The Defect Structure of CdTe: Hall Data*

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A high-temperature Hall effect study as function of cadmium pressure and temperature was carried out for pure and indium-doped CdTe. The results, combined with published data on the Hall effect of quenched crystals and electronic energy level positions, are interpreted on the basis of a detailed point defect model. Parameters of the equilibrium constants of various defect formation reactions are given.

Introduction

An analysis of the defect structure of CdTe given by de Nobel (*1*) and Kröger (*2*), based on the results of Hall effect measurements on pure and doped samples, quenched after annealing under well-defined component pressures at $700 \leqslant T \leqslant 1000°C$, indicates that the defect structure of pure CdTe has three ranges. At high cadmium pressures the electron concentration increases as the square root of p_{Cd}. This was explained by assuming singly ionized native donors ($Cd_i^{\cdot}$ and $V_{Te}^{\cdot}$) and electrons (e') as the main charged species. In this range the temperature dependence of the electron concentration at constant p_{Cd} was found to be negative. At medium p_{Cd} there is a narrow intrinsic range in which electrons and holes are the major charged species. At low p_{Cd} ($=$ high p_{Te_2}) there is a range dominated by holes and singly ionized native acceptors which were believed to be cadmium vacancies (V_{Cd}').

Donor-doped CdTe prepared at high p_{Cd} shows a range in which the electron concentration is equal to the donor concentration and independent of p_{Cd}. At lower p_{Cd} the electron concentration decreases with decreasing p_{Cd} and increasing temperature.

In this range doubly charged native acceptors A_n'' are believed to be major charged species, with $[D^{\cdot}] \approx 2[A_n'']$.

The results on undoped CdTe and the defect model based on it are at variance with the results of experiments by Smith (*3*) on the Hall effect of crystals of undoped CdTe in equilibrium with atmospheres of various p_{Cd} at high temperature and of high-temperature conductivity measurements by Whelan and Shaw (*4*), Zanio (*5*), and Rud and Sanin (*6*), which show that the conductivity and the electron concentration are proportional to $p_{Cd}^{1/3}$. This indicates that the native donors are doubly rather than singly ionized. Further, the electron concentration at constant p_{Cd} increases with increasing temperature rather than decreases as found by de Nobel with quenched crystals.

In order to clarify this discrepancy, we have carried out high-temperature Hall effect measurements on pure and indium-doped crystals. In addition, Cd and Te tracer self-diffusion was studied. The results of the latter will be reported in a subsequent paper, (*10*).

The results of the Hall effect measurements, by Smith and ourselves at high temperature and by de Nobel on cooled crystals, combined with some conclusions based on the self-diffusion study, are used to arrive at a detailed defect model.

Experimental

Sample Preparation

Boules of undoped single crystals of CdTe and of CdTe doped with 10^{17} In cm^{-3} were put at our disposal by Dr. K. Zanio of Hughes Aircraft Research Laboratory, Malibu, CA. Spectrographic analysis shows that impurities, if present, are below the detection limit. Plates of 1-mm thickness were cut from the boules with the aid of a wire saw.

Crystals with an indium content of 2.7×10^{17} cm^{-3} were prepared from the weakly doped material by diffusion. This was done by depositing by vacuum deposition a calculated amount of indium onto one side of a 1-mm-thick plate; a second plate was placed on top of the indium, and the sandwich was annealed at 700°C for 3 weeks in an evacuated quartz tube under a tellurium pressure of 2.2×10^{-2} atm, established by keeping one end of the container, containing some Te, at a temperature of 664°C. A crystal doped with 3.6×10^{18} In cm^{-3} was made by sublimation of weakly doped CdTe in the presence of some additional indium in an atmosphere with $p_{Cd} \approx 0.01$ atm. From this, crystal plates were cut as described above. After polishing the faces to a flatness of ~28 μm, the plates were subdivided in sections of $1 \times 4 \times 4$ mm for the diffusion experiments and $1 \times 10 \times 10$ mm for the Hall effect measurements.

The samples so obtained were washed in trichloroethylene and etched for 100 min with a solution of 10 wt % bromine in methanol. The samples for Hall measurements were given cloverleaf shape as is customary for measurements by the van der Pauw method (7). The indium concentration of the samples was estimated from the high-temperature Hall effect and conductivity as suggested by Zanio (5) under the assumption of indium as a single donor.

Hall Effect Measurements

Hall effect measurements on crystals in equilibrium with atmospheres with well-defined cadmium pressures at 700, 800, and 900°C were carried out in an apparatus as described previously (8). Results for pure and indium-doped crystals are shown in Figs.
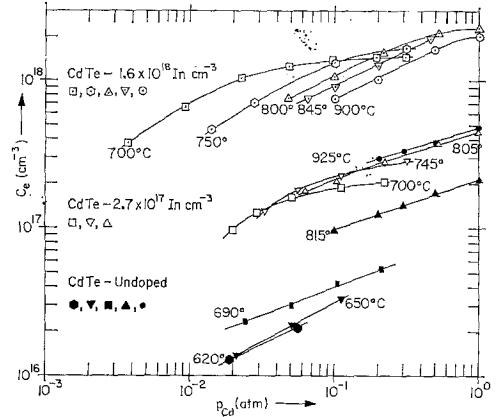

Fig. 1. Electron concentration isotherms for undoped CdTe and CdTe doped, respectively, with 2.7×10^{17} and 1.6×10^{18} In cm^{-3} in equilibrium with vapors of different p_{Cd}.

