# Study of ideal vacancies in CdS (wurtzite)

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The electronic states of ideal vacancies of Cd and S in the CdS lattice with the wurtzite structure are calculated with the use of a Green's-function method. The electronic band structure is computed within a tight-binding approximation by fitting the pseudopotential energy bands obtained by Bergstresser and Cohen. When interactions up to second neighbors are taken into account, both valence and conduction bands are accurately reproduced. We show that cation vacancies may induce bound states inside the fundamental gap while anion vacancies induce bound states in the gap between the conduction $s$ and $p$ cationic states.

## I. INTRODUCTION

In recent years there has been considerable interest in calculating the electronic structure of defects in semiconductors because of the crucial role they play in determining the electrical and optical properties of these materials. The effective-mass approximation has been shown to be able to successfully describe the shallow impurity states.[1] However, concerning the deep-level problem, the dominance of a strong localized potential (as opposed to the long-ranged Coulombic potential for the shallow levels) invalidates the assumptions inherent in the effective-mass theory. Alternative methods must be used, among which those based on the Green's-function technique seem to be the most employed because of their great ability to be used at different levels of sophistication.[2-10] The simplest and the most investigated of the defects giving rise to such deep levels is the simple ideal (unrelaxed) vacancy whose study may serve as a basis for more involved calculations on more realistic models such as the relaxed neutral or charged vacancies, divacancies, self-interstitials, antisite defects, and aggregates of these. Self-consistent calculations have been performed in the case of vacancies in silicon,[9,10] and have been extended recently to study the cation and anion vacancies in AsGa.[11] However, little has been done theoretically on defects in II-VI compounds except for one study on the electronic structure of S vacancies and isoelectronic defects in ZnS in the zinc-blende structure.[12] In this work our intent is to deal with the isolated vacancy problem in hexagonal CdS.

Experimental results seem to indicate the presence of levels induced by S and Cd vacancies in the band gap of this compound.[13,14] It was thus determined it would be interesting to investigate the electronic structure of ideal (unrelaxed) vacancies in this material. For this study the Green's-function method has been used in conjunction with the empirical tight-binding approximation. The tight-binding study of CdS is exposed in Sec. II. In Sec. III we present the results of our calculations on ideal anion and cation vacancies in CdS, while Sec. IV is devoted to some discussions of our results and the conclusion.

## II. TIGHT-BINDING DESCRIPTION OF THE ENERGY BANDS OF CdS

The electronic band structure of CdS in the wurtzite structure has been obtained by a fitting of the pseudopotential energy bands calculated by Bergstresser and Cohen[15] with the empirical tight-binding (ETB) method. The electronic states were modeled with a tight-binding Hamiltonian, which includes the S $3s$ and $3p$ orbitals and the Cd $5s$ and $5p$ orbitals. The Cd $4d$ shell which is expected to lie below the upper valence band[16] has thus been omitted because it can be considered as a core level which is not involved in the chemical bonding. The omission of these cation $d$ states has been in fact a common practice in studying surfaces[17] and defect[12] induced states in II-VI compounds.

Because of the presence of two Cd and S atoms in the unit cell, the resulting ETB Hamiltonian is

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16×16. The fitting has been performed starting from the universal form of the interaction parameters proposed by Froyen and Harrison,[18] and then varying their values and their number until an acceptable description for both the conduction band (CB) and valence band (VB) of Bergstresser was obtained. Taking into account all first- and second-nearest-neighbor interaction, we obtained a rather accurate representation of the valence band and a reasonable agreement for the conduction band. The fitting error was less than 0.3 eV for the valence band and about 0.5 eV for the lowest conduction band which lies below 5 eV. For the higher states our fitting errors were less than 0.7 eV if one excepts the $K_2$ and $K_3$ states which are inverted in our calculation with respect to that of Bergstresser. The most important parameter involved in the fitting procedure was found to be the "ionicity parameter" $X$, defined by Mele and Joannopoulos[19] as the difference between the on-site energies of the cation $s$ and anion $p$ orbitals,

