

over which $V_p(\vec{r})$ is integrated to obtain $V_p(\vec{k})$ is decreased and therefore if $V_p(\vec{k})$ is to be unchanged, the magnitude of $V_p(\vec{r})$ must be increased. Therefore, we can say in the empirical pseudopotential \bar{A}_2 and R_s are two independent parameters (since R_s affects $V_L(\vec{r})$ whereas \bar{A}_2 does not), but in the rigorous pseudopotential R_s and \bar{A}_2 are two depen-

dent parameters; i. e., since both affect only the potential within the R_s sphere, for any value of R_s , one can find an \bar{A}_2 which will locate the d bands correctly but not give their correct width. We thus conclude that the empirical pseudopotential of Fong and Cohen⁵ should yield good energy bands for all members of the transition-metal series.

¹J. C. Phillips and L. Kleinman, Phys. Rev. **116**, 287 (1959).

²B. J. Austin, V. Heine, and L. J. Sham, Phys. Rev. **127**, 276 (1962).

³L. Hodges, H. Ehrenreich, and N. D. Lang, Phys. Rev. **152**, 505 (1966).

⁴F. M. Mueller, Phys. Rev. **153**, 659 (1967).

⁵C. Y. Fong and M. L. Cohen, Phys. Rev. Letters **24**, 306 (1970).

⁶M. H. Cohen and V. Heine, Phys. Rev. **122**, 1821 (1961).

⁷L. Kleinman and R. Shurtleff, Phys. Rev. B **4**, 3284 (1971), have shown that although the usual muffin-tin potential is not accurate in transition metals, a warped-muffin-tin-potential calculated from the self-consistent crystal charge density is (i. e., the charge density may not be spherically averaged).

⁸We use Ry atomic units so the kinetic energy is \hbar^2 .

⁹V. Heine and I. Abarenkov, Phil. Mag. **9**, 451 (1964).

¹⁰L. Kleinman and R. Shurtleff, Phys. Rev. **188**, 1111 (1969).

¹¹The positiveness of the d eigenvalues should not bother

the reader since they are a consequence of our method for calculating the arbitrary zero of energy in the crystal.

¹²Equation (7) is obtained by subtracting $\int \bar{\psi} (-\nabla^2 + \bar{V}(\vec{r})) \times \psi^* d^3r = E \int \bar{\psi} \psi^* d^3r$ from $\int \psi^* (-\nabla^2 + \bar{V}(\vec{r})) \bar{\psi} d^3r = E \int \psi^* \bar{\psi} d^3r$, using Green's theorem and discarding the surface integrals because of the periodicity of the crystal.

¹³M. L. Cohen (private communication).

¹⁴Our $V_p(\vec{r})$ differs from the Fong-Cohen $V_L(\vec{r})$ only in that it is a d pseudopotential whereas $V_L(\vec{r})$ is a local pseudopotential. As far as d waves are concerned they are identical.

¹⁵One might naively expect the states at the bottom of the d band to be more tightly bound. That this is not the case follows from a consideration of the nodal structure of a $3d$ radial function with energy. Below the $3d$ resonance the wave function has no nodes and in fact becomes exponentially large as r gets large. Above the $3d$ resonance a node occurs at a value of r which decreases as the energy increases. The bottom of the d bands lie below the $3d$ resonance while the top of the d bands have an energy such that the node occurs for values of r only slightly greater than the largest inscribed sphere.

Comments on Radiative Capture by Impurities in Semiconductors

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A general relation between the radiative electron-capture cross section and the optical-absorption cross section for impurities in semiconductors is derived in a straightforward way without recourse to detailed balance arguments. The method of derivation is applicable to a wide range of related problems. Specializing the result to a form previously obtained by Blakemore reveals discrepancies in degeneracy factors.

INTRODUCTION

In an earlier paper, Blakemore¹ applied detailed-balance arguments to develop a relationship between the photoionization cross section and the radiative electron-capture cross section of an impurity in a semiconductor. In this note, a more general relationship between the radiative electron-capture cross section $\sigma_{e1}(E_c)$ and the optical-absorption cross section $\sigma(\hbar\omega)$ is derived in a simple and straightforward way without making recourse to detailed-balance arguments. The generalized result is then specialized to the situation treated by

Blakemore. The result obtained differs from Blakemore's only by numerical factors involving degeneracies [cf. Eqs. (8) and (12) below].

