Journal of Optoelectronics and Advanced Materials Vol. 2, No. 3, September 2000, p. 275 - 280

UV-VIS ABSORPTION SPECTRUM OF THE KDP:Pd SYSTEM

Ana Ioanid

Department of Solid State Physics, Faculty of Physics, University of Bucharest,
P.O. Box Mg. 11, 76900 Bucharest Magurele, Romania

The absorption spectrum in the low energies range, 13300÷35000 cm^{-1} exhibits three bands, the high energy band located at 25000 cm^{-1} being intense. The KDP:Pd crystals have yellow color and show no ESR spectrum proofing the existence of the diamagnetic Pd^{2+}-complexes. Setting out from the ability of the Pd^{2+} ion to form the charge transfer complexes with different ligands, an assignement of the absorption observed spectra to the charge transfer transitions of the Pd^{2+} with $H_2PO_4^-$ groups as ligands is suggested. Configurational arguments are given to support the formation a pseudo-square planar complex that is superposed to an axial component with $H_2PO_4^-$ groups as ligands.

(Received March 24; accepted September 11, 2000)

Keywords: Square planar metal-complex, Charge transfer spectrum, Molecular orbital

1. Introduction

Potassium dihydrogen phosphate KH_2PO_4 (KDP) is a well-known ferroelectric crystal which is used in many kinds of optical devices as electrooptical polarizers and harmonics generators. The optical properties of this crystal have mainly been studied from the view points of ferroelectrics or low and high temperature phase transitions [1,2]. The KDP crystal is an insulator with large energy gap exceeding 7 eV. The ferroelectric and optical properties are markedly modifieds by impurities. The KDP:Me systems, Me being a transition metal or rare-earth ion, have characteristic absorption bands in the transparence band of pure KDP crystal. These absorption bands correspond to the transitions between levels arising from the d or f-orbital splitting in the ligand field. The ESR spectra of paramagnetic impurities in the ferroelectric phase give informations for the mechanism of ferroelectricity.

The modern optoelectronic devices industry uses the localized centers, as transition metal or rare-earth impurities in semiconductors and insulators. For exemple, the optoelectronic devices operating in the blue-green range of the spectrum, use the optical transitions associated with localized levels of a rare-earth or transition metal impurity leading to a characteristic luminescence. The total laser efficiency of many rare-earth activator ions is increased by sensitization with strongly absorbing ions, usually from d-transition metal groups which are much better excited by the existing optical pump sources. The important condition for an efficient sensitization is a fast energy transfer from the sensitizer to the activator in order to avoid the de-excitation of the former by its own emission or multiphonon relaxation. All these needs require the knowledge of the absorption spectra both of the sensitizer and the activator.

In this work we present the absorption spectrum of the KDP:Pd system at room temperature. The choice of this d-ion is supported by two reasons: 1) the Pd^{2+} ion is characteristic for nd^8 -transition metal group and 2) the Pd^{2+} ion has the ability to form charge transfer complexes with different ligands. These complexes have the charge transfer absorption bands in the above mentioned spectral range in which both the pure KDP and KDP:Pd crystals have characteristic emission spectra [3].

2. Experimental

The single crystals of KDP and KDP:Pd were grown by slow evaporation of a supersaturated aqueous solution at room temperature. To obtain KDP:Pd single crystals palladium chloride ($PdCl_2$) was added with the concentration of 0.5 mol % against KDP. The transparent KDP:Pd single crystals exhibit yellow color. The transmission spectra in the $(13300 \div 35000)\ \mu m$ spectral range have been performed with a Cary 17D recording spectrophotometer. The absorption spectra have been calculated from the transmission spectra without a reflexion correction. To favour a comparison with the literature the wavenumber scale has been choosen. Fig. 1 shows the absorption spectra of KDP and KDP:Pd systems spectra in the wavenumber range13300÷35000 cm^{-1}.

The absorption spectrum of KDP:Pd crystal shows three additional bands (1,2,3 in the order of increasing energy) whose energy positions are approximately 14930 cm^{-1}, 17540 cm^{-1} and 25000 cm^{-1} respectively. The high energy band is more intense that the lower energy bands. The insert in Fig. 1 shows these two lower energy bands.

