

An Extended Hückel Tight-Binding Calculation of the Cadmium Structure

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The hexagonal close-packed (hcp) structure of cadmium is investigated by using a crystalline extension of the Extended Hückel Tight-Binding program. It is shown that the one-electron theory, including valence orbitals, is suitable to provide the main features of the band dispersion and to conclude that cadmium has an hcp structure with a large c/a value. © 1986 Academic Press, Inc.

I. Introduction

In order to study heterogeneous catalysis, some adsorbate (an organic compound) interacting with a substrate (the metal), the theoretician has to describe the metal-ligand bonds. This is also necessary for organometallic chemistry, and to transfer the "standard parameters" used in the latter field seems a first reasonable approach. However, for surface science problems where the relation between the two partners might be more important to describe than the substrate alone itself, some parametrization has to be done to improve the bulk properties. Calculations using the crystalline extension of the extended Hückel program EH-TB (1). (Tight Binding) are carried out in this paper to test the method's ability to reproduce the bulk properties of cadmium.

Cadmium is an interesting metal to look at. It belongs to the right extreme of the

Mendeleev table, so that together with rubidium [which is the subject of another study, (2)], it would allow by interpolation to estimate the whole line. Cadmium has an hcp structure with a c/a ratio 1.88, which is a noticeable distortion from the ideal value of $(8/3)^{-1/2} = 1.63$. The Cd-Cd distance is 2.98 Å and the cohesive energy is 1.16 eV [(3), the heat of vaporization is 1.04 eV according to catalog s18806, Sargent-Welch, Chicago]. This paper shows that we are able to explain the structure using the EH-TB method.

The use of a given set of H_{ii} parameters must yield a Fermi level not too far from -11.4 eV, the p atomic level of a carbon, to avoid too large electronic transfer between an hydrocarbon adsorbate and the metal. Therefore, one must assume some values which seem overestimated relative to the usual work function measured if one applies the Koopmans' theorem. Note that this may not be a good approximation because of the polarizability of metallic surfaces which reduces the cost of creating a

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TABLE I
PARAMETERS OF THE CADMIUM ATOM

Orbital	H_{ij}	exp 1	exp 2	c1	c2
5s	-13.22	2.32			
5p	-8.20	2.32			
4d	-19.30	6.22	2.53	0.5946	0.5946

Note. Atomic levels, H_{ij} , expressed in electron-volts and Slater exponents, exp. The d functions are double-zeta type.

localized charge. However, assuming that the electronic distribution of the crystal is not significantly distorted from that of the element, a first estimate from the ionization energy of the cadmium atom leads to a Fermi level at -8.99 eV (4). Within such a frame, we will try to determine a set of parameters suitable to improve the description of the substrate itself.

II. Calculation

In these calculations, the H_{ij} matrix elements between Bloch sums are deduced from the S_{ij} , H_{ii} , and H_{jj} values by using the weighted formula (5). The total energies result from an energy averaged over a set of k points as determined by Chadi and Cohen (6). Parameters are listed in Table I, they have been adjusted to reproduce the band structure published by Morruzzi *et al.* (7) which concerns the fcc structure with a Cd-Cd distance of 3.13 \AA , a structure with the same density as the real one. Our result is presented in Fig. 1. The H_{dd} value being fixed at -19.30 eV, the Slater d exponents have been optimized to reproduce the band width at Γ , X , and L . The bottom of the s band is fixed at 18.32 eV, 1.32 eV above the highest d level as in Ref. (7). As it is pure s at Γ , this value depends only on two parameters, H_{ss} , the s atomic level and S_{ss} , the overlap between the Bloch sums. These two are therefore related by the Wolfsberg-Helmholtz formula for the contribution

from different cells. This leads to the following relation between the Bloch terms:

$$H_{ss} = 18.32/(1.75 - 0.75/S_{ss}).$$

The Slater exponent of the s orbital is adjusted through the S_{ss} term to fix the s band width between Γ , X , and L . At the edges of the Brillouin zone (B.Z.), X and L , the s band is above the first p . The s - p crossing between the center and the edge of the B.Z. is responsible for the cohesive energy of the system. Some p bonding character is introduced while some s antibonding character is eliminated. The p Slater exponent has been assumed identical to the s exponent. The H_{pp} values is fixed in the same way as the H_{ss} by adjusting the energy values of the band at X and L .

