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# A quasifermion approach to modelling interatomic interactions in solids

A M Dobrotvorskii and O V Afanasjeva

Lenneftekhim, Zheleznodorozhny Prospekt 40, Saint Petersburg 193148, Russia

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**Abstract.** The quasifermion approximation based on the weakening of conditions imposed on the density matrix of a many-electron system is considered in the present paper. In this approximation, a rather simple construction for the density matrix and for the energy can be obtained. The application of this approximation to a variety of materials science problems is shown to be in good agreement with experimental results.

## 1. Introduction

The solution of theoretical problems of materials science related to mechanisms of destruction, heat, corrosion and radiation resistance and the prediction of useful properties of materials requires computational methods that would permit one to simulate defects, impurities, cracks and grain boundaries as well as the processes of their evolution in solids. Since such processes are usually accompanied by creating and breaking chemical bonds and local rearrangement of electron charge density, the most pertinent form of theory is quantum theory, based on the tight-binding or LCAO approximations [1, 2]. However, the possibility of making use of these methods is essentially limited because adequate models of disturbed crystals should contain several thousands of atoms. Only in this case can the boundary conditions for atoms modelling the essential area of a crystal or of its surface, the lattice relaxation in the vicinity of defects and fracture mechanisms be realistically simulated. Another approach to the problem can be based on the use of the pair potential method [3–5]. Despite the fact that considerable progress has been achieved in the investigation of defects in ionic crystals and metals within the pair potential model, the method has principal shortcomings that do not allow a number of important characteristics of solids to be reproduced, so it is not able to yield the correct values of elastic moduli and to account for the digression from the Cauchy relation  $C_{12} = C_{44}$  for cubic crystals. The vacancy formation energy is always found to be overestimated and about equal to the cohesive energy. Its disadvantages finally become insuperable when we contemplate the simulation of the indirect electron influence on interatomic bonds in solids, which is needed to understand better such phenomena as the embrittlement and the change in self-diffusion rate within contaminated metals.

One of the most promising ways to avoid these difficulties consists of the construction of simple  $N$ -body potentials permitting one to take into account the band character of solid cohesion [6, 7]. However, the potentials determined in such a manner are essentially empirical, which complicates their application to heteroatomic systems. This approach also has the drawback that its fundamental assumption is arbitrary, although there was an

attempt to motivate the functional form of obtained potentials using the second-momentum approximation of tight-binding theory [8].

In this paper we give a brief theoretical foundation of an alternative approach, which makes it possible to treat the multiatomic interactions in solids. It is based on the use of the quasifermion approximation for minimization of the total energy represented as a functional of the density matrix. This enables all the interatomic potentials to be expressed through molecular integrals. Some semiempirical versions of the theory and their applications are discussed as well.

## 2. The quasifermion approximation

Let us consider a multiatomic system with closed shells formed by  $n$  electrons distributed over  $N$  valence atomic orbitals. We shall suppose that one-electron states of the system are described by an energy operator independent of the density matrix. In this case the total electron energy of the system is equal to the sum of energies of occupied one-electron states. In the ground state its value corresponds to the minimum of the functional

$$E = 2\text{Tr}(HP). \quad (1)$$

Here  $H$  is the Hamiltonian and  $P$  is the density matrix, which should obey the following conditions:

$$2\text{Tr}(P) = n \quad (2)$$

$$P^2 = P. \quad (3)$$

The second of these relations is the mathematical expression of the Pauli principle. It considerably complicates the problem of variation of the energy functional and makes it necessary to use numerical methods.

