Universality of the Bond-Breaking Mechanism in Defect Bistability: Observation of Open Volume in the Deep States of In and Ga in CdF$_2$

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Positron annihilation experiments reveal an open-volume defect in the deep state atomic configurations of bistable donors In and Ga in CdF$_2$. The size of the open volume is at least half of a monovacancy. The results are similar to those obtained previously for the *DX* centers in the covalent system Al$_x$Ga$_{1-x}$As. It is therefore likely that the bond-breaking mechanism (substitutional to interstitial atomic motion) responsible for metastability of point defects in covalent semiconductors is more universal and its validity extends to highly ionic compounds, similar to CdF$_2$. [S0031-9007(99)08958-9]

Bistable centers are some of the most fascinating point defects in solids. The charge carriers are captured at these either on localized orbits or in effective mass bound states. The two types of states are separated by a vibronic barrier causing metastability of the shallower effective mass state at low temperature. Such defects are found from highly covalent (e.g., Si in Al$_x$Ga$_{1-x}$As [1]) to highly ionic crystals (e.g., Ga and In in CdF$_2$ [2]). In spite of the very different nature of the bonds in these crystals, bistable defects exhibit largely similar properties. The origin of the metastability is usually attributed to a large lattice relaxation taking place in the transition between the states [3]. In covalent hosts, the bond-breaking mechanism in which atoms change lattice position (e.g., substitutional to interstitial) is responsible for the metastability [4]. This mechanism, being a characteristic feature of the sp^3 bonded defects, was hard to believe as dominant in ionic hosts such as doped CdF$_2$. It was therefore proposed [5] that metastability in these crystals comes simply from a large inward relaxation of neighboring anions upon either ionization or the electron phototransfer to the effective mass delocalized hydrogenic bound states of the donor. This intuitive model got later support from theoretical computations by Song *et al.* [6].

The revival of interest in bistable defects came recently after a series of papers showing that semiconductors doped with such defects are very efficient media for the storage of holograms [7]. Apparently CdF$_2$ crystals doped with Ga [8] are the most promising hosts for this application as the metastability of Ga donors occurs already close to room temperature (about 250 K). After this discovery, new experiments showed that bistable donors in CdF$_2$ crystals form a negative-U system and thus the ground state of these donors is in fact a two-electron state [9,10]. Lattice relaxation involved in the formation of a two-electron state and the metastability may thus be more complex than just a symmetric collapse, as originally suggested. Such a conclusion emerged also from a very recent observation of a macroscopic metastable lattice shrinkage of CdF$_2$ crystals doped with In [11]. Interestingly, most recent theoretical computations of the defect structure of donors in these crystals also suggest a possibility of negative-U [12] and nonsymmetric lattice relaxation with even a substitutional to interstitial dopant motion [13]. Such a relaxation would invariably produce a cationic vacancy, which most easily could be observed by positron annihilation spectroscopy.

Positron annihilation is a well-established method to study vacancy-type defects in solids [14,15]. Positrons get trapped at negative and neutral vacancies due to the missing positive ion core. In a vacancy, the electron density is lower than in the lattice which leads to an increase in the positron lifetime and narrowing of the momentum distribution of the annihilating electron-positron pairs. Among the most exciting discoveries are the direct observations of vacancy-type defects related to the EL2 in GaAs and the *DX* center in Al$_x$Ga$_{1-x}$As [16,17].

In this Letter, we report the first direct experimental evidence on an open-volume defect related to the deep state atomic configurations of In and Ga bistable donors in CdF$_2$. The positron results on the bistable centers in CdF$_2$ are analogous to those on the *DX* center in Al$_x$Ga$_{1-x}$As. Hence, they show unexpected universality of the bond-breaking mechanism of the bistability of defects in semiconductors.

Two standard positron annihilation techniques were used in this work: conventional positron lifetime and Doppler-broadening measurements [14,15]. Two identical sample pieces were sandwiched around a ^{22}NaCl positron source of $20-50$ μCi. The positron lifetime spectra were measured with fast-fast spectrometers whose time resolutions were $210-250$ ps (FWHM). No significant positronium formation was observed in the samples. The Doppler-broadening data were collected with a high-purity Ge detector whose energy resolution was 1.3 keV at 511 keV. The annihilation line shape was characterized with the conventional low electron-momentum parameter S which mainly describes annihilations with valence electrons [14]. It was calculated as the fraction of counts

in the energy interval $|E_\gamma - 511 \text{ keV}| < 0.7$ keV. When positrons annihilate at vacancies, S parameter increases because the Doppler broadening of the annihilation line decreases due to lower electron momenta at vacancies. To be able to vary the state of the bistable defects, the samples were mounted into an optical cryostat ($T = 8-350$ K). The sample illumination was performed with monochromatic light ($h\nu = 1-4$ eV, photon flux $> 10^{12}$ cm^{-2} s^{-1}). (For technical details, see Ref. [18].)

