EFFECTS OF PERTURBATION PARAMETER VARIATION ON THE LOCAL ONE-ELECTRON LEVELS IN AN ALKALI-HALIDE CRYSTAL WITH A DIVALENT ACTIVATOR

V. N. Salomatov

Lifshits's modification of Green's function has now begun to be applied to the electronic states of non-ideal crystals [1-6]. The method has been applied to alkali-halide phosphors to give the local one-electron levels in $KCl - Tl$ [5] and $KCl - Eu^{2+}$ [6-10]. The results are of interest for interpreting the experiments of [8-10]. As regards the nature of the local states, one can merely say they have a genetic relationship to the states of the impurity ion or its neighbors.

It is of interest to examine the nature of the local states by studying the effects of perturbation-parameter change on the local-level system. Major results have been given [10] for $KCl - Eu^{2+}$, and the sets of levels for the various perturbation parameters show that all these parameters are involved in the local-level system, but that a major group of parameters can be distinguished for any particular level as most greatly influencing its position or being responsible for its existence. Levels close to band edges are very sensitive to the perturbation parameters, so some other method must be applied to study them.

A calculation has also been performed [11] for the local one-electron levels in the ground state of $KCl - Sm^{2+}$; it is of interest to compare the perturbation parameters in this case with those for $KCl - Eu^{2+}$ and to see how the differences affect the positions of the local level.

We compare the inducing perturbation parameters [6], which describe the difference between the shifts in the anion levels in the defective and ideal crystals. The subscripts in the $W_{ll}^{\alpha\alpha}$ enumerate the ions in the defective region, as shown in Fig. 1, while the superscripts $\alpha = 1, 2, 3 \rightarrow x, y, z$ indicate the direction of the axis for the 3p function of the anion l along one of the axes of the coordinate system shown in Fig. 1.

Table 1 shows that the inducing parameters fall on the substitution $Eu^{2+} \rightarrow Sm^{2+}$ (the negative parameters increase in absolute magnitude). There should be [10] a downward movement of the local levels lying below the valency band and induced from that band (within the framework of the two-band [5-8] model for the crystal). The results for $KCl - Eu^{2+}$ and $KCl - Sm^{2+}$ (Table 2)* show that this lowering actually occurs, and does so for levels of all symmetries (this result was obtained for levels of symmetry A_1 in [10]).

---

* The values given for $KCl - Eu^{2+}$ in Table 2 differ somewhat from the corresponding ones in [8], but this does not affect the interpretation of the results, though it is responsible for some uncertainty as to the conditions under which the local levels arise.

TABLE 1. Induced-Perturbation Parameters (eV) for the Ground States of $KCl - Eu^{2+}$ and $KCl - Sm^{2+}$

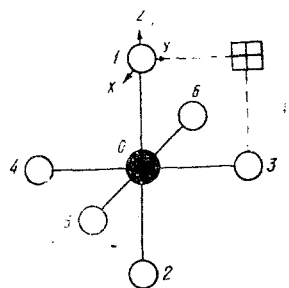|	W_{11}^{33}	W_{11}^{22}	W_{11}^{11}	W_{22}^{33}	W_{22}^{22}	W_{22}^{11}	W_{55}^{11}	W_{55}^{22}
KCl—Eu^{2+}	—5,44	—2,93	—2,64	0,27	—0,06	—0,04	—1,53	—1,10
KCl—Sm^{2+}	—5,63	—3,08	—2,79	0,19	—0,13	—0,11	—1,65	—1,20

Fig. 1. Structure of a center with C_{2v} symmetry (divalent impurity cation together with cation vacancy).

TABLE 2. Local-Level Positions (eV) for the Ground States of $KCl-Eu^{2+}$ and $KCl-Sm^{2+}$. Relative to the Bottom of the Conduction Band

	A_1	A_2	B_1	B_2
$KCl-Eu^{2+}$	—7,10 —10,09 —10,15	—10,18 —11,60	—10,01 —11,40	—1,26 —10,06 —10,72
$KCl-Sm^{2+}$	—7,11 —10,16 —10,26	—10,28 —11,72	—10,18 —11,71	—0,28 —10,27 —10,94

This shows that the levels in $KCl-Eu^{2+}$ and $KCl-Sm^{2+}$ below the valence band are of induced nature (they arise because the potentials of the impurity ion and vacancy differ from the potentials of the regular ions).

This comparison clearly applies for levels that interact only weakly with the one-electron energy bands below the valence band. *

The mixing parameters include the overlap integrals for the impurity ion and neighbors, and they differ little for these two systems. Correspondingly, the position of the hole A_1 level changes by only 0.1 eV on the $Eu^{2+} \rightarrow Sm^{2+}$ substitution.

The B_2 level induced from the conduction band rises in response to the $Eu^{2+} \rightarrow Sm^{2+}$ substitution, because the 4f electrons of Sm^{2+} have less energy than those of Eu^{2+} in KCl. Further research is needed to establish the reasons why the impurity parameters influence the position of the unfilled B_2 level.

LITERATURE CITED

1. G. Koster and J. Slater, Phys. Rev., 95, 1167 (1954); 96, 1208 (1954).
2. N. Kristoffel and G. Zavt, Nuovo Cim., 61B, 331 (1969).
3. F. Bassani, G. Iadonisi, and B. Presiosi, Phys. Rev., 186, 735 (1969).
4. K. Krishan and J. Mahanti, J. Phys. C: Solid State Phys., 3, L 133 (1970).
5. N. N. Kristoffel, G. S. Zavt, and B. V. Shulichenko, Physics of Impurity Centers in Crystals [in Russian], Akad. Nauk ESSR, Tallinin (1972), p. 53.
6. N. N. Kristofel' and V. N. Salomatov, Izv. Akad. Nauk ESSR, Fiz.-Mat., 21, 245 (1972).
7. V. N. Salomatov and N. N. Kristofel', Preprint FAI-14, Tartu (1972).
8. V. N. Salomatov and N. N. Kristofel', Izv. Akad. Nauk ESSR, Fiz.-Mat., 21, 337 (1972).
9. I. A. Parfianovich, V. M. Metsik, V. N. Salomatov, and E. I. Shuraleva, Opt. i Spektroskop., 35, 876 (1973).
10. V. N. Salomatov and N. N. Kristofel', Proceedings of the 21st Conference on Luminescence (Crystal Phosphors) [in Russian], Stavropol' (1973), p. 133; Izv. Akad.Nauk SSSR, Ser.-Fiz.,38 (1974).
11. V. N. Salomatov and N. N. Kristofel', Izv. Akad. Nauk ESSR, Fiz.-Mat., 23 (1974).

* A preliminary consideration indicates that the lower bands affect this system of local levels in $KCl-Eu^{2+}$ and $KCl-Sm^{2+}$ mainly by raising the local levels lying below the valence band.