III. Results

Figure 2 shows the total energy curves of four postulated cadmium structures (bcc, fcc, ideal-hcp, and real-hcp) as a function of the volume of the cell. All of them present a minimum for the same volume. This corre-

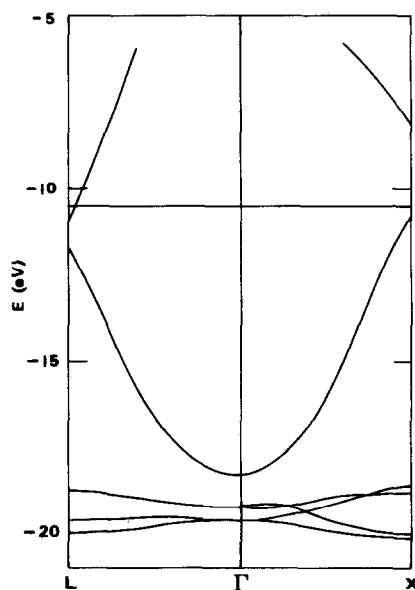


FIG. 1. Band structure of the fcc lattice.

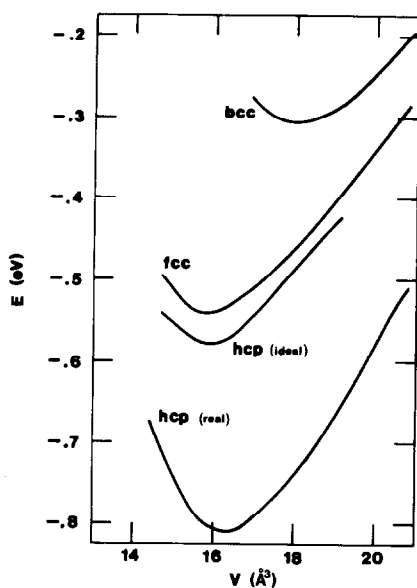
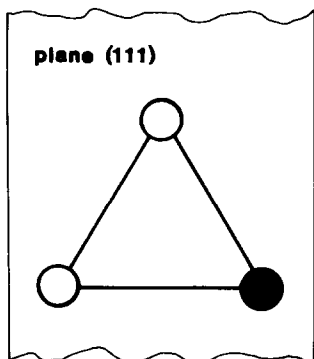


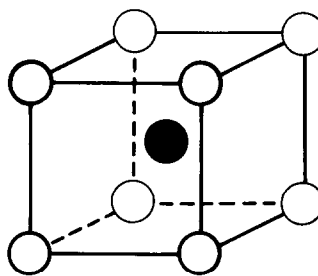
FIG. 2. Cohesive energy curves for the different crystal structures versus the atomic volume.

sponds to a Cd–Cd distance of 2.84 \AA , 5% less than the experimental distance. This is a remarkable result for the EH-TB calculation which does not include explicit repulsive terms. It can suggest that the metal–metal distance is mainly controlled by the valence orbitals.

The real hcp structure is calculated to be the most stable with a cohesive energy of 0.81 eV; the ideal-hcp and the fcc structures are found quite similar with cohesive



SCHEME 1



SCHEME 2

energies of 0.57 and 0.54 eV, respectively; the bcc structure with a cohesive energy of 0.30 eV is found to be worse. The Fermi level of the real hcp structure is calculated to be -9.4 eV , close to -8.99 eV (4), the ionization energy of the element.