1 and 2. For undoped CdTe there is good agreement with results reported by Smith (3). The electron concentration is proportional to $p_{Cd}^{1/3}$. A plot of ln[e'] vs $1/T$ at high p_{Cd} is slightly curved; it has a positive slope, indicating an increase of the electron concentration with decreasing temperature.

Doping with indium increases the electron concentration, in particular at high p_{Cd}. Here the electron concentration has a posi-
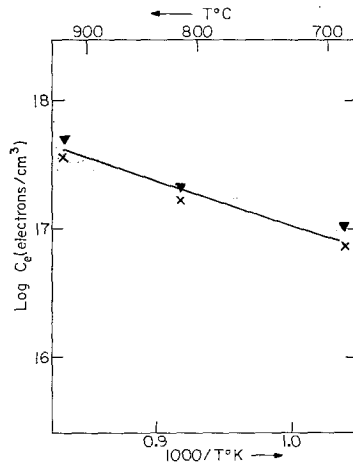

Fig. 2. Electron concentrations as $f(T)$ in undoped CdTe in equilibrium with a vapor with $p_{Cd} = 1$ atm as determined by Hall effect measurements according to Smith (3) and ourselves. Several points are extrapolations. ▼, this paper; × Smith (3).
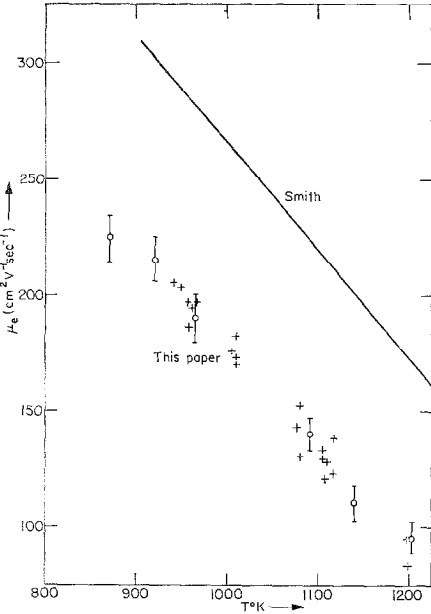
FIG. 3. Electron mobilities in undoped CdTe ($\bigcirc$) and CdTe–2.7×10^{17} In cm^{-3} (+). Smith's results (3) are shown for comparison.

tive temperature dependence. At low p_{Cd} the temperature dependence is negative, just as observed by de Nobel with quenched crystals (1). Resistivities are found to vary with p_{Cd} as the Hall data do. Figure 3 shows electron mobilities of the undoped and the weakly doped crystal as $f(T)$ obtained from the Hall coefficients R_H and the resistivities ρ: $\mu_e = (8/3\pi)R_H/\rho = 6.25 \times 10^{18}/c_e\rho$. These mobilities are considerably smaller than those reported by Smith (3).

Discussion

We now have the task of explaining our experimental data and those of de Nobel on the basis of a detailed defect model. The Hall data have the advantage of giving us electron concentrations which at high p_{Cd} are directly related to atomic defect concentrations.

Under equilibrium conditions the concentrations of point defects are uniquely determined by the values of equilibrium constants of reactions by which defects are formed, the concentration of dopants, and the partial pressure of one component, e.g., p_{Cd} (2). Once the concentrations at one p_{Cd} and one dopant concentration are known, those at all other p_{Cd} and other dopant concentrations are also known, and we can foretell in what way the concentrations of individual defects vary.

Several of these defect reactions and the corresponding mass action relations are shown in Table I.

In cases in which one positive and one negative species dominate the neutrality condition, approximate solutions can be obtained by approximating the neutrality condition accordingly (9). If more species are involved, the exact solution has to be obtained. This is done by combining the complete neutrality condition and dopant balance equation and eliminating from the resultant equation all species but one with the aid of the mass action relations. The equation in the concentration of this single species can be solved numerically. Once the solution has been obtained, the value of each term corresponds to the concentration of a particular defect.

The dependence $[e'] \propto p_{Cd}^{1/3}$ in pure CdTe at high p_{Cd} indicates that doubly ionized native donors $D_n^{\cdot\cdot}$ are involved. These can be $V_{Te}^{\cdot\cdot}$ and/or $Cd_i^{\cdot\cdot}$. Since both the Te self-diffusion at high p_{Cd} and the Cd self-diffusion are proportional to $p_{Cd}^{1/3}$, we cannot decide between these two on this basis. In isotherms the ratio between $[V_{Te}^{\cdot\cdot}]$ and $[Cd_i^{\cdot\cdot}]$ remains constant.

