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Relations between Characteristics of Point Defects and Bulk Properties of Solids

A Criticism of the Varotsos-Alexopoulos Model

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Using the similarity of the effective potentials seen by ions in solids general relations between characteristics of point defects (i.e. the volume v_i , the entropy s_i and the energy Q_i of formation, migration, and activation) and bulk properties of solids are derived. It is shown that the basic assumption of the Varotsos-Alexopoulos-model (VA-model) is not necessarily valid. Using dimensional analysis the validity conditions of this model are expressed in a form of partial differential equation from which relations "derived" by Varotsos and Alexopoulos are obtained. Their relations are different from the here obtained results because the ratios of v_i , s_i , and Q_i are proportional to expressions containing only bulk parameters of the solid, while in the relations obtained by us there are proportionality factors depending on i , i.e. these constants are different for the formation, migration, and activation (formation plus migration) processes. It is also shown that the basic assumption of the VA-model is not valid for a harmonic solid. Experimental data for f.c.c. metals definitely confirm these results instead of those obtained by Varotsos and Alexopoulos.

Unter Nutzung der Ähnlichkeit des effektiven Potentials, das auf die Ionen in Festkörpern wirkt, werden allgemeine Beziehungen zwischen den Charakteristiken von Punktdefekten (z. B. Volumen v_i , Entropie s_i und Bildungs-, Wanderungs- und Aktivierungsenergien Q_i) und Volumeneigenschaften der Festkörper abgeleitet. Es wird gezeigt, daß die Grundannahme des Varotsos-Alexopoulos-Modells (VA-Modells) nicht notwendig gültig ist. Mit der Dimensionsanalyse werden die Gültigkeitsbedingungen dieses Modells in Form einer partiellen Differentialgleichung ausgedrückt, aus der Beziehungen, die von Varotsos und Alexopoulos „abgeleitet“ werden, erhalten werden. Diese sind von den hier erhaltenen Ergebnissen verschieden, weil die Verhältnisse von v_i , s_i und Q_i proportional zu Ausdrücken sind, die nur Volumenparameter des Festkörpers enthalten, während hier in den Beziehungen Proportionalitätsfaktoren existieren, die von i abhängen, d. h. diese Konstanten sind unterschiedlich für die Bildungs-, Wanderungs- (Bildungs- plus Migrations-) und Aktivierungsprozesse. Es wird ebenfalls gezeigt, daß die Grundannahme des VA-Modells nicht gültig ist für einen harmonischen Festkörper. Experimentelle Werte für k.f.z.-Metalle bestätigen definitiv diese Ergebnisse anstelle derjenigen von Varotsos und Alexopoulos.

1. Introduction

In a set of papers Varotsos and Alexopoulos and their coworkers derived empirical relations for the migration (m), formation (f), and activation (a) (i.e. formation plus migration) of defects in different solids. These results were recently collected in their book [1] where it is clearly formulated that in the derivation of these relations they started from the so-called $cB\Omega$ model:

$$g_i = c_i B\Omega, \quad (1)$$

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where g_i ($i = m, f, a$) denotes the Gibbs free energy of the process in question (not including the entropy of mixing); B and Ω are the isothermal bulk modulus and the atomic volume, respectively; c_i is a dimensionless constant assumed to be independent of temperature and pressure. It is also proposed in [1] that c_i can be obtained at absolute zero from (1)

$$c_i = \frac{Q_i}{B_0 \Omega_0}, \quad (2)$$

where Q_i is the corresponding energy and the subscript 0 denotes the values belonging to absolute zero. Obviously, c_i is expected to be different for different processes (i.e. for different i values and for different mechanisms). Taking into account that the defect volumes and entropies are given by

$$v_i = \left(\frac{\partial g_i}{\partial p} \right)_T \quad (3)$$

and

$$s_i = - \left(\frac{\partial g_i}{\partial T} \right)_p, \quad (4)$$

respectively and $B = -\Omega (\partial p / \partial \Omega)_T$, they came to the following results:

$$v_i = c_i \Omega \left[\left(\frac{\partial B}{\partial p} \right)_T - 1 \right] \quad (i = f, m) \quad (5)$$

and

$$s_i = -c_i \left[\frac{\partial (B\Omega)}{\partial T} \right]_p \quad (i = f, m). \quad (6)$$

