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New Method for Treating Lattice Point Defects in Covalent Crystals*

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A new method is proposed for the calculation from first principles of the formation and migration energy of a vacancy or interstitial in covalent crystals. The formation energy of a point imperfection is given by the change in the electrostatic energy of the system of ions arising from the point defect plus the change in energy of the system of valence electrons due to their redistribution associated with the point defect. The redistribution of the valence electrons is determined from a pseudocrystal potential which results from orthogonalizing the valence-electron wave functions to the crystal wave functions of the closed-shell core electrons. The scattering of the valence electrons by the pseudocrystal potential is determined by using the t-matrix approximation. The formation energy of an interstitial in diamond, silicon, and germanium turns out to be 1.76, 1.09, and 0.93 eV, respectively; the migration energy of an interstitial is 0.85, 0.51, and 0.44 eV; the formation energy of a vacancy is 3.68, 2.13, and 1.91 eV; and the migration energy of a vacancy turns out to be 1.85, 1.09, and 0.98 eV. The general method presented for treating point defects in covalent crystals can be readily applied to determine the spectrum of localized states at point defects, which is of interest for optical investigations of point defects. Further, the derived expression for the energy of the system of valence electrons can readily be evaluated to show explicitly its dependence on the displacements of the lattice ions resulting from a point defect. Such an expression is needed, for example, for a self-consistent determination of the lattice distortion due to point defects, and furthermore can be used for calculating the elastic constants or lattice force constants from first principles. An approximate expression for the equation of state of the system of valence electrons is given.

I. INTRODUCTION

In order to analyze in terms of point defects experiments on diamond, silicon, and germanium involving diffusion, quenching, and radiation damage,[1] it is necessary to calculate the formation and migration energy of an interstitial or a vacancy in these semiconductors. For example, it is interesting to check whether self-diffusion in these semiconductors is due to vacancies or interstitials.[2,3] Furthermore, from annealing studies in p-type silicon the activation energy 0.33 eV is assigned to the migration of a positively charged vacancy identified by using electron paramagnetic resonance.[4] The dependence of the vacancy mobility on the charge state has been investigated by some annealing experiments in n-type silicon showing that the change in the mobility is small. The energy of migration for a vacancy in germanium, which also does not seem to depend much on the charge the vacancy carries, is found from quenching experiments to be 0.9 eV for a neutral vacancy.[5] Thus, it is of considerable interest to check theoretically these surprisingly different experimental results for the mobility of a vacancy in silicon and germanium.

So far, interstitials have not been identified experimentally in diamond, silicon, and germanium. The reason might be that interstitials are mobile at very low temperatures. A calculation of the migration energy of an interstitial will tell us then at which temperatures the interstitial might be detected. If interstitials have a migration energy of about 0.3 eV in silicon, for example, it might suggest that the observed point defect in p-type silicon having a migration energy of 0.33 eV is an interstitial identified wrongly as a vacancy. Such a misinterpretation of the observed point defect as a vacancy cannot be ruled out on the basis of present experimental data.

Previous calculations of the formation and migration energy of a vacancy in covalent crystals use a Morse potential[6] or a combination of Born's lattice potential within the harmonic approximation and a Morse potential[7] for describing the interactions among the lattice atoms. This ansatz for the lattice potential is not based on firm theoretical grounds, even in the case of a perfect crystal. The empirically determined parameters involved in the potential describing covalent bonds are assumed to be unchanged in the presence of point defects. Since the interactions among the lattice atoms depend strongly on the distribution of the valence electrons this assumption is valid, if at all, only in lattice regions where the valence-electron distribution is slightly disturbed. If the redistribution of the valence electrons due to a point defect is large, then the potential derived for covalent bonds in the case of a perfect crystal might be totally wrong. For example, this might be the case for the saddle-point configuration of a vacancy and particularly for an interstitial. Therefore, it is not possible to extend the above-mentioned calculations to the case of interstitials, whose properties have not been calculated at all so far. It seems, therefore, desirable to develop a new method treating point defects in covalent crystals from first principles. This is the aim of the present paper and is done as briefly described in

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* Supported in part by the U. S. Atomic Energy Commission.

[1] D. S. Billington and J. H. Crawford, *Radiation Damage in Solids* (Princeton University Press, Princeton, New Jersey, 1961).

[2] M. W. Valenta and C. Ramasastry, Phys. Rev. **106**, 73 (1957).

[3] H. Letaw, W. M. Portnoy, and L. Slifkin, Phys. Rev. **102**, 636 (1956).

[4] G. D. Watkins, J. Phys. Soc. Japan **18**, Suppl. II, 22 (1963).

[5] R. A. Logan, Phys. Rev. **101**, 1455 (1956).

[6] R. A. Swalin, J. Phys. Chem. Solids **18**, 290 (1960).

[7] A. Scholz, Phys. Status Solidi **3**, 43 (1963).

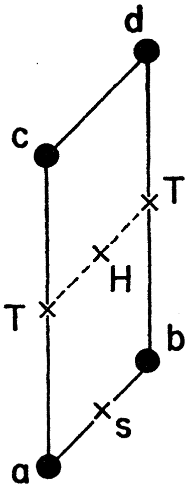

FIG. 1. Illustration of the considered point defect configurations. The atoms a and c, and b and d, respectively, are nearest neighbors along a (001) axis in the diamond lattice. The atoms c and d, and a and b, respectively, are nearest neighbors along a (111) axis. *T* and *H* denote the tetrahedral and, respectively, hexagonal interstitial position. s denotes the saddle point position of the atom a when exchanging places with the vacant lattice site b.

the following. The crystal is represented by a system of ions, e.g., nuclei plus tightly bound core electrons, arranged in a static lattice, and valence electrons moving in a potential field produced by the valence electrons themselves and the ions. The ions interact via a Coulomb potential. The tightly bound core electrons are assumed to be dynamically decoupled from the system of valence electrons and treated within the Hartree-Fock approximation. Since we are dealing with a very open lattice, interactions due to overlapping of tightly bound core electrons usually described by a Born-Mayer potential and van der Waals interactions among the ions are negligible. The distribution of the valence electrons in the imperfect crystal resulting from the scattering of the valence electrons by the lattice ions is determined by using the *t*-matrix approximation.[8]

The crystal potential is strong only within the core region of each ion. The effects of the strong, short-range core parts of the crystal potential are removed as follows.[9] The valence-electron wave functions are orthogonalized to the crystal wave functions of the closed-shell core electrons. One derives then for the effective valence-electron wave function, e.g., original valence-electron wave function minus orthogonalization terms, an effective Hamiltonian representing the crystal potential by a pseudopotential which is usually weak and smooth.[10] To obtain a self-consistent crystal potential the response of the valence electrons to the pseudocrystal potential is determined. The *t*-matrix approximation takes into account a nonlinear response of the valence electrons to the pseudocrystal potential and thus is able to reflect the fine structure of the valence-electron distribution as was shown earlier by the author in claculating Fourier coefficients of the valence electron charge density in diamond.[8] By explicitly taking into account the atomic configuration of the lattice in determining the scattering of the valence electrons, the lattice configuration of the imperfect crystal is clearly reflected in the expression for the energy of the system of valence electrons. Thus it will be readily possible to derive an expression for the energy of the system of valence electrons as a function of the displacements of the ions. It appears that such an expression is required for many problems. For example, in this way a self-consistent calculation of the lattice distortion associated with point defects can be performed.

The formation energy of an interstitial or a vacancy is given by the difference between the ground-state energy of the crystal containing the point defect and the ground-state energy of the perfect crystal. Thus, it is assumed that the localized states introduced by the point defect within the forbidden energy gap between the valence and conduction band are unoccupied. The diamond-type crystal represents a very open lattice. Therefore, the contribution to the formation energy of an interstitial or a vacancy arising from the lattice distortion is presumably small.[7,11,12] Thus we can neglect in our calculations the displacements of the lattice ions. However, it may be noted that in determining the change of the crystal volume associated with a point defect, it is necessary to determine the lattice distortion around the point defect.[11,13]

The diffusion paths for a vacancy or an interstitial are shown in Fig. 1. Two interstitial configurations, chosen according to the lattice symmetry in such a way that the interstitial is farthest away from the surrounding regular lattice ions, are considered. The interstitial position halfway between two next neighboring ions along a (001) lattice axis, called the tetrahedral position, is characterized by four-nearest neighbors at a distance $0.433a$, and six next-nearest neighbors at a distance $0.500a$, where a denotes the lattice constant. The path for interstitial diffusion consists of elements connecting two next-neighboring tetrahedral interstitial positions as indicated in Fig. 1. The interstitial position halfway between two next-neighboring tetrahedral interstitial positions is called the hexagonal-interstitial configuration and is characterized by six nearest neighbors at a distance $0.415a$, and eight next-nearest neighbors at a $0.648a$. It is assumed that these two interstitial positions represent the equilibrium and the saddle-point interstitial configurations.[12] Then the migration energy for an interstitial is calculated by the absolute difference in the formation energy associated with these two interstitial positions. If there is between these two interstitial positions an interstitial position involving a higher formation energy, then the calculation so performed yields at least a lower limit for the migration energy. The diffusion path of a vacancy consists of path elements connecting two next neighboring ions in the

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[8] K. H. Bennemann, Phys. Rev. **133**, A1045 (1964).

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

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

[11] A. Scholz and A. Seeger, Phys. Status Solidi **3**, 1480 (1963).

[12] K. Weiser, Phys. Rev. **126**, 1427 (1962).

[13] K. H. Bennemann and L. Tewordt, Z. Naturforsch. **15a**, 772 (1960).

perfect crystal. The migration energy for a vacancy is calculated by the absolute difference between the formation energies associated with a vacant regular-lattice site and with the saddle-point configuration of the vacancy in which one of the lattice ions located next to the vacancy moved halfway towards the vacancy.

In Sec. II the general method for determining the formation energy of point defects in covalent crystals is outlined. Section III discusses the determination of a self-consistent crystal potential. In Sec. IV the general method described in Secs. II and III is applied to calculate the formation and migration energy of a single interstitial or vacancy in diamond, silicon, and germanium. In Sec. V the limitations of the proposed method are discussed and the numerical results obtained are compared with experimental results. In Appendix A the bound-electron states associated with point defects are briefly discussed. Appendix B treats higher multiple scattering of the valence electrons. In Appendix C an approximate equation of state for the system of valence electrons is derived.

II. GENERAL METHOD

The energy of the static crystal is given by

$$E=\tfrac{1}{2}\sum_{\substack{i,j\\(i\neq j)}}(Z^2e^2/r_{ij})+E_{el}, \tag{II.1}$$

where the first term gives the electrostatic energy of the system of ions with charge Ze, and E_{el} denotes the energy of the system of valence electrons including the energy resulting from the interaction between the valence electrons and the lattice ions. The explicit expression for E_{el} is obtained as follows. The wave functions for the valence electrons are determined by

$$H\psi_k(\mathbf{r})=E(\mathbf{k})\psi_k(\mathbf{r}), \tag{II.2}$$

where the Hamiltonian H is given by

$$H\equiv-(\hbar^2/2m)\nabla^2+V_i(\mathbf{r})+A_{iv}(\mathbf{r})+C(\mathbf{r})+A(\mathbf{r},E). \tag{II.3}$$

V_i is the Coulomb potential due to the lattice ions, e.g., atomic nuclei plus tightly bound core electrons. A_{iv} describes the exchange and correlation interaction between the tightly bound core electrons and the valence electrons. C is the Coulomb potential due to the valence electrons. The operator $A(\mathbf{r},E)$ represents the exchange and residual interaction among the valence electrons. $V_i(\mathbf{r})$ represents a strong negative potential inside the core regions of the ions, thus preventing solution of the wave equation (II.2) by perturbation theory. However, as shown by Phillips and Kleinman[9,14] and others,[10] the energy spectrum $E(\mathbf{k})$ of the valence electrons can be determined from an effective Hamiltonian H' with eigenfunctions Φ_k, where in H' the potential V_i is replaced by a pseudocrystal potential which is in general weak and smooth. The motivation for transforming the Hamiltonian H into an effective Hamiltonian H' arises from the recognition that due to the Pauli exlucsion principle the wave functions ψ_k need be orthogonal to the closed-shell crystal core-electron eigenfunctions. Therefore, the wave functions $\psi_k(\mathbf{r})$ oscillate rapidly inside the core region of an ion. Consequently the valence electrons possess a large positive kinetic energy in the core regions of the ions which represented as a repulsive potential cancels most of the strong negative core part of the potential $V_i(\mathbf{r})$. By expanding ψ_k as

$$\psi_k(\mathbf{r})=\Phi_k(\mathbf{r})-\sum_{t,k'}\langle\varphi_{t,k'}|\Phi_k\rangle\varphi_{t,k'}(\mathbf{r}), \tag{II.4}$$

so that $\psi_k(\mathbf{r})$ is orthogonal to the closed-shell crystal core-electron eigenfunctions $\varphi_{t,k}$, Eq. (II.2) is transformed into

$$H'\Phi_k(\mathbf{r})=E(\mathbf{k})\Phi_k(\mathbf{r}), \tag{II.5}$$

where the effective Hamiltonian H' is given by

$$H'\equiv H+V_R. \tag{II.6}$$

V_R denotes the repulsive potential which cancels most of $V_i(\mathbf{r})$. V_R is in general a nonlocal potential and given by[15]

$$V_R(\mathbf{r},E)|\mathbf{k}\rangle=-\sum_{t,k'}\langle\varphi_{t,k'}|V_i+A_{iv}+C+A|\mathbf{k}\rangle\varphi_{t,k'}(\mathbf{r}). \tag{II.7}$$

Introducing the Green's function $G'(\mathbf{r},\mathbf{r}',k_0)$ defined by

$$[k_0-H'(\mathbf{r},k_0)]G'(\mathbf{r},\mathbf{r}',k_0)=\delta(\mathbf{r}-\mathbf{r}'), \tag{II.8}$$

and boundary conditions which are later explicitly imposed on its Fourier transform, then the energy E_{el} of the system of valence electrons is given by

$$E_{el}=-2i\lim_{\substack{\eta\to+0\\ \mathbf{r}'\to\mathbf{r}}}\int_{-\infty}^{\infty}\frac{dk_0}{2\pi}e^{ik_0\eta}\times\mathrm{Tr}\{(H'(\mathbf{r},k_0)-\tfrac{1}{2}C(\mathbf{r})-\tfrac{1}{2}A(\mathbf{r},k_0))G'(\mathbf{r},\mathbf{r}',k_0)\}. \tag{II.9}$$

Fourier transforming $G'(\mathbf{r},\mathbf{r}',k_0)$ this expression can be rewritten as

$$E_{el}=\frac{-2i}{\Omega^2}\sum_{\mathbf{k},\mathbf{q}}\lim_{\eta\to+0}\int_{-\infty}^{\infty}\frac{dk_0}{2\pi}e^{ik_0\eta}[H'(\mathbf{q},\mathbf{k};k_0)-\tfrac{1}{2}C(\mathbf{q},\mathbf{k})-\tfrac{1}{2}A(\mathbf{q},\mathbf{k};k_0)]G'(\mathbf{k},\mathbf{q},k_0). \tag{II.10}$$

$H'(\mathbf{q},\mathbf{k};k_0)$ is defined by

$$H'(\mathbf{q},\mathbf{k};k_0)\equiv\langle\mathbf{q}|H'|\mathbf{k}\rangle. \tag{II.11}$$

$C(\mathbf{q},\mathbf{k})$ and $A(\mathbf{q},\mathbf{k};k_0)$ are defined analogously. Ω denotes the volume of the crystal. To exhibit explicitly the dependence of E_{el} on the lattice configuration, H' is

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[14] L. Kleinman and J. C. Phillips, Phys. Rev. **118**, 1153 (1960).