3. Discussion

It is important to mention that the KDP:Pd crystal shows no ESR spectrum and this proves the existence of the diamagnetic Pd^{2+} -complexes. The yellow color of the KDP:Pd crystal proves also the existence of the Pd^{2+} ion. This ion is a representative of the nd^8-metal ions having the electronic configuration $[Kr]4d^8$. The absorption spectrum exhibits a strong peak in the UV range, centered at 25000 cm^{-1} and having the absorption coefficient at maximum of the order 5, typical for the charge transfer bands [4]. On the other hand, the strong peaks in the UV range of solutions of some transition metal complexes were proofs of the charge transfer between the ligands and the central ion. This behaviour characterizes for exemple the iron complexes with polyacrylic acid in aqueous solution [5] and the square-planar complexes of Ni^{2+}, Pd^{2+}, Pt^{2+} in aqueous solutions [6].

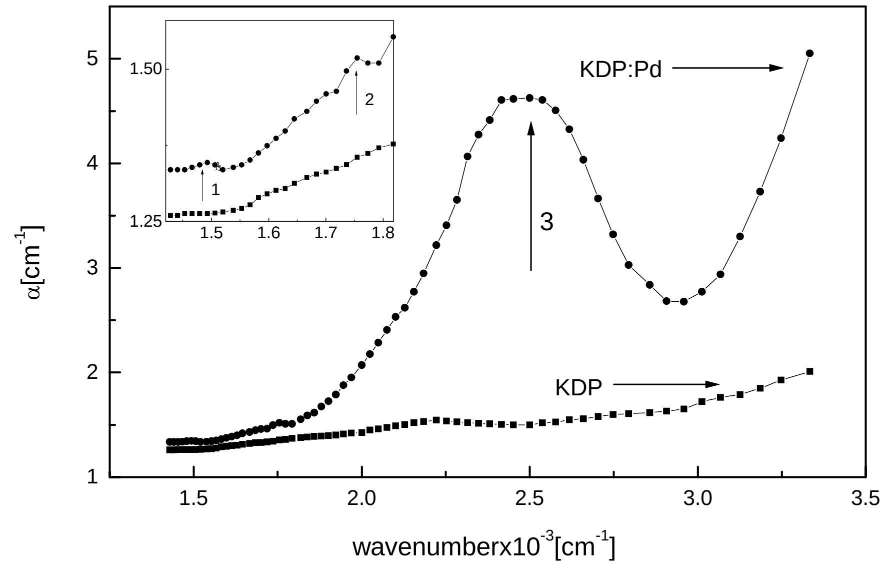

Fig. 1. The absorption spectra of the KDP and KDP:Pd crystals in the 13300÷35000 cm^{-1} spectral range. The insert shows only the low energy spectral range in the same units.

Since the 4d shell lies at the surface of the Pd^{2+} ion, it is strongly influenced by the crystal field and results in the splitting into a number of levels. The number of these levels is determined by the crystallografic symmetry at the position of the d ion. In the following discussion we suppose that the transition metal ion replaces a K^+ cation in KDP structure. At room temperature the crystal structure is a tetragonal one belonging to the point group $\bar{4}2m$. The elementary cell has $a = 7.445$ Å and $c = 6.985$ Å. The KH_2PO_4 crystal has four potassium site per unit cell. Two of them coalesce each other by a translation operation and the rests do the same.The impurity cation may have two sites. One site is potassium lattice site for which one of the eight nearest protons is missing and the other is the potassium lattice site with which a potassium vacancy is associated at one of the nearest sites [7]. The protonic motion in the double minimum potential is one of tunneling between the two potential minima situated along the hydrogen bond, so that it is nearly equal probably to form both $H_2PO_4^-$ and $H_4PO_4^+$ groups. Each from these groups themselves have a $\sigma-$ and a $\pi-$orbital system [8]. On the other hand, it is well-known the tendency of the nd^8 -metal ions to form square planar complexes with different ligands and that this tendency increases in the order $Ni^{2+} < Pd^{2+} < Pt^{2+}$. At room temperature the KDP crystal is in paraelectric phase in which the hydrogen atom lies at the center of the hydrogen bond as in the $H_4PO_4^+$ group. From the electrical point of view the formation of the Pd^{2+} - complex are favorized the $H_2PO_4^-$ groups as ligands. Because in $H_2PO_4^-$ group the hydrogen atoms are nearly frozen, this choice is supported by the observed attenuation of the free carrier absorption mechanism due to the scattering by optical phonons and a shift to long-wavelenghts of the low-energy absorption edge [9,10]. The structure of the Pd^{2+} - complex with the $H_2PO_4^-$ groups as ligands may be established if we consider that the Pd^{2+} ion is located at one potassium lattice site with which a potassium vacancy is associated at one of the nearest sites, as shown in Fig. 2. The first coordination for this position is an axial one and consists in two $H_2PO_4^-$ groups at a distance equal with $d_I = \frac{c}{2} = 3.492$ Å. The second coordination is a pseudo-square planar configuration (originating from a compressed tetrahedral configuration) of four $H_2PO_4^-$ groups, at the distance $d_{II} = \left[\left(\frac{a}{2}\right)^2 + \left(\frac{c}{4}\right)^2\right]^{\frac{1}{2}} = 4.112$ Å.