(For diffusion by a monovacancy mechanism $g_a = g_f + g_m$, $v_a = v_f + v_m$ and defining c_a as $c_f = c_m + c_f$, the relations (5) and (6) are also proposed to be valid for $i = a$). From (2), (5) and (6) directly follows that

$$\frac{v_m}{Q_m} = \frac{v_f}{Q_f} = \frac{\Omega}{B_0 \Omega_0} \left[\left(\frac{\partial B}{\partial p} \right)_T - 1 \right] \quad (7)$$

and

$$\frac{s_m}{Q_m} = \frac{s_f}{Q_f} = - \frac{1}{B_0 \Omega_0} \left(\frac{\partial (B\Omega)}{\partial T} \right)_p. \quad (8)$$

Varotsos and Alexopoulos concluded in [1] that the above $cB\Omega$ model could explain not only the well-known Zener-type relation between s_i and Q_i [2, 3, 4] (i.e. $s_i \sim Q_i/T_m$ where T_m is the melting point), but also the physical meaning of the proportionality constants, the values of which were known before only empirically.

However, we must make critical remarks regarding the results summarized above. From a theoretical point of view it has been shown by different authors (see e.g. [5 to 10]) that correlations between different bulk properties or between parameters of thermally activated processes and other thermodynamical properties (i.e. the corresponding state relationships) in solids can be derived very clearly and simply using a more general basic assumption. Namely, we can use only the very plausible supposition that the interatomic potentials can be written in the form

$$U(\mathbf{r}_1, \dots, \mathbf{r}_N) = \varepsilon_0 \bar{u}(\mathbf{r}_1/\sigma_0, \dots, \mathbf{r}_N/\sigma_0), \quad (9)$$

where \bar{u} is a universal function for all crystals of the same structure and bonding type, $\mathbf{r}_1, \dots, \mathbf{r}_N$ are the positions of nuclei and ε_0 and σ_0 are the bonding strength and the characteristic length parameters varying from one substance to the other. This method avoids the detailed analysis of microscopic processes and so does not need any additional supposition. Consequently, it is not restricted, for instance, only to the elastic continuum theory and makes any speculation about the connection between the concrete thermally activated process and any other bulk process superfluous. For example, it is shown in [6] and [8] that the proportionality between Q_f and T_m or Q_m and T_m in metals does not mean a connection between the vacancy formation or migration and the melting process. In most cases only simple dimensional considerations are necessary (see e.g. [8, 9]). Although this way the atomistic meaning of the proportionality constants in relations cannot be interpreted in details and only their constancy can be stated, this description — because of its very general character — is suitable for showing the validity conditions of relations obtained empirically or semiempirically.

In Section 2 general connections between the properties of point defects and bulk parameters are derived by this method for defect formation, migration, and activation. In Section 3 the validity conditions of the VA model are established: it is shown that the main assumptions included in this model — i.e. the temperature and pressure dependence of the function g_i can be described by the T and p dependence of the scaling parameters ε_0 and σ_0 only — are not generally valid. It is also demonstrated that relations (7) and (8) are not in accordance with the experimental data for f.c.c. metals. In Section 4 we summarize our results and final remarks are made on the application of this method to other pure solids and alloys.

2. General Relations between Properties of Point Defects and Bulk Properties

Using the similarity of the interatomic potentials expressed by (9) it was shown in [8] that at temperatures higher than the Debye temperature the reduced (dimensionless) form of g_i can be given as a function of the reduced pressure $p^* = p(\sigma_0^3/\varepsilon_0)$, and temperature $T^* = kT/\varepsilon_0$ (k is the Boltzmann constant),

$$g_i^* = \frac{\Delta G_i}{N} = \frac{g_i}{\varepsilon_0} = g_{i0}^*(p^*) + \frac{T^*}{N} \sum_{j=1}^{3N} \Delta_i \ln \nu_j^*(p^*, T^*) + \Delta_i E_e^*(p^*, T^*). \quad (10)$$

