

Препринти Інституту фізики конденсованих систем НАН України розповсюджуються серед наукових та інформаційних установ. Вони також доступні по електронній комп'ютерній мережі на WWW-сервері інституту за адресою <http://www.icmp.lviv.ua/>

The preprints of the Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine are distributed to scientific and informational institutions. They also are available by computer network from Institute's WWW server (<http://www.icmp.lviv.ua/>)

Ярослав Йосифович Щур

До ПИТАННЯ ПРО НАДСТРУКТУРНІ ФАЗОВІ ПЕРЕХОДИ В
МОНОКЛІННОМУ КРИСТАЛІ RbD_2PO_4

Роботу отримано 15 листопада 2007 р.

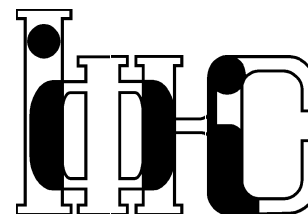
Затверджено до друку Вченою радою ІФКС НАН України

Рекомендовано до друку семінаром відділу теорії модельних
спінових систем

Виготовлено при ІФКС НАН України

© Усі права застережені

Національна академія наук України



ІНСТИТУТ
ФІЗИКИ
КОНДЕНСОВАНИХ
СИСТЕМ

ICMP-07-12E

Ya. Shchur

On the issue of superstructure phase transitions in monoclinic
 RbD_2PO_4 crystal

ЛЬВІВ

УДК: 53.096, 534-16, 536.2.01, 538.913

PACS: 63.20.Dj, 65.40.Ва, 77.80.-e

До питання про надструктурні фазові переходи в моноклінному кристалі RbD_2PO_4

Я.Й. Щур

Анотація. В статті представлені результати теоретико-групового аналізу та симуляції динаміки ґратки моноклінного кристалу RbD_2PO_4 в трьох температурних фазах. Поєднуючи методи теорії груп з аналізом особливостей кристалічної структури у різних структурних фазах, показано, що симетрія кристалу в низькотемпературній фазі повинна бути ацентричною (просторова група $P2_1$). При цьому кристал повинен виявляти антисегнетоелектричні властивості в низькотемпературній фазі, а не сегнетоелектричні, як про це повідомлялось раніше. Моделювання динаміки ґратки проведено в квазі-феноменологічному наближенні, яке враховує кулонівські, короткосяжні, ковалентні, ван-дер-Ваальсівські взаємодії та взаємодії типу водневого зв'язка

On the issue of superstructure phase transitions in monoclinic RbD_2PO_4 crystal

Ya. Shchur

Abstract. The paper presents the results of group-theory analysis and lattice dynamics simulation 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.

Подається в Journal of Physics: Condensed Matter
Submitted to Journal of Physics: Condensed Matter

© Інститут фізики конденсованих систем 2007
Institute for Condensed Matter Physics 2007

1. Introduction

RbD_2PO_4 (DRDP) crystal belongs to the well-known family of KDP type crystals. At an ambient pressure, DRDP undergoes two structural phase transitions with the 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 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 a 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 the phase III as acentric $P2_1$, whereas the relatively fresh neutron scattering investigation [5] suggested the centric $P2_1/n$ space group for this phase. Recently $P2_1$ space group was refined again for the 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 was detected below T_2 point [2] in DRDP, whereas the triple hysteresis loops inherent in ferroelectric state was observed for a mixed $\text{Rb}_{0.7}\text{C}_{0.3}\text{D}_2\text{PO}_4$ compound [2] in phase III. Based on the dielectric and pyroelectric measurements, the authors of paper [10] were unable to determine whether the 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. It 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 the 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 the investigations of other type.

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 a very interesting information since the superstructure phase transitions are associated apparently with the soft mode condensation at the Brillouin zone (BZ) boundary in the $\mathbf{k} = 1/2 \mathbf{b}_3$ (phase I \rightarrow phase II) and $\mathbf{k} = 1/2 \mathbf{b}_1$ (phase II \rightarrow phase III) points. Semi-phenomenological atomistic potential comprising the Coulomb, short-range, covalent, van der Waals and hydrogen-bonded interactions was utilized for simulation in present paper.

