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Optical transitions of the H centers in alkali halides

A. L. Shluger,* V. E. Puchin,† T. Suzuki, K. Tanimura, and N. Itoh
Department of Physics, Nagoya University, Furo-cho, Chikusa-ku, Nagoya-464, Japan

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Comparison is made of the experimentally measured and theoretically calculated absorption spectra of the two types of intrinsic X_2^- hole centers (i.e., V_K and H centers) in several alkali halides (X denotes a halogen atom). The optical absorption spectra of these centers in NaCl, KCl, KBr, KI, and RbI are obtained employing the dichroic spectroscopy. The geometric structure of the V_K and H centers in NaCl, KCl, and KI are determined by optimizing the total energy of the molecular cluster embedded in the crystalline lattice using the Hartree-Fock method, and the defect optical transition energies are calculated using the configuration interaction technique. It is shown that the latter is essential for the correct representation of the wave functions of the excited defect states and for the understanding of the nature of the electronic transitions associated with the defects. The analysis of the spin density in the excited states of the H centers demonstrates the delocalization of these states over several anions surrounding the X_2^- molecular ion. The existence of the optical transitions of the H center higher in energy than the UV band ascribed to the σ_g-σ_u transition is shown theoretically and confirmed experimentally. The difference in the optical properties of the H and V_K centers is discussed in terms of the geometric and electronic structure of the two centers.

I. INTRODUCTION

The dihalogen molecular ion, X_2^- (X denotes a halogen atom), has been studied extensively both in the field of photochemistry and in solid-state physics. In particular, many of the hole-localized centers formed by electronic excitation in metal halide crystals have been shown to have the configuration of the X_2^- molecular ion. The first important finding was the self-trapped hole (STH) in alkali halides where the hole was shown to be localized on the two adjacent halogen ions oriented along the $\langle 110 \rangle$ crystallographic direction and forming a X_2^- molecular ion[1] as shown in Fig. 1(a). Later, it was demonstrated that the STH's of similar structure are formed in many metal halogen crystals and in rare-gas solids.[2] The STH, often called the V_K center, is now regarded as a typical example of the molecular small polaron,[3,4] in which covalent-bond formation plays an essential role in stabilizing the localized state in solids.

It has also been shown that the intrinsic interstitial atom, the H center,[5] formed as a result of the decomposition of the self-trapped excitons[2,6,7] (STE) in alkali halides, may be considered as the X_2^- molecular ion located at an anion site. In some crystals such as LiF[8] and NaCl,[9,10] the molecular axis of the X_2^- in the H center has been shown to be oriented along the $\langle 111 \rangle$ direction, while in other crystals it is oriented along the $\langle 110 \rangle$ direction [see Fig. 1(b)]. From the results of electron-paramagnetic resonance (EPR) studies for the latter configuration, it has been estimated that the spin density of the center is delocalized by about 10% up to the two outer halogens.[5] Based on those results, the H center is sometimes described as X_4^{3-}.

These two types of intrinsic X_2^- hole centers in alkali halides have been studied extensively by several methods including EPR, optical, and Raman spectroscopies. Most of the results concerning their geometric structure and vibrational and electronic properties have been interpreted in terms of a "molecule in solids" model in which the effects of the lattice surrounding the X_2^- can be treated as perturbations. Because of the p character of the halogen valence state, the electronic structure of the X_2^- molecular ion, to a good approximation, can be described in terms of molecular orbitals as linear combinations of p atomic orbitals. In this model, the hole in the ground electronic state $^2\Sigma_u$ is located at the antibonding molecular orbital σ_u. The X_2^--type centers usually show two distinct optical absorption bands, where the one in the UV region is attributed to the σ_g-σ_u transition, and the other near the IR region is attributed to the π_g-σ_u transition.[11-13] This molecular model provides a correct qualitative description of the EPR properties of the H and V_K centers, including the EPR-active electronic transitions, crystal-field effects, and the spin-orbit interaction.[14] Recent resonance Raman studies of the V_K and H centers have revealed a significant difference in the vibrational properties at their ground state; the stretching vibration frequency ω_1 of the X_2^- in the H center was found to be much harder than that in the V_K configuration.[10] A qualitative explanation of this difference is based on the X_2^- molecular ion scheme and takes into account a strong effect of the crystalline potential on the bounding properties of the X_2^- centers.[10]

Although most of the results obtained so far for the V_K and H centers were described satisfactorily in terms of the dihalogen molecular scheme, one problem concerning the optical transition energy of the H center has remained unsolved. In terms of the dihalogen molecular scheme, the energy E_σ of the optical transition between the bonding and antibonding σ hole states should increase as the internuclear spacing[13-16] decreases. As the interionic spacing within the X_2^- ion in the V_K center is

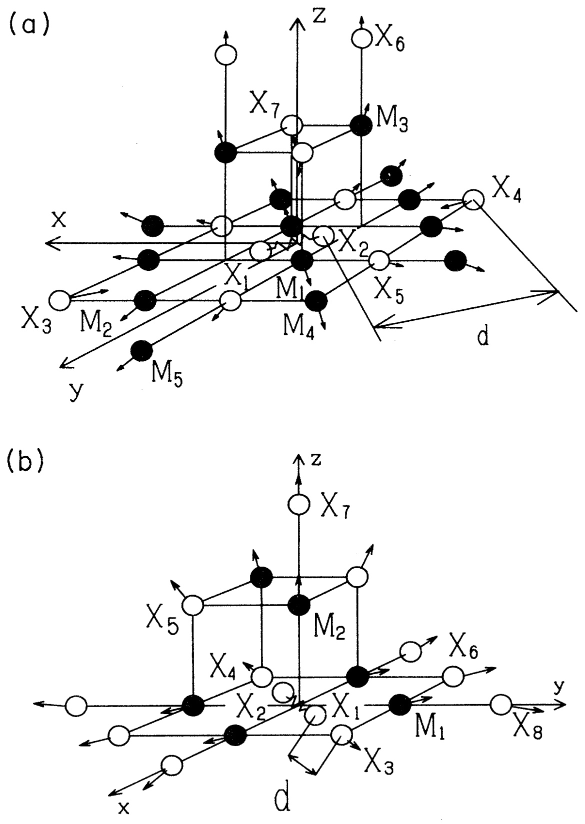

FIG. 1. Schematics of the V_K (a) and H centers (b). Open circles represent anions (X_i) and closed circles represent cations (M_i). Note that similar notations are used in Tables II and III. Part of the ions symmetrical with respect to the xy plane are not shown. Arrows indicate the directions of ionic displacements from ideal sites.

usually much larger than that in the corresponding H center,[17,18] it is naturally expected for the E_σ for the H center to be larger than for the V_K center. This tendency, though qualitative, certainly holds for chlorides, but is totally contradictory for iodides. In particular, in KI, E_σ for the V_K center is 3.1 eV,[12] whereas that for the H center is 2.7 eV.[19] The "reverse" ordering is also the case for RbI, as will be demonstrated later.

Deeper understanding of the nature of the optical transition of the X_2^- centers has become increasingly important in view of the recent extensive studies of the phenomena related to the exciton relaxation in halide crystals. The X_2^- molecular ion is now known as the hole component of the STE in metal halides. According to the present understanding of the structure of the relaxed STE, it consists of the X_2^- molecular ion and an excited electron. The former is displaced from the original STH configuration along a ⟨110⟩ direction upon relaxation after its recombination with an electron. The latter localizes around the adjacent anion vacancy.[20–23] The amount of the displacement of the X_2^- depends on the crystal; in a limiting case, the X_2^- is considered to be transferred to the next anion site creating the H center.[21,23,24] The optical properties of the STE's vary significantly[25–27] with the crystal chemical composition. These variations are attributed to different locations of the X_2^- molecular ion in the STE in different crystals. To substantiate the relation between the atomic structure of the STE's and their optical properties, it is highly desirable to establish the factors which determine the electronic optical transitions associated with the X_2^- molecular ions in different crystalline environments.

