Perturbed-angular-correlation studies of In-vacancy pairs in Hg$_{1-x}$Cd$_x$Te

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(Received 29 July 1997; accepted for publication 23 June 1999)

The interaction of vacancies with $^{111}$In atoms is studied in Hg$_{1-x}$Cd$_x$Te compounds via perturbed-angular correlation (PAC) experiments, for $x = 0.065$, 0.21, 0.44, and 0.95. In the low-$x$ (Hg-rich) compounds, Hg vacancies are created by heating in vacuum. For the $x = 0.21$ alloy, we have previously shown that In$_{c^+}$-vac$_c$ pairs (A centers consisting of an In atom on a cation site and a vacancy at a neighboring cation site) are abundant after quenching from elevated temperatures. These defects are characterized by two PAC signals with quadrupole interaction frequencies $\nu_{Q_1} = 83$ MHz and $\nu_{Q_2} = 92$ MHz, and asymmetry parameters $\eta_1 = \eta_2 = 0.08$. For the $x = 0.065-0.44$ alloys, the data presented in this article show that the fractions $f_1$ and $f_2$ of In atoms associated with these two frequencies vary with $x$ according to whether one or two Hg atoms are nearest neighbors to the Te atom that is bound to the In atom and the vacancy. The data are explained by the polarizable point-ion model. For the $x = 0.95$ compound, PAC signals are observed only when stable In is added to the compound, indicating that the presence of In creates vacancies, and that self-compensation via A centers is dominant. In this case, the well-known frequencies $\nu_{Q_4} = 100$ MHz and $\nu_{Q_5} = 112$ MHz are seen for samples quenched from several different temperatures between 325 and 525 °C, or slow cooled from 475 °C or below. In contrast, for a sample slowly cooled from 525 °C, the frequency $\nu_{Q_6} = 60$ MHz was dominant. This signal could be due to In$_{c^+}$-vac$_c$ pairs in which the vacancy is singly charged, or to In-group I pairs. We attribute the frequencies $\nu_{Q_4} = 100$ MHz and $\nu_{Q_5} = 112$ MHz, like $\nu_{Q_1}$ and $\nu_{Q_2}$, to In$_{c^+}$-vac$_c$ pairs having doubly charged vacancies. © 1999 American Institute of Physics. [S0021-8979(99)01419-X]

I. INTRODUCTION

The compound semiconductors Hg$_{1-x}$Cd$_x$Te (MCT) are of technological interest in both the low $x$ and high $x$ regions.1 The Hg-rich alloys are the basis for a range of technologies, notably detectors of infrared radiation tuned to atmospheric infrared "windows."2 CdTe has applications for optoelectronic devices, radiation detectors, and solar cells.

In MCT, defects and phenomena arising from them are abundant and complex, and directly affect electrical characteristics and device performance. The cation vacancy is the (double) acceptor responsible for the intrinsic $p$-type conductivity of the Hg-rich alloys.3 It is present in quenched MCT, and in MCT heated to temperatures above 300 °C, in sufficient quantity to allow changes in its concentration to be monitored by electrical measurements, or by its interaction with the donor ion indium using perturbed angular correlation (PAC) spectroscopy. The formation of indium-vacancy complexes in the $x = 0.21$ alloy of MCT was studied previ-ously in this laboratory$^4$-7 by PAC. These investigations detected two distinct but very similar electric quadrupole interactions, having characteristic frequencies of $\nu_{Q_1} = 83$ MHz and $\nu_{Q_2} = 92$ MHz. These two interactions both had asymmetry parameters $\eta = 0.08$, and the electric field gradient (EFG) tensor $zz$ axes were oriented close to $\langle 111 \rangle$ crystallographic directions.5 We presented evidence that both of these interactions arose from indium-vacancy pairs (In$_c^-$-vac$_c$), where the indium (donor) ion occupies a cation site and is bound to a vacant (acceptor) site in the first cation shell.