2. Crystal structure and group-theory treatment

The peculiar crystallographic feature of DRDP, such as CsD₂PO₄ (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 D₁ deuterons are ordered near the particular oxygen atoms on the O₁-D₁...O₂ hydrogen bonds in all temperature phases, whereas the D₂ deuterons are disordered between the two possible sites on the O₃-D₂...O₄ bonds in the phases I and II and become ordered in the phase III. Note that the D₂ deuterons being still disordered on the hydrogen bonds in phase II, become distinguished into the two kinds, D₂ and D₃ ones, which are chemically and physically nonequivalent [3]. Contrary to the DCDP case, there is no large difference of the length between the *c*-axis directed O₁-D₂...O₂ and *b*-axis running O₃-D₂(D₃)...O₄ hydrogen bonds.

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 $G^{old} \rightarrow G^{new}$ from the "old" to the "new" space group should satisfy the following condition

$$\frac{1}{n} \sum_{g^{new} \in G^{new}/T^{new}} \chi_k^j(g^{new}) = \text{positive integer}, \quad (2.1)$$

where n is the order of the factor group G/T , $\chi_k^j(g)$ is the character of symmetry element g ($g = \{h|\alpha\}$, α is the non-primitive translation associated with the point symmetry operation h) of j -th irreducible

representation in the \mathbf{k} point of BZ. There is the following relation between $\chi_k^j(g^{new})$ and $\chi_k^j(g^{old})$ for the case of one-vector \mathbf{k} -star (this case is relevant to both phase transitions in DRDP):

$$\chi_k^j(g^{new}) = \exp[-ik(t_0(h) + \alpha^{old})] \chi_k^j(g^{old}), \quad (2.2)$$

where $t_0(h) = \alpha^{new}(h) - \alpha^{old}(h) + \mathbf{s} - h\mathbf{s}$ is the displacement vector and \mathbf{s} is a vector between the origin O' of G^{new} and O of G^{old} [25]. Note, α^{new} is written in terms of the basic translation vectors $\{\mathbf{a}, \mathbf{b}, \mathbf{c}\}$ of "old" phase. Therefore, $\mathbf{t}_0 + \alpha^{old} = 1/2\mathbf{b} + \mathbf{c}$ for the point symmetry operations ℓ and m of $P2_1/c$ group and $\mathbf{t}_0 + \alpha^{old} = \mathbf{a} + 1/2\mathbf{b} + 1/2\mathbf{c}$ for the same symmetry operations ℓ and m of $P2_1/n$ group. Hence, the multiplication factor $\exp[-ik(t_0(h) + \alpha^{old})] = -1$ in (2.2) for the operations ℓ and m of both $P2_1/c$ ($\mathbf{k} = 1/2 \mathbf{b}_3$) and $P2_1/n$ ($\mathbf{k} = 1/2 \mathbf{b}_1$) groups. Using the irreducible representations of $P2_1/m$ ($\mathbf{k} = 1/2 \mathbf{b}_3$), $P2_1/c$ ($\mathbf{k} = 1/2 \mathbf{b}_1$) and $P2_1/n$ ($\mathbf{k} = 0$) groups in corresponding points of BZ (see table 1), and the relations (2.1) and (2.2) 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 transition.

