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Electronic structure of transition-atom impurities in semiconductors:
Substitutional 3d impurities in silicon

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The electronic structure of neutral substitutional 3d transition-metal impurities in an in-
finite silicon host crystal has been calculated for the first time. The calculation is carried
out self-consistently in the local-density-functional formalism to within a high precision.
We use nonlocal, first-principles pseudopotentials and the recently developed quasiband
crystal-field (QBCF) Green's-function method. The elements of the electronic structure of this system are discussed in detail. The calculation reveals the chemical trends in the defect energies (gap states as we11 as resonances) for the impurities Zn, Cu, Ni, Co, Fe, Mn, Cr, V, and Ti, as well as the regularities in the density of states, wave functions, charge distribu-
tions, and screening potentials. For charged impurities, the model explains the remarkable
occurrence of many charge states in the narrow-band-gap region through a new self-regulating mechanism analogous to the homeostasis control in biological systems.

I. INTRODUCTION

A minute contamination of 1 titanium atom per
10 silicon atoms is sufficient

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atom itself. ' For example, a diffusion of a transi-
tion atom into p-type silicon near its melting tern-
perature followed by a relatively slow quenching (a
rather loosely quantified quantity') often produces
impurity-acceptor pairs. A more rapid quench-
ing, however, can also produce isolated interstitials.

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In an all-electron representation, v~, '~'(r)
Z—~/r, where Z~ is the atomic number of atom
P. In

a pseudopotential representation, the effects
of the Zp

—Z~ core electrons are replaced by

a static

external potential. Hence u~, '~'(r)PL

p

is the bare

pseudopotential of atom

P acting on the Lth

1194

a„=0.8
—12.8
0.0
2.88
3.49

—12.5
0.0
3.20
3.78

8.75 —8.32 —2.98

1.39

1.21 —10.21 —7.24 —1.30

2.02
4.11

r, „
I 2s, u
I 15',c
I2,
Ii2

X)„
X4„
X),
Indirect gap
L2', v
Li, u
L3,v

L),
L3,

3.2'
4.15 +0.05'
8.3 +0.1'

—8.48 —3.14
0.78

0.60 —10.39 —7.52 —1.36

1.60
3.69

—2.9'

—9.3 +0.4"
—6.8 +0.2'
—1.2 +0.2'
2.02+0.2'
3.9 +0.1'

TABLE I. Calculated self-consistent single-particle band structure of silicon with the semiempirical local pseudopotential of Ref. 26, employing an exchange coeffi-cient u„=1.For comparison, we give also the results for a„=0.8 and experimental data (Refs. 27—30). The zero of energy is set at the valence-band maximum. The unit-cell volume used is twice the atomic volume 135.188

a.u.. 181 plane waves are used at the I point and a
comparable number at other k points. The self-consistent screening is constructed from the lowest 1471 plane
waves. Four special k points are used to obtain the
ground-state charge density. All components of the pseu-

dopotential up to a momentum q =6 a.u. are included.

Level o,„=1 Experimental —12,5 +0.6'

predictions that reAect the underlying local-density theory (not the computational approximations to it, such as finite clusters, muffin-tin approximations, semiempirical tight-binding parametrizations, etc.) to a level of precision of about 0.1 eV in energies and 1—2% in charge density and potentials. A new computational scheme '

recently developed by us
enables one to achieve this objective very efficiently for an entire group of impurity atoms (e.g., the 3d row) with only modest investment of computer time.

D. Approach

We use the quasiband crystal-field (QBCF) self-consistent Green's-function method. The method was described in detail previously. For our present discussion we need only to describe the wave-function, potential, and density representations. These definitions will aid the analysis of the results (Sec. III).

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structure of isolated atoms. This is done by defining in the host crystal a region r &R, where both VH"'(r) and Vrv'(r) are removed (hence the potential there equals the constant host vacuum level). We have placed in this vacuum the screened pseudopo-

tential [vv,'~(r)+v"'(r)] of a free transition

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If a defect state could have been constructed solely from the Mb pure-host-crystal-band wave functions, then a&~ ——1, whereas if the local quasibands are needed, then a LQq would be sizable. Recall that in the effective-mass approximation Mb = 1 for donor state (Mt, ——3 for acceptor states), a its ——1, and a LQz ——0, and that in tight-binding models Mb ——8—10 and a~QQ —0.

