electrical glow curves reported by Van Heyningen and Brown.[36] These workers observed a number of current peaks during the warming of nominally pure AgCl samples which had been illuminated at liquid helium temperature. They attributed these current peaks to the thermal release of electrons from traps. Although some of the electron traps appeared to be caused by strains, the exact nature of the traps was not determined. Presumably some of the traps could be instrinsic and others could be caused by impurities. In our experiments, nominally pure AgCl samples were continuously illuminated with blue light from a Hg lamp as the

[36] R. S. Van Heyningen and F. C. Brown, Phys. Rev. 111, 462 (1958).

samples were cooled from room to liquid nitrogen temperature in about 2 h and then quenched to helium temperature in less than 2 min. In other experiments, samples were continuously illuminated at liquid helium or nitrogen temperature for 10 to 30 min with either blue light from a Hg lamp or with white light from a tungsten filament lamp. No EPR signals were seen which could be attributed to the illumination. Also, there was no apparent coloration of the samples after these experiments. There exist at least two possible explanations for these failures. First, the electrical glow curve technique is several orders of magnitude more sensitive than EPR in the detection of electron traps. Second, there was no dc electric field applied during the illumination to help prevent electron-hole recombination.

General Method for Determining Lattice Point Defect Configurations Including their Dependence on Electron Redistribution*

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A general method is proposed for determining the equilibrium configurations of single lattice point defects and complexes thereof. The equilibrium configuration of the lattice containing impurities, interstitials, and vacancies is determined by using a variational approach minimizing the energy of the crystal. The energy of the crystal is explicitly expressed in terms of the displacements of the ions. It is assumed that the energy of the system of ions, including the point defects, arises from two-body interactions. The energy of the system of valence or conduction electrons is derived in the general form from a Hamiltonian including the coupling between the distorted lattice and the electrons. The wave functions of the valence or conduction electrons are given by an integral equation derived from the Hartree-Fock equation. The explicit dependence of the wave functions on the displacements of the ions is obtained from the integral equation by using the Born approximation. Using these wave functions the energy of the considered system of electrons is explicitly expressed in terms of the displacements. To apply the method in practice the wave functions and the crystal energy need to be evaluated explicitly.

I. INTRODUCTION

MANY experiments[1-3] have been performed to study the effects of point defects in crystals. To be able to check theoretically the interpretation of these experiments it is necessary to determine the lattice distortion and changes in the distribution of the electrons associated with the various point defects and complexes thereof. In particular, it is of interest to determine the equilibrium configurations and formation energies of an interstitial, a vacancy, a close Frenkel pair (vacancy plus interstitial), a divacancy, and a di-interstitial. In all previous calculations[1-9] of point defect configurations the effect on the lattice distortion arising from the redistribution of the electrons has been neglected. The principal purpose of this paper is, therefore, to determine the lattice distortion by taking into account the coupling between the lattice and the electrons.

The crystal is represented by a system of ions (each ion consists of nucleus plus tighly bound electrons) arranged in a static lattice and valence or conduction electrons moving in a potential field produced by the electrons themselves and the ions. The lattice distortion

[1] A. Seeger, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1955), Vol. 7, Part I, p. 383.
[2] H. G. van Bueren, *Imperfections in Crystals* (North-Holland Publishing Company, Amsterdam, 1960).
[3] F. Seitz and J. S. Koehler, in *Advances in Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 2, p. 305.

[4] R. A. Johnson, G. H. Goedecke, E. Brown, and H. B. Huntington, Bull. Am. Phys. Soc. 5, 181 (1960).
[5] J. B. Gibson, A. N. Goland, M. Milgram, and G. H. Vineyard, Phys. Rev. 120, 1229 (1960).
[6] K. H. Bennemann, Phys. Rev. 124, 669 (1961).
[7] K. H. Bennemann and L. Tewordt, Z. Naturforsch. 15a, 772 (1960).
[8] A. Seeger and E. Mann, J. Phys. Chem. Solids 12, 326 (1960).
[9] L. Tewordt, Phys. Rev. 109, 61 (1958).

produced by the introduction of point defects into the crystal is determined by using a variational approach in which the energy of the system of ions, point defects, and electrons is minimized with respect to the positions of the ions, impurities, and interstitials. The resulting system of equations can be solved by iteration in a manner proposed by Tewordt.[9] The wave functions of the outer electrons in the imperfect crystal are given by an integral equation derived from the Hartree-Fock equation. An approximation scheme which gives the dependence of the wave functions on the displacements of the ions is presented.