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

split into

$$H' \equiv H_0' + \sum_l \Delta H_l', \qquad \text{(II.12)}$$

where l is summed over all lattice ions. H_0' has plane waves as eigenfunctions and is defined as

$$H_0' \equiv -(\hbar^2/2m)\nabla^2 + V_{\mathrm{eff}}{}^0(0,k_0) + \langle C\rangle + A_0(\mathbf{r},k_0). \qquad \text{(II.13)}$$

$V_{\mathrm{eff}}{}^0(0,k_0)$ is given by

$$V_{\mathrm{eff}}{}^0(0,k_0) \equiv \frac{1}{\Omega}\int d^3r\{V_i(\mathbf{r}) + A_{iv}(\mathbf{r}) + [V_R(\mathbf{r},k_0)]_{\mathrm{local}}\}. \qquad \text{(II.14)}$$

$\langle C\rangle$ denotes the space average of C. A_0 results from A for $\sum_l \Delta H_l' \equiv 0$, and $V_R(\mathbf{r},k_0) \equiv 0$. $\Delta H_l'$ is the contribution to $\Delta H' \equiv H' - H_0'$ due to the ion l. Using Eq. (II.12) the equation of motion for the Green's function $G'(\mathbf{r},\mathbf{r}',k_0)$ can be converted into an integral equation as

$$G'(\mathbf{r},\mathbf{r}',k_0) = G_0'(\mathbf{r},\mathbf{r}',k_0) + \sum_l \int d^3r'' G_0'(\mathbf{r},\mathbf{r}'',k_0)\Delta H_l'(\mathbf{r}'',k_0)G'(\mathbf{r}'',\mathbf{r}',k_0). \qquad \text{(II.15)}$$

The Green's function $G_0'(\mathbf{r},\mathbf{r}',k_0)$ is defined by Eq. (II.8) replacing H' by H_0'. Introducing the T operator by

$$T(\mathbf{r},k_0) = \Delta H'(\mathbf{r},k_0) + \int d^3r' \Delta H'(\mathbf{r}',k_0)G_0'(\mathbf{r},\mathbf{r}',k_0)T(\mathbf{r}',k_0), \qquad \text{(II.16)}$$

Eq. (II.15) can be rewritten as

$$G'(\mathbf{r},\mathbf{r}',k_0) = G_0'(\mathbf{r},\mathbf{r}',k_0) + \int d^3r'' G_0'(\mathbf{r},\mathbf{r}'',k_0)T(\mathbf{r}'',k_0)G_0'(\mathbf{r}'',\mathbf{r}',k_0). \qquad \text{(II.17)}$$

Fourier transforming the Green's functions in Eq. (II.17) yields

$$G'(\mathbf{k},\mathbf{q};k_0) = G_0'(\mathbf{k},k_0)(2\pi)^3\delta(\mathbf{q}-\mathbf{k}) + G_0'(\mathbf{k},k_0)T(\mathbf{k},\mathbf{q};k_0)G_0'(\mathbf{q},k_0), \qquad \text{(II.18)}$$

with

$$T(\mathbf{k},\mathbf{q};k_0) \equiv \langle\mathbf{k}|T|\mathbf{q}\rangle, \qquad \text{(II.19)}$$

and

$$G_0'(\mathbf{k},k_0) = 1/[k_0 - E_0'(\mathbf{k}) + i\epsilon\,\mathrm{sgn}(k-k_F)], \epsilon > 0, \qquad \text{(II.20)}$$

where $\mathbf{k}_F$ is the Fermi wave vector and $E_0'(\mathbf{k})$ the eigenvalue of H_0'. Defining the t operator T_l (describing the scattering of the valence electrons due to ΔH_l including multiple scattering arising from the $\Delta H_{l'}$ associated with all the other lattice ions) by

$$T_l(\mathbf{r},\mathbf{r}_l;k_0) = \Delta H_l'(\mathbf{R}_l;k_0) + \sum_{l'} \int d^3r' \Delta H_{l'}'(\mathbf{R}_{l'}',k_0)G_0'(\mathbf{r},\mathbf{r}';k_0) \times T_l(\mathbf{r}',\mathbf{r}_l;k_0), \qquad \text{(II.21)}$$

with

$$\mathbf{R}_l \equiv \mathbf{r} - \mathbf{r}_l, \quad \mathbf{R}_l' \equiv \mathbf{r}' - \mathbf{r}_l, \qquad \text{(II.22)}$$

where $\mathbf{r}_l$ is the position vector of the ion l in the lattice, then $T(\mathbf{r},k_0)$ can be written as

$$T(\mathbf{r},k_0) = \sum_l T_l(\mathbf{r},\mathbf{r}_l;k_0). \qquad \text{(II.23)}$$

Introducing further the t operator describing the single scattering of the propagator $G_0'(\mathbf{r},\mathbf{r}';k_0)$ by one $\Delta H_l'$, which results from T_l if all multiple scattering due to different lattice ions is neglected, by the operator equation

$$t_l(\mathbf{R}_l,k_0) = \Delta H_l'(\mathbf{R}_l,k_0) + \int d^3R_l' \Delta H_l'(\mathbf{R}_l',k_0)G_0'(\mathbf{R}_l,\mathbf{R}_l',k_0)t_l(\mathbf{R}_l',k_0), \qquad \text{(II.24)}$$

then $T_l(\mathbf{k},\mathbf{q},k_0)$ is expressed in terms of

$$t_l(\mathbf{k},\mathbf{q};k_0) = \int d^3r e^{-i\mathbf{k}\cdot\mathbf{R}_l} t_l(\mathbf{R}_l,k_0) e^{i\mathbf{q}\cdot\mathbf{R}_l} \qquad \text{(II.25)}$$

after some operator algebra by

$$T_l(\mathbf{k},\mathbf{q};k_0) = e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}_l}\{t_l(\mathbf{k},\mathbf{q};k_0) + (1/\Omega)\sum_{\substack{l' \\ (l\neq l')}} \sum_{p} e^{i(\mathbf{p}-\mathbf{q})\cdot\mathbf{r}_{ll'}} t_l(\mathbf{k},\mathbf{p};k_0)G_0'(\mathbf{p},k_0)t_{l'}(\mathbf{p},\mathbf{q};k_0) + \cdots\}, \qquad \text{(II.26)}$$

where successive indices are always different. The higher terms in the expansion result from multiple scattering of the valence electrons by the crystal potential. Under certain conditions the expansion given in Eq. (II.26) can be summed up approximately as shown in detail in Appendix B. Using Eq. (II.26), E_{el} can be rewritten as

$$E_{el} = E_{el}{}^0 + \sum_{\substack{l,l' \\ (l\neq l')}} (\Delta E_{el})_{ll'} + \sum_{\substack{l,l',l'' \\ (l'\neq l'',\, l'\neq l,\, l\neq l'')}} (\Delta E_{el})_{ll'l''} + \cdots. \qquad \text{(II.27)}$$

$E_{el}{}^0$ is independent of the lattice configuration and is given by

$$E_{el}{}^0=-2i\sum_k \lim_{\eta\to+0}\int_{-\infty}^{\infty}\frac{dk_0}{2\pi}e^{ik_0\eta}\Big\{G'(\mathbf{k},\mathbf{k};k_0)\Big[\frac{\hbar^2k^2}{2m}+V_{\text{eff}}{}^0(0,k_0)+\frac{\langle C\rangle}{2}+\frac{A_0(\mathbf{k},\mathbf{k};k_0)}{2}\Big]$$
$$+(1/\Omega^2)\sum_l\sum_{\mathbf{q}}G_0'(\mathbf{k},k_0)[\Omega\delta_{k,q}+G_0'(\mathbf{q},k_0)t_l(\mathbf{q},\mathbf{k};k_0)](\Delta V_{\text{eff}}{}^l(\mathbf{k},\mathbf{q};k_0)+\tfrac{1}{2}\Delta C_l(\mathbf{k},\mathbf{q})+\tfrac{1}{2}\Delta A_l(\mathbf{k},\mathbf{q};k_0))\Big\}\,. \quad \text{(II.28)}$$

$(\Delta E_{el})_{ll'}$ is given by

$$(\Delta E_{el})_{ll'}=-\frac{2i}{\Omega^2}\sum_{\mathbf{k},\mathbf{q}}\lim_{\eta\to+0}\int_{-\infty}^{\infty}\frac{dk_0}{2\pi}e^{ik_0\eta}G_0'(\mathbf{q},k_0)G_0'(\mathbf{k},k_0)\{e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}_{ll'}}t_{l'}(\mathbf{q},\mathbf{k};k_0)$$
$$+(1/\Omega)\sum_{\boldsymbol{\lambda}}G_0'(\boldsymbol{\lambda},k_0)[e^{i(\boldsymbol{\lambda}-\mathbf{k})\cdot\mathbf{r}_{ll'}}t_l(\mathbf{q},\boldsymbol{\lambda};k_0)t_{l'}(\boldsymbol{\lambda},\mathbf{k};k_0)+e^{i(\mathbf{q}-\boldsymbol{\lambda})\cdot\mathbf{r}_{ll'}}t_{l'}(\mathbf{q},\boldsymbol{\lambda};k_0)t_l(\boldsymbol{\lambda},\mathbf{k};k_0)]+\cdots\}$$
$$\times(\Delta V_{\text{eff}}{}^l(\mathbf{k},\mathbf{q};k_0)+\tfrac{1}{2}\Delta C_l(\mathbf{k},\mathbf{q})+\Delta A_l(\mathbf{k},\mathbf{q};k_0)). \quad \text{(II.29)}$$

$(\Delta E_{el})_{ll'l''}$ is given by

$$(\Delta E_{el})_{ll'l''}=-\frac{2i}{\Omega^3}\sum_{\mathbf{k},\mathbf{q},\boldsymbol{\lambda}}\lim_{\eta\to+0}\int_{-\infty}^{\infty}\frac{dk_0}{2\pi}e^{ik_0\eta}G_0'(\mathbf{q},k_0)G_0'(\mathbf{k},k_0)G_0'(\boldsymbol{\lambda},k_0)$$
$$\times\{\exp[i(\mathbf{k}\cdot\mathbf{r}_{l''l}+\mathbf{q}\cdot\mathbf{r}_{ll'}+\boldsymbol{\lambda}\cdot\mathbf{r}_{l'l''})]t_{l'}(\mathbf{q},\boldsymbol{\lambda};k_0)t_{l''}(\boldsymbol{\lambda},\mathbf{k};k_0)+\cdots\}$$
$$\times(\Delta V_{\text{eff}}{}^l(\mathbf{k},\mathbf{q};k_0)+\tfrac{1}{2}\Delta C_l(\mathbf{k},\mathbf{q})+\tfrac{1}{2}\Delta A_l(\mathbf{k},\mathbf{q};k_0)). \quad \text{(II.30)}$$

$\langle C\rangle$ is determined by

$$\langle V_i\rangle+\langle C\rangle\cong-\tfrac{2}{3}E_F\,, \qquad \text{(II.31)}$$

where E_F denotes the Fermi energy of the valence electrons. $A_0(\mathbf{r},k_0)$ is in general defined by

$$A_0(\mathbf{r},k_0)|\mathbf{k}\rangle=\int d^3r'\Sigma_0(\mathbf{r},\mathbf{r}';k_0)e^{i\mathbf{k}\cdot\mathbf{r}'}, \qquad \text{(II.32)}$$

where $\sum_0(\mathbf{r},\mathbf{r}';k_0)$ denotes the self-energy of a valence electron with energy k_0 in a uniform electron gas. Approximating the self-energy by[16]

$$\Sigma_0(\mathbf{r},\mathbf{r}';k_0)=i\int\frac{dq_0}{2\pi}V_S{}^0(\mathbf{r},\mathbf{r}';k_0-q_0)G_0(\mathbf{r},\mathbf{r}';q_0), \qquad \text{(II.33)}$$

where $V_S{}^0$ denotes the screened electron-electron interaction in a uniform electron gas and G_0 is obtained from Eq. (II.8) replacing H' by H_0 ,then $A_0(\mathbf{k},\mathbf{k};k_0)$ is given by

$$A_0(\mathbf{k},\mathbf{k};k_0)=i\int\int\frac{d^3q}{(2\pi)^3}\frac{dq_0}{2\pi}$$
$$\times V_S{}^0(|\mathbf{k}-\mathbf{q}|,k_0-q_0)G_0(\mathbf{q},q_0). \qquad \text{(II.34)}$$

The matrix element $\Delta V_{\text{eff}}{}^l(\mathbf{q},\mathbf{k};k_0)$ is defined by

$$\Delta V_{\text{eff}}{}^l(\mathbf{q},\mathbf{k};k_0)=e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}_l}\langle\mathbf{q}|\Delta V_{\text{eff}}{}^l|\mathbf{k}\rangle,$$
$$\Delta V_{\text{eff}}{}^l(\mathbf{r},k_0)\equiv V_{\text{eff}}{}^l(\mathbf{r},k_0)-(V_{\text{eff}}{}^l(0,k_0))^0. \qquad \text{(II.35)}$$

$(V_{\text{eff}}{}^l(0,k_0))^0$ is the contribution to $V_{\text{eff}}{}^0(0,k_0)$ due to ion l. $V_{\text{eff}}{}^l(\mathbf{r},k_0)$ results from $(V_{\text{eff}}{}^l(\mathbf{r},k_0))^0$ replacing $(V_R{}^l)_{\text{local}}$ by $V_R{}^l$. V_{eff} is given by the sum of the terms appearing in the bracket of Eq. (II.14) replacing $(V_R)_{\text{local}}$ by V_R. $\Delta C_l(\mathbf{q},\mathbf{k})$ and $\Delta A_l(\mathbf{q},\mathbf{k};k_0)$ are defined analogously. The matrix elements thus defined are approximately independent of the position vector $\mathbf{r}_l$. $\Delta V_{\text{eff}}{}^l$, ΔC_l, and ΔA_l are the contributions to ΔV_{eff}, ΔC, and ΔA, respectively, due to the ion l. A self-consistent determination of ΔC_l and ΔA_l is performed in the next section.

