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Theory of Interstitial Impurity States in Semiconductors

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The ionization energy and expectation value of the radius corresponding to the states of several interstitial impurities in Ge and Si are calculated. The range of the valence electron of the impurity is divided into two regions; an inner region, which is treated microscopically, and an outer region, which is treated macroscopically. The separation radius, which is primarily a function of the host crystal, is a parameter of the calculation. At a critical separation radius a rapid change of ionization energy and wave-function results. The calculations are carried out for several impurities in column I of the periodic table.

I. INTRODUCTION

CHEMICAL impurities and lattice faults in semiconductors usually produce one or more energy levels in the forbidden energy gap.[1-3] The wave functions corresponding to these levels are localized in the vicinity of the imperfection. When the impurity wave function is spread out over many unit cells of the crystal, as is often the case, then the energy of an eigenstate (donor or acceptor) can be calculated by using the macroscopic concepts of effective mass and dielectric constant.[4-7] When this is the case, the problem of the impurity wave function approximately reduces to the solution of Schrödinger's equation for an electron in the field of a positive point charge. The mass of the electron is changed to the effective mass and the point charge is reduced by the dielectric constant. Solving for the $1s$ state of this system yields an ionization energy of $-(13.6)(m^*/m)(1/\kappa^2)$ ev and an expectation value of the radius of $(3/2)\kappa(m/m^*)a_0$, where m^* is the effective mass and κ the dielectric constant; a_0 is the vacuum Bohr radius, 5.3×10^{-9} cm. This model, the "hydrogenic" model, gives an ionization energy of about 0.01 ev for impurities in Ge and 0.03 ev in Si; the corresponding expectation values of the radius are approximately $100a_0$. These results are independent of the impurity and depend only on the nature of the host crystal. In the vicinity of the impurity, however, the macroscopic concepts do not apply, and this region ought to be treated differently.[8-10] In the case of group III and group V acceptors and donors in Ge and Si, this leads to relatively small corrections to the energy of the impurity state, in good agreement with experiment. Fine details of the impurity core are not important in these cases since the wave function is spread over so many unit cells that only a small fraction resides on the core.

On the other hand, Reiss[11] pointed out that hydrogen does not conform to the "hydrogenic" model. Large amounts of hydrogen, possibly as high as 10^{19} cm^{-3}, are present in crystals of Ge and Si which are normally considered pure.[12] The hydrogen does not affect the electrical properties of the crystal which implies that it does not ionize at room temperature. Reiss shows by a variational calculation on a simple model that the hydrogen impurity level may well be as deep as 1 ev. The model consists of a cavity surrounded by a medium of dielectric constant κ. The radius of the cavity and the dielectric constant are the only crystal parameters entering the calculation. The crystal periodic (effective mass) behavior of the electron is neglected, because in Reiss' calculation the wave function is so concentrated around the impurity atom that fine details of the crystal are unimportant. The energy of a state depends quadratically on κ, but only linearly on (m^*/m). In other words, for the shallow levels, the Schrödinger equation with m^* and κ can be considered as the unperturbed equation and the contribution of the core as a perturbation. For deep levels, the periodic crystal potential and the dielectric constant are considered to perturb the wave function derived from a vacuum Schrödinger equation. Such deep-lying impurity states are not difficult to understand and appear in fact quite naturally in the methodological calculations of Saxon and Hutner[2] and Slater and Koster.[3] The difficulty is to decide in an actual case whether a level will be deep or shallow.

The purpose of this paper is to obtain a qualitative picture of the dependence of impurity states on the properties of both the crystal and the impurity. It is primarily concerned with the calculation of energy levels and wave functions of the outer electrons of impurities in semiconductors. The calculation incorporates the following features in a consistent, though only approximate fashion: The host crystal is characterized by a scalar effective mass m^* and a dielectric constant κ. The impurity atom is described by the electron distribution of the core electrons. A parameter,

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[1] H. M. James, Phys. Rev. **76**, 1611 (1949).
[2] D. S. Saxon and R. A. Hutner, Philips Research Repts. **4**, 81 (1949).
[3] J. C. Slater and G. F. Koster, Phys. Rev. **95**, 1167 (1954).
[4] G. H. Wannier, Phys. Rev. **52**, 191 (1937).
[5] C. H. Kittel and A. H. Mitchell, Phys. Rev. **96**, 802 (1954).
[6] M. A. Lampert, Phys. Rev. **97**, 352 (1955).
[7] J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955).
[8] W. Kohn and J. M. Luttinger, Phys. Rev. **97**, 883 (1955).
[9] W. Kohn and J. M. Luttinger, Phys. Rev. **98**, 915 (1955).
[10] H. Brooks, in *Advances in Electronics and Electron Physics*, edited by L. Marton (Academic Press, Inc., New York, 1955), Vol. 7, p. 85.
[11] H. Reiss, J. Chem. Phys. **25**, 681 (1956).
[12] Thurmond, Guldner, and Beach, J. Electrochem. Soc. **103**, 603 (1956).

the effective cavity radius, will be introduced to separate the microscopic from the macroscopic region.

II. IMPURITY POTENTIAL AND WAVE FUNCTION

1. Hydrogen Impurity Potential

It is useful to look first at the potential due to a single interstitital proton as felt by one electron because, in this case, there is no complication due to other core electrons of the impurity. One can then write down the field in two limiting regions, one far away from the proton and one close to it. If one chooses some characteristic length, L, the two limiting forms are

$$\begin{aligned} E&=e/\kappa r^2, \quad r\gg L \\ E&=e/r^2, \quad r\ll L. \end{aligned} \tag{1}$$

The impurity potential in the two regions is obtained by integration of (1):

$$\begin{aligned} V&=-e/\kappa r, \quad r\gg L \\ V&=-e/r+k, \quad r\ll L. \end{aligned} \tag{2}$$

The radius, L, is related to the lattice spacing. If the integration constant, k, were known, then the impurity potential $V(r)$ would be known over all space, except in the vicinity of L. In that case, extrapolating the two limiting potentials into the region, L, will produce one continuous potential which could be expected to give fairly good results for the energy and wave function of the impurity. The relation between the correct and the extrapolated $V(r)$ is shown schematically in Fig. 1 under the assumption that the correct k is known and that the impurity potential is actually spherically symmetric. The two extrapolated limiting potentials join at a radius, R, which will be called the effective cavity radius. No strict physical reality is to be given to the effective cavity.