Self-trapped holes in alkali halides, V_K centers, have been extensively studied theoretically over the last twenty years, as reviewed in Refs. 4 and 16. In contrast, the number of theoretical studies of the H centers is much smaller and these were mostly concerned with the atomic structure of the center (see, for example, Ref. 15). Several Hartree-Fock calculations of H centers in LiCl, NaCl, and KCl were performed recently in the context of the study of the exciton self-trapping and decomposition into the primary defect pair.[28,29] However, they did not consider the optical absorption of these centers.

In this paper, we present the results of theoretical and experimental studies of the optical properties of the H and V_K centers in alkali halides. The calculations concerning the nature of electronic transitions in these centers were performed using Hartree-Fock embedded molecular cluster techniques. Some detailed optical measurements are made to check the theoretical predictions. The paper is organized as follows. In the next section we survey the experimental results on the optical properties of the V_K and H centers including our experimental data. The results of theoretical calculations are then presented, including a comparison of the methods employed in this study. Finally, based on the theoretical and experimental results, some general discussion is given.

II. EXPERIMENTAL METHODS AND RESULTS

Optical absorption spectra for the V_K and H centers in NaCl, KCl, KBr, KI, and RbI were measured using a conventional spectrophotometer (Shimazu UV-3100). Single crystals of pure specimens except iodides were purchased from Harshaw Chemical Co., and those of iodides from the University of Utah. Single crystals doped with NO_2^-, grown by the Kyropoulos method in a dry Ar atmosphere, were used for measuring the absorption spectra for the V_K centers. Specimens attached on a cold finger of a cryostat, which can be cooled to 5 K, were irradiated with electron pulses generated with a Febetron accelerator (HP-43710A) or by a 222 nm laser pulse generated with an Excimer laser (Lambda Physik EMG-201MSC). In order to obtain the dichroism of the absorption bands, we irradiated the specimens containing the V_K and H centers by polarized monochromatic light, generated by a system consisting of a Xe lamp, a monochromator and a polarizer, with the E vector parallel to the [110] direction, and obtained the difference in the optical absorption measured with light polarized along [110] and [$1\bar{1}0$].

The values of the peak energies and full width at half maxima (FWHM) of the absorption bands due to V_K and

TABLE I. Optical transition energies (in eV) of the V_K and H centers in alkali halides.

	V_K			H		
	E_σ	E_u	E_π	E_σ	E_π	E'
NaCl	3.27			3.89	2.38	4.89
	3.28[a]			3.83[b]		
KCl	3.39[c]		1.73, 1.59[c]	3.69		~4.8
				3.69[d]	2.38[3]	
RbCl	3.40			3.69		
NaBr	3.29	2.65	1.59			
	3.22[a]	2.58[a]	1.58, ~1.3[a]			
KBr	3.25	2.83	1.65	3.24	2.31	4.2, 4.7
				3.25[e]		
	3.22[c]		1.65~1.38[c]	3.26[f]		
RbBr				3.23		
NaI	2.87[f]	2.03[f]	1.41[f]			
KI	3.10[c]	2.12[c]	1.55, 1.08[c]	2.76	2.22	3.8, 4.4
				2.78[g]	2.23[g]	
RbI	3.06[f]	2.21[f]	1.56, ~1.11[f]	2.78	2.16	3.8, 4.4

[a] Values cited in Ref. 14.
[b] From Ref. 30.
[c] From Ref. 11.
[d] From Ref. 13.
[e] From Ref. 31.
[f] From Ref. 32.
[g] From Ref. 19.

H centers in the specimens studied are summarized in Table I, where experimental results obtained by other workers[30-32] are also shown. We use the same notations which have been used in the literature;[12-16] the peak energy of the most prominent band (Σ band) seen in the ultraviolet (UV) region is designated as E_σ, and that of the lowest energy band (Π band) around the visible and near-infrared (IR) region is designated as E_π.[33] The origin of the bands of the V_K center which appear in the energy range between the Σ and Π bands is not yet known,[11] and their peak energies are designated as E_u. All V_K and H centers are oriented along the ⟨110⟩ crystallographic direction, except the H center in NaCl, which is oriented along the ⟨111⟩ direction.

The most striking difference between the transition energies of the V_K and H centers is a significant blueshift of E_π for the H center, which is characteristic for all materials. As one can see in Table I, the E_π for the H centers are higher by 0.6–0.7 eV than those for the V_K centers. According to the dihalogen molecular model, this blueshift of the transition energy can be regarded as a consequence of the shorter interatomic spacing between the two halogens.[15,16] The same trend persists also for the UV absorption band in chlorides, which is traditionally assigned to the σ_u-σ_g hole transition; the peak energy E_σ of the H center has higher energy than that of the V_K center. However, E_σ of the H center in bromides is almost the same, whereas in iodides it is smaller, than that of the V_K center. These results suggest that the shift of the transition energies of the UV absorption band for the H centers with respect to those for the V_K centers is not determined just by the shorter interatomic spacing within the X_2^- molecular ion in the H center. The elucidation of the mechanism which causes the redshift of the E_σ of the H center in iodides is one of the main goals of the present study.

Apart from the variation of the peak energies of the absorption bands, other significant differences in the absorption spectra of the V_K and H centers have to be noted. The first feature is concerned with the difference in the shape of the UV absorption bands of the V_K and H centers. To demonstrate the difference, we compare in Figs. 2 and 3 the dichroic absorption spectra of the V_K and H centers in NaCl and KBr. In each figure, plot (a) shows the absorption spectrum obtained with unpolarized light induced by a pulsed-electron irradiation, and plot (b) shows the dichroic absorption spectra for the H center (solid curve) and for the V_K center (broken curve). As is clearly seen in the figures, the absorption band for the V_K center in the UV region is much wider than the corresponding band for the H center. In KBr, the V_K band is asymmetric; it has a long tail extending to the low-energy side. A recent study of the magnetic circular dichroism (MCD) of the V_K and H centers in KBr has shown that the UV band of the V_K center is a composite which consists of two different bands.[34,35] A similar conclusion was also obtained for NaCl.[36] Therefore, the V_K band in the UV region cannot be assigned simply to the σ_g-σ_u hole transition; other transitions have to be involved to explain the composite nature of the band. In contrast to the V_K band, the UV band of the H center can be well fitted to a single Gaussian. However, as is shown later theoretically, this band has a more compli-

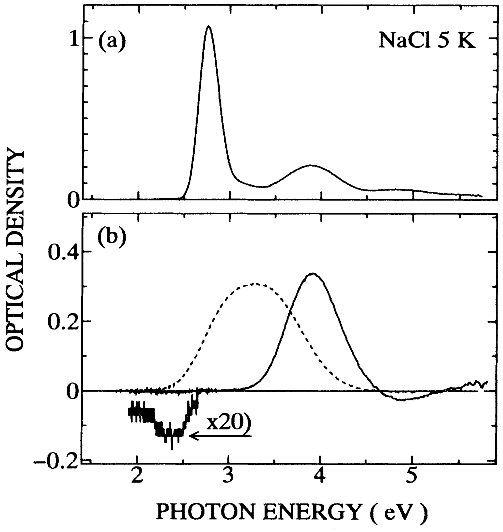

FIG. 2. (a) Optical absorption spectrum measured at 5 K of NaCl irradiated with 1 MeV electron pulse at the same temperature and (b) the dichroic spectrum of the electron-irradiated undoped (solid line) and NO_2^--doped (dashed line) NaCl obtained at 5 K after dichroic breaching along a ⟨110⟩ direction. The former denotes the dichroic spectrum of the H center and the latter that of the V_K center.

