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Self-consistent LCAO calculation of the electronic properties of graphite. II. Point vacancy in the two-dimensional crystal

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The electronic properties of a point vacancy in the two-dimensional graphite crystal are investigated within the Small-periodic-cluster approach using a self-consistent all-valence-electron LCAO (linear combination of atomic orbitals) scheme previously employed for the calculations of the band structure and optical spectra of the regular lattice (part I). Eight crystal bands, 54-96 K points in the Brillouin zone, selected according to the "mean value theorem" and 2 -5 primitive unit cells around the defect site are allowed to interact. A doubly degenerate singly occupied cr defect level is shown to appear in the

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systems, suggest' "that roughly 50 to 70%%u~ of the
defects wave function is localized in a "sphere» surrounding the defect and its nearest neighbors, the remaining tail of the wave function extending onto more distant atoms.

This has a twofold implication: in toms of the theories using the band structure of the regular lattice for

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ready yields a distribution of P'-K, points with weights proportional to the volume they occupy in the BZ, selection of several such%, points ac-cording to the mean value theorem should furnish a good verisimilitude to the totality of points in the BZ. The accuracy of the average of an expectation value calculated from the mean value points is determined by the smoothness of the bands. Owing to the substantial lowering of the dispersion of the original bands in the small BZ representation, this accuracy improves. One canthus set a complete self-consistent calculationon aperfect solid by defining a large unit cell and solving for Bloch type states. in that system using a small number of well-chosen eigenvectors to obtain the ground-state charge density at each iteration. Since the number of general K points projected into a single R point in the SBZ increases rapidly with unit cell size (e.g., Table I}, one might also hope to obtain accurate estimates of properties determined by averaging over the BZ, such as the total energy per atom, elastic constants, etc., by using a few k point repr esentatioris.
This small-periodic-cluster (SPC) scheme is obviously inefficient when one is interested in Perfect periodic systems, (since the large P'h& xj'ho secular equations can be evidently block diagonalized to P' equations of order ho aha using the translational invariance in the primitive unit-cell basis.) We are using it in effect only for de-fect problem, where this type of translational in-
variance does not exist. This is simply done by
repeating the solution of the eigenvalue problem
in the SPC representation after rePlacing a host
atom in the large unit cell by a vacancy. The
self-consistent solution of the Bloch problem in a
vacancy containing large unit cell (P'h —l atomsc4.04 345.848 Td 0.73 Tfhi3 8.36 Tf 1Tj E4.14rding 68lock

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(a) The large number of interacting states in the model result in large dimensions (p'ho &&p'h&x) of the secular equations (each element being a, lat-tice sum in itself) to be solved. This forced us to restore to rather simplified LCAO algorithms (the modified iterative extended Haeckel) for cal-culating the matrix elements. This is certainly an undesirable feature of the present treatment. However, as demonstrated in the previous paper (I), a judicious choice of the I CAO scheme, using only a few parameters taken oyer from essenti-ally atomic (and not solid-state) data, is capable of revealing excellent agreement between experimen-tal and calculated optical interband transition ener-gies, photoelectronspectroscopy (ESCA) data, secondary- electron-emission data, Fermi-surface characteristics, bond lengths,

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tion to this highly localized o defect level, the
valence o band contains an entire distribution of

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of a spin unrestricted Xa cluster calculation for a vacancy in diamond. The situation met in graphite is, however,

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energy by 1.8 eV and by an increase in the degree
of localization of the defect level, from 78 to 86%%uq.

'

The stabilization of the total energy arises from the charge rearrangement in the nonlocalized band
states.

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The increase in the localization of the
defect wave function makes it easier to approach the limit of uninteracting defects in our superlat-tice model when the system is treated self-con-sistently. Self-consistency effects are thus of considerable importance even in the homonuclear

systems and cannot be neglected. ' ' '

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conclusions on the importance of self-consistency and screening effects in defect calculations have been previously emphasized by several auth-
OrS 25 ~ 6 1 ~ 62
The energy required to separate a carbon atom from the cluster and to bring it to infinity in its ground atomic configuration (vacancy self-energy, E„)was calculated from

E„=E„,(N) —[E„,(N —1) +E„,(1) +Euro]j, (2.)

where E&,t (M) denotes the total energy of all the occupied states of a cluster containing M atoms and Ep denotes the promotion energy from the valence sp' state to the ground atomic 'P config-uration. E„,(N) and E„,(N —1) were calculated by sampling the six special points in the C» —G„V and C„—C„V clusters and the promotion energy
was taken from the theoretical results of Goldfarb and Jaffe.