In the quasifermion approximation [9,10], the condition (3) is substituted by the requirement of equality of the traces of the matrices involved. The new condition, imposed with the use of relation (2), can be written in the form

$$2\text{Tr}(P^2) = n. \quad (4)$$

It is evident that this condition is weaker than (3), because it holds for any idempotent matrix and at the same time some non-idempotent matrices satisfying it do exist. Thus the set of matrices on which the functional (1) is minimized proves to be enlarged. The fact that the requirement of idempotency is weakened permits us to minimize functional (1) by the Lagrange multipliers method and obtain the analytical expression for the density matrix

$$P = \xi I - \eta(H - h_1 I) / \sqrt{h_2 - h_1^2} \quad (5)$$

and for the total energy

$$E = 2N(\xi h_1 - \eta \sqrt{h_2 - h_1^2}) \quad (6)$$

where  $\xi = n/2N$  is the mean occupation of one-electron levels,

$$\eta = \sqrt{\xi(1 - \xi)} \quad (7)$$

is a factor of interatomic bonding, which will be discussed below in detail and

$$h_k = (1/N) \text{Tr}(H^k) \quad (8)$$

are moments of the Hamiltonian. As the minimum of functional (1) was found in a set larger than the set of idempotent matrices, the evaluated total energy gives an estimation of its exact magnitude from below.

In [10], it was shown that the solution obtained can be considered as a starting point for the exact one to be constructed. The method of its successive improvement is based on the following statements.

(i) The space of real symmetric matrices commuting with  $H$ , having scalar product  $\text{Tr}(AB)$ , and metric  $\sqrt{\text{Tr}(A-B)^2}$ , is isomorphic to the  $N$ -dimensional Euclidean space  $\mathcal{R}^n$  and the subset of its matrices satisfying conditions (2) and (4) is isomorphic to the  $(N-2)$ -dimensional sphere  $S_q$ .

(ii) The totality of idempotent density matrices  $\{P - i\}$  corresponds to  $C_k^N$  equivalent vertices (where  $k = n/2$  is the number of occupied levels) of permutation polyhedron  $M_k$ , about which the sphere  $S_q$  is circumscribed.

(iii) The quasifermion matrix (5) lies on the sphere  $S_q$  in a Dirichlet region connected with the ground-state matrix  $P_g$  and  $P_g$  proves to be the nearest to it of all matrices  $P_i$  as follows from the inequality

$$\text{Tr}(P_g - P)^2 - \text{Tr}(P_i - P)^2 = (E_g - E_i)/\sqrt{h_2 - h_1^2} \leq 0. \quad (9)$$

(iv) On the sphere  $S_q$  there is a universal functional

$$\Phi(P) = (3/N)q_4 + (1 - 3/N)[(q_3 + 1 - 2\xi)/2\eta]^2 \quad (10)$$

$$q_i = (1/N) \text{Tr}(2P - I)^i \quad (11)$$

which is topologically isomorphic to polyhedron  $M_k$ : its critical points are situated at the points of the sphere corresponding to the centres of the polyhedron faces and the Morse indices [11] of the critical points form the same sequence as the dimensions of the faces. Idempotent matrices  $P_i$  correspond to the minima of functional (10).

Taking into account the properties of the functional  $\Phi(P)$ , the unknown density matrix  $P_g$  can be constructed choosing the quasifermion matrix (5) as a starting approximation and fulfilling a step by step gradient descent procedure.

The calculation procedure just described may be used for acceleration of the iteration process in different versions of the SCF MO LCAO method. On the other hand, the rapid convergence [10], testifying to a good quality of the initial approximation, permits us to develop a specific approximation theory of solid cohesion. In subsequent sections we restrict ourselves to consideration of this theory and its semiempirical versions, using only the simplest expression for the energy (6) obtained in the quasifermion approximation, and modifying it for different types of Hamiltonian.

### 3. The simplest tight-binding Hamiltonian

In the case of the effective Hamiltonian of the tight-binding method the diagonal matrix elements  $\alpha_i$  (Coulomb integrals) have the sense of energies of one-electron atomic levels

and the off-diagonal elements  $\beta_{ij}$  (hopping integrals) are decreasing functions of interatomic distances [12]. Taking into account these notations, relation (6) can be transformed as follows:

$$E = 2N \left( \xi \bar{\alpha} - \eta \sqrt{\bar{\alpha}^2 - \bar{\alpha}^2 + \frac{1}{N} \sum_{A \neq B} \beta_{AB}^2} \right) \quad (12)$$

where  $\bar{\alpha}^i$  is the mean value of powers of Coulomb integrals,  $\beta_{AB}^2$  is a pairwise interatomic interaction