4. Charge-density population analysis

It will be of interest to us to establish the total amount of electronic charge in the central-cell re-gion and its distribution among various I com-
ponents and representations a. We will hence define
Qt to be the electronic charge contribution within
the central-cell region from the 1th component of all
occupied states belonging to the nth representation:
OCC 8

Qt =gN~ f [Gt;(r)] r dr. (15) ~Q =(Q)impurity (Q)vacancy ~ (19a)

properly renormalized by its self-consistent interac-
tions with the host. This requires the definition of
an arbitrary reference state that represents the host
before a substitutional defect is introduced into it.
For this reference state we select the self-consistent

silicon-vacancy system calculated in Ref. 34. We conceptualize that first one prepares a vacancy and then drops into it a noninteracting effective impuri-ty atom that produces an overall electronic distribu-tion which is identical to that of the interacting sys-tem. The effective impurity atom may be different
in its electronic structure from the isolated free-
space impurity atom; that is, it may have nonspheri-
cal components in its charge

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6.

0

-(111) (111)

(a)— (b)

f111)

0.10

IQo 0.08

5.0—

IQ

4.0-

C

3.0—

IQ
CS

2.0—

0$ V 10-

-(111) —Total charge

sgel

Si:Zn --a, only

h
tl

I

IDI 004
0$ V 0.02—

1

l
I

l
I

l

1l
:l
i:

I;

1[' 0 -2

2

0.00

-

—-—'

- 5 -4 0.0 -3

4

5

Disiance {a.u.

)

states with

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15

10

0
0.0 0.5
0.06

0.04
~ ~

0.02

I
L 0.00

~ ~

g -0.02

Q
0
o -0.04

I

& -0.06

0.04

0.00

-0.04

-0.08

-0.12

ll

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0—
-2—

-4- L

-8—
- 10

7

a 6

.

'' L=2

V '"'(r)
i:Ni

y V
Si ZNi="6

V V

ZSi ZNi

- 10

.

'

L=2

-ZF =-26 Fe

rgy, (r)
Si:Fe

V V

ZS.-ZF — 4

r Ayf (r)
Si:Fe

3

100]

rWP" (r)

[X100]

0

00]

V V

ZSi+ ZFe
/=4
[X100]
~ ~ ~ ~ ~

0 4 0

Distance (a.u.)

FIG. 4. External pseudopotential perturbation1 423.68 TdG4 (~)Tj4.

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10
K

8
V~

I I

(a) f'=O
Si:Nl

Si:Fe

0.16 i

0.08

0.04

12 si Ni
/
/
/
/

/ ~

~

/ Exchange
/

/
/ /
/ /

"0.04—

-0.08—

-0.12-

Si:Ni

-0.20 =
6

Distance (8.0.)
'

FIG. 7. Spherical (a) and lowest nonsp ns herical ena (b) components of the r-multip lied I directe Coulomb and exchange screen-ingpe rt urbations for Si:Ni and Si:Fe.

Proaches its point-ion imit of —Az'. Consequent-
y, the total screened perturbation
=6V"'(r)+6V'"'(r) of Eq. (4) is positiue for
I')RN. F'igurC 6 displays on an expann ed scale

V' (r) in the outer central cell. For. r hV 0 & r
nt of the seu-

doopootential en i perturbation), the net effective ec ppotential is ncgativc, tive due to th e dominance om of the attractive
AV'"'(r) over the repulsive b,V', '"'r)r term (compare
1 in Fi s. 4 and S and their

sum for r (1.5 a.u. in Fig. 6). Hence the e ective b, V' screened perturbation (r) delineates e the central '
cell into two distinct regoins, w..ere R orms t e

oint. In the inner central cell 8') the effective potential is attrac iv
and its depth follows the ordering of the barc p

scu-

6V AV g AV g AV etc. Th
3d wave functions of the free T, as we
wave functions of localized TA impurity states in
'1' silicon, are largelyge confined to this region. Hence theor derof effective e potentials also re ec s
der of the 3d ionization energies Ip of free transition I I &Ic, &IT;), as well as the order of

h t central cell the overscreening e ect
causes the effective perturbation to be positive, wi a reversed order o

.