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At this level of approximation, ' E„,(N)
is minimized with respect to the perfect-crystal
unit-cell parameter (yielding a;„=2.482 A com-pared with the experimental value a =2.46A,) but E„,(N - 1) is not minimized with respect to relax-ations of the lattice atoms around the vacancy site. In this static approximation we obtained E„=12.56 and 12.61 eV for C»V and C,9V respectively. The energy of vacancy formation E„fin the unrelaxed latt-ice is. given by subtracting from this the sublim-ation energy E, gained by the system when
the ejected atom is adsorbed on the crystal sur-face. Using the experimental value" E, =7.40 eV for the sublimation energy, one obtains E&- =5.2 eV. Comparison with experiment will be dis-cussed in Sec. IV Bwhere relaxation corrections will be introduced. In our previous calculation on vac-ancy formation" avalue of E~ =3.0 eV was obtained where only the % =0 point was sampled and the
] 7V and C» V clusters were used in a simpl e itera-tive- extended-HUckel calculation, using slightly different atomic parameter. The loss of ~ energy alone upon vacancy formation is calculated here to be 2. 1 eV. This is smaller than the m energy per atom in the regular lattice (part I) signifying that the rearrangement in the electronic structure accompanying.

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FIG. 6. Electrostatic potential difference (in arbi-trary units) between perfect and vacancy-containing clusters, computed from the total valence density along the line shown in the insert to Fig. 5. Site 6 denotes the vacancy, upper numbering refers to Fig. 5.

l6

function receives contributions mainly from the highest occupied o valence bands, justifies the use of the extended-Huckel approximation for des-cribing this state. In a previous paper (part I) it has been shown that the EXH approximation used here yields excellent agreement both with experi-mental data and with first-principles band calcu-lations on the valence bands whereas the high con-duction bands lying some 10 eV above the Fermi level are not properly described by this approxi-
mation.

Figure 6 shows the difference in the electronic electrostatic potentials between the perf ect clus-ter and the one with a vacancy.

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Qa Qe Qs
FIG. 8. Illustration of the three normal modes

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y'(A)

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- FIG. 9. Degree of localization of the defect wave function, energy (ez) of vacancy level, and the vacancy binding energy (E&) (relative to the -unrelaxed vacancy) obtained for the symmetric a' relaxation. Positive-values of the changes in bond length, y indicate inward relaxation.

tion effects accompanying the vacancy formation occur in the more polarizable m system rather than in the relatively rigid 0 system. The relax-ation induced bond shortening associated with the o defect orbital alone [Fig. 9(b)] constitutes only a part of the total bond shortening that results from the stabilization of all occupied bands [Fig. 9(c)]. In fact, most of the stabilization gained by the a' relaxation comes from the n system that forms a part of the occupied valence bands. Though the system is loosing 2.1 eV of its m ener-gy upon vacancy formation, almost 0.80 eV are recovered by the bond shortening accompanying this relaxation.

We now turn to evaluate the role of the Qe and Q, Jahn-Teller distortion modes. These distor-tions will have a direct effect on the defect orbi-tal through both linear and nonlinear Jahn-Teller coupling. Before giving the results of the calcu-lation we briefly discuss the nature of the defect orbitals involved. The doubly degenerate e' de-fect orbital can be described using the defect molecule notation" by t'mo orthogonal hybrid func-
tions:

(4)

where Q„&f&~, and P, denote sP' hybrids of the three dangling bonds associated with atoms a, 6, and c,

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The vibrational

emotion in the well is characterized by &u =410 cm '. The rotational energy of the theory is n=0. 02 eV so that the following ratios are de-
rived:

EJT/he =0.45, p/n= -0.2,
-8.0—

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FIG. 11. Degree of localization of the defect wave
function, energy (~„) of the vacancy level, and the
vacancy binding energy (E&) (relative to the unrelaxed
vacancy). (a) Q& relaxatjon. (b) Q, relaxation.

compared with the value obtained for the- a' distor-
tion Q'P"=y" 3 y' =-0.113 A. The degree of local-
ization is shown to drop to about 83% due to the
outward relaxation. The change in the localization
due to lattice distortions [Figs. 11(a) and ll(b), top] follows different patterns in the Qe and Q,
modes; while in the former case the take off is
characterized by a rather steep slope, in the lat-
ter case a vanishing initial slope is manifested. ' The parameters characterizing the Q~-mode Jahn-Teller effect can be easily extracted from
our numerical calculations (Fig, 11) using the
standard form of the Jahn- Teller Hamiltonian.