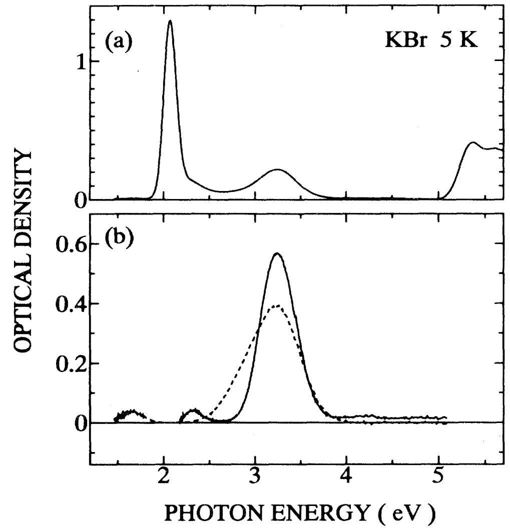

FIG. 3. (a) Optical absorption spectrum measured at 5 K of KBr irradiated with 1 MeV electron pulse at the same temperature and (b) the dichroic spectrum of the electron-irradiated undoped (solid line) and NO_2^--doped (dashed line) KBr obtained at 5 K after dichroic breaching along a ⟨110⟩ direction. The former denotes the dichroic spectrum of the H center and the latter that of the V_K center.

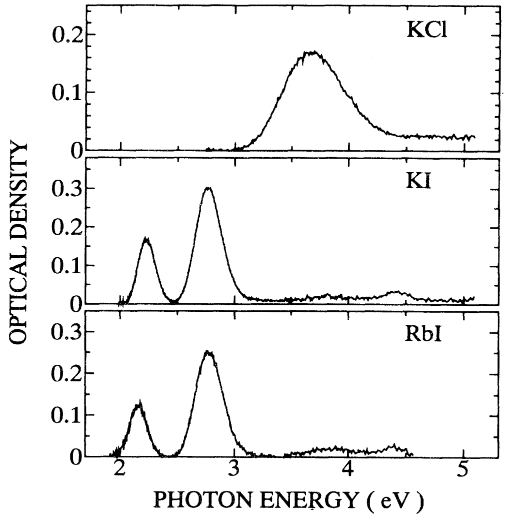

FIG. 4. Dichroic spectra for the H centers in KCl (top), KI (middle), and RbI (bottom).

cated nature than just the σ_g-σ_u hole transition within the X_2^- molecular ion.

Another feature which is present in the absorption spectra of the H centers is the high-energy absorption band (or tail). For instance, an absorption band at 4.8 eV can be definitely seen in the absorption spectrum of the H center in NaCl in Fig. 2(a). The result of the dichroic absorption measurement shows clearly that this band is Π polarized with respect to the molecular axis of the H center [see solid curve in Fig. 2(b)]. To substantiate that the 4.8 eV band is certainly due to the H center, we measured the degree of polarization of this band as a function of preferential bleaching time, and examined its relation to the degree of polarization of the main H band. It has been confirmed that the magnitude of the degree of polarization of the 4.8 eV band is a linear function of that of the 3.89 eV band, which is σ polarized. This proves that the 4.8 eV band is associated directly to the H center. The presence of the absorption bands located at higher energies than the H UV band is not specific to the H center in NaCl, which is oriented along a ⟨111⟩ direction, but is observed for the H centers in other crystals in which the H center is oriented along a ⟨110⟩ direction. In Fig. 3 we present the dichroic absorption spectrum of the H center in KBr. One can see a broad band located at the high-energy side of the main H band. The dichroic absorption spectra of the H centers in KCl, KI, and RbI are shown in Fig. 4. In KCl, similar to the case of KBr, the broad component, which is net σ polarized, is associated with the main H band. For the H centers in KI and RbI, distinct absorption bands are also clearly seen at the high-energy side of the main UV band. To prove that the high-energy band is due to the H center, the relation between the degree of polarization of the high-energy bands and that of the main H band was obtained for KCl, KI, and RbI. For each alkali halide, it was found that both are in proportion to each other, substantiating that the high-energy band is certainly due to the H center. Based on the positive correlation between the degree of polarizations of the H band and these high-energy bands, it can be concluded that the high-energy absorption bands are associated with the H center. On the other hand, for the V_K center, the corresponding bands at the high-energy side of the main UV band were not observed. Therefore, the high-energy absorption band appears to be a characteristic feature of the H center in alkali halides. The theoretical calculations presented in the next section predict that the H centers in alkali halides should have similar high-energy absorption bands.

III. THEORETICAL RESULTS

To gain a better understanding of the relation between the atomic structure of the V_K and H centers and their optical properties, we performed a theoretical study of these centers in NaCl, KCl, and KI. The main difficulties for the quantum-mechanical study of the V_K and H centers concern the fact that the ions comprising the X_2^- molecular ion are located in the low-symmetry interstitial lattice positions; they are polarized, have unusual populations, and in the case of the H center their distances from the nearest anions are much smaller than those in the perfect lattice. Therefore, the number of atoms treated quantum mechanically, the basis set employed, and the details of the lattice distortion play an important role in determining the electronic structure of the center. These as well as additional problems concerned with the calculations of optical absorption energies were discussed in a recent work.[37] In the present study, we combine the advantages of several different methods which are described in the next section.

A. Methods of calculation

Although the V_K and H centers are believed to be quasimolecular by nature, they strongly interact with the crystalline lattice. Therefore, an accurate description of this interaction is essential for this study. Three computational techniques, CLUSTER, ICECAP, and GAUSSIAN 92, based on a molecular cluster model and the Hartree-Fock-Roothaan method, were employed in this work. In the CLUSTER[38] and ICECAP[39] techniques, calculation of a crystal with a defect is made in the model of a molecular cluster embedded in the infinite lattice of polarizable ions. This technique proved to be successful in the previous studies of hole and exciton self-trapping and point defects in several halides and oxides.[4,37] In the GAUSSIAN 92 method, the crystal defect can be treated as a molecule in the electrostatic field of a finite array of point charges simulating the crystalline lattice. Since all three methods have been thoroughly described,[37,40] we present only those details of the calculations which are relevant to the present study.

The important feature of the CLUSTER and ICECAP methods is that they take into account the polarization of the lattice by the defect in a self-consistent manner. The matrix elements of a potential produced by the polarized ions in the dipole approximation are included in both diagonal and nondiagonal elements of the Fock matrix of the quantum cluster. Therefore, the polarization of the lattice directly affects the defect electronic structure and vice versa. Since the V_K center has a positive charge relative to the lattice, it attracts electrons, and the polarization potential produced by the polarized ions is negative. It is different for the ions carrying the hole than for the surrounding anions. This leads to an additional splitting of the electronic states and affects the optical absorption energies of the hole. Although the H center is neutral, it nevertheless produces a considerable elastic distortion of the lattice and polarization of surrounding ions.

In the ICECAP method, the lattice polarization is calculated using the shell model for polarizable ions and a Mott-Littleton calculation technique[41] realized in the HADES code.[37,39] In particular, the interactions between polarizable ions are treated using pair potentials. The pair potentials obtained in Ref. 42 were used in this study for the interactions between the ions in the lattice and those with the two anions forming the V_K and H centers. The ICECAP method was used mainly for the calculation of relaxed configurations of the V_K and H centers. The Bachelet, Hamann, and Schluter (BHS) pseudopotentials[43] were employed for the cores of Na, K, Cl, and I ions. The optimized basis sets for Na, K, and Cl ions have been published elsewhere.[44] The valence portions of the Huzinaga basis set[45] for the I ion were split into three s and p orbitals and augmented with one additional s and p Gaussians with exponents 0.033 and 0.030, respectively. The size of the quantum cluster in these calculations did not exceed 4 anions and 14 nearest-neighbor cations, which is enough for the completely localized hole states. Optical transition energies can be calculated with the ICECAP method using the difference between the self-consistently calculated total energies of the ground and excited states of the defects. This method is effective for strongly localized states. In order to study more delocalized hole states characteristic for the H center, we used the CLUSTER code which allows us to treat a much larger number of ions quantum mechanically and to calculate optical transitions using a configuration interaction technique.