The Hall effect gives us electron concentrations and thus donor concentrations governed by a formation constant $K_{D_n} = [D_n^{\cdot\cdot}][e']^2/p_{Cd}$ that is equal to the sum of the formation constants of $Cd_i^{\cdot\cdot}$ and $V_{Te}^{\cdot\cdot}$, K_{Cdi}'' and K_{TeV}''. Thus K_{D_n} is not a true thermodynamic constant. In particular, if the parameters of the two basic constants are different, i.e., if $Cd_i^{\cdot\cdot}$ and $V_{Te}^{\cdot\cdot}$ have different enthalpies and entropies of formation—and this must in general be expected—a plot of $\ln K_{D_n}$ against $1/T$ will not be a straight line, and the relative contributions of $[Cd_i^{\cdot\cdot}]$ and $[V_{Te}^{\cdot\cdot}]$ to $[D_n^{\cdot\cdot}]$ will vary. This state of affairs may be indicated by the slight curvature of $\ln[e']$ vs $1/T$ that is observed, though it is also possible that this curvature is due to a small inaccuracy in the data.

TABLE I

DEFECT FORMATION REACTIONS FOR CdTe
AND THE CORRESPONDING MASS ACTION RELATIONS

	Reaction		Mass action relations
1	$Cd(g) \rightleftarrows Cd_{Cd}^{\times} \times V_{Te}^{\cdot\cdot} + 2e'$;	H_{TeV}''	$K_{TeV}'' = [V_{Te}^{\cdot\cdot}][e']^2/p_{Cd}$
2	$Cd(g) \times V_i^{\times} \rightleftarrows Cd_i^{\cdot\cdot} + 2e'$;	H_{CdI}''	$K_{CdI}'' = [Cd_i^{\cdot\cdot}][e']^2/p_{Cd}$
3	$Cd_{Cd}^{\times} + 2e' \rightleftarrows Cd(g) + V_{Cd}''$;	H_{CdV}''	$K_{CdV}'' = [V_{Cd}'']p_{Cd}/[e']^2$
4	$Cd_{Cd}^{\times} + e' \rightleftarrows Cd(g) + V_{Cd}'$;	H_{CdV}'	$K_{CdV}' = [V_{Cd}']p_{Cd}/]e']$
5	$CdTe + e' \rightleftarrows Cd(g) + Te_i'$;	H_{TeI}'	$K_{TeI}' = [Te_i']p_{Cd}/[e']$
6	$CdTe \rightleftarrows Cd(g) + Te_i^{\times}$;	$H_{TeI}^{\times}$	$K_{TeI}^{\times} = [Te_i^{\times}]p_{Cd}$
7	$0 \rightleftarrows V_{Cd}'' + V_{Te}^{\cdot\cdot}$;	H_S''	$K_S'' = [V_{Cd}''][V_{Te}^{\cdot\cdot}]$
8	$Cd_{Cd}^{\times} + V_i^{\times} \rightleftarrows Cd_i^{\cdot\cdot} + V_{Cd}''$;	H_F''	$K_F'' = [Cd_i^{\cdot\cdot}][V_{Cd}'']$
9	$0 \rightleftarrows e' + h^{\cdot}$;	E_i	$K_i = [e'][h^{\cdot}]$
10	$V_{Cd}'' \rightleftarrows V_{Cd}' + e'$;	E_{a2V}	$K_{a2V} = [V_{Cd}'][e']/[V_{Cd}'']$
11	$Te_i^{\times} \rightleftarrows Te_i' + h^{\cdot}$;	E_{a1Te}	$K_{a1Te} = [Te_i'][h^{\cdot}]/[Te_i^{\times}]$
12	$V_{Cd}' + In_{Cd}^{\cdot} \rightleftarrows (In_{Cd}\,V_{Cd})'$;	H_P	$K_P = [(In_{Cd}\,V_{Cd})']/[V_{Cd}'][In_{Cd}^{\cdot}]$
13	$CdTe \rightleftarrows Cd(g) + \frac{1}{2}Te_2(g)$;		$K_{CdTe} = p_{Cd}\,p_{Te2}^{1/2}$
14	$\frac{1}{2}Te_2(g) \rightleftarrows Te(g)$;	H_D	$K_D = p_{Te}/p_{Te2}^{1/2}$
15	$CdTe \rightleftarrows Cd(g) + Te(g)$;	$H_{Cd,\,Te}$	$K_{Cd,\,Te} = p_{Cd}\,p_{Te} = K_{CdTe}K_D$

The equilibrium constants should be such that they explain for pure as well as doped crystals both the high-temperature properties and the properties of the quenched crystals.

Let us first consider the electron concentration isotherms for the weakly doped crystals at high p_{Cd}.[1] At 700°C the electron concentration in this range is approximately equal to the indium concentration and only weakly dependent on p_{Cd}. At higher temperatures, the electron concentration reaches values larger than the indium concentration; this must be attributed to nonstoichiometry with the formation of $Cd_i^{\cdot\cdot}$ and $V_{Te}^{\cdot\cdot}$. Yet de Nobel's data on quenched crystals with a similar indium concentration do not show such an increase. Apparently, the extra carriers disappear upon cooling. This can be explained either by trapping of carriers at a deep donor level or by precipitation of the native donor together with its electrons.

As we shall see below, the levels involved in the first ionization of both types of native donors are close to the conduction band. The same probably applies to the second ionization

of V_{Te}; that of Cd_i is deep enough to give rise to some electron trapping at room temperature at the concentrations concerned.