The formation energy of an interstitial or a vacancy is defined as

$$E_F=E-E_0\,, \qquad \text{(II.36)}$$

where E denotes the energy of the crystal containing the point defect and E_0 denotes the energy of the perfect crystal. An interstitial is created by bringing an atom from the surface into the interior of the crystal. A vacancy is produced by removing an atom from a regular lattice site in the interior of the crystal to the surface. It follows from Eq. (II.1), which is rearranged in order to pair off infinite terms, that E_F is given by

$$E_F=\Delta E_1+\Delta E_2+\Delta E_3+\Delta E_4+\Delta E_5\,. \qquad \text{(II.37)}$$

ΔE_1 results from the Coulomb interaction of an ion with the uniform gas of valence electrons and with all the other lattice ions neglecting lattice distortion. ΔE_1 is determined by the Ewald method.[17] One gets for a vacancy

$$\Delta E_1=-\tfrac{1}{2}\varphi(0)\,, \qquad \text{(II.38)}$$

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[16] L. P. Kadanoff and G. Baym, *Quantum Statistical Mechanics* (W. A. Benjamin, Inc., New York, 1962).

[17] K. Fuchs, Proc. Roy. Soc. (London) **A151**, 585 (1935).

and for an interstitial

$$\Delta E_1 = \varphi(x_I) - \tfrac{1}{2}\varphi(0)\,. \tag{II.39}$$

$\mathbf{x}_I$ denotes the position of the interstitial. The lattice potential φ is given by

$$\varphi(\mathbf{x}_\alpha) = (Ze)^2 \left\{ \sum_{l\neq\alpha} \frac{G(|\mathbf{x}_\alpha - \mathbf{x}_l|/(4\eta)^{1/2})}{|\mathbf{x}_\alpha - \mathbf{x}_l|} + \frac{4\pi}{\Omega_0} \sum_{K\neq 0} \frac{\exp(i\mathbf{K}\cdot\mathbf{x}_\alpha - K^2\eta)}{K^2} S(\mathbf{K}) - \frac{4\pi\eta}{\Omega_0} S(0) - \frac{1}{(\pi\eta)^{1/2}} \delta_{\mathbf{x}\alpha,\mathbf{x}\, l_0} \right\}. \tag{II.40}$$

This expression yields $\varphi(0)$ for $\mathbf{x}_\alpha = \mathbf{x}_{l_0} = 0$. $\mathbf{x}_l$ denotes a lattice vector. $\mathbf{K}$ is a reciprocal lattice vector. $\mathbf{x}_{l_0}$ is any lattice vector. The function G is given by

$$G(z) \equiv \frac{2}{\sqrt{\pi}} \int_z^\infty e^{-y^2} dy\,. \tag{II.41}$$

The structure factor $S(\mathbf{K})$ is given by

$$S(\mathbf{K}) \equiv \sum_\nu e^{-i\mathbf{K}\cdot\mathbf{x}_\nu}, \tag{II.42}$$

where ν is summed over all ions within a unit lattice cell of volume Ω_0. η denotes an arbitrary parameter chosen so as to obtain a rapid convergence of the sums occurring in Eq. (II.40).

ΔE_2 gives the change in the electrostatic energy of the ions due to the lattice distortion associated with the point defects. It is

$$\Delta E_2 = -\frac{(Ze)^2}{2} \sum_{i,j} \left\{ \frac{\mathbf{r}_{ij}\cdot\mathbf{v}_{ij}}{r_{ij}^3} - \frac{\mathbf{v}_i\cdot\mathbf{v}_j}{r_{ij}^3} + 3\frac{(\mathbf{v}_i\cdot\mathbf{r}_{ij})(\mathbf{v}_j\cdot\mathbf{r}_{ij})}{r_{ij}^5} + \cdots \right\}, \tag{II.43}$$

with

$$\mathbf{v}_{ij} \equiv \mathbf{v}_i - \mathbf{v}_j\,. \tag{II.44}$$

$\mathbf{v}_i$ denotes the displacement of the ion i with respect to the position $\mathbf{r}_i$. The first term in Eq. (II.43) results from ion-dipole interactions, the next two terms from dipole-dipole interactions, and the higher omitted terms result from interactions involving higher multipoles.

ΔE_3 results from the change $\Delta\Omega$ in the volume of the crystal associated with the lattice point defect. It is

$$\Delta E_3 \equiv E(\Omega + \Delta\Omega) - E(\Omega)\,. \tag{II.45}$$

To determine this contribution the volume dependence of E_{el} must be evaluated explicitly as in Appendix C. One gets then

$$\Delta E_3 = -(\Delta\Omega/\Omega)\{(1.964/r_S^2) - (0.916/r_S) - 0.031 + \theta(r_S) + \sum_{K\neq 0} g_K(r_S)\}\,. \tag{II.46}$$

r_S is the radius of the sphere which contains 1 electron in the uniform gas of valence electrons. The functions $\theta(r_S)$ and $g_K(r_S)$ are explicitly given in Appendix C. Note that Eq. (II.46) yields an extension of the equation of state of a uniform electron gas by taking into account the interactions between the electrons and the static lattice.

ΔE_4 and ΔE_5 result from that part of E_{el} which depends on the lattice configuration. It is

$$\Delta E_4 \equiv \sum_{l\neq D} \{[(\Delta E_{el})_{Dl} - (\Delta E_{el}^0)_{Dl}] + [(\Delta E_{el})_{lD} - (\Delta E_{el}^0)_{lD}]\} + \sum_{\substack{l,\,l' \\ (l\neq l',\, l\neq D,\, l'\neq D)}} \{[(\Delta E_{el})_{Dll'} - (\Delta E_{el}^0)_{Dll'}] + [(\Delta E_{el})_{lDl'} - (\Delta E_{el}^0)_{lDl'}] + [(\Delta E_{el})_{ll'D} - (\Delta E_{el}^0)_{ll'D}]\} + \cdots, \tag{II.47}$$

where D denotes the ion whose removal produced the point defect. $(\Delta E_{el}^0)_{ll'}$ and $(\Delta E_{el}^0)_{ll'l''}$ refer to the perfect crystal, e.g., no vacancy is present and the interstitial is removed to the surface of the crystal. In lowest order approximation, ΔH_l is independent of the lattice configuration. Then ΔE_4 simplifies as

$$\Delta E_4 = 2 \sum_{l\neq D} \{[(\Delta E_{el})_{Dl} - (\Delta E_{el}^0)_{Dl}] + \tfrac{3}{2} \sum_{\substack{l' \\ (l'\neq l,\, l'\neq D)}} [(\Delta E_{el})_{Dll'} - (\Delta E_{el}^0)_{Dll'}]\} + \cdots. \tag{II.48}$$

Finally, ΔE_5 is given by

$$\Delta E_5 \equiv \sum_{\substack{l,\,l' \\ (l\neq l',\, l\neq D,\, l'\neq D)}} \{[(\Delta E_{el})_{ll'} - (\Delta E_{el}^0)_{ll'}] + \sum_{\substack{l'' \\ (D\neq l,\, l',\, l'';\; l''\neq l';\; l''\neq l)}} [(\Delta E_{el})_{ll'l''} - (\Delta E_{el}^0)_{ll'l''}]\}\,. \tag{II.49}$$

To simplify the determinaton of ΔE_4 and ΔE_5, ΔV_{eff}^l and ΔA_l are approximated by local potentials. $(\Delta E_{el})_{ll'}$ is then given by

$$(\Delta E_{el})_{ll'} = 2 \int\!\!\int \frac{d^3k}{(2\pi)^3} \frac{d^3q}{(2\pi)^3} \left\{ e^{i(\mathbf{q}-\mathbf{k})\cdot\mathbf{r}_{ll'}} t_{l'}(\mathbf{q},\mathbf{k}) \frac{f_k(1-f_q)}{E_0'(\mathbf{k}) - E_0'(\mathbf{q})} + 3P \int \frac{d^3p}{(2\pi)^3} \frac{f_p(1-f_k)(1-f_p) - f_k f_p(1-f_q)}{(E_0'(\mathbf{q}) - E_0'(\mathbf{k}))(E_0'(\mathbf{q}) - E_0'(\mathbf{p}))} e^{i(\mathbf{p}-\mathbf{k})\cdot\mathbf{r}_{ll'}} t_{l'}(\mathbf{p},\mathbf{k}) \cdot t_l(\mathbf{q},\mathbf{p}) + \text{c.c.} + \cdots \right\} \times [\Delta V_{\text{eff}}^l(\mathbf{k},\mathbf{q}) + \tfrac{1}{2}(\Delta C_l(\mathbf{k},\mathbf{q})) + \tfrac{1}{2}(\Delta A_l(\mathbf{k},\mathbf{q}))], \tag{II.50}$$

where P indicates that the principal part of the integral must be taken. f_k denotes the Fermi distribution function. $t_l(\mathbf{q};\mathbf{k};k_0)$ averaged with respect to k_0 is denoted by $t_l(\mathbf{q},\mathbf{k})$. Expanding the t matrices, the potentials, and the exponential functions in terms of Legendre polynomials and performing the angular integrations one obtains

$$\begin{aligned}(\Delta E_{el})_{ll'}= \sum_{\substack{g,g',g''\\ \alpha,\beta,m'',m,\sigma}} & D(g0,g'0,g''m'',\alpha m'',\beta m,\sigma 0)\int_0^\infty\int_0^\infty dkdqk^2q^2\Bigg\{j_\sigma(pr_{ll'})j_{g'}(kr_{ll'})\\ &\times[t_{l'}(p,k)]_{g''}\frac{f_k(1-f_q)}{E_0'(k)-E_0'(q)}\delta_{\beta,0}\delta_{m,0}\delta_{g,0}\times\left([\Delta V_{\text{eff}}{}^l(k,q)]_\alpha+\frac{[\Delta C_l(k,q)]_\alpha}{2}+\frac{[\Delta A_l(k,q)]_\alpha}{2}\right)\\ &+\frac{3}{8\pi^3}P\int_0^\infty dpp^2\frac{f_q(1-f_k)(1-f_p)-f_kf_p(1-f_q)}{[E_0'(q)-E_0'(k)][E_0'(q)-E_0'(p)]}j_g(pr_{ll'})j_{g'}(kr_{ll'})(t_{l'}(p,k))_{g''}\\ &\times[t_l(q,p)]_\beta([\Delta V_{\text{eff}}{}^l(k,q)]_\alpha+\tfrac{1}{2}[\Delta C_l(k,q)]_\alpha+\tfrac{1}{2}[\Delta A_l(k,q)]_\alpha)\delta_{\sigma,0}\delta_{m,m''}+\text{c.c.}\Bigg\}\,. \qquad \text{(II.51)}\end{aligned}$$

The coefficient $D(g0,g'0,g''m'',\alpha m'',\beta m'',00)$ is obtained from

$$D(gm,g'm',g''m'',\alpha\nu,\beta\nu',\sigma 0)\equiv i^{g-g'+\sigma}\frac{16}{\pi^{3/2}}\frac{[(2g+1)(2g'+1)(2\sigma+1)]^{1/2}}{(2g''+1)(2\alpha+1)(2\beta+1)}$$

$$\times A(gm,\beta\nu',g''m'')A(g'm',g''m'',\alpha\nu)A(\sigma 0,\alpha\nu,\beta\nu')\,, \qquad \text{(II.52)}$$

$$A(gm,\beta\nu',g''m'')\equiv\int d\Omega Y_{g''m''}{}^*(\theta,\varphi)Y_{gm}(\theta,\varphi)Y_{\beta\nu'}(\theta,\varphi)\,, \qquad \text{(II.53)}$$

for $m=m'=0$, $\nu=\nu'=m''$, $\sigma=0$. The coefficient A is further evaluated as

$$A(gm,\beta\nu'.g''m'')=\left[\frac{(2q+1)(2\beta+1)}{4\pi(2g''+1)}\right]^{1/2}C[g\beta g'',\,m\nu'(m+\nu')]C(g\beta g'',000)\delta_{m'',m+\nu'}\,. \qquad \text{(II.54)}$$

Y_{gm} denotes a spherical harmonic. $C(g\beta g'',0mm)$ is a Clebsch-Gordan coefficient,[18] and j_g a spherical Bessel function. In deriving Eq. (II.51) it has been assumed that the energy $E_0'(\mathbf{k})\cong E_0'(k)$. If $\Delta H_l'(\mathbf{R}_l,0)$ varies slowly with R_l, then the t matrices and potentials in Eq. (II.51) can be averaged with respect to k, q, and p, respectively, and be pulled out of the integral. The remaining integrals contribute then mainly for $\mathbf{k}$, $\mathbf{q}$, and $\mathbf{p}$ close to the Fermi wave vector.