Sif 112.57 138.53 Td (t)7.79 455.7 BT /Xi1.73 Td 38/Xi11 9.12 Tf 123.36 182.455.7 B/Xi11 hV

'

6).

this ~Xi11 10.43 Tf 76.37Xi11 47 Tf 230 Tf 145.4"» Td (AV)Tj ET BT /Xii11 9.42 Tf 2.9 T7 227.0'6 Td (&)Tj ET BT /X111 8.83 f 29426 478.46 Td (the)Tj E free of

their 1

to potential

ori(energies)Tj ET BT /Xi11 9.17Xi1184.1 371.7(Ti6 Td ())Tj ET BT /Xi1 8.51 T913.0283831 Td (as)Tj ET BT /Xi11 5.571Tf 23.35 372.1show Td (an

'1' ect Z)i6 Td ())Tj ET BT /Xi11 8.08 Tf 1200.2 171.9associatscreened si

i

impurity

h

localized

functions wave

scr/Xi11 5.46 th

Si:Fe. "0.

states

f

the
h

Fig.

ere

P

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density fluctuation; cf. Fig. 2). This screening
length is considerably shorter than that expected
from a point-ion Thomas-Fermi model, for a sil-
icon vacancy, or from the bulk linear screening
used in effective-mass calculations. Second, it is

seen that although the screening of the s and p per-turbations are similar (the small-r divergencies result from the occurrence of turning points at Ro and &i for the I.=O and L=1 pseudopotentials; cf. Figs. 4
and

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TABLE III. Energies,

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I I I

0 6

- V8CIflCQ
/
0.4

0.2

0.0

P=-q

[X5]

I

Si:Zn~.

~~ [X5] /
I

-0.8 ——

l"=3

[X25]
l I t I I
C
0 0.8 (

Q
C
U.

Ol

0
N
C
I
c -04- 0
Q. -0.6
0
-0.8—

I S I

Si:Cu

0.4-
[X2]

a p

-0.2

I I I I

I t l I I
0.8-
06 - Si:Fe

0.4
fX2]
0.2-

0,0
-0.2
-0.4

-0.6

-0.8

1 + W I

Si:Ni

Si:CN

repulsiveness as Z decreases. The energy of the
more localized defect levels (as well as the 31 energy
of the free atoms) is controlled by the short-r
behavior (r (2 a.u.) simply because most of the
wave-function and potential amplitudes are confined
there [cf. the (r) 3d values for TA. in Table IV (Ref.
43) and the 1=2 components of the impurity wave functions in Fig. 10]. As Z increases, both the
atomic 3d orbitals and the d portion of the defect
wave functions become more localized. Hence the

positive kinetic-energy contribution to the orbital
energy e; increases with Z. The faster decrease in

gs I t 1 I I l I I l~

0 1 2 3 4 5 60 t 2 3 4 5 6

Distance (a.u.)
FIQ. 10. Angular momentum components G~ (~

r ~

)

[Eq. (Scl] for the tz dangling-bond-hybrid wave functions
of substitutional 3d impurities in silicon, and the silicon
vacancy. Note the various scale factors for the different l components.

the negative and larger potential-energy contribution
causes the well-known increase in binding energy
of atomic 3d orbitals with increasing Z (Table IV). The same behavior occurs for the 3d impurities
whose binding energy (relative to the VBM) in-
creases with increasing Z. The binding energies do
not follow the (reversed) order and the magnitudes of b, V' (r) in the outer central-cell region simply be-
cause the overlap of the wave function and AV' (r)
is far larger in the inner central-cell region.
Notice that the energy of the vacancy t2 level DBH is lower than that of the impurity atoms lighter than Co (Fig. 9) despite the fact that the vacancy poten-tial is more repulsive than the impurity potential. The reason for the absence of pinning of the impuri-ty levels by the vacancy level is that whereas the large and localized I =2 components of the impurity
wave functions have a large positive kinetic contri-
bution to e; (including the centrifugal term), the
smaller and diffused l =2 components of the vacan-cy wave function come with a smaller kinetic term. Thts effect ts mtssed by ttght-btndtng cajcuiattons.
The amount of p-d hybridization in the DBH is
shown in Fig. 11, where the percentage of p and d
charact«[qt; tn Eq. (11)] is depicted across the 3d
series. The DBH begins at Si:Zn as a predominantly
p state (coupling with p-like valence-band states, cf.
Table II). It reaches a 50%—50% p-d character
near the center of the 3d series, after which the p
character increases a little on account of the renewed availability of nearby p-like host states (this time, from the conduction bands). The large extent of p-d hybridization found near the Fermi energy is not en-tirely surprising; it is often found in inorganic chem-
istry of transition-metal tetrahedral coordination
co~pounds [e.g., 25% p character