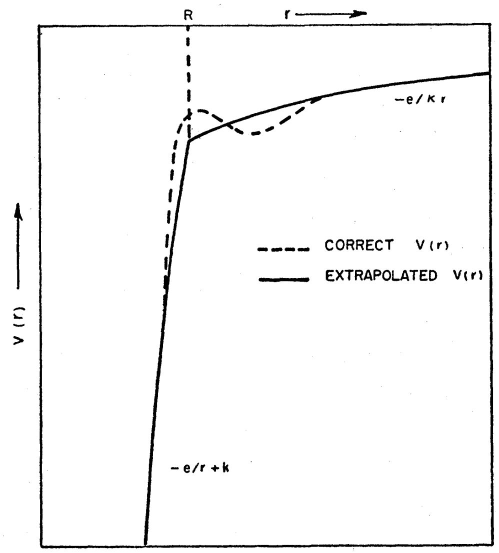

FIG. 1. Schematic representation of correct and extrapolated potential $V(r)$.

The extrapolated potential would be a fair representation of the impurity potential if the constant k were known. This constant, however, depends on the solution of three problems, none of which can be solved without calculations so lengthy that they would not be in the spirit of the present article. Taken up in turn the contributions to k are:

(a) *Integration of the proton field.*—If the field of the interstitial proton is known, it can be integrated from infinity to an arbitrary radius to yield the potential. If this integration is carried to a small $r(\ll L)$, the contribution to the constant k could be obtained. The only region of doubt is the region in the neighborhood of the effective cavity radius, R. This involves the precise way in which the field changes from dielectric behavior into vacuum behavior, a very involved problem. Certainly, spherical symmetry is violated in the neighborhood of R.

(b) *Crystal field.*—To the impurity potential must be added the periodic crystal field. In the region $r>R$ this will be taken into account through the effective-mass formalism. In the region $r<R$, it should be made a part of the potential for the electron having the actual mass. But in this region the impurity potential is generally much stronger than the crystal potential, since we are dealing with an interstitial impurity. Therefore, in the region $r<R$ the crystal potential is approximated by a constant contribution to the total potential.

(c) *Polarization due to the electron.*—The polarization of the crystal due to the interstitial proton is, of course, expressed through the $e/\kappa r$ term in the potential. But the electron polarizes the crystal as well. The problem of the difference in potential experienced by an electron on the two sides of a vacuum-dielectric interface has no unique classical solution. If there is an actual cavity wall, the difference due to the polarization potential is infinite. As a matter of fact, the potential on each side of the cavity becomes infinite, negatively on the vacuum side and positively on the dielectric side. Actually we know, however, that the potential does not behave in this fashion. In the neighborhood of R the classical potential breaks down in such a way that the potential on either side of the cavity differs only by a finite amount, $\bar{k}$. This constant $\bar{k}$ is then the third contribution to the constant k in the potential $V(r)$. This contribution is illustrated in Fig. 2.

The whole question of the constant k is quite analogous to the problem of the potential experienced by an electron near the surface of a metal. The classical picture of mirror charges breaks down near the surface and the potential on either side differs by a constant, the "work function," and not by an infinite amount. When the work function is known, from calculation or experiment, the potential is known everywhere except in the immediate neighborhood of the surface, where it

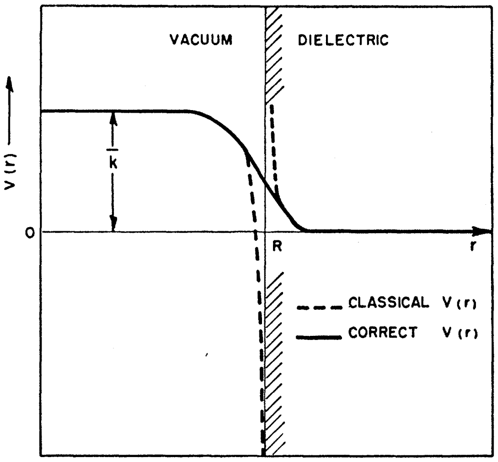

FIG. 2. Schematic representation of potential experienced by the electron due to polarization of the crystal by the electron. For the classical potential k is arbitrary, since the vacuum and dielectric regions cannot be joined continuously.

can be approximated by extrapolation. In the present calculation the constant k takes the place of the work function. If k were known, the potential would be known everywhere, except in the region around R. However, the uncertainties in k due to the three contributions a, b, and c are all of similar magnitude, of the order of electron volts. The calculation is therefore performed by using the extrapolated potential (2) with k as an undetermined parameter. The effective cavity radius R is then a function of k. In practice, it is R which will be used as the undetermined parameter. For the potential (2), the relationship between k and R is given by:

$$k=(e/R)(1-1/\kappa). \tag{3}$$

A change in the effective cavity radius R of $0.5a_0$ corresponds to a change in k of 2 ev when R is of the order of $2.5a_0$. In view of the foregoing discussion, these numbers can serve as a rough estimate of the uncertainty in the effective cavity radius.