II. GENERAL METHOD

The energy of the disturbed crystal containing M point defects is given by $E^M(v_1,v_2,\cdots)$, where the v_i are the displacements of the ions, impurities, and interstitials from suitably chosen starting positions. The displacements v_i are determined by a variational approach whereby the energy E^M is minimized. The displacements of the ions which lie sufficiently far from the point defects are small and vary slowly from ion to ion and correspond, therefore, to an elastic displacement field.[10] The elastic displacement field at r arising from M point defects at $r_i, \cdots, r_M$ is given by

$$v(r)= \sum_{s=1}^{M} v^{(s)}(r-r_s), \qquad (1)$$

where $v^{(s)}(r-r_s)$ is the elastic displacement field due to the point defect s. $v^{(s)}$ is expanded in terms of the elastic solutions $u_1^{(s)}(r-r_s), \cdots, u_n^{(s)}(r-r_s)$ as

$$v^{(s)}(r-r_s)=\beta_1^{(s)}u_1^{(s)}(r-r_s)+\cdots+\beta_n^{(s)}u_n^{(s)}(r-r_s),$$
$$(s=1,\cdots,M), \quad (2)$$

where the constants $\beta_1^{(s)}, \cdots, \beta_n^{(s)}$ are representing the field strengths of the corresponding elastic solutions. The elastic displacement fields $u_1^{(s)}, \cdots, u_n^{(s)}$ are obtained from the derivatives of the fundamental integral of the differential equations for the anisotropic elastic continuum.[11] The $u_1^{(s)}, \cdots, u_n^{(s)}$ are elastic displacement fields due to dipole, quadrupole, etc., forces centered on the point defect s. The number n of these elastic solutions increases with the size of the discretely treated lattice regions $V_1, \cdots, V_M$ around the point defects $1,\cdots$ and M, respectively.

By means of relations (1) and (2), the energy E^M becomes a function of the displacements $v_1, \cdots, v_j$ of the ions, impurities, and interstitials inside the regions $V_1, \cdots, V_M$ and of the coefficients $\beta_1^{(1)}, \cdots, \beta_n^{(M)}$ of the elastic solutions. The minimization of E^M with respect to these arguments yields the following system of

[10] J. D. Eshelby, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 3, p. 79.
[11] E. Kröner, Z. Physik **136**, 402 (1953); and *Kontinuumstheorie der Versetzungen und Eigenspannungen* (Springer-Verlag, Berlin, 1958).

equations:

$$\partial E^M/\partial v_i=0, \quad (i=1, \cdots, j), \qquad (3a)$$

$$\frac{\partial E^M}{\partial \beta_h^{(s)}}=\frac{\partial E^M}{\partial v_{j+1}}\cdot u_h^{(s)}(r_{j+1}-r_s)$$

$$+\frac{\partial E^M}{\partial v_{j+2}}\cdot u_h^{(s)}(r_{j+2}-r_s)+\cdots=0$$

$$[h=1, \cdots, n(s); s=1, \cdots, M], \quad (3b)$$

where $j+1$, $j+2$, $\cdots$ denotes the ions outside the regions $V_1, \cdots, V_M$. Equation (3b) can be simplified by assuming that the distortion of the lattice is negligible at large distances from the point defects. This means the force $(-\partial E^M/\partial v_\nu)$ acting on ion ν vanishes for nearly all ions ν which lie in the lattice region whose distortion is described by the elastic displacement field. The assumption $(\partial E^M/\partial v_\nu \equiv 0)$ for certain ions ν corresponds to a boundary condition guaranteeing the stability of the disturbed lattice.

Equations (3a) and (3b) for the unknowns $v_1, \cdots, v_j$, $\beta_1^{(1)}, \cdots, \beta_n^{(M)}$ are solved, in a manner as originally proposed by Tewordt,[9] by iteration performed on the system of linear algebraic equations derived from Eqs. (3a) and (3b) by approximating all forces $(-\partial E^M/\partial v_\nu)$ by expressions which are linear in the displacements. At each step in the iteration process, the coefficients of the linear algebraic equations are calculated from the linear expansions of the forces $(-\partial E^M/\partial v_\nu)$ in the displacements of the ions, interstitials, and impurities from their positions obtained in the previous step. Thus, the equilibrium state of the disturbed lattice is successively approached. To obtain a rapid convergence of the iteration process, starting positions approximating the equilibrium positions in the disturbed lattice are chosen from which the displacements are calculated. The accuracy of this method of determining lattice distortion is improved as the size of the discretely treated lattice regions $V_1, \cdots, V_M$ increases.

It should be pointed out that the equilibrium state of the disturbed lattice determined as proposed in this paper corresponds, in general, to a relative minimum of energy of the imperfect crystal. Therefore, various equilibrium states of the disturbed lattice can be obtained by choosing different starting positions. In this way it is possible to investigate the migration of the point defects in the lattice.

