

Ionized donor pairs and microwave and far-infrared absorption in semiconducting CdF₂

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The dielectric permittivity $\varepsilon = \varepsilon_1 - i\varepsilon_2$ of semiconducting CdF₂:In, CdF₂:Ga, and CdF₂:Y crystals was studied over the frequency range from 34.0 to 37.5 GHz at temperatures from 1.8 to 100 K. The photoinduced transition from a semi-insulating to a conducting state in photochromic CdF₂:In and CdF₂:Ga crystals results in a significant increase of both the dielectric constant (by $\Delta\varepsilon_1 = 0.5$ to 1.4) and the dielectric-loss factor (by about an order of magnitude). The low-field dielectric-loss factor in these photodecolored crystals and in CdF₂:Y ($\varepsilon_2 = 0.1$ to 0.3) may be decreased by approximately an order of magnitude with an increase in the microwave-field power at 1.8 K. However, ε_2 ceases to depend on the field at $T > 4$ K. These features are explained by the theory of Tanaka *et al.* for resonant-saturated absorption of ionized donor pairs. We have modified this theory to cover the far-IR range of the absorption spectrum of semiconductors with various degree of compensation. Results following from the modified theory were compared with those obtained by three other groups, namely, Blinowski and Mycielski, Efros and Shklovskii, and Baranovskii and Uzakov. We have shown that the ionized donor pairs are responsible for the far-IR absorption in semiconducting CdF₂ studied experimentally by Eisenberger, Pershan, and Bosomworth. The role of impurity clusters in storage of an “excess” impurity and as a source of interstitial F⁻ ions during thermochemical treatment of as-grown crystals (which determines the ultimate semiconductive properties of CdF₂) is also discussed.

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I. INTRODUCTION

CdF₂ is the only fluorite-type crystal and the only highly ionic crystal that can be converted into a semiconducting state via doping with column-III elements of the periodic table and subsequent annealing in reducing atmosphere, for instance, in Cd vapor.¹ During this additive coloration process interstitial fluorine ions F⁻, which are charge compensators of the excess “+1” charge of the dopants, diffuse out of the volume of the crystal to the surface where they recombine with the reducing agent (Cd). The charge neutrality of the crystal is maintained by an opposite current of electrons into the volume. These electrons are localized in the conduction band or at hydrogenic donor orbitals (e_{hydr}) centered on the dopant, embracing at least 12 nearest cations, rather than at the inner atomiclike orbitals of the dopants, as it occurs during additive coloration of other fluorite-type crystals (CaF₂, SrF₂, BaF₂) doped with these elements.² Various authors estimate the Bohr radius of this orbital as 4–16 Å.^{3–8} The donor state in CdF₂ has a binding energy of ~ 100 meV. This is well above the corresponding energy in conventional semiconductors (for comparison, in most of the III-V crystals, this energy is about several meV and in II-VI crystals it amounts to 10–30 meV). The donor state in CdF₂ is responsible for the IR photoionization absorption band ($\lambda_{\text{max}} \approx 7 \mu\text{m}$), which extends to the visible range of the spectrum.^{4,6,9}

The room-temperature electronic conductivity of additively colored CdF₂ crystals can be as high as 10 Ohm⁻¹cm⁻¹. However, the maximum attainable concentration of free electrons does not exceed $\sim 10^{19}$ cm⁻³.^{3,10,11} At low temperatures, this conductivity turns into hopping conductivity between the donor levels.^{10,12}

Electron paramagnetic resonance (EPR) measurements of semiconducting CdF₂ crystals with diamagnetic Lu and Y

dopants reveal free-electron resonances with a g factor of about 2 at room temperature. At low temperatures, strongly broadened spectra of electrons at donor levels are detected.⁹ Neither free nor donor electrons are observed in EPR of CdF₂ crystals doped with paramagnetic rare-earth (RE) ions, probably due to their interactions with 4*f* electrons of the dopants.¹³ It was found that additive coloration of the crystals decreases the EPR signal of paramagnetic RE ions in cubic sites¹⁴ by 10–40%. This means that only 10 to 40% of these ions participate in the reduction process. It was also found that an increase of the dopant concentration from 0.01 to 0.3 mol%, i.e., by a factor of 30, results only in a threefold increase in concentration of electrons in the additively colored crystals.⁹ That is, the concentration of electrons introduced into the crystal during its coloration can be noticeably smaller than that of the dopant. Similar saturation phenomena were also observed in the IR absorption of CdF₂:Y.³ In this case, the intensity of the 7- μm photoionization absorption band tended to saturate as the activator concentration was increased above ~ 0.01 mol%.

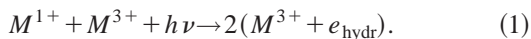
By analogy with Ca, Sr, and Ba fluorides,^{15,16} one may assume for CdF₂ that a limiting concentration of $\sim 10^{20}$ cm⁻³ of RE and Y ions can be introduced into CdF₂ as statistically distributed substitution (cubic) centers. The “redundant” impurities, whose solubility in CdF₂ is as high as 10 mol% or more, form impurity-fluorine clusters, which are readily observed in the optical spectra of RE ions at concentrations of ~ 0.1 mol% or more in the fluorite-type crystals,¹⁵ including CdF₂.¹⁷ The high solubility of some other impurities in CdF₂, such as In,¹⁸ suggests that the cluster formation is a general phenomenon typical for most of column-III impurities in this compound. Probably, that is these clusters which impede the complete removal of interstitial F⁻ ions from doped CdF₂ crystals during additive coloration. The inevitable presence of the interstitial F⁻ ions in

semiconducting CdF_2 crystals is the main result of this study. Therefore, the coexistence of the impurity-fluorine clusters and isolated defects, involving their dynamic interaction during the coloration process, allows us to explain the restrictions imposed on the maximum attainable electron concentration $\sim 10^{19} \text{ cm}^{-3}$, which were reported in Refs. 3, 10, and 11. According to the results of the EPR study,⁹ this concentration is likely to be about 10–40% of that of the cubic impurity centers in any “normal” semiconducting CdF_2 crystal.¹⁹

Among donor impurities in CdF_2 , Ga, and In play a special role, because these dopants form bistable centers in the reduced (semiconducting) crystals. Along with the “shallow” hydrogenic state, they also have a “deep” strongly localized state featuring a large lattice relaxation, i.e., a large shift in the corresponding configuration coordinate.^{20–22} As is shown in Refs. 23–26, the deep state is a two-electron state. The relaxation overcompensates the Coulomb repulsion of the two electrons with opposite spins at the same orbital. Such a large lattice relaxation is typical for two-electron metastable centers (*DX* centers) in conventional semiconductors with ionic-covalent bonds.^{27,28} In the predominantly ionic CdF_2 , this relaxation essentially arises from an increase in the covalence induced by the column IIIa (B subcolumn) dopants. On the contrary, the column IIIb (Sc subcolumn) dopants increase the ionicity of the bond (see Ref. 29 for details).

The microscopic nature of the *DX* centers in $\text{CdF}_2:\text{Ga}$ and $\text{CdF}_2:\text{In}$ was recently identified through direct first-principle calculations.³⁰ The formation of the deep state is accompanied by a [100]-axis displacement of a donor from the normal cation position (surrounded by a cube of eight F^- ions) into an adjacent empty cube of anions. This large lattice relaxation is responsible for the appearance of the energy barrier, which separates the deep state from the metastable substitutional (shallow donor) state. The barrier height is ~ 1 eV for Ga and is less than 0.1 eV for In.²³

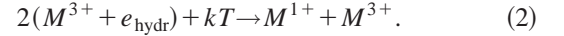
When cooled in the dark, reduced $\text{CdF}_2:\text{Ga}$ and $\text{CdF}_2:\text{In}$ crystals are semi-insulating ones because electrons introduced into the crystals during the coloration are predominantly localized at the deep M^{1+} centers ($M=\text{Ga, In}$). Illumination of the crystals by the light matching the UV-VIS photoionization absorption band of the deep centers results in releasing electrons into the conduction band and their subsequent trapping by ionized (“empty”) centers, which gives rise to the formation of neutral (shallow) donors. In addition, the ionized deep centers spontaneously transform into the shallow state. Thus, the photoionization of the deep centers proceeds as follows:



The quantum yield of this reaction, being equal to two, was experimentally confirmed in Ref. 23.

As a result of reaction Eq. (1), the UV-VIS band disappears, and instead, the $7\text{-}\mu\text{m}$ IR band arises in the absorption spectrum of $\text{CdF}_2:M$ crystals. (Below we refer to this reaction as the “photodecoloration process.”) Due to the above barrier, the photoinduced neutral donors are stable at T

<40 K for In and at $T < 200$ K for Ga.²³ With an increase in temperature, their thermal decay proceeds according to the reaction



In this work, we study the low-temperature complex permittivity of semiconducting $\text{CdF}_2:\text{Ga}$, $\text{CdF}_2:\text{In}$, and $\text{CdF}_2:\text{Y}$ crystals in the microwave range near $\lambda \approx 8$ mm and discuss an important role of the ionized donor pairs in formation of the dielectric response of these crystals in the microwave and far-IR (FIR) spectral regions. The low-temperature (down to 1 K) microwave absorption in semiconducting CdF_2 in magnetic fields up to 100 kG was studied in Ref. 8. Dielectric properties of undoped fluorite-type crystals, including CdF_2 , were reported in Ref. 31 for a wide spectral range.

