

Calculation of diffusion coefficients at any temperature and pressure from a single measurement. I. Self diffusion

P. Varotsos and K. Alexopoulos

Department of Physics, University of Athens, Solonos Str. 104, Athens 144, Greece

(Received 31 August 1978; revised manuscript received 26 February 1980)

A method is proposed which permits the determination of the diffusion coefficient D at any temperature and pressure when it is known for one single experimental situation. In order for the method to be applied, the thermal expansion coefficient and the elastic constants have to be known in the corresponding temperature and pressure range. The method gives good results for the temperature dependence of D of Pb, Cu, Ag, K, and W. The pressure dependence can be checked only for Na because for other metals elastic data are not available at high temperatures under increased pressure.

INTRODUCTION

It is well known that the (tracer) diffusion coefficient D is given by

$$D = \gamma \alpha^2 \nu \exp(-g/kT), \quad (1)$$

where γ is the correlation factor, α is the lattice constant, g the Gibbs energy for the activation process, and ν is a frequency factor which is of the order of the Debye frequency. By considering that $g = h - Ts$ Eq. (1) can be written as

$$D = \gamma \alpha^2 \nu e^{s/k} e^{-h/kT}, \quad (2)$$

where $s = -(\partial g / \partial T)|_P$ and $h = g - T(\partial g / \partial T)|_P$ denote the activation entropy and enthalpy, respectively. In principle h and s may depend on temperature, which means that g does not decrease linearly with T . Even in the simplest case, i.e., when h, s are temperature independent, Eq. (2) indicates that the knowledge of D for a single experimental situation (P_1, T_1) cannot lead to a determination of (h, s); therefore the prediction of D at any temperature and pressure from a single measurement is not possible. It is the object of the present paper to show that regardless of the constancy of h and s this becomes possible when an appropriate expression of g —in function of bulk quantities—is used without the knowledge of any other quantity related to defects.

TEMPERATURE DEPENDENCE OF THE DIFFUSION COEFFICIENT

Recently a connection between the Gibbs activation energy g and the isothermal bulk modulus B has been proposed by the authors¹

$$g = cB\Omega, \quad (3)$$

where Ω is the mean volume per atom and c a constant which is assumed to be temperature and pressure independent. For a given solid, c only

depends on the type of defect that is being activated.

By inserting into Eq. (1) the value of g given by Eq. (3), we get

$$D = \gamma \alpha^2 \nu \exp(-cB\Omega/kT). \quad (4)$$

If the value D_1 has been found experimentally for a temperature T_1 , the value of c can be determined because the pre-exponential factor $\gamma \alpha^2 \nu$ is roughly known. Even if an error of a factor of 2 is introduced by setting ν equal to ν_D , the value of c remains practically the same. Once the value of c has been determined from D_1 , the value D_2 for a temperature T_2 can be found by a direct application of Eq. (4) provided that elastic data and the expansion coefficient β are available for this temperature; the frequency factor $\nu (= \nu_D)$ is assumed to be constant. This latter approximation introduces an insignificant error if one considers that D eventually differs by 7 orders of magnitude (or more). Note also that when c is known from the single measurement (D_1, T_1) the value of the activation enthalpy h can be directly calculated at any temperature from the relation

$$h = c\Omega \left(B - T\beta B - T \frac{\partial B}{\partial T} \Big|_P \right), \quad (5)$$

which immediately results from the relation $h = g - T(\partial g / \partial T)|_P$ by introducing Eq. (3). An inspection of Eq. (5) shows that h varies with temperature. The curvature in the $\ln D$ vs $1/T$ plot therefore depends on the temperature dependence of the bulk quantity $\Omega[B - T\beta B - T(\partial B / \partial T)|_P]$ (see the Appendix). In order to check the reliability of the prediction of D at various T and P we apply it to a few metals.

fcc METALS

We apply Eq. (4) to a "low-melting" metal Pb

and to two "high-melting" metals Cu and Ag.