The $\langle 111 \rangle$ orientation of the EFG tensor, which is also seen in other zincblende semiconductors,3 at first seemed surprising, since the indium-vacancy pair itself has a $\langle 110 \rangle$ symmetry axis, and it is generally assumed that the EFG tensor shares the symmetry of the defect complex.9 Indeed, a first-order point ion calculation, in which ions are treated as point charges affixed to their lattice sites, predicts a $\langle 111 \rangle$ orientation for the EFG $zz$ axis.

We attributed both the $\langle 111 \rangle$ EFG symmetry and the occurrence of the two different frequencies to a polarizable point-ion model,3 whereby the magnitude of the EFGs is due both to point charges (monopoles) and to dipoles caused by the highly polarizable Te ion adjoining the vacancy and the In/Cd probe ion. Since in this model the dipole moment at the Te ion provides an important component of the EFG, the two other nearest-neighbor ions to the Te ion are important. For the $x = 0.21$ compound, the probability is 62% that these ions are both Hg, and 33% that one is Hg and one is Cd. The probability ratio of nearly 2:1 corresponds to the observed...
ratio $f_1/f_2$ of the fractions of the two PAC frequencies.\textsuperscript{4,5} Thus we attributed the lower frequency to the case of two Hg ions adjacent to the Te ion.

If the polarizable point-ion model is correct, then the ratio of $f_1/f_2$ will change as the stoichiometry is changed. In alloys with a larger Hg concentration, $f_1$ should predominate, while in alloys with more Cd, $f_2$ should predominate and a new, third frequency should be measurable, corresponding to the case of two Cd ions neighboring the Te ion. This frequency was not seen in the $x=0.21$ alloy because the probability of this is only 4%. In this work we have measured the ratio of $f_1$ and $f_2$ with stoichiometry, in compounds ranging from almost HgTe to almost CdTe.

The defect properties of CdTe have been studied extensively, utilizing electron paramagnetic resonance (EPR),\textsuperscript{10} optically detected magnetic resonance (ODMR),\textsuperscript{11,12} photoluminescence,\textsuperscript{13} positron annihilation spectroscopy (PAS),\textsuperscript{14} and perturbed angular correlation (PAC) spectroscopy.\textsuperscript{8,9,15–17} After CdTe was annealed for five days at 750 °C in a Te atmosphere to promote the creation of Cd vacancies, isolated Cd vacancies were found by EPR in the singly negatively charged state.\textsuperscript{10} Centers consisting of a Cd vacancy bound to an indium cation donor\textsuperscript{11} or a chlorine anion donor\textsuperscript{12} have been identified by ODMR spectroscopy. They form shallow acceptors with binding energies 0.14 and 0.12 eV, respectively. From PAS data,\textsuperscript{14} it was found that the Cd vacancy concentration did not exceed $10^{16}$ cm$^{-3}$ for undoped CdTe, even when annealed under a Te atmosphere.

The vacancy concentration could be increased to a value of $C_v = 2 \times 10^{17}$ cm$^{-3}$ by adding an equal concentration of In.

Early PAC experiments\textsuperscript{15} for $^{111}$In-implanted pure CdTe showed the presence of a 60 MHz signal, with $\eta = 0.19$, after annealing at 473 K. This signal was attributed to In$_{\text{vac}}$-In$_{\text{vac}}$ pairs. Wegner and Meyer\textsuperscript{9} observed signals at 100 MHz ($\eta < 0.05$), and 111 MHz ($\eta = 0.18$) for CdTe doped with $10^{19}$ In atoms per cm$^3$ by diffusion of stable In together with the radioactive probe ions $^{111}$In, under Cd pressure. The EFG symmetry was $\{111\}$. They also saw a 115 MHz ($\eta = 0.0$) signal after $^{111}$In irradiation of pure CdTe. Both the 60 MHz and 100/111 MHz signals were observed in CdTe by several later experiments. In particular, Ostheimer et al.\textsuperscript{16} found that for In concentrations above about $10^{18}$ cm$^{-3}$, the 60 MHz PAC signal was replaced by the 100/112 MHz pair. They attributed this change to an altered Fermi level caused by the high In concentration, which caused the vacancy in the In$_{\text{vac}}$-In$_{\text{vac}}$ pair to become doubly charged. The 60 MHz signal was then presumed due to the singly charged vacancy.