II. EXPERIMENTAL

Crystals were grown from a melt using a modified Stokbarger-Bridgemen technique. In and Y were introduced into the mixture as fluoride compounds. The distribution coefficients of these dopants in CdF_2 are sufficiently large (0.34 and 1.38, respectively). The concentrations of In and Y ions in the grown crystals, $\sim 2 \times 10^{20} \text{ cm}^{-3}$, were determined by mass-spectrometric analysis. Ga shows low solubility in this crystal (the distribution coefficient being 0.05), and its concentration was $\sim 2 \times 10^{19} \text{ cm}^{-3}$. The additive coloration was performed in a mixture of K+Cd vapors in a chamber which provided separate temperature control of the crystal sample and the metal evaporator. In our typical coloration procedure, a temperature of ~ 500 °C was maintained for 30–40 min at the sample. Then the sample was cooled during ~ 1 h in a He gas flow. When the coloration parameters were varied in a wide range (by increasing the sample temperature, the Cd vapor pressure, and the coloration time), no increase in the concentration of the reduced impurity by more than 50% was observed, but the optical quality of the crystal deteriorated. The concentration of electrons injected into the crystals during coloration (which is equal to the maximum concentration of the neutral donors N_{sh}^0 at low temperatures) was determined from the absorption in the $7\text{-}\mu\text{m}$ IR band to an accuracy of $\sim 50\%$.^{3,5} For $\text{CdF}_2:\text{Ga}$, $\text{CdF}_2:\text{In}$, and $\text{CdF}_2:\text{Y}$ crystals under study, the electron concentrations were $N_{\text{sh}}^0 \approx 7 \times 10^{17}$, 3×10^{18} , and $2 \times 10^{18} \text{ cm}^{-3}$, respectively, being much lower than the total content of the corresponding impurities in the crystals.

The microwave real (ϵ_1) and imaginary (ϵ_2) parts of the dielectric permittivity of $\text{CdF}_2:\text{In}$, $\text{CdF}_2:\text{Ga}$, and $\text{CdF}_2:\text{Y}$ crystals were measured in a frequency range from 34.0 to 37.5 GHz at temperatures from 1.8 to 100 K. The cylindrical crystal samples, 2.0–2.5 mm in diameter, were placed in a cylindrical reflex resonator operating in the TE_{011} mode ($b \approx 6$ mm and $H \approx 7$ mm being, respectively, the radius and the height of the microwave cavity). The empty cavity, its loaded Q factor being $Q_{LO} \approx 5000$, was coupled to a waveguide transmission line and utilized almost the whole input microwave power ($\sim 98\%$) supplied from a Klystron. At the reso-

nance frequency of the cavity, the input microwave power of ~ 10 mW corresponded to an average amplitude of the microwave electric field $E \approx 100$ V/cm in the empty cavity and could be decreased by 0–30 dB with a calibrated attenuator.

The cavity perturbation technique used in these experiments is based on measuring both the loaded Q factor Q_{LS} and the frequency shift of the cavity, which occurs when a CdF_2 sample is inserted into the resonator. Dielectric losses in the sample caused lowering of the Q_{LS} factor and decoupling of the resonator with the waveguide transmission line. This could increase the microwave power reflected from the resonator by up to 100%.

The measurements were made at $T = 1.8$ K both in the dark and after illuminating the samples with UV-VIS light until the deep-to-shallow conversion of the photochromic centers in $\text{CdF}_2:\text{In}$ and $\text{CdF}_2:\text{Ga}$ crystals was completed. The most detailed measurements of the dark ϵ_1 and its shift upon illumination of the crystal $\Delta\epsilon_1$ were carried out for $\text{CdF}_2:\text{Ga}$ at $T = 1.8$ K. A cylindrical rod of ~ 2 mm diameter and ~ 10 mm length was made from the crystal and fixed inside the resonator along its axis in piston holes. In this case, the problem of finding ϵ_1 from the frequency shift of the cavity can be solved exactly.

When measuring ϵ_2 (and also ϵ_1 for $\text{CdF}_2:\text{In}$), the samples were partly inserted into the cavity along its axis by screwing them out of the hole in the upper piston of the resonator by 1.5–2.5 mm. The values of ϵ_1 and η (η being the filling factor, which is equal to the ratio of the energy of the electrical component of the microwave field in the whole volume of the resonator to that in the sample) were determined from the frequency shift by the perturbation-theory calculations. Solutions of the equation for the radial component of the electric field in the TE_{011} resonator with the cylindrical sample were found as the series

$$E(r, z) = \sum_{i=1}^L \sum_{j=1}^L C_{ij} J_1(X_i r/b) \sin(\pi z j/H), \quad (3)$$

where r and z are the cylindrical coordinates of the cavity ($0 \leq r \leq b$ and $0 \leq z \leq H$), and X_i is the i th root of the first-order Bessel function J_1 of the first kind. The number of the variable coefficients C_{ij} to be determined, $LL = 50 \times 50$, was restricted by the computer capacity.

It was assumed that, in the dark, $\epsilon_1 = 8$ (see Ref. 31) when its value was not determined experimentally. The values of ϵ_2 were determined from the ratio

$$\epsilon_2/\epsilon_1 = \tan \delta = \eta(Q_{LS}^{-1} - Q_{LO}^{-1}). \quad (4)$$

At $T = 1.8$ – 4.2 K, as-grown (uncolored) CdF_2 crystals appeared to have no noticeable dielectric losses and did not react to the illumination in any way. However, even in the dark all the reduced samples showed substantial dielectric losses. The microwave dielectric properties of semiconducting $\text{CdF}_2:\text{Y}$ crystal are independent of illumination. In contrast, upon illumination of photochromic $\text{CdF}_2:\text{Ga}$ and $\text{CdF}_2:\text{In}$ samples (cooled to a low temperature in the dark) in the microwave resonant cavity, both a monotonic decrease of the resonator frequency (down to a few hundreds of mega-

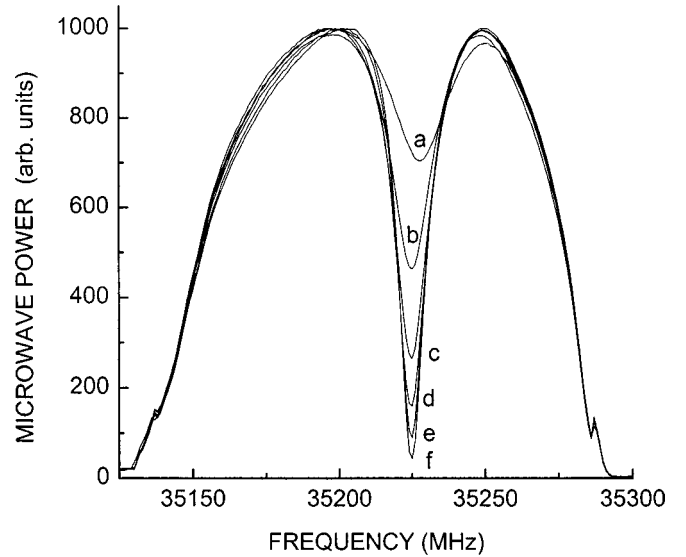


FIG. 1. Normalized frequency dependences of klystron-generated microwave power reflected from the resonant cavity with $\text{CdF}_2:\text{Ga}$ crystal in the dark at different attenuations of the input power (a) 30, (b) 27, (c) 25, (d) 23, (e) 20, and (f) 17 dB. $T = 1.8$ K. $\eta \approx 3.2$.

hertz) and a monotonic increase of the dielectric losses (by about an order of magnitude) were simultaneously observed. These changes reached saturation after continuous illumination. Thus, a substantial increase of both the real and imaginary parts of the complex permittivity was detected during illumination of photochromic $\text{CdF}_2:\text{Ga}$ and $\text{CdF}_2:\text{In}$ crystals. Cessation of the illumination at any time fixed the shift of the complex permittivity at the magnitude reached. The rate of change and, consequently, the time interval that was needed to achieve the maximum permittivity under illumination are governed by the light intensity, as expected for the photodecoloration process.

At $T = 1.8$ K, the saturation of the dielectric losses with the microwave power increase was observed both for non-photochromic $\text{CdF}_2:\text{Y}$ and at any stage of the photodecoloration process in photochromic $\text{CdF}_2:\text{Ga}$ and $\text{CdF}_2:\text{In}$ crystals. In the range of the microwave frequencies studied, the measured value of ϵ_2 could be decreased by about an order of magnitude with an increase in the input microwave power from the minimum level of 30-dB attenuation (see Figs. 1–3). These saturation effects disappeared when the temperature was increased to ~ 4 K.

The temperature dependence of the dielectric loss factor $\epsilon_2(T)$ at various attenuations of the input microwave power was studied both in the dark and under illumination of semiconducting CdF_2 . In the most interesting temperature range 1.8–4.2 K, the dielectric losses were measured in one fixed position of the sample in the resonant cavity. This ensured the maximum reliability of the results. As the temperature increased, a growing value of ϵ_2 called for readjustment of the sample in the cavity. The experimental dependences $\epsilon_2(T)$ for $\text{CdF}_2:\text{Ga}$ at various microwave power levels are shown in Figs. 4 and 5.