In a completely quantum mechanical formalism, many transitions can be thought of in terms of the interchange of energy between two systems, e.g., optical transitions involve energy exchange between an atomic system and a radiative field. It is common to view energy transitions between two quantum mechanical systems exclusively in terms of parameters defined for only one of the systems, e.g., either electron capture involving capture cross sections, electron velocities, electron den-

sity of states, etc., or radiative emission involving optical cross sections, photon density, etc.

DERIVATION

General

While in the example pertinent to this discussion, the radiative electron capture and spontaneous photon emission are normally expressed in terms of equations which look quite different, the two viewpoints have in common the transition rate ω appropriate to the process. This identification is the key to relating the two different cross sections. The equation which relates the transition rate to a corresponding cross section is well known,

$$\omega(E) = \sigma(E) F(E) n_T . \quad (1)$$

Here $\omega(E)$ is the transition rate ($\text{sec}^{-1} \text{cm}^{-3}$), $F(E)$ is the particle flux (number particles $\text{cm}^{-2} \text{sec}^{-1}$), $\sigma(E)$ is the cross section (cm^2), and n_T is the total number of atomic system states per cm^3 which is available to participate in transitions. In the following Eq. (1) is particularized first to a photon flux and second to an electron flux. The two resulting expressions describe the same physical process and are thus equal.

Spontaneous Emission

For photons $F(E) = F(\hbar\omega) = N(\hbar\omega) V_E(\hbar\omega) = \bar{N}G(\hbar\omega) \times V_{\text{EN}}(\hbar\omega)$, where \bar{N} is the average photon occupation number per radiation mode, $V_{\text{EN}}(\hbar\omega)$ is the velocity of propagation of radiative energy, and $G(\hbar\omega)d(\hbar\omega)$ is the number of radiation modes in $d(\hbar\omega)$. We know from quantum mechanical theory that \bar{N} should be replaced by $\bar{N} + 1$ for emission processes.² In the case of spontaneous emission $\bar{N} \sim 0$. The photon flux effective in inducing spontaneous emission is

$$F_{\text{SE}}(\hbar\omega) = V_{\text{EN}}(\hbar\omega) G(\hbar\omega) . \quad (2)$$

The total number of atomic system states, n_T , which can participate in photon emission involving a transition from a filled continuum-conduction-band state to an empty ground state of a donor is given by the product of the probability that an electron is in the continuum state, $g_c f_c$, and the number of ionized donors, $N_D g_D (1 - \bar{f}_D)$,

$$n_T = N_D g_c g_D f_c (1 - \bar{f}_D) . \quad (3)$$

Here, N_D is the total density of donors, g_D is the degeneracy of the donor ground state, $1 - \bar{f}_D$ is the portion of ionized donors, g_c is the conduction-band degeneracy, and f_c is the portion of occupied continuum states. The quantity n_T is conveniently referred to as the density of trapping states.

The ground state of a donor can be empty if the donor is ionized or is in an excited state. Blakemore³ gives a useful discussion about the influence of excited states on distribution functions. For

our purposes, it is adequate to define a new quantity \bar{f}_D to represent the probability that some one of the total set of bound states of the donor is occupied. Then the portion of ionized donors is $1 - \bar{f}_D$. Actually, the computational error introduced by replacing $1 - \bar{f}_D$ by $1 - f_D$ is often negligible, the error being greater for shallow impurities.

The degeneracy factors g_c and g_D have been previously discussed.⁴ The point to be emphasized here is that an ionized donor presents g_D empty ground states to an electron in the conduction band but a neutral donor contains only a single electron in the ground state, i. e., only one of the g_D ground states can be occupied at any one time.

Collecting the results given by Eqs. (2) and (3) into Eq. (1) yields

$$\omega(\hbar\omega) = \sigma(\hbar\omega) V_{\text{EN}}(\hbar\omega) G(\hbar\omega) N_D g_D g_c f_c (1 - \bar{f}_D) \quad (4)$$

for the spontaneous-emission rate involving the radiative recombination of conduction-band electrons with donors.

Electron Capture

Turning now to the electron-capture cross section, the particle flux in Eq. (1) is interpreted as the flux of electrons in the conduction band,

$$F_{e1}(E_c) = V_{e1}(E_c) n(E_c) = V_{e1}(E_c) g_c \rho(E_c) f_c , \quad (5)$$

where $V_{e1}(E_c) = (2\epsilon_c/m_e)^{1/2}$ and $\epsilon_c = E_c - \epsilon_G$. The number of trapping states for electrons is just the number of ionized donors times their degeneracy

$$n_T = g_D N_D (1 - \bar{f}_D) . \quad (6)$$

Combining Eqs. (5) and (6) into (1), the recombination rate expressed in terms of the electron-capture cross section $\sigma_{e1}(E_c)$ reduces to

$$\omega(\hbar\omega) = \sigma_{e1}(E_c) V_{e1}(E_c) \rho(E_c) N_D g_D g_c f_c (1 - \bar{f}_D) . \quad (7)$$

This equation for radiative recombination compares with Eq. (4).