in377.2 349.31 Td (nearby)Tj E368.96 c4T BT /Xi120.ln4 338.1earbBT /Xi15 8.83 Tf 49.05 rifugalCumcBT /Xi15 9.17 Tf 408.04 .169 Td (Iution)T2

—

[X59 ET BT /X6 Tf i15 8.71 T244 301.66 Td (t)T13tive

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TABLE IV. Summary of calculated ground-state one-electron atomic energy levels in eV. The results of the local density (LD) and Hartree-Fock formalisms (Ref. 43) (HF) are shown. The typical size of the atomic d shell is given by the orbital moment (r) 3d in atomic units. Although the LD results for energies are consistently below the HF results, the two calcula-tions produce nearly parallel trends.

Atom Configuration

LD (a„=1)
P —E'd

HF

Zn
Cu

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100% d state, whereas the t2"" is 80—100% d-like.
Both crystal-field resonances commence at the Si:Zn
end as very localized states (percentage of localiza-
tion, 90—100%). In contrast to the DBH,

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M

CCl

z
M

0

M

Oo

I

U'

ch

0

O
V
~ &

Ch
~ W

CC1
CCl

~ 0T~~l

0

~ IH
U5

(0
bQ

U

Ch OO W ~ Ot O~ t Chest

QO

o II

OO ~ M Ch

OG M OH&ooo

~ ~

~ TE M

OOOO QQ

Ch
Ch oo t

O ~

O O rl. Q Q C

O Q Oo
Q Q Q Q

O

O
~ Oo

o II

Ch
Ch W t

O ~ t Q Q

~ ~

~ M

V0CO~t
OQ OOOO

oo HO
Q rt
O O 4 Q O rl.

rl. rt. OOo
Oo OOOO

8
cd

II II II II II ~
o
E

~ ~

~ l~~l

t &Mt '4DO&t -' ~ a' «5 o „II

0

Ch O W w HOW&)n
OH~OOt

Ch
OO

rl O OOOOOQ

O W
Q
QQWOQW

O OO rl O%
OOOO

Oo

O O o II

OO

o w '40 «5 «5 ch

Q Q OOOO

OO OO

O ~
OOWOOW

Q OOOO

Q
II II II II II ~

t2" peak at e[t2]=—0.88 eV. The availability of a high host tq density of states at this region leads to their substantial mixing into this state. This is re-flected by the high percentage of valence-band char-acter for Si:Cr (Table II). These examples illustrate how the details of the host band structure, together with the depth of the external perturbation 5VL"'(r), control the nature of the defect levels. In sharp con-trast to effective-mass impurities, the wave func-tions and energies of the deep Si:TA states are not controlled by host band-edge states.
There are four notable features in the variation of

the main defect levels t2, tq", and e

" with the
impurity

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cdV
cd

0
~ O1K
~ 1+0

'a

cd

MP
V

CA

M

0

I

U'

ch

0

V
CP

Y)