The dielectric permittivities of the samples studied at low

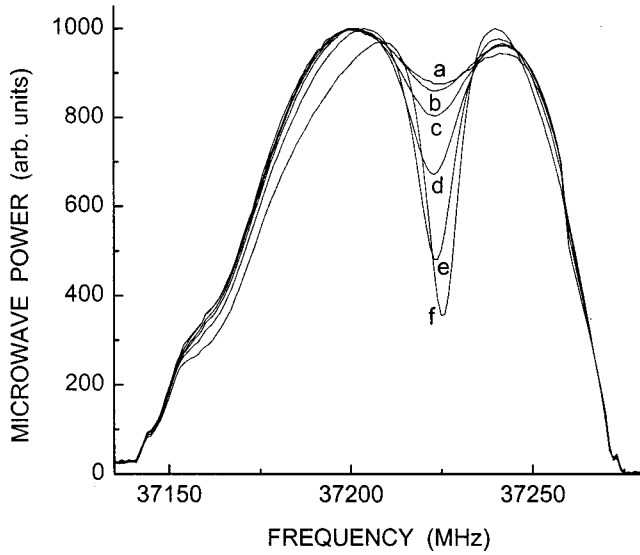


FIG. 2. Normalized frequency dependences of klystron-generated microwave power reflected from the resonant cavity with $\text{CdF}_2:\text{Y}$ crystal at different attenuations of the input power (a) 30, (b) 20, (c) 15, (d) 10, (e) 5, and (f) 0 dB. $T=1.8$ K. $\eta \approx 39$.

microwave fields and the maximum changes in their values observed after illumination at $T=1.8$ K are given in Table I. Within experimental error, all the above results were independent of microwave frequency throughout the frequency range studied.

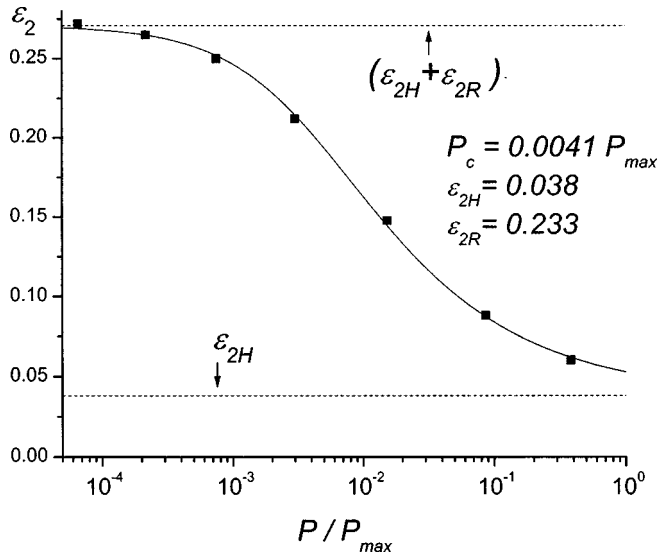


FIG. 3. Values of ϵ_2 for $\text{CdF}_2:\text{Y}$ vs microwave power P stored in the resonant cavity with the sample (in units of the P_{\max} -microwave power stored in the empty cavity at the 0-dB attenuation). Solid line is the least-square fit with the function $\epsilon_2(P) = \epsilon_{2H} + \tilde{\epsilon}_{2R}(P)$ to the experimental data depicted by dots. The field-independent part ϵ_{2H} and the field-dependent part $\tilde{\epsilon}_{2R}(P) = \epsilon_{2R}/(1 + P/P_c)^{1/2}$, of the dielectric loss factor are due to the hopping conductivity and to the resonant absorption, respectively. Dashed lines show the levels of ϵ_{2H} and $(\epsilon_{2H} + \epsilon_{2R})$. The measurements were made with 36 GHz microwaves at $T=1.8$ K and $\eta \approx 39$.

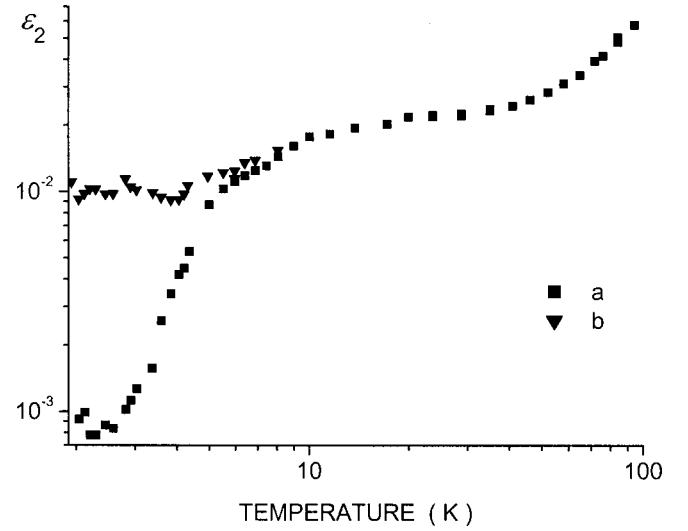


FIG. 4. $\epsilon_2(T)$ dependence for $\text{CdF}_2:\text{Ga}$ crystal in the dark, measured with 36 GHz microwaves. Attenuation of the input microwave power: (a) 0 dB and (b) 30 dB.

III. DISCUSSION OF RESULTS

We have to explain two phenomena observed (i) the saturation of dielectric losses with an increase in the microwave power in semiconducting CdF_2 at $T < 4$ K and (ii) the substantial change of the dielectric permittivity of photochromic $\text{CdF}_2:\text{Ga}$ and $\text{CdF}_2:\text{In}$ after illumination (see Table I). It is shown below that both effects are due to resonant absorption of ionized donor pairs.^{32,33}

All the permittivity changes observed after illumination of photochromic CdF_2 , which are listed in Table I, are apparently due to the deep-to-shallow conversion of the impurity centers in accordance with Eq. (1). The cessation of illumination at $T < 40$ K for In and at $T < 200$ K for Ga “freezes” these changes, because the reverse reaction [see Eq. (2)] proceeds only at higher temperatures. Semiconducting $\text{CdF}_2:\text{Y}$

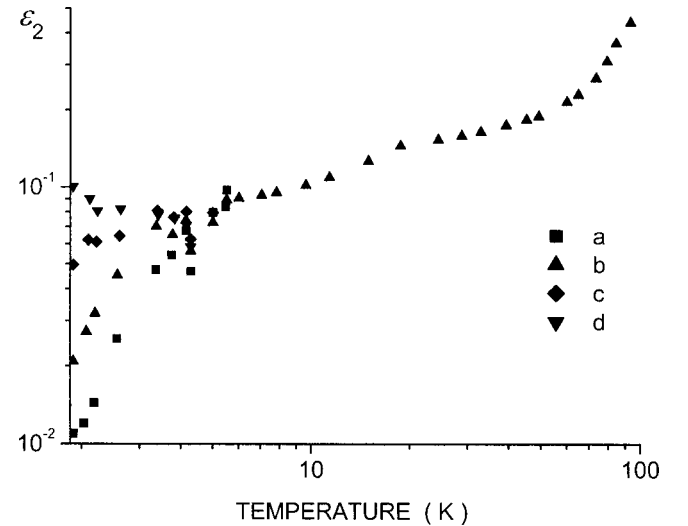


FIG. 5. $\epsilon_2(T)$ dependence for $\text{CdF}_2:\text{Ga}$ crystal after illumination, measured with 36 GHz microwaves. Attenuation of the input microwave power (a) 0 dB, (b) 7 dB, (c) 15 dB, and (d) 25 dB.

TABLE I. Experimental parameters of semiconducting CdF₂ crystals. Permittivity was measured with 8-mm microwaves at $T=1.8$ K .

Sample	Total content of impurity	N_{sh}^0 (cm ⁻³)	ϵ_l in the dark	$\Delta\epsilon_l$ after illumination	$\epsilon_2^{b,c}$	
					in the dark	after illumination
CdF ₂ :Ga	$(2 \pm 1) \times 10^{19}$	$(7 \pm 3) \times 10^{17}$	7.6 ± 0.1^a	0.5 ± 0.1^a	0.01 ± 0.005	0.1 ± 0.05
CdF ₂ :In	$(2 \pm 1) \times 10^{20}$	$(3 \pm 1) \times 10^{18}$		1.4 ± 0.4^b	0.02 ± 0.01	0.1 ± 0.05
CdF ₂ :Y	$(2 \pm 1) \times 10^{20}$	$(2 \pm 1) \times 10^{18}$			0.3 ± 0.1	

^aA cylindrical rod-shaped sample of ~ 2 mm diameter was fixed inside the cavity along its axis in the piston holes of the resonator.

^bA cylindrical sample was partly inserted into the cavity along its axis by screwing it out of the hole in the upper piston of the resonator by 1.5–2.5 mm.

^cMeasured at attenuation of the input microwave power of 30 dB.

crystal is not photochromic, and its illumination does not produce any changes in its dielectric response.