$$X = \epsilon_s^c - \epsilon_p^a .$$

The band gap is actually very sensitive to this energy difference, the role of $s$-$p$ hybridization being of secondary importance. This behavior is markedly different from that of the less ionic III-V and purely covalent group-IV semiconductors where the reverse is true (i.e., it is the hybridization interaction which is responsible for the opening of the gap). We think that it is, in fact, the rather ionic character of CdS which enable us to obtain a realistic TB Hamiltonian describing rather correctly both the valence and the conduction bands, contrary to the more covalent III-V compounds where the conduction band is at most fairly reasonably described by such $s$-$p$ Hamiltonians (see, for example, Table III of Ref. 20). The value attributed to $X$ in our fitting procedure is + 2.4 eV, in close agreement with that assigned to CdS by Mele and Joannopoulos[19] ($\sim 2.7$ eV). This is an important point to be noted, as it has been recognized by a number for authors[6,20,21] that $X$ has a dominant influence on the position of the vacancies induced states, whose determination is the main objective of our work. The final parameters entering our CdS empirical TB Hamiltonian are given in Table I. The resulting band structure is given in Fig. 1(a), while for comparison the pseudopotential energy bands are drawn in Fig. 1(b). Missing from Fig. 1(a) is the lower valence band situated at −8 eV. This band, which is very narrow ($\sim 0.5$ eV), originates from the S 4$s$ states which do not mix appreciably with the other orbitals. The major discrepancy between the two band structures is due to the existence in the TB bands of a gap between the upper ($p$-like) and lower ($s$-like) cationic conduction bands. Although this feature is absent in the pseudopotential calculation of Bergstresser,[15] it must been noted that such a gap is indeed found in the pseudopotential calculation of Collins[22] et al. on CdS and in band-structure calculations of ZnS by Ren and Harrison[23] and Rossler.[16] However, the influence of the upper conduction band on the levels in the vicinity of the fundamental gap has been found to be very weak and not to markedly affect our results on the vacancies' induced levels.

## III. CALCULATION OF THE IDEAL NEUTRAL VACANCY LEVELS

The vacancy-induced states were calculated by the Green's-function method. We here only recall the basic features of this approach, more details can be found, for instance, in Ref. 2.

Let the crystal containing the defect be described by

$$(H_0 + U)|\psi\rangle = E|\psi\rangle , \tag{1}$$

where $H_0$ is the Hamiltonian corresponding to the perfect crystal and $U$ is the potential which characterizes the perturbation introduced by the defect. Integral information about the perturbed crystal can be obtained from the knowledge of the function $D(E)$ defined as:

$$D(E) = \det||1 - G^0(E)U|| , \tag{2}$$

where

$$G^0(E) = (E - H^0 + i\eta)^{-1}, \quad \eta \to 0 \tag{3}$$

is the perfect-crystal Green's operator. The energies of the bound states are determined by

$$D(E) = 0 , \tag{4}$$

while the total change in the density of states is given by

$$\Delta N(E) = \frac{1}{\pi} \frac{d\delta(E)}{dE} , \tag{5}$$

where the phase shift $\delta(E)$ is defined as

$$\delta(E) = -\tan^{-1} \frac{\mathrm{Im}D(E)}{\mathrm{Re}D(E)} . \tag{6}$$

Im and Re, stand, respectively, for imaginary part and real part.