III. EXPANSION OF $\partial E^M/\partial v_\nu$ IN TERMS OF THE DISPLACEMENTS

The forces $(-\partial E^M/\partial v_\nu)$ in Eqs. (3a) and (3b) need be expressed as functions of the displacements $v_1, \cdots$. This is done as follows: First, the energy of the imperfect

crystal is written as the sum of three terms:

$$E^M(\mathbf{v}_1, \cdots) = E_1{}^M(\mathbf{v}_1, \cdots)$$
$$+ E_2{}^M(\mathbf{v}_1, \cdots) + E_3{}^M(\mathbf{v}_1, \cdots). \quad (4)$$

$E_1{}^M$ is the nonelectrostatic interaction energy and $E_2{}^M$ is the electrostatic interaction energy of the system of ions, impurities, and interstitials. $E_3{}^M$ is the energy of the system of valence or conduction electrons including the energy resulting from the interaction between these electrons and the imperfect lattice. Corresponding to Eq. (4), the force $(-\partial E^M/\partial \mathbf{v}_\nu)$ is split into three terms which are explicitly expressed as functions of the displacements.

The nonelectrostatic interaction between the two ions ν and μ, separated by a distance $r_{\nu\mu}'$ in the disturbed lattice, is given by the scalar potential $U_{\nu\mu}(\mathbf{r}_{\nu\mu}')$. The distance of the ions ν and μ, both lying in their starting positions, is denoted by $r_{\nu\mu}$. The displacements of these ions are designated by $\mathbf{v}_\nu$ and $\mathbf{v}_\mu$, respectively. Then $\mathbf{r}_{\nu\mu}'$ is equal to

$$\mathbf{r}_{\nu\mu}' = \mathbf{r}_{\nu\mu} + \mathbf{v}_{\nu\mu}, \quad (5)$$

with

$$\mathbf{v}_{\nu\mu} = \mathbf{v}_\nu - \mathbf{v}_\mu. \quad (6)$$

The force $(-\partial U_{\nu\mu}/\partial \mathbf{v}_\nu)$ acting on ion ν due to ion μ is expanded in a Taylor series in $\mathbf{v}_{\nu\mu}$. Summation over μ yields

$$\frac{\partial E_1{}^M}{\partial \mathbf{v}_\nu} = \sum_\mu \left\{ \frac{\partial U_{\nu\mu}}{\partial \mathbf{r}_{\nu\mu}} + \mathbf{v}_{\nu\mu} \cdot \frac{\partial}{\partial \mathbf{r}_{\nu\mu}} \frac{\partial U_{\nu\mu}}{\partial \mathbf{r}_{\nu\mu}} + \cdots \right\}. \quad (7)$$

In the same way, $(\partial E_2{}^M/\partial \mathbf{v}_\nu)$ is expressed in terms of the displacements. If the potential due to the electrostatic interaction between the ions ν and μ is given by $\phi_{\nu\mu}(\mathbf{r}_{\nu\mu}')$, one obtains

$$\frac{\partial E_2{}^M}{\partial \mathbf{v}_\nu} = \sum_\mu \left\{ \frac{\partial \phi_{\nu\mu}}{\partial \mathbf{r}_{\nu\mu}} + \mathbf{v}_{\nu\mu} \cdot \frac{\partial}{\partial \mathbf{r}_{\nu\mu}} \frac{\partial \phi_{\nu\mu}}{\partial \mathbf{r}_{\nu\mu}} + \cdots \right\}. \quad (8)$$

$(\partial E_3{}^M/\partial \mathbf{v}_\nu)$ is expressed in terms of the displacements using the following procedure: The energy $E_3{}^M$ is split into

$$E_3{}^M = E_{el}{}^M + E_{corr}{}^M, \quad (9)$$

where $E_{el}{}^M$ is obtained by using the Hartree-Fock approximation and $E_{corr}{}^M$ is the correlation energy. The considered system of electrons is characterized by the Hamiltonian

$$H^M = \sum_{l=1}^{N} \left\{ -\frac{\hbar^2}{2m} \nabla_l{}^2 + W^M(\mathbf{r}_l) \right\} + \frac{1}{2} \sum_{l,t(l \neq t)} \frac{e^2}{r_{lt}}, \quad (10)$$

where m is the electron mass and N is the number of electrons. The potential W^M represents the interaction between the imperfect lattice and the lth electron at $\mathbf{r}_l$. The last term describes the Coulomb interaction

between the lth and tth electron. Then $E_{el}{}^M$ is given by

$$E_{el}{}^M = \Sigma_1 + \Sigma_2 + \Sigma_3, \quad (11)$$

with

$$\Sigma_1 = \sum_k \langle \varphi_k{}^M(\mathbf{r}) | -\frac{\hbar^2}{2m} \nabla^2 + W^M(\mathbf{r}) | \varphi_k{}^M(\mathbf{r}) \rangle, \quad (12)$$

$$\Sigma_2 = \frac{e^2}{2} \sum_{k,k'} \langle \varphi_k{}^M(\mathbf{r}_1) \varphi_{k'}{}^M(\mathbf{r}_2) | \frac{1}{r_{12}} | \varphi_{k'}{}^M(\mathbf{r}_2) \varphi_k{}^M(\mathbf{r}_1) \rangle, \quad (13)$$

and

$$\Sigma_3 = -\frac{e^2}{4} \sum_{k,k'} \langle \varphi_k{}^M(\mathbf{r}_1) \varphi_{k'}{}^M(\mathbf{r}_2) | \frac{1}{r_{12}} | \varphi_k{}^M(\mathbf{r}_2) \varphi_{k'}{}^M(\mathbf{r}_1) \rangle. \quad (14)$$