Upon completing the photodecoloration process at a low temperature, photochromic CdF₂:Ga and CdF₂:In crystals have no deep centers, and, in terms of their electrical properties, they are the same objects as any other semiconducting CdF₂, including nonphotochromic CdF₂:Y. All these crystals may be treated as compensated n -type semiconductors with donors having an electron bound to a hydrogenic orbital. Below we assume its Bohr radius $a = 7 \text{ \AA}$ (see Ref. 5). The donors are partly compensated by interstitial F⁻ ions. We further assume that clusters, though they do exist, do not manifest themselves in electron processes. (The role of clusters will be discussed below.)

Thus, the model of semiconducting CdF₂ crystal at low temperatures, which is discussed below, involves the neutral and ionized (positively charged) donor centers with concentrations N_{sh}^0 and N_{sh}^+ , respectively. Interstitial F⁻ ions with concentration $N_F = N_{sh}^+$ act as ionized acceptors. It is obvious that N_{sh}^0 is also the concentration of electrons injected into the crystal in the process of its conversion into the semiconducting state. By introducing the degree of compensation of the semiconductor K and the total concentration of donor centers $N_D \equiv N_{sh}^0 + N_{sh}^+$, N_{sh}^0 , and N_{sh}^+ can be represented as follows: $N_{sh}^0 = N_D(1 - K)$, $N_{sh}^+ = N_D K$.

The dielectric response of a semiconductor is strongly influenced by the nearest pairs of neutral and ionized donors, which are referred to as the “ionized donor pairs.” The resonant absorption of the microwave field by the ionized donor pairs was discovered by Tanaka and Fan in Si.³² A theory of this phenomenon was developed by Tanaka *et al.*,³³ and by Blinowski and Mycielski³⁴ who also found that the resonant absorption shows a maximum at the energy of a quantum of electromagnetic field $\hbar\omega_{\max}$ in the FIR region (lying within 10 to 200 cm⁻¹).³⁴ These FIR bands were experimentally revealed by Milward and Neuringer³⁵ and studied in detail in weakly doped Si and Ge (for example, see Ref. 36).

The theory of Blinowski and Mycielski³⁴ is valid only in the low-compensation case ($K \leq 0.2$). Its version proposed by Baranovskii and Uzakov³⁷ is based on the calculation of the distribution function of the ionized donor pairs $F(\Omega, r)$, so that $4\pi r^2 F(\Omega, r) dr d\Omega$ gives the probability to find in the unit volume the pair of ionized and neutral donors with the

distance between them lying in the range $(r, r + dr)$ and with the energy difference lying in the range $(\Omega, \Omega + d\Omega)$. (The definition of the energy Ω is given below.)

The theory of Tanaka *et al.*³³ also applies to the low-compensation case. However, unlike the theory of Blinowski and Mycielski, it involves the simplifying assumption that all the pairs with $\Omega \leq \hbar\omega$ equally contribute to the absorption at the frequency ω .

For the intermediate-compensation case $0.1 \leq K \leq 0.9$ no analytical solution is available. Nevertheless, rigorous theoretical estimates of the spectral dependence of the absorption coefficient for low and high frequencies relative to the peak ω_{\max} are possible. These estimates were discussed in detail in Efros and Shklovskii’s review³⁸ and are used in our study. In Ref. 39, the $F(\Omega, r)$ function was calculated numerically by simulating the impurity band with the Monte Carlo technique for discrete values of $K = 0.1$ to 0.9. The absorption coefficient was then found for discrete frequencies $\hbar\omega/2E_D = 0.025$ to 0.175, where $E_D = e^2/\epsilon_1 r_D$ is the energy width of the impurity band and $r_D = N_D^{-1/3}$ is the average distance between the donor centers.

Below, basing on the theory of Tanaka *et al.*,³³ we propose simple analytical expressions for the microwave and FIR absorption coefficient for the intermediate-compensation case over the frequency range in which the donor-pair theory is applicable. (Gaussian cgs units are used.) The results are compared with Efros and Shklovskii’s estimates³⁸ for frequencies both larger and smaller than ω_{\max} . The spectral dependences calculated according to our modification of the theory of Tanaka *et al.*³³ are compared with numerical values calculated using tables of Ref. 39 and also with the experimental data of Eisenberger, Pershan, and Bosomworth⁷ on the FIR absorption in semiconducting CdF₂. Experimental values of ϵ_2 at $\hbar\omega = 1.2 \text{ cm}^{-1}$, which corresponds to the microwave quantum energy in the frequency range under study, are compared with those calculated according to our modification of the theory of Tanaka *et al.*, within the Colomb-gap theory³⁸ and the linear conductance theory.⁴⁰

Provided the nearest-neighbor donors are identical, the single electron of the ionized donor pair has an equal probability to be found at each of these donor centers. The situation is similar to that for the molecular H₂⁺ ion. The doubly degenerate ground state of such a system splits into a lower

bonding and excited antibonding states separated by an energy interval W . These two states are described by the symmetric $(1/\sqrt{2})[\Psi_A(r) + \Psi_B(r)]$ and the antisymmetric $(1/\sqrt{2})[\Psi_A(r) - \Psi_B(r)]$ wave functions, respectively. Here, $\Psi_A(r)$ and $\Psi_B(r)$ are the hydrogenic wave functions of the electron at the isolated donor centers A and B that compose the pair. Depending on the distance r_ω between the donors in the pair, the "quantum repulsion" (splitting) energy W , which is resonant to the frequency ω of the electromagnetic field, for $r_\omega > a$ can be fairly accurately represented as³³

$$\hbar\omega = W(r_\omega) \approx (4e^2/3\epsilon_1 a) \frac{r_\omega}{a} \exp(-r_\omega/a). \quad (5)$$

The matrix element of the electric-dipole transition reads

$$P_e = er_\omega/2, \quad (6)$$

where e is the electron charge.

For the following consideration, it is necessary to define the majority and minority donor concentrations of the two types of donor centers in question: $N_{\text{maj}} = \max(N_{sh}^0, N_{sh}^+)$ and $N_{\text{min}} = \min(N_{sh}^0, N_{sh}^+)$.⁴¹ In the statistical distribution of the donors, the probability of any minority donor to find the nearest majority donor within the spherical layer of radius r and thickness dr is as follows:

$$df(r) = \frac{3r^2}{\bar{R}^3} \exp\left[-\left(\frac{r}{\bar{R}}\right)^3\right] dr, \quad (7)$$

where $\bar{R} = (\frac{4}{3}\pi N_{\text{maj}})^{-1/3}$ is the average separation between the majority donors. The density of states for the ionized donor pairs is then

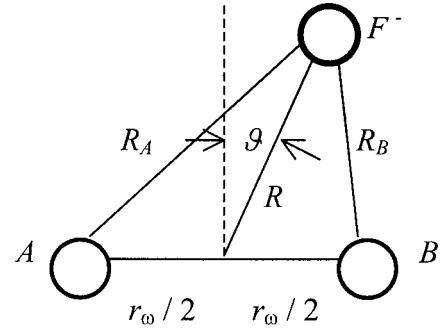
$$\begin{aligned} n(\omega) &= N_{\text{min}} \frac{df(r)}{dr} \frac{dr}{d\omega} = \hbar N_{\text{min}} \frac{df(r)}{dr} \left(\frac{dW}{dr}\right)^{-1} \\ &\cong N_{\text{min}} \frac{3r_\omega^2}{\bar{R}^3} \exp\left[-\left(\frac{r_\omega}{\bar{R}}\right)^3\right] \frac{a}{\omega}. \end{aligned} \quad (8)$$

The donor pairs located within the resonant separation $r_\omega < \bar{R}$ can be considered as isolated ones. However, we suppose that a significant concentration of the interstitial F^- ions and, possibly, of other charged centers causes detuning of the resonance between the energy levels of the pairs by the amount⁴²

$$\Omega \equiv \Omega(r_\omega, R, \sin \vartheta) = \frac{e^2}{\epsilon_1 R_B} - \frac{e^2}{\epsilon_1 R_A} \cong \frac{e^2}{\epsilon_1 R^2} (R_A - R_B). \quad (9)$$

Here R_A , R_B , and R are the distances from the F^- ion to the A and B donors and to their center of gravity, respectively, and θ is the angle of R with the perpendicular to the $A-B$ axis (see Fig. 6). Then, the energy separation between the two lowest levels of the pair is³³

$$\zeta = (W^2 + \Omega^2)^{1/2}. \quad (10)$$



$$\begin{aligned} R_A^2 &= \left(\frac{r_\omega}{2}\right)^2 + R^2 + r_\omega \cdot R \cdot \sin \vartheta \\ R_B^2 &= \left(\frac{r_\omega}{2}\right)^2 + R^2 - r_\omega \cdot R \cdot \sin \vartheta \end{aligned}$$

FIG. 6. Schematic diagram of the ionized donor pair $A-B$ perturbed by an interstitial F^- ion.