Approximating $t_l(\mathbf{k}+\mathbf{q},\,\mathbf{k};k_0)$ by $t_l(\mathbf{q})$, which is $t_l(\mathbf{k}+\mathbf{q},\,\mathbf{k};k_0)$ averaged with respect to k_0 and $\mathbf{k}$, one obtains for $(\Delta E_{el})_{ll'}$ the expression

$$(\Delta E_{el})_{ll'}=2\int\frac{d^3q}{(2\pi)^3}\left\{e^{i\mathbf{q}\cdot\mathbf{r}_{ll'}}\frac{q^2}{8\pi e^2}(\mathcal{E}_0(q,0)-1)t_{l'}(\mathbf{q})+\int\frac{d^3p}{(2\pi)^3}e^{i\mathbf{p}\cdot\mathbf{r}_{ll'}}F(\mathbf{p},\mathbf{q})t_l(\mathbf{q}-\mathbf{p})t_{l'}(\mathbf{p})+\text{c.c.}+\cdots\right\}$$

$$\times(\Delta V_{\text{eff}}{}^l(\mathbf{q})+\tfrac{1}{2}\Delta C_l(\mathbf{q})+\tfrac{1}{2}\Delta A_l(\mathbf{q}))\,, \qquad \text{(II.55)}$$

where $\mathcal{E}_0(q,0)$ is the dielectric function of a uniform gas of valence electrons and where

$$F(\mathbf{p},\mathbf{q})\equiv 3P\int\frac{d^3k}{(2\pi)^3}\frac{f_{k+q}(1-f_k)(1-f_{k+p})-f_kf_{k+p}(1-f_{k+q})}{(E_0'(\mathbf{k}+\mathbf{q})-E_0'(\mathbf{k}))(E_0'(\mathbf{k}+\mathbf{q})-E_0'(\mathbf{k}+\mathbf{p}))}\,. \qquad \text{(II.56)}$$

Equation (II.55) can be further evaluated approximately as

$$(\Delta E_{el})_{ll'}=\frac{1}{\pi^2r_{ll'}}\int_0^\infty dqq\left\{\sin(qr_{ll'})\frac{q^2}{8\pi e^2}(\mathcal{E}_0(q,0)-1)t_{l'}(q)+\frac{1}{2\pi^2}t_l(q)\int_0^\infty dppF'(p,q)t_{l'}(p)\sin(pr_{ll'})+\text{c.c.}+\cdots\right\}$$

$$\times(\Delta V_{\text{eff}}{}^l(q)+\tfrac{1}{2}\Delta C_l(q)+\tfrac{1}{2}\Delta A_l(q))\,, \qquad \text{(II.57)}$$

with

$$F'(p,q)\equiv\int\frac{d\Omega}{4\pi}F(\mathbf{p},\mathbf{q})t_l(\mathbf{q}-\mathbf{p})\,. \qquad \text{(II.58)}$$

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[18] M. E. Rose, *Elementary Theory of Angular Momentum* (John Wiley & Sons, Inc., New York, 1957).

Under the same conditions as used in deriving Eq. (II.50) $(\Delta E_{el})_{ll'l''}$ can be rewritten as

$$(\Delta E_{el})_{ll'l''}=2P\int\frac{d^3k}{(2\pi)^3}P\int\frac{d^3q}{(2\pi)^3}\int\frac{d^3p}{(2\pi)^3}\times\exp[i(\mathbf{k}\cdot\mathbf{r}_{l''l}+\mathbf{q}\cdot\mathbf{r}_{ll'}+\mathbf{p}\cdot\mathbf{r}_{l'l''})]\frac{3[f_q(1-f_k)(1-f_p)-f_kf_p(1-f_q)]}{(E_0'(\mathbf{q})-E_0'(\mathbf{k}))(E_0'(\mathbf{q})-E_0'(\mathbf{p}))}$$
$$\times\{t_{l'}(\mathbf{q},\mathbf{p})t_{l''}(\mathbf{p},\mathbf{k})+\cdots\}(\Delta V_{\text{eff}}{}^l(\mathbf{k},\mathbf{q})+\tfrac{1}{2}\Delta C_l(\mathbf{k},\mathbf{q})+\tfrac{1}{2}\Delta A_l(\mathbf{k},\mathbf{q})).\quad\text{(II.59)}$$

Assuming $E_0'(\mathbf{k})\cong E_0'(k)$, etc., and performing the angular integrations one obtains

$$(\Delta E_{el})_{ll'l''}=\frac{3}{2\pi^2}\sum_{\substack{g,g',g'',\alpha,\beta,\sigma\\ m,m',m''}}\frac{1}{((2g+1)(2g'+1))^{1/2}}D(gm,g'(-m),g''m'',\alpha(m''-m),\beta(mm''-),\sigma0)$$
$$\times Y^*{}_{gm}(\theta_{\mathbf{r}_{l'l''},\mathbf{r}_{ll'}},\varphi_{\mathbf{r}_{l'l''},\mathbf{r}_{ll'}})Y^*{}_{g'm'}(\theta_{\mathbf{r}_{ll''},\mathbf{r}_{ll'}},\varphi_{\mathbf{r}_{ll'},\mathbf{r}_{ll''}})\int_0^\infty\int_0^\infty\int_0^\infty dkdqdp(kqp)^2$$
$$\times\frac{f_q(1-f_k)(1-f_p)-f_kf_p(1-f_q)}{(E_0'(\mathbf{q})-E_0'(\mathbf{k}))(E_0'(\mathbf{q})-E_0'(\mathbf{p}))}\{j_g(pr_{l'l''})j_{g'}(kr_{ll''})j_\sigma(qr_{ll'})(t_{l'}(q,p))_\beta(t_{l''}(p,k))_{g''}+\cdots\}$$
$$\times([\Delta V_{\text{eff}}{}^l(k,q)]_\alpha+\tfrac{1}{2}[\Delta C_l(k,q)]_\alpha+\tfrac{1}{2}[\Delta A_l(k,q)]_\alpha).\quad\text{(II.60)}$$

Again, if $\Delta H_l'$ varies slowly with respect to R_l, then the t matrices and the potentials can be averaged with respect to **k**, **q**, and **p** and be pulled out of the integrals in Eq. (II.60).

Using the same approximations as in deriving Eq. (II.55) one obtains for $(\Delta E_{el})_{ll'l''}$ the expression

$$(\Delta E_{el})_{ll'l''}=2\int\int\frac{d^3p}{(2\pi)^3}\frac{d^3q}{(2\pi)^3}F(\mathbf{p},\mathbf{q})e^{i(\mathbf{q}\cdot\mathbf{r}_{ll'}+\mathbf{p}\cdot\mathbf{r}_{l'l''})}\{t_{l'}(\mathbf{q}-\mathbf{p})t_{l''}(\mathbf{p})+\cdots\}(\Delta V_{\text{eff}}{}^l(\mathbf{q})+\tfrac{1}{2}\Delta C_l(\mathbf{q})+\tfrac{1}{2}\Delta A_l(\mathbf{q})).\quad\text{(II.61)}$$

Performing the angular integrations one gets approximately

$$(\Delta E_{el})_{ll'l''}=\frac{3}{2\pi^4}\sum_{g,g',g'',\alpha}i^{g''+\alpha}\frac{(4\pi(2g''+1))^{1/2}}{(2g+1)(2g'+1)}Y_{\alpha0}(\theta_{\mathbf{r}_{l'l''},\mathbf{r}_{ll'}},0)A(g'0,\alpha0,g0)A(g0,g''0,g'0)\int_0^\infty\int_0^\infty dpdqp^2q^2(F(p'q))_g$$
$$\times\{(t_{l'}(p,q))_{g'}t_{l''}(p)+\cdots\}j_{g''}(qr_{ll'})j_\alpha(pr_{l'l''})(\Delta V_{\text{eff}}{}^l(q)+\tfrac{1}{2}\Delta C_l(q)+\tfrac{1}{2}\Delta A_l(q)).\quad\text{(II.62)}$$

III. SELF-CONSISTENT DETERMINATION OF $\Delta C_l(\mathbf{q},\mathbf{k})$ AND $\Delta A_l(\mathbf{q},\mathbf{k};\,k_0)$

A further calculation of E_{el} needs a detailed determination of $t_l(\mathbf{q},\mathbf{k};k_0)$ and $\Delta H_l'(\mathbf{q},\mathbf{k};k_0)$. It follows from Eq. (II.24) that the matrix $t_l(\mathbf{q},\mathbf{k};k_0)$ is determined by the integral equation

$$t_l(\mathbf{q},\mathbf{k};k_0)=\Delta H_l'(\mathbf{q},\mathbf{k};k_0)+\int\frac{d^3p}{(2\pi)^3}\Delta H_l'(\mathbf{q},\mathbf{p};k_0)G_0'(\mathbf{p},k_0)t_l(\mathbf{p},\mathbf{k};k_0).\quad\text{(III.1)}$$

If the perturbing Hamiltonian $\Delta H_{l'}$ varies slowly as a function of $\mathbf{R}_l$, then Eq. (III.1) is solved by

$$t_l(\mathbf{q},\mathbf{k};k_0)=\left\{\Delta H_l'(\mathbf{q},\mathbf{k};k_0)+\int\frac{d^3p}{(2\pi)^3}G_0'(\mathbf{p},k_0)\Delta H_l'(\mathbf{q},\mathbf{p};k_0)\Delta H_l'(\mathbf{p},\mathbf{k};k_0)\right\}$$
$$\times\left(1-\int\int\frac{d^3p}{(2\pi)^3}\frac{d^3\lambda}{(2\pi)^3}G_0'(\mathbf{p},k_0)G_0'(\boldsymbol{\lambda},k_0)\Delta H_{l'}(\boldsymbol{\lambda},\mathbf{p};k_0)\Delta H_l'(\mathbf{p},\boldsymbol{\lambda};k_0)\right).\quad\text{(III.2)}$$

It is obvious from Eq. (III.1) that in order to determine $t_l(\mathbf{q},\mathbf{k};k_0)$ self-consistently, $\Delta H_l'(\mathbf{q},\mathbf{k};k_0)$ must be determined self-consistently. Assuming that the closed-shell core-electron eigenfunctions $\varphi_{t,k}$ are self-consistent, determination of $\Delta H_l'(\mathbf{q},\mathbf{k};k_0)$ is reduced to the self-consistent determination of $\Delta H_l(\mathbf{q},\mathbf{k};k_0)$ which is defined as the contribution to ΔH due to the ion l, where ΔH is given by $H-H_0$. To determine $\Delta H_l(\mathbf{q},\mathbf{k};k_0)$ self-consistently, the dependence of $\Delta C_l(\mathbf{q},\mathbf{k})$ and $\Delta A_l(\mathbf{q},\mathbf{k};k_0)$ on $\Delta H_l(\mathbf{q},\mathbf{k};k_0)$ must be evaluated explicitly. ΔC_l and ΔA_l are the contributions to $(C-C_0)$ and $(A-A_0)$, respectively, due to the ion l.

Assuming momentum conservation, then to first order in ΔH_l, ΔC_l is approximately given by[8]

$$\Delta C_l(\mathbf{q},\mathbf{k}) = -2i\Omega V_s(\mathbf{q}-\mathbf{k},0)\langle\psi_p|\mathbf{p}\rangle_{\mathrm{av}}\int\int\int \frac{d^3\sigma}{(2\pi)^3}\frac{d^3p}{(2\pi)^3}\frac{dp_0}{2\pi}\langle\boldsymbol{\sigma}|\psi_p\rangle_{\mathrm{av}}G_0(\mathbf{p}+\mathbf{q}-\mathbf{k},p_0) \times G_{H-F}(\mathbf{p},p_0)\Delta H_l(\mathbf{p}+\mathbf{q}-\mathbf{k},\boldsymbol{\sigma};p_0)\,, \qquad \text{(III.3)}$$

which is graphically demonstrated in Fig. 2. $V_s(\mathbf{q}-\mathbf{k},0)$ denotes the screened static interaction among the valence electrons which is given in detail later on in this section. The matrix elements are averaged over all values of $\mathbf{p}$ with $\mathbf{p}\leq\mathbf{p}_F$, where $\mathbf{p}_F$ is the Fermi wave vector. The Fourier transform $G_{H-F}(\mathbf{p},p_0)$ of the Green's function $G_{H-F}(\mathbf{r},\mathbf{r}',p_0)$ given by

$$G_{H-F}(\mathbf{r},\mathbf{r}';p_p) = \sum_{\mathbf{p}}\psi_p(\mathbf{r})\psi_p{}^*(\mathbf{r}')G_{H-F}(\mathbf{p},p_0) \qquad \text{(III.4)}$$

is obtained from Eq. (II.20) replacing $E_0'(\mathbf{p})$ by $E(\mathbf{p})$ as determined from Eq. (II.2). The Green's function G_{H-F} is the Hartree-Fock approximation of the Green's function G. The wave function ψ_p is given by Eq. (II.4) with

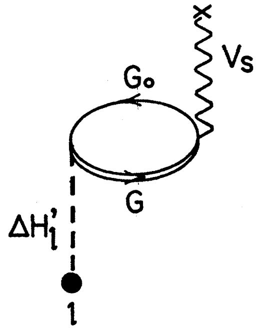

FIG. 2. Graphical representation of ΔC_l.

$$\Phi_p(\mathbf{r}) = |\mathbf{p}\rangle + \int\frac{d^3q}{(2\pi)^3}G_0'(\mathbf{q},p_0(\mathbf{p}))T(\mathbf{q},\mathbf{p};p_0(\mathbf{p}))|\mathbf{q}\rangle\,. \qquad \text{(III.5)}$$

Approximating the self-energy of the valence electrons by[16]

$$\sum(\mathbf{r},\mathbf{r}';k_0) = i\int\frac{dp_0}{2\pi}V_s(\mathbf{r},\mathbf{r}'p_0)G(\mathbf{r},\mathbf{r}',k_0-p_0)\,, \qquad \text{(III.6)}$$

one gets for $\Delta A_l(\mathbf{q},\mathbf{k};k_0)$ the expression

$$\Delta A_l(\mathbf{q},\mathbf{k};k_0) \equiv i\Omega\int\int\int\int\frac{d^3\sigma}{(2\pi)^3}\frac{d^3p'}{(2\pi)^3}\frac{d^3p}{(2\pi)^3}\frac{dp_0}{2\pi}V_s(\mathbf{p},p_0)G_0(\mathbf{q}-\mathbf{p},k_0-p_0)G_{H-F}(\mathbf{p}',k_0-p_0) \times\langle\boldsymbol{\sigma}|\psi_p{}'\rangle\langle\psi_{p'}|\mathbf{k}-\mathbf{p}\rangle\Delta H_l(\mathbf{q}-\mathbf{p},\boldsymbol{\sigma};k_0-p_0)\,. \qquad \text{(III.7)}$$