The correlation energy is given by

$$E_{corr}{}^M = \int d^3r \, F(\mathbf{v}_1, \mathbf{v}_2, \cdots), \quad (15)$$

where F is assumed to be a known function of $\varphi_k{}^M$. The k, k' summations are over all valence or conduction electrons. The one-electron wave functions $\varphi_k{}^M$ are determined by the Hartree-Fock equation

$$(H_k{}^M)^F \varphi_k{}^M = \epsilon_k \varphi_k{}^M, \quad (16)$$

with

$$(H_k{}^M)^F = -\frac{\hbar^2}{2m} \nabla^2 + W^M + C^M + A_k{}^M. \quad (17)$$

$$C^M(\mathbf{r}_1) = e^2 \sum_k \langle \varphi_k{}^M(\mathbf{r}_2) | \frac{1}{r_{12}} | \varphi_k{}^M(\mathbf{r}_2) \rangle \quad (18)$$

is the Coulomb potential of the electrons. The exchange operator $A_k{}^M$ is defined by

$$A_k{}^M \varphi_k{}^M(\mathbf{r}_1)$$
$$= -\frac{e^2}{2} \sum_{k'} \langle \varphi_{k'}{}^M(\mathbf{r}_2) | \frac{1}{r_{12}} | \varphi_k{}^M(\mathbf{r}_2) \rangle \varphi_{k'}{}^M(\mathbf{r}_1). \quad (19)$$

$(H_k{}^M)^F$ is split into

$$(H_k{}^M)^F = H_k{}^0 + \Delta H_k{}^M, \quad (20)$$

where $H_k{}^0$ is the Hartree-Fock operator for the perfect crystal and

$$\Delta H_k{}^M = (W^M - W^0) + (C^M - C^0) + (A_k{}^M - A_k{}^0) \quad (21)$$

represents the perturbing potential arising from the M point defects. Then Eq. (17) can be rewritten as

$$\{H_k{}^0 - \epsilon_k\} \varphi_k{}^M = -\Delta H_k{}^M \varphi_k{}^M. \quad (22)$$

The solution is given by the integral equation[12]

$$\varphi_k{}^M(\mathbf{r}) = \varphi_k{}^0(\mathbf{r}) + \int d^3r' \, G(\mathbf{r}, \mathbf{r}', \mathbf{k}) \Delta H_k{}^M(\mathbf{r}') \varphi_k{}^M(\mathbf{r}'), \quad (23)$$

[12] P. M. Morse and H. Feshbach, *Methods of Theoretical Physics* (McGraw-Hill Book Company, Inc., New York, 1953), Parts I and II.

where the Green's function is determined by

$$\{H_k{}^0 - \epsilon_k\}G(\mathbf{r},\mathbf{r}',\mathbf{k}) = -\delta(\mathbf{r}-\mathbf{r}'). \tag{24}$$

$\varphi_k{}^0$ is the eigenfunction of $H_k{}^0$.

The explicit dependence of the wave functions $\varphi_k{}^M$ upon the displacements $\mathbf{v}_1, \cdots$ is obtained as follows: The potential W^M is given by

$$W^M = \sum_\mu \phi_\mu(\mathbf{r}-\mathbf{r}_\mu') + \sum_{s=1}^{M} \phi_s'(\mathbf{r}-\mathbf{r}_s'). \tag{25}$$

$\phi_\mu(\mathbf{r}-\mathbf{r}_\mu')$ is the potential due to the ion μ located at $\mathbf{r}_\mu'$ and $\phi_s'(\mathbf{r}-\mathbf{r}_s')$ is the potential due to the sth point defect located at $\mathbf{r}_s'$ in the disturbed lattice. A Taylor expansion of ϕ_μ and ϕ_s' in terms of the displacements $\mathbf{v}_\mu$ and $\mathbf{v}_s$, respectively, yields

$$W^M = \sum_\mu \phi_\mu(\mathbf{r}-\mathbf{r}_\mu) + \sum_{s=1}^{M} \phi_s'(\mathbf{r}-\mathbf{r}_s)$$

$$-\sum_\mu \left\{ \mathbf{v}_\mu \cdot \frac{\partial}{\partial \mathbf{r}_\mu} \phi_\mu(\mathbf{r}-\mathbf{r}_\mu) - \cdots \right\}$$

$$-\sum_{s=1}^{M} \left\{ \mathbf{v}_s \cdot \frac{\partial}{\partial \mathbf{r}_s} \phi_s'(\mathbf{r}-\mathbf{r}_s) - \cdots \right\}. \tag{26}$$

