic phonon branch may soften at the BZ boundary at lower temperature, inducing the superstructure phase transition. Note that phonon modes transforming according to the Δ_2 symmetry in the (b_1, b_3) plane (wavevector $\mathbf{k} = \mu_1 b_1 + \mu_3 b_3$, $0 < \mu_1, \mu_3 < \frac{1}{2}$) are compatible with the B_g and A_u irreducible representations both at $\mathbf{k} = 0$ and $\frac{1}{2}b_3$ points. Hence, the $P2_1/m \rightarrow P2_1/c$ phase transition may be the result of multiphonon interaction of B_g and A_u modes. The simulation approach used herein cannot indicate the symmetry of the soft phonon mode. However, as follows from the group-theory consideration presented above, the B_g representation must be responsible for this phase transition.

The low frequency part of the phonon spectrum in the intermediate $P2_1/c$ phase along the b_1 axis is presented in figure 2(b). These dispersion relations are of special interest since the superstructure $P2_1/c \rightarrow P2_1$ phase transition is eventually induced by the soft phonon mode condensation at the BZ boundary at the $\frac{1}{2}b_1$ point. As seen in this figure, the lowest acoustic phonon branch (B_u symmetry at the BZ centre) has an extremely small slope and reaches only 7 cm^{-1} at the BZ boundary ($\frac{1}{2}b_1$ point). At first glance, this finding should speak in favour of the two (B_u and B_g) soft mode scenario for low temperature phase transition. However, this anomalous dispersion of the lowest acoustic branch along the b_1 axis may be the result of the nonlinear interaction not only with the B_g optic mode but also with the mode of other symmetry (i.e. the A_u optic mode). Based solely upon the

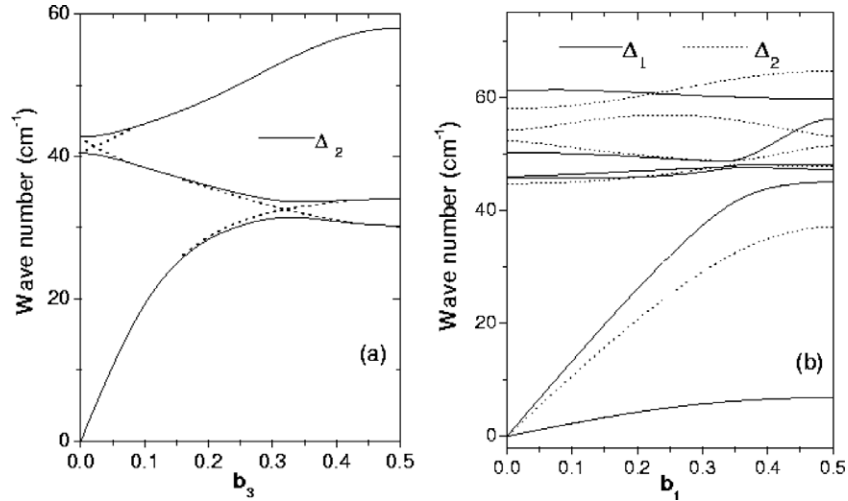


Figure 2. Low frequency part of phonon spectrum simulated in high temperature $P2_1/m$ (a) and intermediate temperature $P2_1/c$ (b) phases along the b_3 and b_1 axes of the BZ, respectively. The dotted lines in (a) indicate the eventual intersection of phonon branches (drawn by eye).

presented lattice dynamics simulation, we cannot establish the symmetry of the soft phonon branch which evokes the $P2_1/c \rightarrow P2_1$ phase transition. One could generally say that the lattice is unstable along the a direction. However, the phenomenological Ginzburg–Landau approach may help to clarify the mechanism of two superstructure phase transition considered here.

Similarly to [26], the generalized form of free energy relevant to both phase II and phase III may be presented as follows:

$$\begin{aligned}
 F_\eta = & \frac{1}{2}\omega_\eta^2(\mathbf{k}_\eta)\eta^2 + \frac{1}{4}\beta_\eta\eta^4 + \sum_{i=1}^3 a_{\eta i}\eta^2 U_i + \frac{1}{2}\sum_{i,j=1}^3 b_{\eta ij}\eta^2 U_i U_j \\
 & + \frac{1}{2}\sum_{j=4}^6 b_{\eta ij}\eta^2 U_j^2 + a_{\eta 5}\eta^2 U_5 + \frac{1}{2}\sum_{i=1}^3 b_{\eta i5}\eta^2 U_i U_5 \\
 & + \frac{1}{2}b_{\eta 46}\eta^2 U_4 U_6
 \end{aligned} \quad (5)$$

