# Electronic structure of cadmium fluoride

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The electronic structure, the densities of states, the dielectric function, and the localization of optical transitions in Brillouin zone of CdF<sub>2</sub> crystals are calculated using the full-potential linear muffin-tin orbital method in the local density approximation. We have also calculated the dielectric function from the two experimental reflectivity spectra using the Kramers-Kronig relations. We have decomposed these calculated  $\varepsilon_2(E)$  spectra into components and compared their parameters with the theoretical results.

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# I. INTRODUCTION

Wide band-gap materials are exceptionally promising in modern optics and optoelectronics, because they can serve as a base for the development of effective and efficient emitters, visible light, and ultraviolet lasers. Ionic crystal CdF<sub>2</sub> with a fluorite structure is characterized with a large gap energy ( $E_g > 9 \text{ eV}$ ) and high transparency in a wide energy range. With doping and a certain thermochemical treatment, it can be carried over into a semiconducting state.<sup>1-4</sup> It is also essential that CdF<sub>2</sub> crystals of quite a large size can be obtained at a relatively low cost.

For CdF<sub>2</sub>, calculations of band structure along some high symmetry directions of the Brillouin zone (BZ) are known that use the tight binding<sup>5</sup> (TB) and pseudopotential<sup>6</sup> (PP) methods. Albert *et al.* had also reported the band structure results on CdF<sub>2</sub>.<sup>7</sup> They used the TB method for the valence bands and the PP method for the conduction bands. The results of these papers<sup>5–7</sup> turned out to be quite similar. Their main drawback is that they lack the calculation of  $\varepsilon_2(E)$ . Hence, the authors analyzed the known experimental reflectivity spectra R(E) only from the band calculations. Reflectivity measurements were reported by Bourdillon and Beaumont,<sup>8</sup> Raisin *et al.*,<sup>9</sup> and Francini *et al.*<sup>10</sup> up to 60 eV. These results have not been compared to each other.

There are two fundamental problems in the spectroscopy of solids: (1) determination of a full set of optical functions<sup>11</sup> (reflectivity R and absorption  $\mu$  coefficients, the real  $\varepsilon_1$  and imaginary  $\varepsilon_2$  parts of dielectric function, indices of refraction *n* and absorption k, etc.); (2) decomposition of the integral  $\varepsilon_2$ spectra into components and determination of their parameters (energies, half-widths, and oscillator strengths or areas). It is common to calculate a full set of optical functions from the experimental R(E) or  $\varepsilon_2(E)$  spectra. Among more than a dozen functions of this set, only  $\varepsilon_1(E)$  and  $\varepsilon_2(E)$  spectra were calculated by Bourdillon and Beaumont<sup>8</sup> from the experimental R(E) spectrum. However, large negative values of  $\varepsilon_2$  in the transparency region and strong underestimation of the first and most intensive maxima make one suppose that the contribution of the nonmeasured regions of the R(E)spectrum had not been considered correctly enough. To the best of our knowledge so far nobody has yet performed a decomposition of  $\varepsilon_2(E)$  spectra into elementary components. Therefore, examination of the electronic structure of  $CdF_2$  crystals in a wide energy range of fundamental absorption is of considerable current interest.

In this work we present a theoretical study of the optical properties of  $CdF_2$  crystals. The paper is organized as follows. We first briefly discuss the calculation method in Sec. II. In Sec. III, our results for the band structure, total and partial densities of states, and dielectric function are presented. We discuss our results for the dielectric properties, which have been obtained theoretically and from the two experimental reflectivity spectra.<sup>8,9</sup> We also calculate the contributions of various interband transitions into the  $\varepsilon_2$  spectrum and their localization in the BZ. We decompose the spectra of dielectric functions into their Lorentz components and determine the components' parameters (energies, halfwidths, intensities, and areas). A summary and conclusions are given in Sec. IV.

