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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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ON THE RELATION BETWEEN BAND AND DISCRETE ABSORPTION IN THE X-RAY SPECTRA OF ATOMS IN POLAR CRYSTALS

(Presented by Academician A. P. Vinogradov, January 30, 1965)

The question of the relation between band and discrete (exciton) absorption in the x-ray spectra of atoms in polar crystals has not yet received a definitive solution. In the present communication it will be considered in the light of new experimental and theoretical results, using as an example the x-ray spectra of the components obtained by us in LiCl, KCl, NaCl, RbCl, and AgCl crystals, shown in Figs. 1–3. The conditions under which the experiments were carried out were the same as in the study of the emission spectra (⁀1). In Figs. 2 and 3 the x-ray spectra are compared with certain results following from analysis of the u.v. spectra of these crystals (⁀2), with data on the external photoeffect (^{3},5)*, and also with the results of the corresponding theoretical calculations (^{7}-10). The position and width of the valence band in the crystals are indicated in accordance with our experiments (⁀1), which are in good agreement with the values of the valence-band widths in alkali-halide crystals calculated in (⁀8).

Fig. 1. $K_{\beta_{1,3}}$-emission bands and the K-absorption edge of chlorine in LiCl, AgCl, NaCl, KCl, and RbCl.
a—experimental curves; —spectra corrected for instrumental distortions and the width of the inner level; —extrapolation of the corrected line contour to zero intensity.

In doing so, as in (⁀11), it was assumed that the characteristic of the valence band is only the K_{β_1}-line, while the line

* According to (⁀4), the magnitude of the threshold of the external photoeffect in NaCl is 6.67 eV (instead of 8.3 according to (⁀3)). However, the method of these authors gives rise to objections (⁀6).

$K_{\beta x}$ arises as a result of double ionization of the chlorine ion. By combining the short-wavelength cutoff of the corrected x-ray emission K_{β_1}-band of radiation

Fig. 2

Figure 2: Fig. 2

and measuring from it the position of the vacuum level (calculated for alkali-halide crystals in (7,8)), one can outline the position of the latter in the K-absorption edges of chlorine and potassium in the spectra studied and, using various estimates (see, for example, (10)), indicate the possible position of the lower boundary of the S-conduction band in the crystals under study (see Figs. 2 and 3). Into this same energy region (region C in Figs. 2 and 3), when it is measured from the top of the valence band,* falls also the energy of the second maximum of the absorption oscillator strength of alkali-halide crystals, which is usually interpreted as a manifestation of a band-to-band transition in these compounds. Thus, the region of the possible position of the lower boundary of the conduction band in alkali-halide crystals, restricted by comparing various experimental data, is designated in the figures by the letter B. As can be seen, its position does not coincide with the value that was determined earlier (12) relative to the position of F-centers, although it is close to it (within the accuracy of the estimate). At the same time it is in more satisfactory agreement with the value of the energy of the lower boundary of the s-band (line and regions A in Figs. 2 and 3), which can be calculated,** using data on the photoelectric effect (3) or oscillator-strength absorption (2) and the width of the valence band (1), as well as the energies

Fig. 2. Comparison of the x-ray K-absorption and emission spectra of chlorine in NaCl and RbCl with data obtained from optical measurements (3) and theoretical calculations (7,9). The designations are the same as in Fig. 1. **V.B.** –valence band; **C.B.** –conduction band according to (9); A –position of the bottom of the conduction band according to x-ray data, taking account of (3); B –region of the possible position of the bottom of the conduction band, obtained from experimental data (2,3); C –maximum possible spread of values for the energy of the band bottom according to experimental and theoretical data

* It should be noted that the condition of momentum conservation in a phototransition may require (10) that, in optical absorption, the electron be ejected from a deeper level of the valence band, and not from its top. However, as can be seen from Fig. 3, this does not qualitatively change our consideration.