Then Eq (23) can be rewritten as

$$\varphi_k{}^M(\mathbf{r}) = \varphi_k{}^0(\mathbf{r}) + \int d^3r' \, G(\mathbf{r},\mathbf{r}',\mathbf{k})$$

$$\times \left\{ \sum_\mu [\phi_\mu(\mathbf{r}'-\mathbf{r}_\mu) - \phi_\mu(\mathbf{r}'-\mathbf{r}_\mu{}^0)] + \sum_{s=1}^{M} \phi_s'(\mathbf{r}'-\mathbf{r}_s) \right.$$

$$\left. + [C^M(\mathbf{r}') - C^0(\mathbf{r}')] + [A_k{}^M(\mathbf{r}') - A_k{}^0(\mathbf{r}')] \right\}$$

$$\times \varphi_k{}^M(\mathbf{r}') - \sum_\mu \left\{ \mathbf{v}_\mu \cdot \int d^3r' \, G(\mathbf{r},\mathbf{r}',\mathbf{k}) \right.$$

$$\times \frac{\partial}{\partial \mathbf{r}_\mu} \phi_\mu(\mathbf{r}'-\mathbf{r}_\mu) \varphi_k{}^M(\mathbf{r}') - \cdots \left. \right\}$$

$$-\sum_{s=1}^{M} \left\{ \mathbf{v}_s \cdot \int d^3r' \, G(\mathbf{r},\mathbf{r}',\mathbf{k}) \right.$$

$$\times \frac{\partial}{\partial \mathbf{r}_s} \phi_s'(\mathbf{r}'-\mathbf{r}_s) \varphi_k{}^M(\mathbf{r}') - \cdots \left. \right\}. \tag{27}$$

$\mathbf{r}_\mu{}^0$ denotes the position of the ion μ in the regular lattice. Equation (27) can be solved by iteration. Denoting the solution of Eq. (27) for $\mathbf{v}_\mu = \mathbf{v}_s = 0$ by $\chi_k{}^M$ and treating in Eq. (27) the terms arising from the displacements by using the Born approximation, $\varphi_k{}^M$ is given in first order by

$$\varphi_k{}^M = \chi_k{}^M + \Delta\chi_k{}^M, \tag{28}$$

with

$$\Delta\chi_k{}^M = -\sum_\mu \left\{ \mathbf{v}_\mu \cdot \int d^3r' \, G(\mathbf{r},\mathbf{r}',\mathbf{k}) \right.$$

$$\times \frac{\partial}{\partial \mathbf{r}_\mu} \phi_\mu(\mathbf{r}'-\mathbf{r}_\mu) \chi_k{}^M(\mathbf{r}') - \cdots \left. \right\}$$

$$-\sum_{s=1}^{M} \left\{ \mathbf{v}_s \cdot \int d^3r' \, G(\mathbf{r},\mathbf{r}',\mathbf{k}) \right.$$

$$\times \frac{\partial}{\partial \mathbf{r}_s} \phi_s'(\mathbf{r}'-\mathbf{r}_s) \chi_k{}^M(\mathbf{r}') - \cdots \left. \right\}. \tag{29}$$

If necessary, this first-order Born approximation can be improved by performing on Eq. (27) the iteration process started with $\varphi_k{}^M$ as given in Eq. (28).

$E_{\mathrm{el}}{}^M$ is in first-order approximation expressed as a function of the displacements by substituting $\varphi_k{}^M$, Eq. (28), into Eqs. (12), (13), and (14). One obtains then

$$\frac{\partial E_{\mathrm{el}}{}^M}{\partial \mathbf{v}_\nu} = \frac{\partial \Sigma_1}{\partial \mathbf{v}_\nu} + \frac{\partial \Sigma_2}{\partial \mathbf{v}_\nu} + \frac{\partial \Sigma_3}{\partial \mathbf{v}_\nu}, \tag{30}$$

with

$$\frac{\partial \Sigma_1}{\partial \mathbf{v}_\nu} = \sum_k \left\{ \left(\left\langle \chi_k{}^M(\mathbf{r}) \left| -\frac{\hbar^2}{2m}\nabla^2 + W^M \right| \frac{\partial}{\partial \mathbf{v}_\nu}\Delta\chi_k{}^M(\mathbf{r}) \right\rangle + \mathrm{c.c.} \right) + \left(\left\langle \Delta\chi_k{}^M(\mathbf{r}) \left| -\frac{\hbar^2}{2m}\nabla^2 + W^M \right| \frac{\partial}{\partial \mathbf{v}_\nu}\Delta\chi_k{}^M(\mathbf{r}) \right\rangle + \mathrm{c.c.} \right) \right.$$