2. Core Potential for $Z\neq 1$

When the impurity is not a simple hydrogen atom, the potential near the impurity has to be modified. Instead of the single positive charge, there is a nucleus of Z positive charges surrounded by $(Z-1)$ negative charges. These make up the core. In vacuum, a fair approximation of the core potential is given through the Thomas-Fermi-Dirac statistical model. This model can still be used here if one makes the assumption that the core containing $(Z-1)$ electrons does not extend beyond the interstitial cavity and is in consequence virtually undisturbed by the crystal. This assumption will hold best for cases, where the $(Z-1)$ electrons form a closed shell. In general, one could always treat electrons which form closed shells as unpertubed and treat the remaining electrons by iterative methods. In the present calculation it will simply be assumed that the core is undisturbed, and it is to be understood that this is a good approximation only for the cases where Z electrons form a closed shell plus one, i.e., for column I of the periodic table. The calculations will be confined to this column.[13]

Adopting the formulation of Latter[14] which assures proper asymptotic behavior of the core potential, the potential for $r<R$ is changed from $-e/r+k$ to

$$V(r)=-(e/r)Zg(r)+k,\quad r<R, \tag{4}$$

where

$$\begin{aligned} Zg(r)&=Z\bar{\varphi}(r/\gamma) &&\text{when}\quad Z\bar{\varphi}(r/\gamma)>1\\ &=1 &&\text{when}\quad Z\bar{\varphi}(r/\gamma)<1, \end{aligned}$$

and

$$Z\bar{\varphi}(r/\gamma)=Z\varphi(r/\gamma)+(9/8\pi^2)^{\frac{1}{2}}[(Zr/a_0)\varphi(r/\gamma)]^{\frac{1}{2}};$$

also $\gamma=0.8853a_0/Z^{\frac{1}{3}}$, and $\varphi(r/\gamma)$ is the universal Thomas-Fermi function.

For $r>R$ the potential is still $-e/\kappa r$. From the continuity of $V(r)$ at $r=R$, the constant k can be given as a function of the effective cavity radius R:

$$k=(e/R)[Zg(R)-1/\kappa]. \tag{5}$$

The discontinuity in the derivative of the potential (4) when first $Z\bar{\varphi}(r/\gamma)$ attains unity, implies in effect at this radius a pileup of charge, which, of course, is fictitious. This is a common feature of the Thomas-Fermi-Dirac potential. In the present calculation the potential is changed to $-e/\kappa r$ at $r=R$. If $Z\bar{\varphi}(R/\gamma)$ is greater than unity, i.e., if the core radius is larger than the cavity radius, all the remaining core charge is concentrated at the cavity radius. In practice, this represents a bigger fictitious concentration than occurs in the vacuum Thomas-Fermi-Dirac case. Nevertheless, for cases of present interest, $R\approx 2.5a_0$, no more than 5% of the core charge fails to be contained in the cavity and thus is concentrated on the cavity wall. This effect is not sufficiently large to change the validity of the calculations. It may be considered as a contribution to the effective cavity radius. This point will be discussed in the last section of the paper.

The impurity potential for all space is now given by the following expression, using (4) and (5):

$$\begin{aligned} eV(r)&=-(e^2/r)Zg(r)+(e^2/R)[Zg(R)-1/\kappa], && r<R\\ eV(r)&=-(e^2/\kappa r), && r>R. \end{aligned} \tag{6}$$

The potential $V(r)$ is depicted for several cases of Z and R in Fig. 3.

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[13] The assumption of the undisturbed core is sensible only in the case of interstitial impurities. In the case of substitutional impurities several electrons, depending on the valence difference between the crystal and the impurity, will be severely disturbed by the bond structure of the crystal and the present potential does not apply. Some remarks in connection with substitutional donors and acceptors are found in Appendix I.

[14] R. Latter, Phys. Rev. **99**, 510 (1955).

3. Wave Function

(a) *Interior region*, $r<R$.—In the cavity region, $r<R$, the Schrödinger equation to be satisfied by the impurity wave function is

$$[(\hbar^2/2m)\Delta - eV(r) + E_i]\psi_i(\mathbf{r}) = 0, \quad r<R. \tag{7}$$

Here $V(r)$ is the potential as defined by (6). The crystal potential is already absorbed in the constant term k. The wave function must fulfill the usual boundary conditions of an atomic orbital at the origin. Since $V(r)$ has spherical symmetry, $\psi_i(\mathbf{r})$ will be expanded in spherical harmonics.

(b) *Exterior region*, $r>R$.—In the exterior region, $r>R$, the periodic crystal potential $U(\mathbf{r})$ must be added to the impurity potential $V(r)$, so that the Schrödinger equation becomes

$$[(\hbar^2/2m)\Delta - eV(r) - U(\mathbf{r}) + E_i]\psi_e(\mathbf{r}) = 0, \quad r>R. \tag{8}$$

In this region $V(r)$ represents a very shallow well, and the effective mass formalism applies. By letting

$$\psi_e(\mathbf{r}) = F(\mathbf{r})u(\mathbf{r}), \tag{9}$$

where $u(\mathbf{r})$ is the Bloch function at the bottom of the conduction band,[15] one obtains

$$[(\hbar^2/2m^*)\Delta - eV(r) + E_i]F(\mathbf{r}) = 0 \quad r>R. \tag{10}$$

The crystal potential has been eliminated by introducing the effective mass m^*. This is a good approximation as long as the envelope function $F(\mathbf{r})$ is slowly varying compared to a typical lattice spacing. Although the effective mass is actually a tensor, obtainable by cyclotron resonance experiments, a scalar effective mass is used in (10) because the tensor mass would make the equations nonseparable. The numerical value of the scalar effective mass m^* is chosen by an energy criterion. The complete tensor equation has been solved variationtionally under the "hydrogenic" assumption that $-e^2/\kappa r$ is the potential all the way to the origin.[5,6] We choose m^* such that the energy for the scalar "hydrogenic" equation is identical to the tensor "hydrogenic" result of Lampert.[6] This gives, for Ge, $(m^*/m) = 0.17$; and for Si, $(m^*/m) = 0.31$.

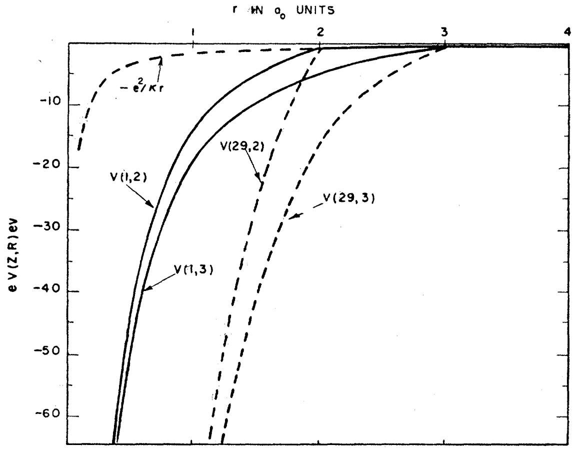

FIG. 3. Impurity potential $V(Z,R)$. To clarify the notation: $V(29,2)$, for example, is the impurity potential for Cu, $Z=29$, with an effective cavity radius $R=2.0a_0$.