Choosing the origin O' of $G^{new} = P2_1/c$ in 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 A_u (B_1^-) soft mode at the I-II phase transition was drawn in ref. [19]. However, the activity of A_u polar mode at $P2_1/m \rightarrow P2_1/c$ transition should induce the polar (antiferroelectric) phase, which contradicts the experimental observation [1,13,16]. On the contrary, the statement regarding the activity of B_g representation adequately describes the physical nature of phase II and the structural changes occurred at the I-II phase transition. Since normal modes transforming in $P2_1/m$ phase according to B_g symmetry are not dipole active, the softening of B_g phonon at the BZ boundary in $\mathbf{k} = 1/2 \mathbf{b}_3$ point induces the non-polar $P2_1/c$ structure in the phase II with 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, assuming their antiparallel type in the neighboring sublattices of $P2_1/c$ phase. Moreover, among the eigenvectors of B_g type in $P2_1/m$ phase there is no eigenvector corresponding to the vibrations of D₂ deuterons tunneling on the O₃-D₂...O₄ hydrogen bonds. This means that the softening of B_g phonon mode should not change the type of D₂ 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 D₂ deuterons.

Table 1. The irreducible multiplier representations of $P2_1/m$ (in the BZ points $\mathbf{k} = 0$, $\mathbf{k} = 1/2 \mathbf{b}_3$), $P2_1/c$ ($\mathbf{k} = 1/2 \mathbf{b}_1$) and $P2_1/n$ ($\mathbf{k} = 0$) space groups.

$P2_1/m$	$\{E 0\}$	$\{2 1/2 \mathbf{b}\}$	$\{m 1/2 \mathbf{b}\}$	$\{I 0\}$
$P2_1/c$	$\{E 0\}$	$\{2 1/2 \mathbf{b} + 1/2 \mathbf{c}\}$	$\{m 1/2 \mathbf{b} + 1/2 \mathbf{c}\}$	$\{I 0\}$
$P2_1/n$	$\{E 0\}$	$\{3 1/2 \mathbf{a} + 1/2 \mathbf{b} + 1/2 \mathbf{c}\}$	$\{m 1/2 \mathbf{a} + 1/2 \mathbf{b} + 1/2 \mathbf{c}\}$	$\{I 0\}$
A_g	1	1	1	1
B_g	1	-1	-1	1
A_u	1	1	-1	-1
B_u	1	-1	1	-1

However, the $P2_1/c \rightarrow P2_1/n$ symmetry transformation induced by the softening of B_g normal mode in the $\mathbf{k} = 1/2 \mathbf{b}_1$ point contradicts both the antiferroelectric and the ferrielectric 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 is transforming according to the B_g irreducible representation in $P2_1/c$ 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 unit cell along a axis) manifests no correlation with the B_g eigenvectors of $P2_1/c$ space group. This means that neither $P2_1/n$ nor other centric space group may correspond to the symmetry of phase III of 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 $P2_1/c \rightarrow P2_1$ phase transition. The first was earlier suggested on the basis of phenomenological approach [26] and consists in the simultaneous condensation of two phonon modes of B_g and B_u symmetry at the BZ boundary in $\mathbf{k} = 1/2 \mathbf{b}_1$ point. This scenario leads to the ferrielectric 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, softening of 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 -axis (antiparallel order, see figure 1(a)). Another eventual scenario of $P2_1/c \rightarrow P2_1$ phase transition is the condensation of A_u phonon mode in $\mathbf{k} = 1/2 \mathbf{b}_1$ 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

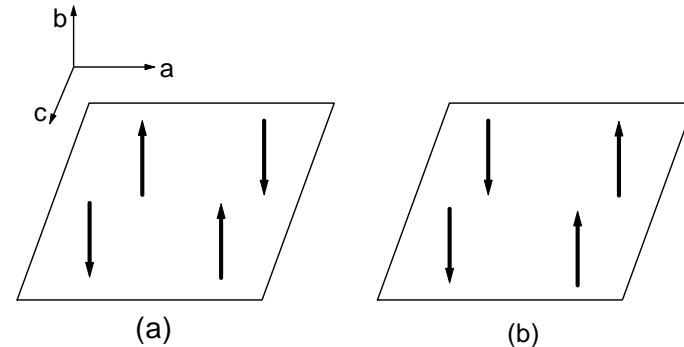


Figure 1. Schematic sketch of the deuteron ordering along the b -axis running deuteron chains in low temperature $P2_1$ phase induced by the eventual softening of B_u (a) and A_u (b) mode at the BZ boundary in $\mathbf{k} = 1/2 \mathbf{b}_1$ point.