Lead. For the evaluation of the pre-exponential factor of Eq. (4) we use the values $\nu_D = 1.8 \times 10^{12} \text{ sec}^{-1}$, $\alpha = 4.94 \text{ \AA}$ (Ref. 2), and $\gamma = 0.78$. As no isothermal bulk modulus values B are available we will use the adiabatic values³ B_s and make a correction with the help of the formula

$$B_s/B = 1 + TVB_s\beta^2/C_P, \quad (6)$$

where C_P is the molar specific heat for constant pressure. From the adiabatic value one obtains for $T_1 = 447 \text{ K}$ the isothermal one $B_1 = 36.96 \times 10^{10} \text{ erg/cm}^3$. Introducing this value and⁴ $D_1 = 4.8 \times 10^{-13} \text{ cm}^2/\text{sec}$, Eq. (4) gives $c = 0.1257$. For $T_2 = 595.6 \text{ K}$ the isothermal bulk modulus is $B_2 = 33.64 \times 10^{10} \text{ erg/cm}^3$. The insertion of these data into Eq. (4) leads to a calculated value of $D_2 = 3.68 \times 10^{-10} \text{ cm}^2/\text{sec}$. Assuming an error of $\pm 1\%$ in the value of B_2 , the calculated D_2 should lie between 3.14 and $4.32 \times 10^{-10} \text{ cm}^2/\text{sec}$. The corresponding experimental⁴ D_2 value is $4.09 \times 10^{-10} \text{ cm}^2/\text{sec}$ which is in quite good agreement with the predicted values.

Copper. All the available experimental data⁵⁻⁸ for self-diffusion in Cu have been inserted in Fig. 1. The value of D varies by 10 orders of magnitude.

Direct experimental values for the adiabatic bulk modulus B_s exist up to 800 K .⁹ In order to extend the calculation to higher temperatures we make first a least-squares fitting to a straight line of the measured B_s values between 500 and 800 K ; then B_s values at higher temperatures are calculated by a linear extrapolation. The isothermal bulk modulus has been obtained by using Eq. (6). For its application we have used the specific heat measurements of Brooks¹⁰ and the expansivity data reported in Metals Handbook.¹¹

The lowest temperature to which the self-diffusion has been measured⁷ is $T_1 = 613.7 \text{ K}$; its value is $D_1 = 1.63 \times 10^{-18} \text{ cm}^2/\text{sec}$. The value of the pre-exponential factor $\gamma\alpha^2\nu$ is obtained by using the values $\gamma = 0.78$ (Ref. 12), $\alpha = 3.61 \text{ \AA}$, and² $\nu_D = 6.52 \times 10^{12} \text{ sec}^{-1}$. By using also the values $B_1 = 1267 \text{ kbar}$ and $\Omega_1 = 11.9017 \text{ \AA}^3$,³ we obtain $c = 0.2025$ from the D_1 value at 613.7 K . Then by applying Eq. (5) for various temperatures T_2 , we obtain the D_2 values inserted in Fig. (1) in the form of a line; it agrees well with the experimental data (points) up to the melting point. Note also that the application of Eq. (5) for $T_1 = 613.7 \text{ K}$ gives $\bar{h} \approx 2.1 \text{ eV}$ which agrees with the experimental value^{8,12} (see the Appendix).