### **II. METHOD OF CALCULATION**

In this paper, we used the self-consistent full potential linear muffin-tin orbitals (FP-LMTO) method in the local density approximation (LDA). As this method has been described in detail elsewhere,<sup>12–14</sup> we will only outline the major steps here. The valence states were calculated in the scalar-relativistic approximation, taking into consideration all the basic relativistic potential corrections except for the spin-orbit correction. The initial configurations of atoms were taken to be  $4d^{10}4p^65s^2$  for Cd and  $2s^22p^5$  for F. The lattice constant of cubic CdF<sub>2</sub> is equal to a=0.5462 nm. The radii of the muffin-tin (MT) spheres were chosen to be proportional to the ionic radii of the elements. They are equal to  $r_{\rm Cd} = 1.896 \, ({\rm Cd}^{2+})$  and  $r_{\rm F} = 2.531 \, {\rm a.u.}({\rm F}^{-})$ , thereby the fluorine MT spheres almost touch each other, while the MT spheres of cadmium in the remaining space touch the fluorine MT spheres. To improve the convergence of the FP-LMTO calculation, an empty sphere was inscribed into the center of the unit cell. We calculated the bands in 252 points of a 1/48th of BZ. The calculation of total and partial densities of states (DOS) and of the  $\varepsilon_2(E)$  spectrum was performed with the tetrahedron method,15 without taking into account the probability of interband direct transitions. It seems to be more appropriate to say that we have determined the joint density of states on the assumption that the matrix elements of the transitions should be independent on their energy and localization in the BZ.

We performed the calculation of the  $\varepsilon_2(E)$  spectra from the experimental reflectivity spectra R(E) (Refs. 8 and 9) with the methods that use the Kramers-Kronig relations. These calculation techniques were described in detail and repeatedly applied in Refs. 11,16 and 17.

The second fundamental problem of spectroscopy is well known in the many fields of physics (optical spectroscopy, x-ray electron spectroscopy, nucleus spectroscopy, effect of Messbauer, etc.). It is an inverse problem that is mathematically incorrect and has an infinite number of solutions. The  $\varepsilon_2(E)$  and other optical function spectra sum contributions of interband transitions and excitons. In general, since the neighbor peaks have large half-widths and are strongly overlapped, we see that some bands of optical transitions are unobservable in the integral total curve. Hence, the number of bands is unknown and may be more than the maxima of the spectrum. Besides, the strength of the oscillator is not determined by the experimental methods. Although the importance of the electron-hole interaction in optical properties has been understood for many years, theoretical calculations, including the many-body effects, have only recently begun to appear. But there are serious discrepancies already in simple systems. (See, e.g., Refs. 18 and 19.) This is a result of the lack of experimental data. Knowledge of the main parameters of elemental components allows more detail and concrete comparison of partial interband transition contributions between couples of valence and conduction bands with the experimental results. Thus the experimental data and resulting calculated are especially important to the development of electronic structure theory. The fine structure of spectra also helps reveal the drawbacks of experimental results.

All known curve-fitting methods are applied on the reproduction of an integral curve by set of N oscillators with 3Nadjusted parameters, where N is also fitted. Otherwise the method of a unified Argand diagram is applied. In our work decomposition of the integral  $\varepsilon_2(E)$  spectra into elementary Lorentz components and determination of their main parameters (energies of the maxima  $E_i$  and the half-widths  $H_i$ , oscillator strengths  $f_i$ , areas of the bands  $S_i$ , etc.) are performed with the method of unified Argand diagrams. Further, we briefly discuss this method.

The frequency dependence of the optical constant may be explained simply on the basis of the classical Lorentz interpretation, where a solid is considered as an assembly of oscillators,<sup>20</sup>

$$\varepsilon_2(E) = \frac{\varepsilon_{2\max} H^2 E_0 E}{(E_0^2 - E^2)^2 + H^2 E^2},$$
(1)

$$\varepsilon_1(E) = 1 + \frac{\varepsilon_{2\max} H E_0(E_0^2 - E^2)}{(E_0^2 - E^2)^2 + H^2 E^2}.$$
 (2)

Here  $\varepsilon_{2\text{max}}$  is the height at the band's maximum, *H* is the half-width, and *E*<sub>0</sub> is the energy of the maximum,



FIG. 1. The Argand diagram for  $E_0=1$  eV,  $\Gamma=0.5$  eV, and  $\varepsilon_{2\text{max}}=1$ .

$$\varepsilon_{2\max} = \frac{4\pi e^2 \hbar^2 f n_{eff} z}{m V H E_0}.$$
(3)

