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Abstract

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PHYSICS

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ENERGY ABSORPTION BY PURE KCl CRYSTALS

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The valence electrons of cations in quasi-ionic crystals (partly with covalent bonding) are excited under the action of the binding energy. In the crystal molecules this causes a decrease in the ionization energy of the atoms. The residual ionization potential (r.i.p.) of the cation (ΔU_i^0) may, in a first approximation, be calculated from the formula

$$\Delta U_i^0 = U_i^0 - (W_c/n), \quad (1)$$

where U_i^0 is the ionization potential of the atom (cation), W_c is the binding energy of the cation in the crystal molecule, and n is the valence of the cation.

For BaSO_4 , $\text{ZnS} \cdot \text{Cu}$ it has been established that the r.i.p. > 0 and coincides with the width of the forbidden band (f.b.) of these crystals, while the maxima of the absorption and emission bands of the energy—with the energies of the lower excited levels of neutral atoms (¹²). Purely ionic crystals have r.i.p. < 0 . Of 20 widely known alkali halides, only Li-, K-, Rb-, CsF, K-, CsCl, and CsBr belong to them. Therefore the binding energy of the valence electron (W_e) with the K^+Cl^- dipole was calculated by proportional geometrical construction ($W_e = 7.7$ eV) and by the formula

$$W_e = [2(U_i^{02} + A^{02}) - \zeta(r_k + r_a)^2]^{0.5}, \quad (2)$$

where A^0 is the magnitude of the electron affinity of the halogen atom, ζ is a scale factor for KCl, close to unity, and r_k and r_a are the radii of the cation and anion, respectively ($W_e = 7.49 \div 7.78$ eV).

This energy corresponds to the longest-wavelength absorption maximum (m.p.) of unexcited crystals and to the width of the f.b. (^{1,2}). Its variations are a consequence of violation of the Franck-Condon principle in interband transitions. For unexcited and excited KCl crystals, from this m.p. up to 14 eV, six common m.p.'s are observed, with $E \approx 8.0$; 8.6; 9.2—9.5; 10.4; 12.2, and 13.0 eV (³⁻⁵). Of these, two correspond to transitions of the valence $3p$ -electron of chlorine

from the ground state of the ionized KCl molecule ($W_c \approx U_{iK}^0 = 4.34$ eV) to the exciton level 5^4D (155 m μ ; 8.0 eV) and into the conduction band—c.b. (143 m μ ; 8.67 eV). The latter transition characterizes the width of the f.b., which was calculated by the formula

$$\Delta U_i^0 = U_{iCl}^0 - U_{iK}^0. \quad (3)$$

The next three m.p.'s of higher energy correspond to transitions into exciton states of neutral chlorine atoms in lattice defects. These electronic transitions occur from the ground level $3^2P_{3/2}^0$ to the excited 4^2P (135 m μ ; 9.2 eV), 4^2D (120 m μ ; 10.4 eV), and 5^4D (100 m μ ; 12.3 eV). The last of the common m.p.'s at 13 eV corresponds to an interband transition in the neutral chlorine atom. All the seven indicated m.p.'s observed in the absorption spectra of excited and unexcited KCl crystals (³⁻⁵) agree well with the calculated ones (Fig. 1B). For five m.p.'s the error is less than 1%, and for the remaining ones about 2%. The m.p.'s of excited KCl crystals with energy less than the width of the f.b. of KCl are represented mainly by electronic transitions in neutral and coagulated potassium atoms (Fig. 1A) in lattice defects or near them and partly by resonant

transitions through virtual levels (⁶) in neutral chlorine atoms and once-ionized KCl molecules.

Electronic resonance transitions in neutral chlorine atoms, corresponding to definite absorption bands (⁷), begin from the ground chlorine level $3^2P_{3/2}^0$ and end at the excited 4^2P , 4^4S^0 , 5^2D^0 , and 5^2F . They all occur with double absorption of quanta with energies of 4.64 , 5.31 , 5.39 , and 6.21 eV, respectively. The discrepancy between the calculated and experimental results is less than 1-2%.

Resonance absorption of energy is also possible in K^+Cl^0 molecules if interionic electronic transitions through a virtual level with $E = 4.33$ eV take part in the formation of an absorption band near 300 m μ (⁷). In such molecules of excited crystals, two more exciton states are possible with $E = 4.9$ and 6.1 eV, which correspond in the spectra to absorption bands near 200 and 254 m μ (⁷). All other absorption bands with energy less than 4 eV are associated with electronic transitions in potassium atoms. The four shortest-wavelength absorption bands, with wavelengths near 334 , 355 , 460 , and 570 m μ (^{5,7}), correspond to electronic transitions from the ground potassium level $4^2S_{1/2}$ in the conduction band (absorption of F -centers) through a virtual level with $E = 2.17$ eV (⁶) and to exciton levels 3^2D , 4^2F^0 , and 5^2D with $E = 2.67$, 3.49 , and 3.37 eV, respectively. Likewise, four electronic transitions occur from the resonance level 4^2P^0 . One of them (in the conduction band) supplements the absorption band at 460 m μ , while the remaining ones—to the levels 5^2D , 4^2F^0 , and 4^2D —correspond to absorption bands near 590 , 660 , and 700 m μ . The last is supplemented by electronic transitions from the level 5^2S in the conduction band, with $E = 1.73$ eV.