At the effective cavity radius, R, the interior wave function ψ_i must be matched to the exterior ψ_e, which gives

$$(\psi_i'/\psi_i)_R = (\psi_e'/\psi_e)_R. \tag{11}$$

In the present calculation the contribution of the Bloch function to the logarithmic derivative at $r=R$ has been neglected. The effect of this approximation is discussed in Appendix II. The matching conditions are now

$$(\psi_i'/\psi_i)_R = (F'/F)_R. \tag{12}$$

Defining a function $\rho_{nl}(r)$:

$$\begin{aligned} \rho_{nl}(r)Y_l^m(\theta,\varphi) &= \psi(\mathbf{r}), \quad r<R \\ &= F(\mathbf{r}), \quad r>R, \end{aligned} \tag{13}$$

the Schrödinger equation to be solved is

$$\begin{aligned} &[(\hbar^2/2m) - eV(r) - (\hbar^2/2m)l(l+1)/r^2 + E_i]\rho_{nl}(r) = 0, \\ &\qquad\qquad\qquad\qquad r<R \\ &[(\hbar^2/2m^*) - eV(r) - (\hbar^2/2m^*)l(l+1)/r^2 + E_i]\rho_{nl}(r) = 0, \\ &\qquad\qquad\qquad\qquad r>R \end{aligned} \tag{14}$$

where $V(r)$ is given by (6) and $\rho_{nl}(r)$ satisfies the usual boundary conditions of radial atomic orbitals. Thus $\rho_{nl}(r)$ has $(n-l-1)$ nodes.

III. CALCULATION AND RESULTS

1. Numerical Procedure

The solutions of the eigenvalue problem (14) were obtained by numerical integration on an IBM 704 computer. A subroutine by Edelman[16] was used as the basis of the program. The integration proceeds basically by a Milne method. The increments of the independent variable are adjusted by a precision criterion. The eigenvalue E_i corresponding to the $(n-l-1)$ node solution of $\rho_{nl}(r)$ is narrowed down to a preassigned number of significant figures. Beside the wave function and eigenvalue, the expectation value of the radius and the square of the radius were also computed.

The computations were carried out for both Ge and Si as the host crystal. For Ge the effective mass ratio (m^*/m) was taken as 0.17 and the dielectric constant κ as 15.8. For Si, $(m^*/m) = 0.31$ and $\kappa = 12.0$. The effective cavity radius R was varied from 1 to 3 a_0 units. (The actual interstitial cavity radius is usually

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[15] Strictly speaking $\psi_e = (1/\sqrt{N})\Sigma_{i=1}^N F^i(\mathbf{r})u^i(\mathbf{r})$ in the case of Ge and Si, because there are several equivalent minima, but, because of the high degree of symmetry of the interstitial cavity, the ground state is represented by (9).

[16] F. Edelman, "A subroutine for the solution of systems of first order ordinary differential equations on the '704' calculator," presented at IBM 704 computer seminar, Endicott, New York, August, 1957.

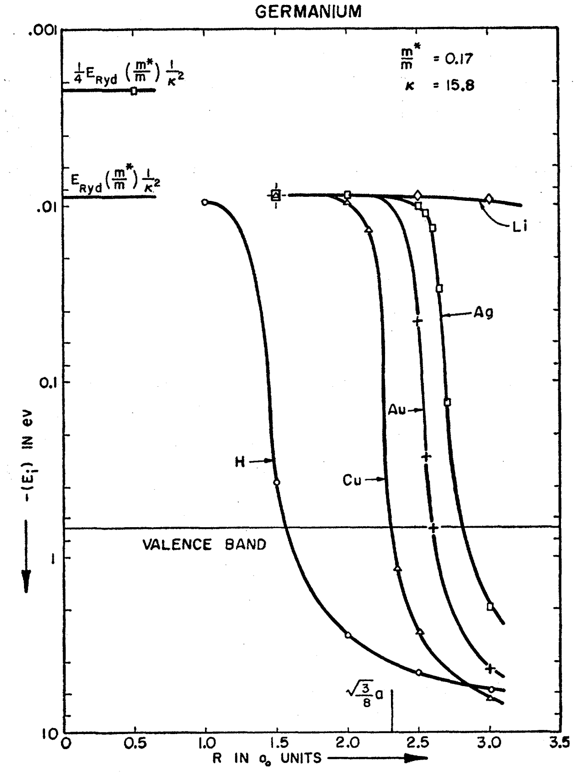

FIG. 4. Ionization energies of impurities in Ge.

considered to be about $2a_0$.) The impurity wave functions calculated were H(1s), Li(2s), Na(3s), Cu(4s), Ag(5s), and Au(6s).

2. Results

The results of the computation are contained in Figs. 4–8. Figures 4 and 5 show the ionization energy E_i as a function of the effective cavity radius, R, for several interstitial impurities. The marked points in the figure are computed energies. The host crystals are Ge and Si, respectively. In each figure $E_i = -(m^*/m)(1/\kappa^2)$ and $E_i = -\frac{1}{4}(m^*/m)(1/\kappa^2)$ have been indicated for reference. These are the $n=1$ and $n=2$ levels of the "hydrogenic" model. The radius $(\sqrt{3}/8)a$, where a is the lattice constant, has also been marked for reference in Figs. 4 through 8. This radius corresponds to half a nearest-neighbor distance in the crystal.

