# Atomic Structure of Acceptors in $Cd_{0.22}Hg_{0.78}Te$: Discrimination between Vacancies and Ions Based on Positron Lifetime and Hall Data

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We demonstrate that positron annihilation provides a direct method to separate vacancy-type and ion-type acceptors in $p$-type $Cd_{0.22}Hg_{0.78}Te$ crystals. We show how to combine positron and Hall data to obtain the concentrations of acceptors, both types, and donors. In crystals with a low concentration of negative ions, there is clear evidence that the vacancies have two ionization levels $2- \rightarrow 1-$ and $1- \rightarrow 0$.

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Hall effect measurements in compound semiconductors show that the free carrier concentrations and their mobilities depend on the growth or annealing process. Various intrinsic defects, acceptor or donor, may modify electrical and optical properties. Information on the atomic nature of the ionized defects is then fundamental to understand these properties.

Positrons due to their positive charge are an ideal probe for negatively charged defects. The annihilation lifetime of trapped positrons is a fingerprint of the size of the open volume of the defect. It is therefore longer for positrons trapped at negative vacancies than for positrons trapped at negative ions [1]. Negative vacancies are also deeper positron traps than negative ions [1]. We demonstrate here that these positron trapping properties provide a powerful way to investigate the atomic structure of acceptors controlling the hole concentration in $p$-type doped crystals. We show furthermore that the concentrations of donors, ion- and vacancy-type acceptors are obtained by analyzing self-consistently positron lifetime and Hall effect data.

We apply the method to $Cd_{0.22}Hg_{0.78}Te$ (CMT) where the role of vacancies as native acceptors is crucial. This narrow gap semiconductor has focused considerable interest due to its leading role as a material for infrared detectors. Depending on the growth and subsequent annealing conditions, these alloys can generally be reversibly converted from $p+$ to $p-$ or even $n$-type materials. This property has been attributed to the presence of mercury vacancies acting as acceptors [2]. Recent positron lifetime measurements have given direct evidence that vacancies are present in $p$-type annealed CMT crystals [3,4]. The vacancy concentration was, however, not found to be proportional to the hole concentration in the saturation range, indicating either a change of charge state of the vacancies or the presence of other defects controlling the hole concentrations [4].

Five pairs of crystals S1 to S5 cut from traveling heater method grown wafers at SAT (France) or at Humboldt University (Germany) were annealed under appropriate temperatures and Hg pressures [4]. Conductivity and Hall effect measurements were performed from 4 to 300 K under various magnetic fields between 0 and 1 T. The pair S1 was $n$ type after stoichiometric annealing [4] with $4 \times 10^{15}$ $cm^{-3}$ electrons at 77 K. The four other pairs were $p$ type. Between 20 and 150 K, the Hall data were analyzed [5] with either one type or two types of holes, light and heavy. The differences in concentrations between the analysis with one or two types of holes were less than 25%. At temperatures above 150–200 K, analysis included the contribution from heavy holes and electrons [5]. The hole concentration at 77 K varies from $6 \times 10^{15}$ to $3.1 \times 10^{16}$ $cm^{-3}$ (Table I). The data $p(T)$ in S2 and S3 can be analyzed using a model (1) where a divalent acceptor controls the carrier ionization. There is need to use a model (2) introducing an additional independent acceptor level to analyze the data S4 and S5. Both analyses can be performed with or without compensation. One notices in Fig. 1 that the ionization of acceptors starts at lower temperature in S4 than in S3, although the hole concentrations are nearly the same above 50 K with $p_{77\,K}$ equal to $1.2 \times 10^{16}$ and $1.3 \times 10^{16}$ $cm^{-3}$, respectively.

Positron lifetime spectra were measured as described earlier [4] using a spectrometer system with a time resolution of 220 ps. After source and background corrections, the spectra were fitted by a sum of exponential components, $\sum_i I_i \exp(-t/\tau_i^*)$, convoluted with the Gaussian resolution function of the spectrometer. The average positron lifetime $\tau = \sum_i I_i \tau_i^*$ is determined with a high accuracy of $\pm 0.5$ ps. The lifetime components $\tau_i^*$ are used to determine the annihilation lifetime $\tau_i$ in the different annihilation states.