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 softening. That means that the phase III should reveal a strict antiferroelectric order with the $P2_1$ symmetry, rather than the ferrielectric state reported repeatedly [1,2,13,14].

3. Model of lattice dynamics

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

$$\Phi(r_{kk'}) = \frac{e^2}{4\pi\epsilon_0} \frac{Z(k)Z(k')}{r_{kk'}} + Sa \exp\left(-\frac{br_{kk'}}{R(k) + R(k')}\right) + (3.1) \\ + D_{0j} \exp\left(-\frac{n}{2} \frac{(r_{kk'} - r_{0j})^2}{r_{kk'}^6}\right) - \frac{w}{r_{kk'}^6},$$

The first term in (3.2) 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' type. S , D_j , n_j , r_{0j} and w are adjustable parameters. The third term in (3) was also used for the simulation of oxygen-deuterium interactions within hydrogen bonds.

We used the same values of model parameters both in high temperature $P2_1/m$ and in intermediate $P2_1/c$ phase of DRDP. These values were the same as those utilized for lattice dynamics simulation of DCDP in 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 difference length 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 $\text{O}_3\text{-D}_2(\text{D}_3)\dots\text{O}_4$ hydrogen bonds we treated them to be located at the middle of 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 the 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 $\text{O}_3\text{-D}_2(\text{D}_3)\dots\text{O}_4$ 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:

$$Z(\text{O}_3) = -1.058; Z(\text{O}_4) = -0.910; R(\text{O}_3) = 1.466 \text{ \AA}; R(\text{O}_4) = 1.166 \text{ \AA}$$

$$r_{02} = 1.608 \text{ \AA} \text{ (for } \text{O}_4\text{-D}_2\text{)}; r_{05} = 1.24 \text{ \AA} \text{ (for } \text{O}_3\text{-D}_2\text{)}$$

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 Ref. [5] as $P2_1/n$ and does not match our conclusion regarding the $P2_1$ symmetry of this phase, obtained herein above by means of group theory analysis. However, we utilized the results of Ref. [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 in 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 ($T=403$ 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 ($T=332$ K). The average disagreement between the experiment [7,20] and the simulation for phonon frequencies of A symmetry calculated in 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 \mathbf{b}_3 direction of BZ in $P2_1/m$ phase ($T=403$ K) are depicted in figure 2(a). Note that our simulation was performed in the quasi-harmonic approximation assuming the 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 the point near $\mathbf{k} \approx 0.32 \mathbf{b}_3$ and the other crossing between two lowest optic modes near $\mathbf{k} \approx 0.02 \mathbf{b}_3$ 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 $1/2 \mathbf{b}_3$ point of BZ. Since the current simulation was performed at the temperature higher by 22 K than the phase transition point, one may expect that due to the non-linear phonon interaction

the lowest Δ_2 optic phonon branch may soften at the BZ boundary at

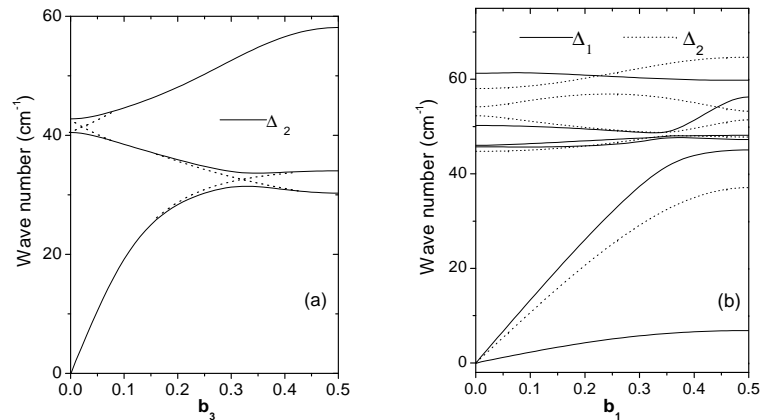


Figure 2. Low frequency part of phonon spectrum simulated in high temperature $P2_1/m$ (a) and intermediate temperature $P2_1/c$ (b) phase along the \mathbf{b}_3 and \mathbf{b}_1 axis of BZ, respectively. The dotted lines in figure 2 (a) indicate the eventual intersection of phonon branches (are drawn by eye).