Figures 6 and 7 show $\langle r\rangle$, the expectation value of the radius as a function of R computed with the wave functions of the same impurities. The "hydrogenic" $n=1$ and $n=2$ expectation values, $\langle r\rangle = \frac{3}{2}\kappa(m/m^*)a_0$ and $\langle r\rangle = 6\kappa(m/m^*)a_0$, are indicated for reference. Figure 8 shows $[r\rho_{nl}(r)]^{\frac{1}{3}}$ as a function of r for two effective cavity radii, $R=2.0a_0$ and $R=2.5a_0$. There is no physical significance to the cube root of the wave function. It is chosen merely for convenience of plotting. The functions in Fig. 8 are not normalized, but rather have the same initial slope. The vertical mark on each of the two curves indicates the location of effective cavity radius. The impurity is Cu; the host crystal Ge.

The most striking feature of these results is the sudden change of the ionization energy and expectation value of the radius once a critical effective cavity radius, R, is reached. When R becomes sufficiently large, the wave function rapidly changes from "hydrogenic" to vacuum behavior. In the critical region the rate of change of E_i with R is as high as 10 ev$/a_0$ and the rate of change of $\langle r\rangle$ with R as high as 300. The mathematical reason for this rapid change is best understood in connection with Figs. 8 and 3. Both wave functions in Fig. 8 are 4s functions and therefore have three nodes. In the interior region, $r<R$, the potential is so large, that the wave functions are virtually unaffected by the energy eigenvalue. When the function for $R=2.0a_0$ reaches the cavity wall, it has noded three times, but its logarithmic derivative is still positive. It can therefore match into a "hydrogenic" 1s function, which is an appropriate solution for $r>R$. The resulting energy and expectation value are $E_i \approx -0.01$ ev and $\langle r\rangle \approx 100a_0$, the usual "hydrogenic" result. On the other hand, the wave function for $R=2.5a_0$ has a somewhat deeper well in the region $r<R$ as can be seen from Fig. 3. This causes a larger second derivative of the wave function. The cavity wall is also reached at a larger radius. The two effects combine to make the logarithmic derivative of

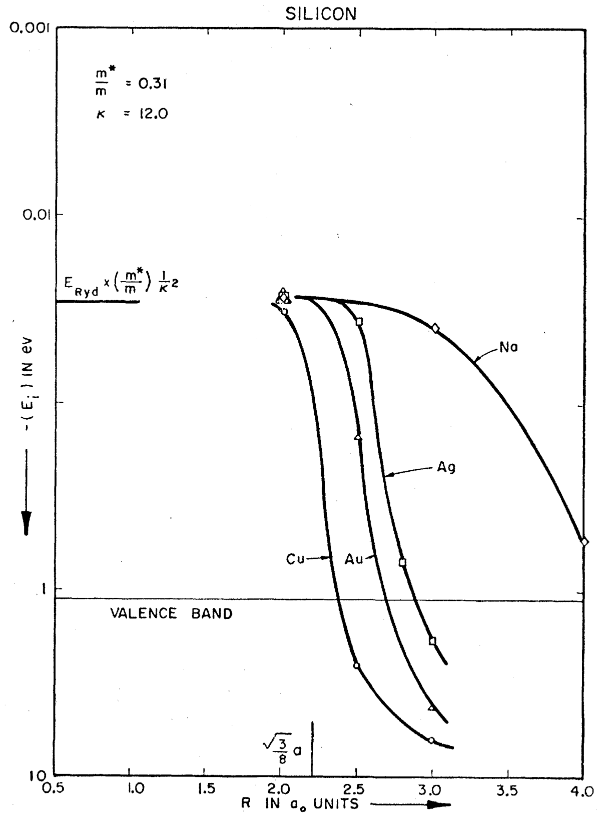

FIG. 5. Ionization energies of impurities in Si.

the wave function negative at $r=R$. The interior wave function can no longer match into a "hydrogenic" function but must decay exponentially. The energy eigenvalue and radius are therefore more characteristic of the vacuum behavior of Cu. They are $E_i \approx -3$ ev and $\langle r\rangle \approx 4a_0$.

Another, more physical, reason for the sudden shrinking of the wave function is the fact that in the region of the critical radius, the potential $V(r)$ for the interior region alone becomes binding for the wave function in question, as shown by the change in logarithmic derivative when R changes from $2.0a_0$ to $2.5a_0$ in the case depicted in Fig. 8. The interior potential is very steep, and once it is binding it causes a rapid change in the ionization energy.

3. Discussion

As we have seen, the computation results in numerical values of the ionization energy E_i and the expectation value $\langle r\rangle$ for several group I impurities, interstitial in Ge and Si. The crystal is characterized by a scalar effective mass m^* and a dielectric constant κ. The impurity core is described by a Fermi-Thomas-Dirac potential $\bar{\varphi}(r/\gamma)$.

In order to evaluate the results, R must be specified. It is clear from the discussion in II, Sec. 1, that R is not a function of the impurity, but rather of the host crystal, as long as the impurity core is smaller than the interstitial cavity and is virtually undisturbed by the crystal. This assumption is consistent with the assumptions which go into the derivation of the potential (6). As was pointed out in that discussion, the assumption of the undisturbed core is almost satisfied. We therefore conclude that R is almost, but not quite, independent of the impurity and a function of the host crystal alone. An estimate of the magnitude of R can be obtained through comparison with experimental observations of energy levels, if possible, in the critical region where the rate of change of E_i with R is large. This means a deep level. Such donor levels, however, are very rare, as is to be expected in the region of large derivative. The only level which may meet this criterion is the Au level in Ge and Si. This level is at 0.05 ev above the valence band[17,18] in Ge and at 0.33 ev above the valence band[19,20] in Si. It is not certain that the observed donor level is due to interstitial Au. The discussion in Appendix I, however, makes it quite plausible that Au would give rise to three acceptor levels in the gap when it is substitutional and to one donor level, when it is