In the CLUSTER method, the lattice polarization is treated in a polarizable ion model and Mott-Littleton approximation as described in Refs. 38 and 46. The ionic polarizabilities and crystal dielectric constants were taken from Ref. 47. The electronic structure of the system is calculated using the unrestricted Hartree-Fock method within the approximation of intermediate neglect of differential overlap (INDO).[48,49] In this approximation only pair interactions between atoms are included and part of the Fock matrix is calculated using numerical parameters. In the calculations of the NaCl and KCl crystals we employed the set of parameters which were published in Ref. 49. The parameters for the K and I ions were optimized in this work in order to reproduce the characteristics of the KI perfect crystal as well as those of KI and I_2^- molecules. The calculations of the band structure of the perfect KI crystal were made using a large unit cell (LUC) method[50] for the unit cell $K_{32}I_{32}$. This allows us to take into account 8 **k** points of the Brillouin zone. The lattice constant a of KI obtained in our calculations is equal to 6.7 a.u. (6.676 is the experimental value[9]). The optical absorption energies for the V_K and H centers were calculated using a configuration interaction technique including single excitations in the whole space of valence states[51] (CIS). This technique is discussed in more detail in the next section. The band gap for KI calculated using this technique is equal to 5.9 eV, which is slightly smaller than the experimental value of 6.3 eV.[9] Boundary effects in the quantum cluster embedded in the lattice can affect the displacements of ions surrounding the defect. In order to check the importance of this effect we also made calculations using periodic boundary conditions for a unit cell $K_{32}I_{32}$. Since the unit cell should be neutral in the case of the V_K center, it included an Ag^+ ion in one of the cation sites. The latter is known as a good electron-trapping center and is often used in hole studies. The INDO parameters for this ion were taken from the previous calculations[52] of the hole trapping in AgCl. In the triplet state of the system the excited electron becomes completely localized in the Ag^0 state where the hole is delocalized by the unit cell if no special lattice relaxation is included.

To compare the optical transitions obtained using an approximation CLUSTER method with the results of a more accurate *ab initio* technique, we employed the GAUSSIAN 92 code.[40] Comparison of the results of our previous calculations for the geometry of the neutral H center in alkali chlorides obtained using the ICECAP technique and those obtained using the DICAP code, which does not include the full polarization of the lattice outside the cluster, demonstrated good agreement of the displacements of ions neighboring the Cl$_2^-$.[44] Therefore, the calculations of the optical transitions were made for the H center in KCl and KI using the atomic positions obtained in the ICECAP calculations. The quantum cluster included four Cl(1) ions and 38 nearest-neighbor cations which were situated in the center of the crystalline block of $9 \times 9 \times 9$ ions located in the perfect lattice sites. These point ions produced the electrostatic potential which simulated that of the infinite lattice. Six cations nearest to the X_2^- molecular ion [cations M_1 and M_2 in Fig. 1(a)] had a basis set, whereas all other cations included in the calculations were treated as bare pseudopotentials. Due to the program restrictions, different sets of pseudopotentials were employed in the ICECAP and GAUSSIAN 92 calculations: the semilocal norm-conserving pseudopotentials of Hay and Wadt[53] were used to describe the cores of K, Cl, and I ions. Although these pseudopotentials are slightly different from the BHS pseudopotentials used in the ICECAP calculations, we believe that the use of extended basis sets of the same quality makes the techniques complementary. The standard basis sets optimized for the K, Cl, and I atoms with the pseudopotentials[53] included 3*s* and 3*p* Gaussians and were augmented by diffuse *s* and *p* orbitals with the exponents equal to 0.067 and 0.085 for the Cl ion and 0.045 and 0.035 for the I ion, respectively. The optical transition energies were calculated using the CIS technique.[51]

B. Results of calculations

1. Geometric structure and lattice relaxation

The atomic and electronic structures of the V_K and H centers were calculated using both the ICECAP and CLUSTER codes. In the ICECAP method the quantum clusters used for the calculations of the V_K and H centers in NaCl and KCl were $M_{10}\mathrm{Cl}_4$ and $M_{14}\mathrm{Cl}_4$, correspondingly (where M=Na, K). For KI the calculations were made for the quantum cluster I_2^- embedded in the polarizable lattice of classical ions. With the CLUSTER technique, both the cluster model accounting for the lattice polarization and the periodic LUC model were employed; $M_{24}X_{24}$ and $M_{38}X_{38}$ quantum clusters for the V_K and H centers and $M_{32}X_{32}$ unit cell were used in these studies (where X=Cl,I). The three techniques gave similar qualitative results for displacements of ions nearest to the X_2^- ion carrying the hole and the difference in the ionic displacements for completely relaxed states did not exceed $0.02a$ (where a is the interionic distance). The directions of ionic displacements are shown in Figs. 1(a) and 1(b) by arrows. The coordinates of several ions with the most significant displacements obtained using the ICECAP code are presented in Tables II and III. The ionic displacements are qualitatively similar for the V_K centers in all crystals considered; therefore, as a characteristic example we presented the coordinates only for this center in KCl. Our displacements are close to those obtained by Cade, Stoneham, and Tasker in atomistic simulations of the V_K centers in all alkali halides using the CASCADE code[54] and are presented in that paper. The H centers in NaCl and KCl (KI) are oriented along different axes and it is instructive to present data for both of them. Numerical data characterizing the geometrical structure of the center are presented in Table III. These are the interatomic separations within the free X_2^- molecule, R_e^f, ion and that in the V_K and H centers, R_e, and the distances between the cores of one of the ions forming the X_2^- and the nearest-neighbor anion along the $\langle 110 \rangle$ axis, d.

TABLE II. Coordinates of ions in V_K center in KCl in units of interionic distance a ($a = 3.116$ Å). The system of coordinates and ion notations is given in Fig. 1(a). The displacements of other ions in the crystal are less than $0.01a$.

Ion	Coordinates
X_1	0.308;0.308;0.00
X_3	1.48;1.48;0.00
X_5	1.55;−0.50;0.00
X_6	0.50;−0.50;0.98
X_7	0.50;0.50;2.02
M_1	0.617;−0.617;0.00
M_2	1.56;0.48;0.00
M_3	0.50;0.50;1.06
M_4	1.52;−1.52;0.00
M_5	2.53;−0.51;0.00

The data presented in Tables II and III demonstrate clearly that the X_2^- molecular ion in the H center is compressed compared to the free X_2^- molecule or the V_K center. This results mainly from the large gradient of the crystalline potential near the anion site and the short-range repulsion from surrounding ions. In particular, the distances between the anions forming the X_2^- molecule ion and the surrounding anions are much smaller for the H center than for the V_K center. These geometrical features are thoroughly discussed in the recent paper[10] in the context of the interpretation of the experimentally measured Raman spectra of H carriers in several alkali halides. The new results of the present study are concerned with the difference in the electronic structure of both centers, and the nature of related optical transitions which come out from their geometry. Quantitatively, these differences depend on the method of calculation, the quality of the basis sets, the treatment of the surrounding lattice, and other factors. However, the

TABLE III. Coordinates of ions in the H center in NaCl and KCl in units of interionic distance a ($a = 2.789$ Å for NaCl and $a = 3.116$ Å for KCl). The system of coordinates and ion notations is given in Fig. 1(b). The displacements of other ions in the crystal are less than $0.01a$.

Ion	Coordinates NaCl	 KCl
X_1	0.26;0.26;0.26	0.289;0.289;0.00
X_3	1.03;1.03;−0.02	1.02;1.02;0.00
X_5	1.04;−0.02;1.04	1.01;−0.01;0.99
X_6	1.01;−1.01;0.00	1.03;−1.03;0.00
X_7	2.04;0.00;0.00	2.05;0.00;0.00
M_1	1.10;−0.04;−0.04	1.13;−0.07;0.00
M_2	−0.04;−0.04;1.10	0.00;0.00;0.96

qualitative features are general and can be summarized as follows.