$$\beta_{AB}^2 = \sum_{i \in A} \sum_{j \in B} \beta_{ij}^2. \quad (13)$$

Expression (12) has a clear physical meaning. The first term within parentheses corresponds to the electron energy of isolated atoms. The second term describes the energy of chemical bonds between the atoms. It contains the contribution from the donor-acceptor interaction given by the dispersion of Coulomb integrals and the pairwise summation connected with the delocalization of electrons under the creation of covalent or metallic bonds. It is to be noted that the form of cohesion energy obtained here looks very like the standard second-moment model of tight-binding theory [13-16]. Furthermore, for a half-filled band the resemblance becomes complete. In the particular case of a two-level system, the two solutions are proved to coincide with the exact one from the secular equation. Nevertheless, our result has an important advantage due to it being derived without any additional assumption except for the quasifermion approximation referred to the picture of density of states or the valence band occupation. The charge state of atoms was not restricted either as has been done elsewhere [17]. The specificity of the quasifermion total energy consists of the presence of the occupation-dependent coefficient  $\eta$  before the square root. Owing to relation (7), this multiplier reaches its maximal value at half band occupation and vanishes for completely free and completely filled shells. It allows the model discussed here to be employed at arbitrary valence band filling.

The functional dependence of total energy on atomic and structural parameters obtained in the quasifermion approximation permits one to give a qualitative analysis and to explain the regularities in different properties in the rows of chemical elements and chemical compounds. For example, let us consider the dependence of vibration frequencies of 3d transition metal dimers on the atomic number. Supposing that the second derivatives of two-centre integrals at the points corresponding to equilibrium interatomic distances are approximately the same for the elements of the same row, we can expect a symbatic character of the change of the vibrational frequencies and the coefficient  $\eta$  along the row. The results of non-empirical calculation [18] on dimer vibrations (figure 1) justify such a supposition reasonably well.

A similar approach makes it possible to explain the periodic trends of heats of chemisorption on metals, heats and temperatures of melting and activation energies of self-diffusion, the influence of impurities on strength and cohesion properties of metals, etc [19-21].

#### 4. The energy operator of the Hartree-Fock-Roothaan approximation

Within the Hartree-Fock method the total electron energy is described by a functional quadratic with respect to the density matrix [22]. Let us restrict ourselves to systems

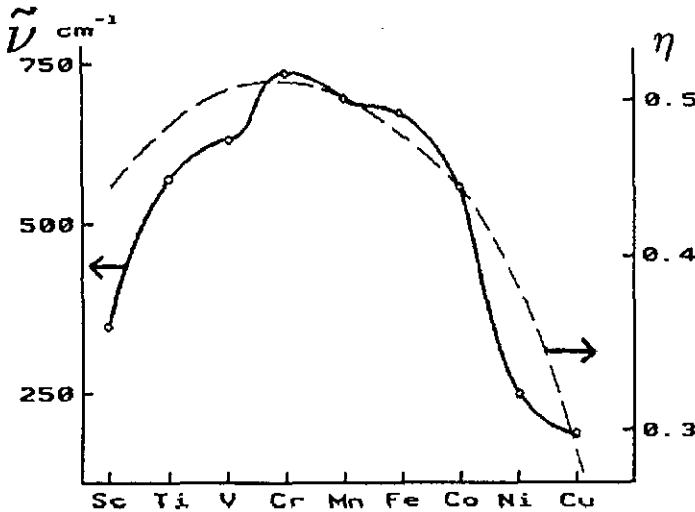


Figure 1. The vibration frequencies and the values of parameter  $\eta$  for 3d metal dimers (bold curve, experiment; dashed curve, theory).

permitting its linearization. They include, for instance, metals and homoatomic covalent crystals for which the charge transfer between atoms is absent, alloys, impurity defects and chemisorption complexes involving elements with not too diverse electronegativities as well as ionic crystals.

