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Identification of defect centers in $Hg_{1-x}Cd_xTe$ using their energy level composition dependence

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(Received 11 September 1984; accepted for publication 15 February 1985)

We have extended the Kobayashi, Sankey, and Dow [Phys. Rev. B **25**, 6367 (1982)] theory of deep levels in $Hg_{1-x}Cd_xTe$ to include (vacancy, impurity) nearest-neighbor pairs. In qualitative agreement with the results obtained by these workers for isolated point defects, we find that the composition dependences (dE/dx) of the defect energy levels associated with such complexes depend on the site occupied by the impurity atom. Furthermore, we find that the composition dependences of *some* of the defect levels produced by such a complex are very different than the dE/dx of levels associated with the corresponding isolated point defects. We thus suggest that this theory can often be used as an aid in the identification of the defect center producing an observed energy level. In particular, it can be used to obtain site information about an observed level and, in favorable cases, to distinguish between levels produced by isolated point defects and those produced by complexes. As an example, we compare our theoretical predictions for the dE/dx of levels associated with (vacancy, impurity) pairs to the experimental slopes of the energy levels observed in deep level transient spectroscopy by Jones, Nair, and Polla [Appl. Phys. Lett. **39**, 248 (1981)] and find that the theory lends support to these workers' interpretation of their data. In addition, we present new photoluminescence data on both a previously observed and identified acceptor and on an unknown center in $Hg_{1-x}Cd_xTe$. As a further example of the usefulness of our theory, we compare the theoretical slopes of energy levels associated with (vacancy, impurity) pairs with the composition dependences of the defect levels extracted from the photoluminescence data. The results of both of the theoretical-experimental comparisons show that the theory can be used successfully, in conjunction with experimental data, to aid in the identification of the defect center which produces an observed energy level.

I. INTRODUCTION

The importance of the variable band-gap semiconductor $Hg_{1-x}Cd_xTe$ for use in infrared detection devices is well known.[1] It is also well understood that the performance characteristics of such devices can be severely limited by effects which are related to defects in this material. In particular, such defects may produce electronic energy levels which lie in or near the fundamental band gap and these levels can greatly influence the optoelectronic properties of the material.[2] As a step towards the theoretical treatment of defects in this material, Kobayashi *et al.*[3] have applied the Hjalmarson *et al.*[4] theory of deep levels to obtain predictions of the alloy composition (x) dependences ("chemical trends") of the energy levels due to isolated point defects in $Hg_{1-x}Cd_xTe$. We have extended this theory to include (vacancy, impurity) nearest-neighbor pairs, the simplest possible vacancy-associated complexes. In this paper we (1) present some results of calculations obtained using this generalized theory, (2) discuss the use of this theory to provide impurity site information for both (vacancy, impurity) pairs and isolated impurities, (3) discuss how, in favorable uses, this theory can be used to help distinguish between observed energy levels due to complexes and those due to isolated point defects, (4) illustrate these points by a comparison of the composition dependences of theoretical energy levels produced by (vacancy, impurity) pairs with the x dependences of energy levels observed by Jones *et al.*[5] in deep level transient spectroscopy (DLTS) measurements, (5) present some new photoluminescence data on both a previously observed acceptor and an unknown center in $Hg_{1-x}Cd_xTe$, and (6) apply the theory to an analysis of our photoluminescence data.

The results of our calculations of the defect energy levels produced by (vacancy, impurity) pairs and those of Kobayashi *et al.*[3] of the levels associated with isolated point defects show that the variations with composition (dE/dx) of the energy levels due to a particular defect depend strongly on the atomic site (anion or cation) occupied by the impurity. However, we also find that the composition dependences of *some* of the defect levels which are produced by such a vacancy-associated complex are very different than the dE/dx of levels due to the corresponding isolated impurity or vacancy. Thus, *the dE/dx of a defect level is not only indicative of which site the impurity occupies but can also be used, in favorable cases, to distinguish between observed levels due to isolated point defects and those due to complexes.*

At present, most theories of deep level defects cannot reliably predict absolute defect energy levels. The scheme we discuss here does *not* require such absolute level predictions; instead it requires only that the theory correctly predict the

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variation of defect energy levels with x. To illustrate the utility of our scheme, we compare the composition dependences of the defect levels observed in DLTS by Jones *et al.*[5] and of the defect levels extracted from our photoluminescence data with the theoretical slopes of particular levels of a (vacancy, impurity) pair. These comparisons show that the theory can be successfully used, in conjunction with experimental data, as an aid in the identification of the defect center which produces an observed energy level. In particular, site information about such centers can certainly be obtained from such experimental-theoretical comparisons and in some cases, they can be used to obtain information about whether an observed energy level is due to a complex or to a point defect.

II. THEORY: SUMMARY OF THE METHOD

Our theory is an extension to $Hg_{1-x}Cd_xTe$ of the theory of deep levels produced by (vacancy, impurity) nearest-neighbor pairs in III-V semiconductors, recently developed by Myles and Sankey.[6] While other theories have been published which have predicted deep levels due to such complexes,[7-12] these have usually only considered a few particular cases in a few materials. On the other hand, the theory discussed in Ref. 6 is a global theory which can straightforwardly be used to predict the trends in the deep levels due to such complexes as a function of both defect and host. It is thus a natural approach to use to explore such trends with alloy composition x in $Hg_{1-x}Cd_xTe$.