If $\Omega \gg W$, the matrix element of the electric-dipole transition P_e decreases with increasing Ω as

$$P_e = (W/\Omega)er_\omega/2. \quad (11)$$

Let us restrict our discussion to an ionized donor pair and the nearest interstitial F^- ion (or any other charge center). We assume that they may be considered separately from the remaining ensemble of the impurities. This means the fulfillment of the inequality $r_\omega < R_p$, where R_p is the average distance between the pair and the nearest perturbing impurity whose total concentrations is $N_p \gg N_F$. It is very likely that in "ordinary" semiconductor $R_p = \bar{R}$ (see below). By analogy with Tanaka *et al.*,³³ we assume that all the pairs with $\Omega \leq W = \hbar\omega$ contribute equally⁴³ to the resonant absorption of the donor pairs at frequency ω , and their resonant length r_ω and P_e values are defined by Eqs. (5) and (6). For any given ω and R , we can find the limiting angle θ_{lim} ($0 \leq \theta_{\text{lim}} \leq \pi/2$) for which $\Omega = W$, as well as the limiting distance

$$R_{\text{max}}(\omega) \cong \left(\frac{e^2 r_\omega}{\epsilon_1 \hbar \omega}\right)^{1/2}, \quad (12)$$

for which $\theta_{\text{lim}} = \pi/2$. The perturbing influence of the charge impurity can evidently be neglected at $R \geq R_{\text{max}}$. Let us define the function $\Phi(\omega, r) = \sin(\theta_{\text{lim}})$ at $R \leq R_{\text{max}}$ and $\Phi(\omega, r) = 1$ at $R \geq R_{\text{max}}$. The relative number of all the donor pairs $S_p(\omega) \leq 1$, with the separation r_ω , which contribute to the resonant absorption at the frequency ω is then

$$S_p(\omega) = \int_0^\infty \frac{3x^2}{R_p^3} \exp[-(x/R_p)^3] \Phi(\omega, x) dx. \quad (13)$$

Finally, the frequency dependence of the imaginary part of permittivity $\epsilon_2(\omega)$ related to the resonant absorption of ionized donor pairs can be written as⁴⁴

$$\begin{aligned}
\varepsilon_2(\omega) &= \frac{4\pi^2}{3\hbar} N_{\min} n(\omega) S_p(\omega) P_e(\omega)^2 \\
&\quad \times (1 + E^2/E_c^2)^{-1/2} \tanh\left(\frac{\hbar\omega}{2kT}\right) \\
&= \frac{\pi^2}{\hbar\omega} N_{\min} S_p(\omega) e^2 \bar{R} a \left(\frac{r_\omega}{\bar{R}}\right)^4 \exp\left[-\left(\frac{r_\omega}{\bar{R}}\right)^3\right] \\
&\quad \times (1 + E^2/E_c^2)^{-1/2} \tanh\left(\frac{\hbar\omega}{2kT}\right). \quad (14)
\end{aligned}$$

Here, k is the Boltzmann constant, E is the amplitude of the ac electric field, and E_c is its critical value. Using the relation

$$\alpha(\omega) = \sqrt{2} \frac{\omega}{c} [(\varepsilon_1^2 + \varepsilon_2^2)^{1/2} - \varepsilon_1]^{1/2} \cong \frac{\omega}{c} \frac{\varepsilon_2(\omega)}{\sqrt{\varepsilon_1}}, \quad (15)$$

one can also derive the frequency dependence of the optical absorption coefficient $\alpha(\omega)$.

It should be noted that Eq. (14) is valid in a wide range of frequencies, in contrast to the basic formula for the ac conductivity $\sigma(\omega) = \omega\varepsilon_2(\omega)/4\pi$, derived in the work of Tanaka *et al.*³³ in the low-frequency approximation⁴⁵ (see below).

Thus, the ionized donor pairs feature a continuous and fairly broad energy spectrum. Since the energy splittings between their bonding and antibonding states are much smaller than the donor ionization energy, at low temperatures these pairs can be considered as “electron” two-level systems (TLS’s) with the effective spin $S = \frac{1}{2}$, which are formally similar⁴⁶ to the well-known “ion” TLS’s observed in glasses⁴⁷ and crystals.^{15,48} This similarity allows us to derive Eq. (14) for the dielectric loss factor on the basis of the TLS theory.^{44,49} However, we use the $n(\omega)$, $S_p(\omega)$, and $P_e(\omega)$ dependences and E_c parameter that are specific for the ionized donor pairs.

The conventional “ion” TLS’s are produced by atoms or groups of atoms tunneling in amorphous dielectrics or in glass-like features of the crystals with extended “porous” defects. In particular noteworthy are the studies of the ion TLS’s in dielectric crystals with the fluorite-type structure,^{50–52} in which a broadband resonant microwave and FIR absorption was also found. All the experimental facts discussed here are clear evidence of the electronic nature of the observed TLS. Among these facts are the existence of the resonant absorption only in reduced samples and its significant increase after illumination of photochromic CdF₂ crystals (due to an increase in concentration of electrons at the shallow donor levels).

The experimental dependences of the microwave absorption on temperature and microwave power can be explained using Eq. (14) in terms of TLS theory.^{44,49} In the absence of the electromagnetic field, the thermal equilibrium leads to the Boltzmann population of the TLS. High-power field $E \gg E_c$ can be eliminate the differences in population of the levels whose splittings are resonant with the field. As a result, a “hole” appears in the broad absorption spectrum of

the TLS. Its width is proportional to $\sim E \sim P^{1/2}$ (where P is the microwave power stored in the resonant cavity). The microwave power absorbed by the TLS increases by the same square root law. However, the ratio of absorbed to input microwave power P_{in} accordingly decreases as $\sim E^{-1} \sim P^{-1/2} \sim P_{\text{in}}^{-1/2}$. This explains the saturation of the dielectric loss factor with increased microwave power observed at temperatures from 1.8 to 4 K (see Figs. 4 and 5). The same processes are responsible for the “improvement” of the resonator curve with an increase in the input microwave power (see Figs. 1 and 2). In this case, the Q_{LS} factor of the cavity with the sample increases, the resonator coupling with the waveguide transmission line is partly restored, and the microwave power reflected from the resonator decreases.

The saturation of dielectric losses with increasing input microwave power is evidence of the mainly resonant absorption of the ionized donor pairs at 1.8 K. Figure 3 shows that the decrease in the field-dependent part of the dielectric loss factor with an increase of the microwave power agrees well with the theoretical dependence [Eq. (14)] for the resonant absorption in a wide range of P values.⁵³ It should be noted that the saturation phenomenon discards the supposition of Ref. 9 about the quasi-free motion of electrons in some restricted areas in semiconducting CdF₂ at low temperatures.⁵⁴

In all the crystals studied, the saturation of the dielectric losses disappears at $T > 4$ K (see Figs. 4 and 5). Here, the resonant absorption (which must fall with increasing T as $\sim \hbar\omega/kT$) is evidently replaced by the relaxation absorption. The latter is due to phonon-assisted hopping of electrons between energy levels of the polar pairs with length r and energy gap $\zeta \sim kT$ modulated by $\Delta\zeta \approx 2e(\mathbf{r} \cdot \mathbf{E})$ in the ac electric field.^{12,33,44}

It is interesting to compare the resonant absorption of donor pairs in CdF₂ and in a conventional semiconductor, e.g., in the n -type Si (see Refs. 32–34). The small compensation of such a semiconductor $K < 0.1$ is obtained via introduction of small amount of acceptors N_A ($N_A \ll N_{sh}^0$). At low temperatures, all the acceptors are charged by trapping electrons from the donors, and a hopping conductivity of the same amount of the electron vacancies N_A over donor levels can arise ($N_{sh}^+ = N_A$). After trapping an electron, each of the N_A acceptor acquires an effective charge “−1,” which attracts an electron vacancy (a hole) to the nearest donor, rendering it ionized. Since the same charge perturbs the ionized donor pair formed by this ionized donor and the next-nearest neutral donor, the donor pairs in the n -type Si are “tied” to the perturbing impurities. Consequently, in this case $R_p = \bar{R}$, i.e., the average distance between the pair and the nearest perturbing impurity (acceptor) is equal to that between the neutral (majority) donors ($N_{\text{maj}} = N_{sh}^0$). The same appears to hold for donor pairs in semiconducting CdF₂ at $N_p = N_F = N_{sh}^+ < N_{sh}^0$, where interstitial F[−] ions act as ionized acceptors. However, the concentration of the perturbing impurity in semiconducting CdF₂ usually exceeds that of the neutral donors, i.e., $N_p = N_F = N_{sh}^+ > N_{sh}^0$. In this case, $R_p = \bar{R}$ as well, because the average distance between the pair and the nearest perturbing impurity is determined by the concentra-

tion of the ionized (majority) donors ($N_{\text{maj}} = N_{sh}^+$). Thus, the equality $R_p = \bar{R}$ appears to be true at any degree of compensation, and $S_p(\omega)$ is independent of concentration of the minority donors N_{min} . Hence, it follows from Eqs. (14) and (15) that, for a given value of N_{maj} , the spectra $\varepsilon_2(\omega)/N_{\text{min}}$, and $\alpha(\omega)/N_{\text{min}}$ are independent of N_{min} .

The donor-pair approach is known to be applicable under the following conditions:³⁸

$$r_\omega \ll r_D, \quad \hbar\omega \ll E_D, \quad \text{and} \quad \hbar\omega \ll e^2/\varepsilon_1 r_\omega. \quad (16)$$

These conditions are evidently equivalent to the inequality

$$W(r_D) \ll \hbar\omega \ll E_D. \quad (17)$$

Let us compare spectral dependences of FIR absorption given by Eqs. (14) and (15) at various K with Efros and Shklovskii's estimates³⁸ obtained in the low- and high-frequency approximations.