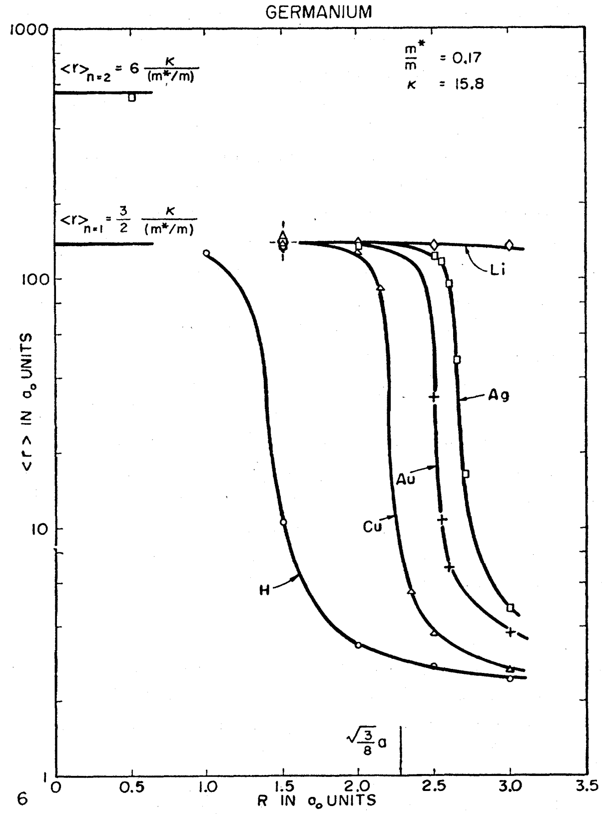

FIG. 6. Expectation values of the radius for impurities in Ge.

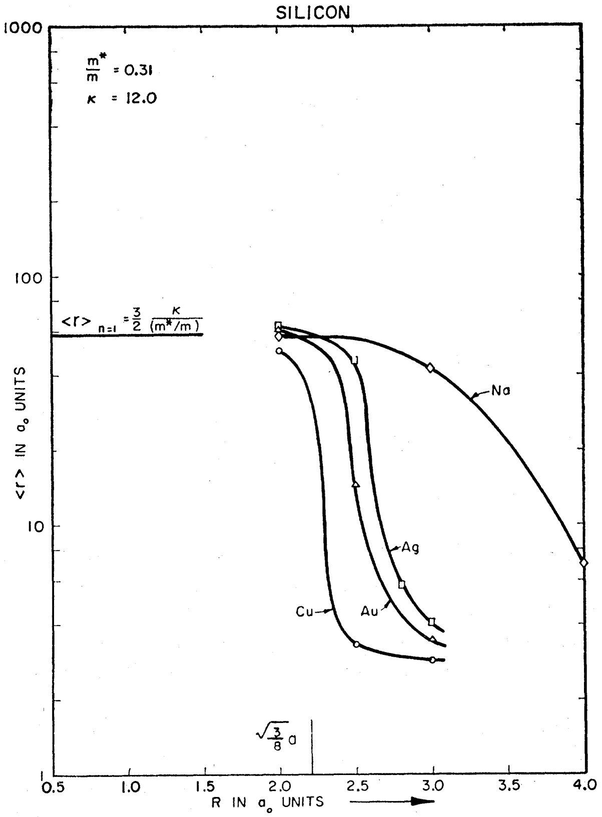

FIG. 7. Expectation values of the radius for impurities in Si.

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[17] W. C. Dunlap, Jr., Phys. Rev. **97**, 614 (1955).

[18] W. C. Dunlap, Jr., Phys. Rev. **98**, 1535(A) (1955); **100**, 1629 (1955).

[19] F. J. Morin and J. P. Maita, Phys. Rev. **90**, 337 (1953).

[20] Morin, Maita, Schulman, and Hannay, Phys. Rev. **96**, 833 (1954).

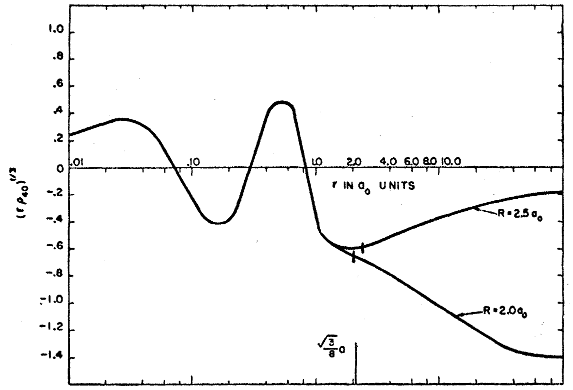

FIG. 8. 4s wave functions ($n=4$, $l=0$) of Cu in Ge, for $R=2.0a_0$ and $R=2.5a_0$. The vertical mark on each wave function corresponds to the effective cavity radius R. The wave functions are not normalized, but rather correspond to the condition $[d(r\rho_{nl})/dr]_{r=0}=1/\gamma$.

interstitial. If the donor level in Si and Ge is due to interstitial Au, then the correct level is obtained if $R=2.6a_0$. In any case $R>2.4a_0$ in both Ge and Si, because Cu has no donor level in the gap although it is known at times to occupy interstitial positions in the lattice.

The results are tabulated in Table I. The first two columns give the impurity element and the main quantum number n. Columns 3 and 5 give the ionization energy $-E_i$ and the expectation value of the radius $\langle r\rangle$, insofar as such numbers can be taken literally,† where R has been so chosen as to give the observed Au donor level. As has been pointed out, R is not expected to be entirely independent of the impurity. If we assume a spread of $0.4a_0$ in R, which corresponds to a spread of 1.6 ev in k, from (4) and (5), then the corresponding spread in E_i and $\langle r\rangle$ is given in columns 4 and 6. From the Cu evidence, the range $2.4a_0<R<2.8a_0$ is reasonable, whether the Au level is due to the impurity in an interstitial position or not.

A not very sensitive check with experiment is the observation that, in the whole range of possible R values, Li and Na are certainly "hydrogenic," while H is not, in accordance with the results of Reiss.[11] Cu exhibits vacuum behavior, while Ag and Au are in the critical region.

TABLE I. Tabulation of results. The ionization energy and expectation value of the radius are given for the effective cavity radius $2.6a_0$ as well as for the range $2.4a_0<R<2.6a_0$.