2. *One-electron picture*

In the molecular orbital linear combination of atomic orbitals Hartree-Fock calculation of the quantum cluster, one obtains the discrete spectrum of one-electron states localized within the cluster. The wave functions of these states are linear combinations of the atomic orbitals (AO's) centered on the two ions constituting the X_2^- and the nearest cations and anions. However, the character of these states in the two centers is different. In the V_K center, the admixture of the orbitals centered on surrounding ions into the "molecular" states produced by the AO's of the X_2^- ion is small compared to the H center. This results from two main factors: (i) relatively large interionic separation between the X_2^- and other anions (see, for example, Table I) and (ii) the difference in the matrix elements of the polarization potential, which are much smaller on the surrounding anions than on the ions constituting the X_2^- ion and additionally split the corresponding states. Essentially, the V_K center can be well described in these terms as a "molecular" center. In the H center, the distances between the ions of the X_2^- and nearest anions are comparable. This leads to the formation of one-electron states comprised of the atomic orbitals of the X_2^- and surrounding anions with comparable coefficients. The character of each particular state is determined by its symmetry. Consider, for example, the σ_g states. In the case where the center is oriented along the $\langle 110\rangle$ axis, these are formed mainly by the atomic orbitals of the X_2^- and the two nearest anions along this axis (see Fig. 1). Two possible bonding combinations of the atomic orbitals are shown in Fig. 5. There is also a series of the π states which are linear combinations of the AO's of the X_2^- and the anions in the (100) plane and in two parallel planes (for the z-type states).

Optical transitions related to the topic of our study take place from the double-occupied one-electron states described above to the single-occupied σ_u hole state, and from that state to the unoccupied states formed by the surrounding cations. In the V_K center, the σ_u state is almost the X_2^- molecular state, whereas in the H center it is more strongly delocalized over at least four anions.

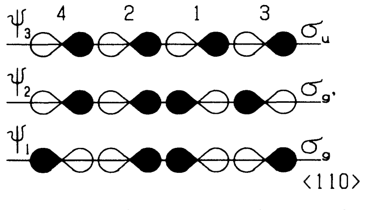

FIG. 5. Schematic of the two double-occupied σ_g and one single-occupied σ_u electronic states of the V_K and H centers representing three possible bonding combinations of the p atomic orbitals of four nearest anions along the same axis. Numbers 1–4 correspond to the anions in Fig. 1 and Tables II and III. The lowest is the completely bonding state; the next state is bonding between ions 1 and 2 and antibonding between ions 1–2 and 2–4; the upper state is the completely antibonding electronic state.

To discuss different features of the optical absorption bands for the two centers, we will first use the simplified model based on the one-electron picture of the electron transitions. The energy of the electron transition between two molecular orbital states μ and a can be written as

$$\varepsilon_{\mu a}=\varepsilon_\mu-\varepsilon_a-(\mu\mu|aa)+(\mu a|\mu a)\ , \tag{1}$$

where ε_μ and ε_a are the one-electron energies of these states, and $(\mu\mu|aa)$ and $(\mu a|\mu a)$ are the Coulomb and exchange integrals, respectively, calculated for the molecular orbitals. In this model one can qualitatively discuss the one-electron transitions between different electronic states. In these terms the qualitative difference between the transitions within the quantum clusters with the V_K and H centers results first from the difference in the intramolecular distances within the X_2^- molecular ion, R_e. In the H center, where R_e is much smaller than in the V_K center, molecularlike Σ and Π-polarized allowed transitions have much higher energies than corresponding transitions in the V_K center. In particular, the energy of the $\sigma_g\rightarrow\sigma_u$ transition (in notations of electron transfer) calculated using Eq. (1) in the CLUSTER code for the H center in KCl in 4.52 eV, whereas the energy of the similar transition in the V_K center is only 3.3 eV. The former value is close to the interpolation of the Hartree-Fock calculation of the Cl_2^- molecular ion by Gilbert and Wahl[17] as discussed by Stoneham in Ref. 15, and is much larger than the experimentally observed transition energy. At the same time the energy obtained for the V_K center is much closer to the experimentally observed 3.4 eV. However, the model based on the transitions between the one-electronic occupied and unoccupied states is often oversimplified, as it does not take into account the relaxation of the system wave function after the electronic transition.

3. *Configuration interaction*

To obtain more accurate wave functions of the excited states and transition energies, one can consider a linear combination of the many-electron wave functions (determinants) corresponding to all such transitions in the system and take into account the interaction between the different excited states. The coefficients in this linear combination and the transition energies are normalized eigenvectors and eigenvalues which can be deduced from the Hamiltonian matrix.

$$\langle\Psi_{\mu a}|H|\Psi_{\nu b}\rangle=[E_{\mathrm{HF}}+\varepsilon_a-\varepsilon_\mu]\delta_{\mu\nu}\delta_{ab}-(\mu a|\nu b)\ , \tag{2}$$

where H is the Hamiltonian and E_{HF} is the Hartree-Fock total energy of the ground state. This is the essence of the CIS technique described in Ref. 51. Solving the CIS equations one obtains the whole spectrum of excitations for the electrons included in the quantum cluster. The latter may consist of several hundred or even thousand transitions, dependent on the basis set employed in the calculations. Due to the quasimolecular nature and the relatively high symmetry of the V_K and H centers, the assignment of the lowest calculated transitions can be easily made by their polarization and transition matrix elements. In our remaining discussion we will mainly focus on the lowest allowed π and σ polarized transitions. Transitions with higher energies are discussed in the next section.

The characteristic optical absorption energies calculated for the V_K and H centers in NaCl, KCl, and KI using the CIS method and the CLUSTER code are presented in Table IV. Several general features can be noted. First, the Π polarized transitions in the H center have higher energies than in the V_K center. This results from the smaller R_e value. Second, the energy of the lowest σ-polarized transition in the H center in NaCl is much larger, in KCl is close, and in KI is smaller than the energy of the corresponding σ transition in the V_K center. This results from the geometrical structure of the center and the interaction of the different electronic configurations. Finally, there are several transitions with much higher energies than those traditionally attributed to the V_K and H centers and which also belong to these centers.

Let us now consider in more detail the nature of the first two features. Although the CIS calculations in our study involve several hundred determinants, in many cases due to the symmetry and difference in energies only few of them mix in a particular excited state with appreciable coefficients. This allows us to use a simplified model for discussion of the Σ-polarized transitions in the H center in KCl and KI, in which the states shown in Fig. 5 play the most significant role. The wave functions of the two excited states of this center resulting from the electron transitions from Ψ_1 and Ψ_2 to Ψ_3 can be approximately written as

$$\Psi^1 = c_1\Psi_{13} + c_2\Psi_{23} \ , \tag{3}$$

$$\Psi^2 = c_3\Psi_{13} - c_4\Psi_{23} \ , \tag{4}$$

where $\Psi_{\mu 3}$ is a Slater determinant of the system ground state in which the unoccupied molecular orbital 3 is substituted by one of the occupied orbitals $\mu = 1,2$ (see Fig. 5). The absolute values of the coefficients c_1 and c_4, and c_2 and c_3 in this particular case, are close to each other because of the small admixture of other transitions. For instance, in the CLUSTER calculations of the H center in KCl these coefficients are equal to 0.72 and 0.68. Such a large mixing of the two transitions is accompanied by a strong splitting of the energies of the one-electron transitions. Prior to the interaction between the configurations being taken into account, the transition energies calculated using Eq. (1) were 4.52 and 4.62 eV for $\varepsilon_{2\rightarrow 3}$ and $\varepsilon_{1\rightarrow 3}$, respectively. The transition energies calculated for the H center using the CIS technique are 3.74 and 5.5 eV. Similarly, for the H center in KI the same transitions were initially 5.14 and 3.15 eV. Note that in this case the transition from the more delocalized Ψ_2 state has initially much smaller energy than that from the completely bonding Ψ_1 state. After solving the CIS equations one obtains 2.90 eV for the lowest σ-polarized transition and 5.4 eV for the higher one. The weight of the 2→3 transition (the coefficient c_2 before the corresponding determinant) in the wave function of the excited state (3) is 0.94 in the CLUSTER calculation. Qualitatively, one can say that due to this admixture, the high energy of the one-electron σ-polarized transition is shifted to smaller energies.

To check dependence of the results on the method of calculation and the basis set we have calculated optical transitions for the H center in KCl and KI using the GAUSSIAN 92 computer code and the CIS technique. The initial atomic configurations of the centers were the same as those obtained in the ICECAP calculations. Variation of the atomic coordinates has shown that these configurations are also close to the energy minimum in the GAUSSIAN 92 method, though difference in the ionic displacements occurred due to the absence of short-range repulsion between the ions on the border of the cluster and neighboring lattice. The optical transition energies

TABLE IV. Geometrical parameters (in Å) and optical absorption energies (in eV) for the V_K and H centers in NaCl, KCl, and KI. Polarizations of the UV transitions are given in parentheses.