$$\left. + \left\langle \chi_k{}^M(\mathbf{r}) \left| \frac{\partial W^M}{\partial \mathbf{v}_\nu} \right| \chi_k{}^M(\mathbf{r}) \right\rangle + \left(\left\langle \chi_k{}^M(\mathbf{r}) \left| \frac{\partial W^M}{\partial \mathbf{v}_\nu} \right| \Delta\chi_k{}^M(\mathbf{r}) \right\rangle + \mathrm{c.c.} \right) + \left\langle \Delta\chi_k{}^M(\mathbf{r}) \left| \frac{\partial W^M}{\partial \mathbf{v}_\nu} \right| \Delta\chi_k{}^M(\mathbf{r}) \right\rangle \right\}, \tag{31}$$

$$\frac{\partial \Sigma_2}{\partial \mathbf{v}_\nu} = e^2 \sum_{k,k'} \left\{ \left(\left\langle \chi_k{}^M(\mathbf{r}_1)\chi_{k'}{}^M(\mathbf{r}_2) \left| \frac{1}{r_{12}} \right| \frac{\partial}{\partial \mathbf{v}_\nu}\Delta\chi_{k'}{}^M(\mathbf{r}_2)\chi_k{}^M(\mathbf{r}_1) \right\rangle + \mathrm{c.c.} \right) \right.$$

$$+ \left(\left\langle \Delta\chi_k{}^M(\mathbf{r}_1)\chi_{k'}{}^M(\mathbf{r}_2) \left| \frac{1}{r_{12}} \right| \chi_{k'}{}^M(\mathbf{r}_2)\frac{\partial}{\partial \mathbf{v}_\nu}\Delta\chi_k{}^M(\mathbf{r}_1) \right\rangle + \mathrm{c.c.} \right)$$

$$\left. + \left(\left\langle \chi_k{}^M(\mathbf{r}_1) \left| \left\langle \chi_{k'}{}^M(\mathbf{r}_2) \left| \frac{1}{r_{12}} \right| \Delta\chi_{k'}{}^M(\mathbf{r}_2) \right\rangle + \mathrm{c.c.} \right| \frac{\partial}{\partial \mathbf{v}_\nu}\Delta\chi_k{}^M(\mathbf{r}_1) \right\rangle + \mathrm{c.c.} \right) + \cdots \right\}, \tag{32}$$

and

$$\frac{\partial \Sigma_3}{\partial v_\nu} = -\frac{e^2}{2} \sum_{k,k'} \left\{ \left(\left\langle \chi_k{}^M(\mathbf{r}_1)\chi_{k'}{}^M(\mathbf{r}_2) \left| \frac{1}{r_{12}} \right| \chi_k{}^M(\mathbf{r}_2)\frac{\partial}{\partial v_\nu}\Delta\chi_{k'}{}^M(\mathbf{r}_1) \right\rangle + \text{c.c.} \right) \right.$$

$$+ \left(\left\langle \chi_k{}^M(\mathbf{r}_1)\Delta\chi_{k'}{}^M(\mathbf{r}_2) \left| \frac{1}{r_{12}} \right| \chi_k{}^M(\mathbf{r}_2)\frac{\partial}{\partial v_\nu}\Delta\chi_{k'}{}^M(\mathbf{r}_1) \right\rangle + \text{c.c.} \right)$$

$$+ \left(\left\langle \chi_k{}^M(\mathbf{r}_1)\frac{\partial}{\partial v_\nu}\Delta\chi_{k'}{}^M(\mathbf{r}_2) \left| \frac{1}{r_{12}} \right| \Delta\chi_k{}^M(\mathbf{r}_2)\chi_{k'}{}^M(\mathbf{r}_1) \right\rangle + \text{c.c.} \right)$$

$$\left. + \left(\left\langle \chi_k{}^M(\mathbf{r}_1)\chi_{k'}{}^M(\mathbf{r}_2) \left| \frac{1}{r_{12}} \right| \Delta\chi_k{}^M(\mathbf{r}_2)\frac{\partial}{\partial v_\nu}\Delta\chi_{k'}{}^M(\mathbf{r}_1) \right\rangle + \text{c.c.} \right) + \cdots \right\}. \quad (33)$$