~ 1H
Ch
~ ~

cd
cd

~ 0f~~l

C4 0

~ W
QO

'a

bQ
cd

O
Q

O~'4 OO
Q Q ~

0

Ql

V~ p~l

M
CA

CA

CA

N

QNOOOt

V
cd

M t

rt. O ~ OOOOOO

Ch

OOO rt' QONOON

OO O Q OOOO~

~t ~V)t

Ch ~ Ch
Ch M t

OO Q Q 0

t '4)Mt

Ch m Q t

Ch Q O~nOOt

OO~ OOQOOO

~ ~

~ %+~I

t

OO O H OO&OO

Q OOQQ

8

oo ~ II II II II II ~
0
8

OO

O

II O o

OO W OO Ch mt ~~OO
OHOQOn

ChQ oo Ch Q OOOOOQ

eh O
OOOOOO

'PROQ OOOO

Vl & Ch O t nlnC) OO~
II rl OO~0

OO Wt QChCh W m e4 ~ Ch
O & rP O O '4

Ch Ch

OOOQOO

Ch

ChQ VO OQOOQO

Q

Ch

Q OOOO

Q
II II II II II ~

ing combination is predominantly Si-like and resides
in the valence band, whereas the antibonding TA-
like states appear at much higher energies and do not contribute to the occupied states.
This phenomena is very well known in the chem-istry of transition-atom compounds: when a TA forms a binary compound with an element Xhaving a lower-lying valence s orbital (e.g., X =Cl in CuCl), the I ~ „bottom of the occupied valence band is composed predominantly of the X-atom s orbitals (ap, +bp, with a »b), whereas the antibonding counterpart of this state is the empty conduction-band level I"

~, composed primarily of the TA s orbi-
tals (cP, —dP,, with d »c). Note, however, that
although anchored at the TA site, this wave func-

tion may have most of its amplitude on the anion. "
Hence, the TA s orbital gets effectively depopulated relative to its atomic ground state. The extent of this depopulation increases with the increased separation in the atomic s energies of the two atoms. Considering the trends in the atomic energies given in Table IV, one expects the effective s occupation
of a TA in silicon to decrease as Z decreases. The
a~ valence-band resonances are accordingly mostly hostlike, whereas the atomic 4s state of the TA is expected to be mostly empty (diffused throughout the conduction

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Defect Charge Q„at(e)

0,5 0.0 -0.5 -1.0

(b)
S.O— 0.2
O

CO

O
C
hl

Ud 0

~gap I

7.5— I

U 0
e 7.0 0

I
U

(a) I 3.0-

CA

6$
0

—0.0

Qgsp e

SeO

O

0 Ql
0 -45 CO

0 Gyp 0 U 0 0

2.5—

(N Nc)q;, wh—ere q; is the gap-level charge per electron given by Eq. (11). Similarly, in an
effective-mass donor model, Qvs(N) is conceptual-
ized to remain almost constant as the system is
charged, since ZH of the impurity electrons are used to "heal" the vacancy site, and the remaining
(Zt"—ZH +N Np) impurit—y electrons occupy the
extended donor-gap levd. Furthermore, in a non-
self-consistent calculation for a deep impurity,
Qvs(N) would likewise be independent of N, and
Qs»(N) would increase linearly with N Nc. —
Figure 15(a) shows for Si:Mn the variations in
QvB(N) and Qs,„(N)with N, as obtained by per-forming separate self-consistent calculations for each value of N. It is seen that whereas Qg,&(N) in-
creases nearly linearly with X, as expected, the
valence-band contribution Qvs(N) decreases with N,
leading to Q(N) that varies with N considerably

slower than Q„„=NNc or Qs,~(N) a—lone. Much
like a pool below a waterfall, as electrons are poured into the gap level the valence-band states rearrange
themselves so that they leak out of the central ce11 to
partially compensate for the disturbance. This self-
regulating behavior of the system, in response to an
external perturbation, is remarkably analogous to
the homeostasis control mechanisms in biology or to
servomechanisms in machine operations. In such systems, despite the existence of

Qs, in3 484.earranT BT /Xi22 7.78 Tf3190.02 30 205.484.by partialT BT /Xi22 8.25 Tf 143.41 674.482(~gap)Tj BT /Xi22 3.63 Tf7169.86 19 126.483(electroT BT /Xi22 10.05 T 171.4 6798.16 483(3)Tj ET BT /Xi22 7.98 Tf 169.86 180.95 483(compensT BT /Xi22 10.05 T 200.11 679.3 for 73

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0.2

0.1

~ 0.0

I—-0.1

I
0 -0.2
lg
s- -0.3

~ 0.6 Q
U
C~

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C
o

Cl 5-
V
o 4 '.-
Q
3 le&a
0

C
N

0

I
0.3—
~ ~

CL og— E
I~
0 $ V
I
LLI

12
I

I
10

9
~ 0~
8

Qj

~~

C 6
V
5

O 4-
V

Q 3~(+
1.2
~ ISO

1.0
CL

E 0.8

0.6
0.4

LLj 0.2'

l) l

(b)-

0.0

t I

Zn Cu Ni Co Fe Mn Cr V Ti

0.0

1

Zn Cu Ni Co Fe Mn Cr V Ti

FIG. 17. Electronic configuration of an effective transition atom embedded substitutionally in silicon. (a) Representa-tion occupations b Q [Eq. (19a)], and (b) orbita1 occupation r3,Q~ [Eq. (19b}]. For comparison the total number of va1ence electrons Zp is shown as a dashed line.