Silver. The adiabatic elastic data have been

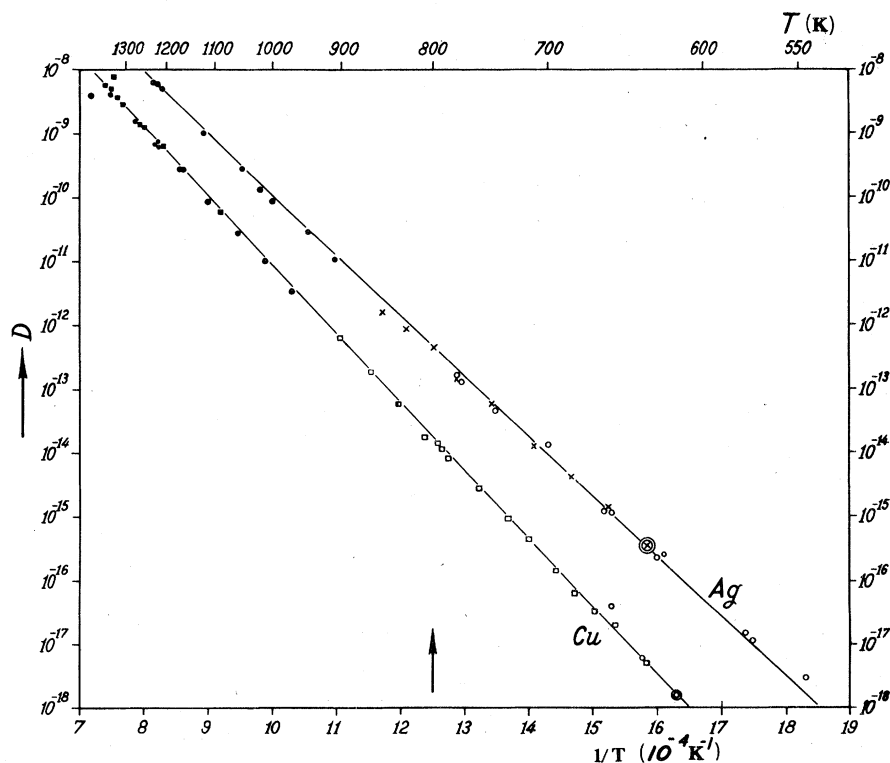


FIG. 1. Diffusion coefficients as a function of temperature. Measured points for copper: (●) Ref. 5; (□) Ref. 6; (○) Ref. 7; (■) Ref. 8. Measured points for silver: (×) Ref. 15; (○) Ref. 16; (●) Ref. 17. The arrow indicates the highest temperature for which elastic data are available. Full line: calculated.

quoted by Varshni¹³ up to 800 K. The isothermal bulk modulus was obtained by inserting into Eq. (6) the isobaric specific heat values¹⁴ and the expansivity data.¹¹ The value of the pre-exponential factor is found from $\gamma = 0.78$, $\alpha = 4.08 \text{ \AA}$ and $\nu_D = 4.7 \times 10^{12} \text{ sec}^{-1}$. Starting from the value $D_1 = 3.38 \times 10^{-16} \text{ cm}^2/\text{sec}$ given by Backus, Bakker, and Mehrer¹⁵ for $T_1 = 630.7 \text{ K}$, one finds $c = 0.1629$. By applying Eq. (4) for various temperatures T_2 up to 800 K, one gets the line drawn in Fig. (1). It agrees well with the experimental values^{15,16} (points). At higher temperatures a linear extension of the adiabatic bulk modulus has been assumed. The computed line agrees well with the general trend of the experimental data¹⁷ but is systematically slightly higher than the experimental ones. However, by accepting the plausible error, 2% in the values of the isothermal bulk modulus, the calculated values come to lie within the margin of the experimental errors.

Equation (5) when applied for $T = 630.7 \text{ K}$ gives $h \approx 1.88 \text{ eV}$ which agrees with the value 1.86 eV derived from a least-squares fitting (to a straight line) of the diffusion data.¹⁸

bcc METALS

We have chosen for the application of Eq. (4) a low-melting metal (K) and a high-melting one (W).