The area of the band S and the oscillator strength f are obtained as follows:

$$f = \frac{mV}{4\pi\hbar^2 e^2 z} \frac{E_0 H \varepsilon_{2\text{max}}}{n_{eff}},\tag{4}$$

$$S = \frac{1}{2} \frac{\varepsilon_{2\text{max}} H E_0}{\sqrt{4E_0^2 - H^2}} \left[ \pi + 2 \arctan\left(\frac{2E_0^2 - H^2}{H\sqrt{4E_0^2 - H^2}}\right) \right], \quad (5)$$

where V is the unit-cell volume, z is the number of functional modules (atoms or molecules) in the unit cell, and  $n_{eff}$  is the effective number of electrons contributing to the optical properties up to an energy  $E_0$ ,

$$n_{eff}(E_0) = \frac{m}{2\pi^2 e^2} \int_0^{E_0} E\varepsilon_2(E) dE.$$
 (6)

Assuming  $H \ll E_0$ , we obtained from Eq. (5) the trivial formula,

$$S \approx \frac{\pi}{2} H \varepsilon_{2\text{max}}.$$
 (7)

An individual oscillator on Argand diagram  $\varepsilon_2 = f(\varepsilon_1)$  is presented by a curve (Fig. 1) that is almost a circle by relation<sup>20</sup>

$$\varepsilon_2^2 + \varepsilon_2 \varepsilon_{2\max} + (\varepsilon_1 - 1)^2 - (\varepsilon_1 - 1)\varepsilon_{2\max} H/(E_0 + E) = 0.$$
(8)

On the integral Argand diagram there are several sections which can be well described with circles. It is easier to begin with the most intensive peak. For this peak we construct the full circle on the diagram of Argand. For such a circle, the parameters of the oscillator are obtained and the oscillator is subtracted from the  $\varepsilon_1$  and  $\varepsilon_2$  curves. Remainders of both integral functions ( $\varepsilon_1$  and  $\varepsilon_2$ ) are determined. For the remain-



ders, a new Argand diagram is plotted and the process is repeated. Thus we decompose the spectra of  $\varepsilon_1$  and  $\varepsilon_2$  without any adjusted parameters on the minimal set of Lorentz oscillators. This decomposition is unique and can be easily reproduced.

### **III. RESULTS OF CALCULATIONS**

#### A. Band structure and densities of states

The calculated band structure for CdF<sub>2</sub> is shown in Fig. 2. Band-gap width has proved to be equal to 4.2 eV, which is 2.2 times smaller than the value obtained by the estimation from the  $\varepsilon_2$  spectra calculated from the experimental reflectivity spectra ( $E_g \approx 9.2$  eV). The underestimation of  $E_g$  is typical of all the calculations based on the LDA functional. There are many approaches to overcome this shortcoming, ranging from the very simple scissors operator to more sophisticated approaches such as self-interaction correction (SIC) and GW methods. The scissors operator accounts for a rigid shift of all conduction bands to fit the experimental gap.

In all, we obtained 13 valence bands  $(V_1-V_{13})$ , numbered from the bottom upwards). The overall width of the six upper valence bands  $(V_8-V_{13})$  was found to be 3.4 eV, which agrees well with the experimental value  $\Delta E_{v1} \approx 3.8$  eV obtained from the photoemission spectra.<sup>6,9,21</sup> The top of the highest valence band (HVB) is located at point *W*. However, at points  $\Gamma$ , *X*, and *L*, the states of HVB are lower only by 0.392, 0.087, and 0.329 eV, respectively. Below  $V_8$ , five narrow bands  $(V_3-V_7)$  are located with overall width  $\Delta E_{v2} \approx 1.7 \text{ eV}$ , the forbidden energy gap between bands  $V_8$ and  $V_7$  being equal to 0.25 eV. Albert *et al.*<sup>7</sup> obtained only two bands with  $\Delta E_{v2} \approx 0.7 \text{ eV}$ , instead of five. Our value of  $\Delta E_{v2}$  is in better agreement with the photoemission results (~2 eV), but the location of bands  $V_3 - V_7$  is overestimated by ~1.5 eV. Two core bands  $V_1$  and  $V_2$  are located at 19.3–20.5 eV, below the top of HVB.

The lowest conduction band (LCB, $C_1$ ) has a minimum at point  $\Gamma$ , and it weakly depends on the wave vector **k** along directions *X*-*W*-*L*. The LCB is separated from higher bands with the forbidden energy gap at ~1.7 eV. Within the range 10–30 eV, 13 unoccupied bands ( $C_2-C_{14}$ ) are located.