In Eqs. (32) and (33) only the terms up to the first order in the displacements have been written down explicitly. One obtains from Eq. (29)

$$\frac{\partial\Delta\chi_k{}^M}{\partial v_\nu} = -\sum_\mu \left\{ \delta_{\nu\mu} \int d^3r' \, G(\mathbf{r},\mathbf{r}',k)\frac{\partial}{\partial r_\mu}\phi_\mu(\mathbf{r}'-\mathbf{r}_\mu)\chi_k{}^M(\mathbf{r}') - \cdots \right\}$$

$$- \sum_{s=1}^M \left\{ \delta_{\nu s} \int d^3r' \, G(\mathbf{r},\mathbf{r}',k)\frac{\partial}{\partial r_s}\phi_s(\mathbf{r}'-\mathbf{r}_s)\chi_k{}^M(\mathbf{r}') - \cdots \right\}, \quad (34)$$

and from Eq. (26)

$$\frac{\partial W^M}{\partial v_\nu} = -\sum_\mu \left\{ \delta_{\nu\mu}\frac{\partial}{\partial r_\mu}\phi_\mu(\mathbf{r}-\mathbf{r}_\mu) - \cdots \right\} - \sum_{s=1}^M \left\{ \delta_{\nu s}\frac{\partial}{\partial r_s}\phi_s'(\mathbf{r}-\mathbf{r}_s) - \cdots \right\}. \quad (35)$$

Finally, $(\partial E_{\text{corr}}{}^M/\partial v_\nu)$ will be expressed as a function of the displacements. The expansion of F, Eq. (15), in a Taylor series in terms of the displacements yields

$$\frac{\partial E_{\text{corr}}{}^M}{\partial v_\nu} = \int d^3r \left\{ 1 + \sum_\mu v_\mu \cdot \left(\frac{\partial F}{\partial v_\mu}\right)_{v_t=0} + \cdots \right\}\left(\frac{\partial F}{\partial v_\nu}\right)_{v_t=0}, \quad (t=1,2,\cdots). \quad (36)$$

All forces contributing to $(-\partial E^M/\partial v_\nu)$ are now explicitly expressed in terms of the displacements. The wave functions $\chi_k{}^M$ are determined as follows. The wave functions obtained as solutions of Eq. (27) by neglecting all lattice distortion, i.e., $\mathbf{r}_\mu = \mathbf{r}_\mu{}^0$, $v_\mu = v_s = 0$, are denoted by $\Gamma_k{}^M$. By making then the same approximation which leads to Eq. (28), one gets from Eq. (27)

$$\chi_k{}^M = \Gamma_k{}^M + \Delta\Gamma_k{}^M, \quad (37)$$

where

$$\Delta\Gamma_k{}^M = -\sum_\mu \left\{ (\mathbf{r}-\mathbf{r}_\mu{}^0) \int d^3r' \, G(\mathbf{r},\mathbf{r}',k) \right.$$

$$\left. \times \frac{\partial}{\partial r_\mu{}^0}\phi(\mathbf{r}'-\mathbf{r}_\mu{}^0)\Gamma_k{}^M(\mathbf{r}') - \cdots \right\}, \quad (38)$$

and

$$\Gamma_k{}^M = \varphi_k{}^0 + \int d^3r' \, G(\mathbf{r},\mathbf{r}',k)$$

$$\times \left\{ \sum_{s=1}^M \phi_s'(\mathbf{r}'-\mathbf{r}_s) + [C^M(\mathbf{r}') - C^0(\mathbf{r}')] \right.$$

$$\left. + [A_k{}^M(\mathbf{r}') - A_k{}^0(\mathbf{r}')] \right\}\Gamma_k{}^M(\mathbf{r}'). \quad (39)$$

$\Delta\Gamma_k{}^M$ is the change of the wave function $\Gamma_k{}^M$ due to the lattice distortion associated with the starting positions of the ions. Equation (39) can be solved by iteration starting with

$$\Gamma_k{}^{M(0)} = \varphi_k{}^0 + \sum_{s=1}^M \Delta\varphi_k{}^s, \quad (40)$$

where the $\Delta\varphi_k{}^s$ are the scattered waves due to the single point defects acting independently. The effect of the iteration process is to include multiple scattering in the wave functions. $\Delta\varphi_k{}^s$ is defined as

$$\Delta\varphi_k{}^s = \varphi_k{}^s - \varphi_k{}^0, \quad (41)$$

where $\varphi_k{}^s$ is determined from

$$\varphi_k{}^s(\mathbf{r}) = \varphi_k{}^0(\mathbf{r}) + \int d^3r' \, G(\mathbf{r},\mathbf{r}',k)$$

$$\times \{\phi_s'(\mathbf{r}'-\mathbf{r}_s) + [C^s(\mathbf{r}') - C^0(\mathbf{r}')]$$

$$+ [A_k{}^s(\mathbf{r}') - A_k{}^0(\mathbf{r}')]\}\varphi_k{}^s(\mathbf{r}'). \quad (42)$$

$(c^s - c^0)$ and $(A_k{}^s - A_k{}^0)$ are the perturbations in the

Coulomb and exchange potentials due to the point defect s.