Host	Impurity	n	$R=2.6a_0$ $-E_i$ (ev)	$2.4a_0<R<2.8a_0$ $-E_i$ (ev)	$R=2.6a_0$ $\langle r\rangle/a_0$	$2.4a_0<R<2.8a_0$ $\langle r\rangle/a_0$
Ge	H	1	4.9	4.3–5.4	2.7	2.8–2.6
Ge	Li	2	0.0092	0.0090–0.0094	138	140–135
Ge	Cu	4	3.6	1.8–5.4	3.4	4.7–2.9
Ge	Ag	5	0.014	0.0094–0.60	95	130–7.8
Ge	Au	6	0.63	0.013–2.8	7	110–4.7
Si	Na	3	0.030	0.028–0.032	54	57–49
Si	Cu	4	5.0	1.3–5.0	3.2	3.8–2.8
Si	Ag	5	0.16	0.030–0.70	20	52–5.8
Si	Au	6	0.72	0.056–2.2	7.6	40–4.3

The ionization energy calculated for $R=0.5a_0$, for the arbitrarily chosen case of the Ag 5s level in Ge, is of special interest (see Fig. 4). It corresponds to an excited ($n=2$) "hydrogenic" level. The explanation is that the cavity here is so small that not all the nodes can be accommodated in it. In that case the last node may lie outside the cavity. The inside wave function then matches into a 2s "hydrogenic" function, which in the spirit of the "hydrogenic" model represents an excited state. Of course, the level is not excited in the ordinary sense since it really represents the ground state of the system. None of the impurities computed here exhibits such "excited" levels in the reasonable range of R, but the possibility that more complex impurities may have an "excited" ground state cannot be ruled out.

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APPENDIX I. SUBSTITUTIONAL DONORS AND ACCEPTORS

The removal of a germanium or silicon atom from the crystal interrupts the tetrahedral four-bond structure. When an impurity is placed in the vacancy, this structure tends to re-establish itself. This means that all the electrons of the impurity which are loosely bound, i.e., the valence electrons, will be seriously distorted from their vacuum distribution. It is possible to sketch the potential under the assumption that the tetrahedral bond structure is completely re-established. The potential will consist of a virtually undisturbed closed shell core potential to which has to be added a potential originating from the charge distribution of the bond electrons. If the net charge of nucleus, core, and bond electrons is positive, then this potential is to be thought of as acting on the remaining impurity electrons. If the net charge is negative, this is to be interpreted to mean that the impurity has borrowed electrons from other bonding sites. In that case, the missing bonds can be treated as positively charged particles (holes) on which the potential acts. Schematically the interior potential can be written as follows:

$$V_i=V_c+V_b+k',\quad r<R_s.$$

Here V_c is the potential due to the nucleus and inner core electrons. V_b is the potential due to the bond electrons. Let us say there are q_c electrons making up the closed shells. There are q_b electron charges arising from the bond electrons (four in the case of the tetrahedral bond structure). R_s is the substitutional effective cavity radius not equal to the interstitial cavity radius. k' is an

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† *Note added in proof.*—The results can certainly not be taken literally when $-E_i$ becomes comparable to the forbidden energy gap. A localized state, such as is described here, cannot exist in the valence band.

additive constant different from k in the interstitial case. As in the interstitial case, V_c may be assumed to be virtually undisturbed and can be described by an appropriate Fermi-Thomas potential. On the other hand, V_b depends on a detailed knowledge of the charge density of bond electrons in the undisturbed crystal and is therefore the least well-known part of V_1.

The exterior potential represents the Coulomb potential of the unscreened charge to which has to be added the crystal potential:

$$V_e = -e(Z-q_c-q_b)/\kappa r + U(\mathbf{r}), \quad r > R_s.$$

Here Z is the atomic number of the impurity. The total charge giving rise to V_e is $e(Z-q_c-q_b)=eQ$. If Q is positive, the potential acts on the Q remaining electrons, which make up the neutral impurity atom. There will therefore be Q donor states.

If Q is negative, then the neutral impurity atom has attracted $|Q|$ electrons from other bond sites and the potential will be felt by $|Q|$ disrupted bonds or holes. The states arising from holes moving in V are acceptor states, and there will be $|Q|$ such states. Since the potential is felt by a positively charged particle, the core part, which is attractive in the donor case, will be repulsive in the acceptor case. Electron and hole potentials are shown in Fig. 9.

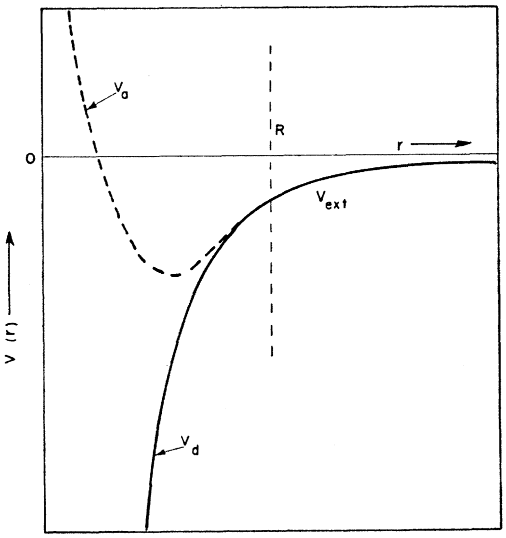

FIG. 9. Schematic representation of substitutional donor and acceptor potential. The donor potential, V_d, is drawn as the potential felt by an electron. The acceptor potential V_a, is drawn as felt by a hole.

From this simple picture one can then conclude that column V elements, substitutional in a crystal with the tetrahedral bond structure, will give rise to a single donor level because for column V we have $(Z-q_c)=5$ and for the tetrahedral bond structure, $q_b=4$. This gives $Q=1$. Similarly column III elements will produce a single acceptor level. This, of course, is in accordance with well known facts. For the transition metals the $3d$ shell is filling up, but is more tightly bound than the $4s^2$ electrons, which are therefore the valence electrons. For these, as well as Zn and Ca, $Q=-2$, which produces two acceptor states.