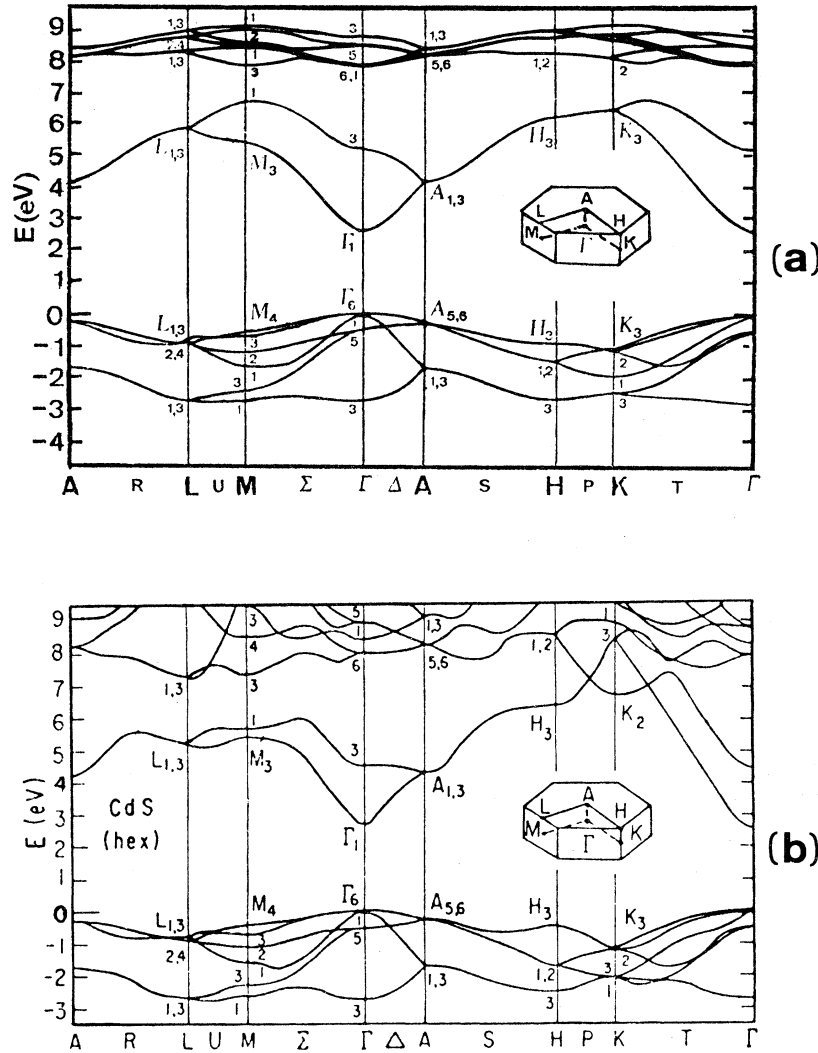In the case of an ideal vacancy, the defect potential is obtained by removing from the periodic

FIG. 1. (a) ETB energy bands compared to (b) pseudopotential energy bands of bulk CdS.

solid the corresponding atom. This removal was accomplished by shifting to infinity the on-site energies of this atom. Further simplification was gained by symmetrizing the orbitals with respect to the symmetry group of the vacancy, which is $C_{3v}$ in the wurtzite structure. $s$ and $p$ orbitals induce the irreducible representations (IR) $A_1$ and $E$ of this group, $s$ and $p_z$ being basis partners of the one-dimensional IR $A_1$ and $p_x, p_y$ basis functions of the two-dimensional IR $E$. The matrix elements of the Green's function $G^0_{\alpha\alpha'}(E)$ have been calculated as

$$G^0_{\alpha\alpha'}(E) = P \int \frac{A_{\alpha\alpha'}(E')}{E - E'} dE' - i\pi A_{\alpha\alpha'}(E) , \quad (7)$$

where $P$ stands for principal part and the spectral density of states $A_{\alpha\alpha'}(E)$ is given by

$$A_{\alpha\alpha'}(E) = \sum_{n(\vec{k})} \langle \alpha \mid n\vec{k} \rangle \langle n\vec{k} \mid a' \rangle \delta(E - E_n(\vec{k}))$$

$$(8)$$

TABLE I. ETB parameters for bulk CdS. Energies are in eV. Sign + refers to Cd and sign − to S; 1 refers to first nearest neighbors and 2 to second-nearest neighbors.

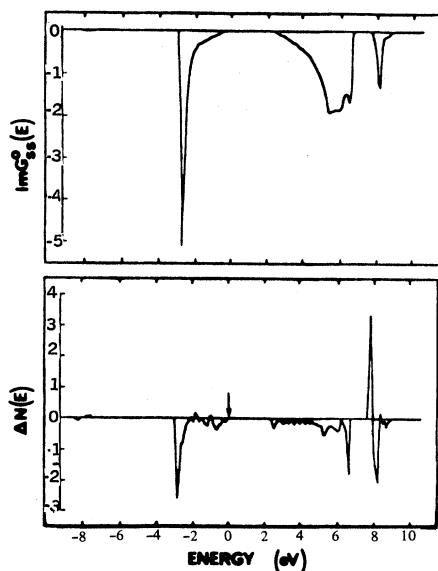| | |
|---|---|
| $E_s^- = -20.8$ | $(s_+ s_+ \sigma)_2 = -0.057$ |
| $E_p^- = -12.86$ | $(p_+ p_+ \sigma)_2 = 0.07$ |
| $E_p^+ = -10.47$ | $(p_+ p_+ \pi)_2 = -0.018$ |
| $E_s^+ = -6.9$ | $(s_+ p_+ \sigma)_2 = 0.059$ |
| $(s_+ s_0 \sigma)_1 = -0.18$ | $(s_- s_- \sigma)_2 = 0.027$ |
| $(p_+ p_- \sigma)_1 = 2.746$ | $(p_- p_- \sigma)_2 = 0.062$ |
| $(p_+ p_- \pi)_1 = -0.42$ | $(p_- p_- \pi)_2 = -0.02$ |
| $(s_+ p_- \sigma)_1 = 1.945$ | $(s_- p_- \pi)_2 = 0.041$ |
| $(s_- p_+ \sigma)_1 = 1.865$ | |