Here ΔG_i is the change of the total Gibbs free energy of the system (not including the entropy of mixing [3]) and N is the number of atoms. The first two terms on the r.h.s. of (10) are the changes in the reduced Gibbs free energy of phonons (the subscript again refers to absolute zero) in quasi-harmonic approximation. The non-reduced form of these is well-known from the classical rate theory (see e.g. [3]). The vibrational frequencies ν_j^* are expressed now (across the $V^*(p^*, T^*)$ function) as a function of pressure and temperature and $g_{i0}^* = v_{i0}^* + p^* v_{i0}^*$. The third term denotes the change in the reduced Gibbs free energy of the valence electrons (its nonreduced form is given e.g. in [10]),

$$\Delta_i E_e^*(p^*, T^*) = \Delta_i E_e^* \left[1 - T^* \frac{5}{3} \frac{\pi^2 z^2}{E_e^*} \right]. \quad (11)$$

Here $E_e^* = 3/5 (z E_{F0}/\varepsilon_0)$, z is the valence, E_{F0} is the Fermi energy at $T = 0$ K, and the symbol Δ_i in (10) and (11) denotes the change in the quantities during the process in question. Now, using the standard thermodynamical definitions of $v_i^* = v_i/\sigma_0^3$,

$s_i^* = s_i/k$ and $h_i^* = h_i^*/\varepsilon_0$ we have

$$v_i^* = v_{0i}^* + \frac{T^*}{N} \sum_{j=1}^{3N} \Delta_i \left[\frac{1}{v_i^*} \left(\frac{\partial v_1^*}{\partial p^*} \right)_{T^*} \right] + \Delta_i \left(\frac{\partial E_e^*}{\partial p^*} \right)_{T^*}, \quad (12)$$

$$s_i^* = -\frac{1}{N} \sum_{j=1}^{3N} \Delta_i \ln v_j^* - \frac{T^*}{N} \sum_{j=1}^{3N} \frac{1}{v_j^*} \left(\frac{\partial v_j}{\partial T^*} \right)_{p^*} + \Delta_i \left(\frac{\partial E_e^*}{\partial p^*} \right)_{T^*}, \quad (13)$$

$$h_i^* = g_{i0}^*(p^*) - \frac{T^{*2}}{N} \sum_{j=2}^{3N} \Delta_i \left[\frac{1}{v_j^*} \left(\frac{\partial v_j^*}{\partial T^*} \right)_{p^*} \right] + \Delta_i E_e^*. \quad (14)$$

It can be noted that the phonon parts of (10), (12), (13), and (14) are given in quasi-harmonic approximation, which takes partial account of anharmonicity as well and only those effects of anharmonicity are neglected which are described by the first anharmonic correction to the Gibbs free energy (see (10) in [8] where it was shown that this correction is proportional to T^{*2}).

It is also worth mentioning that e.g. Nowick and Dienes [12] obtained the same result for the phonon parts in the nonreduced form, and their expression e.g. for h_i could be easily obtained rewriting (14), using familiar thermodynamical relations. Accordingly, neglecting the electronic parts and taking into account that at high temperatures [8]

$$c_v^* = c_v/k = 3, \quad -\frac{V^*}{v_j^*} \frac{\partial v_i^*}{\partial V^*} = \gamma_j^*, \quad \frac{1}{3N} \sum_{j=1}^{3N} \gamma_j^* = \gamma^* = \gamma,$$

$\gamma^* c_v = V^* \alpha^* B^*$ and $c_p^* = c_v^* = T^* V^* \alpha^* B^*$, where $\gamma^* = \gamma$ is the Grüneisen parameter, α^* is the reduced thermal expansion coefficient, c_p^* and c_v^* are the reduced heat capacity at constant pressure and at constant volume, respectively, (12), (13) and (14) can be rewritten as

$$v_i^* = v_{0i}^* - T^* \Delta_i [V^* \alpha^*], \quad (15)$$

$$s_i^* = -\frac{1}{N} \sum_{j=1}^{3N} \Delta_i \ln v_j^* - \Delta_i c_p^*, \quad (16)$$

$$h_i^* = u_{0i}^* + p^* v_{0i}^* + T^* \Delta_i c_p^*. \quad (17)$$

We can see from (12), (13), and (14) or (15), (16), and (17) that the reduced volume, entropy and enthalpy are *universal functions of the reduced temperature and pressure* if we neglect the electronic terms in their expressions.

