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A MECHANISM OF FORMATION OF RADICALS IN CRYSTAL KDP (KH₂PO₄)

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Abstract

The mechanisms of formation of A-radicals in the crystal K₂SO₄. Calculations established that the excitation of oscillations on the O-H bond in the triplet excitons in the excited state leads to a situation vibronic instability leading to the disintegration of the exciton with the formation of hydrogen atoms and A- radical.

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1. Introduction

Now one of authentically established radiation induced defects in crystals of KDP is intercluster atoms of hydrogen. Its existence is proved by the analysis of ranges of EPR. In work as Liu et al. (2003) methods of quantum chemistry it is shown that the proton occupying knot in the hydrogen subsystem of a crystal lattice of KDP, can take an electron. In this case the position of hydrogen atom in the corresponding knot of the crystal lattice becomes unstable. It is pushed out into the intercluster. In the hydrogen sublattice of crystals of KDP vacancies which can be considered as the L-centers are formed. However at radiation formation of L-defects there are complementary defects of U₂ type but not the Byerum D-defects.

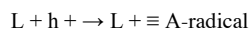
The intercluster hydrogen centers are found not only in KDP crystals, but also in DKDP (by Setzler et al. (1998)). Thermal properties of the centers like (H[•])_i and (D[•])_i are similar. The signal of EPR of these radiation induced centers when heating decreases about 120 K. However it is not known what it is connected with. There are two reasons of decrease intensity of signal of EPR when heating: thermal annealing of the paramagnetic centers or increase in probability of spin-lattice relaxation.

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The EPR method in crystals of potassium dihydrophosphate existence of the autolocalized holes is established. In literature these hole pointwise defects are called as B-radicals. The properties and structure of the autolocalized holes in crystals KDP and DKDP are similar. The B-radical represents a quasimolecule $(\text{H}_2\text{PO}_4)^0$. Literary data reveal essential contradictions on thermal stability of B-radical. The mechanism of disintegration of this radiation defect is not established. B-center structure is $(\text{H}_2\text{PO}_4)^0$ is absolutely established fact.

Another paramagnetic hole center established in crystals of KDP and DKDP, is A-radical. For the first time the signal of EPR of this defect was described in 1956 by M.P. Tonkonogov. Earlier the structure of this center, i.e. in 1951 was established by N. Byerum: this center represents a quasimolecule (H_2PO_4) - i.e. the hole center with hydrogen vacancy. The hole is localized on the oxygen interfacing to hydrogen vacancy. From data of EPR it is known (Chirila et al. (2003)) that intensity of a paramagnetic resonance from this radiation defect decreases to about 170 - 200 K. Therefore, TSL peak in KDP crystal at 180 K can be connected with disintegration of the hole center like A-radical.

The mechanisms of formation and disintegration of this radiation defect are not discussed in literature. It is known, that concentration of A-radical and intercluster atoms of Hydrogen are identical. On this basis work by Ogorodnikov et al. (2001) it is claimed that A-radical and $(\text{H}_1)^0$ centers form complementary pairs. In principle it is possible. At ionization of phosphatic anion the electron is taken by the proton next to it. However, this mechanism contradicts the following facts: it is apparent that formation of B-radicals occurs in the results of ionization of phosphatic anions. If A-radicals and $(\text{H}_1)^0$ centers make complementary pairs, drain channels for the free electrons are not clear at formation of B-radicals. Besides, in work (Chirila et al. (2003)) it is shown that EPR signal from A-radicals increases in the temperature range 90-140 K, i.e. in temperature area of decrease of EPR signal from B-radicals. It allows to assume that A-radicals are the secondary defects which are formed in the post-radiation stage. At radiation stage the creation of A-radicals can occur according to the following mechanism (by Ogorodnikov et al. (2001)):



Ionization of radiation induced or the pre-radiation Byerum defects can lead to the formation of A-radical. Realization of this mechanism assumes that introduction of the heterovalent impurities ions into the crystal lattice of KDP leading to emergence of complementary hydrogen vacancies, has to lead to increase in probability of A-radical formation. Dominance of this mechanism contradicts the experimental fact of increase of the corresponding signal of EPR when heating the irradiated crystals of KDP. Plurality of channels of formation of this hole center is represented as the most probable one.

This paper presents the results of a study of mechanisms of formation of A-radicals in KDP crystals (KH_2PO_4), which play a major role in recombination luminescence in wideband crystals. An A-radical is a hole node with a hydrogen vacancy $-(\text{HPO}_4)^-$.

For KDP crystals there are no models of recombination processes, aside from general statements about the recombination of electrons and holes without specifying the nature of their carriers.

2. Experimental procedures

The monocrystals of KH_2PO_4 were grown from saturated aqueous solutions by isothermal evaporation of the solvent at the temperature of 40 °C. Prior to usage the source material of the grade "ultrapure" was purified by recrystallization. During the recrystallization only the crystals formed from the second third of the original solution were selected. This approach significantly reduces the concentration of impurities. Poorly soluble impurities mainly fall out during the evaporation of the first third of source solution, while easily soluble ones remain in the in the final third. After 10-12 days crystals of sizes from 5 mm to 40 mm were obtained from saturated KDP solution.