Assuming momentum conservation, one gets $\mathbf{q}=\mathbf{k}=\mathbf{p}+\mathbf{p}'$. Then Eq. (III.7) can approximately be rewritten as

$$\Delta A_l(\mathbf{q},\mathbf{k};k_0) = i\Omega(2\pi)^3\delta(\mathbf{q}-\mathbf{k})\langle\psi_{q-p}|\mathbf{q}-\mathbf{p}\rangle_{\mathrm{av}}\int\int\int\int\frac{d^3\sigma}{(2\pi)^3}\frac{d^3p}{(2\pi)^3}\frac{dp_0}{2\pi}\langle\boldsymbol{\sigma}|\psi_{\mathbf{q}-\mathbf{p}}\rangle_{\mathrm{av}} \times V_s(\mathbf{p},p_0)G_0(\mathbf{q}-\mathbf{p},k_0-p_0)G_{H-F}(\mathbf{q}-\mathbf{p},k_0-p_0)\Delta H_l(\mathbf{q}-\mathbf{p},\boldsymbol{\sigma};k_0-p_0)\,, \qquad \text{(III.8)}$$

where the matrix elements are averaged over all values of $\mathbf{p}$ lying within the Fermi sea. Assuming that ΔA_l is slowly varying with R_l, then Eq. (III.8) is approximately solved by

$$\Delta A_l(\mathbf{q},\mathbf{k};k_0) = \frac{i\Omega(2\pi)^3\delta(q-k)\langle\psi_{q-p}|q-p\rangle_{\mathrm{av}}}{K(\mathbf{q},k_0)}\int\int\int\frac{d^3\sigma}{(2\pi)^3}\frac{d^3p}{(2\pi)^3}\frac{dp_0}{2\pi}\langle\boldsymbol{\sigma}|\psi_{q-p}\rangle_{\mathrm{av}} \times V_s(\mathbf{p},p_0)G_0(\mathbf{q}-\mathbf{p},k_0-p_0)G_{H-F}(\mathbf{q}-\mathbf{p},k_0-p_0)\{\Delta V_i{}^l(\mathbf{q}-\mathbf{p},\boldsymbol{\sigma})+\Delta A_{iv}{}^l(\mathbf{q}-\mathbf{p},\boldsymbol{\sigma})+\Delta C_l(\mathbf{q}-\mathbf{p},\boldsymbol{\sigma})\}\,, \qquad \text{(III.9)}$$

with

$$K(\mathbf{q},k_0) \equiv 1 - i\Omega\langle\psi_{q-p}|\mathbf{q}-\mathbf{p}\rangle_{\mathrm{av}}\int\int\int\frac{d^3\sigma}{(2\pi)^3}\frac{d^3p}{(2\pi)^3}\frac{dp_0}{2\pi}\langle\boldsymbol{\sigma}|\psi_{q-p}\rangle_{\mathrm{av}}V_s(\mathbf{p},p_0)G_0(\mathbf{q}-\mathbf{p},k_0-p_0)G_{H-F}(\mathbf{q}-\mathbf{p},k_0-p_0)\,. \qquad \text{(III.10)}$$

Assuming that ΔC_l varies slowly in $\mathbf{R}_l$, using Eq. (III.9), then Eq. (III.3) is solved by

$$\Delta C_l(\mathbf{q},\mathbf{k}) = \frac{1-\mathcal{E}(\mathbf{q}-\mathbf{k},0)}{\mathcal{E}(\mathbf{q}-\mathbf{k},0)}\{V_i{}^l(\mathbf{q},\mathbf{k})+A_{iv}{}^l(\mathbf{q},\mathbf{k})\}\,, \qquad \text{(III.11)}$$

where the dielectric function $\mathcal{E}(\mathbf{q}-\mathbf{k},0)$ is given by

$$\mathcal{E}(\mathbf{q}-\mathbf{k},0)\equiv 1+i\Omega V_s(\mathbf{q}-\mathbf{k},0)\pi(\mathbf{q}-\mathbf{k},0)\,, \tag{III.12}$$

with the irreducible polarization propagator $\pi(\mathbf{q}-\mathbf{k},0)$ determined by

$$\pi(\mathbf{q}-\mathbf{k},0)=\langle\psi_p|\mathbf{p}\rangle_{\text{av}}\int\frac{d^3\sigma}{(2\pi)^3}\langle\boldsymbol{\sigma}|\psi_p\rangle_{\text{av}}P_0(\mathbf{q}-\mathbf{k},0)\{1+\beta(\mathbf{q}-\mathbf{k},0)\}\,. \tag{III.13}$$

The term $\beta(\mathbf{q}-\mathbf{k},0)$ arises from ΔA_l and is given by

$$\beta(\mathbf{q}-\mathbf{k},0)\equiv i\Omega\frac{\langle\mathbf{p}+\mathbf{q}-\mathbf{k}|\psi_p\rangle_{\text{av}}}{\int d^3\sigma/(2\pi)^3\langle\boldsymbol{\sigma}|\psi_p\rangle_{\text{av}}}\int\frac{dk_0}{2\pi}\frac{\langle\psi_{p+q-k-p'}|\mathbf{p}+\mathbf{q}-\mathbf{k}-\mathbf{p}'\rangle_{\text{av,av}}}{\langle K(\mathbf{p}+\mathbf{q}-\mathbf{k},k_0)\rangle_{\text{av}}}\int\!\!\int\!\!\int\frac{d^3\sigma}{(2\pi)^3}\frac{d^3p'}{(2\pi)^3}\frac{dp_0'}{2\pi}$$
$$\times\langle\boldsymbol{\sigma}|\psi_{p+q-k-p'}\rangle_{\text{av}}V_s(\mathbf{p}',p_0')\langle G_0(\mathbf{p}+\mathbf{q}-\mathbf{k}-\mathbf{p}',k_0-p_0')\rangle_{\text{av}}\langle G_{H-F}(\mathbf{p}+\mathbf{q}-\mathbf{k}-\mathbf{p}',k_0-p_0')\rangle_{\text{av}}\,. \tag{III.14}$$

The matrix element $\langle\psi_{p+q-k-p'}|\mathbf{p}+\mathbf{q}-\mathbf{k}-\mathbf{p}\rangle_{\text{av,av}}$ is averaged over all values of $\mathbf{p}$ and $\mathbf{p}'$ within the Fermi sea of the valence electrons. It has been assumed that $K(\mathbf{p}+\mathbf{q}-\mathbf{k},k_0)$ varies slowly as a function of $\mathbf{p}$ over the range of integration. $\langle K(\mathbf{p}+\mathbf{q}-\mathbf{k},k_0)\rangle_{\text{av}}$ is averaged over all values of $\mathbf{p}$ within the Fermi sea. The Green's functions G_0 and G_{H-F} are averaged with respect to all $\mathbf{p}\leq\mathbf{p}_F$. $P_0(\mathbf{q}-\mathbf{k},0)$ is defined as

$$P_0(\mathbf{q}-\mathbf{k},0)=2\int\!\!\int\frac{d^3p}{(2\pi)^3}\frac{dp_0}{2\pi}\times G_0(\mathbf{p}+\mathbf{q}-\mathbf{k},p_0)G_{H-F}(\mathbf{p},p_0)\,. \tag{III.15}$$

Replacing the Green's function $G_{H-F}(\mathbf{p},p_0)$ by the free-particle Green's function $G_0(\mathbf{p},p_0)$ then $P_0(\mathbf{q}-\mathbf{k},0)$ reduces to the polarization propagator P_{00} obtained in the random-phase approximation for a uniform electron gas[16] for which an explicit expression is given by Lindhard.[19] Substituting in Eq. (III.9) for ΔC_l the expression given by Eq. (III.11), then ΔA_l is given as a function of V_i^l and A_{iv}^l only. This completes, within the approximation used, the self-consistent determination of ΔC_l and ΔA_l. The wave functions ψ_p occurring in the matrix elements involved in the formulas for ΔC_l and ΔA_l can be approximated by the wave functions ψ_p which result from Eqs. (II.4) and (III.5) approximating $T(\mathbf{q},\mathbf{p};p_0(\mathbf{p}))$ by $\sum_l e^{i(\mathbf{p}-\mathbf{q})\cdot\mathbf{r}_l}t_l(\mathbf{q},\mathbf{p};p_0(\mathbf{p}))$, where t_l is determined from $\Delta H_l'$ with ΔC_l as obtained by using for the dielectric function $\mathcal{E}$ the static dielectric constant $\mathcal{E}_0$ for a uniform electron gas.

Assuming momentum conservation, then the screened interaction $V_s(\mathbf{p},p_0)$ among the valence electrons is approximately given by[8]

$$V_s(\mathbf{p},p_0)=\frac{4\pi e^2}{p^2}\left[1+i\frac{4\pi e^2}{p^2}|\langle\psi_{p+q}|e^{i\mathbf{p}\cdot\mathbf{r}}|\psi_q\rangle_{\text{av}}|^2P(\mathbf{p},p_0)\right]^{-1}, \tag{III.16}$$

with

$$P(\mathbf{p},p_0)\equiv\int\!\!\int\frac{d^3q}{(2\pi)^3}\frac{dq_0}{2\pi}\times G_{H-F}(\mathbf{q},q_0)G_{H-F}(\mathbf{q}+\mathbf{p},q_0+p_0)\,. \tag{III.17}$$

A further evaluation of $P(\mathbf{p},p_0)$ is only feasible if a model is chosen for the crystal electron bands with a simple energy spectrum $E(\mathbf{q})$.[20]

In deriving Eq. (III.11) it has been assumed that ΔH_l can be approximated by a local potential. This can be achieved, for example, by approximating ΔA_l by the appropriate Thomas-Fermi-Slater exchange potential.[21,22] Thus, it may be noted, that the approximations used in deriving Eq. (III.11) are less restrictive if one neglects ΔA_l, e.g., for $\beta\equiv 0$. The approximations involved in deriving Eq. (III.11) are equivalent to those used by Cohen and Phillips[23] in determining self-consistently the screening of ΔV_{eff}^l by the valence electrons. However, these authors take only a linear response of the valence electrons to the pseudocrystal potential into account, thus neglecting local field effects in determining the dielectric function $\mathcal{E}$, while the dielectric function determined by Eq. (III.12) includes local-field corrections. Finally, it follows that ΔH_l can be written as

$$\Delta H_l(\mathbf{q},\mathbf{k};k_0)=\frac{\Delta V_i^l(\mathbf{q},\mathbf{k})+\Delta A_{iv}^l(\mathbf{q},\mathbf{k})}{\mathcal{E}(\mathbf{q}-\mathbf{k},0)}+\Delta A_l(\mathbf{q},\mathbf{k};k_0)\,. \tag{III.18}$$

The first term in Eq. (III.18) gives for $\Delta A_l\equiv 0$ the same result for ΔH_l as obtained within the random-phase approximation or self-consistent Hartree approximation.[24]

For the following the matrix element $\Delta V_R^l(\mathbf{q},\mathbf{k};k_0)$ of the nonlocal repulsive potential ΔV_R^l must be

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[19] J. Lindhard, Kgl. Danske Videnskab. Selskab, Mat.-Fys. Medd. **28**, 8 (1954).

[20] D. R. Penn, Phys. Rev. **128**, 2093 (1962).

[21] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[22] J. C. Phillips and L. Kleinman, Phys. Rev. **128**, 2098 (1962).

[23] M. H. Cohen and J. C. Phillips, Phys. Rev. **124**, 1818 (1961).

[24] H. Ehrenreich and M. H. Cohen, Phys. Rev. **115**, 786 (1959).

evaluated in more detail. It follows from Eq. (II.7) that

$$\Delta V_R{}^l(\mathbf{q},\mathbf{k};k_0)=-\sum_{t,k'}\langle\varphi_{t,k'}|\Delta H_l|\mathbf{k}\rangle\langle\mathbf{q}|\varphi_{t,k'}\rangle. \qquad \text{(III.19)}$$

Writing $\varphi_{t,k}$ in the form

$$\varphi_{t,k}(\mathbf{r})=\sum_s U_{tk}{}^s(\mathbf{r}_s)\varphi_t{}^s(\mathbf{R}_s), \qquad \text{(III.20)}$$

using

$$\sum_k U_{tk}{}^{s*}(\mathbf{r}_s)U_{tk}{}^{s'}(\mathbf{r}_{s'})=\langle\varphi_t{}^s|\varphi_t{}^{s'}\rangle, \qquad \text{(III.21)}$$

and assuming that $\varphi_t{}^s$ and $\varphi_t{}^{s'}$, and ΔH_s and $\Delta H_{s'}$ for $s\neq s'$ are not appreciably overlapping, then one gets

$$\Delta V_R{}^l(\mathbf{q},\mathbf{k};k_0)$$

$$=-\sum_t\int\frac{d^3p}{(2\pi)^3}\Delta H_l(\mathbf{p},\mathbf{k};k_0)a_t{}^l(\mathbf{p})a_t{}^{l*}(\mathbf{q}), \qquad \text{(III.22)}$$

with

$$a_t{}^l(\mathbf{p})\equiv\langle\varphi_t{}^l|\mathbf{p}\rangle. \qquad \text{(III.23)}$$

Expanding $|\mathbf{p}\rangle$ in spherical harmonics and writing $\varphi_t{}^l$ as

$$\varphi_t{}^l(\mathbf{R}_l)=\sum_m(P_{tm}{}^l(\mathbf{R}_l)/R_l)Y_{tm}(\theta_{\mathbf{R}l},\varphi_{\mathbf{R}l}), \qquad \text{(III.24)}$$

one gets

$$a_t{}^l(\mathbf{p})=(4\pi)^{1/2}(2t+1)^{1/2}i^t\int_0^\infty drrP_{tm}{}^{l*}(r)j_t(pr). \qquad \text{(III.25)}$$

In order to evaluate further $\Delta V_R{}^l(\mathbf{q},\mathbf{k};k_0)$, it is assumed that $\Delta A_l(\mathbf{q},\mathbf{k};k_0)$ can be approximated by $\Delta A_l(k)$ and $\beta(\mathbf{q}-\mathbf{k},0)$ by $\beta(|\mathbf{q}-\mathbf{k}|,0.)$ Then, $\Delta H_l(\mathbf{p},\mathbf{k};k_0)$ can be expanded in Legendre polynomials as

$$\Delta H_l(\mathbf{p},\mathbf{k};k_0)=\sum_{g=0}^{\infty}\{\Delta H_l(p,k;k_0)\}_gP_g(\cos\theta_{\mathbf{p},\mathbf{k}}). \qquad \text{(III.26)}$$

This yields

$$\Delta V_R{}^l(\mathbf{q},\mathbf{k};k_0)=-\sum_t a_t{}^{l*}(\mathbf{q})b_t{}^l(k,k_0), \qquad \text{(III.27)}$$

with

$$b_t{}^l(k,k_0)\equiv\frac{1}{2\pi^2}\int_0^\infty dpp^2\{\Delta H_l(p,k;k_0)\}_0a_t{}^l(\mathbf{p}). \qquad \text{(III.28)}$$

It follows that $\Delta H_l{}'$ can be expanded in the same way as ΔH_l. Therefore, $t_l(\mathbf{q},\mathbf{k};k_0)$ can be expanded in Legendre polynomials in the same way as $\Delta H_l{}'(\mathbf{q},\mathbf{k};k_0)$.