Potassium. For this metal, values of the isothermal bulk modulus are directly available.¹⁹⁻²¹ The pre-exponential factor was calculated from $\alpha = 5.225 \text{ \AA}$, $\gamma = 0.727$, and $\nu_D = 1.9 \times 10^{12} \text{ sec}^{-1}$. By using in Eq. (4) the values $T_1 = 220.8 \text{ K}$, $B_1 = 32.68 \text{ kbar}$, and $D_1 = 9.02 \times 10^{-11} \text{ cm}^2/\text{sec}$, we get $c \approx 0.224$. Then Eq. (4) gives for $T_2 = 288 \text{ K}$ (where $B_2 = 30.97 \text{ kbar}$) the result $D_2 = 0.9(-0.2, +0.3) \times 10^{-8} \text{ cm}^2/\text{sec}$ which is in satisfactory agreement with the experimental value²² $D_2 = 1.15 \times 10^{-8} \text{ cm}^2/\text{sec}$.

Tungsten. The self-diffusion of W has been studied very recently by Mundy, Rothman, Lam, Hoff, and Nowicki²³ from 1700 to 3400 K. The pre-exponential factor was calculated from $\alpha = 3.18 \text{ \AA}$, $\nu_D = 8.33 \times 10^{12} \text{ sec}^{-1}$, and $\gamma = 0.727$. The elastic constants have only been measured²⁴ up to 1800 K; they follow a second-degree law²⁵ which we assume as correct up to 3400 K. The data for the correction of the bulk modulus from adiabatic to isothermal are also only available²⁶ at low temperatures, however, this correction is not very critical. Equation (4) for $T_1 = 1705 \text{ K}$ gives $c = 0.1915$ if we use the values $B_1 = 2682 \text{ kbar}$ and $D_1 = 1.37 \times 10^{-18} \text{ cm}^2/\text{sec}$. Then by using the existing elastic, isobaric specific heat, and expansivity data up to a temperature of 3400 K, various values of D_2 can be calculated from Eq. (4). The results have been plotted as a continuous line in Fig. 2. At higher temperatures a systematic difference appears for D_2 of about a factor of two between calculated and experimental values. This can easily be explained by assuming that at temperatures nearing the melting point the bulk modulus starts falling faster than in the lower temperature regions, an effect that has been noticed in other solids.²⁷ A reduction of B by about 4% from the second-degree law is sufficient to produce this increase of D_2 .

By using the values $B = 2682 \text{ kbar}$, $\beta = 18 \times 10^{-6} \text{ K}^{-1}$, and $(\partial B/\partial T)|_P = -2.68 \text{ kbar/K}$, Eq. (5) gives for $T = 1705 \text{ K}$ the result $h = 5.6 \text{ eV}$; this is in satisfactory agreement with experiments if one considers that the monovacancy formation and migration enthalpy is $4.0 \pm 0.3 \text{ eV}$ and $1.5 \pm 0.3 \text{ eV}$, respectively.²⁸

PRESSURE DEPENDENCE OF D

In the following the symbol (0) indicates values at zero pressure. By dividing the equations

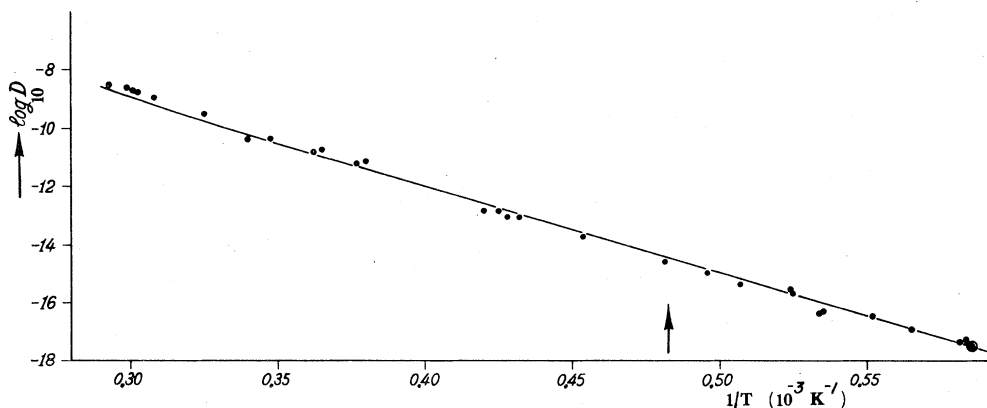


FIG. 2. Diffusion coefficient of W as a function of temperature. Measured points: (●) Ref. 22. The arrow indicates the highest temperature for which elastic data are available. Full line: calculated.