The theory is based upon the sp^3s^* semiempirical tight-binding band-structure theory for CdTe and HgTe, developed by Kobayashi *et al.*,[3] and on the Hjalmarson *et al.*[4] theory of deep levels, as extended to (vacancy, impurity) pairs by Myles and Sankey.[6] This theory was designed to predict *chemical trends* in the *ordering* of the deep levels, both as a function of x and as a function of defect. The Hjalmarson *et al.*[4] theory and its various extensions and generalizations, while containing uncertainties in its results for absolute defect energies, has proven remarkably successful in its predictions of such chemical trends in numerous previous applications.[6,9,12-14] Accordingly, our proposed impurity center identification scheme is based entirely on a comparison of the dE/dx of experimental and theoretical defect energy levels and *not* on the absolute energy of a specific level. If, however, some observed defect level could be unambiguously associated with a particular defect, and thus used as a calibration, the resulting adjusted predictions of the theory should give a correct semiquantitative picture of deep levels in $Hg_{1-x}Cd_xTe$. Clearly, this scheme is not restricted to this material, but should also find use as an aid to defect center identification in other alloy semiconductors.[13]

In this paper, we thus describe the host Hamiltonian for $Hg_{1-x}Cd_xTe$ in the model of Kobayashi *et al.*,[3] where the electronic bandstructures of the alloy constituents CdTe and HgTe are modeled in a semiempirical tightbinding approximation and alloy effects are treated in the virtual crystal approximation. This Hamiltonian is presented and discussed in detail in Ref. 3. The defects we consider are restricted to ideal vacancies paired with nearest-neighbor sp^3 bonded substitutional impurities. The defect potential due to such a complex is taken to be the same as that discussed by Myles and Sankey[6] and is thus described in detail in Ref. 6. We note that in combining the defect potential of Ref. 6 with the bandstructures of Ref. 3, we have included spin-orbit coupling effects in the host bandstructures, but have neglected them in the treatment of the defect potential. Details of the theory will be discussed in a later publication.[15]

III. THEORETICAL RESULTS

We first discuss the results of our calculations of deep levels produced by (vacancy, impurity) pairs in $Hg_{1-x}Cd_xTe$ in a general, qualitative fashion. Following this, we present and discuss our quantitative results for both a (cation vacancy, anion impurity) pair and an (anion vacancy, cation impurity) pair for a particular choice of impurity.

A. Qualitative discussion

The results of our calculations show that the composition dependence (dE/dx) of an energy level which is associated with a particular complex depends strongly on whether the impurity occupies the cation or the anion site of the host crystal. This is in qualitative agreement with the results of Kobayashi *et al.*[3] for isolated point defects in the same material and also in qualitative agreement with the recent isolated impurity results of Tuncay and Tomak,[16] which were obtained using different host bandstructures for $Hg_{1-x}Cd_xTe$. This dependence of the dE/dx on the impurity site has also been found before (for isolated impurities) in other semiconducting alloys,[17] but it does not appear to have been utilized as a means to obtain site information from experimentally obtained defect levels, as we are proposing here. It should also be emphasized that one of the new results of the present paper is that this strong dependence of the slope of a defect energy level on the impurity site is valid for the energy levels produced by a vacancy associated complex as well as for those due to isolated impurities.

In particular, the results of the present calculations, taken together with the results of Ref. 3, show that both isolated anion-site impurities and vacancy complexes which contain such an impurity usually produce energy levels which have a small dE/dx; such levels thus often appear to be nearly "attached" to the valence band edge. On the other hand, the energy levels produced by either an isolated cation-site impurity or by a complex containing such an impurity usually have much stronger x dependences than their anion-site counterparts; the slopes of such levels are often comparable to the conduction band variation dE_g/dx. The cation and anion isolated vacancy levels are also distinguishable by their dE/dx.[3] In both cases, they have slopes which are smaller than those of the levels due to any isolated impurity on the same site; some of the cation vacancy levels are almost independent of x, while some of the anion vacancy levels have a negative dE/dx.

Another result that we find from our calculations of deep levels due to (vacancy,impurity) pairs in $Hg_{1-x}Cd_xTe$ is that the slope of an energy level of particular symmetry which is produced by a particular type of vacancy associated complex (either an anion vacancy paired with a cation impu-

rity or a cation vacancy paired with an anion impurity) is almost independent of which impurity is present in the complex, even though the energy of such a level certainly does depend on the impurity. The dE/dx of a level due to such a complex is instead primarily controlled by the *site* of the impurity atom and on the level *symmetry*. This is also in qualitative agreement with previous results for defect levels due to isolated impurities in this same material.[3,16]

A significant new finding of our theory is that the dE/dx for some of the energy levels produced by a (vacancy, impurity) pair, in particular those whose wavefunctions are primarily vacancylike, can be *significantly* different from either those produced by the corresponding isolated defects or those produced by the complex and whose wavefunctions are primarily impuritylike. This raises the possibility of distinguishing *at least some* of the energy levels produced by vacancy associated complexes from those produced by isolated impurities on the basis of their experimental slopes.