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From the mean depths of the wells in the bottom parts of Fig, 11(a) we obtain E&T-0.023 eV arising from the linear vibronic coupling, while the dif-ference between the well depths or the comparison with the well depths in Fig. 11(b) yields the
strength of the ndnlinear coupling as P =-0.04 eV. The notation of Ref. 69 (see glossary there) is followed. The figures lead to a force constant of 1.2x10' dyn/cm compared to about 5.6x10' dyn/cm
obtained (paper I) for the perfect lattice and to the
value of =6.7x 10' dyn/cm deduced from experi-

Normalized amplitudes of distortion at equilibri-
um are:

Qe'" ——v 6 y;„=0.068 A
and

Qm =42 y' =-0.068 A

indicating moderate linear and weak nonlinear coupling. Other vibronic parameters of the sys-tem (using the definitions of Ref. 69), are:
L —= 0.082 eV; K=0.023 eV, and 1V-=O, L, K, and N being the linear, quadratic, and cubic coupling
coefficients, respectively. The numerical values
given ln tIlls section lnvolvlng as they do high-or-der energy derivatives, must be accepted as merely aPP~oximative. The following qualitative conclusions are, however, significant: the stable

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would expect a slightly larger hE '

value in gra-
phite. These arguments would suggest roughly
E„f=4 eV in graphite.
.Both the macroscopic model and the corrected
defect molecule model lead-to values of E„f that are in substantial agreement with that of the pre-
sent study. Phenomenological models using var-
ious forms of atom-atom potentials seem rather crude for systems containing both a relatively rigid 0 skeleton and a polarizable m system. It has been realized some time ago"'' that simple atom-atom potentials that neglect the many-body coupling of the atoms surrounding the given atom-ic pair, fail to predict the stable conformation and the correct lattice dynamics of aromatic and ionic crystals and one has to introduce a quantum-
mechanical description of the role of the delocal-
ized m system on the potential surface.
The average theoretical contraction ha/a of the basal plane of graphite due to relaxation of the
atoms around a.single vacancy, was calculated in

the present work to be -0.18/o per bond. The ob-
served value (b,a/a), bs obtained by irradiating at
- 196 Q (where defect aggregation is assumed to be very small) can be partitioned into a contribu-tion originating from a Poisson-ratio effect"

"

denoted (~a/I). and to the vacancy-induced Poisson
relaxation part (b,a/a)„„. The former contribution arises from the increase in the c spacing hc/c due
to interstitial formation and is proportional to the
compliance ratio S»/S», i.e., (ha/a)p„.,„„=(hc/c) (S»/S»). Using the observed Poisson ratio" and the hc/c and b,a/a values measured by Pluchery'
and by Henson and Reynolds, '

one obtains (Aa/a), «
- —(0.13-0.05)%. Only rough agreement is obtain-ed with the present extended-Nickel SPC calcula-
tion. Using an average bond-order bond-length
correlations" in a simple m-electron model,
KeQy'~ obtained a theoretical estimate of C„' (La/a)„„=-0.14 where C„' is the number of atoms associated with each vacancy. Since in our model only the bonds involving the three nearest and six
next-nearest neighbors ar e affected by the presence
of the vacancy (i.e., C„' =9), our results can be
written approximately as C „'(b.a/a)v« -0.144 in
good agreement with Kelly's suggestion. It thus
seems that although the simple semiempirical LCAO technique employed here is too crude for
obtaining realistic atomic conformations at equil-
ibrium, the overall expected trends are correctly
reproduced.
The energetic position of the vacancy level with respect to the valence crystal bands can not at prese~t be conclusively compared with experi-
ment, owing to the lack of detailed optical spectra
of irradiated graphite. A preliminary study of the
optical spectra of neutron irradiated graphite88 at

80 'C revealed an absorption at 2.6 eV that disap-
pears completely upon annealing and is not present
in the unirradiated samples. Since only neutral

vacancies are expected to be stable at normal con-n ditions,

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