Finally, it may be noted, that if $\Delta H_l{}'(\mathbf{R}_l,k_0)$ varies slowly with R_l and if the angular dependence of $t_l(\mathbf{k},\mathbf{p};k_0)$ can be expressed by the angles $\theta_{\mathbf{k},\mathbf{p}}$ and $\varphi_{\mathbf{k},\mathbf{p}}$, then expanding t_l in terms of Legendre polynomials it follows from Eq. (III.1) that $(t_l(k,p;k_0))_g$ is given by

$$(t_l(k,p;k_0))_g=\left\{(\Delta H_l{}'(k,p;k_0))_g+\frac{1}{2\pi^2}\frac{1}{2g+1}\int_0^\infty dqq^2G_0{}'(q,k_0)(\Delta H_l{}'(k,q;k_0))_g(\Delta H_{l'}(q,p;k_0))_g\right\}$$
$$\times\left(1-\frac{1}{2\pi^2}\frac{1}{2g+1}\int_0^\infty\int_0^\infty dqd\lambda(q\lambda)^2G_0{}'(q,k_0)G_0{}'(\lambda,k_0)(\Delta H_l{}'(\lambda,q;k_0))_g(\Delta H_{l'}(q,\lambda;k_0))_g\right)^{-1}. \qquad \text{(III.29)}$$

IV. NUMERICAL RESULTS FOR THE ENERGY OF FORMATION AND MIGRATION OF AN INTERSTITIAL AND A VACANCY

The general method outlined in Secs. II and III is used to calculate the formation and migration energy of an interstitial and a vacancy in diamond, silicon, and germanium. The calculations are carried out for the point-defect configurations indicated in Fig. 1, e.g., for the tetrahedral and hexagonal interstitial position, for a vacancy at the lattice site "*b*," and for two vacancies at the sides "*a*" and "*b*" and a lattice atom at the position "*s*." Lattice distortion associated with the point defect is neglected. Then the formation energy is calculated from

$$E_F=\Delta E_1+\Delta E_3=\Delta E_4. \qquad \text{(IV.1)}$$

ΔE_1 is determined by Eqs. (II.38) and (II.39). ΔE_3 is approximately determined from Eq. (II.45) approximating the volume change of the crystal $\Delta\Omega$ by Ω_0 in the case of a vacancy and by $(-\Omega_0)$ in the case of an interstitial. Thus we neglect the contribution to $\Delta\Omega$ resulting from the lattice relaxation associated with the point defect.[11] ΔE_4 is determined from Eqs. (II.48), (II.55), and (II.62) as follows. t_l is assumed to be independent of l. Defining

$$\Delta E_1(\mathbf{q})\equiv4\left\{\frac{q^2}{8\pi e^2}(\mathcal{E}(q,0)-1)t_{l'0}(\mathbf{q})\left(\Delta V_{\text{eff}}{}^{l0}(\mathbf{q})+\frac{\Delta C_{l0}(\mathbf{q})}{2}+\frac{\Delta A_{l0}(\mathbf{q})}{2}\right)\right.$$
$$\left.+\int\frac{d^3p}{(2\pi)^3}(F(\mathbf{p},\mathbf{q})t_{l'0}(\mathbf{q})t_{l0}(\mathbf{p}-\mathbf{q})+\text{c.c.})\left(\Delta V_{\text{eff}}{}^{l0}(\mathbf{p})+\frac{\Delta C_{l0}(\mathbf{p})}{2}+\frac{\Delta A_{l0}(\mathbf{p})}{2}\right)+\cdots\right\}, \qquad \text{(IV.2)}$$

and

$$\Delta E_2(\mathbf{p},\mathbf{q})\equiv6F(\mathbf{p},\mathbf{q})\{t_{l'0}(\mathbf{q}-\mathbf{p})t_{l''0}(\mathbf{p})+\cdots\}(\Delta V_{\text{eff}}{}^{l0}(\mathbf{q})+\tfrac{1}{2}\Delta C_{l0}(\mathbf{q})+\tfrac{1}{2}\Delta A_{l0}(\mathbf{q})), \qquad \text{(IV.3)}$$

where l_0, l_0', l_0'' refer to any lattice ion, then Eq. (II.48) is rewritten as

$$\Delta E_4=\Delta E_4^{(1)}+\Delta E_4^{(2)}\,, \tag{IV.4}$$

with

$$\Delta E_4^{(1)}=\sum_{\mathbf{q}} N(\mathbf{q})\Delta E_1(\mathbf{q})\,, \tag{IV.5}$$

and

$$\Delta E_4^{(2)}\equiv\sum_{\mathbf{q},\mathbf{p}} M(\mathbf{p},\mathbf{q})\Delta E_2(\mathbf{p},\mathbf{q})\,. \tag{IV.6}$$

$N(\mathbf{q})$ and $M(\mathbf{p},\mathbf{q})$ are defined as

$$N(\mathbf{q})\equiv\pm(1/\Omega)\sum_{l'\neq D}(e^{i\mathbf{q}\cdot\mathbf{r}_{Dl'}}-e^{i\mathbf{q}\cdot\mathbf{r}_{Dl'}{}^0})\,, \tag{IV.7}$$

$$\mathbf{r}_{Dl'}{}^0\equiv\mathbf{r}_D{}^0-\mathbf{r}_{l'}\,,$$

and

$$M(\mathbf{p},\mathbf{q})\equiv\pm(1/\Omega^2)\times\sum_{\substack{l',l''\\(l'\neq l'',\,(l',l'')\neq D)}}(\exp i[(\mathbf{q}-\mathbf{p})\cdot\mathbf{r}_{Dl'}+\mathbf{p}\cdot\mathbf{r}_{Dl''}]-\exp i[(\mathbf{q}-\mathbf{p})\cdot\mathbf{r}_{Dl'}{}^0+\mathbf{p}\cdot\mathbf{r}_{Dl''}{}^0])\,. \tag{IV.8}$$

$\mathbf{r}_D$ refers to the position of the ion D in the interior of the crystal and $\mathbf{r}_D{}^0$ refers to the position of the ion D at the surface of the crystal. The minus signs in front of $1/\Omega$ and $1/\Omega^2$ refer to a vacancy. Defining

$$Q(\mathbf{q})\equiv(1/\Omega)\sum_{l'\neq D}e^{i\mathbf{q}\cdot\mathbf{r}_{Dl'}}\,, \tag{IV.9}$$

where l' is summed over all lattice ions beside the ion D, one gets

$$N(\mathbf{q})=\pm\{Q(\mathbf{q})-\tfrac{1}{2}Q^0(\mathbf{q})\}\,, \tag{IV.10}$$

where $Q^0(\mathbf{q})$ is given by Eq. (IV.9) replacing $\mathbf{r}_D$ by $\mathbf{r}_D{}^0$, and

$$M(\mathbf{p},\mathbf{q})=\pm\{[Q(\mathbf{q}-\mathbf{p})Q(\mathbf{p})-Q(\mathbf{q})]-\tfrac{1}{2}[\tfrac{1}{2}Q^0(\mathbf{q}-\mathbf{p})Q^0(\mathbf{p})-Q^0(\mathbf{q})]\}\,. \tag{IV.11}$$

It is

$$Q_I(\mathbf{q})=e^{0\mathbf{K}\cdot\mathbf{r}_0}S(\mathbf{K})\delta_{\mathbf{q},\mathbf{K}}\,, \tag{IV.12}$$

and

$$Q_V(\mathbf{q})=Q^0(\mathbf{q})\,,$$

$$Q^0(\mathbf{q})=e^{i\mathbf{K}\cdot\mathbf{r}_D{}^0}S(\mathbf{K})\delta_{\mathbf{q},\mathbf{K}}-\frac{1}{\Omega}\,, \tag{IV.13}$$

where $\mathbf{K}$ is a reciprocal lattice vector and I and V refer to the interstitial and vacancy, respectively.

In determining ΔE_4, $\Delta H_l(\mathbf{q},\mathbf{k};\mathbf{k}_0)$ is approximately given by Eq. (III.18) replacing the dielectric constant by $\mathcal{E}_H{}^0$ representing the dielectric function of a uniform electron gas in the Hartree approximation and with $\Delta A_l(\mathbf{q},\mathbf{k};0)$ determined by using the Thomas-Fermi-Slater approximation.[21,22] $\mathcal{E}_H{}^0$ is obtained from Eq. (III.12) by replacing the electron-electron interaction potential V_s by $V_s{}^0$, which refers to a uniform electron gas, and by approximating in the polarization propagator π all wave functions ψ_k by plane waves and putting $\beta\equiv0$. Using the Thomas-Fermi-Slater approximation one gets for ΔA_l the approximate expression

$$\Delta A_l(\mathbf{q},\mathbf{k};0)=-(0.92e^2/3r_s)\Delta\rho_l(\mathbf{q},\mathbf{k})\,. \tag{IV.14}$$

$\Delta\rho_l(\mathbf{q},\mathbf{k})$ is defined as

$$\Delta\rho_l(\mathbf{q},\mathbf{k})\equiv\int d^3R_l e^{-i\mathbf{q}\cdot\mathbf{R}_l}\Delta\rho_l(\mathbf{R}_l)e^{i\mathbf{k}\cdot\mathbf{R}_l}\,, \tag{IV.15}$$

where $\Delta\rho_l(\mathbf{R}_l)$ is the change in the density of valence electrons associated with $\Delta\rho_l(\mathbf{R}_l,0)$. It follows from Secs. II and III that $\Delta\rho_l(\mathbf{q},\mathbf{k})$ can be written as

$$\Delta\rho_l(\mathbf{q},\mathbf{k})=\sum_p\int\int\frac{d^3\sigma}{(2\pi)^3}\frac{d^3\gamma}{(2\pi)^3}f_p(1-f_\sigma)e^{i(\gamma-\sigma+\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_l}\left[\frac{1}{E(\mathbf{p})-E_0(\boldsymbol{\sigma})+i\eta}-\frac{1}{E(\boldsymbol{\sigma})-E_0(\mathbf{p})-i\eta}\right]\times\Delta H_l(\boldsymbol{\sigma},\boldsymbol{\gamma};0)\langle\boldsymbol{\gamma}|\psi_p\rangle\langle\psi_p|\boldsymbol{\sigma}+\mathbf{k}-\mathbf{q}\rangle\,. \tag{IV.16}$$

Then a self-consistent expression for $\Delta\rho_l(\mathbf{q},\mathbf{k})$ is approximately obtained by

$$\Delta\rho_l(\mathbf{q},\mathbf{k})=\frac{1-\omega(\mathbf{q},\mathbf{k})}{\omega(\mathbf{q},\mathbf{k})}\,\frac{\Delta V_i{}^l(\mathbf{q},\mathbf{k})+\Delta A_{iv}{}^l(\mathbf{q},\mathbf{k})}{\mathcal{E}_H(\mathbf{q}-\mathbf{k},0)}\,, \tag{IV.17}$$

with

$$\omega(\mathbf{q},\mathbf{k})\equiv1-\sum_p\int\int\frac{d^3\sigma}{(2\pi)^3}\frac{d^3\gamma}{(2\pi)^3}f_p(1-f_\sigma)\times e^{i(\gamma-\sigma+\mathbf{k}-\mathbf{q})\cdot\mathbf{r}_l}\left[\frac{1}{E(\mathbf{p})-E_0(\boldsymbol{\sigma})+i\eta}-\frac{1}{E(\boldsymbol{\sigma})-E_0(\mathbf{p})-i\eta}\right]\langle\boldsymbol{\gamma}|\psi_p\rangle\langle\psi_p|\boldsymbol{\sigma}+\mathbf{k}-\mathbf{q}\rangle\,. \tag{IV.18}$$

$\omega(\mathbf{q},\mathbf{k})$ is approximately given by replacing the energies E by E_0 and by averaging the matrix elements with respect to $\mathbf{p}$. For the numerical calculation the wave function ψ_p is approximated in Eq. (IV.18) by a normalized plane wave, and in Eq. (IV.17) $\mathcal{E}_H$ is approximated by $\mathcal{E}_H{}^0$.

$\Delta V_R{}^l(\mathbf{q},\mathbf{k};0)$ is determined from Eq. (III.27). The closed-shell core electron wave functions $\varphi_t{}^l$ are determined using earlier results given by Herman[25] for diamond, by Kleinman and Phillips[14] for silicon, and by Hartree *et al.*[26] for germanium.

The numerical results obtained for the energy of formation and migration of a single interstitial and of a single vacancy in diamond, silicon, and germanium are listed in Table I and discussed in the following section. The following tables contain the results obtained in the Hartree and Hartree-Fock approximation and display the importance of the *t*-matrix approximation, and particularly the importance of multiple scattering. The interpretation of the results in physical terms becomes obvious from the fact that multiple scattering is responsible for covalent bonding and that exchange increases the formation of covalent bonds. The formation energies of the interstitial refer to the tetrahedral interstitial position, which turns out to be the equilibrium position. (See Table II to Table VIII.) In order to demonstrate the potential associated with a single lattice ion, which is the basic quantity in the outlined method, Fig. 3 shows for diamond, silicon, and germanium

$$V_l(q)=V_i^l(q)+A_{iv}^l(q)+V_R^l(q)+[C(q)/N]+[A(q)/N]. \qquad \text{(IV.19)}$$

Figure 3 shows that in all three cases $V_l(q)$ decreases rapidly with increasing q indicating a smooth pseudocrystal potential as assumed.