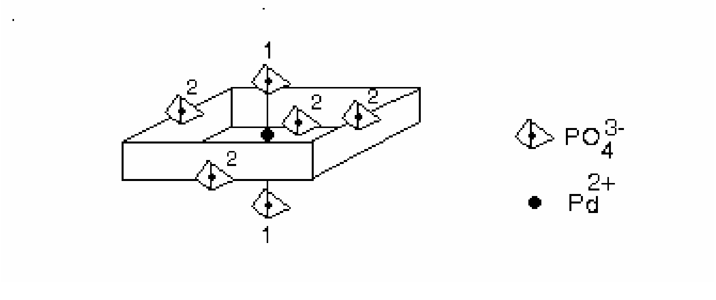

Fig. 2. The presumed configuration of the Pd^{2+} -complex in KDP:Pd crystal. For clarity the protons have been omitted.

Taken into account the $H_2PO_4^-$ groups as ligands, we can write a possible formula of the Pd^{2+} pseudo-square planar complex as $Pd\left[H_2PO_4^-\right]_4^{2-}$. In this case the energy positions of the $4d_{z^2}$ and $4d_{xz,yz}$ metal orbitals are modified at higer energies that in the pure square planar complex due to the axial component of the ligand field.

The intensity of ligand field transitions is generally low since they are forbidden due to the parity selection rule. Unlike ligand field transitions, the charge transfer transition which are generally allowed give rise to intense absorption bands so that the d-d bands for the most part are obscured by the charge transfer bands. In the molecular orbital method it is assumed the normal non-bonding electrons in the t_{2g} d orbitals of the transition metal ion forming π bonds with suitable ligand orbitals. Fig. 3 shows the molecular orbital energy level scheme for a square planar transition metal complex in which the ligands (for instance $H_2PO_4^-$ groups) themselves have a $\pi-$orbital system.

In the frame of this theory, two features of the molecular orbital bonding scheme are consistent with this observation:

i) In the pure square planar configuration, the $nd_{x^2-y^2}, (n+1)s, (n+1)p_x, (n+1)p_y$ metal orbitals account for most $\sigma-$bonding and nd_{z^2} makes only a minor contribution and may be considered a non-bonding orbital. In the KDP:Pd crystal case, with a strongly axial ligand field component, the addition a fifth ligand ($H_2PO_4^-$ group) above the basical square drastically decreases the stability of the ring $\pi-$bonding by linking the $5p_z$ orbital in $\sigma-$bonding. The $4d_{z^2}$ orbital is more unstable than $4d_{xz,yz}$ orbital because it makes a greater contribution for $\sigma-$bonding of the metal complex. As a result, any changes in the molecular orbital energy level scheme are expected. In Fig. 3 we have schematically drawn the d orbital energy positions in the pure square planar configuration (a), [6], and the proposed positions in the Pd^{2+} -complex with the $H_2PO_4^-$ groups as ligands in the KDP:Pd crystal, (b).

ii) The $a_{2u}(\pi^*)$ molecular orbital consisting of the $(n+1)p_z$ metal orbital and a combination of the four ligand π vertical orbitals, gives a very stable $\pi-$bonding orbital which may be called the ring $\pi-$orbital and which is responsible for the diamagnetism of the complex. Because the $H_2PO_4^-$ ligands themselves have a $\pi-$orbital system, for palladium complexes both π-bonding (π^b) and π-antibonding (π^*) ligand orbitals must be considered. The nd^8 metal complexes exhibit the expected three charge transfer bands because the d-d bands for the most part are obscured by these charge transfer bands. The charge transfer occurs probably by metal-ligand transitions or ligand-metal transitions. Two typical features of the spectrum should serve as a guide in assigning the charge transfer as ligand (π orbital)-metal or metal-ligand ($a_{2u}(\pi^*)$).