In Fig. 1, it is clear that the d band can be considered as a set of core orbitals and that one low-lying band above them is filled. This one is essentially the s band which mixes at the edge of the Brillouin zone with some p . If we consider that in a first approximation, the s band is filled, the struc-

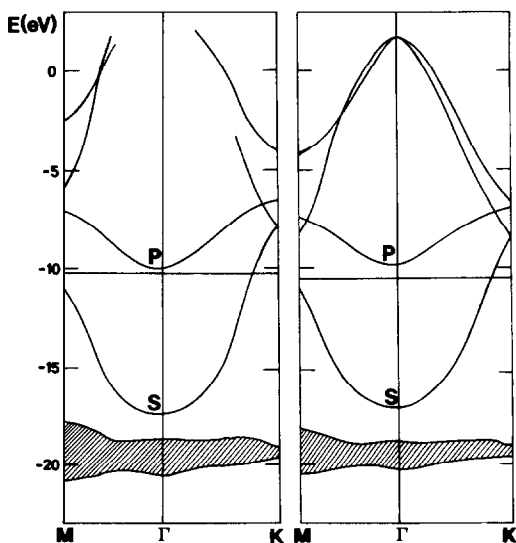


FIG. 3. Band structure of the two-dimensional hexagonal lattice (one (100) plane of the hcp system or one 111 plane of the fcc system). The shaded regions correspond to the d bands.