** The energy of the s-boundary of the conduction band in the chlorine K-absorption spectrum is equal to $K_{\beta_1}(\mathrm{Cl}^-) + \text{osc. str.} = 2824.5$ eV; the boundary in the potassium K-spectrum is $K_{\beta_5}(\mathrm{K}^+) + \text{osc. str.} = 3610.7$ eV; in the chlorine L-spectrum $[K_{\beta_1}(\mathrm{Cl}^-) - K_{\alpha}(\mathrm{Cl}^-)] + \text{osc. str.} = 202.9$ eV, and in the L_{III}- and L_{II}-spectra of potassium, 297.3 and 300.3 eV. In these calculations, naturally, the assumption was made that the distance between the corresponding energy levels in the atom does not undergo significant changes in the presence of a vacancy in the K-shell.

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

$(3p-2p)$ in the Cl^- ion*, determined from x-ray spectra. Using the procedure already applied for this purpose in (^{13}), one can, from the formula $(M_{\mathrm{I}}^{\mathrm{abs}} - L_{\mathrm{III}}^{\mathrm{abs}}) + 182.75$ eV, also determine for KCl the energy separation $4p-4s$ and indicate the region of the possible position of the lower boundary of the p-continuum of states in the spectra of both components of alkali-halide crystals.

Fig. 3. Comparison of the x-ray K-absorption and emission spectra of potassium (a) and chlorine (b) in KCl with the optical-study data (^{2,3}) and calculation results (^{7,8}). For notation see Fig. 2. M is the region of possible appearance of exciton absorption according to the calculations (^{15}); D is the region of the possible position of the boundary of the p-continuum, calculated by the authors by the method of (^{13}); H is the position of the bottom of the conduction band, determined in (^{12}) relative to the maximum of absorption by F-centers.

As is known (^{14}), the weak K_{β_5}-line in the emission spectrum of potassium in a KCl crystal arises owing to the cross transition $1s(K^+) \to 3p(Cl^-)$. This was recently confirmed independently in (^{1}). Therefore the K-spectra of both components in KCl can be compared with one another by superposing the maxima of the K_{β_5}- and K_{β_1}-emission bands in the spectra of potassium and chlorine, respectively. If one uses the distance between the top of the potassium $3p$-band and the vacuum energy level (23.6 eV) from (^{7}) and marks the position of the latter on the K-absorption spectrum of potassium in KCl, we also obtain good agreement with the position determined in the analysis of the x-ray spectrum of the other component of the compound.

[*] In doing so, the natural assumption is made that ultraviolet absorption [$3p(Cl^-) \to$ bottom of the conduction band] and absorption in the x-ray region [$2p(Cl^-) \to$ s-bottom of the conduction band] occur into one and the same system of levels.

Summarizing what has been said, one may conclude that in all, without exception, x-ray absorption spectra of the components of the polar crystals studied there is a fairly extended region (of the order of several electron volts) lying below the boundary of the conduction band, whose origin should naturally be associated with the transition of photoelectrons to exciton energy levels. As can be seen (Fig. 3), it is precisely into this region that the maxima of exciton x-ray absorption, calculated in (15) and marked in the figure by the letter M, should fall.*

Fig. 4. Comparison of the x-ray L-absorption spectra of chlorine (a) and

potassium (b) in KCl (16), and also of sodium (c) in NaCl (17), with optical data (2,3) and with the results of calculations (7,8). The designations are the same as in the preceding figures. The shaded regions are the positions of levels in vacuum relative to the maximum of the K_{β_1}-line (long-wavelength boundary of the region) and the K_{β_5} emission band of potassium (short-wavelength boundary of the region), according to the authors' calculation by the method of (13).

Analogous exciton origin (Fig. 4) is evidently also possessed by the first two sharp maxima in the $L_{\text{II,III}}$-absorption spectra of chlorine in NaCl and KCl crystals (16) and by the narrow long-wavelength maximum in the spectrum of Na (17) in the same crystal. This is also confirmed by the results of our recent calculation, with the aid of the Dykman–Overhauser model, of the energy of the ground state of the x-ray exciton in NaCl.

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* The comparison we have made of the absorption spectra of chlorine and potassium in KCl also shows the validity of the conclusion of the authors of (15) concerning the greater remoteness from the bottom of the conduction band of the ground state of the localized x-ray exciton K^+ (3.39 eV) than of Cl^- (2.5 eV).

Note: Figure translations are in progress. See original paper for figures.

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