Within the energy range 0–3.5 eV, the spectrum of the density of valence states N(E) contains three peaks with their major maxima at 0.41, 1.97, and 3.40 eV [Fig. 3(a)]. The energy distance between the first and third peaks is in good agreement with the photoemission results, while the position of the second maximum seems to be overestimated by ~0.3 eV. The calculation of the partial contributions of the states of Cd<sup>2+</sup> and F<sup>-</sup> shows that the main contribution to these bands is made by the 2*p* states of F<sup>-</sup> [Fig. 3(b)]. However, the contribution of the 4*d* states of Cd<sup>2+</sup> is also quite large, the largest contribution being made to the first and third maxima of N(E) (~20% and 40%, respectively).

Two more doublet peaks of the N(E) spectrum are observed in the energy ranges 3.8–5.5 eV and 19–20.5 eV. The first of them has its maxima at 3.95 and 4.97 eV and is caused mainly by the 4*d* states of Cd<sup>2+</sup>. Besides, there is a contribution of the 2*p* states of F<sup>-</sup>; in the lower energy component of the doublet, this contribution amounts to ~30%. The other doublet of the N(E) spectrum is caused by the 2*s* states of F<sup>-</sup>.

In the unoccupied states's spectrum N(E), one can observe a doublet peak with maxima at 7.35 and 7.75 eV, a peak with a maximum at 10.14 eV, one more doublet peak with maxima at 12.79 and 13.47 eV, and a peak with a maximum at 14.42 eV. The LCB is caused mainly by the 5*s* states of Cd<sup>2+</sup> [Fig. 3(c)]. In the energy range 10–20 eV, the peaks of N(E) are caused by the 5*p* states of Cd<sup>2+</sup>.

# **B.** Optical properties

The reflectivity spectra R(E) of CdF<sub>2</sub> crystals were measured at 300 K in the energy range 0–45 eV on freshly cleaved surfaces<sup>9</sup> and in the range 4–56 eV on polished surfaces.<sup>8</sup> From these results, we calculated full sets of the optical functions of CdF<sub>2</sub>. For the sake of brevity, let us consider only the results of the calculation of the  $\varepsilon_2(E)$  spectra. Further on, we will refer to these spectra as the experimental-calculated spectra. Case 1 concerns the  $\varepsilon_2$ spectrum, calculated from the R(E) spectrum by Raisin *et al.*<sup>9</sup> while case 2 concerns the  $\varepsilon_2$  spectrum, calculated from the R(E) spectrum by Bourdillon<sup>8</sup> and Beaumont (Arrows and figures in Fig. 4 show the maxima of the peaks of spectrum 1.)

The  $\varepsilon_2$  spectra of the two calculations are qualitatively similar; one can find in both of them ten main and most intensive peaks in the energy range of intrinsic absorption 6–45 eV. In the energy range 6–17 eV, we observed consid-



FIG. 3. Total density of states N(E) of CdF<sub>2</sub> (a) and partial contributions of fluorine 2s, 2p states, cadmium 4d states (b), and of cadmium 5s, 5p states (c).

erable discrepancies in intensities and positions of the maxima of curves 1 and 2. In case 1, the maxima of the peaks are located at the following energies: 7.5 (No. 1), 12.7 (No. 3), 15.0 (No. 4), 17.6 (No. 5), 22.0 (No. 6), 26.4 (No. 7), 28.2 (No. 8), 36.1 eV (No. 10). Peaks Nos. 2 and 9 manifested themselves only in spectrum 2 with maxima at 10.3 (No. 2) and 32.5 eV (No. 9). At the same time, a wide shoulder in the energy range 8–10.5 eV is observed in spectrum 1. The maxima of the peaks of curve 2 in the range E < 17 eV are shifted to higher energies by 0.1 (No. 1), 0.4 (no. 3), and 0.1 eV (no. 4).

The case 2 spectrum at E < 17 eV is 1.1–1.8 times underestimated in intensity. At higher energies, both  $\varepsilon_2$  spectra agree well in intensities and in positions of the peaks. The



FIG. 4. The  $\varepsilon_2(E)$  spectra of CdF<sub>2</sub>, calculated theoretically (3, dotted line) and from the experimental R(E) spectra of Ref. 8 (2, dashed line) and Ref. 9 (1, solid line).

discrepancies of the spectra in the energy range 6-17 eV are, apparently, caused by poor quality of the samples's surfaces used by Bourdillon and Beaumont.<sup>8</sup>

The theoretical  $\varepsilon_2(E)$  spectrum (curve 3 in Fig. 4) was shifted by 5.0 eV by applying the scissors operator in order to align the experimental and theoretical values of  $E_g$ . The most intensive transitions are concentrated in the energy range 9–25 eV. The three major peaks are located in the energy ranges 9–14, 14–17.5, 20–24 eV, while the broad shoulder is in the range 17.5–20 eV. All the peaks are of complex structure and contain two or three maxima. At E > 25 eV, decay of intensity of the theoretical  $\varepsilon_2(E)$  spectrum was observed.