In the present study, in the pure samples, a regimen of isochronal anneals with various cooling rates did not result in the formation of a measurable fraction of In atom-vacancy pairs, suggesting that in these samples the concentration of vacancies was quite low. In contrast, in samples doped during growth with $10^{19}$ In cm$^{-3}$, large fractions of the indium probe ions, as many as 70%, were bound to vacancies. From this we conclude that the formation of these pairs in significant quantity is an extrinsic phenomenon, depending on the purity of the sample. We compare these results to MCT alloys having higher Hg concentration in order to show that the 100/112 MHz frequencies are due to the doubly charged vacancy-In/Cd defect.

II. EXPERIMENTAL PROCEDURE

We studied Hg$_{1-x}$Cd$_x$Te (MCT) grown by the traveling heater method,\textsuperscript{18} with $x = 0.065$, $x = 0.44$, and $x = 0.95$, and compared the results with earlier measurements\textsuperscript{4,19} for the $x = 0.21$ alloy, grown by solid state recrystallization (supplied by Texas Instruments). The $x = 0.44$ sample and two of the $x = 0.95$ samples were doped during growth with $10^{19}$ In atoms per cm$^3$.

In these experiments the $^{111}$In PAC probe atoms were diffused into the material at temperatures between 325 °C (for $x = 0.065$) and 575 °C (for $x = 0.95$). It was found that annealing at higher temperatures caused the material to decompose. Each sample was first etched in a Br–methanol solution, then placed in a HF-etched, DI-water-rinsed quartz tube into which a very small quantity of $^{111}$In (in the form of InCl$_3$ in a HCl solution) had been deposited, and then sealed in a vacuum of order $10^{-5}$ Torr. The sample was then annealed in the evacuated ampoule and slowly cooled, or quenched to room temperature by dropping from a vertical furnace into a bath of cool water. For all anneals and PAC measurements, the samples remained enclosed in the quartz ampoules. All PAC measurements were performed at room temperature using a typical setup of four NaI detectors at 90° and standard slow–fast (time-energy) coincidence electronics.

We prepared two samples of the $x = 0.95$ material from an undoped wafer, and two samples from an In-doped wafer. One sample from each wafer was isochronally annealed for 4 h at sequentially higher temperatures between 325 and 575 °C, and allowed to cool to room temperature over several hours. The other samples were first preannealed at 475 °C and cooled slowly to room temperature. They were then subjected to a similar isochronal annealing sequence, except that each sample was quenched rapidly to room temperature as described above. A PAC measurement was done after each anneal.

Perturbed-angular-correlation (PAC) spectroscopy is used to detect hyperfine fields at the sites of radioactive probe nuclei ($^{111}$In in the present experiments) by measuring the effect of the induced nuclear precession on the radiation pattern emitted from the ensemble of decaying nuclei.\textsuperscript{20} Electric field gradients (EFGs), such as those arising from nearby crystal lattice defects, interact with electric quadrupole moments of probe nuclei, causing a perturbation of the radiation pattern, the functional form of which is known exactly. One useful characteristic of PAC spectroscopy is the small number of probe atoms required, on the order of $10^{11}$. This assures that the atoms are "good probes" in that they do not significantly alter the properties of the material being studied; in undoped samples the tiny concentration of indium probe atoms does not affect the electrical properties of the concentration of intrinsic defects, and in the samples doped with In during growth the radioactive indium atoms are chemically identical to the indium introduced into the melt, so their environments may be considered to be typical of all
the indium ions. However, the depth profile of the diffused probe ions will typically be shallower than that of the indium introduced during growth.

Via PAC one measures the absolute fraction of the total number of probe ions in a particular environment. One can, therefore, determine the fraction of indium ions involved in indium-vacancy complexes, which is proportional to the concentration of vacancies and a Boltzmann factor involving the complex’s binding energy. It follows that, in a given material, at a given temperature, the measured fraction of indium-vacancy pairs is directly proportional to the concentration of vacancies.