where η is the order parameter, which has the meaning of the soft phonon mode coordinates transforming according to B_g ($P2_1/m \rightarrow P2_1/c$ phase transition, $\mathbf{k} = \frac{1}{2}\mathbf{b}_3$) or to A_u ($P2_1/c \rightarrow P2_1$ phase transition, $\mathbf{k} = \frac{1}{2}\mathbf{b}_1$) representation. $\omega_\eta^2(\mathbf{k}) = A_\eta(T - T_\eta)$ can be treated as the soft phonon mode frequency at the BZ boundary points $\mathbf{k} = \frac{1}{2}\mathbf{b}_3$ or $\frac{1}{2}\mathbf{b}_1$, $T_\eta = T_1$ or T_2 . The coupling between the order parameter η and strain components U_i is accounted for in (5) as well.

As pointed out above, there is an eventual interaction between the lowest Δ_2 optic phonon branch (B_g symmetry at the BZ centre) and the Δ_2 acoustic branch along the b_3 direction in phase I (see figure 2(a)). The slope of this Δ_2 acoustic mode evaluated near the BZ centre corresponds to the V_{ZY} velocity of the pure transfer acoustic wave (Z -direction of wave propagation, Y -direction of wave polarization). Using the relations between acoustic wave velocities and elastic constants

$$\begin{aligned}
 \rho V_{ZY}^2 &= C_{44} \\
 \rho V_{XZ}^2 &= C_{11} + C_{55} - \sqrt{(C_{11} - C_{55})^2 + 4C_{15}^2}
 \end{aligned} \quad (6)$$

and the relations corresponding to changes of complex elastic constants in the region of phase transition [26]

$$\begin{aligned}
 \Delta C_{ii}^* &= b_{\eta ii}\eta_0^2 - \frac{a_{\eta i}^2\eta_0^2}{\omega_\eta^2(1 + i\Omega\tau_\eta)}, \quad i = 1, 5 \\
 \Delta C_{15}^* &= \frac{1}{2}b_{\eta 15}\eta_0^2, \\
 \Delta C_{44}^* &= \frac{1}{2}b_{\eta 44}\eta_0^2
 \end{aligned} \quad (7)$$

where $\eta_0^2 = -\frac{A_\eta(T - T_\eta)}{2\beta_\eta}$ is the equilibrium value of the corresponding order parameter, $\Omega = 2\pi f$ is the acoustic wave frequency and τ_η is the soft mode relaxation time, one may infer that the fourth-order anharmonic interaction ($b_{\eta 44}$ coefficient) between the B_g soft phonon mode and the pure transverse A_u acoustic mode (V_{ZY} velocity) is allowed in phase I. This fact correlates well with the data of our simulation (figure 2(a)). Hence, we have the evidence from the phenomenological theory that the $P2_1/m \rightarrow P2_1/c$ phase transition may be the result of B_g soft phonon mode and A_u acoustic mode interaction.

The similar mechanism of anharmonic fourth-order interaction ($b_{\eta 11}$, $b_{\eta 55}$ and $b_{\eta 15}$) between the order parameter and the strain components may govern the low temperature $P2_1/c \rightarrow P2_1$ phase transition (see equations (5)–(7)). However, as follows from (7), in this case the third-order anharmonic interaction ($a_{\eta 1}$ and $a_{\eta 5}$) plays an essential role, especially within the phase transition region, significantly decreasing the V_{XZ} velocity of the transverse acoustic wave (X and Z are the directions of wave propagation and wave polarization, respectively). The extremely small slope of the Δ_1 acoustic branch simulated along the b_1 axis (see figure 2(b)), corresponding to the V_{XZ} velocity, seems to agree well with the results of phenomenological analysis.

According to our group-theory analysis, the soft mode evoking the low temperature phase transition has the A_u symmetry at the $\mathbf{k} = \frac{1}{2}\mathbf{b}_1$ point. Assuming the results of lattice dynamics simulation (figure 2(b)) and the phenomenological treatment presented here, one may conclude