The above relations can be useful and experimentally checked if we know the three parameters ε_0 , σ_0 , and M (M is the mass of the atoms) characterizing the individual members of a given similarity class. For practical purposes we can use macroscopic (thermodynamical) quantities scaling ε_0 and σ_0 . It was shown in one of our previous papers [8] that in metals the melting point $T_m(0)$ at $p = 0$ Pa and the atomic volume Ω_0 at $T = 0$ K and at $p = 0$ Pa are suitable parameters scaling ε_0 and σ_0^3 , respectively. (Because of the weak pressure dependence of the macroscopic quantities in solid state, the values taken at normal pressure can be used instead of their limit values at $p = 0$ Pa). Thus

$$\varepsilon_0 = k T_m(0) c_{TM} \quad (18)$$

and

$$\sigma_0^3 = c_0 \Omega_0 = c_0 \frac{V_0}{N}, \quad (19)$$

where c_{TM} and c_0 are universal (dimensionless) constants for all crystals of the same structure and bonding type.

In [8] an analytical expression for the reduced reciprocal isothermal bulk modulus was given. Furthermore, it was also shown that at $T = 0$ K the electronic contributions in the reduced bulk modulus cause a systematic variation (about 30%) in alkali metals (Table 2 in [8]). The reason for this is that, although the phonon terms in B^* are the same functions of their variables for all metals of a given similarity class (i.e. with the same bonding type and crystal structure), the reduced electronic term in B^* (depending on z and E_{F0}) is different for different metals. However, if we neglect the electronic terms the $B_0\Omega_0$ product (B_0 is the bulk modulus at $T = 0$ K and $p = 0$ Pa) can also be used as a scaling parameter for ε_0 , i.e.

$$\varepsilon_0 = c_B B_0 \Omega_0 \quad (20)$$

and c_B is dimensionless and approximately constant for all members of a similarity class.

Let us turn back to expressions (15), (16), and (17) and first neglect the temperature dependence. Thus it is found at $p^* \approx 0$ (at normal pressure) that v_i^* , s_i^* , and h_i^* are universal constants for a class of similar metals, i.e.

$$v_i = v_{i0}^* \sigma_0^3 = v_{i0}^* c_0 \Omega_0 = a_i^* \Omega_0, \quad (21)$$

$$s_i = s_i^* k, \quad (22)$$

and

$$h_i(0) = Q_i = Q_{i0}^* = Q_i^* c_{TM} k T_m(0) = b_i^* T_m(0) = b_i'^* B_0 \Omega_0. \quad (23)$$

Consequently, the activation volume, v_i , is proportional to the atomic volume, the activation entropy is a universal constant and the activation energy is proportional to the melting point (or to the $B_0\Omega_0$ product). The proportionality factors (b_i^* , $b_i'^*$, a_i^* , and s_i^*) are expected to be constants for a given process ($i = f, m, a$) and for all metals of the same bonding type and crystal structure. Furthermore, from (22) and (23) we have

$$\frac{s_i}{Q_i} = \frac{s_i^* k}{b_i^* T_m} = \frac{s_i^* k}{b_i'^* B_0 \Omega_0} \quad (24)$$

and similarly from (21) and (22) as well as from (21) and (23) we can write

$$\frac{s_i}{v_i} = \frac{s_i^* k}{a_i^* \Omega_0} \quad (25)$$

and

$$\frac{v_i}{Q_i} = \frac{a_i^*}{b_i'^* B_0} = \frac{a_i^*}{b_i^* T_m(0)} \frac{\Omega_0}{T_m(0)}, \quad (26)$$

respectively.

The above relations are also well-known as empirical laws and e.g. (22), (23), and (24) were derived in the same way previously in [6], [8], and [9]. Equation (25) — using the Grüneisen equation (according to which $V = \gamma c_v / \alpha B$) — can be rewritten in the form

$$\frac{s_i}{v_i} \sim \alpha_0 B_0 \quad (27)$$

which is also known as a semi-empirical relation in the literature (see e.g. [13] or [14]) and (26) is just another semi-empirical law ($v_i/Q_i \sim 1/B$) derived from the Zener model (see [14]) as well.

We must emphasize that *the three independent proportionality constants in (21) to (26) are different for different i and so relations (5) to (8) cannot be derived from these without further additional supposition(s). In other words, in the VA model only one proportionality constant, c_i , is present and the above additional supposition is equivalent to the expressions for a_i^* and s_i^* in (21) and (22) by means of the pressure and temperature derivatives of the $B\Omega$ product.* This problem will be analyzed in the next section.