Cu and Au, with a Q of -3, are expected to give rise to three acceptor states. These are observed[17] when these elements are substitutional in Ge. In the case of Au an additional donor level 0.05 ev above the valence band is observed. This donor level could be due to interstitial or substitutional Au. If it is due to interstitial Au, it is a donor level in the usual sense. If it is due to substitutional Au, however, it represents the state of a bond electron, since the three acceptor states prove that the single Au valence electron takes part in the bond structure of Ge. This is not a donor state in the usual sense of the word, in which donor and acceptor states are states of nonbonding electrons and holes. Since the bond structure is certainly strained in the neighborhood of the impurity, this concept of a bond-donor is not inconsistent, but the Au donor state, if it is due to substitutional Au, is unique in this respect.

This Appendix is not meant to give a good potential for the calculation of impurity states due to substitutional impurities, but is only meant to stress some of the ingredients which would go into such a potential and to point out the difference between the substitutional and the interstitial cases.

APPENDIX II. DISCUSSION OF MATCHING CONDITION

Equation (12) expresses the fact that the inside wave function ψ_i is matched to the envelope function $F(\mathbf{r})$ and not to the total exterior wave function ψ_e. In order to get a better understanding of the error involved, we write

$$\psi_e(\mathbf{r}, -i\nabla) = u(\mathbf{r}, -i\nabla)F(\mathbf{r}).$$

Expanding in the momentum operator, this leads to

$$\psi_e(\mathbf{r}) = u_0(\mathbf{r})F(\mathbf{r}) + \mathbf{u}_1(\mathbf{r})\cdot\nabla F(\mathbf{r}) + \cdots,$$

where the Bloch function near the bottom of the band is given by

$$W(\mathbf{k},\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}}[u_0(\mathbf{r}) + i\mathbf{k}\cdot\mathbf{u}_1(\mathbf{r}) + \cdots].$$

The matching conditions arising from $\psi_e(\mathbf{r})$ depend critically on the Bloch functions. For the case of substitutional impurities, the conditions have been investigated by Brooks and Fletcher.[21,22] By matching at the Wigner-Seitz sphere, they were able to relate the Bloch function to the effective mass. For simple bands this usually leads to new matching conditions which would not produce very significant changes in the results which were computed, using (12).

However, the matching conditions are obviously a function of R as can be seen from the expression for ψ_e.

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[21] H. Brooks and N. Fletcher (unpublished).

[22] N. Fletcher, thesis, Harvard University, Cambridge, Massachusetts, 1955 (unpublished).

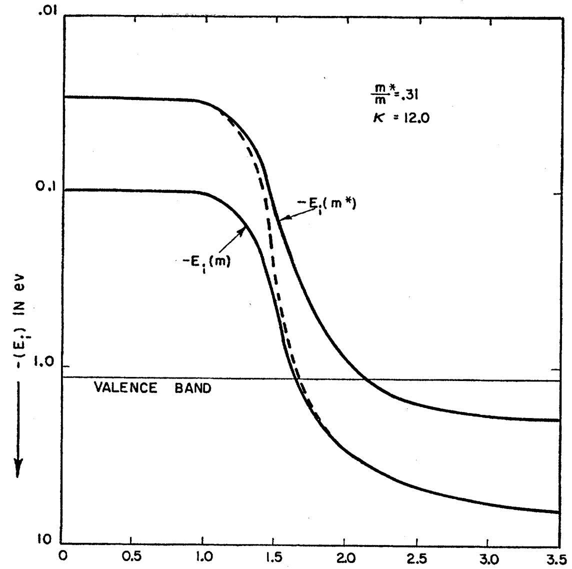

FIG. 10. Upper and lower limits of ionization energy. The curve marked $-E_i(m)$ is the ionization energy when the real mass is used throughout; the curve marked $-E_i(m^*)$, when the effective mass is used throughout. The dashed curve is the ionization energy, when interior and exterior solutions are matched at R. The impurity is H, the host crystal is Si.

To put reasonable limits on the error, therefore, involves a detailed analysis of the crystal wave function near the edge of the conduction band. Fortunately, however, it is possible to set upper and lower bounds, which are adequate for our present purpose, without any involved calculations. The main point to realize is that the radius at which the matching should occur is, within broad limits, quite arbitrary. It is true that somewhere in the region of the impurity the effective-mass behavior does not apply, but the transition from effective to real mass at exactly the same radius at which the inside and the outside potential meet was only a convenience in the computation. The ionization energy is not nearly as sensitive to the radius at which m changes to m^*, as it is to the radius at which the dielectric becomes effective. This is because the effective mass appears linearly and the dielectric constant quadratically in the energy. It would therefore have been equally justified, keeping the potential the same, to change from interior to exterior function at a different radius as, for instance, at the surface nearest to R along which the logarithmic derivative of the Bloch function is small. If that surface lies totally outside the sphere of radius R, then the correct ionization energy is certainly lower than the one obtained by matching at R since the crystal potential has now been neglected between R and the matching radius. If the surface lies totally inside R, the correct ionization energy is higher. Absolute lower and upper limits are therefore given by matching, respectively, at infinity or at the origin, that is solving the Schrödinger equation with m or m^*.

The Schrödinger equation with the potential (6) has been solved for the case of hydrogen, using m and m^*, respectively, as the mass terms. The resulting ionization energies are shown in Fig. 10. It is seen that even though the ionization energy at any particular R can be off by a factor of five, the qualitative behavior of the solution is unaltered in the steep region, the uncertainty in R nowhere being more than $0.4a_0$.

A more careful investigation could probably make the limits narrower. It seems almost obvious that since $u(\mathbf{r})$ is a crystal periodic function, it would be sufficient to take as the limiting matching radii the cavity radius R plus or minus a fraction of the lattice constant, depending on the harmonic nature of $u(\mathbf{r})$. Also, depending on the harmonic nature of $u(\mathbf{r})$ the correct curve will either cut the computed curve repeatedly or, if the logarithmic derivative of $u(\mathbf{r})$ is a slowly varying function of $\mathbf{r}$, the correct curve may stay on one side of the computed curve throughout the critical region. Since $u(\mathbf{r})$ does not depend on the impurity, the effect would then be that all the curves of ionization energy and expectation value of the radius would be pushed to the right or left.