On the basis of all of these results we thus suggest that the experimentally observed dE/dx of a defect energy level can often be used to identify the site occupied by an impurity. Furthermore, *in favorable cases, it can also be used to distinguish between levels produced by isolated point defects and those produced by vacancy associated complexes.*

A final interesting and important qualitative result of our calculations is that complexing an impurity with a vacancy can produce energy levels whose *positions* are substantially altered in comparison with those of either the isolated impurity or the isolated vacancy. This has been noted before by Myles and Sankey[6] in their paper on deep levels produced by (vacancy, impurity) pairs in III-V semiconductors.

B. Quantitative results for (vacancy, indium impurity) pairs

As is mentioned above, although spin-orbit coupling effects are included in the host band structures of $Hg_{1-x}Cd_xTe$,[3] in the present theory we neglect these effects in our treatment of the defect potential. The point group for an isolated point defect in a tetrahedrally symmetric zinc-blende semiconductor is T_d. Point defects with sp^3 hybrid bonding can thus have defect states (neglecting spin-orbit coupling) with either nondegenerate A_1 (s-like) or triply degenerate T_2 (p-like) symmetry. Paired nearest-neighbor defects in the same zinc-blende hosts are described (again neglecting spin-orbit coupling) by a reduced "molecular" C_{3v} symmetry group. This results in splittings of the T_2 levels and mixing of the "atomic" A_1 and T_2 levels on both sites. The resulting "molecular" states are nondegenerate a_1-symmetric (σ-like) levels, whose energies can be very different than either the A_1 or the T_2 levels of the isolated defects, and doubly degenerate e-symmetric (π-like) levels, whose energies are almost identical to the isolated defect T_2 levels.

In Fig. 1 we show typical results of our calculations. Figure 1(a) shows our predictions for the x dependence of the a_1-symmetric (σ-like) and e-symmetric (π-like) levels produced by a cation vacancy complexed with a nearest-neighbor substitional indium impurity on the anion site. Figure 1(b) shows our results for the opposite case, where the vacancy is on the anion site, and the indium impurity has replaced the host cation. There are two pair levels of each symmetry type in the region near the band gap; for one, the associated wave function is derived mainly from the impurity and for the other, the wave function is derived mainly from the vacancy (labelled "impuritylike" and "vacancylike," respectively, in Fig. 1). The e-symmetric, vacancylike level which is produced by an anion vacancy paired with an indium impurity on the cation site occurs at an energy which is above the scale of Fig. 1(b). It is thus not shown in that figure. We show the results of our calculations for (vacancy, indium impurity) defect pairs because the samples from which we obtained the photoluminescence spectra discussed below are believed to contain indium related defects. Our predictions for the x dependences of levels produced by other (vacancy, impurity) pairs in $Hg_{1-x}Cd_xTe$ will be presented in a later publication.[15] As is discussed above, we find that while the absolute energy level depths certainly vary with the choice of impurity, the dE/dx of a level associated with a particular site and symmetry is almost independent of which impurity is present in the (vacancy, impurity) complex. Thus, the *slopes* of the levels shown in Figs. 1(a) and 1(b) can, to a good approximation, be taken as the slopes of energy levels derived from a (vacancy, impurity) pair complex and associated with a particular site and symmetry, independent of the choice of impurity. This fact will be utilized below in our comparisons of the theoretical slopes of defect energy levels with the dE/dx of various measured levels.

Both the impuritylike and vacancylike a_1-symmetric levels predicted in Fig. 1 occur at energies which are substantially shifted from the corresponding isolated point defect levels predicted by Kobayashi *et al.*[3] One finding of these calculations that is true generally is thus that complexing with a vacancy can alter the position of an isolated point defect level by a substantial amount. Also, the impuritylike levels of both symmetries predicted in Fig. 1 have similar x dependences as the corresponding isolated impurity levels found in Ref. 3. Another finding of these calculations is thus that the impuritylike levels produced by a (vacancy, impurity) pair cannot easily be distinguished, on the basis of their dE/dx, from the corresponding isolated impurity levels.

The case of the vacancylike energy levels produced by such a vacancy associated complex is, however, very different. In particular, the vacancylike, a_1-symmetric levels, shown in Fig. 1, not only occur at very different energies than those for the corresponding isolated defects, but they also have strikingly different x dependences than those predicted in Ref. 3 for either isolated defect. One of the most important results of the present theory is thus that a *vacancy-like a_1-symmetric level due to a (vacancy, impurity) complex can be distinguished from an isolated impurity level by its x dependence.* This gives one the possibility of, at least in some cases, being able to use the dE/dx of observed levels distinguish between isolated point defect levels and levels produced by vacancy associated complexes.