The eigenfunctions $\varphi_k{}^0$ of $H_k{}^0$ are the Bloch waves

$$\varphi_{nk}{}^0(\mathbf{r}) = u_n(\mathbf{r},\mathbf{k})e^{i\mathbf{k}\cdot\mathbf{r}}, \tag{43}$$

which form a complete orthonormal set of eigenfunctions with eigenvalues $\epsilon_n{}^0(\mathbf{k})$. n denotes the energy bands. The Green's function $G(\mathbf{r},\mathbf{r}',\mathbf{k})$, defined in Eq. (24), is then given by[12]

$$G(\mathbf{r},\mathbf{r}',\mathbf{k}) = \frac{1}{(2\pi)^3}\sum_l \int d^3k' \frac{\varphi_{lk'}{}^{0*}(\mathbf{r}')\varphi_{lk'}{}^0(\mathbf{r})}{\epsilon_n{}^0(\mathbf{k}) - \epsilon_l{}^0(\mathbf{k}') + i\eta}, \tag{44}$$

where η is a positive infinitesimal parameter ensuring that only an outgoing scattered wave is obtained. Substituting this Green's function and the Bloch wave $\varphi_{nk}{}^0$, Eq. (43), into Eq. (39), the wave function $\Gamma_k{}^M$ is in principle determined. However, in order to carry out an explicit analytical determination of $\Gamma_k{}^M$ a suitable approximation procedure, corresponding to the considered type of crystal, has to be developed.

IV. CONCLUDING REMARKS

After replacing the forces $(-\partial E_1{}^M/\partial\mathbf{v}_\nu)$, $(-\partial E_2{}^M/\partial\mathbf{v}_\nu)$, $(-\partial E_{el}{}^M/\partial\mathbf{v}_\nu)$, and $(-\partial E_{corr}{}^M/\partial\mathbf{v}_\nu)$ by their linearized expansions, the system of Eqs. (3a), (3b) is explicitly expressed in the unknowns. By taking into account the coupling between the electrons and the lattice, the determination of the lattice distortion becomes very complicated. However, some simplifications can be introduced in performing the calculation. First, the lattice distortion is determined by using as starting positions the positions of the ions, impurities, and interstitials which result from Eqs. (3a) and (3b) by neglecting the forces $(-\partial E_{el}{}^M/\partial\mathbf{v}_\nu)$ and $(-\partial E_{corr}{}^M/\partial\mathbf{v}_\nu)$. Further, the determination of $\Delta\chi_k{}^M$, Eq. (29), is greatly simplified by approximating $\chi_k{}^M$ by $\Gamma_k{}^M$ at each step in the iteration process performed on Eqs. (3a) and (3b). As can be seen from Eqs. (28) and (29), this approximation is good if the displacements are small. If the point defects lie sufficiently far apart from each other or if the Bloch wave $\Gamma_k{}^M$ is well localized, as in ionic and valence crystals, then those terms in $\Delta\Gamma_k{}^M$ which arise from multiple scattering can be neglected. Assuming that the potentials $\phi_\nu(\mathbf{r} - \mathbf{r}_\nu)$ and $\phi_s{}'(\mathbf{r} - \mathbf{r}_s)$ vary rapidly only within a small region around $\mathbf{r}_\nu$ and $\mathbf{r}_s$, respectively,

the derivatives of these potentials resemble the Dirac function and as such allow immediate solution of most of the multiple center integrals occurring in the calculations.

It becomes obvious from Eqs. (27), (28), and (29) that for small displacements the corrections to $\varphi_k{}^M$ arising from the iteration process are negligible. The Born approximation leading to Eq. (28) is valid if multiple electron scattering due to the displacements is negligible.

So far, the outlined method for determining lattice distortion is applicable to an arbitrary type of crystal. However, to solve the linear system of equations for a special crystal in practice, its coefficients need be determined numerically. This can be done by using explicit expressions for the two-body forces describing the interactions among the ions, impurities, and interstitials and, further, by computing the energy of the system of valence and conduction electrons, including its interaction with the imperfect lattice, by using suitable approximations depending on the considered type of crystal and, therefore, developed in detail from case to case. In particular, to obtain from Eq. (44) an explicit expression for the Green's function $G(\mathbf{r},\mathbf{r}',\mathbf{k})$, a suitable approximation of the Bloch waves has to be chosen.

The formation energy of M point defects is given by

$$E_F{}^M = E^M - E^0, \tag{45}$$

where E^0 is the energy of the perfect crystal. The interaction energy of M point defects is given by

$$E_{int}{}^M = E_F{}^M - \sum_{s=1}^{M} E_F{}^s, \tag{46}$$

where $E_F{}^s$ is the formation energy of the point defect s. The volume change of the crystal due to the M point defects can be calculated from the elastic displacement field $\mathbf{v}(\mathbf{r})$, Eq. (1).

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