FIG. 2. Imaginary part of the Green's function and change in the density of states for an ideal Cd vacancy: symmetry $A_1(s)$ (a.u.). Vertical arrow indicates the zero of the Green's function corresponding to the ideal vacancy-induced states.
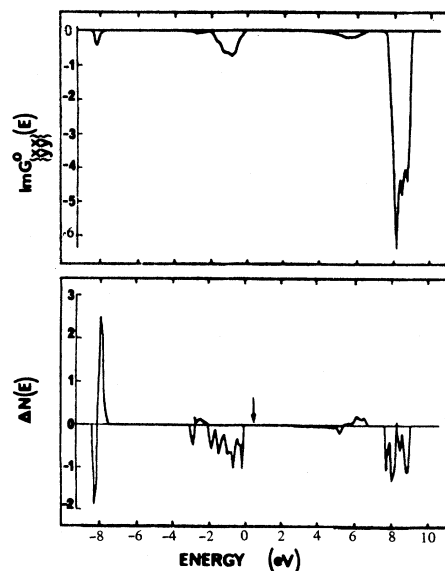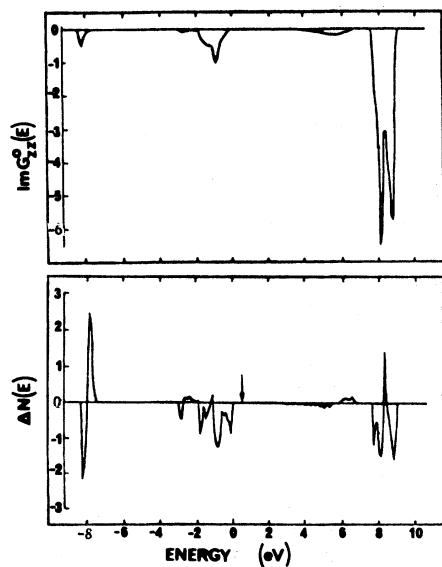
FIG. 4. Imaginary part of the Green's function and change in the density of states for an ideal Cd vacancy: symmetry $E(p_x$ or $p_y)$ (a.u.). Vertical arrow indicates the zero of the Green's function corresponding to the ideal vacancy-induced states.

FIG. 3. Imaginary part of the Green's function and change in the density of states for an ideal Cd vacancy: symmetry $A_1(p_z)$ (a.u.). Vertical arrow indicates the zero of the Green's function corresponding to the ideal vacancy-induced states.
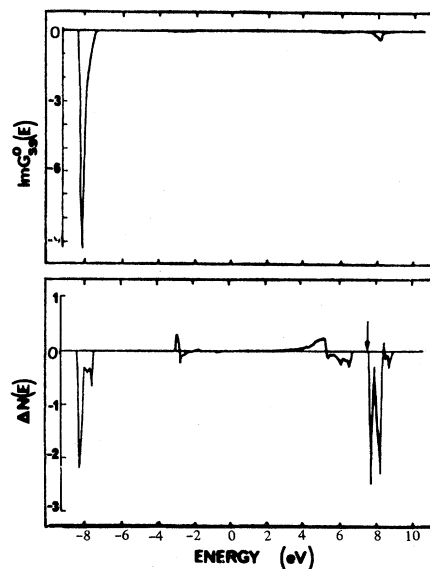
FIG. 5. Imaginary part of Green's function and change in the density of states for an ideal S vacancy: symmetry $A_1(s)$ (a.u.). Vertical arrow indicates the zero of the Green's function corresponding to the ideal vacancy-induced state.
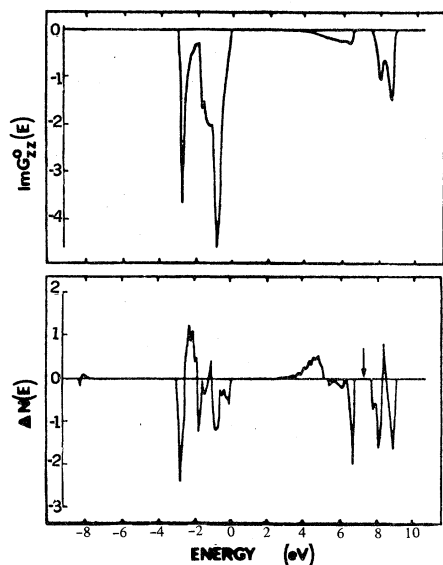
FIG. 6. Imaginary part of the Green's function and change in the density of states for an ideal S vacancy: symmetry $A_1(p_z)$ (a.u.). Vertical arrow indicates the zero of the Green's function corresponding to the ideal vacancy-induced state.