In the case of closed shells and a non-orthogonal set of atomic orbitals, the linearized energy functional has the form

$$E = W + 2\text{Tr}(PS^{1/2}F(D)S^{-1/2}) - 2\text{Tr}[DG(D)] \tag{14}$$

where  $D$  denotes a diagonal matrix of orbital occupation numbers for neutral atoms or for ions,  $S$  is the overlap matrix,  $W$  is the potential energy of atomic core interaction,  $G$  is the electron interaction matrix,  $F = H + 2G$  is the Fock operator matrix and  $H$  is the matrix of the operator

$$\hat{H} = -\frac{1}{2}\nabla^2 + \hat{V}(r) \tag{15}$$

which includes the lattice potential  $\hat{V}(r)$ .

The minimization of the functional (14) using the quasifermion approximation leads to the following result

$$E = W + 2N(\xi f_1 - g - \eta\sqrt{f_2 - f_1^2}) \tag{16}$$

$$f_k = (1/N) \text{Tr}[S^{1/2}F(D)S^{-1/2}]^k \tag{17}$$

$$g = (1/N) \text{Tr}[DG(D)]. \tag{18}$$

According to equation (16), all the calculations are now reduced to the evaluation of quantities  $f_k$  and  $g$ , representing the convolutions of molecular integrals. It is essential that such evaluation does not require preliminary construction of  $\hat{F}$  and  $\hat{G}$  operator matrices.

Moreover, by virtue of the invariance of matrix traces under unitary transformation of the basis orbital set, the calculation of the integrals is simplified greatly since formulae convenient for applications can be obtained directly for convolutions themselves. Further simplification can be gained if we make use of several assumptions usual for semiempirical methods of quantum chemistry to estimate the traces of matrix products given by relations (17) and (18). For this purpose, let us replace the  $S^{1/2}$  matrix by the initial terms of its truncated power series over the off-diagonal part of the overlap matrix, take the NDO approximation for multicentre integrals and adopt the conventional approximate formula  $F_{ij} = 0.5\beta(f_{ii} + F_{jj})S_{ij}$  for off-diagonal elements of the Hartree-Fock matrix including a semiempirical parameter  $\beta_{AB}$ . With these assumptions, the total energy (16) can be written as

$$E = U_0 + \frac{1}{2} \sum_{A \neq B} U_{AB} - \eta \sqrt{W_0 + \frac{1}{2} \sum_{A \neq B} W_{AB}^2}. \quad (19)$$

Here  $U_0$  and  $W_0$  are quantities independent of interatomic distances that represent the total energy of non-interacting atoms and the dispersion of atomic level energies  $\epsilon_l$ , respectively. Each of them is a sum of site contributions over all atoms of the system

$$U_0 = \sum_A u_{0A} = 2 \sum_A \sum_{l \in A} N_l (\xi \epsilon_l - \xi_l g_l) \quad (20)$$

$$W_0^2 = \sum_A w_{0A}^2 = N \sum_A \sum_{l \in A} B_l \epsilon_l^2 - \left( \sum_A \sum_{l \in A} N_l \epsilon_l \right)^2 \quad (21)$$

$$\epsilon_l = t_l + v_l + 2g_l \quad (22)$$

where  $\xi_l = n_l/(2N_l)$ ,  $N_l$  is the number of atomic orbitals in the subshell with orbital quantum number  $l$ ,  $n_l$  is the occupation of the subshell and  $t_l$ ,  $v_l$  and  $g_l$  are the values of one-centre integrals of kinetic energy, interaction with the core, and electron interaction, respectively averaged over the subshell.

The pairwise terms  $U_{AB}$  and  $W_{AB}$  in equation (19) can be expressed through the two-centre integrals. They have the simplest form in the first order in the overlap matrix

$$U_{AB} = U_{AB}^0 + 4 \sum_{l \in A} \sum_{l' \in B} [(1 - \beta_{AB})(\epsilon_l + \epsilon_{l'}) \sigma_{ll'}]^2 \quad (23)$$

$$W_{AB}^2 = 2N \sum_{l \in A} \sum_{l' \in B} [(1 - \beta_{AB})(\epsilon_l + \epsilon_{l'}) \sigma_{ll'}]^2 \quad (24)$$

where  $U_{AB}^0$  denotes the energy of Coulomb interaction of charge densities of neutral atoms (or ions in the case of ionic crystals)

$$\gamma_{ll'} = \sum_{m=-l}^l \sum_{m'=-l'}^{l'} \int \int \frac{\phi_{lm}^2(\mathbf{r}) \phi_{l'm'}^2(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{v} d\mathbf{v}' \quad (25)$$

$$\sigma_{ll'}^2 = \sum_{m=-l}^l \sum_{m'=-l'}^{l'} \int \phi_{lm}(\mathbf{r}) \phi_{l'm'}(\mathbf{r}) d\mathbf{v}. \quad (26)$$