The bulk CdF$_2$ crystals were grown by the modified Bridgman method. Two of the samples (#1 and #2) were doped with Ga, one (#3) with In, and one (#4) with Y (concentrations were in the range $10^{18}-10^{19}$ cm^{-3}). All of the samples were annealed in reducing Cd atmosphere to remove compensating F interstitials. Sample #2 was annealed more thoroughly than sample #1 to vary the concentration of bistable defects in the samples. The Y doped sample was suitable as a reference since Y is a simple effective mass shallow donor in CdF$_2$ crystals [2].

The average positron lifetime results, measured in darkness from 10 to 300 K, are shown in Fig. 1. When positrons are trapped at open volume defects, the average lifetime τ_{av} increases compared with the value τ_{bulk} in the lattice. In all of our samples, the lowest average lifetimes were measured at temperatures below 50 K. Raising the sample temperature towards room temperature leads to an increase of $5-15$ ps in the lifetime values depending on the sample. The most natural explanation for this temperature dependence is positron trapping at two different types of point defects: some open-volume defects and some negative centers without any open volume [14]. At low temperatures, a considerable fraction of positrons gets trapped at negative ion-type defects, which prevents them from getting trapped at vacancies. Above 60 K, positrons are able

FIG. 1. The average positron lifetime in darkness as a function of the measurement temperature. The solid lines are guides to the eye.

to escape from the shallow state around the negative ions, which enhances trapping at vacancies, i.e., increases the average lifetime.

In a recent theoretical work, Mattila $et\ al.$ performed $ab\ initio$ calculations on the formation energies of point defects in CdF$_2$ [12]. They suggest that in n-type material the Cd vacancy is the most abundant vacancy defect. As shown, we observe native vacancies in Y, Ga, and In doped material and it is thus natural to attribute them to V_{Cd}. In addition, the calculations [12] confirm the traditional assumption that F interstitials are abundantly formed as negatively charged compensating defects in n-type CdF$_2$. The positron data indicates the presence of negative ions in Y, Ga, and In doped crystals. These defects are most probably the F interstitials.

The key experiment concerning defect bistability is to study whether illumination has an influence upon positron trapping. Illumination is known to induce deep-shallow transition of the bistable centers [2]. A most pronounced effect is observed in both In and Ga doped crystals at 15 K: The mean positron lifetime decreases with increasing photon fluence and saturates to a value of $1-4$ ps lower than obtained before illumination. The changes are persistent at 15 K: After an illumination the average lifetime remains constant for days. In contrast to these effects, the illumination has no influence on the positron lifetime in the Y doped sample.

To study the thermal stability of the observed persistent change in the average lifetime, we performed an isochronal annealing experiment (Fig. 2). The samples were first illuminated with 1.95 eV (In doped) or 3.0 eV (Ga doped) photons whereafter the measurements and the heat treatments were performed in the dark. In In doped CdF$_2$, annealing in the range from 60 to 75 K restores the lifetime at the initial level before illumination. In the case of the Ga doped CdF$_2$, the recovery occurs between 200 and 250 K. These temperatures are the same at which the bistable centers make the transition from the shallow state to the deep state [2].

The positron lifetime can be directly correlated with the optical absorption of the bistable defects by performing the experiment as a function of the photon energy. The absorption related to the deep states of Ga and In begins to increase at 2.5 and 1.5 eV, respectively (Fig. 3). In the positron experiment the samples were illuminated at 15 K to a constant photon fluence. The positron lifetime spectra were measured in the dark at 15 K after each illumination (Fig. 3). In the Ga and In doped samples τ_{av} starts to decrease at about 2.7 and 1.5 eV, respectively. The average lifetime decreases with increasing absorption until the level corresponding to prolonged illumination (fully depleted deep state) is reached. The photon energy ranges at which τ_{av} decreases and the absorption increases match very well [19].

