1. INTRODUCTION

Electronic structure of crystals consist of impurities sufficiently differs from ideal picture of solid state. Electronic density distribution and ionic radius of component and doping ion is unlike, naturally. Violation of translation symmetry of a crystal due to substitution of the component ion by doped one is the main cause of appearance point defects and change in electronic structure of crystals. This substitution sometime is the main cause of change in optical, electrical etc. properties of compounds. Concentration of doped ions, as controlled and uncontrolled ones in crystals changes from $10^{-9}$ to $10^{-1}$ wt %. When doped ions amount grows more than 1 wt % we may say about appearence of a new compound. Strong interests to doped crystals focussed on compounds doped with ions including unfilled nd and nf (nl ions, shortly) electronic shells due to unrestricted area of application of the materials.

The electronic state (valence) of component or doped ions entering in the composition of solids is responsible of the solid ground properties. In particular, the oxidation state of the ions and the symmetry of the crystalline lattice determine the structure of the energy bands, optical, dielectrical and other properties of the crystals [1–3]. Detail consideration of interaction of impurity with crystalline lattice ions is important for progress in understanding of properties of doped crystals and mixed solids, in total.

Irradiation in the most of compounds doped with nl ions creates different color and point defects that induce optical additional absorption bands, AA, in crystals [3–5]. The types of color center (charge trapped in anion or cation vacancy, change in oxidation state, interstitial ions and more complex defects) and the intensity of the optical absorption (emission) bands depend on the crystallographic structure of the compounds as well as on the crystal growth conditions along with the types and concentration of impurities. Spectroscopic methods were widely used to study the radiation induced defects in crystals but not so far successfully [3–5].

It is well known that the ions of iron (Me), lanthanum (RE) and actinium (AC) group elements, shortly—ME, show oxidation states from “+2” to “+6” and even “+7” in different compounds. Thermal treatment, irradiation, variation in the crystal growth conditions, etc. may induce changes in oxidation state of the ions (components and impurities). For example, Sr$^{2+}$Ti$^{4+}$O$_3$ single crystals can contain more than 20 % of Ti$^{3+}$ ions upon a thermal treatment [3–5]. In papers [5–7] shown that K$^+$ ion in KCl single crystals change its oxidation state to neutral K$^0$ atom under the influence of UV, X ray, $\gamma$-irradiation.

Doped nl ions change their oxidation state more efficiently upon irradiation or thermal treatment than the regular crystal component ones [2–3, 7–9]. Defect accumulation during irradiation induces also changes in the doped ion oxidation state. For Me or RE ions, this effect may be studied by using ESR, optical absorption (or emission), thermo-stimulated processes such as thermo-stimulated conductivity (TSC) and thermo-stimulated luminescence (TSL) and other methods [9–13]. It should be noticed that the experimental determination of the ion oxidation state for most of the doped and component ions in the solid is a complex problem. For this purpose, we propose an...
effective method based on the valence shift of X Ray lines called VSXRL [3–5].

The radiation induced defects in ruby, α-Al2O3 : Cr, in crystals with perovskite type crystalline lattice, such as strontium titanate, SrTiO3, or yttrium alumininate, YAO3 : Cr, in crystals with garnets structure: Y3Al5O12 : Cr : Nd, Gd3Sc2Al3O12 : Cr : Ca (GSAG) or Gd3Se2Gd3O12 : Cr : Cs (GSGG) etc. [12–14] for doses higher than 102 Gy give rise to additional optical absorption bands at 217, 260, 360 and 460 nm for ruby [9], 295, 370, 425 and 500 nm for the YAO3 : Cr [13], and 253, 282, 417 and 488 nm for Y3Al5O12 : Cr garnet [15]. The concentration of the Cr3+ ions can be in crystals with perovskite type crystalline lattice, such as oxides, fluorides or other (first of all wide band gap crystals and so-called optical materials) creates local electron or hole level. Average doped ion energy $E_0$ in a crystal depends on electronic configuration, type of compound, naturally. For doped ions with unfilled nd or nf electron shell there is of around Fermi’s energy. Interaction inside of nlN electron configuration of the doping ion and Stark’s splitting due to interaction of nl ion and crystalline lattice creates energy level scheme of nl ion in a crystal. Estimation of the $E_0$ may be made during calculation of Madelung’s constant value $\alpha_{\text{M}}$ for cation side in the crystal and ion ionization energy [3–5]. The doped ion ground state is near valence band. Calculation of the ground state energy of impurity $E_{gr}$ is quite complex task.

2. AB INITIO SELF-CONSISTENT FIELD THEORY FOR CLUSTERS AND DOPED CRYSTALS

2.1. Energy Position of Doping Ion in a Crystal

One in important solid state physics backgrounds declares that any case of crystal lattice symmetry violation creates new energy level in crystal’s forbidden zone. Every ion substituted crystal component ion in different compounds such as oxides, fluorides or other creates local electron or hole level. Average doped ion energy $E_0$ in a crystal depends on electronic configuration, type of compound, naturally. For doped ions with unfilled nd or nf electron shell there is of around Fermi’s energy. Interaction inside of nlN electron configuration of the doping ion and Stark’s splitting due to interaction of nl ion and crystalline lattice creates energy level scheme of nl ion in a crystal. Estimation of the $E_0$ may be made during calculation of Madelung’s constant value $\alpha_{\text{M}}$ for cation side in the crystal and ion ionization energy [3–5]. The doped ion ground state is near valence band. Calculation of the ground state energy of impurity $E_{gr}$ is quite complex task.

2.2. Energy Level Scheme of nl Ion in a Crystal

Energy level scheme of doped ion in a crystal may be considered in the framework of modified crystalline lattice field theory [33–35]. A symbiosis of the Hartree-Fock-Pauli approach and the Heitler-London model has been used to study the electronic structure of clusters and solids [21–31]. The theoretical values are compared to experimental ones for optical and X ray spectra of Me and RE/AC ions in wide band gap crystals [3, 20, 36–37].

The foundation of the theory is the well known Born-Oppenheimer approximation for unrestricted ME$n^+$: $[L]$ cluster. For the electronic part of the total wave function of the crystal, we may write the following equation:

$$\left[{-\frac12 \sum_i \Delta_i - \sum_i V(r_i, R) + \sum_{i<j}^1 \frac1{|r_i-r_j|}}\right] \Psi_j(r, R) = W_j(R)\Psi_j(r, R).$$

(1)

For ME ion Eq.(1) may be written as:

$$[H_{\text{free}}(r) + H_{\text{int}}(r, R)] \Psi_j(r, R) = E_j(R)\Psi_j(r, R),$$

(2)