

SPONTANEOUS POLARIZATION AND ITS EFFECT ON PHYSICAL CHARACTERISTICS OF POTASSIUM, RUBIDIUM AND CAESIUM DIHYDROPHOSPHATES AND ARSENATES

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INTRODUCTION

KDP ferroelectrics (ferroelectrics) are isomorphous crystals of dihydrophosphates and arsenates of potassium, rubidium, caesium KH_2PO_4 , RbH_2PO_4 , CsH_2PO_4 , RbH_2AsO_4 , CsH_2AsO_4 and their deuterated analogues. The physical properties of these crystals are described in monographs [1-5]. It has been established that the phase transition from para- to ferrophase is the transition of ordering type and the dipolar and deformational ordering occurs in *KDP* crystals. In the neighbourhood of phase transition temperature the physical properties of *KDP* crystals undergo the distinctive changes that manifest themselves as peaks, breaks, V-shaped minimums on the curves of temperature dependence of heat capacity, direct and inverse dielectric permittivity, thermal conductivity coefficient, spontaneous deformation degree, elasticity constants, and the like.

The consideration of statistical theory of *KDP* crystals, explanation and justification of their physical properties on the basis of molecular-kinetic concept are of interest to physical engineers.

RESULTS AND DISCUSSION

It is common knowledge that KH_2PO_4 crystals have H_{22} tetragonal structure (Fig. 1) and are in paraelectric phase at high temperatures. With temperature decrease the displacement of potassium K and phosphorus P atoms takes place by and against the c-axis (Fig. 1) and ferroelectric phase is formed. The directions of preferential displacements of base units are marked off by arrows, lattice constants a_1 , a_2 , c and intersite distances r_1 , r_2 , r_3 , r_4 , for which the interactions of structural units are taken into account in calculations, are shown in the Fig. 1

The internal energy, Helmholtz free energy and Gibbs thermodynamic potential have been calculated under the assumption of crystal single-domain, perfect crystal lattice and in approximation of pair interaction of the nearest atoms. From these formulae the equations of system thermodynamic equilibrium have been derived.

The temperature dependence of polarizational order parameter $\xi(T)$ is determined by the following formula

$$kT \ln \frac{1+\xi}{1-\xi} = 2(\omega + 2\alpha\xi^2)\xi,$$

on which the temperature of phase transition (Curie point) is defined $kT_0 = \omega$. The spontaneous

polarization has undergone the ever-change, but increases sharply near Curie temperature.

The temperature dependence of configuration heat capacity $C(T)$ has been calculated and this equation can be written as

$$C/k = \frac{\left(1 + 2\frac{\alpha}{\omega}\xi^2\right)\xi \ln \frac{1+\xi}{1-\xi}}{2\left(\frac{kT/\omega}{1-\xi^2} - 1 - 6\frac{\alpha}{\omega}\xi^2\right)}.$$

As it is turned out this dependence is peak-shaped near Curie point.

The dependence of parameter of polarizational order on the intensity of external electric field $\xi(E)$ is defined by the following expression

$$\frac{E}{\omega} = \left(2\frac{\alpha}{\omega}\xi^2 + 1\right)\xi - \frac{1}{2}(1-x) \ln \frac{1+\xi}{1-\xi}, \quad x = \frac{(T-T_0)}{T_0}.$$

At $\xi \rightarrow 0$ the approximate formula is true

$$\frac{E}{\omega} = 2\frac{\alpha}{\omega}\xi^3 + x\xi.$$

It has been found that this dependence $\xi(E)$ show evidence of non-linearity with temperature increase.

The temperature dependence of inverse $1/\chi$ and direct χ dielectric susceptibility is equal to

$$\frac{1}{\chi} = \begin{cases} -2x \left[1 + \frac{1+x}{2(x-2\alpha/\omega)} \right] & \text{at } \xi \neq 0, \\ x & \text{at } \xi = 0. \end{cases}$$

The dielectric susceptibility χ increases to infinity at $x \rightarrow 0$ ($T \rightarrow T_0$).

The following notation is used in formulae: ω and α are energetic parameters in terms of interaction energies of α , $\beta = \text{K, P}$ pairs; k is Boltzmann's constant, T is absolute temperature, x is degree of deformation.

The plots of all mentioned dependences $\xi(T)$, $C(T)$, $\xi(E)$, $\chi(x)$ have been constructed in the paper on the basis of these derived equations. The theory gives results in qualitative agreement with experimental data.

CONCLUSIONS

Thus, the developed statistical theory of spontaneous polarization and deformation in *KDP* crystals with consideration for interpretation of paraelectrician-ferroelectrician phase transition as of ordering type allows the elucidation and explanation for

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the temperature dependence of order parameter (the nature of this dependence is close to the transition of first kind). This theory permits also the substantiation of the order parameter dependence on the intensity of external electric field, the elucidation of special feature of configuration heat capacity dependence on temperature. As described in the paper, this dependence is close to experimental just for the case of phase transition of first kind. Theory results allow the conclusions that temperature dependences of direct and inverse dielectric susceptibility are such that the Curie-Weiss law (linear dependence of $1/\chi$ quantity on temperature) and the rule of negative two near Curie point are true.