				Optical absorption energies		
Crystal	Defect	R_e[a]	d	E_σ	E_π	E_{UV}
NaCl	V_K	2.74	4.5	3.1	1.3	4.0 (Π[b]), 4.1 (Σ[b])
	H	2.52	3.2	3.7	1.7	5.4 (Π), 5.6 (Σ)
KCl	V_K	2.73	5.1	3.4	1.4	4.1 (Π) 4.2 (Σ)
	H	2.60	3.3	3.7	1.9	4.2 (Π), 5.3 (Π), 5.5 (Σ)
				3.7[c]	2.3[c]	6.2[c] (Σ)
KI	V_K	3.55	5.5	3.2	1.4	4.0 (Π) 4.1 (Σ)
	H	3.23	3.5	2.9	2.4	4.4 (Π), 4.6 (Π), 4.7 (Σ) 5.4 (Σ)
				2.5[c]	2.2[c]	5.9[c] (Σ)

[a] The equilibrium distances in the Cl_2^- and I_2^- molecules were calculated to be 2.71 and 3.28 Å, correspondingly.

[b] Predominant polarization.

[c] The results of GAUSSIAN 92 calculations.

calculated using the GAUSSIAN 92 are presented in Table IV. They are close to those obtained using the CLUSTER code.

More appropriate and a visual way of presentation of the electron or hole distribution within the defect is based on the analysis of spin density. This is the difference between the total electron densities for the electrons with spins up and down. The results of calculations of the spin-density distribution of the hole demonstrated qualitatively similar features in both the CLUSTER and GAUSSIAN 92 techniques. Sections of the spin densities for the ground state and two σ-polarized excited states of the H center in KCl and KI obtained in the GAUSSIAN 92 calculation are presented in Figs. 6 and 7. In these figures (a) corresponds to the ground state, (b) corresponds to the final state of the lowest Σ-polarized transitions, whereas (c) corresponds to the higher Σ transition. Note that in both cases considered above, i.e., in the H center in KCl and KI, the hole in the ground state is almost completely localized on the X_2^- molecular ion in the antibonding state, although the spin density on outer anions is much higher in KI than in KCl. This results from the fact that the R_e and d values (see Table IV) are very close in KI. Considerable redistribution of the hole to outer anions in the excited states can be clearly seen. Nevertheless, for the first σ-polarized transition the hole is still predominantly localized within the X_2^- molecular ion in both KCl and KI. Thus, this transition can be qualitatively described as "intramolecular." In contrast, the higher Σ-polarized transition is accompanied by a strong hole redistribution on the outer anions, especially in KI. We should stress, however, that although the qualitative effect of the hole redistribution in the excited state persists in all calculations, quantitatively it depends on the basis set and the method of calculation. In particular, in the CLUSTER calculations of KCl for the first Σ-polarized transition, almost 0.7 of the hole is still localized on ions 1 and 2 constituting the X_2^- molecular ion. In the case of the H center in KI the distribution of the hole in this

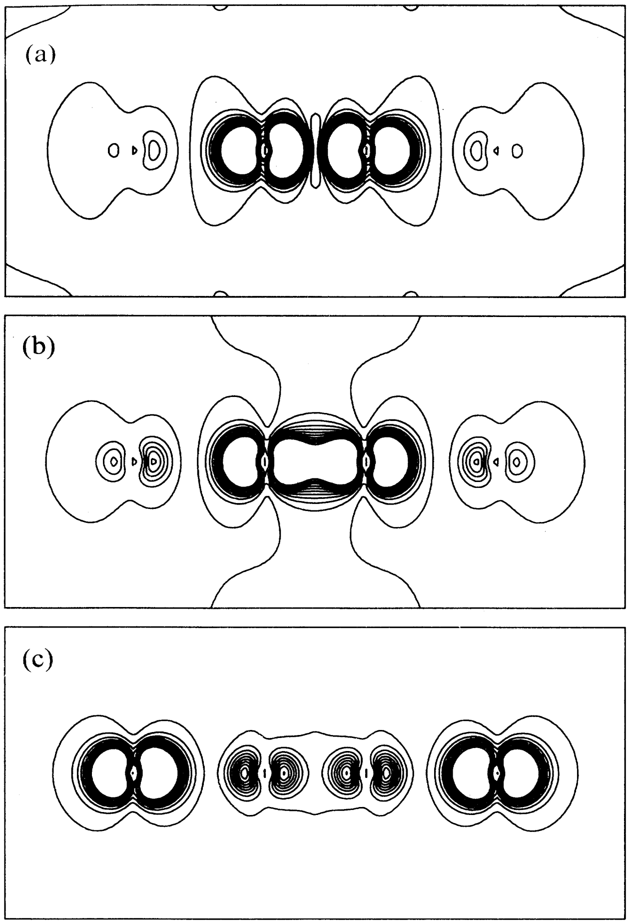

FIG. 6. The spin density plots in the xy plane for the H center in KCl: (a) the ground state; (b) after the lowest Σ-polarized electronic transition; (c) after the far-UV Σ-polarized transition. The wave functions of excited states (b) and (c) can be approximately presented by Eqs. (3) and (4) in the text and correspond to the hole transfer to states 1 and 2 in Fig. 5. Note the delocalization of state (c). The isolines are drawn in the logarithmic scale; the smallest density is equal to 10^{-5} and progressively increases with the coefficient equal to 8.

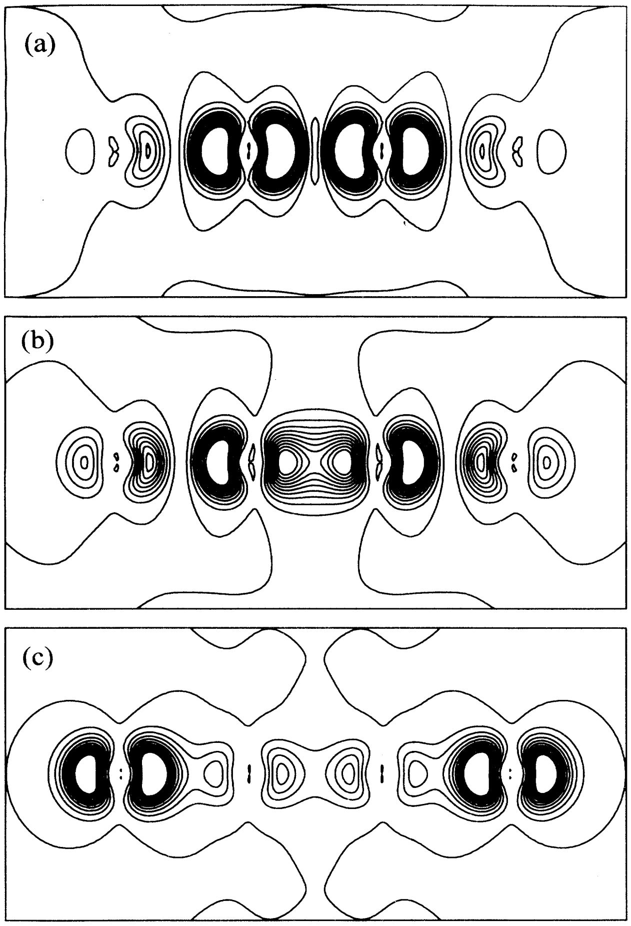

FIG. 7. The spin-density plots for the H center in KCl in the xy plane. See Fig. 6 for notations.

transition is more uniform an only about 0.5 of the spin density is localized on ions 1 and 2.

Due to the ⟨110⟩ orientation of the H center in KCl and KI, the configuration interaction affects the Σ-polarized transitions stronger than the Π. This results mainly from the smaller overlap between the p orbitals. The energies of the Π-polarized transitions are larger in the H center than those in the V_K center mostly due to the smaller intramolecular distance within the X_2^- molecular ion. The situation is more complicated, however, in the H center in NaCl, which is oriented along the ⟨111⟩ axis. Due to the lower symmetry, the number of mixing configurations in this case is larger, although the qualitative features of the transitions remain the same.