3. Experimental results and discussion

It is known, that in the region of 110-140 K the growth of EPR signal intensity is observed, which is linked to A-radicals.

In literature two possible channels of formation of A-radical (Lushchik, Ch.B. et al. (1989)) which represent the hole centers having hydrogen vacancy $(\text{HPO}_4)^-$ are considered. The first is bound to ionization of the growth L-defects, the second – at oscillation by radiation in a crystal of zonal electrons and holes leads to hydrogen leaving in intercluster at an electron capture. Hole localization on the atom of oxygen next to formed vacancy leads to emergence of A-radical. The first and second mechanisms of formation of the paramagnetic centers $(\text{HPO}_4)^-$ are realized only at a radiation stage, i.e. in the course of exaltation of crystals by the ionizing radiation. The increase in concentration of A-radical on post-radiation has no stage in literature of adequate explanation.

In the field of 110-130 K there is disintegration of B-radical and in the same temperature area formation of new A-radical. We consider that these processes are bound. On offered above model disintegration of the B-radical results from "assembly" of excitons. In their turn excitons have two channels of deactivation – radiating and nonradiating. The first gives an observed luminescence.

There are also two nonradiating channels of disintegration of characteristic electronic exaltations: the birth of phonons and disintegration on structural defects. The greatest interest represents the last one. It is most studied in alkali-halide crystals. Alkaline and halide crystals are connections with pronounced ionic character of a chemical bond. Therefore bond energy at this group of crystals is rather high. However, nonradiating disintegration of the autolocalized excitons on F-, H-pairs is one of the main reasons for radiation instability of these connections (Lushchik, Ch.B. et al. (1989)).

In work by Lushchik, Ch.B. et al. (1989) criteria by means of which realization the exciton mechanism of a defect formation can be realized are formulated: power and time. The energy accumulated in an exciton, has to be enough for cleavage.

The exciton lifetime in cluster of a crystal lattice has to be more period of the lattice fluctuations. In KDP crystals both of these criteria are carried out. Width of the forbidden region at these crystals lies in the range of 8.0-8.8 eV. Energy of a hydrogen bridge makes the tenth shares of eV. By quantum and chemical calculation by us it is shown that energy is necessary for deprotonation from a phosphatic anion at 0.21 eV Hole in KDP crystals is autolocalized (B-radical). Therefore autolocalization of excitons is possible as well. Really, in work by Ogorodnikov et al. (2012) emission band with maximum at 4.75 eV is connected with the autolocalized excitons.

Thus, in KDP Ch.B. Lushchik power and time criteria for disintegration of electronic exaltation on structural defects of a crystal lattice are carried out (Lushchik, Ch.B. et al. (1989)).

We have carried out computer simulations of the structure and decay of excitons in KDP crystals by half-empirical MNDO method. Selection of the cluster was due to the desire to take into account the nearest environment around central phosphate anion and hydrogen atoms associated with it.

In Fig. 1 the type of cluster ($8K^+ 5PO_4^{3-} 2H^+$) on which calculations by the MNDO method were carried out is presented. Geometrical parameters of this cluster are taken from known values of lengths of communications in KDP lattice. The choice of cluster is caused by aspiration to consider the immediate environment of the central phosphatic anion and the related atoms of hydrogen. The last are designated in drawing in figures 1 and 2. The most short O-H communication by hydrogen number 2. Initial geometrical parameters of a phosphatic anion and length of communications of O-H are specified in table 1.

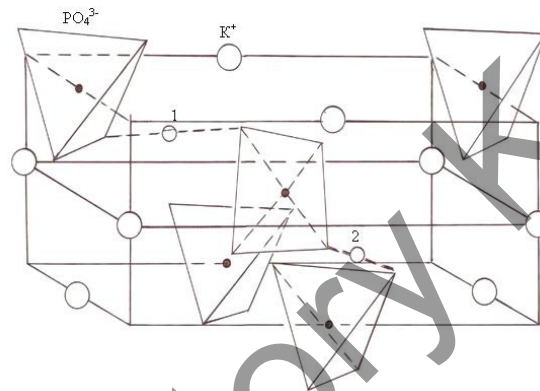


Fig. 1. The type of cluster ($8K^+ 5PO_4^{3-} 2H^+$).

Calculations on the given cluster of the geometrical structure of the exciton ($H_2PO_4^-$) in the excited triplet state yielded the results given in Table 1. When carrying out calculations the variation of valence angles was not carried out.