Therefore, the theoretical  $\varepsilon_2(E)$  spectrum reproduces well the most intensive maxima of the spectra of cases 1 and 2 in the energy range 8.6–25 eV; however, maxima nos. 4 and 5 are shifted to higher energies, while the intensity of maximum no. 3 has been strongly overestimated.

The calculation of the partial contributions of the transitions between pairs of bands showed that, as in CaF<sub>2</sub>,<sup>17</sup> the majority of the transitions occurred not at the points of high symmetry directions, but at considerable distances from them. (See Table I and Fig. 5.) The analysis of the localizations of many transitions showed that they all occurred in the volume of BZ (Fig. 5). Furthermore, most of them are not grouped in the central part near point  $\Gamma$  (inside tetrahedron  $\Gamma LNR$ ), instead they are located mainly near the points of planes *LNR*, *LNX*, *LKX*. (Point *R* is the middle point of interval  $\Gamma X$ , while point *N* is the projection of point *L* onto line  $\Gamma K$ .)

According to our results, all the intensive peaks of  $\varepsilon_2(E)$  are sums of separate transition peaks between many pairs of bands across the whole volume of BZ. Maximum No. 3 is mainly caused by transitions  $V_{12}$ ,  $V_{13} \rightarrow C_1$  and a small contribution is also made by transitions  $V_8 - V_{11} \rightarrow C_1$ . Maximum

No. <sup>a</sup>	$E_{exp}^{\ \ b}$	$E_{theor}^{\ \ c}$	Origin and localization of the components			
1	7.5		Exciton at point $\Gamma$			
2	9.3	9.1	$V_{13}-C_1$ , near point $\Gamma$			
5	12.8	12.6	$V_{13}-C_1$ , near plane <i>LKX</i>			
		12.7	$V_{12}-C_1$ , near points K and U and on plane LKX			
6	15.0	14.9	$V_{13}-C_2$ , near plane LNX			
		15.0	$V_{12}-C_2$ , near plane $\Gamma KWX$ on lines NR and NX			
		15.6	$V_8 - C_1$ , near line $LX$			
		15.9	$V_6 - C_1$ , near point X			
7	16.3	16.0	$V_{11}-C_2$ , near L, $V_7-C_1$ near point X			
		16.3	$V_6 - C_1$ , near points X and K			
		16.7	$V_{10} - C_2$ , near N, $V_5 - C_1$ near X			
		17.0	$V_3 - C_1$ , $V_4 - C_1$ on plane LNW			
8	17.7	17.5	$V_8 - C_2$ , near point $\Gamma$ , $V_{13} - C_3$			
		17.8	$V_{12} - C_3$			
		18.0	$V_{13}-C_4, V_{11}-C_3, V_{12}-C_4$			
		18.1	$V_{11}-C_4, V_{12}-C_4$			
		18.4	$V_7 - C_2$ , near R, $V_6 - C_2$ , near the center of line NX			
		18.9	$V_5 - C_2$ , near R, $V_{13} - C_5$			
		19.1	$V_{12} - C_5$			
		19.2	$V_4 - C_2$ , on plane LNX, $V_9 - C_3$			
		19.4	$V_3 - C_2$			
		19.6	$V_{10} - C_4$			
9	20.2	20.8	$V_7 - C_3, V_8 - C_4$			
		21.0	$V_{6} - C_{3}$			
10	22.0	21.5	$V_5 - C_3, V_7 - C_4, V_6 - C_4, V_{13} - C_6$			
		21.7	$V_8 - C_5, V_{12} - C_6$			
		21.9	$V_4 - C_3, V_5 - C_4, V_{11} - C_6, V_3 - C_3$			
11	23.0	23.0	$V_{10} - C_6, V_7 - C_5, V_5 - C_5$			
		23.2	$V_3 - C_4, V_6 - C_5$			
		23.5	$V_9 - C_6$			

TABLE I. Energy (eV), origin, and localization of transitions of CdF<sub>2</sub>.