3. Criticism of the Varotsos-Alexopoulos Model

As it was mentioned in Section 1, the law of corresponding states is a consequence of the similarity of the interatomic potentials (9). Accordingly, for solids of the same similarity class, all materials characteristics must depend on the parameters ε_0 , σ_0 and the atomic mass M . In other words, any thermodynamical quantity, q , characterizing one bulk property of solids, is a function of seven quantities: p , T , k , h , ε_0 , σ_0 , and M , where h is the Planck constant [4, 15]. Now, using k , ε_0 , σ_0 , and M as fundamental quantities (there is no dimensionless combination of them), q can be expressed as [16]

$$q = k^a M^b \varepsilon_0^c \sigma_0^d q(T^*, p^*, \lambda^*), \quad (28)$$

where $\lambda^* = h/(\sigma_0 \sqrt{M\varepsilon_0})$ is the reduced de Broglie wavelength. Here q^* is a universal function of its arguments and its nature depends on the nature of the reduced potential function only. Consequently, the temperature and pressure dependence of ε' and σ' being proportional to ε_0 and σ_0 (say at $p = 0$ Pa and $T = 0$ K) can be generally given by

$$\frac{\varepsilon'}{\varepsilon_0} = \varepsilon'^*(p^*, T^*, \lambda^*)$$

as well as

$$\frac{\sigma'}{\sigma_0} = \sigma'^*(p^*, T^*, \lambda^*).$$

Now let us suppose that the temperature and pressure dependence of q can be described by the temperature and pressure dependence of the scaling parameters only (i.e. changing p and T the *shape* of the reduced potential remains unchanged). Then q will be a function of five quantities: h , k , $\varepsilon'(p, T)$, $\sigma'(p, T)$, and M , and it can be given by

$$q = k^a M^b \varepsilon'^c(p, T) \sigma'^d(p, T) q^*(\lambda'^*). \quad (29)$$

Since it was supposed that \bar{u} remained the same in (9), q^* must be the same function of $\lambda'^* = h/(\sigma' \sqrt{M\varepsilon'})$ as q^* of λ^* at fixed p^* and T^* . This means that the $q/\varepsilon'^c \sigma'^d$ ratio must be independent of p and T . But this is a very rigorous condition and it is not expected to be generally valid for thermodynamical quantities.

Consequently, the above supposition is not automatically valid for the function g_i and so the basic assumption (used by Varotsos and Alexopoulos) which also states that the T and p dependence of g_i can be given by the T and p dependence of the product $B\Omega$ is also questionable. It must be noted, furthermore, that (1) means e.g. that the explicit temperature dependence of g_i (given by the $-Ts$ term) is described by the anharmonic effects, since the temperature dependence of the $B\Omega$ product originates from pure anharmonicity. But the entropy of activation is not zero even for a harmonic solid [3] and so the entropy term does not vanish in g_i .

Let us now suppose that only the pressure dependence of g can be described by pressure dependent scaling parameters. (This is obviously less rigorous condition than (29).) In this case — taking into account that q will be a function of the following six quantities, h , k , $\varepsilon'(p)$, $\sigma'(p)$, M , and T — we can write

$$q = k^a M^b \varepsilon'^c(p) \sigma'^d(p) q'^*(T'^*, \lambda'^*), \quad (30)$$

where $T'^* = kT/\varepsilon'(p)$, $\lambda'^* = h/\sigma'(p) \sqrt{M\varepsilon'(p)}$ and the $q/\varepsilon'^c(p) \sigma'^d(p)$ ratio must generally depend on the variable $T/\varepsilon'(p)$ and explicitly does not depend on p . Similarly, using temperature-dependent scaling parameters, we find that the $q/\varepsilon'^c(T) \sigma'^d(T)$ ratio must explicitly depend on $p'^* = p\sigma'(T)/\varepsilon'(T)$, but it does not have an explicit T dependence.