Fig. 1. Band scheme of pure KCl crystals

Figure 1: Fig. 1. Band scheme of pure KCl crystals

An absorption band with wavelength near 1μ may be explained by electronic transitions in neutral potassium atoms from the level 5^2P^0 into the conduction band ($970\text{ m}\mu$, 1.28 eV). In addition to the listed absorption bands, two more absorption bands with wavelengths near 730 and $850\text{ m}\mu$ are observed in the spectra, for which there are no analogues in the band schemes considered. There are indications of the coagulation nature of these absorption bands (^{3,5,7}), etc.

Fig. 1. Band scheme of pure KCl crystals. **A** –for crystals consisting of neutral (K^0) and coagulated potassium atoms: K_2 –by two, K_\perp and K_Δ –by three in straight and equilateral positions; **B** –for crystals consisting of neutral (K^+Cl^-) and once-ionized (K^+Cl^0) molecules and atoms (Cl^0). Whole numbers denote wavelengths in $\text{m}\mu$; fractional numbers denote energies in eV ; dashed lines denote virtual levels according to (⁶).

As regards the first of them, it is known that it corresponds either to an anion vacancy that has captured two electrons (⁸), etc., or to the smallest colloids–dispersely distributed metallic centers (⁹), etc., or to two anion vacancies that have each captured one electron (¹⁰). The supposition of one anion vacancy with two electrons does not withst–

is subject to criticism, since the electron affinity energy of potassium is 0.82 eV , while the destruction of these centers occurs at 1.7 eV . The second and third are in fact expressions of one and the same entity: these are two coagulated potassium atoms–an elementary double potassium coagulate. Its preferential location is in cation sites next to two anion vacancies. In such a coagulate each atom perturbs and attracts the valence electron of the other with an electron affinity energy ($A_K^0 = 0.82\text{ eV}$), as a result of which the electrons are removed from their atoms. This lowers the ionization potential of the atoms. Owing to this, the ability of the atoms to attract “foreign” electrons increases, i.e., each atom, losing its own electron, tries more strongly to attract the electron of the other atom. Thus, if the ionization potential of an atom decreases by the amount of the atom’s affinity for an electron, then the fraction by which the bond of the electron with its own atom is weakened may be represented as (A^0/U_i^0). Obviously, by the same fraction the electron affinity energy of this atom must increase, i.e., it may be written as $A^0(A^0/U_i^0)$. Therefore, in the second approximation the affinity energy will have the perturbed form

$$A^{0*} = A^0 [1 + (A^0/U_i^0)]. \quad (4)$$

Then the R.I.P. for either of the two covalently interacting identical potassium atoms can be determined from the formula

$$\Delta U_{i2}^0 = U_i^0 - A_2^{0*}, \quad (5)$$

or, substituting the value (4), we obtain for the double coagulate

$$\Delta U_{i2}^0 = U_i^0 - A^0 (1 + A^0/U_i^0). \quad (6)$$

The calculated value $\Delta U_{iK2}^0 = 3.36$ eV is almost twice the value of the energy at the absorption maximum. It turns out that the whole point is that almost exactly in the middle of the b.g. of this coagulate lies the exciton level 3^2D of neutral potassium. Thus energy absorption by two-atom potassium coagulates is effected by quasi-resonant electronic transitions from the ground level of the coagulate to the exciton quasi-resonant level 3^2D , and from it into the c.b., with energies of 1.68 and 1.67 eV, respectively. The absorption maximum near 850 m μ obviously must belong to more complex—triple—coagulates ⁽¹¹⁾. They may have a right-angled (\perp) and an equiangular (Δ) arrangement of atoms. The first corresponds to the atoms being located in cation sites. The atom at the vertex of the right angle will then be the most perturbed. The perturbation of its electron is about $1.41A^0 \approx 1.16$ eV, and the R.I.P. of such a coagulate will be

$$\Delta U_{i\perp}^0 = U_i^0 - 1.41A^0 \approx 3.18 \text{ eV}. \quad (7)$$

In the present case, energy absorption is evidently effected through a virtual level in the middle of the b.g., which gives an error relative to experiment of only about 2%. For an equiangular coagulate the perturbation of the valence electrons is the same and equals $1.73A^0$, which for potassium atoms is 1.42 eV. Therefore the R.I.P. will be