lower temperature inducing the superstructure phase transition. Note that phonon modes transforming according to the Δ_2 symmetry in the $(\mathbf{b}_1, \mathbf{b}_3)$ plane (wave vector $\mathbf{k} = \mu_1 \mathbf{b}_1 + \mu_3 \mathbf{b}_3$, $0 < \mu_1, \mu_3 < 1/2$) are compatible with the B_g and A_u irreducible representations both at $\mathbf{k} = 0$ and $\mathbf{k} = 1/2 \mathbf{b}_3$ point. 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 soft phonon mode. However, as follows from the group-theory consideration presented above, the B_g representation should be responsible for this phase transition.

The low-frequency part of phonon spectrum in the intermediate $P2_1/c$ phase along \mathbf{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 in $1/2 \mathbf{b}_1$ point. As seen in this figure, the lowest acoustic phonon branch (B_u symmetry at BZ centre) has an extremely small slope and reaches only 7 cm^{-1} at the BZ boundary ($1/2 \mathbf{b}_1$ 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. How-

ever, this anomalous dispersion of the lowest acoustic branch along \mathbf{b}_1 axis may be the result of the non-linear interaction not only with B_g optic mode but also with the mode of other symmetry (i.e. A_u mode). Basing solely upon the presented 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 a direction. However, there are two reasons for such an instability. Firstly, similarly to the case of high temperature phase transition ($P2_1/m \rightarrow P2_1/c$), the lower phase transition may be the result of multiphonon interaction too. In this case the phase transformation may be treated as a displacive-type transition. Secondly, the deuteron ordering along the b -axis directed hydrogen bonds below the T_2 point may evoke the softening of some phonon mode of the heavy ions. This 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 to the superstructure phase transitions in DRDP crystal we have computed the partial density of phonon states (PDOS) within the $1/4$ of irreducible BZ. Note that PDOS is associated with the vibrations of the certain kind of atoms. Let us inspect the medium-frequency part ($500 - 800 \text{ cm}^{-1}$) of PDOS spectrum of oxygen and deuterium atoms involved in the short $\text{O}_3\text{-D}_2\text{...O}_4$ hydrogen bonds, since this spectral range contains the vibrations of the both types of atoms. Figure 3 presents the corresponding frequency range of 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 the 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 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 $P2_1/c$ 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. The 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