In the most common PAC data analysis, the coincidence counting rates as a function of time are used to form a ratio $R(t)$ of angular correlation data measured between detectors at different angles. Each unique defect structure causes a unique quadrupole interaction and a term:

$$s_0 + \sum_{n=1}^{3} s_n \cos \omega_n t,$$

in $R(t)$. Each defect configuration is manifested as three nonzero frequency components in $R(t)$, which are seen in the Fourier transform of $R(t)$ (see Fig. 2). The strength $\nu_Q$ and asymmetry parameter $\eta$ of the quadrupole interaction determine the frequencies $\omega_n$. The coefficients $s_n$ depend on both the asymmetry parameter $\eta$ and (in single-crystal specimens) the orientation of the electric field gradient tensor relative to the detectors. The magnitude, symmetry, and orientation of the tensor describing the gradient of the electric field can be deduced by fitting the theoretical equation to experimental PAC data. A careful and thorough PAC analysis, correlating changes in the microscopic configuration of the indium ions with macroscopic factors like temperature, doping, and the orientation of a single crystal relative to the detectors, can yield useful information about the behavior of defect-impurity complexes and, in favorable cases, their structure.

$^{111}$In decays to $^{111}$Cd just before the EFG is “sampled” by the probe atom nucleus. This means that, although the vacancy is initially bound to an indium atom, when the measurement which made the vacancy is isolated: the indium atom has converted to cadmium, a native cation in these materials.

### III. RESULTS

#### A. Alloys with $x=0.065-0.44$

Figure 1 shows $R(t)$ spectra for: (a) an $x=0.065$ sample (annealed 2 h at 475 °C and quenched), (b) an $x=0.21$ sample (annealed 2 h at 350 °C and quenched, then aged for 8 h at 85 °C), and (c) an $x=0.44$ sample (annealed 4 h at 475 °C and quenched). The solid lines in Fig. 1 are least-square fits to the data, using Eq. (1). The frequency of modulation of the $R(t)$ signals is proportional to the strength of the EFG at the probe nuclei. The amplitude of the modulation directly gives the fraction of probe ions having a given EFG. The data of the middle panel ($x=0.21$) show a splitting of the modulations for times longer than 100 ns, indicating the presence of two closely spaced EFGs. In the top two panels, the relatively flat baseline value of $R(t)$ at about $-0.04$ represents the fraction of probe ions that have EFGs near zero, and thus are in cubic symmetry sites. This baseline signal decays gradually with time, indicating small, random variations from cubic symmetry. In the bottom panel, the baseline signal is rather strongly damped.

The Fourier transforms of the $R(t)$ data of Fig. 1 are shown in Fig. 2. Frequency triplets corresponding to a particular EFG, as determined by a least-squares fit to the theoretical function of Eq. (1), are indicated in the figure by linked vertical bars. Only one triplet is resolved in Fig. 2(a), for the $x=0.065$ sample, at a frequency $\nu_Q=83$ MHz, and $\eta=0.05$. The fit is improved by the inclusion of 8% of a second fraction with a somewhat higher $\nu_Q$, varying from 88 to 92 MHz depending on the starting fit parameters.

In Fig. 2(b) two frequency triplets are seen, characterized by fundamental quadrupole interaction frequencies $\nu_Q$ of 83 and 92 MHz, both having asymmetry parameters of $\eta=0.08$. The fractions of In atoms associated with those frequencies are $f_1=38\%$ and $f_2=20\%$. The separation of the two components is clearest at the second and...
third “harmonics” of the frequency triplets, which show up as double peaks near 165 and 250 Mrad/s.

The $x=0.44$ data of Fig. 2 show evidence for a third, higher, frequency. In this alloy all of the frequencies have increased, as a result of a balance of several factors including changes in the lattice constant and the density of conduction-electronic charge. The two fractions seen previously now occur at $\nu_{Q_1}=87$ MHz and $\nu_{Q_2}=96$ MHz, respectively. Though impossible to measure with any precision in this sample, the asymmetry parameter $\eta$ is consistent with those of the other alloys. The third triplet has a fundamental quadrupole interaction frequency $\nu_{Q_3}$ of about 105 MHz. There is an uncertainty in this measurement of about 5 MHz. As in the $x=0.21$ alloy, the frequencies can be resolved most clearly in the second peaks of each frequency triplet. Note that the three frequencies are equally spaced, each 9–10 MHz apart from the neighboring peaks.