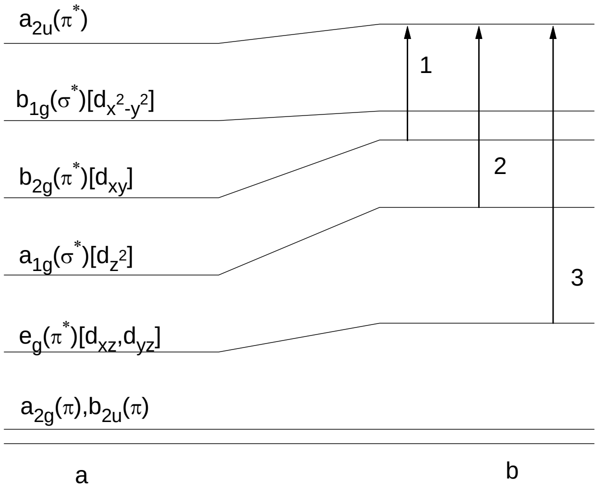

Fig. 3. Molecular orbital energy level scheme; **a**- for pure square planar transition metal complex in which the ligands themselves have a $\pi-$orbital system and **b**- presumed scheme for pseudo-square planar Pd^{2+}--complex in KDP:Pd crystal.

1) For pure square planar metal complexes in which the ligands themselves a $\pi-$orbital system, the charge transfer bands are expected to involve transitions from the highest filled metal orbitals to the most stable empty ligand antibonding molecular orbital $a_{2u}(\pi^*)$. Thus, the first charge transfer band, in increasing energy, corresponds to the orbitally forbiden transition $b_{2g}(\pi^*) \to a_{2u}(\pi^*)$. The second and the third charge transfer bands correspond to the allowed transitions $a_{1g}(\sigma^*) \to a_{2u}(\pi^*)$, $e_g(\pi^*) \to a_{2u}(\pi^*)$ respectively, with the $e_g(\pi^*) \to a_{2u}(\pi^*)$ band expected to have considerably greater intensity. The bands have an intensity order $e_g(\pi^*) \to a_{2u}(\pi^*) > a_{1g}(\sigma^*) \to a_{2u}(\pi^*) > b_{2g}(\pi^*) \to a_{2u}(\pi^*)$.

2) In the pure square planar complexes the two orbitally allowed metal-ligand transitions $a_{1g}(\sigma^*) \to a_{2u}(\pi^*)$, $e_g(\pi^*) \to a_{2u}(\pi^*)$ are only $2000 \div 3000\ \mathrm{cm}^{-1}$ apart because the $a_{1g}(\sigma^*)$ and $e_g(\pi^*)$ metal orbitals are virtually non-bonding and thus nearly equal in energy. For the palladium complex in KDP:Pd crystal, according to ii), $a_{1g}(\sigma^*)$ and $e_g(\pi^*)$ metal orbital are not non-bonding as well as $b_{2g}(\pi^*)$ and $b_{1g}(\sigma^*)$. Thus the metal-ligand transitions $b_{2g}(\pi^*) \to a_{2u}(\pi^*)$, $a_{1g}(\sigma^*) \to a_{2u}(\pi^*)$ have close energies and lower energies than those for pure square planar complex.

Using the scheme from Fig. 3 for the Pd^{2+} -complex in KDP, we can ascribe the 1, 2, 3 absorption bands of the spectrum from Fig. 1 to the three transitions metal-ligand as in Table 1. The wavenumber positions and their relative intensities are also given. For comparison the same quantities for the square planar $Pd\left[CH^-\right]_4^{2-}$ in which ligands themselves have a $\pi-$orbital system [6] are also given.

Table 1. The energy positions and the relative intensities of the metal-ligand transitions generating charge transfer bands of the $Pd\left[H_2PO_4^-\right]_4^{2-}$ and $Pd\left[CH^-\right]_4^{2-}$ complexes.