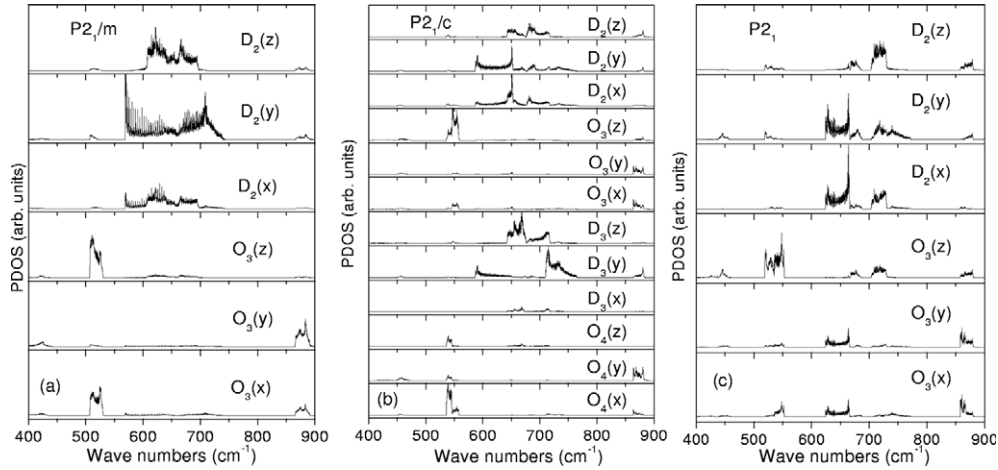


Figure 3. Intermediate frequency part of PDOS spectra corresponding to O_3 , O_4 and D_2 atoms in three $P2_1/m$ (a), $P2_1/c$ (b) and $P2_1$ (c) temperature phases. Notation x, y, z corresponds to the Cartesian system ($x \perp (b, c)$, $y \parallel b, z \parallel c$).

that the low temperature phase transition is the consequence of multiphonon interaction of the lowest soft A_u optic (Δ_2 symmetry along b_1 axis) and the acoustic B_u (Δ_1 symmetry along b_1) branch near the $k = \frac{1}{2}b_1$ point. Since the low frequency soft A_u mode involves mainly the vibrations of heavy ions, the phase transition into the lowest polar phase III may be treated as a displacive type transition. However, the deuteron ordering along the b -axis directed hydrogen bonds below the T_2 point indicates that the real mechanism of phase transition is in fact more complicated. The mixed order–disorder and displacive type of phase transition was traditionally suggested for KH_2PO_4 crystals [30, 31], and seems to have found the confirmation in KDP through the first principal calculation [32].

In order to check the validity of this mechanism for the superstructure phase transitions in the DRDP crystal we have computed the partial density of phonon states (PDOS) within one-quarter of the irreducible BZ. Note that the PDOS is associated with the vibrations of a certain kind of atoms. Let us inspect the medium frequency part ($500\text{--}800\text{ cm}^{-1}$) of the PDOS spectrum of the oxygen and deuterium atoms involved in the short $O_3\text{--}D_2 \cdots O_4$ hydrogen bonds, since this spectral range contains the vibrations of both types of atoms. Figure 3 presents the corresponding frequency range of the PDOS calculated in three phases. As seen in this figure, there is a narrow but distinct frequency gap ($\sim 40\text{ cm}^{-1}$) between the oxygen and deuterium vibrations in the high temperature phase I. O_3 and O_4 atoms vibrate with the same frequencies because they are symmetrically connected through the mirror plane. There is generally a similar picture in the intermediate phase II. Although the energy gap between oxygen and deuterium vibrations becomes smaller ($\sim 30\text{ cm}^{-1}$), there is practically no visible mixing between the vibrations of the two kinds of atoms. It is worth noting that the physical and chemical nonequivalence of D_2 and D_3 deuteriums located on the short hydrogen bonds in the $P2_1/c$ phase has a clear manifestation in the PDOS spectra. Vibrations of D_3 atoms placed near $590\text{--}760\text{ cm}^{-1}$ are mainly polarized in the (y, z) plane, whereas the vibrations of D_2 atoms demonstrate no significant space

anisotropy in this frequency range. A similar feature is relevant to the highest frequency deuteron vibrations. The phonon modes located near 2025 cm^{-1} are formed mainly due to the D_2 vibrations polarized almost uniformly along three x, y , and z directions, while the strong phonon modes centred around 2002 cm^{-1} originate from the D_3 vibrations in the (x, z) plane. However, the situation is changed in the low temperature $P2_1$ phase. The range of $625\text{--}665\text{ cm}^{-1}$ corresponds to the vibrations of both D_2 and O_3 atoms in the (x, y) plane and the region of $705\text{--}730\text{ cm}^{-1}$ contains the z -polarized vibrations of O_3 atoms and almost space isotropic vibrations of D_2 . This should clearly manifest the coupled deuteron–phonon vibrations in the ordered phase III. However, assuming that the PDOS spectra in the intermediate phase II were calculated at a temperature higher by 22 K than the phase II–phase III transition point, one may suppose that approaching the temperature of lower phase transition the coupling of deuteron and oxygen vibrations should play an increasingly important role in the mechanism of phase transition.