IV. COMPARISON WITH THE DATA OF JONES, NAIR, AND POLLA

As an example of the utility of our theory, we have analyzed some published DLTS data of Jones *et al.*[5] on defects

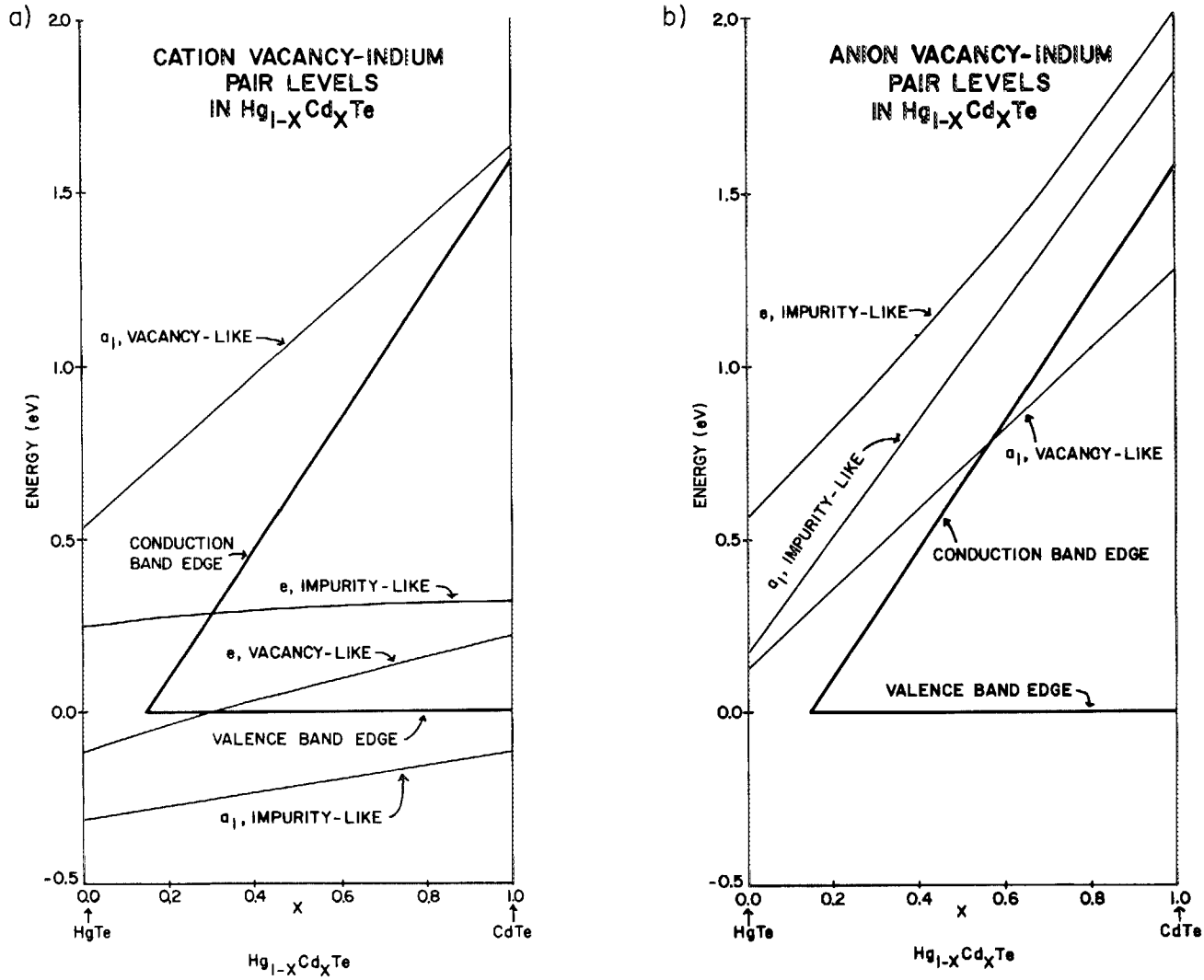

FIG. 1. Theoretical predictions of the energy level positions and the x dependences produced by a (vacancy, indium impurity) nearest-neighbor pair in $Hg_{1-x}Cd_xTe$. The slope of a level of a given site and symmetry is almost independent of the particular impurity contained in the complex. The slopes of the impuritylike levels are almost the same as those obtained in Ref. 3 for the corresponding isolated impurity: (a) cation vacancy paired with an indium on the anion site; (b) anion vacancy paired with an indium on the cation site. In this case, the e-symmetric, vacancylike level occurs at energies which are above the scale of the figure; it is thus not shown.

in p-type $Hg_{1-x}Cd_xTe$. These workers have found two defect levels with energies varying nearly as $(1/2)E_g(x)$ and $(3/4)E_g(x)$, where $E_g(x)$ is the variation of the band-gap energy or conduction band edge with composition x. They have associated the $(1/2)E_g$ level with a cation vacancy related defect and state that the origin of the $(3/4)E_g$ level is unknown.

The results of the theoretical-experimental comparison in this case are shown in Fig. 2. In that figure we have plotted the composition dependences of the two defect energy levels observed by Jones *et al.*[5] The data for the $(1/2)E_g$ level is represented by the closed circles and that for the $(3/4)E_g$ level is represented by the plus signs. The solid lines drawn through these two sets of data points are reproduced from Ref. 5 and are included as a guide to the eye. The conduction band-edge composition dependence shown in the figure is that obtained from the present theory. Also shown in that figure are the x dependences of the a_1-symmetric, vacancylike level produced by a (cation vacancy, anion impurity) nearest-neighbor pair and the e-symmetric, impuritylike level associated with an (anion vacancy, cation impurity) pair. These are shown as dashed lines in the figure. The theoretical curves are derived from the energy levels of Figs. 1(a) and 1(b) by shifting the latter levels in energy (keeping their dE/dx unchanged) until they pass through the region of the experimental points. This makes direct use of and reemphasizes the fact that the *slope* of a particular level produced by a (vacancy, impurity) complex depends very little on which impurity is present in the complex, even though the absolute energy of such a level does depend on the impurity atom. Instead, the dE/dx of a complex-produced level depends primarily on the *site* of the impurity and on the symmetry of the level. It should be noted that the slopes of the other theoretical levels shown in Fig. 1 will not provide a good description of the data.