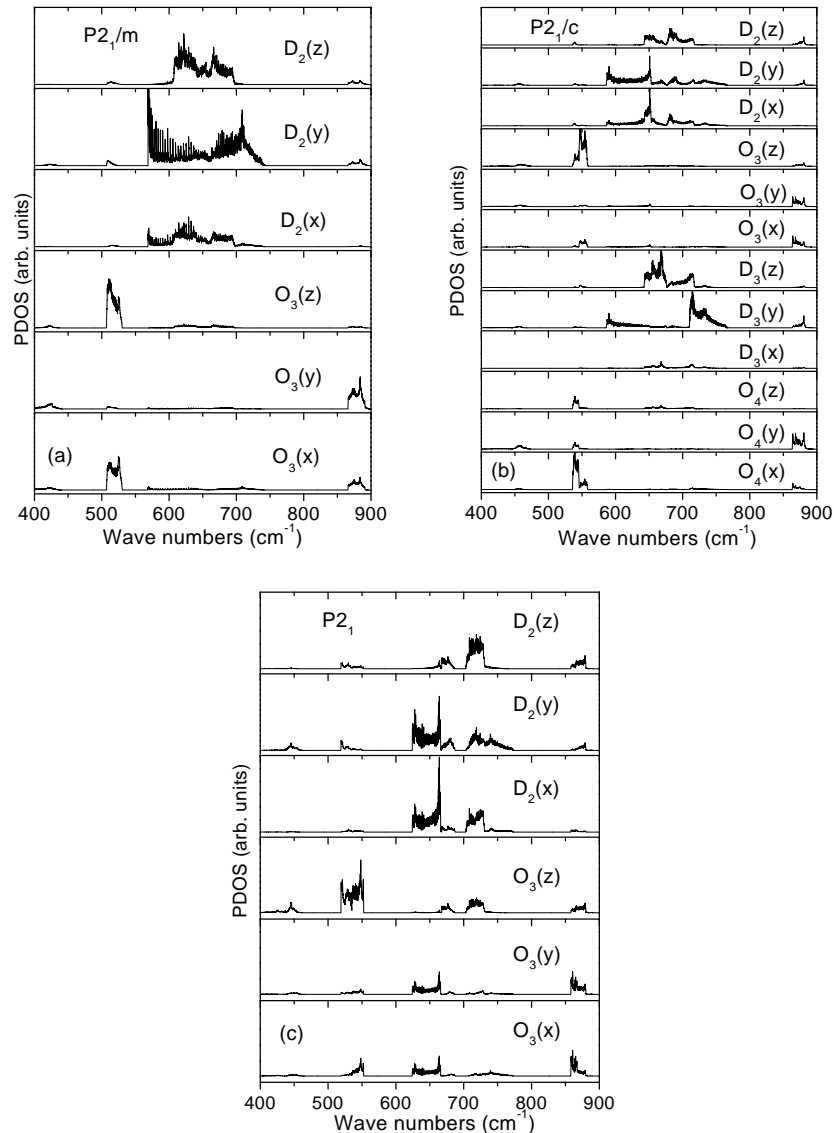


Figure 3. Intermediate frequency part of PDOS spectra corresponding to O_3 , O_4 and D_2 atoms in three $P2_1/m$ (a), $P2_1/c$ (b) and $P2_1$ (c) temperature phases. Notation x, y, z corresponds to the Cartesian system ($x \perp (b, c)$, $y \parallel b, z \parallel c$).

centered around 2002 cm^{-1} originate from the D_3 vibrations in (x, z) plane. However, the situation is changed in low-temperature $P2_1$ phase. The range of $625 - 665 \text{ cm}^{-1}$ corresponds to the vibrations of both D_2 and O_3 atoms in (x, y) plane and the region of $705 - 730 \text{ cm}^{-1}$ 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 the 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 (see figure 4). Since the DOS function $g(\omega)$ was calculated at the three certain temperatures

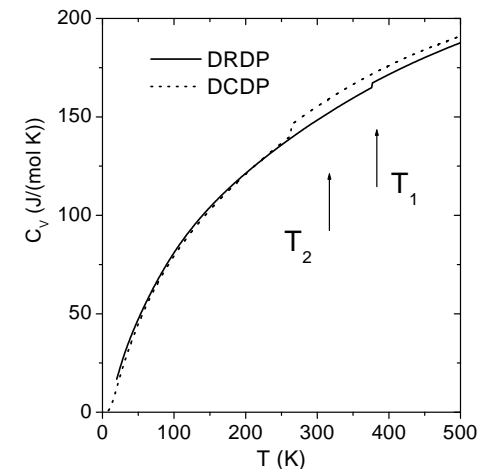


Figure 4. Temperature dependence of the simulated C_V specific heat of DRDP crystal. The data for DCDP are taken from ref. [27].

in three phases, respectively, the temperature evolution of $C_V(T)$ was extended in each phase through the following relationship:

$$C_V(T) = 3N_A k \int_0^\infty \left(\frac{\hbar\omega}{2kT}\right)^2 \csc^2\left(\frac{\hbar\omega}{2kT}\right) g(\omega) d\omega. \quad (4.1)$$

It is rather surprising that there is no visible jump in $C_V(T)$ near

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

5. Conclusions

The 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 of the standard group theory approach it was established that the B_g irreducible representation is responsible for the $P2_1/m \rightarrow P2_1/c$ 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 strict antiferroelectric properties rather than the ferrielectric state. In this case the A_u irreducible representation is responsible for $P2_1/c \rightarrow P2_1$ phase transition.