Furthermore, in order to have more insight into the physical background of the conclusions obtained above, we can derive a differential equation for q satisfying (29) or (30). Let us restrict ourselves to the classical limit only, where T is higher than the Debye temperature, θ_D , i.e. the λ^* dependence of q disappears from (24) and (25) [8]. Taking the partial derivatives of q by p and T we have from (29)

$$\frac{\partial q}{\partial p} = \frac{\partial q}{\partial T} \frac{cE(p) + dF(p)}{cE(T) + dF(T)}, \quad (31)$$

where $E(p) = 1/\varepsilon'(\partial\varepsilon'/\partial p)_T$, $F(p) = 1/\sigma'(\partial\sigma'/\partial p)_T$, $E(T) = 1/\varepsilon'(\partial\varepsilon'/\partial T)_p$, and $F(T) = 1/\sigma'(\partial\sigma'/\partial T)_p$. Similarly, we can get from (30) (or from the equivalent expression using temperature-dependent scaling parameters)

$$\frac{\partial q}{\partial p} - cqE(p) - dqF(p) = -TE(p) \frac{\partial q}{\partial T} \quad (32)$$

or

$$\frac{\partial q}{\partial T} - cqE(T) - dqF(T) = p[3F(T) - E(T)] \frac{\partial q}{\partial p}, \quad (33)$$

respectively.

In order to show that the Varotsos-Alexopoulos model is equivalent to the supposition expressed in (29), let us suppose that g_i obeys (31). Then we have with (3) and (4)

$$\frac{s_i}{v_i} = - \frac{E(T)}{E(p)}. \quad (34)$$

Furthermore, according to (29)

$$g_i = C_i \varepsilon', \quad (35)$$

where C_i is a constant independent of p and T . Obviously, (35) is equivalent to (1) if we use $\varepsilon' = c_B B\Omega$ (see also (20)) and from (34) and (35) we could get the same results summarized in the form of (2) and (5) to (8). In this case, since $E(p) = (1/8) [(\partial B/\partial p) - 1]$ and $E(T) = (1/B\Omega) (B\Omega/\partial T) = \alpha + (1/B) (\partial B/\partial T)$, (34) can be rewritten as

$$\frac{s_i}{v_i} = \frac{\alpha B}{\left(\frac{\partial B}{\partial p} - 1\right)} - \frac{\frac{\partial B}{\partial T}}{\left(\frac{\partial B}{\partial T} - 1\right)} \quad (36)$$

and this is equal to the ratio of (6) and (5).

Summarizing our results we must emphasize that the validity of (1) or (31) — i.e. the fact that the ratio $g_i/B\Omega$ does not explicitly depend on p and T — is not necessarily the case for arbitrary g_i . All those “theories” trying to confirm (1) or a similar relation (for example in the strain energy model Zener [4] and Keyes [17] the shear modulus, G , is used instead of B) are only approximate and should not be expected to follow from the more sophisticated theories (see also [18]). For example — criticizing the strain energy model — Flynn [3] established: “... in this model the entropy change between the saddle point and the ground state at constant volume is small and, second, it is assumed that the volume dependence of elastic constants at high temperatures gives a reasonable measure of the volume dependence of the phonon frequencies. It is not expected that either assumption is very accurate ...”.

Several further critical remarks can also be added:

a) The experimental justification of (5) to (8) is also questionable. For example, it is known that in f.c.c. metals $v_m/v_a \approx 0.2$ [19], i.e. $v_m/v_f \approx 0.25$. On the other hand, $Q_m/Q_f = 0.89$ for self-diffusion (see e.g. [20]), and so $v_m/v_f \neq Q_m/Q_f$. Furthermore, after a careful analysis of literature data it was obtained in [21] that $s_m/s_f \approx 3$ which is in contrast to (8), if we take into account again that $Q_m/Q_f = 0.89$. It is also well-known that in the Zener relation (24) the proportionality constant is different for vacancy formation and migration (see also [21]) and it is inconsistent with (8) as well.

b) As it was mentioned before the ratio $g_i/B\Omega$ has an explicit temperature dependence (at fixed p) for a harmonic solid and so (29) is not valid for g_i in this case.

