DX Centers in Ionic Semiconductor CdF$_2$:Ga

A. I. Ryskin, A. S. Shcheulin, and D. E. Onopko

S. I. Vavilov State Optical Institute, 199034, St. Petersburg, Russia
(Received 27 February 1997)

Analysis of thermally and optically induced transformations of metastable Ga centers in the wide-gap, predominantly ionic semiconductor CdF$_2$ points to the existence of two metastable states of the center. The configuration-coordinate model of the center is discussed and its energy parameters are determined. It is concluded that this center is not just "*DX*-like," as was initially assumed, but is a true *DX* center with a shallow donor and two deep negative-*U* states.   [S0031-9007(98)05594-X]

The metastable *DX*-like centers observed in covalent and ionic-covalent semiconductors also occur in the wide-gap, predominantly ionic CdF$_2$ crystals with fluorite structure doped with the trivalent impurities In or Ga and annealed (additively colored) in a hydrogen or metal-vapor atmosphere. The annealing procedure transfers the crystals into a semiconducting state.

As is well known, the deep state of the *DX* centers in semiconductors is formed by the capture of a second electron at a neutral donor [1]. On the other hand, it was initially assumed that the two states of the bistable center in CdF$_2$ correspond to the donor electron localized either at the intrinsic atomiclike orbital (M^{2+} configuration, $M =$ In, Ga, "deep" center) or at the hydrogenic one ($M^{3+} + e_{\text{hydr}}$, "shallow" donor center). Thus, transformation of the center was assumed to proceed without a change in its charge [2–4]. Within this framework, In and Ga bistable centers are treated as the examples of intrinsic self-trapping after Toyozawa [5].

Our studies of optical and thermal transformations of M centers in CdF$_2$ showed that, in fact, a change in the center's state is accompanied by a change in its charge. The bimolecular kinetics of thermal destruction of shallow centers and the quantum yield $\eta \simeq 2$ of the photochemical reaction of the deep-shallow center transformation clearly indicate that two shallow centers participate in the formation of one deep center and *vice versa* [6]. This means that the ground state of the M center corresponds to the localization of two electrons thus testifying to the formally single-valent character of this state, i.e., its negative-*U* nature.

Direct evidence for the two-electron nature of the deep center was found in measurements of the magnetic moment J of CdF$_2$:In crystals. In these experiments, no magnetic moment was observed in the deep state of the In center. However, it appeared ($J = 1/2$) when the shallow state was populated by photoexcitation of the deep state [7].

Metastability of the nontransition impurities in CdF$_2$ was explained by the sequence of filling of the valent atomic shells for these dopants; on the other hand, transition-metal and rare-earth impurities produce only shallow-donor states in this crystal [8].

This paper shows that *two* types of *DX* centers exist in semiconducting CdF$_2$:Ga. Parameters of the configuration-coordinate model are determined from the analysis of thermal and optical transformations of the centers. Together with previous studies [6–8], the present Letter reports similar properties of the metastable centers in typical semiconductors and semiconducting CdF$_2$. We conclude that CdF$_2$ is the most highly ionic crystal among those in which *DX* centers are observed.

CdF$_2$:Ga crystals with the dopant concentration $N_{\text{Ga}} = [(1.5–7.0) \pm 0.3] \times 10^{17}$ cm^{-3} were grown from the melt and annealed in metal vapor to convert impurities into the metastable state. The value of N_{Ga} was obtained by shallow-center absorption measurement (see below). After crystals are cooled in the dark to $T = 5$ K, nearly one half of the Ga ions appear in the "optically silent" Ga^{3+} state. An equal quantity of ions form deep Ga^{1+} centers which are responsible for a photoionization absorption band in the ultraviolet-visible (UV-VIS) region of the spectrum. This band composes a photochromic portion of intensive UV-VIS absorption typical of additively colored CdF$_2$:Ga [Fig. 1(a)]. The nautre of the nonphotochromic portion of this absorption will be considered elsewhere. Figure 1(a) also shows the short-wavelength tail of a wide infrared (IR) band ($\lambda_{\max} \approx 7$ μm, Fig. 1, inset). The IR band corresponds to photoionization of the shallow centers (Ga$^{3+} + e_{\text{hydr}}$), a small number of which exist in the rapidly cooled crystals. In [9] a relation between the peak absorption of the IR band $\alpha_{\max}$ and the dopant concentration in CdF$_2$:Y was reported. Since the IR band shape is almost independent of the chemical nature of the trivalent impurity [10], we use this relation to determine N_{Ga} by $\alpha_{\max}$.