Similar analysis of the optical transitions in the V_K center in NaCl, KCl, and KI reveals much stronger localization of the spin density of the hole in the ground state and after the lowest Π- and Σ-polarized transitions than that in the H center. The fact that the hole states in the V_K center are localized stronger than in the H center is connected with the difference in geometrical structure of the two centers (see Tables II and III). This is also reflected in the much better agreement of the energies of the optical transitions within the free X_2^- molecule with those in the V_K center than in the H center.

We should note that because of the lattice stress around the H center, the transition energies strongly depend on the atomic configuration of the center, i.e., the displacements of surrounding ions. The basis set of atomic orbitals may also affect the results of calculations. Therefore, it is important to check the reliability of our qualitative conclusions using different sizes of quantum clusters and different calculation techniques. The former can be accomplished at present only using the CLUSTER code. Since in KI the H center seems to be more delocalized than in KCl or NaCl, we performed the calculations for this center in the clusters $K_{14}I_4$, $K_{14}I_{10}$, and $K_{38}I_{38}$. Due to the different number of electrons involved in these three cases, we obtained the difference in the values of transition energies within 0.15 eV. All qualitative conclusions, though, remained the same.

4. Far-UV part of the absorption spectra

Both CLUSTER and GAUSSIAN 92 calculations have demonstrated that along with the Σ- and Π-polarized transitions in the energy range which is traditionally attributed to the V_K and H centers, there are series of transitions with higher energies which are also due to the electron excitations associated with the defect. For convenience, we will further call them UV transitions. The calculated energies, E', of these transitions in the energy range less than 6.0 eV are presented in Table IV. These transitions originate from the σ-like states involving the atomic orbitals of the central X_2^- molecular ion and of the nearest-neighbor anions. For the Σ- and part of the Π-polarized transitions these are mainly the anions X_3 and X_4 (see Table II) located within the plane of the X_2^- molecular ion. For the Π_z-polarized transitions the AO's of anions X_5 (see Table II) also contribute to the wave functions. Such transitions, differing only in energy and value of the transition matrix element, exist for all the defects studied. Because of the more delocalized wave functions, these transitions have the dipole transition matrix elements several times smaller that those for the Σ- and Π-polarized transitions discussed above. Besides, in this energy range there are also the "ionizing" transitions with an appreciable transition matrix element originating from the single occupied defect state to the unoccupied states due to the nearest-neighbor cations.

To compare the theoretical predictions with the experimental spectra, it is important to understand whether the experimentally observed absorption bands are due to the electron transitions from the local or from the quasilocal (resonant) electronic states. The optical transitions from the quasilocal states generally have much smaller oscillator strength than the optical transitions between the well-localized local states (see, for example, Ref. 55). Since the defect wave functions are localized within the cluster due to the molecular nature of the calculation, the quasilocal states cannot be easily distinguished from the local states. Especially, one can expect the quasilocal states to be more delocalized than can be predicted in our calculations due to the strong interaction with the band states, and their energies to overlap with the valence or conduction crystal bands. This may affect both transition energies and matrix elements.

To classify the defect optical transitions, we have calculated the position of the defect ground state, E_h, of the V_K and H centers with respect to the optical excitation from the top of the valence band. This is the lower limit of the "optical" energy for the hole delocalization, which determines an approximate energy range within which the optical electronic transitions are originated from the local states. It can be determined as $E_h = E_g - A$ from the energy cycle involving the interband excitation with further electron trapping on the defect center, where E_g is the optical band gap and A is the Franck-Condon electron affinity of the particular center. The A values calculated for the H centers using the ICECAP code are equal to 2.6 eV for NaCl, 1.9 eV for KCl, and 2.2 eV for KI. Using the experimental values for E_g, one obtains the E_h values equal to about 5, 6.7, and 4.1 eV in these crystals, respectively. Alternatively, one can calculate the energies of the electron transitions from the delocalized "band" states to the single-occupied σ_u hole state in a large quantum cluster. In particular, the electron transitions from the most delocalized "band" states to the hole state, calculated using the CIS and the CLUSTER code in the cluster $K_{14}Cl_{14}$, have an edge at 7.1 eV. Similar calculation for the cluster $K_{38}I_{38}$ simulating the H center in KI gives 4.7 eV. The about 0.5 eV difference in the E_h values obtained by different methods is caused by the fact that all the one-electron states, even in relatively large clusters are perturbed by the defect. However, a reasonable agreement between the results suggests that the values of E_h given above are realistic. In a similar calculation for the "vertical" electron affinity of the V_K center in KCl we obtained the value of A equal to 5.1 eV. This suggests that the hole state in this case is located about 3.5 eV above the top of the valence band.

As was shown in our experimental study given in Sec. II, the transitions in the far-UV energy region were indeed observed in some crystals as a long tail with much lower intensity than the "main" σ band, whereas in others, as distinct absorption bands. Comparison of the values of E_h with the theoretically calculated (see Table IV) and the experimentally observed positions, E', of the maxima of the high-energy bands (see Table I) suggests that most of these transitions in the *H* center in NaCl and KCl and part of them in KI are originated from the local states. The results for the *H* centers presented in Table IV are in reasonable agreement with the experimentally observed transitions. At the same time, the UV transitions in the V_K centers most likely originate from the quasilocal states in the valence band. Therefore, they should have much smaller probabilities and their energies determined theoretically are less reliable as they can be affected by the interaction with the band states.

IV. SUMMARY AND CONCLUSIONS

Although the intrinsic X_2^- hole centers in alkali halides, the V_K and *H* centers, are certainly among the best studied point defects in ionic crystals, some of the fundamental optical properties of these centers still remain unclear. We compared the experimentally measured and theoretically calculated absorption spectra of these centers in several alkali halides. The experimental results reveal that the π_g-σ_u transition energies are systematically larger for the *H* centers than for the V_K centers, in qualitative agreement with the molecular dihalogen model of both centers and the general understanding that the halogen-halogen distance for the *H* center is smaller than that in the V_K center. However, the σ_g-σ_u transition energies for the *H* centers are found to be larger than those for the V_K center only in chlorides, nearly the same in bromides, and smaller in iodides. These results suggest that the shift of the transition energies of the UV absorption band for the *H* centers with respect to those for the V_K centers is not determined just by the shorter interatomic spacing within the X_2^- molecular ion in the *H* center.

Theoretically, it is shown that correct representation of the wave function of the excited defect states including the interaction of the appropriate excited electronic configurations is essential for the understanding of the nature of the defect electronic transitions. It appears that this effect is particularly important for the hole centers which cause strong distortion of the surrounding lattice. The account for the interaction between the intramolecular one-electron transitions within the halogen molecular ion and these transitions from the surrounding anions to the single occupied hole state allowed us to explain the relative transition energies for the *H* center with respect to the V_K center. The analysis of the spin density in the excited states of the *H* and V_K centers demonstrated the considerable delocalization of these states over several anions surrounding the X_2^- molecular ion. The existence of the optical transitions of the *H* center in the ultraviolet range higher than the σ_g-σ_u transition energy has been shown theoretically and confirmed experimentally.

However, some optical properties of the V_K centers cannot be explained in the present model, in particular, that the σ_g-σ_u optical absorption band of the V_K centers is much broader than that of the *H* centers, and the existence of the E_u band. The effect that is not taken into account in the present calculations is that of the electron-electron correlation. Preliminary calculations show that the energy of the electron correlation differs strongly for the ground and excited states of the V_K center, and that the electronic transitions from the delocalized states for the center may have much smaller energies than calculated in this study. Work in this direction is in progress.

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[*] Present address: The Royal Institution of Great Britain, 21 Albemarle St., London W1X 4BS, U.K.

[†] Permanent address: Institute of Chemical Physics, University of Latvia, 19 Rainis Blvd., Riga LV1098, Latvia.

[1] W. Kanzig, Phys. Rev. **99**, 1890 (1955); T. G. Kastner and W. Kanzig, J. Phys. Chem. Solids **3**, 178 (1957).