The data in Figs. 2 and 3 show that the average positron lifetime is sensitive to the state of the bistable centers.
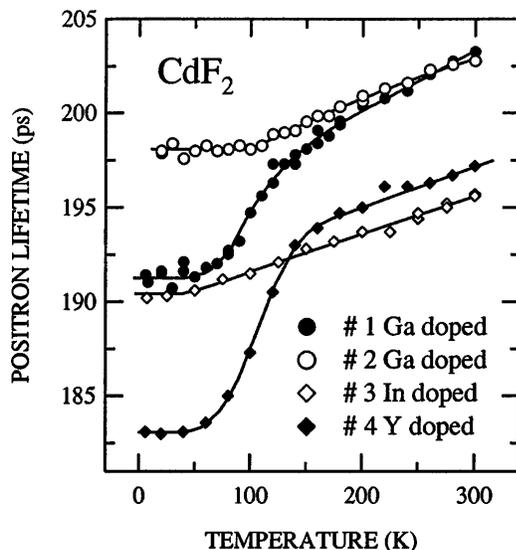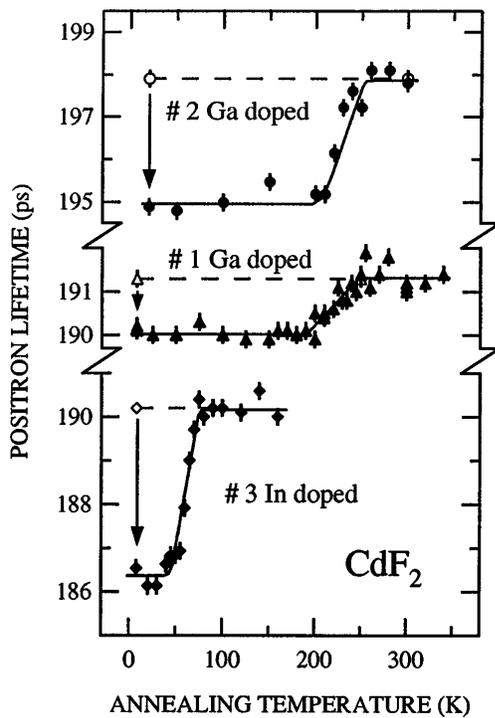
FIG. 2. The average positron lifetime measured at 15 K in darkness as a function of the annealing temperature. Before each 10-min annealing the samples were illuminated at 15 K with 1.95 eV (In doped) or 3.0 eV (Ga doped) light. The illumination was long enough to saturate the change in the average positron lifetime (photon fluence 2×10^{17} cm^{-2}). The open symbols and the dashed lines represent the lifetime levels before illumination. The solid lines are guides to the eye.

Positron trapping at open-volume defects is enhanced, i.e., more vacancies are detected, when the deep state is occupied. However, Cd vacancies are observed in the In and Ga doped samples also when the bistable centers are in the shallow state. This is evident since the average lifetime after illumination (Fig. 2) is higher than the lowest value 183 ps measured in the Y doped specimen (Fig. 1). In order to differentiate between various open-volume defects seen by positrons [14], we plot the low electron-momentum parameter S vs the average lifetime measured in sample #2 at different temperatures (15–180 K) in the dark before and after illumination (Fig. 4). The data measured after illumination form a straight line which can be explained with positrons annihilating at only two states: as localized in a Cd vacancy and delocalized in the lattice. Before illumination, the data do not fall on the same line which indicates that positrons annihilate also in a vacancy defect whose characteristic S parameter and positron lifetime are not the same as those of V_{Cd}.

When the deep state of In and Ga is occupied, positrons are thus trapped at vacancy defects which are different from V_{Cd} (Fig. 4). The vacancy ceases trapping positrons when In and Ga are converted to the shallow state by illumination (Figs. 2 and 3). We thus infer that the vacancy
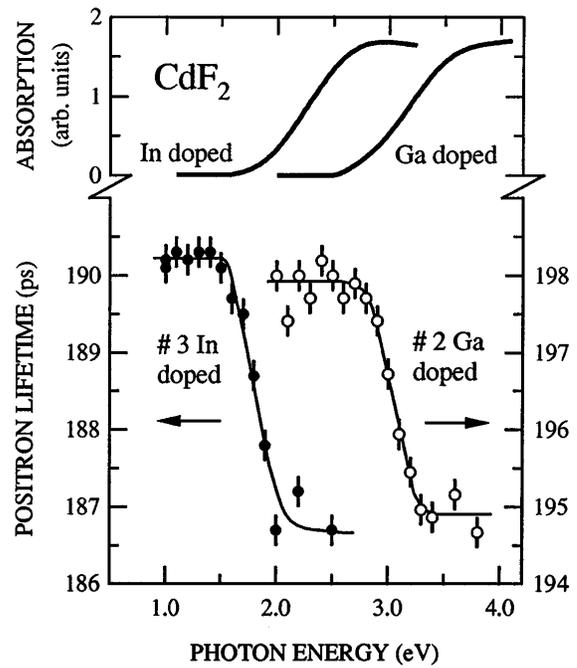
FIG. 3. The absorption spectra and the average positron lifetime vs the photon energy. The absorption data show a typical result for In and Ga in the deep state. The positron measurements were performed in darkness at 15 K after illuminating the sample to a constant fluence (3.6×10^{15} cm^{-2} for sample #2 and 8.0×10^{16} cm^{-2} for sample #3). After each measurement the samples were annealed at 300 K. The solid lines are guides to the eye.