The spectra in $n$-type S1 are of one component with lifetimes of $278 \pm 1$ ps at 20 K and $280 \pm 1$ ps at 300 K (Fig. 2). These are the lowest ones that we measure and characterize annihilation in the lattice as discussed earlier

  

TABLE I. Values of (i) $m$, $k_v$(105 K), $E_1(-/0)$, $E_2(2-/-)$, $E_b$, $c_{st}$, $\mu_{st}$ (20 K) and of (ii) $c_v$, $\mu_{2-}$(20 K), $N_d^+$ in $p$-type $Cd_{0.22}Hg_{0.78}Te$ crystals. The (i) values are determined from the fitting of the temperature dependence of the positron average lifetime. The (ii) values are determined from the combined analysis of Hall and positron data. In the last three columns, the concentration of donors $N_d^+$, ion-type $N_a^-$ ($N_a^- = c_{st}$) and vacancy-type ($V_{Hg}$) $c_v$ acceptors are compared. Typical errors are given in the text or in the figures.

| | $p_{77\,K}$ ($10^{15}$ cm$^{-3}$) | $m$ | $k_v$ (105 K) ($10^9$ s$^{-1}$) | $E_1$ (−/0) (meV) | $E_2$ (2−/−) (meV) | $E_b$ (meV) | $c_{st}$ ($10^{15}$ cm$^{-3}$) | $\mu_{st}$ (20 K) ($10^{16}$ atoms s$^{-1}$) | $c_v$ ($10^{15}$ cm$^{-3}$) | $\mu_{2-}$ (20 K) ($10^{16}$ atoms s$^{-1}$) | $N_d^+$ ($10^{15}$ cm$^{-3}$) | $\frac{N_d^+}{N_a^-}$ | $\frac{N_d^+ - N_a^-}{c_v}$ | $\frac{N_a^-}{c_v}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| S2 | 6.1 | 1.5 | 7 | 10 | 32 | 48 | — | — | 6.2 | 8.0 | 3.8 | >>> | 0.61 | 0 |
| S3 | 13 | 1.5 | 10 | 11 | 51 | 48 | 2 | 8.9 | 19 | 6.3 | 6.7 | 3.3 | 0.24 | 0.10 |
| S4 | 12 | 1.8 | 6 | — | 41 | 49 | 7 | 10.6 | 9.8 | 5.7 | 5.5 | 0.78 | <0 | 0.71 |
| S5 | 31 | 1.5 | 10 | — | 31 | 50 | 15 | 9.5 | 22 | 5.0 | 8.6 | 0.57 | <0 | 0.68 |

[4]. The average positron lifetime $\tau$ has a strong temperature dependence in all $p$-type samples (Fig. 2). At a temperature $T_{max}$ ranging from 80 to 140 K depending on the sample, $\tau$ goes through a maximum especially well marked in S4 and S5. The spectra can be resolved into two components except below 100 K in S4 and S5. The long component $\tau_2$, as shown for S3 and S4 in Fig. 1, has a value of 305 ± 5 ps. Below 100 K in S4 and S5, the two-component decomposition can be forced by fixing $\tau_2$ to the value 305 ps.

The annihilation properties in $p$-type crystals indicate that positrons are trapped at vacancy-type defects. The 305 ps lifetime characterizes the defect we have previously proposed to be the mercury vacancy [4]. The one defect trapping model is valid for the decomposition with the 305 ps lifetime when the lifetime $\tau_{mod} = (I_1/\tau_1 + I_2/\tau_2)^{-1}$ calculated from the decomposition becomes equal to the lifetime in lattice $\tau_b$ measured in crystal S1. This occurs only above 225 K in S2 and 270 K in S3, S4, and S5. Let us examine what occurs at lower temperatures. In Fig. 2, we observe that, above $T_{max}$, the average lifetime $\tau$ increases with decreasing temperature as expected for positron trapping vacancies [1,6]. Below $T_{max}$, $\tau$ decreases, indicating that the fraction of positrons annihilating at $V_{Hg}$ vacancies decreases in all $p$-type crystals. If the $V_{Hg}$ vacancy is indeed a double acceptor, a charge state transition $2- \rightarrow 1-$ or $1- \rightarrow 0$ of the $V_{Hg}$ vacancy as the Fermi level goes down in the gap with decreasing temperature can induce such a decrease. There is indeed theoretical [1] and