It is clear from Fig. 2 that the slope that we find for the a_1-symmetric, vacancylike level derived from the cation vacancy associated complex is nearly the same as the slope of the experimental data for the $(1/2)E_g$ trap. As has been emphasized above, a vacancy-like pair level has a very different

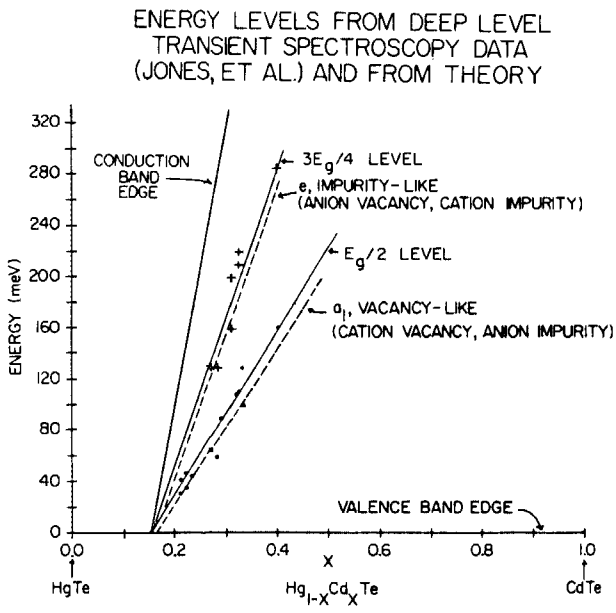

FIG. 2. Deep level transient spectroscopy data of Jones, Nair, and Polla (Ref. 5) for the x dependences of the $(1/2)E_g$ level (solid circles) and the $(3/4)E_g$ level (plus signs) in $Hg_{1-x}Cd_xTe$, along with the theoretical slopes for the a_1-symmetric, vacancylike level produced by a (cation vacancy, anion impurity) pair and the e-symmetric, impuritylike level produced by an (anion vacancy, cation impurity) pair (dashed lines). The solid lines through the data are guides to the eye. It should be noted that the slope of the latter level and the results of Kobayashi *et al.* (Ref. 3) for the slope of a T_2-symmetric level produced by an isolated cation impurity are very nearly the same. The conduction band edge shown is the one resulting from the present theory.

dE/dx than the corresponding isolated impurity or vacancy level. This enables such a pair related level to be distinguished from an isolated point defect level. The close agreement between the theoretical and experimental slopes in this case thus leads us to suggest that the $(1/2)E_g$ trap is associated with a (cation vacancy, anion impurity) complex. This result is consistent with the interpretation of Jones *et al.*[5] for this defect level and illustrates the utility of the theory for distinguishing between complex related and point defect produced energy levels.

From Fig. 2 it is also clear that the slope of the experimental data for the $(3/4)E_g$ trap and the theoretical slope that we find for the e-symmetric, impuritylike level produced by an (anion vacancy, cation impurity) complex are very nearly the same. Unfortunately, as is discussed above, the impuritylike levels produced by such a complex have almost the same slopes as the corresponding isolated impurity levels found by Kobayashi *et al.*[3] These cation impurity-related slopes are, however, very different than the slopes of energy levels produced by anion impurities or complexes containing such impurities. Thus, while the theory in this case is unable to distinguish between an isolated impurity and a vacancy associated complex, we can conclude that the $(3/4)E_g$ level is probably associated with a defect containing a cation site impurity. This comparison therefore shows the usefulness of the theory for obtaining site information about experimentally observed levels.

V. PHOTOLUMINESCENCE EXPERIMENTS AND COMPARISON WITH THEORY

A. Experimental details

Photoluminescence experiments were carried out using n-type samples fabricated with the solid-state recrystallization technique. The samples were nominally 1×20 mm, were chemically etched prior to post annealing, and were subsequently cleaned with a bromine-methanol etch. A helium-neon laser was used for excitation, and a Perkin Elmer Model E1 spectrometer provided spectral discrimination. A cooled photovoltaic InSb detector was used for emission wavelengths down to 5.35 μm, and cooled photoconductive Ge:Hg and Ge:Cu detectors to 13.7 and 20 μm, respectively were used.

Photoluminescence spectra for three x values are shown in Fig. 3. In these spectra, two clearly resolved peaks which we label A and B can be seen. In most spectra there is also a broader, more poorly resolved feature which we label C in the figure. In Fig. 3(c), feature C is not clearly separable from the tail of peak B, and we show as dashed and dot-dashed curves Lorentzians centered at 74.7 and 69.0 meV, respectively, to aid in this separation. Similar spectra have been reported for $x = 0.32$ and $x = 0.48$ by Hunter and McGill,[18] who identified the peak corresponding to our peak A as being produced by either band-to-band or bound exciton recombination, and the peak corresponding to our peak B as being associated with either a free-to-acceptor or donor-to-acceptor transition. They also observe a feature on the low-energy side of this peak, similar to the feature we label C, which they do not identify. We note that there is considerable variation in the linewidths of each of the spectral features. We attribute this effect to compositional variations across the 0.1- mm diameter of the focussed excitation laser beam. This interpretation is consistent with the estimated local variation of x on this scale.[1]