Illumination of the crystals in the UV-VIS band causes its partial bleaching and a simultaneous strong increase in the IR band intensity [Fig. 1(a)]. This photochemical reaction corresponds to deep-to-shallow center conversion. The giant photochromic effect in CdF$_2$:M was recently used for writing holographic gratings in these crystals [11–13].

To study deep Ga centers and their energy parameters, we analyzed the shallow-center thermally induced decay.
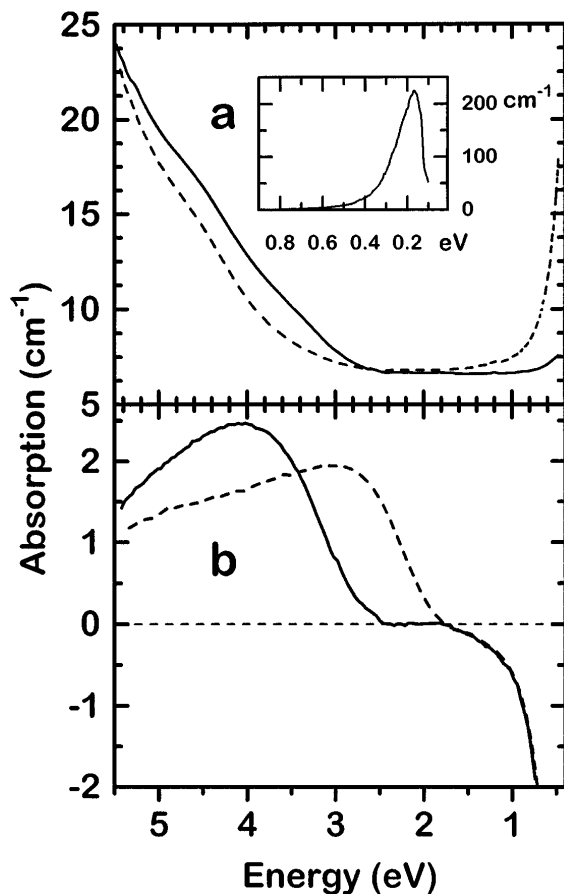
FIG. 1. Absorption spectra of a CdF_2:Ga crystal ($N_{Ga} = 7.0 \times 10^{17}$ cm^{-3}) cooled in the dark to $T = 5$ K (solid line) and bleached in the UV-VIS band at the same temperature (dashed line) (a) and differential absorption spectra of crystal with DX (solid line) and DX' (dashed line) centers ($N_{Ga} = 1.5 \times 10^{17}$ cm^{-3}, $T = 5$ K) (b). In the inset, the IR absorption band for a bleached crystal with $N_{Ga} = 7.0 \times 10^{17}$ cm^{-3} at $T = 77$ K is shown.

After bleaching in the UV-VIS band at $T = 5$ K, crystals were slowly heated at a constant rate 0.05 deg/s. The change of the IR band intensity with temperature represents the temperature dependence of the shallow-center concentration N_{hydr} neglecting a slight modification of the band shape with T [9]. Shallow centers are stable below 20 K. Above this temperature an electron from such a center is thermally excited into the conduction band and can be captured by another shallow center. Such capture is also thermally activated because it proceeds only with the overcoming of the potential barrier. The decay of shallow Ga centers predominates over their formation in two ranges of the temperature decrease of the IR absorption: $20 < T < 90-110$ K ("first range") and $190-220 < T < 260-280$ K ("second range," Fig. 2; the interval limits weakly depend on N_{Ga}). These results testify to the existence of three states of the Ga center: the DX-type ground state which is formed in the second range of the shallow-center decay [6] and two metastable states. The latter are
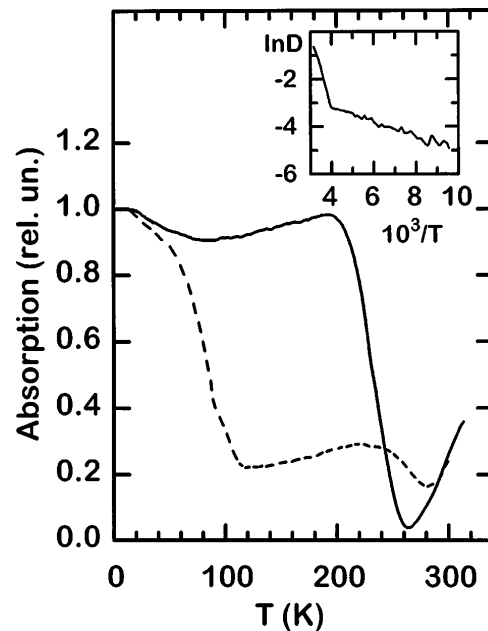