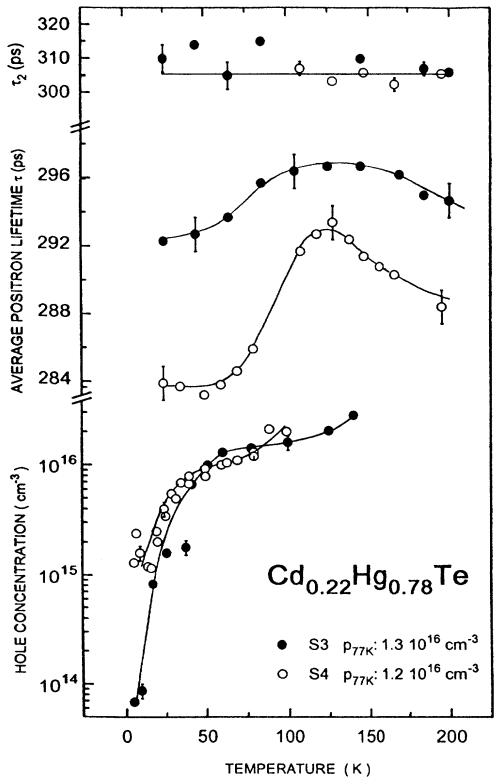


FIG. 1. Hole concentration, average positron lifetime, and long component $\tau_2$ vs temperature in $p$-type $Cd_{0.22}Hg_{0.78}Te$ crystals with the same hole concentration at 77 K.

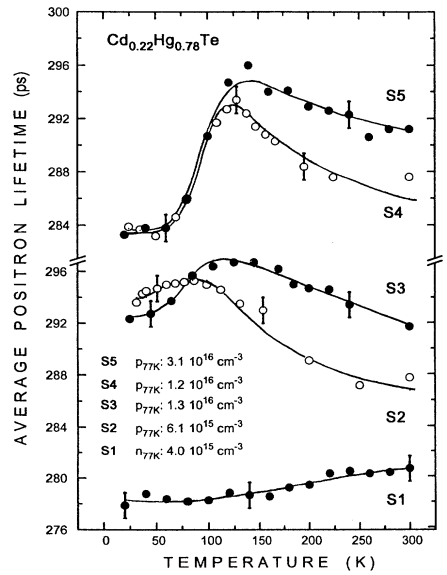


FIG. 2. Average positron lifetime as a function of temperature in $Cd_{0.22}Hg_{0.78}Te$ grown by the traveling heater method and annealed under various conditions of temperature and Hg pressure. The solid and open points correspond to the experimental data. The lines for $p$-type crystals are obtained from parameter fitting.

experimental evidence [6] that the positron trapping coefficient $\mu_v$ at vacancies is lower in the neutral state than in the negative one. Another process is, however, clearly going on in S4 and S5 where the decrease of $\tau$ at low temperatures is much stronger than in S2 and S3 and where the 305 ps is no longer freely resolved. We focus on S4 and S3 which have the same $p_{77\,\mathrm{K}}$ to investigate this other process.

The lifetime at 300 K in S4, 287 ps, being lower than in S3, 292 ps, it follows that S4 contains less vacancies than S3. As $p_{77\,\mathrm{K}}$ is the same, the conclusion is that defects other than $V_{\mathrm{Hg}}$ vacancies control the doping. We can infer that either (i) S4 contains less donors than S3 or (ii) S4 contains more acceptors than S3. The positron behavior at low temperatures indicates that other defects than vacancies trap positrons at low temperature in S4 where the lifetime 305 ps is no longer freely resolved below 100 K. These defects give rise to lifetimes shorter than 305 ps since the average lifetime decreases. This behavior suggests that in addition to vacancies negative ions trap positrons in S4. This idea is consistent with Hall data which require the addition of an extra acceptor level to fit the hole concentration in this sample.