The lattice dynamics simulation performed within the framework of semi-phenomenological approach reveals the peculiarities of phonon spectrum along the b_3 axis of BZ in the high temperature $P2_1/m$ 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 b_3 axis, which might evoke the phase transition accompanied by the unit cell multiplication along the c axis.

The phonon spectrum calculated in $P2_1/c$ phase demonstrates the instability of acoustic branch (B_u symmetry at the BZ center) along the b_1 axis. We lack the 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.

References

1. Y. Makita, M. Sumita, T. Osaka, and S. Suzuki, *Ferroelectrics* **39**, 1017 (1981).
2. M. Sumita, T. Osaka, and Y. Makita, *J. Phys. Soc. Jpn.* **50**, 154 (1981).
3. T. Hagiwara, K. Itoh, E. Nakamura, M. Komukae, and Y. Makita, *Acta Cryst. C* **40**, 718 (1984).
4. S. Suzuki, K. Arai, M. Sumita, and Y. Makita, *J. Phys. Soc. Jpn.* **52**, 2394 (1983).
5. S. Mattau, Untersuchung der strukturellen Phasenubergänge und Domanenbildung in der ferroischen Modellsubstanzen RbH_2PO_4 und RbD_2PO_4 , PhD thesis, Technischen Hochschule Aachen (2002) <http://darwin.bth.rwth-aachen.de/opus/volltexte/2003/545/>.
6. W. Bronowska, *Materials Science-Poland* **24**, 229 (2006) <http://www.materialsscience.pwr.wroc.pl/>.
7. B. Marchon, A. Novak, R. Blinc, *J. Raman spectrosc.* **18**, 447 (1987).
8. O. Jarh, J. Dolinsek, B. Topic, B. Zeks, R. Blinc, V. H. Schmidt, L. A. Shuvalov, and A. I. Baranov, *Phys. Rev. B* **39**, 2004 (1989).
9. M. Sumita, T. Osaka, and Y. Makita, *J. Phys. Soc. Jpn* **53**, 2784 (1984).
10. H. Pykacz, Z. Czapla, and J. Mroz, *Acta Physica Pol* **A66** 639 (1984).
11. K. Gesi, K. Ozawa, T. Osaka, and Y. Makita, *J. Phys. Soc. Jpn.* **52**, 2538 (1983).
12. M. Komukae, and Y. Makita, *J. Phys. Soc. Jpn.* **54**, 4359 (1985).
13. A. I. Baranov, V. A. Sandler, L. A. Shuvalov, and R. M. Fedosyuk, *Ferroelectrics Letters* **5**, 119 (1986).
14. A. I. Baranov, R. M. Fedosyuk, N. R. Ivanov, V. A. Sandler, L. A. Shuvalov, J. Grigas, and R. Mizeris, *Ferroelectrics* **72**, 59 (1987).
15. R. R. Levitskii, I. R. Zachek, I. V. Kutny, Ya. I. Shchur, J. Grigas, and R. Mizeris, *Ferroelectrics* **110**, 85 (1990).
16. M. Komukae, K. Kawashima, and T. Osaka, *J. Phys. Soc. Jpn.* **69**, 2076 (2000).
17. M. Komukae, K. Kawashima, and T. Osaka, *Ferroelectrics* **272**, 291 (2002).
18. C. Moriyoshi, T. Fujii, K. Itoh, and M. Komukae *Ferroelectrics* **269**, 273 (2002).
19. C. Moriyoshi, T. Fujii, and K. Itoh, *Ferroelectrics* **285**, 75 (2003).
20. Ya. Shchur, V. Dzhalal, O. Vlokh, and I. Klymiv, *phys.stat.sol.(a)* **144**, K17 (1994).