to approach a noble-metal configuration. This is in
marked contradiction to the Ludwig-%oodbury
model which hypothesized that for substitutional
3d elements, the 3d electrons will be promoted into
the sp subshell to form a tetrahedral hybrid (i.e.,
d"s ~d" s'p, or d" +'s' —+d" s'p). We find
that for the completely filled d-subshell elements Zn and Cu, where the 3d shell cannot accommodate any s electrons, the latter are being promoted into a p state, yielding =s p

'

d

'

for Zn and

so'9p084d9'9z for Cu. The Ni impurity has the in-termediate occupation of s

'

p d; hence Ni in

silicon forms a noble-metal-like compound with a
nearly filled d subshell. This should be contrasted with the effective electronic configurations deduced

for the bulk elemental metals of s' d, s' d

s "d', and s' d for Cr, Fe, Ni, and Cu, respec-
tively, showing a much higher occupation of the s
orbitals.

A calculation of the charge-density components
5I(r) of the effective impurity atom [Eq. (19c)] shows them to be very similar to those of a free atom (in fact, almost indistinguishable on a

the585 Td (chaegatiTf 1619 Td (at305 Tf 162.74 137.82 Td /X9-metal-like)H.8c24 9.32Tf 15T /l.'bot)Tj ET BT /Xi24 7.89c /Xi24 81T /Xi.2 204.71 To.n9.22 TTd

a

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Atomic

Model

SC Model

q

-3.13
tg

K 11

9

~ 0~
lg

L

Q.

C

Ql
~~

C
I

I 5
V
lh

I

3.5

I

4.5

I

0.5

I

1.0

I

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2 I I I I I I I I I

(Potential Sell-Consistency

c 8-
6-

4
2

0 0
So -2

~~ o =$500mRy

Self-Consistent Model

0=8.2 mRy

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(ii) Slater's transition-state (TS) concept approxi-
mates the first three terms on the

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tal-field splitting depends on the l =4 potential component alone'.

traps near the top of the VB were shown '" to be due
to complexes with acceptor impurities such as boron (the most

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The logic of the model is then as follows: If the electronic configuration of the free atom is d"s~, but only 2S&n+m spins are observed in the im-pure system, one needs to

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ism appropriate for shallow effective-mass impuri-
ties.

(v) The consequence of the special screening in
this system is that whereas in the inner central cell (r &1.

5 a.u.

) the screened perturbation b,

V follows

the atomically determined order of the bare pseudo-potentials, b, V "&hV '&hV ', etc., (and hence that of the atomic 3d ionization energies); in the outer central cell (r &2 a.u.

) the order is reversed.
This may lead to the interesting possibility that de-fect energy levels e;(Z) associated with very local-ized wave functions will exhibit an opposite ordering with the atomic number

Z to that characteristic of
delocalized wave functions (e.g.

, excited states).
(vi) Although impurities encompassing Zn to

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Rev. Lett. 1, 295 (1958); G. Finn, Phys. Rev. 91, 754
(1953);R. O. Carlson, ibid. 104, 937 (1954).
F. D. M. Haldane and P. W. Anderson, Phys. Rev. 8 13,
2553 (1976).
Some examples are the following: M. M. Akhmedova, L.
S. Berman, L. S. Kostina, and A. A. Lebedev, Fiz.