On the basis of the above discussions, we propose to fit the lifetime data in Fig. 2 with a model where positrons are trapped at $V_{\mathrm{Hg}}$ vacancies which may exist in neutral, $V^0_{\mathrm{Hg}}$, singly, $V^-_{\mathrm{Hg}}$, and doubly negative, $V^{2-}_{\mathrm{Hg}}$, charge states and at negative ions. Positrons annihilate (i) delocalized in the lattice with a lifetime $\tau_b(T)$ given by the data (S1) in Fig. 2, (ii) localized at negative ions with a lifetime $\tau_{\mathrm{st}}(T)$ equal to $\tau_b(T)$, and (iii) localized at $V_{\mathrm{Hg}}$ vacancies with a lifetime $\tau_v = 305$ ps. We calculate the fraction $f_i$ of positrons annihilating at the state $i$ by using the stationary solution of the kinetic equation describing positron transitions from the lattice state to the localized ones ([7] and references therein). For the negative ions, the trapping rate $k_{\mathrm{st}} = \mu_{\mathrm{st}} c_{\mathrm{st}}$ and detrapping rate $\delta$ are related by the expression (1)

$$\frac{\delta}{k_{\mathrm{st}}} = \frac{1}{c_{\mathrm{st}}} \left( \frac{m_+ k_B T}{2\pi\hbar^2} \right)^{3/2} \exp\left( -\frac{E_b}{k_B T} \right), \qquad (1)$$

where $E_b$ is the positron binding energy at the negative ions, $c_{\mathrm{st}}$ their concentration, and $m_+$ the positron conduction band effective mass $m_+ = m_e$ [1]. We assume [1] that the trapping coefficient at the negative ions $\mu_{\mathrm{st}}$ varies as $T^{-0.5}$. For the mercury vacancy, we take $(g_-/g_0 = 2/4)$ and $(g_{2-}/g_- = 1/2)$ as degeneracy factors for the first $E_1$, $(1- \rightarrow 0)$, and the second $E_2$ $(2- \rightarrow 1-)$ ionization levels, respectively [8]. We take the lifetime $\tau_v$ to be independent of the charge state because the long components in the lifetime spectra fall in the narrow range $305 \pm 5$ ps. For the trapping coefficient in the negative charge states, we assume the same temperature dependence for $V^-_{\mathrm{Hg}}$ as $V^{2-}_{\mathrm{Hg}}$ but scale the coefficients by a factor of 2, $\mu_{2-} = 2\mu_-$ [1]. In agreement with the model describing positron trapping at negative vacancies via Rydberg-like states [1], we found that after electron irradiation in $n$-type converted CMT [9] the temperature dependence of $\mu_{2-}$ at $V^{2-}_{\mathrm{Hg}}$ can be approximated as $T^{-0.5}$ from 20 to $\approx$105 K and as $T^{-m}$ from $\approx$105 to 300 K with $m$ near 1.5. The trapping coefficient at the neutral vacancy $\mu_0$ is independent of temperature and can reasonably be scaled to $\mu_{2-}$ by a ratio $\mu_0/\mu_2(300\ \mathrm{K}) = 1/10, \ldots, 1/2$ [1]. The trapping rate at the vacancies, $k_v = (\mu_0 f_0 + \mu_- f_- + \mu_{2-} f_{2-}) c_v$, depends on the Fermi level and ionization levels $E_1$ and $E_2$ via the fractions of vacancies $f_0$, $f_-$, and $f_{2-}$ in the charge states 0, $-$, and $2-$, respectively [10].