B. Alloys with $x=0.95$

Results for the $x=0.95$ material are shown in Figs. 3–6. Figure 3 shows the $R(t)$ spectrum for an undoped sample after annealing at 475 °C for 4 h, followed by slow cooling. This spectrum was typical of the undoped samples, both quenched and cooled slowly: no In-vacancy pairs were seen at any point in the annealing regimen of the undoped samples. In these samples, all of the indium ions occupy sites of nearly cubic symmetry; almost certainly they are substi-

FIG. 3. $R(t)$ data for $^{111}$In in undoped Hg$_{0.05}$Cd$_{0.95}$Te after annealing at 475 °C and cooling slowly to room temperature. This spectrum is typical of the undoped samples.

FIG. 4. $R(t)$ spectra for Hg$_{0.05}$Cd$_{0.95}$Te doped with $10^{19}$ In atoms per cm$^3$, after quenching from 425 °C (top panel), 475 °C (middle panel), and 525 °C (bottom panel).
tuting for metal ions, as they are known to do in their electrically active state. As in the Hg-rich alloys there are slight deviations from cubic symmetry, reflected in the slight exponential decay of the $R(t)$ spectra.

Figures 4–6 show the data for $x = 0.95$ samples that were doped during growth with $10^{19}$ In atoms per cm$^3$. Figure 4 shows $R(t)$ spectra for a sample quenched from 425, 475, and 525 °C. Figure 5 shows $R(t)$ spectra from an identical sample, after anneals at the same temperatures, but slowly cooled instead of quenched. Figure 6 shows the Fourier transforms for the data of Fig. 5.

In the quenching sequence of Fig. 4 (which followed the initial preanneal at 475 °C), about 47% of the indium ions are involved in complexes having interaction frequencies close to 105 MHz and an asymmetry parameter between 0 and 0.1. There are two distinct peaks here, i.e., a frequency doublet, reported previously$^{9,16}$ for CdTe as the 100/112 MHz doublet. In the present case the doublet has frequencies of $\nu_{Q_4} = 100$ MHz and $\nu_{Q_5} = 112$ MHz as well, with an uncertainty of about 5 MHz for the lower frequency, and about 3 MHz for the higher frequency. For quenches from 425 to 525 °C, the fraction of In ions associated with this doublet are some-

what lower than for quenches from 325 and 375 °C (see Table I, but the frequencies of the interactions remain the same. Although there are two distinct peaks, they are not resolved well enough to allow us to make an accurate measurement of the two different fractions. The fit parameters for all of the spectra are shown in Table I.

In contrast to the quenching sequence, the data for the slow-cooled sequence (Table I, Figs. 5 and 6) show a transition. After slow cooling from 425 °C and below, 58%–63% of the probe ions occupy sites identical to those observed in the quenched samples. The 425 °C $R(t)$ data and their Fourier transform (Figs. 5 and 6, top panels) are very similar to the data for all the quenched samples (Fig. 4). The 475 °C data (center panels of Figs. 5 and 6) show a feature not seen in any of the others: about 14% of the probe ions exhibit a new interaction, characterized by $\nu_{Q} = 83$ MHz, and $\eta = 0$. Slow cooling from 525 °C drastically alters the situation: in this case, and subsequently after slow cooling from higher temperatures, about 45%, of the indium ions occupy a state having a frequency $\nu_{Q_6} = 60$ MHz, which is very similar to that reported$^{8,15}$ for the indium-vacancy pair in high purity CdTe. The asymmetry parameter for this interaction is near

![FIG. 5. $R(t)$ spectra for Hg$_{0.05}$Cd$_{0.95}$Te doped with $10^{19}$ In atoms per cm$^3$, after slow cooling from temperatures of 425 °C (top panel), 475 °C (middle panel), and 525 °C (bottom panel).](image1)