defect is a constituent of the deep state atomic structure of the bistable centers in CdF$_2$. A likely configuration is a pair of V_{Cd} and Ga or In interstitial in its close vicinity. Such defect complex has an overall negative charge as In and Ga bistable donors form a negative-U system [9,10].
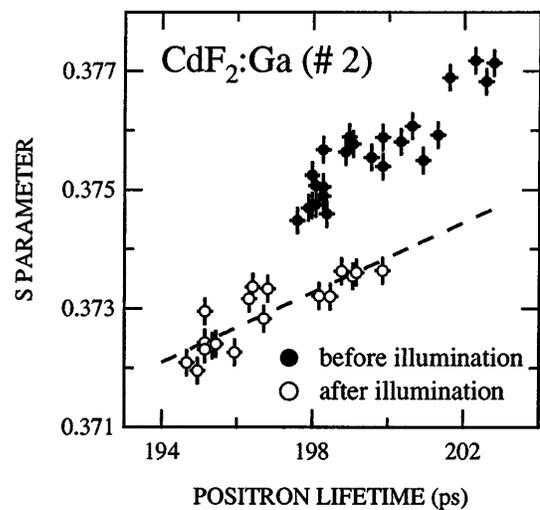
FIG. 4. The S parameter vs average lifetime τ_{av} in sample #2 (Ga doped) before and after illumination. The data points correspond to simultaneous measurements of S and τ_{av} at different temperatures between 15 and 180 K.

In sample #2, τ_{av} at 15 K decreases from 198 to 195 ps when the bistable centers are converted from the deep to the shallow state (Fig. 2). This implies that the characteristic positron lifetime in the deep state related vacancy $\tau_{DS} \gtrsim 198$ ps. It is thus at least 15 ps longer than the lifetime in the lattice ($\tau_{bulk} \lesssim 183$ ps). On the other hand, the theoretical difference between τ_{bulk} and $\tau_{V_{Cd}}$ is about 35 ps [20]. Hence, we can deduce that the open volume in the deep state atomic configuration of the bistable centers is at least half of a Cd monovacancy.

The concentrations of the different defects D_i can be estimated as follows: At the high concentration limit ($[D_{tot}] = \sum_i[D_i] \gtrsim 10^{18}$ cm^{-3}), the average positron lifetime $\tau_{av} \approx \sum_i([D_i]/[D_{tot}])\tau_i$ [14], where τ_i is the lifetime at defect D_i ($\tau_{F_i} = \tau_{bulk} = 180$ ps, $\tau_{DS} = 205$ ps, and $\tau_{V_{Cd}} = 215$ ps from theory [20]). Assuming that all Ga and In dopant atoms are either singly positive as shallow donors or singly negative in the deep state, the charge neutrality condition can be written as $[Ga(In)]_{tot} = 2[DS^{1-}] + 2[V_{Cd}^{2-}] + [F_i^{1-}]$ (charges from [12]). By applying these expressions for our results at 15 K both in darkness ($D_i = V_{Cd}$, F_i, DS) and after illumination ($D_i = V_{Cd}$, F_i) we can solve the concentrations.

As a result, we find that $[V_{Cd}]$ and $[F_i]$ are of the order of 10^{17}–10^{18} cm^{-3} which are reasonable values in CdF$_2$. Furthermore, the concentration of the deep states $[DS]$ is about 10^{18} cm^{-3} which is the same order of magnitude as estimated from electrical and optical measurements. This supports quantitatively our identification of the vacancy defect in the atomic structure of the deep state of In and Ga in CdF$_2$.

Most excitingly, the positron annihilation results on the DX center in Al$_x$Ga$_{1-x}$As [14,17] are qualitatively very similar to those in CdF$_2$. In Al$_x$Ga$_{1-x}$As, the donor atom is believed to make a substitutional-interstitial jump leaving an open volume behind which positrons detect [14,17]. Very recent calculations by Park and Chadi [13] suggest that also in CdF$_2$ In and Ga atoms can move from the substitutional site to an interstitial site in the neighboring lattice cell. This model is fully compatible with our positron data and indicates unexpected universality of the bond-breaking mechanism of bistability of defects in semiconductors.

In summary, we have studied n-type CdF$_2$ crystals doped with Y, Ga, and In by positron annihilation spectroscopies. We found that an open-volume defect is included in the atomic configuration of the deep state of the bistable In and Ga related defects. Our data indicate that the size of the open volume is at least half a Cd monovacancy. The positron results imply that the bond-breaking mechanism resulting in asymmetric lattice relaxations is of much more general validity than previously thought; it applies from covalent to predominantly ionic systems.

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