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Comments on the calculation of the formation volume of vacancies in solids

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We establish contact between two stress-assisted diffusion theories. The first theory is formal and has been developed by the author by a consistent use of the principles of modern continuum mechanics. The second theory is microscopic, based on solid-state physics arguments and has been published in a recent issue of Phys. Rev. B by Varotsos *et al.* We show that both theories are compatible within the low-pressure regime. As a result of this compatibility the phenomenological coefficients of the formal theory can be explicitly calculated in terms of microscopic parameters. Furthermore, an interesting experimental result which cannot be modeled within the formal theory is now adequately explained. The present findings seem to provide additional supporting evidence to the validity of the Varotsos *et al.* proposition.

I. INTRODUCTION

In this short communication we report an interesting observation regarding the relationship between two different stress-assisted diffusion theories. The first theory is purely phenomenological and was derived by Aifantis *et al.*[1-3] by adopting the approach of modern continuum mechanics. The second theory was established by Varotsos *et al.*[4-6] by using solid-state physics arguments. The first theory is inherently linear modeling, in particular, diffusion in materials elastically stressed and, therefore, it is applicable to many interesting engineering applications. The second theory is nonlinear and it claims to model diffusion processes in materials subjected to extremely high hydrostatic pressures.

It has been shown[2,3] that the linear theory is in accordance with experimental data for certain diffusion systems and when the applied stresses are relatively low. The relevant plots are given in a previous paper.[2] Two comments are important to be made here[2,3]: (i) the value of the various phenomenological coefficients can only be determined by the experimental data; (ii) certain plots show a strong dependence on temperature, a fact which cannot be justified by considering the small temperature dependence of the elastic constants.

The above two questions are reconsidered here within the nonlinear theory proposed by Varotsos *et al.*[4-6] In particular, we show how a linearization procedure establishes compatibility for both theories in the low-pressure regime. The compatibility requirement yields an explicit calculation of an important phenomenological constant in terms of microscopic parameters. The calculation agrees with the experimental data. Furthermore, the above mentioned temperature dependence is sufficiently explained. In this connection, the present paper can be thought of as supplement to the analysis contained in a paper by Varotsos, Ludwig, and Alexopoulos.[6]

II. CONTINUUM MECHANICS APPROACH

By employing arguments of modern continuum mechanics it has been recently shown[1-3] that diffusion in a solid elastically stressed is described by the equation

$$\frac{\partial \rho}{\partial t} = D^* \nabla^2 \rho - M \nabla \sigma \cdot \nabla \rho , \tag{1a}$$

$$D^* = D + N\sigma , \tag{1b}$$

where ρ is the concentration of the diffusing species, D the diffusion coefficient of the unstressed solid, σ is the trace of the stress tensor, and M and N are phenomenological constants. Certain microscopic arguments have been invoked[7,8] to relate the constant M to diffusivity D, the activation volume v, the Boltzmann's constant k, and the absolute temperature T. However, no such theory has been developed for the constant N whose determination is, thus, exclusively left to experiment.

Equation (1b) can be rearranged to read

$$\left(\frac{D^*}{D} - 1\right) / \sigma = \frac{N}{D} = A , \tag{2}$$

where A is a new constant. Equation (2) suggests that for small stresses the ratio $(D^*/D - 1)/\sigma$ must be a constant. This fact has been experimentally confirmed for certain systems.[2,3] It has also been experimentally observed that the constant A varies with temperature, in particular, it decreases as temperature increases. A theoretical calculation of the constant A and a justification of its dependence on the temperature is not possible within the framework of continuum mechanics which is based on purely phenomenological arguments. Below we examine the validity of Eq. (2) within a physical model proposed by Varotsos, Ludwig, and Alexopoulos.[6] We show that this model is consistent with Eq. (2) in the low-pressure regime. In addition, we show that the model provides a theoretical calculation for the constant A and explains its temperature variation, in agreement with the experimental data.