Thus, for trapping to be responsible for the removal of excess carriers during cooling, we must assume that $Cd_i^{\cdot\cdot}$ is dominant at $T \geqslant 800°C$. Even then, however, at most half of the extra electrons will be removed; the other half will remain free. Such a limitation does not exist if the carriers are removed by precipitation of the donors. From self-diffusion data (10) we know that $Cd_i^{\cdot\cdot}$ diffuses much faster than $V_{Te}^{\cdot\cdot}$. Therefore, it is probably the former that precipitates during cooling, and this defect must be the one dominant in $D_n^{\cdot\cdot}$ at $T \geqslant 800°C$.

As we shall see later, explanation of the properties of undoped crystals requires that the nonprecipitating donor ($V_{Te}^{\cdot\cdot}$) is dominant at 700°C. We have arbitrarily chosen constants of formation of $Cd_i^{\cdot\cdot}$ and $V_{Te}^{\cdot\cdot}$ that lead to concentration ratios $[Cd_i^{\cdot\cdot}]/[V_{Te}^{\cdot\cdot}] \approx 3{:}1$ at 900°C, 1.3:1 at 800°C and 1:2 at 700°C. A much stronger variation would require formation constants for the two defects with parameters that are unacceptably different.

At lower p_{Cd} the electron concentrations drop below the indium concentration levels and show a negative temperature dependence. This effect results from an increase in the

concentrations of atomic defects with a negative effective charge which gradually displace e' as the main charge-compensating species. These negative species may be V'_{Cd}, V''_{Cd}, Te'_i, Te''_i, or associates of these with the donor dopant: $(In_{Cd}V_{Cd})'$ or $(In_{Cd}Te_i)'$.

In cooled crystals de Nobel reports a sharp cutoff of the concentration of free carriers at a particular p_{Cd} which is the higher, the lower the annealing temperature. This effect is attributed to the trapping of electrons at deep levels caused by either V'_{Cd} or Te'_i. Insufficiently rapid cooling led to a shift of the cutoff to lower p_{Cd}'s, which was attributed to precipitation of the trapping centres. In addition to V'_{Cd} and Te'_i, doubly charged V''_{Cd} or Te''_i and pairs between these species and the donor must be present.

Relative concentrations of single defects and pairs may be estimated using plausible values for the pairing constants. This shows that pairing must be expected at the 10^{18} doping level but it is negligible in the weakly doped samples at $T \geqslant 700°C$.

In isotherms, single species with the same charge behave in a similar way, while the ratio of their concentration remains unchanged. Therefore, it is useful to introduce native acceptors A_n with

$$[A'_n] = [V'_{Cd}] + [Te'_i], \quad [A''_n] = [V''_{Cd}] + [Te''_i]$$

Approximate values of the ratio $[A'_n]/[A''_n]$ can be obtained from an analysis of the shape of self-diffusion isotherms (10). It is found that at the point where $[e'] \approx [h']$, $[A'_n]/[A''_n] \approx$ 8 at 700°C, 5 at 800°C, and 2.8 at 900°C independently of the species contributing to A'_n and A''_n.

A decision concerning relative contributions of V_{Cd} and Te_i to A_n can be made on the basis of the electron trapping observed in the cooled crystals and plausible assignments of defects

TABLE II

Donor levels	Position	References	Assignment	References
Energy levels				
D_1	$E_c - 0.01$ ev	a, b	$Cd_i^{\times}$, $V_{Te}^{\times}$	
D_2	$E_c - 0.035$ eV	c	$V_{Te}^{\cdot}$	
D_3	$E_c - (0.14-0.21$ eV$)$	$b-d$	$Cd_i^{\cdot}$	
D_4	$E_2 + 0.55$ eV	e		
Acceptor levels				
A_1	$E_c - 0.06$ eV	$f-k$	Te''_i	
A_2	$E_c - (0.6-0.7$ eV$)$	a, e, j, l, m	V''_{Cd}	
A_3	$E_v + 0.15$ eV	a, l, n	Te_i' or $(In_{Cd}V_{Cd})'$	p
A_4	$E_v + 0.05$ eV	c, j, l	V'_{Cd}	h, j, l
A_5	$E_v + (0.3-0.4$ eV$)$	j, l	Ag'_{Cd}, Cu'_{Cd}, Au'_{Cd}	j

^{a} Reference 1.

^{b} Yu V. Rud and K. V. Sanin, *Sov. Phys.–Semicond.* **5**, 244 (1971).

^{c} V. S. Ivanov, V. B. Stopachinskii, and V. A. Chapin, *Sov. Phys.–Semicond.* **5**, 83. (1971).

^{d} Reference 4.

^{e} N. V. Agrinskaya, E. N. Arkad'eva, and O. A. Matveev, *Sov. Phys.–Semicond.* **4**, 306 (1970).

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^{g} M. R. Lorenz and H. H. Woodbury, *Phys. Rev. Lett.* **10**, 215 (1963).

^{h} M. R. Lorenz, M. Aven, and H. H. Woodbury, *Phys. Rev.* **132**, 143 (1963).

^{j} M. R. Lorenz and B. Segall, *Phys. Lett*, **7**, 18 (1963); M. R. Lorenz, B. Segall, and H. H. Woodbury, *Phys. Rev.* **134**, 751 (1963).

^{k} A. A. Abramov, V. S. Vavilov, and I. K. Vodop'yanov, *Sov. Phys. –Semicond.* **4**, 219 (1970).

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^{m} K. Zanio, W. M. Akutagawa, and R. Kikuchi, *J. Appl. Phys.* **39**, 2818 (1968).