![FIG. 6. Fourier transforms calculated from the $R(t)$ data of Fig. 5. Top panel: 425 °C, middle panel: 475 °C, bottom panel: 525 °C. Frequency triplets corresponding to a particular $\nu_Q$, as determined by a least-squares fit to the theoretical function of Eq. (1), are indicated by linked vertical bars.](image2)
zero, apparently smaller than the value most often reported in the literature, though values of \( \eta = 0 \) have also been reported. The 100/112 MHz interaction has vanished completely. The remaining indium ions occupy near-cubic, substitutional metal sites.

IV. DISCUSSION

A. Stoichiometry dependence of defect fractions

According to the polarizable point ion model, the magnitude of the EFG caused by In\(_{xC}\)-vac\(_C\) pairs depends strongly on the other two nearest cation neighbors to the highly polarizable Te ion that is adjacent to both the vacancy and the In ion. In MCT, these ions can be Hg–Hg, Hg–Cd, or Cd–Cd. The character of the Te–Cd bond is somewhat different from the character of the Te–Hg bond. In the simplest image, this difference can be expressed in terms of the amount of electronic charge transferred away from the Te ion and towards the cation, which, according to the results of our experiment, is larger for the Hg–Te bond than for the Cd–Te bond. A Te ion coordinated with more Hg ions has a smaller total charge, hence a smaller polarizability, than a Te ion coordinated with more Cd ions. This is consistent with the fact that the Cd–Te bond is more “ionic” than the Hg–Te bond. The EFG arising from the polarized Te ion is larger when it has more Cd ions as nearest neighbors. Thus one should observe three different EFGs caused by In\(_{xC}\)-vac\(_C\) pairs of a given charge in MCT compounds (as we have observed in Figs. 1 and 2), depending on whether the Te neighbors are Hg–Hg, Hg–Cd, or Cd–Cd.

The fractions of the probe ions associated with those EFGs should vary with the stoichiometry, or \( x \) value, if the cations are randomly distributed in the compound. The predicted fractions of the indium probe ions having Hg–Hg, Hg–Cd, and Cd–Cd nearest neighbors to Te, calculated by multiplying the probabilities by the observed total vacancy fraction, are shown in Table II for the different compositions. The observed fractions \( f_1, f_2, \) and \( f_3 \) having frequencies \( \nu_{Q_1}, \nu_{Q_2}, \) and \( \nu_{Q_3} \) are also shown in Table II. The ratios of the observed fractions shown in Table II agree within experimental error with the calculated probabilities of Hg–Hg, Hg–Cd, and Cd–Cd neighbors. For the \( x = 0.065 \) specimen, only the frequency \( \nu_{Q_1} = 83 \) MHz is clearly visible in the Fourier transform [Fig. 2(a)], although a small fraction \( f_2 \) (about 8%) of the second frequency, \( \nu_{Q_2} = 92 \) MHz, corresponding to the defect coordinated by one Cd ion and one Hg ion, improves the fit. For the \( x = 0.21 \) sample, a second frequency triplet is apparent [Fig. 2(b)], and the relative fractions are consistent with the model of random occupancy, which predicts that 62% of the indium ions are coordinated (in the quadrant containing the vacancy) by two Hg ions, 33% by one Hg ion and one Cd ion, and a little more than 4% by two Cd ions. In the \( x = 0.44 \) sample a