No. of the band	Transition	Transition energy [cm^{-1}]		Energies ratio	Relative intensity in this work, and in [6]
		this work	From [6]		
1	$b_{2g}(\pi^*) \to a_{2u}(\pi^*)$	14930	41600	2.78	small
2	$a_{1g}(\sigma^*) \to a_{2u}(\pi^*)$	17540	45400	2.58	intermediate
3	$e_g(\pi^*) \to a_{2u}(\pi^*)$	25000	47200	1.88	large

Comparing these results about the absorption features of $Pd\left[H_2PO_4^-\right]_4^{2-}$ in KDP:Pd crystal and $Pd\left[CH^-\right]_4^{2-}$ in aqueous solution we summarize the following main observations:

-the absorption spectra consist in three bands whose relative intensities are in order $I_1 < I_2 < I_3$ corresponding intensities being less for $Pd\left[H_2PO_4^-\right]_4^{2-}$ complex;

-for $Pd\left[H_2PO_4^-\right]_4^{2-}$ complex, the transitions metal-ligand occured at lower energies that for $Pd\left[CH^-\right]_4^{2-}$ complex. The energy ratios show that the transitions implying the $4d_{xy}$ and $4d_{z^2}$ metal orbitals have considerably greater value;

-the transitions impliying the $4\,\mathrm{d}_{z^2}$ and $4\,\mathrm{d}_{xz,yz}$ metal orbitals have nearly energy for $\mathrm{Pd}\left[\mathrm{CH}^-\right]_4^{2-}$ while for $\mathrm{Pd}\left[\mathrm{H_2PO_4^-}\right]_4^{2-}$ the difference between energy positions of transitions from $4\,\mathrm{d}_{xy}$ and $4\,\mathrm{d}_{z^2}$ is very little.

These observations are consistent with the above discussions 1) and 2). In addition, the electron distribution of the d^8 ion in the square planar ligand field may be written $\left(\mathrm{d}_{xz,yz}\right)^4\left(\mathrm{d}_{z^2}\right)^2\left(\mathrm{d}_{xy}\right)^2\left(\mathrm{d}_{x^2-y^2}\right)^0$. The intensity of the $\mathrm{e_g}(\pi^*)\left[\mathrm{d}_{xz,yz}\right]\rightarrow \mathrm{a_{2u}}(\pi^*)$ transition is large because the low orbital level is filled with four electrons. The small difference between the energy positions of the transitions $\mathrm{b_{2g}}(\pi^*)\rightarrow \mathrm{a_{2u}}(\pi^*)$, $\mathrm{a_{1g}}(\sigma^*)\rightarrow \mathrm{a_{2u}}(\pi^*)$ and the lower energy positions of the transitions metal-ligand in the $\mathrm{Pd}\left[\mathrm{H_2PO_4^-}\right]_4^{2-}$ complex are both sensitive to the axial component of the ligand field.

4. Conclusions

Using our experimental result compared to those from literature, we could conclude that the absorption spectrum of the KDP:Pd crystal is characterized as a charge transfer spectrum. The three charge transfer bands correspond to the metal-ligand transitions from metal levels arising from the d-splitting in a quasi-square planar Pd^{2+}-complex with the $\mathrm{H_2PO_4^-}$ groups as ligands that is superposed to an axial component, to stable $\pi-$antibonding orbital levels of the ligands. A comparison of these results with those of steady-state photocurent under uniform illumination is in progress.

References

[1] A. Otani, S. Makishima, J. Phys. Soc. Japan, **26** , 85 (1969).
[2] A. Ioanid, M. Popescu, N. Vlahovici, I. Bunget, phys. stat. sol., (a) **82**, K125, (1984).
[3] A.Ioanid A., to be published in J. Optoel. Adv. Mat., Vol. 2., No. 5, (2000)
[4] H. L. Schlafer, G. Glieman, Basic Principles of Ligand Field Theory, Wiley, London, 1969.
[5] S. Frunza, M. Fiti, L. Frunza, D. N. Stoenescu, R. Moldovan, T. Beica, Liq. Cryst. **16**, 277 (1994).
[6] H. Gray, C. J. Ballhausen, J. Am. Chem. Soc., **85**, No.1, 260 (1963).
[7] Y. Tsutsumi, M. Kunitomo, T. Terao, T. Hashi, J. Phys. Soc., Japan, **26**, 16 (1969).
[8] S. Saito, K. Wada, R. Onaka, J. Phys. Soc., Japan, **37**, No.3, 711 (1974).
[9] A. Ioanid, A. Moise, accepted for Rom. Rep. Phys., (January, 1999).
[10] Němec P., J. Oswald, M. Frumar, B. Frumarová, Journal of Optoelectronics and Advanced Materials, vol. **1**, No.4, 33 (1999).