^{n} N. V. Agrinskaya, E. N. Arkad'eva, and O. A. Matveev, *Sov. Phys.–Semicond.* **4**, 347 (1970).

^{p} N. V. Agrinskaya, E. N. Arkad'eva, and O. A. Matveev, *Sov. Phys.–Semicond.* **5**, 767 (1971).

to known electronic energy levels listed in Table II.

We are inclined to assign the acceptor levels A_1 and A_2 to Te_i'' and V_{Cd}''. If we arbitrarily assume $A_1 \equiv Te_i''$, then a simple statistical calculation, using $E_g = E_c - E_v = (1.6 - \alpha T)$ eV = 1.1 eV at 700°C (where α is the temperature dependence of the gap of 3×10^{-4} eV/deg (11), shows that at the Cd pressure at which the fermi level E_F lies at the center of the gap, i.e., $E_F = E_c - 0.55$ eV, $[Te_i''] \leqslant [Te_i']/100$. On the other hand, we saw that $[A_n''] \geqslant [A_n']/8$. Therefore in this case, A_n'' must consist almost exclusively of V_{Cd}'', i.e., $A_2 \equiv V_{Cd}''$.

The cutoff of the free carrier concentration observed by de Nobel must involve trapping at either V_{Cd}' or Te_i' but, if either of these is to act as an effective electron trap, its empty level (i.e., the V_{Cd}'' or Te_i'' level) must be far from the conduction band. Since we assumed Te_i'' close to the conduction band, V_{Cd}' must be the deep trap. In order to have strong trapping, we need a considerable concentration of traps; therefore, V_{Cd}' must be dominant in A_n'.

If we would have started by assuming $A_1 \equiv V_{Cd}''$, we would find $A_2 \equiv Te_i''$, with Te_i' the deep trap. Kumar and Kröger (12) assumed V_{Cd}'' to be the main doubly charged species in CdS on the basis of the fact that In_2S_3 has the same structure as CdS. However, this only indicates that vacancies will dominate at very high In concentrations. The dominance of a certain species promoted by a low concentration of dopant remains an inherent property of the mother crystal. Yet we believe that V_{Cd}'' is dominant because of the dependence of the electron trapping effects on the quenching rate observed by de Nobel (1): Slow quenching reduces trapping, which is attributed to precipitation of the trapping centers.

Precipitation involves migration of the defects and thus of Cd for V_{Cd}', Te for Te_i'. It is known that $D_{Cd} \gg D_{Te}$ (10). Therefore, precipitation is likely to involve V_{Cd}' rather than Te_i'; i.e., V_{Cd}' is the trapping center. Evidence for the precipitation of cadmium vacancies in tellurium-rich crystals has in fact been obtained by Shiozawa et al. (13),

who observed the formation of cubic voids, partly filled with amorphous material which was believed to be tellurium; these experiments, of course, do not differentiate between V_{Cd}' and V_{Cd}''. On the basis of the arguments given, the level assignments must be as first assumed; these are given in Table II. The level A_3 may be assigned to Te_i' and/or $(In_{Cd}V_{Cd})'$.

The assignment of A_2 to V_{Cd}'' seems not to be in agreement with an observation by Zanio et al. (14) that a level at $E_c - 0.58$ eV ($\approx A_2$), present at a concentration of 10^{10} cm^{-3} in semiinsulating CdTe had a cross section for the trapping of electrons of 10^{-11} cm^2. Such a large cross section is not to be expected for a negatively charged species V_{Cd}' as the trap. There are two ways by which this discrepancy may be removed.

Zanio et al. based their analysis on the assumption that in the nonirradiated crystal all the trap levels were empty, but then the concentration arrived at by them represents the total concentration of the species involved. They found 10^{10} cm^{-3}, which is about 5 orders of magnitude smaller than the concentrations of other defects we find in CdTe. If the basis of the analysis was wrong, much higher concentrations of trap species may have been present and the capture cross section for electrons would come out much smaller, which would thus remove the objection against our identification of the trapping level with V_{Cd}'' (the trap being V_{Cd}'). It is also possible that there are two species involved, one responsible for the electron concentration cutoff (V_{Cd}') while the other acts as a recombination trap—but both with an empty level close to $E_c - 0.6$ eV. Zanio et al. suggested that the latter might be Te_i^x. In this case certainly the total trap species concentration ($c_{Te_i^x} + c_{Te_i}$) must have been greater than 10^{10} cm^{-3}; Zanio's 10^{10} cm^{-3} value would have been unfounded and the very reason to put the Te_i' level at $E_c - 0.58$ eV disappears. Further, we have to reject Te_i^x as the cut off trap for the same reason earlier reported for Te_i': It migrates too slowly to give the rapid precipitation which is a characteristic of the cutoff trap. Another objection against our assignment of the V_{Cd}'' level is found in the luminescence work of Bryant et al. (15), who assign

lines at 1.534 and 1.572 eV to transitions from the conduction band to the levels of V''_{Cd} and V'_{Cd}. A gap of only 0.038 eV between these two levels seems unacceptably small. Therefore, we shall maintain our assignments $A_2 \equiv V''_{Cd}$ and also keep $A_3 \equiv Te'_i$ in spite of the fact that there are no strong arguments in favor of the latter. Let us now consider the donor levels.