With the position of the Fermi level calculated from the Hall data, we can then fit the average lifetime $\tau = \tau_{\mathrm{st}} f_{\mathrm{st}} + \tau_b f_b + \tau_v f_v$ to the data in Fig. 2 using the quantities $k_{\mathrm{st}}(20\ \mathrm{K})$, $k_v(105\ \mathrm{K})$, $c_{\mathrm{st}}$, $E_b$, $E_1$ and $E_2$, $m$ as adjustable parameters, and the ratio $\mu_0/\mu_{2-}(300\ \mathrm{K})$ as a fixed parameter. The results obtained in the fitting are insensitive to the value of this ratio 1/10 or 1/2, because, at low temperatures, the trapping coefficient at neutral vacancies is much lower than those at negative vacancies and ions. The full lines in Fig. 2 are calculated using the fitted values given in Table I. Several results of these fittings deserve attention. First, the temperature dependence of $\mu_{2-}$ at the negative vacancies $m = 1.65 \pm 0.15$ is the same as that found after electron irradiation. Second, the positron behavior in S3 and S2 is consistent with the existence of neutral and negative vacancies. The ionization energies $E_1$ $(1- \rightarrow 0)$ and $E_2$ $(2- \rightarrow 1-)$ are at $E_{v^+}(10 \pm 1)$ meV and $E_{v^+}(41 \pm 9)$ meV. Third, it is impossible to fit the data in S4 and S5 by allowing the neutral state for the vacancies. The fit is possible when only negative vacancies are considered. An ionization level $(2- \rightarrow 1-)$ can still be found at $E_{v^+}(36 \pm 5)$ meV in good agreement with these values found in S2 and S3. Fourth, the positron binding energy at negative ions is $49 \pm 1$ meV, a value consistent with those calculated by effective mass theory for Rydberg-like states. The trapping coefficient $\mu_{\mathrm{st}}(20\ \mathrm{K})$ calculated from the adjusted values $k_{\mathrm{st}}(20\ \mathrm{K})$ and $c_{\mathrm{st}}$, $\mu_{\mathrm{st}}(20\ \mathrm{K}) = k_{\mathrm{st}}(20\ \mathrm{K})/c_{\mathrm{st}}$, has the high value of $(9.6 \pm 0.9) \times 10^{16}\ \mathrm{s}^{-1}$ in agreement with theory [1]. The concentration of negative ions is about 3–5 times higher in S4 and S5 than in S3 and below the detection limit in S2.

The ionization energies we determine for the $V_{\mathrm{Hg}}$ fall in the range proposed by other authors ([10] and references therein). The charge state transitions induce only very weak atomic relaxations because the annihilation lifetime at $V_{\mathrm{Hg}}$ is independent of the position of the Fermi level. Our results demonstrate that the steep decrease of the lifetime at low temperatures in S4 and S5 are due to trapping at negative ions, and we can state that the decrease in the S parameter is incorrectly attributed in Ref. [11] to the charge transition of the vacancy. This is the reason why those authors found higher ionization energies than we did and needed to have the trapping coefficient at neutral vacancies higher than at negative vacancies at room temperature.

The Hall data in Fig. 1 indicate that the ionization of acceptors occurs at lower temperature in S4 which, according to positron lifetime data, contains more negative ions and less $V_{Hg}$ vacancies than S3. This suggests that the negative ions ionize at lower temperature than the $V_{Hg}$ vacancies. In the temperature range where the ionization of ions is exhausted, the vacancy ionization controls the hole concentration. The electroneutrality gives $p = N_a^- - N^+d + c_v(f_- + 2f_{2-})$, where $N_d^+$ and $N_a^-$ are the effective donor and acceptor concentration, i.e., $N_d^+ = \sum_i iN_d^{i+}$ and $N_a^- = \sum_i iN_a^{i-}$. The hole concentration $p(T)$ is a linear function of the vacancy charge occupancy $f_- + 2f_{2-}$ with $c_v$ fixing the slope and $N_a^- - N_d^+$ the coordinate at the origin. We then combine the Hall and positron data to determine $c_v$, $N_a^-$, and $N_d^+$ as follows.

In Fig. 3, we have plotted the experimental data $p(T)$ against the values $f_- + 2f_{2-}$ calculated with the ionization levels obtained from the fitting of the positron lifetimes $\tau(T)$. For S4 and S5 where the fraction of positron trapping at neutral vacancies is too small to contribute to $\tau = f(T)$, we have fixed $E_1$ equal to $E_v + 11$ meV. The straight lines calculated by linear regression in Fig. 3 give values of $c_v$ around $10^{16}$ cm$^{-3}$ (Table I). Once $c_v$ is known, we calculate the values of $\mu_0(T)$, $\mu_-(T)$, and $\mu_{2-}(T)$ from the adjusted values of $k_v(T)$ and $f_0$, $f_-$, and $f_{2-}$. We find them to be in good agreement in the four samples with $\mu_{2-}(20\ \text{K}) = (6.5 \pm 2.0) \times 10^{16}\ \text{s}^{-1}$ and $\mu_{2-}(300\ \text{K}) = (3.5 \pm 2.0) \times 10^{15}\ \text{s}^{-1}$. The trapping coefficient at the negative vacancies at 20 K, $\mu_{2-}(20\ \text{K})$, is of the same order of magnitude as that found at negative ions, consistent with a trapping mechanism mediated via Rydberg-like states at the vacancies [1].