$$D(0) = \gamma \alpha^2(0) \nu(0) \exp[-g(0)/kT],$$

$$D = \gamma \alpha^2 \nu \exp(-g/kT),$$

and taking the approximation $\nu(0) \approx \nu$ and $\alpha(0) \approx \alpha$ one obtains

$$D/D(0) = \exp[cB(0)\Omega(0)/kT - cB\Omega/kT]. \quad (7)$$

c can be determined as before from $D(0)$. The bulk modulus has to be expressed in terms of the compressibility $\kappa (\equiv 1/B)$; the latter is defined as $\kappa = -(1/\Omega)d\Omega/dP$ and hence,

$$\Omega = \Omega(0) \exp\left(\int_0^P -\kappa dP\right).$$

Therefore, Eq. (7) becomes

$$\frac{D}{D(0)} = \exp\left\{\frac{c\Omega(0)}{kT} \left[B(0) - B \exp\left(\int_0^P -\kappa dP\right)\right]\right\}. \quad (8)$$

Equation (8) permits the calculation of D from $D(0)$ for any pressure provided that the variation of the elastic constants with the pressure is known.

Sodium. The pressure variation of the isothermal bulk modulus has been measured by Grover, Getting, and Kennedy²⁹ from which we extracted $\partial^2 B/\partial P^2 = 0.068$ (kbar)⁻¹. In Table I we give all the data required for the calculation of the quantity $\exp(\int_0^P \kappa dP)$ at $T = 300$ K for pressures up to 7 kbar. Mundy³⁰ for $T = 298.2$ K reported $D(0) = 5.81 \times 10^{-9}$ cm²/sec. By using $\alpha = 4.225$ Å, $\gamma = 0.727$ (Ref. 12), $\nu_D = 3.33 \times 10^{12}$ sec⁻¹, and accepting for 298.2 K the values given in Table I for 300 K, an application of Eq. (4) given $c = 0.24$; then Eq. (8) gives $D = 2 \times 10^{-10}$ cm²/sec for 7 kbar. For this pressure the experimental value³⁰ is 5×10^{-10} cm²/sec in agreement with the calculated value if one considers the large experimental error in κ and $d\kappa/dP$. To the best of our knowledge no other high-temperature elastic data under pressure for high-melting materials are available so that Eq. (10) cannot be checked for such materials.

TABLE I. Elastic data for sodium at $T = 300$ K.

P (kbar)	B (kbar)	$\frac{dB}{dP}$	$\int_0^P \kappa dP (10^{-2})$
0	59.90	4.06	0
1	63.86	3.99	1.50
2	67.61	3.92	3.14
3	71.16	3.86	4.58
4	74.51	3.79	5.96
5	77.66	3.72	7.27
6	80.60	3.65	8.53
7	83.34	3.59	9.76

APPENDIX: DISCUSSION OF THE CURVATURE OBSERVED IN Cu

An inspection of the calculated curve of Fig. 1 shows a slight upward curvature which seems to be comparable to that observed experimentally. In the frame of a single mechanism this curvature implies that the activation enthalpy increases with temperature. Once the value of c has been determined from a single D_1 value, Eq. (5) permits the direct computation of h for each temperature. Unfortunately, as mentioned, direct elastic data at high temperatures—where the $\ln D$ vs $1/T$ plot is curved—are not available so that an accurate plot of the calculated h values as a function of T is not possible. However, as an approximation, we have applied Eq. (5) by using the extrapolated B_s values mentioned above. These indicative results are given in Table II. We notice a small increase of h as the temperature increases.