[2] A. K. S. Song and R. T. Williams, in *Self-Trapped Excitons*, edited by M. Cardona, Springer Series in Solid-State Sciences Vol. 105 (Springer, Berlin, 1993).

[3] N. F. Mott and A. M. Stoneham, J. Phys. C **10**, 3391 (1977).

[4] A. L. Shluger and A. M. Stoneham, J. Phys. Condens. Matter **5**, 3049 (1993).

[5] W. Kanzig and T. O. Woodruff, J. Phys. Chem. Solids **9**, 70 (1958).

[6] N. Itoh, Adv. Phys. **31**, 491 (1982).

[7] N. Itoh and K. Tanimura, J. Phys. Chem. Solids **51**, 717 (1990).

[8] M. L. Dakss and R. L. Mieher, Phys. Rev. Lett. **18**, 1056 (1968); Phys. Rev. **187**, 1053 (1969).

[9] Ch. B. Lushchik and A. Ch. Lushchik, *Decay of Electronic Excitations with Defect Formation in Solids* (Nauka, Moscow, 1989).

[10] T. Suzuki, K. Tanimura, and N. Itoh, Phys. Rev. B **48**, 9298 (1993).

[11] C. J. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. **111**, 1235 (1958); C. J. Delbezq, W. Hayes, and P. H. Yuster, *ibid.* **121**, 1043 (1961).

[12] A. N. Jette, T. L. Gilbert, and T. P. Das, Phys. Rev. **184**, 884 (1969).

[13] C. J. Delbecq, J. L. Kolpus, E. U. Yasaitis, and P. H. Yuster, Phys. Rev. **154**, 866 (1967).

[14] D. Schoemaker, Phys. Rev. B **7**, 786 (1973).

[15] A. M. Stoneham, *Theory of Defects in Solids* (Oxford University Press, Oxford, 1975).

[16] M. N. Kabler, in *Point Defects in Solids,* edtied by J. H. Crawford, Jr. and L. M. Slifkin (Plenum, New York, 1972), p. 327.

[17] T. L. Gilbert and A. C. Wahl, J. Chem. Phys. **55**, 5249 (1971).

[18] G. J. Dienes, R. D. Hatcher, and R. Smolouchowski, Phys. Rev. **157**, 692 (1967).

[19] J. D. Konitzer and H. N. Hersh, J. Phys. Chem. Solids **27**, 771 (1966).

[20] D. Block, A. Wasiela, and Y. Merle d'Aubigne, J. Phys. C **11**, 4101 (1978).

[21] G. B. Brunet, C. H. Leung, and K. S. Song, Solid State Commun. **53**, 607 (1985); C. H. Leung, G. B. Brunet, and K. S. Song, J. Phys. C **18**, 4459 (1985).

[22] A. L. Shluger, R. W. Grimes, and C. R. A. Catlow, J. Phys. Condens. Matter **3**, 3125 (1991).

[23] K. Tanimura, T. Suzuki, and N. Itoh, Phys. Rev. Lett. **68**, 635 (1992); T. Suzuki, K. Tanimura, and N. Itoh, Phys. Rev. B **49**, 7233 (1994).

[24] K. Kan'no, K. Tanaka, and T. Hayashi, Rev. Solid State Sci. **4**, 383 (1990).

[25] R. T. Williams and M. N. Kabler, Phys. Rev. B **4**, 1897 (1974).

[26] K. Tanimura and N. Itoh, Phys. Rev. B **45**, 1432 (1992).

[27] K. Edamatsu, M. Sumita, S. Hirota, and M. Hirai, Phys. Rev. B **47**, 6747 (1993).

[28] A. L. Shluger, N. Itoh, V. E. Puchin, and E. N. Heifets, Phys. Rev. B **44**, 1499 (1991),

[29] V. E. Puchin, A. L. Shluger, K. Tanimura, and N. Itoh, Phys. Rev. B **47**, 6226 (1993).

[30] M. Ikezawa, K. Shirahata, and T. Kojima, Sci. Rep. Tohoku Univ. I **L11**, 45 (1969).

[31] K. Bachman and W. Känzig, Phys. Konden. Mat. **7**, 284 (1968).

[32] R. B. Murray and F. J. Keller, Phys. Rev. **153**, 993 (1967).

[33] The absorption band of the V_K center in the visible region is strongly σ polarized in bromides and iodides. The role of spin-orbit coupling for the transition dipole moment responsible for the low-energy absorption band of the V_K center has been discussed in Ref. 16.

[34] U. Rogulis, W. Meise, and J.-M. Spaeth, in *Proceedings of the XII International Conference on Defects in Insulating Materials,* edited by O. Kanert and J.-M. Spaeth (World Scientific, Singapore, 1993), p. 468.

[35] J.-M. Spaeth, W. Meise, and K. S. Song, J. Phys. Condens. Matter **6**, 1801 (1994).

[36] J-M. Spaeth (private communication).

[37] A. L. Shluger, A. H. Harker, V. E. Puchin, N. Itoh, and C. R. A. Catlow, Model Simulations Mater. Sci. Eng. **1**, 673 (1993).

[38] A. L. Shluger, E. A. Kotomin, and L. N. Kantorovich, J. Phys. C **19**, 4183 (1986).

[39] J. M. Vail, R. Pandey, and B. Kunz, Rev. Solid State Sci. **5**, 241 (1991).

[40] A. M. J. Frisch, G. W. Trucks, M. Head-Gordon, F. M. W. Gill, M. W. Wong, J. B. Foresman, B. G. Jonson, H. B. Schlegel, M. A. Robb, E. S. Reploge, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart, and J. A. Pople, GAUSSIAN 92 (Gaussian, Pittsburgh, PA, 1992).

[41] N. F. Mott and M. J. Littleton, Trans. Faraday Soc. **34**, 485 (1938); this technique has been described in a special issue of J. Chem. Soc. Faraday Trans. II **85** (1989).

[42] A. M. Stoneham, *Handbook of Interatomic Potentials. I. Ionic Crystals* (UKAEA, Harwell, 1981).

[43] G. B. Bachelet, D. R. Hamann, and M. Schluter, Phys. Rev. B **26**, 4199 (1982).

[44] V. E. Puchin, A. L. Shluger, K. Tanimura, and N. Itoh, Phys. Rev. B **47**, 6226 (1993).

[45] *Gaussian Basis Sets for Molecular Calculations,* edited by S. Huzinaga, Physical Science Data Vol. 16 (Elsevier, Amsterdam, 1984).

[46] K. B. Tolpygo, Ukr. Fiz. Zh. **2**, 242 (1957); K. B. Tolpygo and O. F. Tomasevich, *ibid.* **3**, 145 (1958); L. N. Kantorovich, J. Phys. C **21**, 5041 (1988).

[47] F. Dochy, Phys. Status Solidi A **59**, 531 (1980).

[48] J. A. Pople and D. L. Beverige, *Approximate Molecular Orbitla Theory* (McGraw-Hill, New York, 1970).

[49] E. V. Stefanovich, E. K. Shidlovskaya, A. L. Shluger, and M. A. Zakharov, Phys. Status Solidi B **160**, 529 (1990).

[50] R. A. Evarestov, *Quantum-Chemical Methods of Solid State Theory* (Leningrad University Press, Leningrad, 1982); A. L. Shluger and E. V. Stefanovich, Phys. Rev. B **42**, 9664 (1990).

[51] J. B. Foresman, M. Head-Gordon, J. A. Pople, and M. J. Frisch, J. Phys. Chem. **96**, 135 (1992).

[52] E. N. Heifets and A. L. Shluger, J. Phys. Condens. Matter **4**, 8311 (1992).

[53] W. R. Wadt and P. J. Hay, J. Chem. Phys. **82**, 284 (1985).

[54] P. E. Cade, A. M. Stoneham, and P. W. Tasker, Phys. Rev. B **30**, 4621 (1984).

[55] A. L. Shluger, S. N. Mysovsky, and A. I. Nepomnyaschikh, J. Phys. Chem. Solids **49**, 1043 (1988).