<table>
<thead>
<tr>
<th>Alloy ( x ) value</th>
<th>( f_1 ) (%)</th>
<th>( f_2 ) (%)</th>
<th>( f_3 ) (%)</th>
<th>Hg–Hg (%)</th>
<th>Hg–Cd (%)</th>
<th>Cd–Cd (%)</th>
</tr>
</thead>
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<tr>
<td>0.065</td>
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<td>8±2</td>
<td>0</td>
<td>61</td>
<td>8</td>
<td>~0</td>
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<tr>
<td>0.21</td>
<td>38±3</td>
<td>20±3</td>
<td>0</td>
<td>36</td>
<td>19</td>
<td>2</td>
</tr>
<tr>
<td>0.44</td>
<td>21±4</td>
<td>30±6</td>
<td>6±2</td>
<td>16</td>
<td>25</td>
<td>10</td>
</tr>
<tr>
<td>0.95</td>
<td>0</td>
<td>0</td>
<td>52±5</td>
<td>~0</td>
<td>5</td>
<td>47</td>
</tr>
</tbody>
</table>
third fraction \( f_3 \), having a higher frequency \( \nu_{Q_1} = 105 \text{ MHz} \) is seen in Fig. 2(c), corresponding to the case where the polarized Te ion is coordinated by two Cd ions. In this case, the errors in the fitted defect fractions are considerably higher. This is to be expected because of difficulty in fitting highly damped spectra. The agreement with the prediction of random occupancy is less exact, but the trend is clear: the highly damped spectra. The agreement with the prediction of the errors in the fitted defect fractions are considerably compensation via vacancy production centers. In the case of donor doping, the importance of self-

As was mentioned in Sec. III A, the rate of decay of the baseline signal in Fig. 1 increases with \( x \) and is especially pronounced in Fig. 1(c). This stoichiometry dependence suggests that the damping is caused by small, (quasi-) random efgs resulting from the quasirandom distribution of Cd ions on the cation lattice. However, the strong damping seen in Fig. 1(c) was not seen in thin-film samples of similar stoichiometry,\(^{19}\) suggesting either that the cations were more ordered in those thin film samples, or that the damping arises from some other cause, such as lattice strain.

To summarize, PAC data for Hg-rich MCT alloys are consistent with the predictions of the polarizable point-ion model, assuming a quasirandom distribution of cations.

**B. Vacancy concentration and charge in Cd-rich alloy**

In wide-band-gap semiconductors, it has been observed that the carrier concentration is often very much smaller than the concentration of dopant ions. Several possibilities\(^{28}\) have been proposed to explain this observation, including self-compensation, residual impurities, solubility limits, and DX centers. In the case of donor doping, the importance of self-compensation via vacancy production (and subsequent A-center creation) has been known for some time. However, its importance has been questioned in the case of CdTe\(^{12}\).

In the undoped \( x = 0.95 \) samples, which contain only residual impurities and a vanishingly small number of indium probe ions (Fig. 3), there is no measurable pairing between indium probe ions and vacancies. All of the indium ions occupy substitutional metal sites, regardless of the annealing temperature and cooling rate. In the samples of Fig. 4 and Table I, which contain large concentrations of indium ions introduced during growth, the fraction of \( \text{In}_{c-app} \) pairs is close to 50%. These results show that self-compensation is important in near-CdTe MCT alloys doped with In. The absence of indium-vacancy pairs in undoped, Cd-rich samples is consistent with a trend observed in our laboratory in undoped MCT samples of intermediate stoichiometry: as \( x \) increases the fraction of indium ions bound to vacancies gets smaller. In undoped samples with \( x > 0.5 \) it is difficult to see these pairs at all, except for occasional exceptions arising, perhaps, from unintentional contamination. These results suggest that the nature and origin of vacancies is different in Cd-rich materials than in Cd-doped samples: in Hg-rich alloys thermal history has an important effect on vacancy concen-

tration, which in turn is relatively insensitive to doping; in Cd-rich alloys the vacancy concentration does not depend in an important way on the thermal history, depending instead primarily on doping. In contrast to the case of Hg-rich alloys, the pairing of indium ions with vacancies in CdTe and Cd-rich alloys is primarily an extrinsic phenomenon, related to the impurity concentration (intentional or unintentional), and not an intrinsic property of the crystal itself. This conclusion was also reached in the experiments of Wegner and Meyer.\(^{9}\)