Low-frequency range: $\hbar\omega \ll E_D r_\omega / r_D$. The low-frequency range condition is equivalent to the inequality $\bar{R} \ll R_{\text{max}}(\omega)$. (It is this condition which was used by Tanaka *et al.*³³) One can easily see that, from $\bar{R}^2 \ll R_{\text{max}}^2 = e^2 r_\omega / \varepsilon_1 \hbar\omega$, it follows that $\hbar\omega \ll e^2 r_\omega / \varepsilon_1 \bar{R}^2 \sim E_D r_\omega / r_D$. The main contribution to the integral for the function $S_p(\omega)$ in Eq. (13) comes from the area $x \sim R_p = \bar{R} \ll R_{\text{max}}$. Finally, we have

$$\begin{aligned} \Omega &\cong \frac{e^2}{\varepsilon_1 R^2} (R_A - R_B) \cong \frac{e^2 r_\omega}{\varepsilon_1 R^2} \sin(\vartheta_{\text{lim}}) = \hbar\omega, \\ \Phi(\omega, R) &\approx \frac{\varepsilon_1 \hbar\omega R^2}{e^2 r_\omega} = \frac{R^2}{R_{\text{max}}^2}, \\ S_p(\omega) &\approx \frac{\varepsilon_1 \hbar\omega R_p^2}{e^2 r_\omega} \Gamma\left(\frac{5}{3}\right) \approx \frac{\varepsilon_1 \hbar\omega \bar{R}^2}{e^2 r_\omega} = \frac{\bar{R}^2}{R_{\text{max}}^2(\omega)}. \end{aligned} \quad (18)$$

It follows from Eqs. (12), (14), (15), and (18) that at $\hbar\omega \gg kT$ and $E \ll E_c$:

$$\begin{aligned} \alpha(\omega) &= \frac{\pi^2}{c} \sqrt{\varepsilon_1} \frac{a}{\bar{R}} \omega r_\omega^3 N_{\text{min}} \\ &= \left(\frac{4}{3}\pi\right)^{1/3} \frac{\pi^2}{c} \sqrt{\varepsilon_1} a \omega r_\omega^3 N_{\text{min}}^{1/3} N_{\text{maj}}^{2/3} \\ &= \left(\frac{4}{3}\pi\right)^{1/3} \frac{\pi^2}{c} \sqrt{\varepsilon_1} a \omega r_\omega^3 N_D^{4/3} K^+(1-K)^{1/3} \\ &\approx \frac{4\pi^3}{6c} \sqrt{\varepsilon_1} a \omega r_\omega^3 N_D^{4/3} K(1-K). \end{aligned} \quad (19)$$

Here, $K^+ = \min(K, 1-K)$ and the latter approximate equality is fairly accurate in the whole range $0 \leq K \leq 1$. Equation (19) is similar to Efros and Shklovskii's estimate

$$\alpha(\omega) = \frac{4\pi^3}{6c} \sqrt{\varepsilon_1} a \omega r_\omega^3 N_D^{4/3} K f(K), \quad (20)$$

where $f(K)$ is a function of the compensation.³⁸

High-frequency range: $\hbar\omega \gg E_D r_\omega / r_D$. This condition is equivalent to $\bar{R} \gg R_{\text{max}}(\omega)$. In this case, the main contribution to the integral for the function $S_p(\omega)$ in Eq. (13) comes from $x \sim R_p = \bar{R} \gg R_{\text{max}}$. Here, $\Phi(\omega, x) \approx 1$ and, consequently, $S_p(\omega) \approx 1$. Finally, we have

$$\begin{aligned} \alpha(\omega) &= \frac{\pi^2 e^2}{\hbar c \sqrt{\varepsilon_1}} \frac{a}{\bar{R}^3} r_\omega^4 N_{\text{min}} = \frac{4\pi^3}{3} \frac{e^2}{\hbar c \sqrt{\varepsilon_1}} a r_\omega^4 N_{\text{min}} N_{\text{maj}} \\ &= \frac{4\pi^3}{3} \frac{e^2}{\hbar c \sqrt{\varepsilon_1}} a r_\omega^4 N_D^2 K(1-K), \end{aligned} \quad (21)$$

which is again similar to Efros and Shklovskii's estimate

$$\alpha(\omega) = \frac{4\pi^3}{3} \frac{e^2}{\hbar c \sqrt{\varepsilon_1}} a r_\omega^4 N_D^2 K f(K). \quad (22)$$

Thus, the spectral dependences of FIR absorption in both the low-frequency and high-frequency approximations obtained according to our modification of the theory of Tanaka *et al.* are very close to Efros and Shklovskii's estimates at any value of K . However, Eqs. (14) and (15) describe optical absorption in the whole spectral range determined by Eqs. (16) and (17), and we will use them further.

Very-low frequency range. This is the range in which the donor-pair approach is inapplicable. It was shown in Ref. 38 that, due to the long-range electrostatic interaction between impurity centers in weakly doped semiconductors, the density of electron states decreases in the vicinity of the Fermi level, and the Coulomb gap arises. For the intermediate-compensation case, the width of the gap Δ_c is of the same order of magnitude as the width of the impurity band (E_D). For very low frequencies, when $\hbar\omega \ll e^2/\varepsilon_1 r_\omega \ll \Delta_c$, which is equivalent to the condition $r_\omega \gg r_D$, the frequency dependence of the absorption coefficient is given by³⁸

$$\alpha(\omega) \sim \omega / r_\omega. \quad (23)$$

This relationship corresponds to the super-linear frequency dependence of the absorption coefficient. This dependence is $\sim r_\omega^4$ times steeper than that predicted by the donor-pair theory for the low-frequency range [see Eqs. (19) and (20)].

However, experimental data are available³⁶ that show linear dependence of $\alpha(\omega)$ on the frequency in semiconductors with really statistical and homogeneous distribution of the dopant, as in the p -type Ge prepared with the neutron transmutation doping technique:

$$\alpha(\omega) \sim \omega. \quad (24)$$

Phillips⁴⁰ has proposed a linear conductance theory which employs an electron compartmentalization model and explains this dependence at frequencies down to $\omega \rightarrow 0$.

Note the presence of the exponential term $\exp[-(r_\omega/\bar{R})^3]$, in Eq. (14), which provides an abrupt decrease of the absorption at the boundary of applicability of the donor-pair theory at $r_\omega > \bar{R} \sim r_D$ due to the allowance for

TABLE II. Some numerical parameters for semiconducting CdF₂ with ionized donor pairs ($a=7 \text{ \AA}$).

	$N_{sh}^0 = 7 \times 10^{17} \text{ cm}^{-3}$					$N_{sh}^0 = 2 \times 10^{18} \text{ cm}^{-3}$				
	$K=0.1$	$K=0.3$	$K=0.5$	$K=0.7$	$K=0.9$	$K=0.1$	$K=0.3$	$K=0.5$	$K=0.7$	$K=0.9$
N_D (10^{18} cm^{-3})	0.78	1.0	1.4	2.3	7.0	2.2	2.9	4.0	6.7	20
N_F (10^{18} cm^{-3})	0.08	0.3	0.7	1.6	6.3	0.2	0.9	2.0	4.7	18
\bar{R} (\AA)	70	70	70	53	34	49	49	49	37	24
r_D (\AA)	109	100	89	75	52	77	71	63	53	37
$W(r_D)$ (cm^{-1})	0.008	0.025	0.10	0.62	11.7	0.53	1.2	3.1	10.5	75
E_D (cm^{-1})	132	144	161	191	276	188	204	229	271	391
$r_{\omega \max}^T$ (\AA)	37	37	37	34	28	33	33	33	29	22
$\hbar \omega_{\max}^T$ (cm^{-1})	71	71	71	106	210	117	117	117	180	368
$\hbar \omega_{\max}^{\text{BM}}$ (cm^{-1})	73					118				
r_{ω}/r_D^a	0.65	0.70	0.79	0.93	1.3	0.92	1.0	1.1	1.3	1.9
S_p^a	0.0077	0.0077	0.0077	0.0056	0.0043	0.0053	0.0053	0.0053	0.0045	0.0044
$\varepsilon_2^{\text{Ta}}$	0.044	0.171	0.400	0.175	6×10^{-4}	0.038	0.145	0.339	0.014	2×10^{-10}
$\varepsilon_2^{\text{BMa}}$	0.050					0.181				
$\varepsilon_2^{\text{ESa}}$	0.019	0.053	0.065	0.052	0.010	0.046	0.098	0.102	0.094	0.051
$\varepsilon_2^{\text{Pa}}$	0.024	0.066	0.083	0.068	0.014	0.060	0.130	0.138	0.131	0.093

^aParameters are given for the microwave electromagnetic field with $\hbar \omega = 1.2 \text{ cm}^{-1}$.

only “isolated” donor pairs. This is the fundamental difference between the theory of Tanaka *et al.*³³ and the theory of Blinowski and Mycielski.^{34,37} The latter allows also for “nonisolated” pairs, and the exponential factor does not appear there.