Following Hunter and McGill,[18] we identify our peak A with a transition involving the recombination of a bound exciton. We then make use of this identification to determine the band gap for each spectrum. To do so, we assume that the ionization energy of the exciton scales with x in the same way as the band gap,

$$E_{be}(x) = \alpha E_g(x), \tag{1}$$

where $E_{be}(x)$ is the energy of the bound exciton and $E_g(x)$ is the band-gap energy for the composition x. In Eq. (1), α is a constant determined from the pure CdTe values by

$$E_{be}(1) = \alpha E_g(1). \tag{2}$$

In pure CdTe, the free exciton lies 10 meV below the band edge.[19] Assuming that the exciton is bound by an additional 5 meV and combining Eqs.(1) and (2) then gives band gaps of 401, 275, and 86.9 meV for the samples for which photoluminescence spectra are shown in Fig. 3(a), 3(b), and 3(c), respectively. Finally, we obtain the average alloy composition x for our samples by making use of the data of Schmit and Stelzer[20] relating x to the band gap. The resulting x values are 0.364, 0.297, and 0.197 for the samples for which spectra are displayed in Figs. 3(a), 3(b), and 3(c), respectively. These values agree to within 20% with the x values obtained by

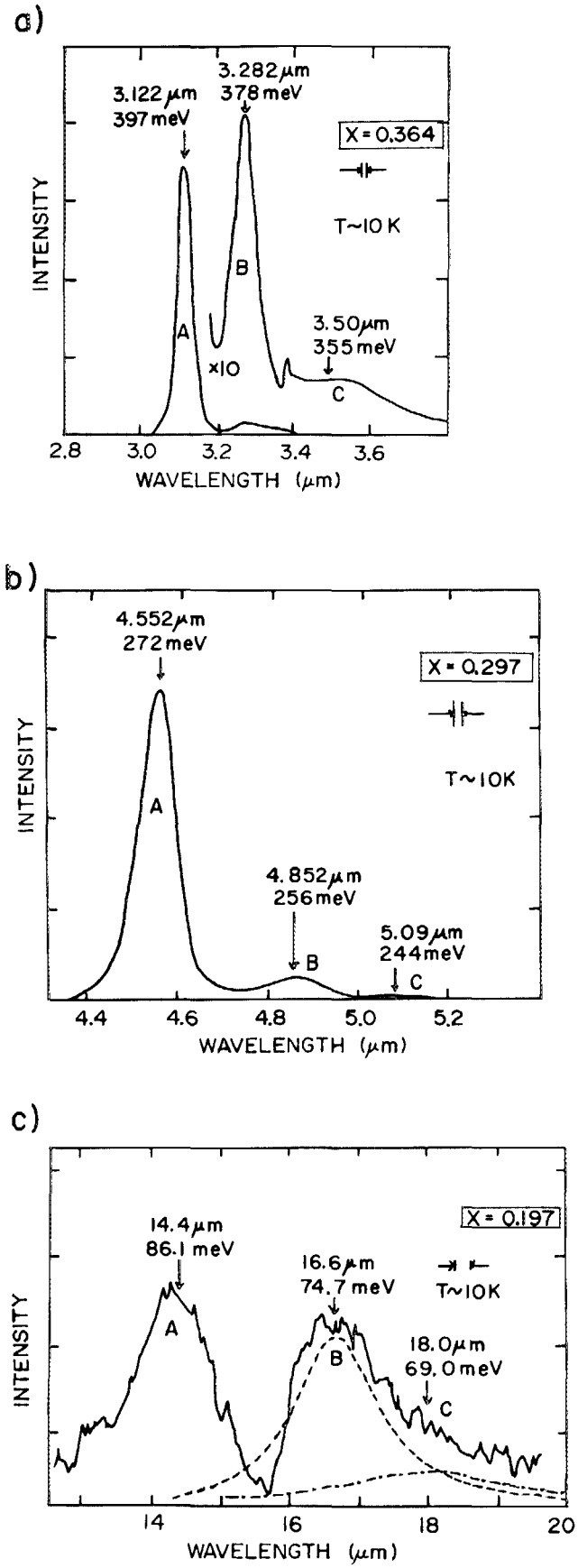

FIG. 3. Typical photoluminescence spectra in $Hg_{1-x}Cd_xTe$ showing spectral features A, B, and C. (a) $x = 0.364$, (b) $x = 0.297$, (c) $x = 0.197$. The dashed and dot-dashed curves in (c) are Lorentzians in energy, centered at 74.7 and 69.0 meV, respectively, which are shown as aid to the eye in resolving spectral feature C.

Brau using Hall effect measurements on the same samples.[21]

Once the band gap is known and if we assume that peaks B and C result from free to bound transitions, the energies of the levels associated with these peaks can then be determined for each x. Uncertainties in the exact positioning of the band-gap for each x may introduce a systematic error in the absolute positioning of the levels of up to 3 meV. In order to make the experimental-theoretical comparison discussed below, however, we are primarily interested in the x dependence of these levels. Since such uncertainties have only a second order effect on the slopes of the levels, they will not seriously affect the resulting experimental slopes of the defect levels. We estimate that in a worst possible case, such errors introduce less than a 10% error in the slopes of the levels derived from our data.