It is evident that in solving particular problems of materials science different approaches to calculation or approximate evaluation of quantities entering the relations (16) and (19)

may be used in place of those described above. In order to choose the most appropriate computational scheme, attention should be paid to both the experience accumulated in the quantum solid state theory and the physical nature of the solids under consideration.

It should be also emphasized that the square root term in equation (19)—non-additive with respect to pairwise interactions—is the simplest in its  $N$ -body potential structure. For metals with an ideal lattice, its form coincides with the potential from [6] with accuracy up to the  $W_0^2$  term, which in this case is usually small. At the same time, when we deal with solids that possess a more complex structure or composition the situation is different because the form of the covalent bond energy constructed by the authors of [6] incorporates a sum over all atoms of a square root cohesive function. For each type of atom this function is written as the simple  $N$ -body potential with the square root structure described above. The same result, however, can be derived from quasifermion theory as well, if we go from the many-atomic model to the model of an 'atom in a solid'. Evaluating the energies of separate atoms embedded in the crystal by means of the basic relation (19) and summing the atomic contributions obtained in this manner we find the following expression for the total energy:

$$E = U_0 + \frac{1}{2} \sum_{A \neq B} U_{AB} - \eta \sum_A \sqrt{w_{0a}^2 + \frac{1}{2} \sum_B W_{AB}^2}. \quad (27)$$

Thus, the quasifermion theory gives us a flexible computational technique applicable to investigation of a large variety of solid state models. We now briefly discuss some of its applications.

## 5. Calculation of metal properties

The possibility of using the  $N$ -body potential constructed within the quasifermion approximation for calculation of elastic properties and point defect energetics can be judged from the results for aluminium. The calculations were carried out within the  $sp$  basis. To take into account the inner electron shells, a simple effective core potential [23] has been employed. The exponents of Slater-type valence atomic orbitals have been optimized by means of the Hartree-Fock procedure. The properties of the metal were calculated for two different electronic configurations of the Al atom: (i) the ground state  $s^2 p^1$  and (ii) a hybrid state with uniform occupation of valence atomic orbitals. The interatomic interactions entering equation (19) were determined for eight atomic spheres farther from which all the pair potentials appeared to become small and may be neglected. For each of two electron configurations the only fitting parameter  $\beta$  was chosen so as to reproduce equilibrium values of the Al lattice constant. The results of calculations (table 1) show that not only the elastic moduli of second order but also the theoretical value of the derivative of the bulk modulus with respect to pressure are in fair accordance with experiment.

It is noteworthy that values of the anisotropy coefficient of the Young's modulus and the parameter  $q = (C_{12} - C_{44})/C_{12}$  characterizing the deviation from the Cauchy relation are very reasonable. This emphasizes the substantial advantage of the  $N$ -body potential constructed here compared with the pair potential model. The energies of point defect formation and migration in aluminium  $E_v^f = 1.17$  eV,  $E_v^m = 0.81$  eV and  $E_i^f = 2.85$  eV calculated in the framework of the cluster model within the same assumptions referred to the atomic parameters (the second type of electron configuration was considered) also agree



Table 1. The elastic properties of aluminium.

Elastic constants (GPa)	Calculations		Experiment	
	1	2	[24]	[25]
$K$	66.7	71.1	79.4	76.0
$\partial K/\partial P$	3.93	3.99	4.26	3.45
$C_{11}$	98.6	100.0	114.3	107.0
$C_{12}$	50.7	56.7	62.0	60.7
$C_{44}$	27.7	25.4	31.5	28.2
$E_{100}$	64.2	58.9	70.8	62.5
$E_{111}$	68.9	63.6	77.2	68.6
$E_{100}/E_{111}$	0.93	0.93	0.92	0.91
$q$	0.53	0.62	0.49	0.61

with experimental data, although a slightly overestimated value was found in the case of vacancy formation [26].