From the fact that double ionization is observed at 700°C at electron concentrations as high as 4×10^{17} cm^{-3}, it can be concluded that the second ionization level(s) of the active donor(s) are at or above the Fermi level under these conditions. Calculation using

$$c_e = 2(2\pi m_e^* kT/h^2)^{3/2} \exp((E_F - E_c)/kT)$$

with $m_e^* = 0.096\, m$ (16) gives $E_F \approx E_c - 0.2$ eV. Thus D_1, D_2, and D_3 can be levels of the native donors, but D_4 cannot. Assignment of D_2 to V'_{Te} and D_3 to Cd_i can be made on the basis of the fact that in CdS the Cd_i levels are deeper than the V_S levels (12). If we accept the level assignments of Table II, we can calculate the ratio $[V'_{Cd}]/[V''_{Cd}]$ at the point where $[e'] \approx]h']$. One finds this ratio to be 3.3 at 700°C and 1.2 at 900°C. This, combined with the estimate of $[A''_n]/[A''_n]$ arrived at earlier and $[A''_n] \approx [V''_{Cd}]$, gives $[Te'_i]/[V'_{Cd}] = (8 - 3.3)/3.3 \approx 1.4$ at 700°C, and $(2.8 - 1.2)/1.2 \approx 1.3$ at 900°C. Although these estimates are not very accurate, they indicate that the two acceptor species are present in about the same concentration and that their ratio does not vary appreciably with temperature. Parameters of the formation constants describing the generation of the various defects in approximately the required ratios are given in Table III.

Figures 4 and 5 show isotherms for CdTe–2.7×10^{17} In cm^{-3} at 700 and 800°C, calculated using these constants. The figures also

TABLE III

PARAMETERS OF DEFECT FORMATION REACTIONS: $K = K_0 \exp(H/RT)$ [a]

	K	K_0 (site fractions)	H (eV)	Remarks
1	$K''_{D_n} = K''_{TeV} + K''_{CdI}$	7.65×10^{-7}	1.86	
2	K''_{TeV}	2.4×10^{-9}	1.47	
	K''_{CdI}	1.9×10^{-5}	2.28	
	K''_{CdV}	3.56×10^{8}	0.88	
4	K'_{CdV}	9.8×10^{7}	2.08	
5	K'_{TeI}	3.95×10^{3}	1.19	
6	$K^{\times}_{TeI}$	2.75×10^{3}	3.6	$(A_3 \equiv Te'_i)$
7	K''_S	0.85	2.35	$K''_S = K''_{CdV} K''_{TeV}$
8	K''_F	6.8×10^{3}	3.16	$K''_F = K''_{CdV} K''_{CdI}$
9	K_i	3.1×10^{-2}	1.92	(Adjusted from Smith (3) by increasing the activation energy, leaving the absolute values at 800°C unchanged
			1.32 [b]	
		(1.44×10^{-4}) [c]	(1.73) [c]	
10	K_{a_2V}	$1.07 \times 1.0^{-2}\ (9 \times 10^{-4})$ [c]	$0.66\ (0.6)$ [c]	
11	K_{a_1Te}	4.8×10^{-2}	0.275	$(A_3 \equiv Te'_i,$ at $E_v + 0.15)$
12	K_p	0.43	-0.83	
13	K_{CdTe}	5.7×10^{9}	2.98	
14	K_D	5.39	1.18	
15	K_{CdTe}	3.06×10^{12}	4.16	$K_{CdTe} \times K_D$

[a] There are 1.48×10^{22} CdTe cm^{-3}.

[b] Data according to (3).

[c] Data in parentheses are according to de Nobel as given in (2).

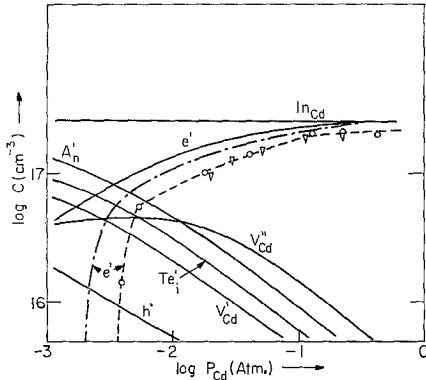FIG. 4. Isotherms for defect concentrations as $f(p_{Cd})$ in CdTe–2.7×10^{17} In cm^{-3} at 700°C, electron concentrations after quenching to room temperature, and electron concentrations in quenched crystals of CdTe–2×10^{17} In cm^{-3} according to de Nobel (1). ∇ c_e exp; —— calcd (high T); —·—· calcd (cooled); ——○—— exp (cooled; de Nobel (1) 2×10^{17} In).

show de Nobel's results for the electron concentration in a quenched crystal, CdTe–2×10^{17} In cm^{-3}, and a calculated curve for the electron concentration after cooling with the assumption of electron trapping at V'_{Cd} and complete precipitation of Cd$_i^{··}$:
Cd$_i^{··}$ + $2e'$ → Cd$_{precip}$.