Considerable evidence has accumulated from\(^{11}\) in PAC experiments in CdTe that the signal with frequency 60 MHz and \( \eta = 0.1-0 \) (having \( (111) \) symmetry) corresponds to the \( \text{In}_{c-vac} \) pair (A center), probably with the vacancy in the singly charged state.\(^{8,15,26}\) Recent support for this charge state has been provided by evidence that the fraction of defects associated with the 60 MHz signal is larger at room temperature than at 77 K, where the Fermi level is reduced.\(^ {27}\) This frequency was replaced by the 100/112 MHz signals (also having \( (111) \) EFG symmetry) in samples doped with more than \( 10^{18} \) In cm\(^{-3} \) and similar results were found for other II–VI compounds.\(^{16}\) The change has been attributed to a higher Fermi level in the highly doped samples, which caused the vacancy in the \( \text{In}_{c-vac} \) pair to trap two electrons. It is therefore tempting to conclude that the 100/112 MHz signals in CdTe and in Cd-rich MCT, along with the 83/92 MHZ signals in Hg-rich alloys are due to single acceptor \( \text{In}_{c-vac} \) pairs (doubly charged vacancy), and the 60 MHz signal is due to neutral \( \text{In}_{c-vac} \) pairs (singly charge vacancy). However, there have been several recent reports which indicate that PAC signals characterized by frequencies near 60 MHz can also be caused by\(^{111}\) In-group I ions pairs, where both ions are on cation sites. Rib et al.\(^{17}\) observed frequencies of 60 MHz and \( \eta = 0.15 \) for Ag-doped CdTe, and a frequency of 57.5 MHz and \( \eta = 0.16 \) for Cu-doped CdTe. Recently, Wolf et al. have studied both\(^{11}\)\(^{11}\) Ag and\(^{11}\)\(^{11}\) In in CdTe via PAC measurements. For\(^{11}\)\(^{11}\) In they observed signals with 57 MHz (\( \eta = 0.1 \)) and 61 MHz (\( \eta = 0.18 \)) which they attributed to \( \text{In}_{c-Ag} \) pairs and \( \text{In}_{c-vac} \) pairs respectively.\(^{28}\) The Ag results showed that the Ag atoms occupied Cd sites in the lattice. Austin et al.\(^{19}\) showed that in a sample of MCT with \( x = 0.45 \) both the 60 and 87 MHz signals occurred, and that the latter was replaced by the former during aging at room temperature over a period of several hours. The timing of this process indicated that ionic diffusion was involved, and led to speculation that the transformation was due to the filling of vacancies by fast-diffusing impurities, perhaps group I ions like Li, Cu, or Ag. Also unexplained is the wide range of asymmetry parameters that have been reported for 60 MHz interactions in CdTe and related alloys. All of these factors lead to uncertainty in the attribution of the 60 MHz signal.

**V. CONCLUSIONS**

The present experiments support the polarizable point-ion model\(^{5}\) for calculation of EFGs caused by point defects. According to this model, the magnitudes of the EFGs caused by \( \text{In}_{c-vac} \) pairs in MCT are dependent on the other two nearest cations to the Te ion adjoining the vacancy and the
In/Cd probe ion. Thus three different frequencies are expected (for a specific charge state of the vacancy), depending on whether those cations are Hg–Hg, Hg–Cd, or Cd–Cd. We observe three frequencies, in the present experiments for Hg$_{1-x}$Cd$_x$Te compounds with $x = 0.065$, 0.21, 0.44, and 0.95, and the fractions of In probe ions having the different frequencies are seen to be roughly proportional to the probability that the Te atom has Hg–Hg, Hg–Cd, or Cd–Cd neighbors.

In the compound with $x = 0.95$, In$_C$–vac$_C$ pairs (A centers) do not occur in very pure material in sufficient numbers to be seen by PAC. They do, however, dominate in material doped during growth with large concentration of indium, indicating that self-compensation is very important. Because the Fermi level is high in this case, we infer that the vacancies in these pairs have a charge state of $-2$, and that the PAC frequency doublet at 100/112 MHz (as well as the 87 and 92 MHz frequencies observed for the other MCT compounds) corresponds to doubly charged vacancies. The PAC frequency near 60 MHz that is observed in these experiments, and also in other research for lightly doped material, can be due to neutral In$_C$–vac$_C$ pairs (vacancy charge of $-1$), or to In-group I pairs.

ACKNOWLEDGMENTS