Here $|n\vec{k}\rangle$ are the unperturbed eigenstates of the crystal with energies $E_n(\vec{k})$. These spectral densities of states were obtained by the Gilat-Raubenheimer method,[24] summing over 250 $\vec{k}$ points in the irreducible $\frac{1}{12}$ Brillouin zone. However, it was
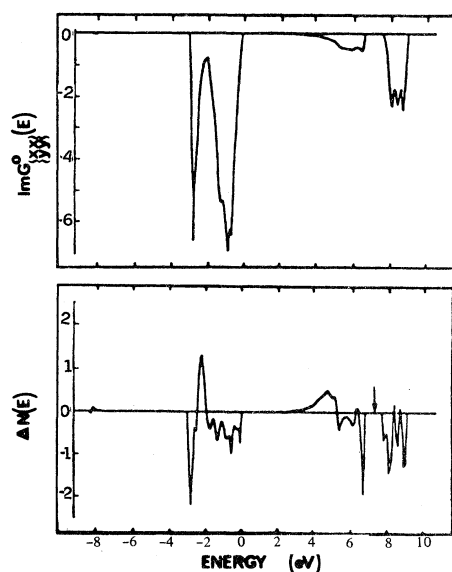


FIG. 7. Imaginary part of the Green's function and change in the density of states for an ideal S vacancy: symmetry $E(p_x$ or $p_y)$ (a.u.). Vertical arrow indicates the zero of the Green's function corresponding to the ideal vacancy-induced state.

TABLE II. Energies of the states induced by ideal vacancies in CdS. Energies in eV are measured from the top of the valence band.

| | $A_1(s)$ | $A_1(p_z)$ | $E(p_x,p_y)$ |
|---|---|---|---|
| $V_{Cd}$ | 0.2 | 0.35 | 0.35 |
| $V_S$ | 7.6 | 7.4 | 7.4 |

found in the case of $A_1$ symmetry that the coupling between the $s$ and $p_z$ states, i.e., the matrix elements $G_{sz}^0(E)$ was negligibly small which allowed us to treat these two states separately. Equation (4), which determines the position of the bound states now simplifies as

$$G_{\alpha\alpha}^0(E)=0 , \qquad (9)$$

while the phase shifts are determined by

$$\delta_\alpha(E)=-\tan^{-1}\frac{\mathrm{Im}G_{\alpha\alpha}^0(E)}{\mathrm{Re}G_{\alpha\alpha}^0(E)} , \qquad (10)$$

where $\alpha$ is $s$, $p_z$, or any of $p_x$ and $p_y$ orbitals at the vacancy site. The changes in the density of states induced by the vacancy is then given by Eq. (5). The imaginary part of the Green's functions which is proportional to the spectral densities of states of the perfect crystal and the changes in these densities of states induced by the vacancies are plotted in Figs. 2—7. The top panels of these figures give the relative contributions of the sulphur and cadmium $s$ and $p$ orbitals to the total density of states in CdS. The ionic character of CdS is apparent in this figure, each band being principally formed by one type of orbital, the mixing between them being rather weak. It can also be seen from this figure that the contributions of the $p_z$ and the $p_x$ (or $p_y$) orbitals to the total density of states is almost the same. It is in fact only the introduction of the second-neighbor interactions which differentiates their contributions. The position of the bound states in the gap (if any) can be determined from the zero of the real part of the Green's function. Cd vacancies are found to give bound levels in the fundamental gap, while S vacancies give rise to levels situated in the gap between the conduction $s$ and $p$ cationic states. The positions of these levels are given in Table II. The $p_z$ $A_1$ states are found to be quasidegenerated with the $(p_x,p_y)$ states of symmetry $E$; their separation is due to the second-neighbor interaction which differentiates the wurtzite from zinc-blende structure in which these $p$ states are threefold degenerate. Such interactions have been taken to be rather weak in our calculation, which explains this quasidegenerescence. The
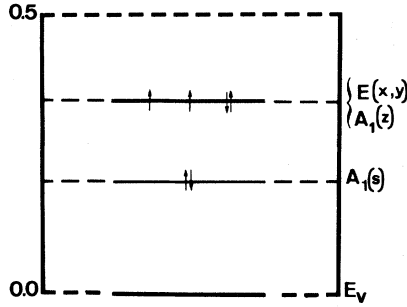
FIG. 8. Position (in eV) in the gap and occupancy of the bound states induced by a neutral Cd vacancy in CdS.