c) The ratios of v_i , s_i , and Q_i , derived from (1) are independent of i and they depend only on the bulk properties of the solids. On the other hand, from the use of the similarity of the interatomic potentials only we got the relations (24), (25), and (26) containing proportionality constants depending on i . The lack of these constants from (7) and (8) is also not expected from a more sophisticated theory of defect formation and migration. For example, it was shown theoretically in [22] that s_f/k and s_m/k are proportional to $\ln ||\bar{C}^g||/||\bar{C}^f||$ and $\ln ||\bar{C}^g||/||\bar{C}^m||$, respectively, where $||\bar{C}^g||$, $||\bar{C}^f||$, and $||\bar{C}^m||$ are the determinants of the reduced dynamical matrix of the crystal (i.e. their elements are the second derivatives of the reduced potential, \bar{u} , by the reduced Descartes coordinates of the displacement vectors of the atoms) in the ground state, in a presence of a vacancy and in the saddle-point configuration, respectively. Now $Q_f = \varepsilon \Delta \bar{u}_f$ and $Q_m = \varepsilon \Delta \bar{u}_m$, where $\Delta \bar{u}_f$ and $\Delta \bar{u}_m$ are obviously different from each other since they are connected with the change in the reduced potential during the formation or migration of a vacancy. Then, it is not necessarily expected that the ratio of the change of \bar{u} and the change of the logarithm of its second derivatives is the same for the formation and migration processes, and so e.g. (8) is not expected to be valid.

d) Since both g_i and the product $B\Omega$ — in first approximation — have a linear pressure and temperature dependence, their ratio can more slightly depend on p and T . Even if — not concerning the above remarks — one has the impression that this ratio can be considered approximately constant, the logically only right way to check the validity of (1), is the precise comparison of the relations “derived” with the experimental facts. If they are not confirmed by the measured data — and we have illustrated this for f.c.c. metals — then (1) or (29) is not valid for g_i and cannot be used as a basic supposition in deriving further relations as it was done in [1].

4. Conclusions and Final Remarks

1) From the similarity of the interatomic potentials (9) it follows that v_i is proportional to the atomic volume, Q_i is proportional to ε_0 (or to the melting point or to the product $B\Omega$) and s_i is constant for the formation, migration, and activation (forma-

tion plus migration) of defects. Equations (21) to (26) were obtained as general relations between properties of point defects and bulk properties of solids.

2) We have shown that the basic assumption of the Varotsos-Alexopoulos model is not necessarily valid for arbitrary g_i . Using dimensional analysis we got the validity conditions of (1) in a form of a partial differential equation from which the relations "derived" by Varotsos and Alexopoulos (or earlier by Lawson [13], Keyes [17], and Wert and Zener [2]) were obtained. It was shown from the experimental data that these are not generally valid for vacancy formation, migration, and activation in f.c.c. metals. Nevertheless, it was found — using only the similarity of the interatomic potentials — that the ratios of v_i , s_i , and Q_i can be generally given by similar relations but with proportionality constants depending on i . These proportionality constants can be determined by their comparison to the experimental data or by detailed atomistic calculations (using concrete forms of the interatomic potentials) of the formation and migration processes.

3) It is also interesting to investigate the validity conditions of the empirical relations proposed by Nachtrieb et al. [23] according to which the pressure dependence of the diffusion coefficient can be described by the pressure dependence of the melting point and so [14]

$$\frac{v_i}{Q_i} = \frac{1}{T_m} \frac{dT_m}{dp} \quad \text{for } i = a. \quad (37)$$

It is easy to show that this rule can be derived if we suppose that (30) (or (32) which is a less rigorous condition than (29)) is valid for g_i , since from (32) we have at $p = 0$ Pa

$$\frac{v_i}{Q_i} = E(p) \quad (38)$$

and this is right if we use pressure dependent T_m in (18). On the other hand, comparing (37) to (26) we can conclude that the Nachtrieb rule is valid if