The computed density of states was used in order to evaluate the specific heat at constant volume C_V of DRDP. Since the DOS function $g(\omega)$ was calculated at three certain temperatures in three phases, respectively, the temperature evolution of $C_V(T)$ was extended in each phase through the following relationship:

$$C_V = 3N_A k \int_0^\infty \left(\frac{\hbar\omega}{2kT} \right)^2 \operatorname{cosec} h^2 \left(\frac{\hbar\omega}{2kT} \right) g(\omega) d\omega. \quad (8)$$

It is rather surprising that there is no visible jump in $C_V(T)$ near the T_2 phase transition temperature, especially taking into account that the $C_V(T)$ dependency was computed based on the two different crystal structures with different numbers of molecules in a unit cell ($Z = 4$ and 8 in phases II and III, respectively). This should argue in favour of the reliability of the model lattice dynamics approach used in the current work. Since there are no experimental data concerning the heat capacity of monoclinic DRDP, in figure 4 we present the calculated $C_V(T)$ dependence for the monoclinic DCDP

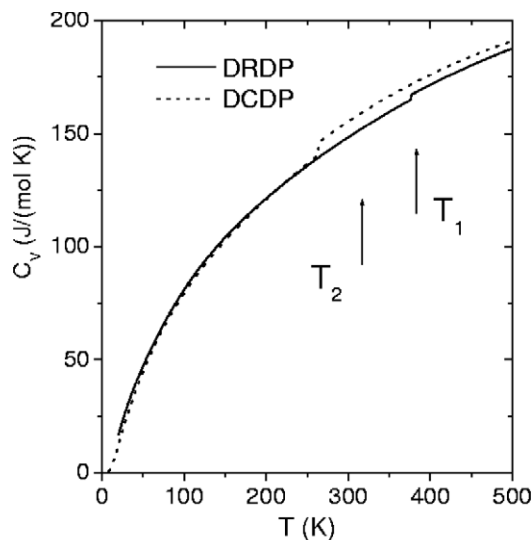


Figure 4. Temperature dependence of the simulated C_V specific heat of the DRDP crystal. The data for DCDP are taken from [27].

crystal [27]. As seen in this figure, the isomorphous Rb–Cs substitution slightly influences the thermodynamic properties of these compounds.

5. Conclusions

This paper presents the results of the group-theory consideration of a controversial question concerning the mechanism of phase transitions and the physical nature of the low temperature phase of monoclinic DRDP. Using the standard group-theory approach it was established that the B_g irreducible representation is responsible for the $P_{2_1/m} \rightarrow P_{2_1/c}$ phase transition. Taking into consideration the type of deuteron order within the b -axis directed deuteron chains observed experimentally in the ordered phase III [5], one may assert that the low temperature phase should reveal the strict antiferroelectric properties rather than the ferroelectric state. In this case the A_u irreducible representation is responsible for the $P_{2_1/c} \rightarrow P_{2_1}$ phase transition.

The lattice dynamics simulation performed within the framework of the semi-phenomenological approach reveals the peculiarities of the phonon spectrum along the b_3 axis of BZ in the high temperature $P_{2_1/m}$ phase. Assuming the possibility of interaction of phonon branches, one may state that the lowest Δ_2 optic phonon branch has the minimum at the BZ boundary along the b_3 axis, which might evoke the phase transition accompanied by the unit cell multiplication along the c axis.

The phonon spectrum calculated in the $P_{2_1/c}$ phase demonstrates the instability of the acoustic branch (B_u symmetry at the BZ centre) along the b_1 axis. We lack undoubted evidence that the phonon branch having the A_u symmetry at the BZ boundary is active. Probably, the real picture of the low temperature phase transition is more complicated and cannot be properly described within the simple quasi-harmonic approximation allowing no interaction of phonon branches. One may only suppose that the anomalous dispersion of the acoustic branch may be the result of

multiphonon interaction with the active phonon or pseudospin mode.

The phenomenological analysis performed within the Landau–Ginzburg theory allows the anharmonic multiphonon interaction for both $P_{2_1/m} \rightarrow P_{2_1/c}$ and $P_{2_1/c} \rightarrow P_{2_1}$ phase transitions.

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