DISCUSSION

Since Eqs. (4) and (7) described the same physical process, they are obviously equal; hence the relation

$$\sigma_{e1}(E_c) = \sigma(\hbar\omega) \left[\frac{V_{\text{EN}}(\hbar\omega) G(\hbar\omega)}{V_{e1}(E_c) \rho(E_c)} \right] \quad (8)$$

must be satisfied. Equation (8) is a generalized form of a result recently obtained by Blakemore.¹ In the form presented in Eq. (8) the relationship between $\sigma_{e1}(E_c)$ and $\sigma(\hbar\omega)$ is intuitively clear.

This general result can be specialized to the form given by Blakemore by taking the energy and group velocities as equal, $V_{\text{EN}} = V_G$,⁵ and substitut-

ing in the defining relations:

$$G(\hbar\omega) = n^2(\hbar\omega)(\hbar\omega)^2/(\pi c)^2 V_G, \quad (9)$$

$$\rho(E_c) = (2\pi)^{-2}(2m_c/\hbar^2)^{3/2}\epsilon_c^{1/2}, \quad (10)$$

and

$$V_{e1}(E_c) = (2\epsilon_c/m_c)^{1/2}, \quad (11)$$

all valid for parabolic bands. Equation (8) then reduces to

$$\sigma_{e1}(E_c) = \sigma(\hbar\omega) \left[\frac{[n(\hbar\omega)/c]^2(\hbar\omega)^2}{m_c \epsilon_c} \right], \quad (12)$$

where $\hbar\omega = \epsilon_D + \epsilon_c$. Equation (12) compares with Blakemore's Eq. (12). Differences in the way impurity and band degeneracies enter Eq. (12) can occur because of the degree of arbitrariness available in defining cross sections. However, the

occurrence of g_D in Blakemore's Eq. (12) appears to be in error; the additional factor of $\frac{1}{2}$ in his Eq. (12) is correct because his photon cross section σ_i includes the spin degeneracy while $\sigma(\hbar\omega)$ defined herein does not, i. e., $\frac{1}{2}\sigma_i = \sigma(\hbar\omega)$. The normalization of $\sigma(\hbar\omega)$ used here is precisely defined by Eqs. (23) and (24) of Ref. 4.

The point of view exemplified in arriving at Eq. (8) or (12) is of general utility and intuitive simplicity. The arguments are clearly trivially applicable to acceptors. Further, no recourse to detailed balance is required.

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Isolated Interstitials in Silicon. II*

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An isolated interstitial in silicon at the bond-centered position is investigated using the theory of solid-state scattering and a pseudopotential for the defect potential. The present study is an extension of the work reported recently for the interstitial at the nominal site. One feature is common to the two cases, namely, no bound state is found in the band gap associated with this defect. However, owing to stronger interactions between the atoms at the small distances in this case, the change in the one-electron energy due to the interstitial is larger and the bound state below the valence band lies much deeper.

In a recent article¹ (hereafter referred to as I), an isolated interstitial in silicon at the nominal site (tetrahedral position) was studied using the techniques of solid-state scattering theory.² In this approach, one expands the wave function of the defect system in terms of the Wannier functions for the perfect crystal and generates the matrices for the defect potential and the Green's function on the Wannier-function basis. The relevant results are then obtained in terms of a determinantal equation. The change in the one-electron energy arising from the interstitial was found to be -0.67 Ry, and no bound state associated with this defect was found in the band gap. The vacancy formation energy thus obtained (1.00 Ry) was far too high, even allowing for the fact that inclusion of lattice relaxation around the defects and the changes in Coulomb interaction due to redistribution of charge would

lower the value of the formation energy.

A more plausible position for the interstitial was suggested by Watkins^{3,4} to be the bond-centered position where, owing to shorter distances between the atoms, the interstitial contribution will be much larger thus bringing the value of the formation energy down. Watkins *et al.*⁴ suggested several alternative positions. The bond center is only one of them. This article reports the results of studying the interstitial at the bond-centered position.

The calculations were performed using the method and some of the quantities obtained in I. The same type of symmetry relations between the potential matrix elements holds [Eq. (4.6) of I] except that \vec{R}_β is now replaced by zero. The matrix elements for different lattice-site vectors \vec{R}_μ break into groups such that a vector \vec{R}_μ can be connected with