$$\frac{dT_m}{dp} = \frac{a_i^*}{b_i^*} \Omega_0. \quad (39)$$

Now, it was shown in [8] — also as a consequence of (9) — that

$$\frac{dT_m}{dp} = \delta \Omega_0, \quad (40)$$

where δ is a constant and its value is 6.0×10^2 K/eV [24] for f.c.c. metals. Comparing (39) and (40) it can be seen that (38) can be fulfilled if the a_i^*/b_i^* ratio is equal to δ for $i = a$, and it is also obvious that (38) cannot be valid at one and the same time, for the vacancy concentration, vacancy migration, and the atomic diffusion coefficient because $v_f/Q_f \neq v_m/Q_m \neq v_a/Q_a$ (see Section 3). Nevertheless, the numerical values of a_i^*/b_i^* can be estimated: it is well-known from experimental data that a_a^* lies between 0.7 and 1.0 for f.c.c. metals [19, 25], and $b_i^* = 1.57 \times 10^{-3}$ eV/K [20, 25]. Accordingly, the average values of $a_a^*/b_a^* = 5.44 \times 10^2$ K/eV, and similarly, — using that $v_m/v_a = a_m^*/a_a^* = 0.2$ [19] and $Q_m/Q_a = 0.47$ [20] — we have $a_f^*/b_f^* = 8.16 \times 10^2$ K/eV and $a_m^*/b_m^* = 2.34 \times 10^2$ K/eV. Consequently, the empirical rule for the pressure dependence of D can be valid for f.c.c. metals, but the same rule cannot be fulfilled at the same time for the vacancy concentration and/or migration. It can be noted that the agreement of δ and a_a^*/b_a^* could be accidental in the sense that this rule is not expected to be automatically valid for b.c.c. metals (or other solids) as well. In all cases the comparison of δ values with the experimental a_i^*/b_i^* ratios is necessary to

decide for which i the above rule could be approximately fulfilled, if there is such a coincidence at all.

4) In our considerations the effect of the change of the electronic structure (the third term in (10)) was neglected. This could lead to some scatter in the reduced (universal) maps from one metal to the other in the same similarity class. This problem was investigated in more details in [8].

5) We have shown that the temperature and pressure dependence of the reduced v_i , s_i , and Q_i quantities (i.e. v_i/Ω , s_i/k , and Q_i/ε or Q_i/kT_m or $Q_i/B\Omega$) must be universal. This means that, for example, the logarithm of the reduced diffusion coefficient versus the reduced reciprocal temperature (say T/T_m or $kT/B\Omega$) must be the same function at a fixed reduced pressure, regardless of the fact whether this is a straight line or not. It is also expected to be valid even if the curvature of the Arrhenius plot is caused not by the inherent temperature dependence of s_i and Q_i , but when the diffusion coefficients are the sum of two (or more) diffusion coefficients of thermally activated defects. In this case the reduced D must also generally depend on T^* and p^* and e.g. the ratio of the two diffusion coefficients (which is dimensionless and so reduced) must be constant at the same T^* and p^* . For example at normal pressure ($p^* = 0$) and at $T^* = 1$ (at the melting point in metals where kT_m is a good measure of ε) it was observed that the ratio of the divacancy and the monovacancy diffusion coefficients is about 0.5 for Ag, Au, Cu, and Pt (and somewhat less for Ni) [26]. The universal curvature of the Arrhenius plot can be connected with the inherent temperature dependence of s_i and Q_i as well. From the measurements and analysis of D values alone it is not possible to decide equivocally whether two mechanisms or the temperature dependence of the entropy and energy (or both) are responsible for the curvature. We emphasize that the careful analysis of the measured $D(p, T)$ values, isotope effects, and the defect annealing kinetics lead to the conclusion that in f.c.c. metals the divacancy contribution is significant at high temperatures [27]. On the other hand, Varotsos and Alexopoulos [1] stated that the above curvature is caused by the temperature dependence of s_i and Q_i can be fully described by the temperature dependence of $B\Omega$. In the light of the experimental facts cited above it is hard to accept and it was also shown in [21] — using more reliable B values — that the VA model is unable to describe the curvature of the Arrhenius plot in f.c.c. metals.

6) In this paper the experimental examples were taken from the experimentally very well investigated group of f.c.c. metals, for which the mechanism of diffusion is vacancy mechanism (with a considerable contribution of divacancies at high temperatures). Obviously, our results ((21) to (26)) are expected to be valid e.g. for the diffusion in b.c.c. metals and so for the selfinterstitial mechanism (which is believed to be significant at high temperatures [28]) as well. Similarly, it is expected that these relations are valid for diffusion in ionic crystals, or semiconductors — where the product $B\Omega$ is a better measure of ε than the melting point [8] — if we consider the formation and migration of the same defect within a similarity group. (Obviously for ionic crystals the two different sublattices must be separately considered.)

Furthermore, the correlations derived by Varotsos and Alexopoulos — as a generalization of (1) — for the impurity diffusion have to be reconsidered similarly, to the cases when e.g. (23) or (24) were generalized in [21] and [9] respectively, or as these relations were generalized for the case of random binary alloys in [10].

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