FIG. 2. Temperature evolution of the normalized IR absorption under the slow heating of CdF_2:Ga crystals with $N_{Ga} = 7.0 \times 10^{17}$ cm^{-3} ($\lambda = 1.45$ μm, solid line) and $N_{Ga} = 1.5 \times 10^{17}$ cm^{-3} ($\lambda = 1.8$ μm, dashed line) above $T = 5$ K. In the inset, the Arrhenius plot for the optical density in the IR band ($\lambda = 1.45$ μm) of the former crystal under slow cooling below $T = 300$ K is shown.

the hydrogenic state and a deeper state into which the former is transformed in the first temperature range.

The question arises as to whether the latter state is a two-electron state as well, i.e., DX-type, or a single-electron metastable state with its own smaller capture barrier. To answer this question, we have analyzed the kinetics of the shallow-center thermal decay for both temperature ranges for a crystal with $N_{Ga} = 1.5 \times 10^{17}$ cm^{-3} [14]. For this crystal both of the stages of decay are well pronounced. The crystal was cooled to T of the first or the second range and bleached in the UV-VIS band after which the decrease of absorption in the IR band with time (due to decay of the shallow centers) was measured. Excluding a short time interval in which the fast decay occurs, it was found that, as for the second range, the decay curve for the first range is well described by a hyperboliclike dependence typical of a bimolecular reaction (Fig. 3) [15]. This characteristic of the shallow-center decay clearly indicates that, in any case, two one-electronic shallow centers are involved in the elementary act of their thermal destruction. The centers which are being formed when the shallow centers are destroyed are thus shown to be two-electron states. Below, we denote the centers formed in the first range as DX' to distinguish them from the ground-state DX centers formed in the second range.

The faster decay in the initial stages is explained by the relatively high mobility of photoexcited electrons due to the small quantity of Ga^{3+} ions which trap electrons;
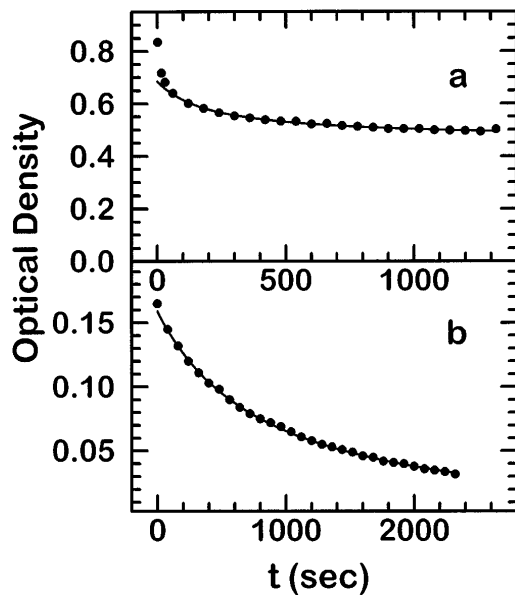
FIG. 3. Decay of IR (shallow center) absorption in CdF_2:Ga ($N_{Ga} = 1.5 \times 10^{17}$ cm^{-3}, $\lambda = 1.8$ μm) after switching off the bleaching UV-VIS light at $T = 82$ K (a) and $T = 254$ K (b). Black circles are experimental points, solid lines show the hyperbolic-cotangent dependence fitted to experimental data.

FIG. 4. Generalized configuration-coordinate model of Ga centers in CdF_2:Ga.

an increase of these ions during the decay decreases the electron mobility and results in the hyperbolic-type dependence when the mobility approaches its equilibrium value (for the temperature of experiment). The "nonhyperbolic" fragment of the decay is less pronounced in the second range as compared with the first range since the difference between the initial concentration $N_{hydr}(0)$, from which decay begins after switching off the bleaching light, and equilibrium concentration $N_{hydr}(\infty)$ is lower for this range.