B. Theoretical-experimental comparisons; interpretation of experimental results

In Fig. 4, we plot the results of this data analysis for the x dependence of the energies of photoluminesence peaks B (closed circles) and C (plus signs) for all compositions for which we have data. Also shown in this figure are the composition dependences of the e-symmetric impuritylike and vacancylike, and the a_1-symmetric, impuritylike levels produced by a (cation vacancy, anion impurity) nearest-neighbor pair (dashed lines). At $x = 1$, we show the energy ranges of two known defect levels in CdTe: an acceptor level in the range 40–60 meV, believed to be due to an anion-site impurity,[22,23] and a level in the 140–150 meV range, believed to be due to a (vacancy, impurity) complex.[22,23] The solid straight lines drawn through the two sets of data points are least-

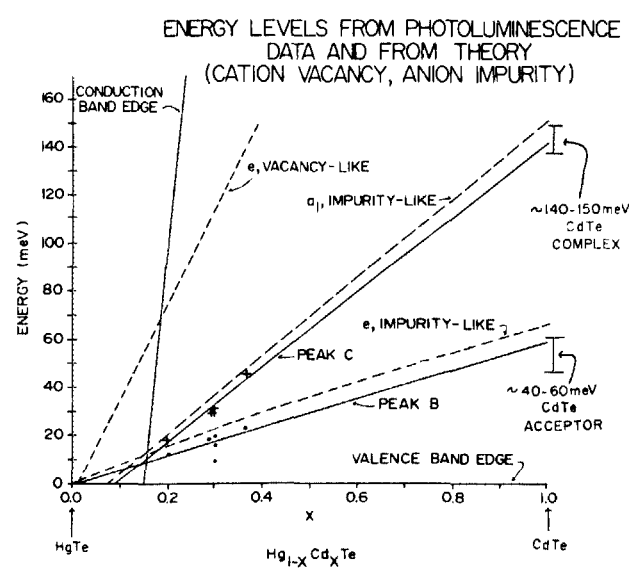

FIG. 4. Composition dependences of the energy levels extracted from the photoluminescence data for spectral features B (closed circles) and C (plus signs), along with theoretical slopes for the e-symmetric, impuritylike and vacancylike and the a_1-symmetric, impuritylike levels produced by a (cation vacancy, anion impurity) pair (dashed lines). The solid lines are least squares fits to the data. Also shown at $x = 1$ are the energy regions where an acceptor level associated with an anion-site impurity (40–60 meV) and a level related to a cation-site vacancy complex (140–150 meV) have been identified in CdTe (Refs. 22 and 23). The conduction band edge shown is the one resulting from the present theory.

squares fits to the data. The percentage uncertainties in the positions of the experimental energy levels, which are attributable to inaccuracies in our determination of the centers of the luminescence peaks, are greater for spectral feature C than for B at all x and become larger as x decreases. For the smallest composition at which we have obtained data ($x = 0.197$), we estimate the uncertainties in the positions of peaks B and C to be 1.1 and 2.1 meV, respectively. The conduction band edge shown in Fig. 4 is the one calculated on the basis of the present theory.

Similar to the case for Fig. 2 discussed above, in Fig. 4 the theoretical curves are obtained by shifting the theoretical energy levels of Fig. 1(a) in energy, but keeping their variation with composition (dE/dx) unchanged, until they pass through the region of the data. This again utilizes and emphasizes that the dE/dx of a particular level associated with a (vacancy, impurity) pair is essentially independent of which impurity is present in the complex.

It is evident from Fig. 4 that the slope of the e-symmetric, vacancylike level produced by a (cation vacancy, anion impurity) complex will not provide a good description of the data. Further, the slopes of the data and those of the other levels shown in Fig. 1 but not reproduced in Fig. 4 (particularly those due to the anion vacancy-related complex) diverge even more. On the other hand, the slopes of the e- and a_1-symmetric, impuritylike levels associated with this same complex and reproduced in Fig. 4 closely match those of the least-squares fits to the luminescence data of peaks B and C. These facts suggest that both spectral features and thus the energy levels extracted from the data for them are associated with defect centers where the impurity atom has replaced an anion host (Te) atom. However, because the impuritylike levels for a (vacancy, impurity) pair have a very similar dE/dx as the corresponding isolated point defect levels found by Kobayashi *et al.*,[3] we cannot say definitively on the basis of the theory alone whether peaks B and C are produced by isolated anion impurities or by cation vacancy related complexes containing such impurities.

In both cases, however, we can tentatively make such identifications by other means. An acceptor level at nearly the same energy as we find for peak B has been previously observed in $Hg_{1-x}Cd_xTe$ and associated with an isolated anion-site impurity thought to be either As or P.[18,24] Further, the least squares fit to our data for that peak extrapolates at $x = 1$ to an energy (59 meV) within the range of that of the above-mentioned known acceptor level in CdTe.[22,23] These observations, taken together with the experimental-theoretical comparison discussed above, are consistent with and strongly support the assignment of the energy level extracted from the data for spectral feature B to an isolated anion-site impurity. This assignment again illustrates the utility of the theory for use, in conjunction with experimental data, in obtaining impurity site information about experimentally obtained defect energy levels.