In calculating the elastic coefficients for transition metals, the computational scheme adopted was somewhat different. In this case, we have made use of effective core potentials and atomic orbitals from [27]. The atomic value configuration and the parameter  $\beta$  for each metal were fitted to the experimental lattice constant and bulk modulus. Other details of the calculation have been reported earlier [28]. We restrict ourselves here to the discussion of data obtained for  $\alpha$ -iron, nickel and chromium (table 2).

Table 2. The elastic properties of transition metals.

Elastic constants (GPa)	$\alpha$ -Fe		Ni		Cr	
	Calculation	Experiment [24]	Calculation	Experiment [24]	Calculation	Experiment [24]
$K$	166.2	173.1	186.8	168.8	188.6	173.1
$\partial K/\partial P$	3.1	3.7	5.7	6.2	3.3	3.7
$C_{11}$	217.8	243.1	254.4	261.2	240.8	394.1
$C_{12}$	140.4	138.1	153.1	150.8	162.5	88.5
$C_{44}$	134.8	121.9	128.1	131.7	127.0	103.8
$q$	0.04	0.12	0.16	0.13	0.22	-0.17

In the two former cases, the moduli calculated are in reasonably good agreement with experimental values [24] and could be further improved by more accurately varying the initial parameters. At the same time, the  $N$ -body potentials constructed by us fail to give rise to results of the same quality for Cr. The reason for this lies in the fact that Cr is the only transition metal with a negative deviation from the Cauchy relation. By carrying out the mathematical deviation analogous to those leading to the equality  $C_{12} = C_{44}$  for central two-body interactions in cubic crystals it is possible to show that in the case of the  $N$ -body potential (19) the difference  $C_{12} - C_{44}$  is always non-negative and, consequently, the anomaly under consideration cannot be explained. The same is true for the  $N$ -body potential from [6]. To solve this problem, it is necessary to introduce corrections connected with the procedure of successive approximations for the density matrix and the total energy, described above.

The method we are discussing is of special interest in connection with the heteroatomic system problem, in particular with the problem of 'hydrogen in metal'. Such calculations were performed for a number of metal-hydrogen systems [28-31]. In [28] and [31], the

results of computer simulation of lattice relaxation for different H impurity positions and for diffusion processes of H in Al,  $\alpha$ -Fe and Fe-Cr alloys have been reported. It was shown that on the basis of these calculations reliable evaluations can be made not only of the activation barriers but also of pre-exponential factors of the diffusion coefficient.

In [29] and [30], it has been demonstrated that the quasifermion approximation can be used for investigation of the influence of H on cohesive properties of metals, such as ideal strength, and on defect formation and self-diffusion. Table 3 shows the results of calculations of the bulk modulus and the ideal tensile strength for  $\alpha$ -Fe crystals at different impurity concentrations.

Table 3. Influence of hydrogen on mechanical properties of  $\alpha$ -Fe.

$v_H$ (at.%)	$K$ (GPa)	$\sigma_{100}$ (GPa)
0	168.4	40.7
0.155	167.0	39.6
0.930	160.8	38.0
1.860	153.6	35.7
3.720	140.6	30.5

These data confirm the estimation made in the decohesive theory of H embrittlement, according to which the decrease of cohesive forces is about 3–30% at.% H in the local areas of metal enriched by dissolved gas [32].

## 6. Conclusions

The method developed in this paper in the framework of the quasifermion approximation has considerable advantages over the pair potential approach as well as over the method based on building the simple empirical  $N$ -body potential into the conventional pairwise model. It can be applied to calculation of the total energy of multi-atomic systems containing components of different chemical nature and, hence it permits one to simulate a wide range of processes in solids.