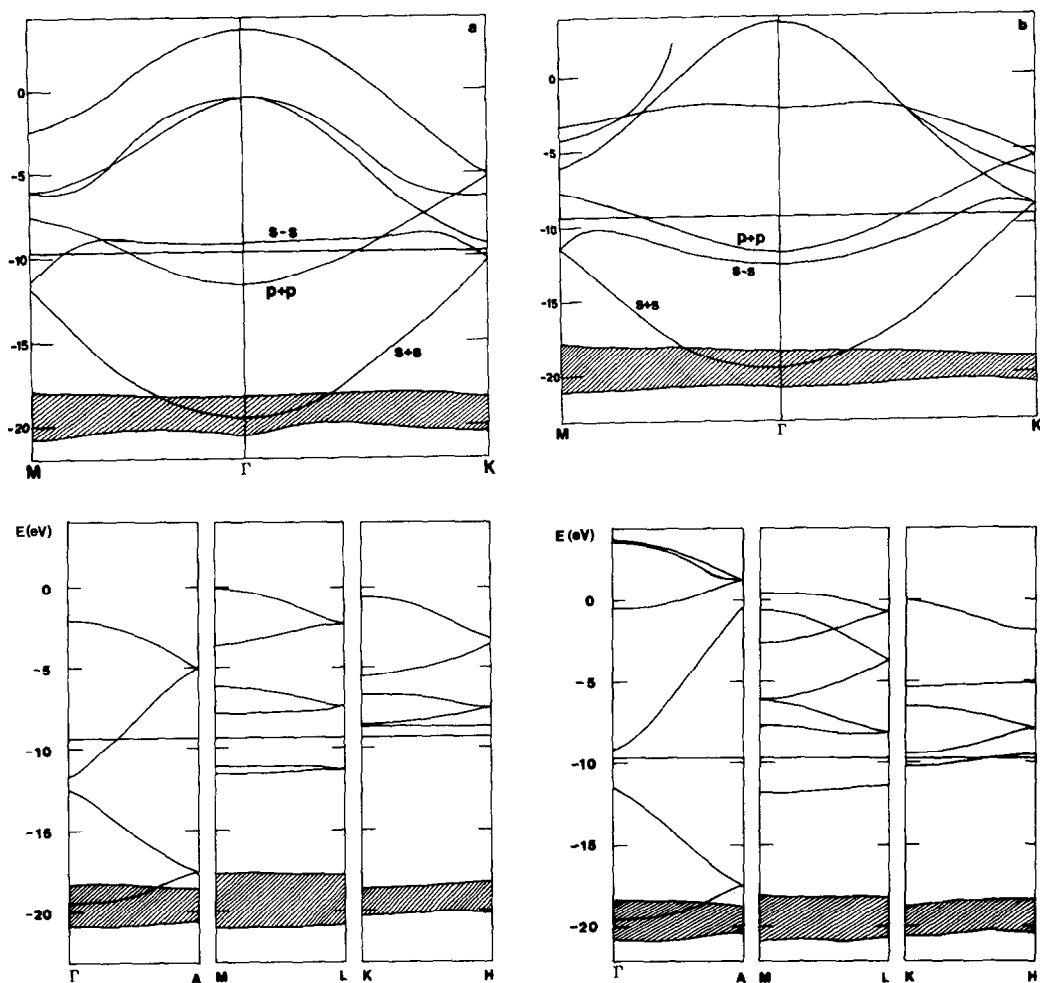


FIG. 4. Band structure of the hcp lattice (a) ideal $c/a = 1.63$, (b) real $c/a = 1.88$. ΓK and ΓM account for the wave vectors pointing in the hexagonal planes and ΓA , ML , and KH correspond to the wave vectors perpendicular to those planes. The shaded regions correspond to the d bands.

ture has to avoid introducing large $s - s$ antibonding character. The bcc is clearly inadequate for that; indeed in a bcc structure the atoms can be divided into two sets forming an alternant system, all the eight first neighbors of an atom from one set being attributed to the other. Such a system allows the maximum antibonding character (see Scheme 1). The highest crystal orbital is out-of-phase between all the nearest neighbor atoms at the edge of the B.Z. It is not the case for the fcc and hcp structures

because they possess triangular patterns in their planes of high density (see Scheme 2). The presence of triangles makes it impossible to divide the atoms into two sets (non-alternant system). Two atoms which are bound out-of-phase to a third one in a triangular mode are related "in-phase" to one another. No such large antibonding character as in the bcc structure can therefore be introduced. This explains why the bcc structure is not adequate for cadmium.

In Fig. 3 are reproduced the band struc-

ture of the (100) plane of the hcp systems (ideal and real). The real situation corresponds to a contraction of the structure in the plane. This one corresponds to an increase in the s/s overlap and to the best situation.

In Fig. 4 are reproduced band structures for the hcp bulk structures. Figure 4a concerns the hcp structure with the ideal c/a ratio of 1.63 and Fig. 4b, the real one with the c/a ratio of 1.88. Both structures have the same density. As the unit cell of the hcp structure contains two atoms, there are now two occupied bands over the d bands which have mainly an $s + s$ and $s - s$ character, the + or - qualifying the phase between the two atoms. The in-phase combinations are rather insensitive to the distortion. Indeed, this one only induces a small relative variation of the overlap term, which is large. The antibonding levels $s - s$ and $p - p$ exhibit much larger relative variations. At Γ , the bottom of the $p + p$ band (a bonding crystal orbital) lies under the Fermi level. A small portion (with the largest bonding character) of the $p + p$ band is filled. Along the Γ -A, the M -L, and the K -H directions, the $p + p$ band is very flat and remains close to the Fermi level. Decreasing the c/a value increases the p_z/p_z splitting and the s/s splitting. This can be seen by comparing Figs. 4a and b along the Γ -M and the Γ -K directions. The $s - s$ band is pushed up above the Fermi level in the ideal situation (the smaller c/a value). This explains the difference in stability of the two structures. The raise of the $s - s$ level is not compensated by a significant lowering of the $p + p$ level. The Fermi level of the ideal structure is very slightly pushed down. This corresponds to the existence of flat p energy surfaces close to the Fermi

level (see Γ -A, M -L, and K -H). The averaged s value of the two s levels at Γ is a reminiscence of the in-plane bonding character. This value is for the real case 1.66 eV below the ideal case value. The splitting of the two levels results from the interplane interaction. It is smaller for the real case (7 eV) than for the ideal one (10.3 eV).

IV. Conclusion

hcp structure is observed because it allows a distortion c/a which does not exist for the fcc. Without this distortion, the two structures are found to be very similar. The distortion is the result of the large s occupancy. It allows a decrease in the antibonding character of the high-lying occupied s states. EH-TB calculations, though limited to monoelectronic terms and to valence orbitals, provide a correct order of magnitude for the intermetallic distance and the cohesive energy. It leads to the correct structure and is useful in explaining it.

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