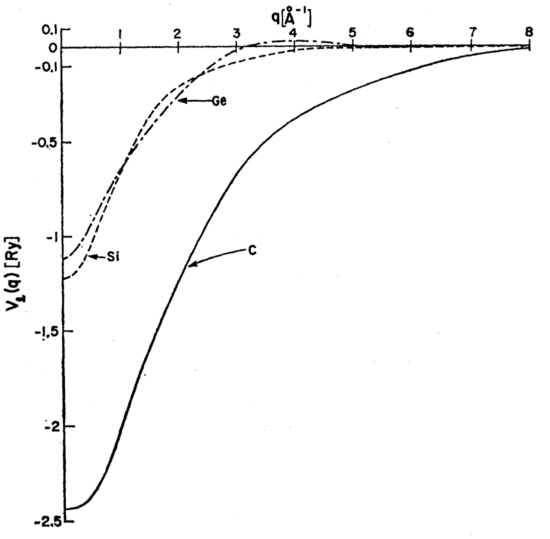

FIG. 3. Plots of the potential $V_l(\mathbf{q})$, which is defined as the sum of $V_i^l(\mathbf{q})$, $A_{iv}^l(\mathbf{q})$, $V_R^l(\mathbf{q})$, $C(q)/N$, and $A(\mathbf{q})/N$, for C, Si, and Ge.

V. DISCUSSION

A general method is presented for determining from first principles properties of point defects in covalent crystals. The scattering of the valence electrons by the effective crystal potential is treated by taking into account the atomic configuration of the lattice. In this way the response of the valence electrons to the effective crystal potential can be determined taking into account nonlinear screening, e.g., local field corrections. The redistribution of the valence electrons reflects strongly the atomic configuration of the imperfect lattice. Thus, the energy of the system of valence electrons is obtained as a function of the positions of the ions. This will be used in a continuing paper to express the energy of the system of valence electrons in terms of the ionic displacements arising from the point defect. Such an expression is required for many problems, for example, for a self-consistent determination of the equilibrium configuration of an imperfect crystal.[27]

TABLE I. E_F^v and E_M^v denote the energy of formation and migration, respectively, of a vacancy. $E_D^v\equiv E_F^v+E_M^v$ denotes the activation energy for vacancy diffusion. E_F^I and E_M^I denote the energy of formation and migration, respectively, of an interstitial. $E_D^I\equiv E_F^I+E_M^I$ denotes the activation energy for interstitial diffusion.

Substance	E_F^v (eV)	E_M^v (eV)	E_D^v (eV)	E_F^I (eV)	E_M^I (eV)	E_D^I (eV)
C	3.68	1.85	5.53	1.76	0.85	2.61
Si	2.13	1.09	3.22	1.09	0.51	1.60
Ge	1.91	0.98	2.89	0.93	0.44	1.37

The *t*-matrix approximation is valid even if the crystal potential is strong and represents, therefore, an extension of orthogonal-plane-wave method and is very useful if the pseudocrystal potential is not weak and for treating those valence electron states for which the repulsive potential vanishes for symmetry reasons. For example, in diamond, valence electrons in *s* states see no repulsive potential. Another advantage of the *t*-matrix approach is its ease of physical interpretation, which is very useful for finding good approximations. Further, the *t*-matrix approximation is very convenient for treating multiple scattering of the valence electrons by the lattice which is essential in covalent crystals. Multiple scattering is important for determining the fine structure of the valence-electron distribution reflecting, for example, the sizes of the lattice ions. Multiple electron scattering will in general become more and more important with decreasing distance among neighboring lattice ions.

The orthogonalization of the valence-electron wave functions to the closed-shell core-electron wave functions yields two main advantages. First, the crystal potential is transformed into an effective crystal potential, which is usually weak and smooth. Second, the electronic structure of the ion cores is taken into account, guaranteeing that the valence electrons will not occupy closed-shell core-electron states. The cancellation of the crystal potential by the repulsive potential is discussed in detail by Cohen and Heine[10] and by others.[14] However, it may be noted that if the closed-shell core-

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[25] F. Herman, Phys. Rev. **88**, 1210 (1952).

[26] W. Hartree, D. R. Hartree, and M. F. Manning, Phys. Rev. **59**, 306 (1941).

[27] K. H. Bennemann, Phys. Rev. **130**, 1757 (1963).

TABLE II. The contributions ΔE_1, ΔE_3, and ΔE_4 for a vacancy. The energies are in rydbergs.

	C	Si	Ge
$\Delta E_1{}^V$	6.458	4.223	4.069
$\Delta E_3{}^V$	-1.801	-1.156	-1.088
$\Delta E_4{}^V$	-4.387	-2.911	-2.841
$E_F{}^V$	0.270	0.156	0.140

electron states are distributed over the strongest inner core part of the potential and if no strong admixture of core levels into valence levels occurs, then the pseudocrystal potential is weak. In general the cancellation of the crystal potential is less complete for higher valence-electron states. However, valence electrons in higher states also interact more weakly with the crystal potential.

The general method studies the determination of a self-consistent crystal potential taking into account correlation among the valence electrons,[22,28] thus presenting an extension of usual band theory. The valence electrons interact with a static lattice. However, the proposed method can be extended to take into account the dynamics of the lattice by adding the polarization propagator of the lattice to the polarization propagator of the valence electrons in the dielectric function. The application of the proposed general method to other crystal types is mainly limited by the fact that the tightly bound core electrons are treated as dynamically independent of the valence electrons. The neglect of correlation between core and valence electrons is valid if electron transitions between tightly bound core-electron states and valence-electron states are negligible and if the excitation energies of tightly bound core electrons are large compared to excitation energies of the valence electrons, for example, the plasma energy. Under these two conditions the core-valence electron interactions are essentially unscreened and thus can be treated within the Hartree-Fock approximation. This is the case, for example, for small ion cores. However, in noble metals and transition metals the interaction between conduction electrons and core electrons—for example, s-d electron interactions—is remarkably strong, and then the above assumption will fail. Then the coupled wave equations for the core electrons and the valence electrons must be solved self-consistently.

TABLE III. The contributions ΔE_1, ΔE_3, and ΔE_4 for the saddle-point configuration of the vacancy. All energies are in rydbergs.

	C	Si	Ge
$\Delta E_1{}^V$	5.076	3.320	3.197
$\Delta E_3{}^V$	-1.801	-1.156	-1.088
$\Delta E_4{}^V$	-2.869	-1.928	-1.898
$E_F{}^V$	0.406	0.236	0.211

TABLE IV. The contributions ΔE_1, ΔE_3, and ΔE_4 for the interstitial. All energies are in rydbergs.

Interstitial site		C	Si	Ge
T	$\Delta E_1{}^I$	1.965	1.289	1.239
	$\Delta E_3{}^I$	1.801	1.156	1.088
	$\Delta E_4{}^I$	-3.637	-2.367	-2.258
	$E_F{}^I$	0.129	0.078	0.069
H	$\Delta E_1{}^I$	2.401	1.572	1.513
	$\Delta E_3{}^I$	1.801	1.156	1.088
	$\Delta E_4{}^I$	-4.031	-2.628	-2.511
	$E_F{}^I$	0.171	0.100	0.090

TABLE V. Vacancy formation and migration energy as resulting from various approximations for the scattering matrix T_l. All energies are in eV.

Approximation for T_l		C	Si	Ge
ΔH_l	$E_F{}^V$	0.64	0.47	0.43
t_l	$E_F{}^V$	0.92	0.64	0.59
$t_l+\sum_{l'\neq l} t_l G_0 t_{l'}$	$E_F{}^V$	3.68	2.13	1.91
ΔH_l	$E_M{}^V$	1.27	0.86	0.78
t_l	$E_M{}^V$	0.91	0.60	0.52
$t_l+\sum_{l'\neq l} t_l G_0 t_{l'}$	$E_M{}^V$	1.85	1.09	0.98

If the closed-shell core-electron wave functions $\varphi_t{}^l$ belonging to different ions overlap, then the resulting repulsive interaction can approximately be described by a Born-Mayer potential. It needs to be investigated from case to case whether the exchange-correlation potential can be approximated by a local potential. As has been discussed by Phillips and Kleinman[22] a local exchange potential represents a fairly good approximation in the three semiconductors considered in this paper.

TABLE VI. Vacancy formation and migration energy in the Hartree and Hartree-Fock approximation. The energies are in eV.

Approximation		C	Si	Ge
Hartree	$E_F{}^V$	2.52	1.62	1.47
Hartree-Fock	$E_F{}^V$	3.68	2.13	1.91
Hartree	$E_M{}^V$	1.45	0.87	0.80
Hartree-Fock	$E_M{}^V$	1.85	1.09	0.97

The general method was concerned with determining the nonlocalized valence-electron states resulting from the electron scattering by the imperfect crystal. However, there will in general also be bound states associated with point defects. In the text, the sum over the wave

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[28] F. Bassani, J. Robinson, B. Goodman, and J. R. Schrieffer, Phys. Rev. **127**, 1969 (1962).

TABLE VII. Interstitial formation and migration energy as resulting from various approximations for the scattering matrix T_l. The formation energy refers to the T site, the equilibrium configuration. All energies are in eV.

Approximations for T_l		C	Si	Ge
ΔH_l	E_F^I	0.49	0.33	0.30
t_l	E_F^I	0.71	0.48	0.42
$t_l+\sum_{l'\neq l} t_l G_0 t_{l'}$	E_F^I	1.76	1.09	0.93
ΔH_l	E_M^I	1.75	0.84	0.75
t_l	E_M^I	2.15	1.06	0.97
$t_l+\sum_{l'\neq l} t_l G_0 t_{l'}$	E_M^I	0.85	0.51	0.44

vector of a valence electron has always been converted into an integral in a way implying that the bound states lying in the energy gap between the valence and conduction band are unoccupied. This will in general be the case if the crystal is in its ground state, but not at high temperatures and in strongly doped *n*- or *p*-type crystals. The existence of bound states might complicate the kinetics of point defects. However, it is observed that the migration of a vacancy does not depend much on its charged state[5] resulting from trapping valence electrons in bound states. A brief mathematical formulation of bound states is given in Appendix A.

The proposed method can readily be used to determine correlations among point defects, for example, to calculate the interaction among two interstitials, two vacancies, an impurity and a vacancy, etc. Such correlations play a role in diffusion and quenching experiments.

The further main approximations used in the application of the general method to diamond, silicon, and germanium are that the dielectric function $\mathcal{E}$ is approximated by $\mathcal{E}_H{}^0$, that the renormalization of the valence-electron wave functions is neglected, that the exchange potential is determined using a Thomas-Fermi-Slater approximation, and that the lattice distortion and resulting volume change of the crystal is neglected. The error resulting from these approximations in determining formation energies is roughly estimated as about 20%. However, the error involved in determining the migration energies will in general be less.

TABLE VIII. Interstitial formation and migration energy in the Hartree and Hartree-Fock approximation. The formation energy refers to the T site, the equilibrium configuration. All energies are in eV.

Approximation		C	Si	Ge
Hartree	E_F^I	1.30	0.83	0.71
Hartree-Fock	E_F^I	1.76	1.09	0.93
Hartree	E_M^I	0.68	0.40	0.35
Hartree-Fock	E_M^I	0.85	0.51	0.44

It follows from Table I that the migration energy of an interstitial is much smaller than the migration energy of a vacancy. Since the atoms in the diamond-type lattice are strongly bound by covalent bonds to each other and the vacancy migration involves the successive rupture and reformation of three covalent bonds, it is expected that the presumably loosely bound interstitial is much more mobile than the vacancy.

In the following, the results given in Table I are compared to results found by experiments and earlier calculations. By using a Morse potential in which parameters are determined phenomenologically from force constant data, Swalin[6] calculated for the energy of formation of a vacancy in diamond, silicon, and germanium 4.16, 2.32, and 2.07 eV, respectively. Swalin obtains further for the vacancy migration energy in diamond, silicon, and germanium 2.02, 1.06, and 0.95 eV, respectively. By describing the covalent bonds by a Morse potential and determining the lattice distortion due to the vacancy from Born's lattice energy within the harmonic approximation, Scholz[7] calculates the formation energy of a vacancy in germanium. Depending on the potential used Scholz obtains results between 1.62 and 2.52 eV.

The following experimental results are available. From quenching in *n*- or *p*-type germanium it is found that the energy of formation of the involved point defect, believed to be a vacancy, is 2.0±0.3 eV.[5] Also, the data can be fitted using 0.9±0.07 eV for the energy of motion. The activation energy for self-diffusion in pure germanium was measured to be 2.96±0.05 eV.[3] The energy of formation and migration is found to be the same irrespective of whether the vacancy is in *n*- or *p*-type material, thus indicating that the energies of formation and migration do not depend much on the charged state of the vacancy. Watkins[4] obtained from annealing studies in *p*-type silicon an energy of motion of 0.33±0.03 eV for the vacancy identified by means of electron paramagnetic resonance (EPR). This result is inconsistent with others. It may be noted that some experiments performed in *n*-type silicon demonstrate that the dependence of the vacancy mobility on the charge state is small. Also, Fig. 3 suggests that diffusion in silicon and germanium should be rather similar. Judging from impurity measurements the activation energy of diffusion in silicon is about 3.5 eV.[4] Assigning it to vacancy motion, Watkin's results would imply a formation energy for the vacancy of about 3 eV, which is remarkably different from germanium. Probably further EPR studies are necessary before point defects can be firmly identified.

Hasiguti[4] estimated from measurements that the migration energy of an interstitial in *p*-type germanium is about 0.5–0.6 eV and the migration energy of a vacancy in *n*-type germanium about 1.2–1.3 eV.

Accurate experimental results about formation and migration energies of point defects in diamond are not yet given in the literature.