One can note that the formation of DX' centers in samples with relatively high dopant concentration is strongly suppressed (Fig. 2, see below).

To describe the temperature dependence of the shallow-center thermal decay we employed a model similar to that which Thio *et al.* [16] used for analysis of deep donors in $Cd_{1-x}Zn_x$Te:Cl (Fig. 4). This model includes two DX-type states, namely, the shallower (DX') and the deeper (DX) states, the hydrogenic state (HS), and the conduction band (CB). At $T < 20$ K, thermal excitation of electrons from the shallow-donor centers is practically impossible. At higher temperatures, this process occurs, accompanied by DX'- or DX-center formation. According to the process described above of deep center formation, the kinetics of the shallow-center thermal decay corresponds to the bimolecular mechanism with activation energy $E_{ac} = E_{hydr} + E_{cap'}(E_{cap})$ for the first (second) range of the decay. From an analysis of the kinetics we determine E_{ac} (details of this procedure are given in [6]). Then, using the known value of the shallow-center binding energy $E_{hydr} = 0.116$ eV [10], we calculate the barrier height $E_{cap'} < 0.1$ eV for the first range

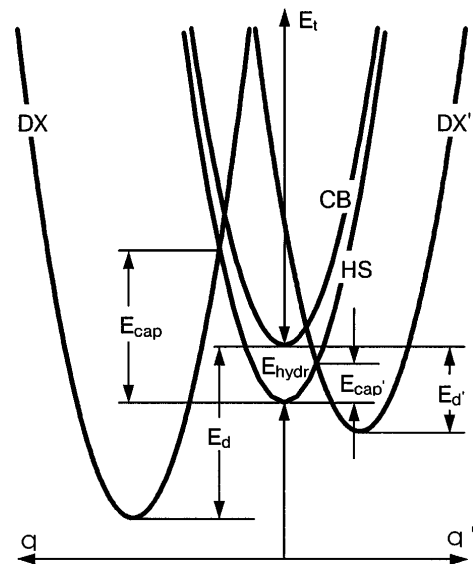and $E_{cap} = 1.12$ eV for the second range. A comparison of these values shows the significantly larger lattice distortion of the DX center as compared with the DX' center. Probably, the large lattice relaxation required for the DX-center formation explains "freezing" of the small (nonequilibrium) concentration of shallow centers during the relatively fast cooling of crystals in the dark [Fig. 1(a)].

The ranges of the temperature increase of the IR absorption correspond to equilibrium between shallow and DX' centers ($90-110 < T < 190-210$ K) and among all three centers involved ($T > 260-280$ K). The binding energies of the deep centers E_d and $E_{d'}$ were determined from the dependence of the IR absorption on $1/T$ under slow (0.05 deg/s) crystal cooling from room temperature (Fig. 2, inset). To obtain these energies, E_{hydr} must be added to the values found from this dependence. In the crystal with $N_{Ga} = 7.0 \times 10^{17}$ cm^{-3} the binding energies are $E_d = 0.39$ eV, $E_{d'} = 0.14$ eV. Thus, the binding energy of DX' centers is only slightly larger than that of the shallow-donor centers.

One can speculate that the suppression of the first stage of the shallow-center thermal decay in high-concentration samples is due to the autoionization of DX' centers in the random electric field induced by charged Ga^{1+} and Ga^{3+} ions. This process, being opposite to the shallow-center decay, increases the concentration of the shallow centers. The higher is N_{Ga}, the more pronounced is this effect. Probably, the relatively low binding energy of DX' centers promotes their autoionization which does not occur for DX centers even at the highest doping levels studied.

Evidently, DX and DX' centers should have significantly different photoionization absorption spectra. To confirm this, the spectrum of a CdF_2:Ga crystal with $N_{Ga} = 1.5 \times 10^{17}$ cm^3 was measured after (i) crystal cooling to $T = 5$ K in the dark; (ii) crystal bleaching

in the UV-VIS band at this temperature (this spectrum shows the lattice absorption and absorption of the non-photochromic impurities; (iii) subsequent slow heating to $T = 77$ K and fast cooling to 5 K. In accordance with the above considerations, the differential spectra (iii)-(ii) and (i)-(ii) [Fig. 1(b)] present the predominant absorption of DX' and DX centers, respectively. The energies of the corresponding band maxima are $\sim$3 eV for the DX' center and $\sim$4 eV for the DX center.