<sup>a</sup>Index number of oscillator. (See Table II.)

<sup>b</sup>Energies of the components of the  $\varepsilon_2$  spectrum (case 1).

<sup>c</sup>Energies of the theoretical band transitions.

No. 4 is caused by the transitions from valence bands  $V_9-V_{13}$  to conduction band  $C_2$  and from  $V_3-V_8$  to  $C_1$ . Shoulder No. 5 is associated with many transitions from  $V_9-V_{13}$  to  $C_3-C_5$  and from  $V_3-V_8$  to  $C_2$ . Maximum No. 6—with transitions from  $V_9-V_{13} \rightarrow C_6$ ,  $C_7$  and from  $V_3-V_8 \rightarrow C_3-C_5$ . Albert *et al.*<sup>7</sup> proposed the exciton nature of peaks Nos. 3 and 4: however, the structures of the experimental-calculated  $\varepsilon_2(E)$  spectra in the range 10–20 eV are very well reproduced by our theoretical calculation within the one-electron approximation.

### C. Decomposition of the integral dielectric spectra

In order to determine the fine structures of the  $\varepsilon_2$  spectra, calculated from the experimental R(E) spectra, and to compare them in more detail with the theoretical results, we decomposed these spectra into elementary Lorentz compo-

nents, using the method of unified Argand diagrams. In all, we obtained 22 different components: 17 and 21 for cases 1 and 2, respectively (Table II). Only 12 oscillators appeared in the integral curves as the maxima.

The discrepancies between the two integral  $\varepsilon_2(E)$  spectra naturally appeared in the oscillator parameters. This is especially noticeable for components nos. 1–7. The components of case 1 were shifted to lower energies by 0.1–0.4 (Nos. 1, 5, 6, and 11), 1.0 (No. 2), and 1.1 eV (Nos. 3 and 21), relative to the peaks of spectrum 2. At the same time, the majority of the oscillators have large half-widths  $H_i > 1$  eV. Their values, as well as the heights  $\varepsilon_{2max}$ , are in good agreement for the two variants of decomposition. The areas of most components are in the interval 0.8–2.5, except for component Nos. 5, 6, 8, and 10. The values of heights, halfwidths, and areas are more than possible errors of calculations and decomposition techniques. This means that



FIG. 5. Localization of transitions of CdF<sub>2</sub> in BZ. Circles and crosses indicate the centers of the tetrahedra that make the largest contribution, while the perpendiculars show their heights above the plane  $\Gamma XKW$ . White circles mark transitions  $V_{13} \rightarrow C_1$  (a),  $V_{13} \rightarrow C_2$  (b),  $V_{12} \rightarrow C_2$  (c),  $V_4 \rightarrow C_1$  (d). Black circles mark  $V_{12} \rightarrow C_1$  (a),  $V_6 \rightarrow C_1$  (b),  $V_8 \rightarrow C_1$  (c),  $V_{10} \rightarrow C_2$  (d). Crosses mark  $V_5 \rightarrow C_1$  (d).

considered oscillators cannot be artifacts of the decomposition procedure and they are not neglected.

According to our theoretical calculations, the majority of the found components are caused by many transitions between various pairs of bands. Oscillator No. 1 is clearly caused by excitation of free excitons at point  $\Gamma$ , while oscillator No. 2 corresponds to the first interband transition in the vicinity of the center of BZ (Table I). In this case, binding energy  $E_b$  of the longest wavelength exciton is 1.75 eV. Peaks Nos. 3–6 are caused by the transitions from the HVB to two lower conduction bands. Oscillator No. 7 is mainly caused by excitations of the states of the valence bands  $V_3-V_7$ , while the transitions from both bands to the higher conduction band participate in the formation of components Nos. 8–16, and get strongly overlapped at that.

At E > 28 eV, transitions from a half-core band, formed by the 2s states of  $F^-$ , should be observed. The intensity of the theoretical curve in this energy interval is noticeably lower, however, than the intensity of the  $\varepsilon_2$  spectra obtained from the experimental results. This defect is, apparently, caused by not taking into account the matrix elements of the transitions.