Table II shows the parameters of the theory and the results of calculations for semiconducting CdF₂ crystals with two different electron concentrations $N_{sh}^0 \approx 7 \times 10^{17} \text{ cm}^{-3}$ and $2 \times 10^{18} \text{ cm}^{-3}$, and the degrees of compensation ranging from $0.1 \leq K \leq 0.9$. These parameters are the following: the total donor concentration N_D , the concentration of the interstitial F⁻ ions N_F , the average distance between donors r_D , the average distance between majority donors \bar{R} , the energy of the resonant splitting $W(r_D)$ of the donor pair with the separation r_D , the width of the impurity band E_D , the position of the maximum of the FIR absorption calculated from Eqs. (14) and (15) ($\hbar \omega_{\max}^T$) and according to Blinowski and Mycielski’s theory^{34,37} ($\hbar \omega_{\max}^{\text{BM}}$), and the separation $r_{\omega \max}^T$ at which the equality $\hbar \omega_{\max}^T = W(r_{\omega \max}^T)$ holds.

For the microwave electromagnetic field with $\hbar \omega = 1.2 \text{ cm}^{-1}$, the following quantities are also given: the ratio r_{ω}/r_D , the fraction $S_p = S_p(\omega)$ of all the donor pairs with the resonant separation r_{ω} for which the inequality $\Omega \leq \hbar \omega$ is satisfied, the dielectric loss factor calculated from Eq. (14) ($\varepsilon_2^{\text{Ta}}$) and according to Blinowski and Mycielski’s theory^{34,37} ($\varepsilon_2^{\text{BMa}}$), Efros and Shklovski’s theory of Coulomb gap³⁸ ($\varepsilon_2^{\text{ESa}}$), and Phillips’ theory of linear conductance⁴⁰ ($\varepsilon_2^{\text{Pa}}$). In the latter two cases, the extrapolation of “exact” values found using Baranowski and Uzakow’s tables³⁹ for the minimum frequency of $\hbar \omega/2E_D = 0.025$ to those for a microwave field with $\hbar \omega = 1.2 \text{ cm}^{-1}$ was made using Eqs. (23) and (24).

One can see from Table II that, for a fixed concentration of electrons at the donor levels N_{sh}^0 the dielectric loss factor ε_2 has a maximum at the compensation $K \approx 0.5$ and decreases noticeably for both larger and smaller values of K .

Experimental results (see Table I) reveal no correlation between N_{sh}^0 and ε_2 in the crystals under study. Apparently, this is due to variation in their compensations. For photodecolored CdF₂:Ga and CdF₂:In crystals, and for CdF₂:Y, the experimental values of ε_2 in low microwave fields at 1.8 K agree within an order of magnitude⁵⁵ with this quantity calculated in any approach (see Table II) in the range of compensation degree from $0.1 \leq K \leq 0.9$.

In Ref. 8, in which the microwave absorption of donor pairs in semiconducting CdF₂ was discussed, the effect of perturbing impurity was ignored. The magnitude of the parameter S_p given in Table II shows, however, that its influence is essential. It lowers the microwave dielectric losses in semiconducting CdF₂ by more than two orders of magnitude.

So far we have considered photochromic CdF₂:In and CdF₂:Ga crystals after completion of the photodecoloration process when the stationary concentrations N_{sh}^0 and N_{sh}^+ are established. Now, we will briefly discuss the photodecoloration stage at $T = 1.8 \text{ K}$. In a partly decolored crystal, i.e., in a crystal with partial deep-to-shallow center conversion, the neutral- and ionized-center concentrations \tilde{N}_{sh}^0 and \tilde{N}_{sh}^+ are variable quantities. Their values depend on the degree of photodecoloration of the deep centers γ , where $0 \leq \gamma \leq 1$:

$$\begin{aligned} \tilde{N}_{sh}^0 &= \gamma N_{sh}^0, \\ N_p = \tilde{N}_{sh}^+ &= N_F + \frac{1-\gamma}{2} N_{sh}^0. \end{aligned} \quad (25)$$

Here, the parameter N_{sh}^0 is, as before, the maximum attainable concentration of the neutral donors in the crystal. In the dark, $\gamma \approx 0$, $\tilde{N}_{sh}^0 \approx 0$, the degree of compensation K is close to unity, and the ionized donor pairs are (almost) absent. After switching the UV-VIS illumination on, γ changes continuously from 0 to 1. Photodestruction of the deep centers

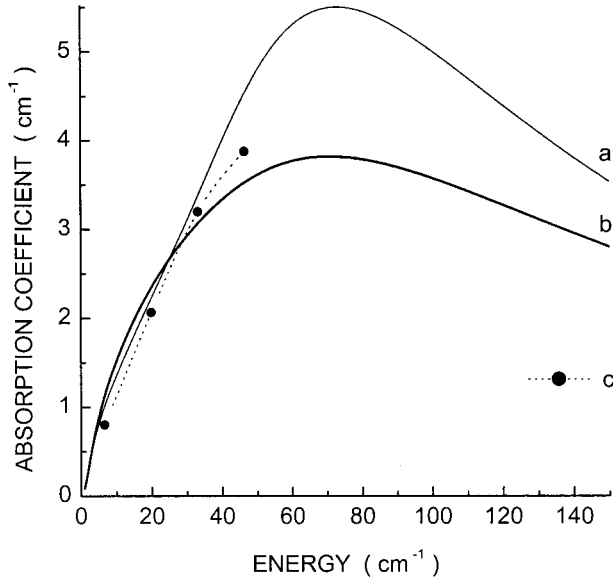


FIG. 7. FIR absorption spectra of CdF_2 with $N_{sh}^0 = 7 \times 10^{17} \text{ cm}^{-3}$ and $K=0.1$ as calculated according to (a) Blinowski-Mycielski's theory (Refs. 34,37), (b) Eqs. (14) and (15), and (c) Baranovskii-Uzakov's model³⁹ for $a = 7 \text{ \AA}$.

causes an increase in the neutral donor concentration $\tilde{N}_{sh}^0 \rightarrow N_{sh}^0$ and a decrease in concentration of the perturbing impurities $N_p = \tilde{N}_{sh}^+ \rightarrow N_F$. The degree of compensation K falls as the ratio $\tilde{N}_{sh}^+ / (\tilde{N}_{sh}^0 + \tilde{N}_{sh}^+)$. It can be easily seen that, in the process of photodecoloration, the total concentration of the ionized donor pairs and corresponding changes in dielectric response would reach their maximum upon attaining $K = 0.5$, and then would go down with concentration of the minority donors (in the case of $N_F < N_{sh}^0$). However, the experimentally found monotonic increase of both the dielectric loss factor and the dielectric constant under illumination of photochromic $\text{CdF}_2:\text{Ga}$ and $\text{CdF}_2:\text{In}$ crystals testify clearly to the fact that value of $K=0.5$ is not passed over. Thus, we find that $N_F \geq N_{sh}^0$ and $K \geq 0.5$ in photodecolored $\text{CdF}_2:\text{Ga}$ and $\text{CdF}_2:\text{In}$ crystals.

Eisenberger, Pershan, and Bosomworth⁷ observed the FIR absorption band from ~ 10 to $\sim 150 \text{ cm}^{-1}$ in a number of semiconducting CdF_2 crystals and found an approximately linear dependence of its intensity on the electron concentration. The FIR absorption was initially ascribed to the polaron effect⁷ and, later on, to the resonant absorption of the ionized donor pairs.⁸ Our calculations support the latter suggestion.

Figure 7 shows spectral dependences of the FIR absorption calculated from Eqs. (14) and (15), according to Blinowski and Mycielski's theory^{34,37} and to Baranovskii and Uzakov's model³⁹ for a crystal with $N_{sh}^0 = 7 \times 10^{17} \text{ cm}^{-3}$ and $K=0.1$. One can see a similarity of all these curves.

In Figs. 8 and 9, the solid lines show spectral dependences of the FIR absorption calculated from Eqs. (14) and (15) for two CdF_2 crystals with $N_{sh}^0 = 7 \times 10^{17} \text{ cm}^{-3}$ and $2 \times 10^{18} \text{ cm}^{-3}$, and $K=0.1, 0.3, 0.5, 0.7$, and 0.9 . Dots depict the absorption coefficients for the same parameters N_{sh}^0 and K calculated according to Baranovskii and Uzakov's model

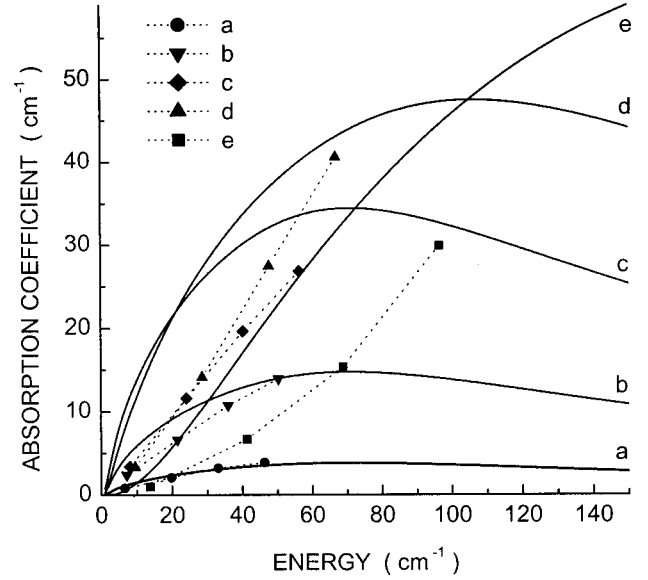


FIG. 8. FIR absorption spectra of CdF_2 with $N_{sh}^0 = 7 \times 10^{17} \text{ cm}^{-3}$ as calculated by Eqs. (14) and (15) (solid lines) and according to Baranovskii-Uzakov's model (Ref. 39) (dots) for $a = 7 \text{ \AA}$ at various compensations (a) $K=0.1$, (b) $K=0.3$, (c) $K=0.5$, (d) $K=0.7$, and (e) $K=0.9$.