Thus, we have discovered two deep (two-electron, strongly relaxed) Ga centers in semiconducting CdF_2. The existence of several local energy minima in configuration-coordinate space, i.e., the presence of several DX centers differing in their structure and energy, was predicted for many DX systems (for instance, [17–20]); possibly, this is a general property of the structure-unstable centers of this type.

In general, [6–8] and this study prove that the metastable centers in semiconducting CdF_2 are not just "DX-like," as was initially proposed, but are true DX centers with all of their typical features. This conclusion is nontrivial considering the relatively high ionicity of this crystal. It testifies to the strong hybridization of impurity orbitals with the band states of the crystal that ensures the existence of charge states of the impurity with a different, by a factor of 2, number of valence electrons (Ga^{3+} and Ga^{1+}). Such hybridization, while usual for covalent and ionic-covalent semiconductors, is surprising in such a highly ionic compound as cadmium fluoride. As a measure of the ionicity of crystal, one can take the longitudinal-transversal splitting of optical phonons normalized to the optical phonon frequency. This value is 0.08–0.16 for typical III-V and II-VI compounds in which DX centers occur and 0.42 for cadmium fluoride [9]. Thus, CdF_2 is the most highly ionic crystal in which DX centers have been observed thus far.

[1] D. J. Chadi and K. J. Chang, Phys. Rev. Lett. **61**, 873 (1988); Phys. Rev. B **39**, 10 063 (1989).

[2] U. Piekara, J. M. Langer, and K. Krukowska-Fulde, Solid State Commun. **23**, 583 (1977).

[3] J. E. Dmochowski *et al.,* Acta Phys. Pol. A **73**, 247 (1988).

[4] J. M. Langer, *Lecture Notes in Physics* (Springer, New York, 1980), Vol. 122, p. 123; J. Phys. Soc. Jpn. Suppl. **49A**, 207 (1980); Radiat. Eff. **72**, 55 (1983); Rev. Solid State Sci. **4**, 297 (1990).

[5] Y. Toyozawa, Solid State Electron. **21**, 313 (1978); Physica (Amsterdam) **116B**, 7 (1983); Semicond. Insul. **5**, 175 (1983).

[6] A. S. Shcheulin *et al.,* Phys. Lett. A **222**, 107 (1996).

[7] S. A. Kazanskii, A. I. Ryskin, and V. V. Romanov, Appl. Phys. Lett. **70**, 1272 (1970); Phys. Solid State **39**, 1067 (1970).

[8] A. I. Ryskin and P. P. Fedorov, Phys. Solid State **39**, 943 (1997).

[9] F. Moser, D. Matz, and S. Lyu, Phys. Rev. **182**, 808 (1969).

[10] J. M. Langer *et al.,* Phys. Status Solidi (b) **66**, 537 (1974).

[11] A. I. Ryskin *et al.,* Appl. Phys. Lett. **67**, 31 (1995).

[12] B. Koziarska *et al.,* Acta Phys. Pol. **88**, 1010 (1995); Mater. Sci. Forum **196–201**, 1103 (1995); A. Suchocki *et al.,* Appl. Phys. Lett. **70**, 22 (1997).

[13] A. I. Ryskin *et al.,* J. Appl. Phys. **83**, 2215 (1998).

[14] Earlier, such analysis has been cited only for the second temperature range [A. S. Shcheulin *et al.,* Phys. Lett. A **222**, 107 (1996)].

[15] This hyperbolic-cotangent dependence takes into account the "reverse" process of the deep-center thermal decay. When this process can be neglected, this dependence reduces to the first-order hyperbola.

[16] T. Thio, J. W. Bennett, and P. Becla, Phys. Rev. B **54**, 1754 (1996).

[17] D. J. Chadi, Phys. Rev. B **46**, 6777 (1992).

[18] C. H. Park and D. J. Chadi, Appl. Phys. Lett. **66**, 534 (1995).

[19] D. J. Chadi and C. H. Park, Mater. Sci. Forum **196–201**, 285 (1995).

[20] C. H. Park and D. J. Chadi, Phys. Rev. B **54**, R14 246 (1996).