In the strongly doped crystals the behavior at low p_{Cd} is similar to that in the weakly doped crystals. At high p_{Cd}, however, there is a difference. Calculation shows that the increase
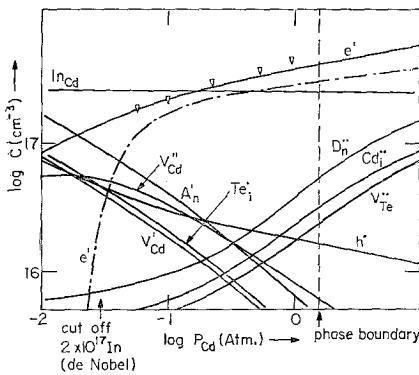

FIG. 5. Isotherms for defect concentrations as $f(p_{Cd})$ for CdTe–2.7×10^{17} In cm^{-3} at 800°C; triangles are experimental points. Electron concentrations expected in quenched crystals are also given. ∇ c_e exp; —— calcd (high T); —·—· c_e calcd (cooled).
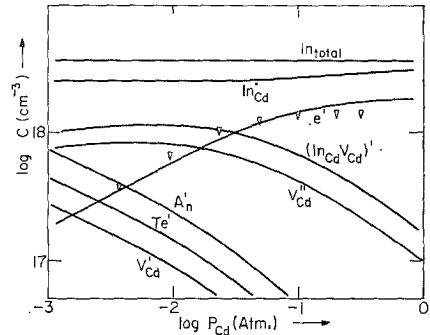

FIG. 6. Defect concentration isotherms for CdTe–3.6×10^{18} In cm^{-3} at 800°C; ∇ c_e exp.

in the electron concentration with increasing temperature observed in this range cannot be explained by the formation of native donors. It can be explained if we assume that pairing between In$_{Cd}^{·}$ and V''_{Cd} occurs at all temperatures, but to a degree decreasing with increasing temperature; pairing increases the fraction of donors compensated by vacancies, and thus a decrease in pairing, by reducing this fraction, increases the fraction of donors compensated by electrons. A pairing constant designed to give the required change is given in Table III.

Isotherms for CdTe–1.6×10^{18} In cm^3 at 700, 800, and 900°C calculated with the constants of Table III are shown in Figs. 6–8. Figure 8 also shows the expected variation of the electron concentration in a cooled crystal, which shows again a sharp cutoff due to trapping of electrons at V'_{Cd}.

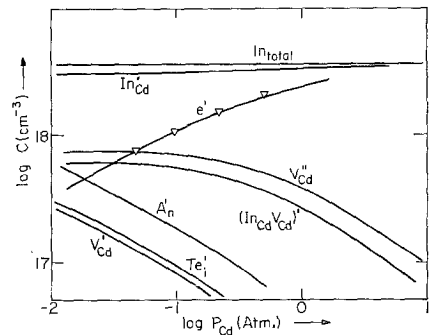The same constants should account for the properties of undoped CdTe.

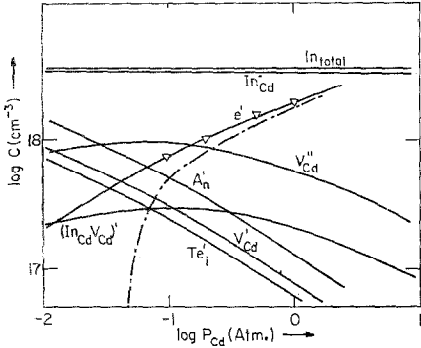FIG. 7. Defect concentration isotherms for CdTe–3.6×10^{18} In cm^{-3} at 800°C; ∇ c_e exp.

FIG. 8. Defect concentration isotherms for CdTe–3.6×10^{18} In cm^{-3} at 900°C. ∇ c_e exp; —— calcd (high T); —·—·—· calcd (cooled).

If we compare the concentrations of electrons found at high p_{Cd} with concentrations found by de Nobel in cooled crystals, we see that at 700°C these are approximately equal; at 800 and 900°C, however, there is a difference which increases with increasing temperature: Whereas the high-temperature concentrations increase, those in the cooled crystals decrease with increasing temperature. This can again be explained by precipitation of one of the native donors ($Cd_i^{\cdot\cdot}$) if we assume that these are increasingly dominant at
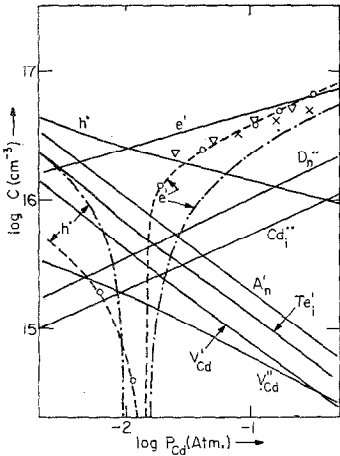

FIG. 9. Defect concentration isotherms for undoped CdTe at 700°C. Also shown are the concentrations of e' and $h^{\cdot}$ after quenching and values for these quantities observed by de Nobel (*1*). ∇ c_e exp (this paper); $\times$ c_e exp (Smith (*3*)); —— calcd; — — — c_e cooled crystal (de Nobel (*1*)); — — — — c_e cooled crystal, calcd.
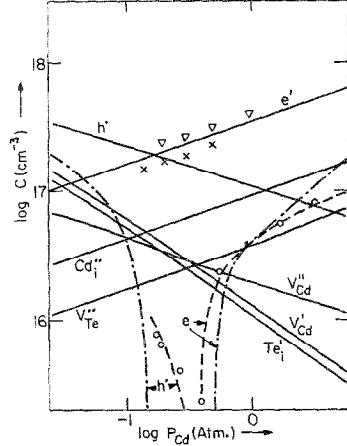

FIG. 10. Defect concentration isotherms for undoped CdTe at 900°C. Also shown are the concentrations of e' and $h^{\cdot}$ after quenching and values for these quantities observed by de Nobel (*1*) ∇ c (high T, this paper); $\times$ c_e (high T, Smith (*3*)); —○— c_e, c_h (quenched, de Nobel (*1*)); — — — calcd (quenched).