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APPENDIX A: BOUND STATES

In the previous sections, the valence-electron states resulting from the scattering of the valence electrons due to the perturbing Hamiltonian ΔH have been determined. In the following we outline briefly the determination of the bound states associated with point defects. The shallow localized states due to imperfections in semiconductors can be adequately determined in terms of the effective mass theory developed by Kohn.[29] However, this theory is not valid for deep localized states at point defects. The shallow as well as deep bound states resulting from point defects are determined by the poles of the t matrix T_l associated with an interstitial, impurity, or displaced lattice ion. Thus the localized states are determined by the homogeneous integral equation

$$T_l(\mathbf{q},\mathbf{k};k_0)=\int\frac{d^3p}{(2\pi)^3}V_l(\mathbf{q},\mathbf{p};k_0)G_0(p,k_0)T_l(\mathbf{p},\mathbf{k};k_0)+\sum_{\substack{l'\\(l'\neq l)}}\int\frac{d^3p}{(2\pi)^3}e^{i(\mathbf{q}-\mathbf{p})\cdot\mathbf{r}_{ll'}}V_{l'}(\mathbf{q},\mathbf{p};k_0)G_0(p,k_0)T_l(\mathbf{p},\mathbf{k};k_0)\,,\tag{A.1}$$

with

$$V_l(\mathbf{q},\mathbf{p};k_0)=V_{\mathrm{eff}}{}^l(\mathbf{q},\mathbf{p};k_0)+C_0(\mathbf{q},\mathbf{p})/N+A_0(\mathbf{q},\mathbf{p};k_0)/N+\Delta C_l(\mathbf{q},\mathbf{p})+\Delta A_l(\mathbf{q},\mathbf{p};k_0)\,,\tag{A.2}$$

N being the total number of lattice atoms, and with

$$G_0(p,k_0)=\frac{1}{k_0-(\hbar^2/2m)p^2+i\epsilon\,\mathrm{sgn}(p-p_F)}\,,\quad \epsilon>0.\tag{A.3}$$

T_l is approximately expanded in Legendre polynomials as

$$T_l(\mathbf{q},\mathbf{k};k_0)=\sum\nolimits_g\,[T_l(q,k;k_0)]_gP_g(\cos\vartheta_{\mathbf{q},\mathbf{k}}).\tag{A.4}$$

One gets then from Eq. (A.1)

$$[T_l(q,k;k_0)]_g=\frac{1}{2\pi^2}\frac{1}{2g+1}\int_0^\infty dpp^2G_0(p,k_0)[V_l(q,p;k_0)]_g[T_l(p,k;k_0]_g$$
$$+\sum_{\substack{l'\\(l'\neq l)}}\int\frac{d^3p}{(2\pi)^3}e^{i(\mathbf{q}-\mathbf{p})\cdot\mathbf{r}_{ll'}}G_0(p,k_0)V_{l'}(\mathbf{q},\mathbf{p};k_0)[T_l(p,k;k_0)]_g(P_g(\cos\vartheta_{\mathbf{p},\mathbf{k}})/P_g(\cos\vartheta_{\mathbf{q},\mathbf{k}})).\tag{A.5}$$

Assuming that V_l varies slowly in space, then Eq. (A.5) can approximately be rewritten as

$$[T_l(q,k;k_0)]_g=\frac{1}{2\pi^2}\frac{1}{2g+1}\int_0^\infty dpp^2G_0(p,k_0)[V_l(q,p;k_0)]_g[T_l(p,k;k_0)]_g$$
$$+\sum_{\substack{l'\\(l'\neq l)}}\sum_{g'}\frac{P_{g'}(1)}{2\pi^2}\times\int_0^\infty dpp^2G_0(p,k_0)\frac{\sin qr_{ll'}}{qr_{ll'}}\frac{\sin pr_{ll'}}{pr_{ll'}}[V_{l'}(q,p;k_0)]_{g'}[T_l(p,k;k_0)]_g.\tag{A.6}$$

It follows from Eq. (A.6) that the poles of $[T_l(q,k;k_0)]_g$ respectively, the energies k_0 of the bound states are approximately determined by

$$1-\frac{1}{4\pi^4}\left(\frac{1}{2g+1}\right)\int_0^\infty\int_0^\infty dpdp'p^2(p')^2G_0(p,k_0)G_0(p',k_0)[V_l(p,p';k_0)]_g$$
$$\times\left\{\frac{1}{2g+1}[V_l(p',p;k_0)]_g+\sum_{\substack{l'\\(l'\neq l)}}\sum_{g'}P_{g'}(1)[V_{l'}(p',p;k_0)]_{g'}(\sin p'r_{ll'}/p'r_{ll'})(\sin pr_{ll'}/pr_{ll'})\right\}=0.\tag{A.7}$$

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[29] W. Kohn, *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957).

APPENDIX B: MULTIPLE SCATTERING

The t matrix t_l describes the scattering of the electrons due to the single perturbing Hamiltonian $\Delta H_l'$ when separated from the toal ensemble of scatterers representing the crystal. The t-matrix T_l describes the scattering arising from $\Delta H_l'$ in the presence of the crystal. The effect of the crystal on the valence electron scattering due to $\Delta H_l'$ is given by the multiple scattering occurring among $\Delta H_l'$ and the surrounding crystal. All multiple scattering contributions to T_l are summed up in the integral equation derived for T_l. This integral equation can be solved by using Fredholm's general theory.[30] If $\Delta H_l'(\boldsymbol{\sigma},\mathbf{k};k_0)$ is sharply peaked at $\mathbf{q}\approx\mathbf{k}$, e.g., $\Delta H_l'(\mathbf{R}_l,k_0)$ a smoothly varying function in $\mathbf{R}_l$, then the integral equation for $T_l(\mathbf{q},\mathbf{k};k_0)$ is approximately solved by

$$T_l(\mathbf{q},\mathbf{k};k_0)=\left(\Delta H_l'(\mathbf{q},\mathbf{k};k_0)+\sum_{l'}\int\frac{d^3p}{(2\pi)^3}e^{i(\mathbf{q}-\mathbf{p})\cdot\mathbf{r}_{ll'}}\Delta H_{l'}'(\mathbf{q},\mathbf{p};k_0)G_0'(\mathbf{p},k_0)\Delta H_l'(\mathbf{p},\mathbf{k};k_0)\right)$$
$$\times\left(1-\sum_{l',l''}\int\int\frac{d^3p}{(2\pi)^3}\frac{d^3s}{2(\pi)^3}e^{i(\mathbf{q}-\mathbf{p})\cdot\mathbf{r}_{ll'}}e^{i(\mathbf{p}-\mathbf{s})\cdot\mathbf{r}_{ll''}}\Delta H_{l'}'(\mathbf{q},\mathbf{p};k_0)G_0'(\mathbf{p},k_0)\Delta H_{l''}'(\mathbf{p},\mathbf{s};k_0,G_0'(\mathbf{s},k_0)\right)^{-1}. \quad \text{(B.1)}$$

A further approximation replaces $\Delta H_{l'}'(\mathbf{q},\mathbf{p};k_0)$ in the second bracket by $\Delta H_{l'}'(\mathbf{s},\mathbf{p};k_0)$. If $\Delta H_l'$ is independent of l, which is the case for a perfect, monoatomic crystal or for a monoatomic crystal in general, and if $\Delta H_l'$ is approximated by the expression resulting for a regular lattice ion l, then Eq. (B.1) can be rewritten as

$$T_l(\mathbf{q},\mathbf{k};k_0)=\left(\Delta H_{l_0}'(\mathbf{q},\mathbf{k};k_0)+\int\frac{d^3p}{(2\pi)^3}\Delta H_{l_0}'(\mathbf{q},\mathbf{p};k_0)G_0'(\mathbf{p},k_0)\Delta H_{l_0}'(\mathbf{p},\mathbf{k};k_0)C_l(\mathbf{p},\mathbf{q})\right)$$
$$\times\left(1-\int\int\frac{d^3p}{(2\pi)^3}\frac{d^3s}{(2\pi)^3}\Delta H_{l_0}'(\mathbf{q},\mathbf{p};k_0)G_0'(\mathbf{p},k_0)\Delta H_{l_0}'(\mathbf{p},\mathbf{s};k_\prime)G_0'(\mathbf{s},k_0)C_l(\mathbf{p},\mathbf{q})C_l(\mathbf{s},\mathbf{p})\right)^{-1}, \quad \text{(B.2)}$$

$$C_l(\mathbf{p},\mathbf{q})\equiv\sum_{l'}e^{i(\mathbf{q}-\mathbf{p})\cdot\mathbf{r}_{ll'}}. \quad \text{(B.3)}$$

If $\Delta H_l'(\mathbf{q},\mathbf{k};k_0)$ is only sharply peaked at $q\approx k$, then the integral equation resulting for $[T_l(q,k;k_0)]_a$ is approximately solved in a way as outlined in Appendix A.

APPENDIX C: EQUATION OF STATE OF VALENCE ELECTRONS

To determine ΔE_3 the dependence of E_{el} on the crystal volume must be evaluated explicitly. Approximating V_R and A by local potentials one gets approximately from Eqs. (II.10) and (II.31)

$$E_{el}-n\frac{C_0}{2}=n\left\{\frac{0.982}{r_s^2}-\frac{0.916}{r_s}+E_{\text{corr}}(r_s)+\langle V_R(r_s)\rangle+\sum_{\mathbf{K}\neq0}f_{\mathbf{K}}(r_s)\right\}. \quad \text{(C.1)}$$

C_0 results from C for $\sum_l\Delta H_l'\equiv0$ and $V_R\equiv0$. n is the total number of valence electrons. r_s is given by

$$r_s=\left(\frac{3}{32\pi Z}\right)^{1/3}a. \quad \text{(C.2)}$$

a is the lattice constant. The correlation energy E_{corr} is approximately given by[31]

$$E_{\text{corr}}=(-0.115+0.031\ln r_s). \quad \text{(C.3)}$$

The repulsive potential V_R is given as a function of r_s by

$$V_R(\mathbf{p})=-\int\frac{d^3q}{(2\pi)^3}\gamma(\mathbf{q},\mathbf{p})\times\left\{\frac{1+\Lambda(q)}{\mathcal{E}(q,0)}V_{\text{eff}}(q)-V_R(q)\right\}, \quad \text{(C.4)}$$

with

$$\gamma(\mathbf{q},\mathbf{p})\equiv\sum_{t,k}a_{tk}(\mathbf{q})a_{tk}^*(\mathbf{p}),$$
$$a_{tk}(\mathbf{q})\equiv\int d^3r\,\varphi_{tk}^*(\mathbf{r})e^{i\mathbf{q}\cdot\mathbf{r}}, \quad \text{(C.5)}$$

$$\Lambda(\mathbf{q})\equiv-(0.916/r_s)\tfrac{1}{3}(q^2/8\pi e^2)[1-\mathcal{E}(q,0)], \quad \text{(C.6)}$$

and

$$V_{\text{eff}}\equiv V_i'+A_{iv}+V_R, \quad V_i'\equiv V_i+C'+A'. \quad \text{(C.7)}$$

C' and A' denote the contributions to C and A, respectively, resulting from the part $(\psi_k-\Phi_k)$ of the total wave function of the valence electrons. On the right side in Eq. (C.4) V_R might be approximated by the expression obtained from Eq. (C.4) by replacing the expression in brackets by $(V_i'+A_{iv})$. $\gamma(\mathbf{q},\mathbf{p})$ and $(V_i'+A_{iv})$ are approximately independent of r_s. The dielectric function $\mathcal{E}(\mathbf{q},0)$ is given approximately by[19]

$$\mathcal{E}(q,0)=1+0.165r_s[u(x)/x^2], \quad x\equiv\frac{q}{2k_f}, \quad \text{(C.8)}$$

where

$$u(x)\equiv\frac{1}{2}\left\{1+\frac{1-x^2}{2x}\ln\left|\frac{1+x}{1-x}\right|\right\}. \quad \text{(C.9)}$$

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[30] E. Whittaker and G. Watson, *A Course of Modern Analysis* (University Press, Cambridge, England, 1946).

[31] D. Pines, *The Many-Body Problem* (W. A. Benjamin, Inc., New York, 1961).

The Fermi wave vector k_F is related to r_s as

$$k_F=\left(\frac{9\pi}{4}\right)^{1/3}\frac{1}{r_s}. \qquad \text{(C.10)}$$

The function $f_{\mathbf{K}}(r_s)$ is given by

$$f_{\mathbf{K}}(r_s)=S(\mathbf{K})S^*(\mathbf{K})\frac{K^2\Omega_0}{16\pi e^2 Z}\frac{1+\Lambda(K)}{\mathcal{E}(K,0)} \times\frac{1+\Lambda(K)+\mathcal{E}(K,0)}{\mathcal{E}(K,0)}V_{\text{eff}}^2(K). \qquad \text{(C.11)}$$

The above formulas yield an approximate expression for the equation of state of the system of valence electrons taking into account within the Born approximation the interaction between the pseudocrystal potential and the valence electrons. The exact treatment of the electron-lattice interaction replaces $[(1/\mathcal{E}+\Lambda/\mathcal{E})V_{\text{eff}}]$ in Eq. (C.11) by the corresponding t matrix and in all formulas $\mathcal{E}$ by the exact dielectric function.

ΔE_3 is now determined as follows. r_s' which refers to the crystal with volume $\Omega+\Delta\Omega$ is related to r_s, which refers to the crystal with volume Ω as

$$r_s'=(1+C)^{1/3}r_s\,, \qquad \text{(C.12)}$$

with

$$C\equiv\Delta\Omega/\Omega=\alpha(Z/n)\,,\quad \Delta\Omega\equiv\alpha\Omega_0\,,\quad \Omega_0=a^3/8. \qquad \text{(C.13)}$$

One gets then

$$\Delta E_3=-\frac{C}{3}\left\{\frac{1.964}{r_s^2}-\frac{0.916}{r_s}-0.031 +\theta(r_s)+\sum_{\mathbf{K}\neq 0}g_{\mathbf{K}}(r_s)\right\}n, \qquad \text{(C.14)}$$

with

$$\theta(r_s)=-\int\frac{d^3q}{(2\pi)^3}\gamma(q,0)H(q)V_{\text{eff}}(q)\,, \qquad \text{(C.15)}$$

$$H(q)\equiv\frac{1}{\mathcal{E}(q,0)}\left\{\frac{0.165r_s}{\mathcal{E}(q,0)}\frac{2x^2-1}{2x^3}\ln\left|\frac{1+x}{1-x}\right| \times\left(1-\frac{0.916}{3r_s}\frac{q^2}{8\pi e^2}\right)+\Lambda(q)\right\}, \qquad \text{(C.16)}$$

and

$$g_{\mathbf{K}}(r_s)\equiv S(\mathbf{K})S^*(\mathbf{K})\frac{K^2\Omega_0}{16\pi e^2 Z}H(K)V_{\text{eff}}^2(K)\left\{2\frac{1+\Lambda(K)}{\mathcal{E}(K,0)}+1 +2\frac{1+\Lambda(K)}{\mathcal{E}(K,0)}\left(\frac{1+\Lambda(K)}{\mathcal{E}(K,0)}+1\right)\frac{\Theta_K(r_s)}{V_{\text{eff}}(K)H(K)}\right\}, \qquad \text{(C.17)}$$

where θ_K is obtained from Eq. (C.15) replacing $\gamma(q,0)$ by $\gamma(g,K)$.