Peak C is a heretofore unobserved spectral feature in $Hg_{1-x}Cd_xTe$, although Hunter and McGill[18] have observed, but not identified, a similar feature on the low-energy side of the peak in their data which corresponds to our peak B. In this case, our theory, used in conjunction with other information, can again be useful in helping to obtain at least site information about the center which is associated with this feature. The theoretical-experimental comparison discussed above suggests that the energy level extracted from the data for peak C is anion impurity related. Furthermore, we note that the least-squares fit to the data, in this case, extrapolates at $x = 1$ to an energy (142 meV) in the range of a level previously observed in CdTe and attributed to a (cation vacancy, anion impurity) complex.[22,23] These facts suggest that spectral feature C is associated with a (vacancy, impurity) complex where the impurity occupies the anion (Te) site. We, therefore tentatively make such an identification for this peak, while again emphasizing that such an identification cannot be made on the basis of the theory alone, since the dE/dx for isolated impurity levels and for the impuritylike levels derived from a (vacancy, impurity) complex are (for the impurity on the same site in both cases) similar. This assignment is yet another illustration of the utility of the theory, along with information obtained from data, for helping in the identification of the centers which produce observed defect energy levels.

As a final comment on our data, we note that we have considered the possibility that peak C is a phonon replica of peak B. However, both its energy differences with peak B and its variation with x are wrong for this explanation.[25] We thus reject this explanation for that spectral feature in favor of that just discussed.

VI. SUMMARY AND CONCLUSIONS

In summary, we have generalized the Kobayashi *et al.*[3] theory of deep energy levels produced by point defects in $Hg_{1-x}Cd_xTe$ to the case of (vacancy, impurity) nearest-neighbor pairs. The theory is based upon the theory of deep levels due to (vacancy, impurity) pairs in semiconductors developed by Myles and Sankey[6] and on the Kobayashi *et al.*[3] semi-empirical tightbinding bandstructures for $Hg_{1-x}Cd_xTe$. Furthermore, we have shown that, similar to the case of point defects,[3] the slopes of the resulting vacancy complex related energy levels as a function of alloy composition are strongly dependent upon the site occupied by the impurity. *A significant finding of our theory is that the a_1-symmetric vacancylike energy levels produced by such a (vacancy, impurity) complex have very different x dependences than either the impuritylike levels coming from the same complex or the corresponding isolated point defect levels.* These facts suggest that the theory can be useful, when used in an analysis of experimental data on defect energy levels in $Hg_{1-x}Cd_xTe$, to help to obtain impurity site information about the defect centers which produce such levels and, *in favorable cases, to help to distinguish between a vacancy complex produced level and an isolated point defect level.*

We have illustrated these points by comparing the predictions of our theory for the slopes of defect energy levels as a function of x to the observed composition dependences of such levels in $Hg_{1-x}Cd_xTe$ in two different cases. In the first case, we have made such a comparison with the so-called $(1/2)E_g$ and $(3/4)E_g$ levels observed in DLTS by Jones *et al.*[5] In that case, we have shown that the theory can be used, in conjunction with the data analysis of Ref. 5 to essen-

tially unambiguously associate the $(1/2)E_g$ level with a cation vacancy related complex (consistent with the interpretation of Jones *et al.*[5]) and the $(3/4)E_g$ level with a cation impurity related defect center. In the second case, we have presented some new photoluminescence data on both a known acceptor level and an unknown spectral feature. In that case, we have shown that the theory can be used, in conjunction with this and other data, to associate the known acceptor level with an anion impurity-related defect center (consistent with other assignments for this level[22,23]) and the unknown spectral feature with an anion impurity related defect center that probably also contains a cation vacancy.

The theory can thus be utilized to help in the identification of the defect centers which produce observed energy levels in $Hg_{1-x}Cd_xTe$. Clearly, the utility of this type of theory is not restricted to the analysis of data on defect centers in this material, but should be useful for similar analyses in other semiconducting alloys. Work along these lines,[13] as well as efforts to generalize our theory to include the effects of the spin-orbit splittings of the defect levels, is underway.

Finally, we note that Tuncay and Tomak[16] have recently developed a theory of isolated point defect states in $Hg_{1-x}Cd_xTe$, using the tightbinding host bandstructures of Podgorny and Czyzyk[26] as a starting point. The x dependences that they predict for both cation and anion site defects are in qualitative agreement both with those found by Kobayashi *et al.*[3] and with those that we find for the impuritylike levels produced by (vacancy, impurity) pairs. This suggests that our conclusions regarding the correlation of the dE/dx of an energy level with the site occupied by an associated impurity are independent of the model used for the host band structure.

ACKNOWLEDGMENTS

C.W.M. and P.F.W. are grateful to Texas Instruments, Inc. for a grant which partially supported this work and to Texas Tech University for a grant of computer time to perform these calculations. We are also grateful to A. J. Syllaios for several helpful suggestions, for many stimulating conversations, and for a critical reading of the manuscript. C.W.M. thanks O. F. Sankey, A. Kobayashi, and J. D. Dow for many stimulating conversations and for use of the computer codes and tightbinding parameter data which generated the $Hg_{1-x}Cd_xTe$ band structures. We thank M. J. Brau for supplying the samples from which we obtained the photoluminescence data.

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