III. SOLID-STATE PHYSICS APPROACH

It is well known from statistical thermodynamics that the diffusion coefficient D is related to the Gibb's activation energy g by

$$D(P)=D_0\exp\left(-\frac{g(P)}{kT}\right) , \tag{3}$$

where P denotes the applied hydrostatic pressure, k is Boltzmann's constant, T is the absolute temperature, and the pre-exponential term can be considered as constant. By following the terminology of Sec. II we have

$$D\equiv D(0)=D_0\exp\left(-\frac{g(0)}{kT}\right) . \tag{4}$$

For small pressures we expand Eq. (3) in Taylor's series to obtain

$$D(P)=D(0)+D'(0)P+\tfrac{1}{2}D''(0)P^2+\cdots , \tag{5}$$

where a prime denotes differentiation with respect to P. We neglect the second-order term and, in conformity with the terminology of Sec. II, we denote by D^* the linear variation of $D(P)$. We also use definition (4) and Eq. (3) to compute $D'(0)$. Then, Eq. (5) reads

$$D^*=D-\frac{D}{kT}\frac{\partial g}{\partial P}P . \tag{6}$$

The value of $\partial g/\partial P$ can be obtained from the Varotsos-Ludwig-Alexopoulos model[6] as

$$\frac{\partial g}{\partial P}=c\left(\frac{dB}{dP}-1\right)\Omega , \tag{7}$$

where B is the isothermal bulk modulus, Ω the mean volume per atom, and c is a known constant independent of temperature and pressure. The value of c is given[6] by

$$c=\frac{h_0}{B_0\Omega_0} , \tag{8}$$

where h_0 is the activation enthalpy at absolute zero and B_0 and Ω_0 are the corresponding values of B and Ω at absolute zero. Combining Eqs. (6) – (8) we obtain

$$\left(\frac{D^*}{D}-1\right)/P=-\frac{h_0}{kT}\frac{\Omega}{\Omega_0}\left(\frac{dB}{dP}-1\right)\frac{1}{B_0} . \tag{9}$$

By recalling that $P=-\frac{1}{3}\sigma$, we observe that Eq. (9) is compatible with Eq. (2). This compatibility is established by taking

$$A=\frac{h_0}{3kT}\frac{\Omega}{\Omega_0}\left(\frac{dB}{dP}-1\right)\frac{1}{B_0} , \tag{10}$$

which provides a theoretical calculation of the constant A in terms of known microscopic parameters. In addition, expression (10) suggests that A is decreasing with temperature, roughly as $\sim 1/T$, in agreement with the experimental data. To illustrate further the above observation we searched in the literature[9,10] specific values for Cu, i.e.,

$dB/dP\simeq 5.65$ (at room temperature),

$h_0=2.2$ eV, $\Omega_0=11.66\times 10^{-24}$ cm^3 ,

$\Omega/\Omega_0\simeq 1.08$, $B_0\simeq 1.45\times 10^{12}$ erg/cm^3 .

These values, in conjunction with Eq. (10), predict

$$A\simeq 3\times 10^{-8}\frac{1}{T}\ {}^\circ\mathrm{K}\frac{\mathrm{dyn}}{\mathrm{cm}^2} .$$

However, the value of A should be about 30% larger than the above due to the increase of dB/dP with temperature (we used the value of dB/dP in room temperature since there are no relevant experimental values for higher temperatures). Thus, the value that A predicted from Eq. (10) is comparable with this predicted from experiment.[2]

IV. CONCLUSION

We have shown that formal continuum mechanics theories can be substantiated by invoking solid-state physics arguments. In particular, we have shown that the Varotsos-Ludwig-Alexopoulos physical model is compatible with the author's formal theory in the low-pressure regime. Also, the parameter A which in the formal theory is an experimental constant was found here to depend explicitly on the bulk properties $\{\Omega, \Omega_0, B_0, dB/dP\}$, the diffusion process through the value of h_0, and the inverse of absolute temperature $1/T$.

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[1] E. C. Aifantis, Mech. Res. Commun. 3, 245 (1976).

[2] E. C. Aifantis, W. W. Gerberich, and D. E. Beskos, Arch. Mech. Stosow. 29, 339 (1977).

[3] E. C. Aifantis and W. W. Gerberich, Acta Mech. 29, 169 (1978).

[4] P. Varotsos, J. Phys. Lett. 38, L455 (1977).

[5] P. Varotsos and W. Ludwig, J. Phys. C 11, L309 (1978); 11, L315 (1978).

[6] P. Varotsos, W. Ludwig, and K. Alexopoulos, Phys. Rev. B 18, 2683 (1978).

[7] H. P. Van Leeuwen, J. Corrosion 29, 197 (1973).

[8] P. G. Shewmon, *Diffusion in Solids* (McGraw-Hill, New York, 1963), p. 23.

[9] G. R. Barsch and Z. P. Chang, Phys. Status Solidi 19, 139 (1967).

[10] Y. A. Chang and L. Himmel, J. Appl. Phys. 37, 3569 (1966).