for four discrete frequencies within $\hbar\omega/2E_D = 0.025$ to 0.175 , which are listed in Ref. 39. The available tabulated data for $r_\omega/r_D = 0.1$ to 1.1 were extrapolated to the actual value of this ratio for each of these frequencies. For $N_{sh}^0 = 2 \times 10^{18} \text{ cm}^{-3}$ and $K=0.9$, the absorption coefficients were calculated only for three frequencies (see Fig. 9), as far as the ratio r_ω/r_D exceeds 1.1 for $\hbar\omega/2E_D = 0.025$. Unfortunately, Baranovskii and Uzakov made the calculations³⁹

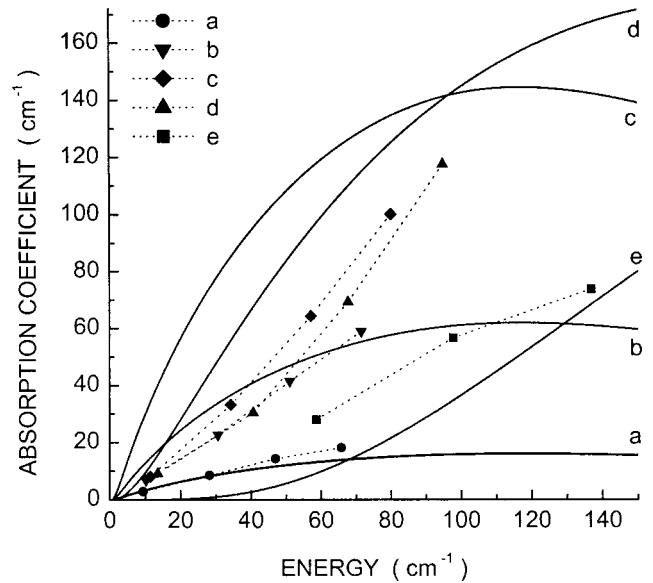


FIG. 9. FIR absorption spectra of CdF_2 with $N_{sh}^0 = 2 \times 10^{18} \text{ cm}^{-3}$ as calculated by Eqs. (14) and (15) (solid lines) and according to Baranovskii-Uzakov's model (Ref. 39) (dots) for $a = 7 \text{ \AA}$ at various compensations (a) $K=0.1$, (b) $K=0.3$, (c) $K=0.5$, (d) $K=0.7$, and (e) $K=0.9$.

only for frequencies below the maximum of the FIR absorption. Nevertheless, from Figs. 7–9, one can see a fair agreement between spectral dependences of the FIR absorption at $K=0.1$ obtained from Eqs. (14) and (15) and those calculated according to Baranowskii and Uzakov's model. For larger $K=0.3$ to 0.9 , only qualitative agreement is achieved. Both approaches give similar displacements of the FIR spectra to higher frequencies with an increase of K from 0.1 to 0.9 and reveal crossing of the spectral curves for various K values in the low-frequency range.

The spectral dependences of the FIR absorption calculated by Eqs. (14) and (15) for the degree of compensation from $0.5 \leq K \leq 0.9$ [see Figs. 7(c)–7(e) and 8(c)–8(e)] well agree, both in the band shape and in the absorption coefficient values, with the experimental spectra (see Ref. 7) of semiconducting CdF_2 crystals with concentration of the neutral donors of $\sim 10^{18} \text{ cm}^{-3}$. Thus, our calculations of the FIR absorption may be considered as direct evidence for the moderate compensation degree $0.5 \leq K \leq 0.9$ of the trivalent impurity in additively colored CdF_2 crystals.

From analysis of the microwave and FIR absorption, we have obtained restrictions on the degree of compensation, that is, $0.5 \leq K \leq 0.9$ in semiconducting CdF_2 crystals. Now, we can estimate the concentration of interstitial F^- ions and the total concentration of donors in the crystals studied. The concentration of the interstitial F^- ions, $N_F = N_{sh}^0 K / (1 - K)$, in the crystals under study does not exceed $\sim 3 \times 10^{19} \text{ cm}^{-3}$. The total concentration of donors in $\text{CdF}_2:\text{Y}$ crystal studied, which is equal to the concentration of “isolated” Y^{3+} ions in CdF_2 lattice, $N_D = N_{sh}^0 / (1 - K) < 3 \times 10^{19} \text{ cm}^{-3}$, appears to be at least by a factor of 5 smaller than the total content of this impurity in the crystal ($\sim 2 \times 10^{20} \text{ cm}^{-3}$). This means that more than 80% of Y^{3+} ions are bound to clusters. Similar reasoning shows that no more than 30% of In ions form the simple cubic centers that make up the donor levels and participate in electron processes in $\text{CdF}_2:\text{In}$ crystals under study. The remaining more than 70% of In ions are bound to clusters and do not act as donors. The clusters seem to clear the crystal lattice of the “redundant” impurity.

It is necessary to determine a source of the appreciable increase of the real part of permittivity $\Delta \epsilon_1$ after illumination of photochromic $\text{CdF}_2:\text{Ga}$ and $\text{CdF}_2:\text{In}$ crystals (see Table I). Using the Kramers-Kronig relations, it is possible to estimate the expected value of $\Delta \epsilon_1(\omega)$ associated with a substantial photoinduced growth of the number of electrons on the donor levels

$$\Delta \epsilon_1(\omega) = \frac{2}{\pi} \int_0^\infty \frac{x \epsilon_2(x)}{x^2 - \omega^2} dx \cong \frac{2}{\pi} c \int_0^\infty \frac{\sqrt{\epsilon_1(x)} \alpha(x)}{x^2 - \omega^2} dx. \quad (26)$$

It follows from Eq. (26) that the photoinduced buildup of the $7\text{-}\mu\text{m}$ absorption band of the shallow donor centers yields $\Delta \epsilon_1(\omega \rightarrow 0) \approx 4 \times 10^{-2}$. It is by an order of magnitude smaller than the experimental value. However, with due account of the FIR absorption band either calculated (see Figs. 8 and 9) or experimentally recorded in Ref. 7, we obtain

$\Delta \epsilon_1(\omega \rightarrow 0) \sim 2$ (for $N_{sh}^0 \sim 10^{18} \text{ cm}^{-3}$ and $K=0.5$), which agrees with the experimental data.

IV. CONCLUSIONS

The occurrence of microwave and FIR broadband absorption, as well as the saturation of the microwave absorption in high electromagnetic fields observed in semiconducting CdF_2 crystals are due to the coexistence of the neutral and charged donors, which form ionized donor pairs. The change of dielectric response upon illumination of photochromic $\text{CdF}_2:\text{Ga}$ and $\text{CdF}_2:\text{In}$ crystals at low temperatures is caused by the photoinduced increase in concentration of donor electrons, and, consequently, by the increase in concentration of donor pairs.

It is possible to estimate the degree of compensation K of semiconducting CdF_2 from the dielectric-loss factor and the FIR absorption spectrum. The value of the dielectric-loss factor at low temperature $T=1.8 \text{ K}$, the monotonic character of variation of the complex permittivity throughout photodecoloration of photochromic crystals, and the spectral dependence and value of the FIR absorption coefficient are evidence that the degree of compensation is restricted by the inequality $0.5 \leq K \leq 0.9$ for typical semiconducting CdF_2 . These restrictions on the K value are in good agreement with the results of the EPR study of Eisenberger and Pershan⁹ (see the Introduction). Hence, in semiconducting CdF_2 , the concentration of the ionized donors (equal to the concentration of the interstitial F^- ions) exceeds that of the neutral donors.

Thus, this study demonstrates that during additive coloration of CdF_2 doped with column-III elements, total chemical reduction of the impurity and, consequently, total removal of the interstitial F^- ions from the crystal lattice, is unachievable. This inference (which is confirmed by the experimental data of Refs. 3, 9, and 10) implies the presence of some sources in doped CdF_2 that supply the crystals with F^- ions during chemical reduction of the impurity. Evidently, these sources are the impurity-fluorine clusters, which are supposed to scavenge interstitial F^- ions.¹⁷ The clusters already exist in the crystal lattice of as-grown CdF_2 when the latter is in the semi-insulating state and, possibly, undergo some restructuring during the thermochemical process of conversion.¹⁷

The clusters (whose structure may be different for various dopants) appear to be responsible for the high solubility of many column-III elements in CdF_2 . A substantial part of the donor impurity is certainly collected into clusters. Hence, it is impossible to obtain a semiconducting CdF_2 crystal with the compensation degree of less than 0.5 and with concentration of free or weakly bound electrons exceeding $\sim 10^{19} \text{ cm}^{-3}$.

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