$$\Delta U_{i\Delta}^0 = U_i^0 - 1.73A^0 = 2.92 \text{ eV}. \quad (8)$$

If it is assumed that in this case also a resonant transition occurs through a virtual level in the middle of the band, then the discrepancy with the calculation reaches 5%. This should be explained by the fact that coagulates of 4 and more atoms were not taken into account. All the described absorption maxima and the corresponding electronic transitions are collected in Table 1. It follows from it that all observed and verified absorption maxima of energy in KCl crystals can be well interpreted with the aid of the residual ionization potential, excited levels, the ionization potential, and the electron affinity energy of the neutral atoms composing a (quasi-)ionic crystal. The concept of the R.I.P. can be used to interpret the absorption spectra not only of quasi-ionic but also of ionized purely ionic crystals and co-

Table 1

Experimental and calculated characteristics of absorption maxima of pure KCl crystals at room temperature

Maxima in spectra 3-5, 7-9, etc., λ , $m\mu$	Maxima in spectra 3-5, 7-9, etc., E , eV	Energy of calculated maxima, eV	$\Delta E/E$, %	Absorption centers	Electronic transitions, designation	Electronic transitions, multiplicity
95	13.0	13.01	< 1	Cl^0	v.b.-c.b.	1
102	12.2	12.3	< 1	Cl^0	v.b.- 5^4D	1
119	10.4	10.4	< 1	Cl^0	v.b.- 4^2D	1
130-135	9.2-9.5	9.2	0-3	Cl^0	v.b.- 4^2P	1
144	8.6	8.67	< 1	K^+Cl^0*	v.b.-c.b.	1
155	8.0	8.0	~ 0	K^+Cl^0*	v.b.- 5^4D	1
155-162	7.65-8.0	7.49-7.78	~ 2	K^+Cl^-*	v.b.-c.b.	1
200	6.2	6.21	< 1	Cl^0	v.b.-v.l.- 5^2F	2
200	6.2	6.1	< 2	K^+Cl^0*	v.b.- 4^4D	1
212	5.85	5.93	< 2	Cl^0	v.b.-v.l.- 5^2D^0	2
230	5.39	5.31	< 2	Cl^0	v.b.-v.l.- 4^4S^0	2
250-266	4.66-4.96	4.64-4.90	< 1	Cl^0	v.b.-v.l.- 4^2P	2
250-266	4.66-4.96	-4.90	< 2	K^+Cl^0*	v.b.- 4^2P	1
290-300	4.13-4.27	4.33	1-5	K^+Cl^0*	v.b.-v.l.-c.b.	2
334	3.72	3.73	< 1	K^0	v.b.- 5^2D	1
350-358	3.46-3.54	3.49	~ 1	K^0	v.b.- 4^2F^0	1
460	2.70	2.67-	~ 1	K^0	v.b.- 3^2D	1

Maxima in spectra 3-5, 7-9, etc., λ , $m\mu$	Maxima in spectra 3-5, 7-9, etc., E , eV	Energy of calcu- lated maxima, eV	$\Delta E/E$, %	Absorption centers	Electronic transi- tions, designa- tion	Electronic transi- tions, multi- plicity
460	2.70	-2.73	~ 1	K^0	4^2P- c.b.	1
555-568	2.18- 2.22	2.17	~ 1	K^0	v.b.-v.l. -c.b.	2
590	2.10	2.12	< 1	K^0	4^2P^0- 5^2D	1
655-675	1.84- 1.89	1.88	~ 1	K^0	4^2P^0- 4^2F^0	1
709	1.75	1.79-	~ 2	K^0	4^2P^0- 4^2D	1
709	1.75	-1.73	~ 1	K^0	5^2S- c.b.	1
725-730	1.70- 1.71	1.68	< 2	K_2^0	v.b.- 3^2D- c.b.	2
800-890	1.55- 1.39	1.59-	~ 2	K_3^0L	v.b.-v.l. -c.b.	2
800-890	1.55- 1.39	-1.46	~ 5	$K_{3\Delta}^0$	v.b.-v.l. -c.b.	2
980	1.27	1.28	< 1	K^0	5^2P^0- c.b.	1

Designations: * -excited atom of an ionized molecule; v.b., v.l., and c.b. -valence band, virtual level (according to V. L. Levshin ⁽⁶⁾), and conduction band, respectively.

coagulating atoms. For pure ionic single crystals of KCl, for which o.m.p. < 0 , a single m.p. is observed, corresponding to the electronic transition from the ground state of a crystal molecule into the conduction band. The remaining 21 m.p. correspond to various crystal defects; of these, 8 are due to electronic transitions in neutral chlorine atoms, 5 in ionized KCl molecules, 8 in neutral and 2 in coagulating potassium atoms. More than 50% of the electronic transitions begin in the valence band, and more than 30% are of resonant nature.

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