$T \geqslant 800°C$ but a minority relative to $V_{Te}^{\cdot\cdot}$ at $T < 800°C$. In fact, the parameters of the formation constants $K_{CdI}^{\cdot\cdot}$ and $K_{TeV}^{\cdot\cdot}$ given in Table III were based on this requirement, giving $[Cd_i^{\cdot\cdot}]/[V_{Te}^{\cdot\cdot}] = 3$ at 900°C and 0.5 at 700°C (giving a ratio of 1.3 at 800°C). Trapping of electrons at the empty $Cd_i^{\cdot\cdot}$ level would remove only half of the electrons generated by Cd_i and cannot lead to a negative temperature dependence of the electron concentration after cooling.

Figures 9 and 10 give calculated defect isotherms for undoped CdTe at 700 and 900°C. There is good agreement with our experimental data. Since several defects have concentrations that are of the same order of magnitude, Brouwer's approximation method could not be used; the exact solution had to be obtained by the method indicated earlier. The figures also give electron and hole concentrations after cooling, under the assumption of complete precipitation of $Cd_i^{\cdot\cdot} + 2e'$ and redistribution of electrons and holes over the levels of the remaining centers. This involves electron trapping at V_{Cd}' and hole trapping at V_{Cd}''. This leads to pinning of the Fermi level at the V_{Cd}'' level and leads to an almost carrier-free material at medium Cd pressures. De Nobel's data for electron and hole concen-

trations after cooling are shown for comparison. The fact that our model predicts a wider high-resistance region at 900°C than de Nobel observed may be due to precipitation of some of the trapping centers during cooling in his crystals.

Note that nowhere is the $p_{Cd}^{1/3}$ dependence of the electron concentration observed at high temperatures found after cooling. This indicates that the slope $\frac{1}{2}$ found by de Nobel for the electron concentration in cooled crystals prepared at high p_{Cd} is not a characteristic slope of a Brouwer approximation as assumed by him. It arises by the removal of electrons by recombination with holes and trapping at V'_{Cd} and has, in fact, all values between $\frac{1}{3}$ and ∞. Therefore, de Nobel's conclusion that the donors are singly ionized is obviously incorrect.

Figure 11 shows defect concentrations as a function of temperature in undoped CdTe at $p_{Cd} = 1$ atm.

Given the concentrations of Te'_i and holes, a Te'_i level position at $E_v + 0.15$ eV, and an effective hole mass $m_h^* = 0.63m_0$ (17), we can calculate the concentrations of Te_i^x. Typical values at $p_{Cd} = 0.1$ atm are 7.7×10^{11} at 700°C and 2.9×10^{14} at 900°C. Parameters of
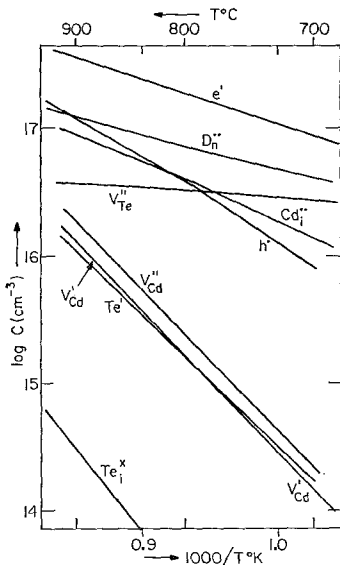
the formation constant calculated on this basis are included in Table III. If we would place the Te'_i at $E_c - 0.58$ eV as suggested by Zanio et al. (14), we would find the Te_i^x concentration larger by $\exp(\Delta E/kT)$, with $\Delta E = (E_c - 0.58) - (E + 0.15) = E_i - 0.73$ eV ≈ 0.37 eV at 700°C, leading to a concentration of Te_i^x at 700°C and $p_{Cd} = 0.1$ atm of 6.4×10^{13} cm^{-3}.

The concentration in cooled crystals would, of course, be much smaller. Using the data of Fig. 4 for indium-doped CdTe prepared at 700°C under $p_{Cd} = 10^{-3}$ atm, we find after quenching to room temperature $c_e = 2 \times 10^{16}$ cm^{-3}, $c_{Te'_i} \approx 10^{17}$ cm^{-3}, and

$$c_{Te_i^x} \approx (c_{Te'_i}/c_e)(2\pi m_e^* kT/h^2)^{3/2} \exp -0.58$$
$$\text{eV}/kT \approx 3 \times 10^8 \text{ cm}^{-3}.$$

Summary

The point defect structure of pure and donor-doped CdTe is determined by an analysis of Hall data obtained at high temperature under equilibrium conditions and after cooling, with some input from a self-diffusion study.

FIG. 11. Concentrations of native defects in undoped CdTe at $p_{Cd} = 1$ atm.

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