Tekh. Poloprovdn. 9, 2351 (1975) [Sov. Phys.— Semicond. 9, 1516 (1975)];M. A. Abdugafurova, L. M.
Kapitonova, L. S. Kostina, A. A. Lebedev, and S. Ma-khkamov, ibid 9,.450 (1975) [ibid 9, 6. 85 (1975)]; S. A. Azimov, N. A. Sultanov, L. Islamov, and R. N.
Nagmatov, ibid 7, 1.837 (1974) [ibid 7, 1.227 {1974)];
M. K. Bakhadyrkhanov, S. S. Nigmankhodzhaev, and
A. T. Teshabaev, ibid. 10, 743 (1976) [ibid 10,. 441 (1976)]; A. A. Lebedev and M. M. Akhmedova, ibid. 10, 1894 (1976) [ibid 10, 1.130 (1976)].
In the work of Ref. 3, "slow quenching" is achieved by dropping an encapsulated sample held at 1250'C into water, whereas "rapid quenching" is obtained by blow-ing the sample into ethylene glycol. In the work of Ref. 4 the sample held at 1070'C was pulled quickly into the cool region (27'C) of the furnace. In the work of Ref. 5 a "rapid quenching" was obtained by dropping the hot sample into liquid nitrogen. Different quenching rates control the site preference (substitutional versus inter-stitial) of the diffused impurity. The substrates are similarly prepared in different techniques. In Ref. 3 the silicon is grown by a pull technique, in Ref. 4 by crucible float zone, and in Ref. 5 by the Czochralski
method. It is likely that different native defects exist in
these samples.
G. %. Ludwig, H. H. Woodbury, and R. O. Carlson, J. Phys. Chem. Solids 8, 490 (1954).
S. H. Muller, G. M. Tuynman, E. G. Sierverts, and C. A. J. Ammerlaan, Phys. Rev. 8 25, 25 (1982).
W. Bergholtz and W. Schroter, in International Confer ence on Radiation Effects in Semiconductors, Nice,

1978, edited by J. H. Albany (IOP, London, 1979), p.
572.

~4F. S. Ham and G. W. Ludwig, in Paramagnetic Reso-
nance, Proceedings of the First International Jerusalem
Conference, Israel 1962, edited by W. Low (Academic,
New York, 1963), Vol. 1, p. 131.
K. B. Tolpygo, Fiz. Tverd. Tela. (Leningrad) 11, 2846 (1969) [Sov. Phys.—Solid State 11,2304 {1970)].
L. S. Kogan, and K. B. Tolpygo, Fiz. Tverd. Tela. (Len-
ingrad) 16, 3176 (1974) [Sov. Phys.—Solid State, 16,
2067 (1975)]; ibid 15, 1544 (197.3) [ibid 15, 1034.
(1973)].
A. B. Roitsin and L. A. Firshtein, Fiz Tverd. Tela.
(Leningrad) 13, 63 (1971) [Sov. Phys.—Solid State 13,
50 {1971)].
(a) L. K. Ermakov, Fiz. Tekh. Poluprovodn. 12, 1230 (1978) [Sov. Phys.—Semicond. 12, 732 (1978)]; (b) R. L. Kleinhenz, V. A. Singh, and J. %. Corbett (unpub-lished).

(a) B. G. Cartling, 8. Roos, and U. %'ahlgren, Chem. Phys. Lett. 21, 380 (1973);8. G. Cartling, J. Phys. C 8,

3171 (1975); 8, 3183 (1975); (b) L. A. Hemstreet and J. O. Dimmock, Phys. Rev. 8 20, 1527 (1979).
L. A. Hemstreet, Phys. Rev. 8 15, 834 (1977).
(a) G. G. DeLeo, G. D. Watkins, and W. B. Fowler, Phys. Rev. 8 23, 1851 (1981); (b) G. G. Deleo, G. D. Watkins, and W. 8. Fowler, Phys. Rev. 8 25, 4962 (1982); 25, 4972 (1982), and (unpublished).
J. E. Lowther, J. Phys. C 13, 3681 (1980).
3A preliminary report has been given in A. Zunger and U. Lindefelt, Phys. Rev. 8 26, 846 (1982).
W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).
(a) A. Zunger and M. L. Cohen, Phys. Rev. 8 18, 5449 (1978); 20, 4082 (1979); (b) P. K. Lam, M. L. Cohen, and A. Zunger, ibid.

t2T BT 3.45 511.25 Tdr7 (A.)Tj ET BT /Xi32l.92 Tf 516.22 598.81 Td (and)TK99.02 555.56 Td (T BT /Xi3dET BT8.82 Tf 267.7 Tf 320(Sham,)Tj ET BT /Xi35c4.)Tj ET612ET BT

H.