Table 1. Geometric parameters of the ($H_2PO_4^-$) in the triplet state

Parameter	Value (nm)
P-O (nearest to the H ₁)	0.158
P-O (nearest to the H ₂)	0.146
other P-O	0.154
O-H ₁	0.150
O-H ₂	0.095
Charge in units of "e" on	
H ₁	+0.82
H ₂	+0.62

The charge on the hydrogen next to the phosphates' anion in case of the exciton in the excited triplet state makes 0.62e. Thus, in an excited triplet state in the complex ($H_2PO_4^-$) there is an essential redistribution of electrons on orbitals and between displaced hydrogen and the oxygen next to it there is the covalent binding. Energy of transition from excited triplet in the ground singlet state makes 9.85 eV. This result is overestimated in comparison with the experimental assessment for width of the forbidden region of KDP given above.

By means of calculations it is established that energy of this transition decreases at increase in length of communication of the H-O bond. For example, when finding hydrogen in its initial ideal position in a crystal lattice of KDP it makes 6.23 eV. The given values of energies of transitions in size will be coordinated with the experimental data not really well. However, from them it is possible to draw an important qualitative conclusion: at KDP exciton in a triplet state vibronny instability is observed at initiation of fluctuations on H-O bond. The similar mechanism of vibronny instability at exaltation of shift fashions fluctuation is cornerstone of the modern ideas of mechanisms of disintegration electronic exaltation on structural defects alkaline and haloid crystals (Lushchik, Ch.B. et al. (1989)).

In Fig. 2 the potential curve for KDP exciton is given in an excited triplet state from hydrogen shift in the direction, perpendicular H-O bond. From this figure it is visible that threshold energy of the separation makes about 0.35 eV.

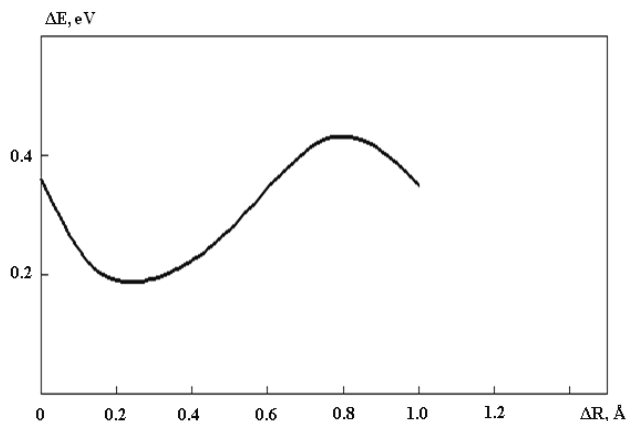
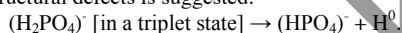


Fig. 2. The potential curve for KDP.

In Fig. 3 dependence of size of a charge (Q) of hydrogen is presented at change of length of H-O of connection (\AA). It is visible that there is a formation of H^0 . It explains the type of the potential curve given in Fig. 3, i.e. at formation of atom of hydrogen the mechanism of its instability in cluster of the crystal lattice turns on. Based on the results of the study the following mechanism of a decay of KDP excitons to structural defects is suggested:



Changing the length of the H-O bond in the exciton leads to a decrease of the transition energy from the excited triplet state to the ground singlet state. It increases probability of nonradiating disintegration as in one act of this process the smaller number of phonons has to be born. As, H-O bond is strongly anharmonic because of the considerable distinction of values of oscillating masses exists the increased probability of localization of vibration energy on this connection. As a result at nonradiating disintegration of excitons the A-radical and atom of hydrogen are formed which is localized in the intercluster.

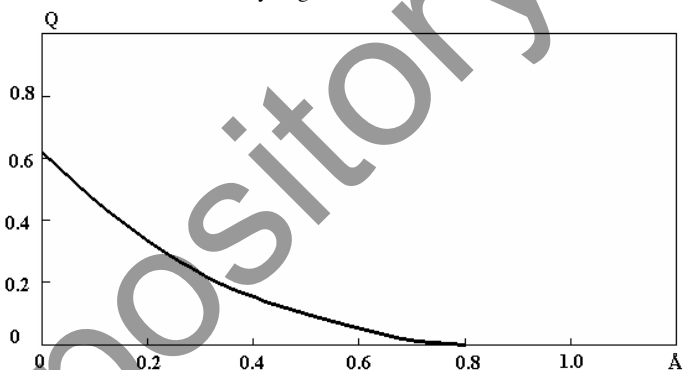


Fig. 3. The dependence of size of a charge (Q) of hydrogen is presented at change of length of H-O of connection (\AA).

Therefore, the intercluster atom of H^0 hydrogen is complementary defect not only for the autolocalized hole (B-radical), but also can be that to the A-radical that arises at nonradiating disintegration of the exciton (Kim et al. (2008)).

4. Conclusion

Thus, we present the following model of formation of A-radicals during the post-radiation stage: the excitons are formed when interstitial hydrogen atoms recombine with B-radicals. Our calculations show that the excitation of oscillations on the O-H bond in excitons in the triplet excited state leads to a situation of vibronic instability, which in turn leads to the collapse of the exciton with the formation of a hydrogen atom and an A-radical.

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