21. B. Topic, R. Blinc, and L. A. Shuvalov, *phys. stat. sol. (a)* **85** 409 (1984).
 22. E. Yakushkin, *Crystallografia* **31**, 606 (1986).
 23. Z. Hu, C. W. Garland, and J. A. Gonzalo, *Ferroelectrics* **112**, 217 (1990).
 24. O. G. Vlokh, Ya. I. Shchur, I. S. Girnyk, and I. M. Klymiv, *Fiz. Tverd. Tela (Leningrad)* **36**, 2890 (1994).
 25. B. B. Lavrencic, and T. Shigenari, *Solid State Communic.* **13**, 1329 (1973).
 26. I. V. Kityk, Ya. I. Shchur, L. P. Lutsiv-Shumskii, and O. G. Vlokh, *J. Phys.: Condens. Matter* **6**, 699 (1994).
 27. Ya. Shchur, *Phys. Rev. B* **74**, 054301 (2006).
 28. Ya. Shchur, *phys. stat. sol. (b)* **244**, 569 (2007).
 29. Ya. Shchur, *Phase Transitions* **80**, 17 (2007).
 30. K. Kobayashi, *J. Phys. Soc. Jpn.* **24**, 497 (1968).
 31. A. Bussmann-Holder, and K. H. Michel, *Phys. Rev. Lett.* **80**, 2173 (1998).
 32. S. Koval, J. Kohanoff, J. Lasave, G. Colizzi, and R. L. Migoni, *Phys. Rev. B* **71**, 184102 (2005).
-

CONDENSED MATTER PHYSICS

The journal **Condensed Matter Physics** is founded in 1993 and published by Institute for Condensed Matter Physics of the National Academy of Sciences of Ukraine.

AIMS AND SCOPE: The journal **Condensed Matter Physics** contains research and review articles in the field of statistical mechanics and condensed matter theory. The main attention is paid to physics of solid, liquid and amorphous systems, phase equilibria and phase transitions, thermal, structural, electric, magnetic and optical properties of condensed matter. Condensed Matter Physics is published quarterly.

ABSTRACTED/INDEXED IN:

- Chemical Abstract Service, Current Contents/Physical, Chemical&Earth Sciences
- ISI Science Citation Index-Expanded, ISI Alerting Services
- INSPEC
- Elsevier Bibliographic Databases (EMBASE, EMNursing, Compendex, GEOBASE, Scopus)
- “Referativnyi Zhurnal”
- “Dzhirelo”

EDITOR IN CHIEF: Ihor Yukhnovskii

EDITORIAL BOARD: T. Arimitsu, *Tsukuba*; J.-P. Badiali, *Paris*; B. Berche, *Nancy*; J.-M. Caillol, *Orsay*; C. von Ferber, *Freiburg*; R. Folk, *Linz*; D. Henderson, *Provo*; Yu. Holovatch, *Lviv*; M. Holovko, *Lviv*; O. Ivankiv, *Lviv*; M. Korynevskii, *Lviv*; Yu. Kozitsky, *Lublin*; M. Kozlovskii, *Lviv*; H. Krienke, *Regensburg*; R. Levitskii, *Lviv*; V. Morozov, *Moscow*; I. Mryglod, *Lviv*; O. Patsahan (Assistant Editor), *Lviv*; N. Plakida, *Dubna*; G. Röpke, *Rostock*; Yu. Rudavskii, *Lviv*; I. Stasyuk (Associate Editor), *Lviv*; M. Tokarchuk, *Lviv*; I. Vakarchuk, *Lviv*; M. Vavrukh, *Lviv*; A. Zagorodny, *Kyiv*.

CONTACT INFORMATION:

Institute for Condensed Matter Physics
of the National Academy of Sciences of Ukraine
1 Svientsitskii Str., 79011 Lviv, Ukraine
Tel: +380(322)760908; Fax: +380(322)761158
E-mail: cmp@icmp.lviv.ua <http://www.icmp.lviv.ua>