There is an evident logical connection of the present method with quantum mechanical equations that allows convenient expressions for interatomic potentials to be derived and experience accumulated in quantum theory of solids to be used for the purpose of applied calculations. A minimal number of semiempirical parameters is required to fulfill such calculations. The relative simplicity of the method makes it possible to use it for investigations of models including hundreds of atoms and to take into account not only direct atom-atom interactions but also the effects connected with electron delocalization and charge transfer. The flexibility of the method makes it promising for solving several theoretical problems of materials science.

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## References

- [1] Hayns H R 1982 *J. Quantum Chem.* **21** 231
- [2] Dobrotvorskii A M 1987 *Zh. Strukt. Khim.* **28** 152 (in Russian)
- [3] Dederichs P H, Lechmann C, Schober H R, Scholz A and Zeller R 1977 *J. Nucl. Mater.* **69&70** 176
- [4] Wolf D 1985 *Physica B+C* **191** 53
- [5] Lidiard A B 1988 *Phil. Mag.* **A 58** 3
- [6] Finnis M W and Sinklair J A 1984 *Phil. Mag.* **A 50** 45
- [7] Dow M S and Bakes M I 1985 *Phys. Rev. Lett.* **50** 1285
- [8] Ackland G T, Finnis M W and Vitek V 1988 *J. Phys. F: Met. Phys.* **18** L153
- [9] Dobrotvorskii A M 1984 *Dok. Akad. Nauk.* **279** 915 (in Russian)
- [10] Dobrotvorskii A M 1990 *Teor. Eksp. Khim.* **26** 1 (in Russian)
- [11] Milnor T 1963 *Morse Theory* (Princeton, NJ: Princeton University Press)
- [12] Harrison W A 1980 *Electronic Structure and Properties of Solids* (San Francisco: Freeman)
- [13] Cyrot-Lackmann F 1969 *Surf. Sci.* **15** 535
- [14] Allan G 1970 *Ann. Phys., Paris* **5** 169
- [15] Ducastelle F and Cyrot-Lackmann F 1971 *J. Phys. Chem. Solids* **32** 285
- [16] Allan G and Lanno M 1976 *J. Phys. Chem. Solids* **37** 699
- [17] Masuda K and Sato A 1981 *Phil. Mag.* **A 44** 799
- [18] Wolf A and Schmidtke 1980 *Int. J. Quantum Chem.* **5** 1187
- [19] Dobrotvorskii A M 1985 *Koord. Khim.* **11** 307 (in Russian)
- [20] Dobrotvorskii A M, Afanasjeva O V and Archakov Y I 1984 *Fiz. Metall. Metalloved.* **58** 330 (in Russian)
- [21] Afanasjeva O V, Dobrotvorskii A M and Archakov Y I 1984 *Zh. Prikl. Khim.* **10** 2366 (in Russian)
- [22] McWeeny R and Sutcliffe B T 1969 *Methods of Molecular Quantum Mechanics* (London: Academic)
- [23] Dutchak J I, Jakibchuk P N and Zhovtanetskii M I 1976 *Ukr. Fiz. Zh.* **21** 34
- [24] Francevich I N, Voronov F F and Bacuta S A 1982 *Elastic Constants and Elastic Module of Metals and Nonmetals* (Kiev: Naukova Dumka) (in Russian)
- [25] Leibfrid T and Broier N 1981 *The Point Defects in Metals. The Introduction to Theory* (Moskow: Mir) (in Russian)
- [26] Wollenberger H J 1983 *Point Defects in Physical Metallurgy* (Amsterdam: North-Holland)
- [27] Hay P J and Wadt W R 1985 *J. Chem. Phys.* **82** 270
- [28] Dobrotvorskii A M 1991 *Teor. Exp. Khim.* **27** 437 (in Russian)
- [29] Dobrotvorskii A M and Archakov Y I 1989 *Fiz.-Khim. Mech. Mater.* **25** 3 (in Russian)
- [30] Dobrotvorskii A M and Archakov Y I 1990 *Fiz.-Khim. Mech. Mater.* **26** 42 (in Russian)
- [31] Dobrotvorskii A M, Afanasjeva O V and Archakov Y I *Fiz.-Khim. Mech. Mater.* at press (in Russian)
- [32] Oriani R A and Josephic P H 1974 *Acta Metall.* **22** 1965