Further, unrepresented in one-electron theoretical calculations, oscillators can be also assigned with excitons. Of course, the majority of the considered oscillators may also contain the contributions of metastable excitons; however, such calculations for CdF<sub>2</sub> have not been made so far. Clearly, precise analysis for the origins of elemental components and peaks of spectrum  $\varepsilon_2(E)$  requires a knowledge of full set of oscillators and their parameters, total and partial spectra  $\varepsilon_2(E)$  of one-electron models, and models including the electron-hole interaction. For the CdF<sub>2</sub> crystal, we see that most oscillators in the range 10–25 eV are well repro-

TABLE II. Energy E(eV), half-width H(eV), height  $\varepsilon_{2\text{max}}$ , area S(eV), and oscillator strength f of the components of the  $\varepsilon_2$  spectra, calculated from the R(E) spectra by Raisin *et al.* (Ref. 9) (columns 1) and by Bourdillon and Beaumont (Ref. 8) (columns 2).

	E		Н		ε <sub>2max</sub>		S			
No	1	2	1	2	1	2	1	2	1	2
1	7.5	7.6	0.4	0.3	3.60	2.10	2.3	1.1	1.16	1.45
1′	8.4	9.4	0.3	1.5	0.23	0.18	0.1	0.4	0.08	0.25
2	9.3	10.3	1.3	1.9	0.83	0.54	1.7	1.5	0.43	0.67
3	10.7	11.8	2.7	2.4	0.83	0.53	3.3	1.9	0.69	0.54
4	12.0		1.0		0.90		1.4		0.22	
5	12.8	13.2	1.5	1.2	2.70	1.58	6.3	2.8	0.81	0.53
6	15.0	15.2	1.8	2.3	2.10	1.90	5.6	6.6	0.50	0.81
7	16.3	16.2	2.3	0.5	0.57	0.30	2.0	0.2	0.15	0.02
8	17.7	17.7	3.1	2.1	0.70	0.92	3.2	2.9	0.23	0.27
9	20.2	20.2	2.2	2.0	0.40	0.54	1.4	1.6	0.09	0.13
10	22.0	22.0	3.4	3.5	0.72	0.82	3.7	4.3	0.24	0.32
11	23.0	23.4	1.4	1.5	0.20	0.16	0.4	0.4	0.03	0.03
12		25.0		1.0		0.30		0.5		0.03
13	26.5	26.2	3.4	2.2	0.45	0.57	2.3	1.9	0.15	0.13
14		27.1		2.3		0.19		0.7		0.04
15	29.0	28.8	2.7	1.9	0.44	0.40	1.8	1.2	0.11	0.07
16		29.9		2.2		0.22		0.8		0.05
17	32.7	32.6	4.6	2.4	0.19	0.35	1.3	1.3	0.08	0.08
18		34.6		2.2		0.24		0.8		0.05
19	36.2	36.3	3.7	2.7	0.37	0.29	2.1	1.2	0.13	0.07
20		39.6		3.7		0.22		1.2		0.08
21	42.2	43.3	3.7	2.7	0.24	0.20	1.4	0.8	0.09	0.05

duced in the one-electron theory without taking into account dipole matrix elements. In the energy range E>25 eV two variants of decomposition have different numbers of components due to discrepancies in calculated  $\varepsilon_2$  spectra. Besides, the underestimate of the theoretical  $\varepsilon_2$  spectrum encumbers the evaluation of the specific nature of components Nos. 12–21. We hope that further calculation will surely help correct it.

### **IV. SUMMARY**

In the present paper, we calculated theoretically the bands and the total and partial densities of states of  $CdF_2$ ; besides, we performed a theoretical calculation of the spectrum of the imaginary part of the dielectric function, presenting the results also in terms of the contributions of transitions between individual pairs of bands, taking into account the bands's localizations in Brillouin zone. From the experimental reflectivity spectra, we obtained full sets of the optical functions. This made it possible to compare in detail the results of two experimental papers with the results of our theoretical calculations and to discover their good agreement.

We found the parameters of the components of the fine structures of the  $\varepsilon_2$  spectra of CdF<sub>2</sub> in the wide energy region of fundamental absorption, obtaining, thereby, the most comprehensive experimental and calculated information on the energies and intensities of more than twenty principal transitions. For these transitions, we offered a theoretical explanation of their nature based on the model of direct interband transitions. An exception to this explanation is made by the longest wavelength and most intensive peak caused by the lowest energy exciton. It should be noted that both the majority of the remaining maxima of the integral  $\varepsilon_2(E)$  spectra and their components that we have found can be of exciton nature.

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