The obtained results of computer-aided design have been compared with literature experimental data for crystals with H_{22} structure, the comparison shows their qualitative correspondence.

REFERENCES

1. Matysina ZA, Zaginaichenko SYu, Schur DV; Hydrogen solubility in alloys under pressure, International journal of hydrogen energy, 21, 11, 1085-1089, 1996, Pergamon
2. Schur DV, Lyashenko AA, Adejev VM, Voitovich VB, Zaginaichenko S Yu; Niobium as a construction material for a hydrogen energy system, International journal of hydrogen energy, 20, 5, 405-407, 1995, Elsevier
3. Трефилов ВИ, Лавренко ВА, Щур ДВ, Нищенко ММ, Тикун ВЛ, Морозова РА; Одно- и трехстадийное гидрирование сплавов цирконий-железо, Доклады АН УССР сер. А. физ-мат и техн. науки, 6, 21-24, 1987
4. Schur DV, Trefilov VI, Pishuk VK, Zaginaichenko SYu; Investigation of metal-hydrogen systems for the purpose of their use for hydrogen storage, Proceedings of the Second int. Symposium on New Materials for Fuel Cell and Modern Battery Systems, Montreal (Quebec), Canada, 601-609, 1997
5. Trefilov VI, Schur DV, Pishuk VK, Zaginaichenko SYu; The behaviour of zirconium as a material for energy storage, Proceedings of Florence World Energy Research Symposium (FLOWERS 97) Clean Energy for the New Century, Florence, Italy, 487-494, 1997
6. Tarasov BP, Shul'ga Yu M, Fokin VN, Vasilets VN, Shul'ga NYu, Schur DV, Yartys VA; Deuterofullerene C 60 D 24 studied by XRD, IR and XPS, Journal of alloys and compounds, 314, 1, 296-300, 2001, Elsevier
7. Tarasov BP, Fokin VN, Moravsky AP, Shul'ga Yu M, Yartys VA, Schur DV; Promotion of fullerene hydride synthesis by intermetallic compounds, HYDROGEN ENERGY PROGRESS, 2, 1221-1230, 1998
8. Schur DV, Lavrenko VA, Adejev VM, Kirjakova IE; Studies of the hydride formation mechanism in metals, International journal of hydrogen energy, 19, 3, 265-268, 1994, Elsevier
9. Schur DV, Lavrenko VA; Studies of titanium-hydrogen plasma interaction, Vacuum, 44, 9, 897-898, 1993, Elsevier
10. Schur DV, Pishuk VK, Zaginaichenko SY, Adejev VM, Voitovich VB; Phase transformations in metals hydrides, Hydrogen energy progress, 2, 1235-1244, 1996, UNIVERSITY OF CENTRAL FLORIDA
11. Zaginaichenko S Yu, Matysina ZA, Schur DV; The influence of nitrogen, oxygen, carbon, boron, silicon and phosphorus on hydrogen solubility in crystals, International journal of hydrogen energy, 21, 11, 1073-1083, 1996, Pergamon
12. Trefilov VI, Schur DV, Pishuk VK, Zaginaichenko SYu, Choba AV, Nagornaya NR; The solar furnaces for scientific and technological investigation, Renewable energy, 16, 1, 757-760, 1999, Elsevier
13. Трефилов ВИ, Щур ДВ, Загинайченко СЮ; Фуллерены-основа материалов будущего, 2001, Laboratory 67

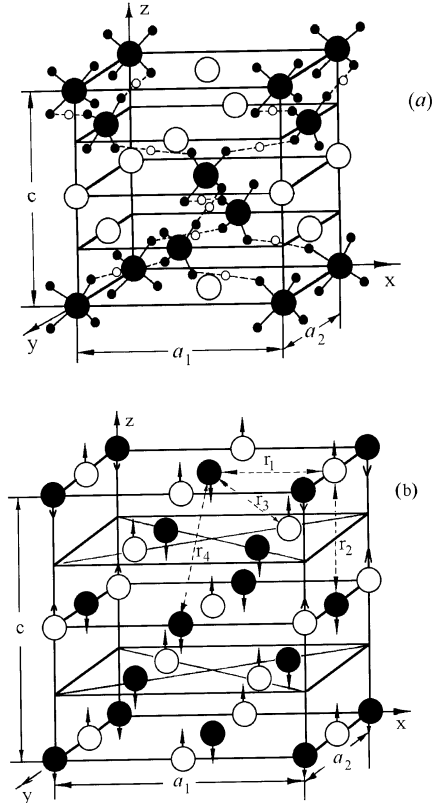


Fig. 1. Elementary cell of crystal lattice of potassium dihydrophosphate KH_2PO_4 .

- (a) tetragonal structure of paraelectric modification by West [6],
- (b) orthorhombic structure of ferroelectric modification by Frazer [7, 8] (oxygen and hydrogen atoms are not shown). The displacements directions of potassium K and phosphorus P atoms are indicated by arrows.
- - potassium K atoms, ● - phosphorus P atoms,
 • - oxygen O atoms, ◦ - hydrogen H atoms.