lower panels of Figs. 2—7 give the relative contributions of $s$ and $p$ states to the total change in the density of states and to the phase shifts induced by the Cd and S vacancies. The number of states gained (or lost) in the energy interval $E_1 - E_2$ is related to the difference in the phase shift at the limit of the interval by

$$\int_{E_1}^{E_2} \delta N(E)dE = -\frac{1}{\pi}[\delta(E_1) - \delta(E_2)] . \quad (11)$$

In particular, for each cation or anion vacancy calculation, it is found that when the changes in the densities of states of all symmetries are summed up, the integral of $\delta N(E)$ over the energy bands including the bound states is $-4$ (not counting spin), in accordance with Levinson's theorem, as four states have been removed from the lattice to infinity.

The position of the Fermi level, and thus the occupancy of the bound states in the fundamental gap, is determined by the charge neutrality condition

$$\int_{-\infty}^{E_F} \delta N(E)dE = -M , \quad (12)$$

where $M$ is the number of valence electrons that are removed ($M = 2$ for a neutral Cd vacancy and $M = 6$ for a neutral S vacancy). The occupancy of these bound states is given in Fig. 8 in the case of a neutral Cd vacancy. The twofold degenerate $E$ level is thus partially occupied and is thus expected to be unstable with respect to a Jahn-Teller distortion.

## IV. SUMMARY AND CONCLUSION

In this work we have studied the electronic structure of ideal vacancies in hexagonal CdS. We

have first constructed an empirical TB Hamiltonian describing the energy bands in the vicinity of the fundamental gap. This Hamiltonian, which involves first- and second-nearest-neighbor interactions of the $s$ and $p$ orbitals of the constituent ions, reproduces reasonably accurately the band structure obtained by the pseudopotential method. Anion and cation ideal vacancies were then considered. The densities of states as well as the energies of the bound states were determined by a Green's-function method. Two singly degenerate $A_1$ levels and one twofold degenerate $E$ level are found in the fundamental gap in the case of Cd vacancies, while S vacancies are found to induce levels between the conduction cationic $s$ and $p$ bands.

Several authors[6,20,21] have argued that the ionicity parameter $X = \epsilon_s^c - \epsilon_p^a$ has a major influence on the position of the vacancies' bound states. They found[6,20], in fact, in III-V compounds (where $X$ is $< 0$) the cation (anion) vacancy levels tend to move towards the lower (upper) edge of the gap as the ionicity $X$ is increased. On such grounds they speculated that in the strongly ionic II-VI compounds ($X > 0$) no vacancy levels are to be found inside the fundamental gap. This is in fact what is found here in the case of the anion S vacancy levels which are situated $\sim 8$ eV above the bottom of the conduction band. However, our calculation shows that cation vacancies may induce bound states inside the fundamental gap. Yet it must be said that before definite statements must be made about the precise positions of such ideal vacancy states, more sophisticated self-consistent calculations should be performed, taking into account the change in the charge density produced by the removal of an atom in the solid. Although at this stage a rather crude calculation like this is not to be compared with experimental data, our results are not inconsistent with experimental works[13,14] which attribute levels near the top of the valence band to Cd vacancies. This calculation, which is the first pertaining to defect states in II-VI wurtzite compounds, seems thus sufficiently hopeful to stimulate more sophisticated calculations involving self-consistency studies of vacancies' charged states and calculations of Jahn-Teller distortions. However, it is felt that before seeking more reliable quantitative results, more experimental work is needed, for example, the knowledge of the symmetry of the relaxed vacancies should be very useful for future theoretical work.

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