The offset at the origin of the straight line in Fig. 3 corresponds to the difference $N_a^- - N_d^+$. As discussed above, we can identify the shallow acceptors $N_a^-$ with the negative ions $c_{st}$ trapping positrons. Taking for $N_a^-$ the values $c_{st}$ in Table I, we calculate the concentrations of donors which vary from $4 \times 10^{15}$ cm$^{-3}$ in S2 to $9 \times 10^{15}$ cm$^{-3}$ in S5 (Table I). The ratio $N_d^+/N_a^-$ in Table I shows that the donors are totally compensated for by acceptors of ion type in S4 and S5, whereas a fraction of the vacancies is compensated in S2, ≈61%, and S3, ≈24%. The ratio $N_a^-/c_v$ in Table I shows that the dominant acceptors are vacancies in S2 and S3.

In conclusion, we introduce a novel method based on a self-consistent analysis of positron lifetime and Hall effect data to determine the respective concentrations of ion- and vacancy-type acceptors, and donors in $p$-type semiconductors. We demonstrate that we can directly investigate whether $p$-type doping is due to $V_{Hg}$ vacancies or negative ions in CMT crystals. We can then give a correct determination of the energy of the ionization levels of the $V_{Hg}$ vacancy.

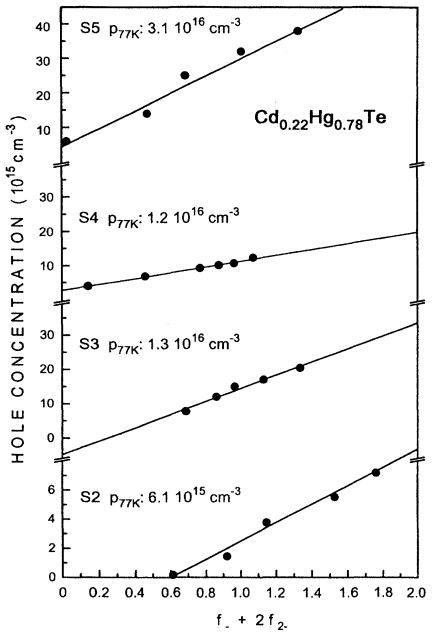


FIG. 3. Hole concentration as a function of the occupancy of the vacancy charge state $f_- + 2f_{2-}$.

[1] M. J. Puska, C. Corbel, and R. M. Nieminen, Phys. Rev. B **41**, 9980 (1990).
[2] H. R. Vydyanath, J. Electrochem. Soc. **xx**, 2609 (1981); J. Vac. Sci. Technol. B **9**, 1716 (1991).
[3] R. Krause, A. Klimakow, F. M. Kiessling, A. Polity, P. Gille, and M. Schenk, J. Cryst. Growth **101**, 512 (1990).
[4] C. Gély-Sykes, C. Corbel, R. Triboulet, F. Soisson, and L. Baroux, Ann. Chim. Fr. **16**, 541 (1991); J. Phys. C **2**, 4763 (1990).
[5] S. Rolland, A. Lasbley, A. Seyni, R. Granger, and R. Triboulet, Rev. Phys. Appl. **24**, 795 (1989).
[6] J. Mäkinen, P. Hautojärvi, and C. Corbel, J. Phys. Condens. Matter **4**, 5137 (1992).
[7] C. Corbel, F. Pierre, K. Saarinen, P. Hautojärvi, and P. Moser, Phys. Rev. B **45**, 3386 (1992).
[8] C. Blanchard and P. Girault, Semicond. Sci. Technol. **6**, A127 (1991).
[9] F. M. Kiessling, C. Corbel, L. Baroux, S. Rolland, and R. Triboulet (to be published).
[10] P. Höschl, P. Moravac, V. Prosser, V. Szöcs, and R. Grill, Phys. Status Solidi (b) **145**, 637 (1988).
[11] C. D. Smith, P. Rice-Evans, and N. Shaw, Phys. Rev. Lett. **72**, 1108 (1994).