The calculated h values are not unreasonable. For instance, the simultaneous least-square fitting of the high-temperature self-diffusion data reported by Rothman and Peterson⁵ (700–1060 °C) and by Bartdorff, Neumann, and Reimers (737–1079 °C) gives⁸ an activation enthalpy of about 2.18 eV. This value is comparable to the calculated h values, at the same temperature region, if one considers an uncertainty of, at least 1% (due mainly to the experimental uncertainty of B).

The fact that the expression $g = cB\Omega$ predicts an upwards curvature of the Arrhenius plot may be viewed in an alternative way. According to Gilder and Lazarus³² the specific heat c_p per vacancy is given by the approximate relation

$$c_p \equiv \frac{\partial h}{\partial T} \Big|_P = \frac{T\nu\beta^2}{\kappa} \left(2 \frac{\beta^v}{\beta} - \frac{\kappa^v}{\kappa}\right), \quad (A1)$$

where β^v and κ^v are the thermal expansion coefficient and the compressibility of the activation volume v . Nowick and Dienes³³ by assuming, in the lack of the direct experimental values that

TABLE II. The activation enthalpy in copper as calculated from Eq. (5). The value $c = 0.2025$ has been determined from D_1 value at $T = 613.7$ K.

T (K)	h (eV) calc. from Eq. (5)
613.7	2.134
700	2.134
800	2.135
900	2.136
1000	2.135
1100	2.137
1200	2.139
1300	2.155

$\beta^v/\beta = 1$, $\kappa^v/\kappa = 1$ found a very small value of c_P , of the order of a few tenths of k_B . This would lead to a nondetectable curvature of the Arrhenius plot. However, Eq. (3) leads¹ to

$$\beta^v = \beta + \frac{\partial}{\partial T} \frac{\partial B}{\partial P} \left/ \left(\frac{\partial B}{\partial P} - 1 \right) \right. \quad (\text{A2})$$

and

$$\kappa^v = \kappa - \frac{\partial^2 B}{\partial P^2} \left/ \left(\frac{\partial B}{\partial P} - 1 \right) \right. \quad (\text{A3})$$

Experiments in copper have shown that the quantity $\partial B/\partial P$ increases with temperature³⁴ and decreases with pressure²⁹ so that $\beta^v > \beta$ and $\kappa^v > \kappa$.

In order to get an idea of the order of magnitude of c_P we calculate the ratios β^v/β and κ^v/κ . By considering that $\partial B/\partial P$ increases by 10% from liquid nitrogen up to RT,³⁴ Eq. (A2) shows that the ratio β^v/β is of the order of 10. Furthermore by considering that $-B\partial^2 B/\partial P^2 \approx \partial B/\partial P$, Eq. (A3) indicates that the ratio κ^v/κ is around 2. Therefore the term $(2\beta^v/\beta - \kappa^v/\kappa)$ in Eq. (A1) is far from unity.

The value of c_P now becomes larger by one order of magnitude in comparison to the value estimated by Nowick and Dienes.³³ The new value of c_P is sufficient to account for an observable curvature of the Arrhenius plot.

- ¹P. Varotsos, W. Ludwig, and K. Alexopoulos, *Phys. Rev. B* **18**, 2683 (1978).
- ²C. Kittel, *Introduction to Solid State Physics*, 4th ed. (Wiley, New York, 1971), p. 219.
- ³C. L. Vold, M. E. Glicksman, E. W. Kammer, and L. C. Cardinal, *J. Phys. Chem. Solids* **38**, 157 (1977).
- ⁴N. H. Nachtrieb, H. A. Resing, and S. A. Rice, *J. Chem. Phys.* **31**, 135 (1959).
- ⁵S. J. Rothman and N. L. Peterson, *Phys. Status Solidi* **35**, 305 (1969).
- ⁶K. Maier, C. Bassani, and W. Schule, *Phys. Lett.* **A44**, 539 (1973).
- ⁷Nghi Q. Lam, S. J. Rothman, and L. J. Nowicki, *Phys. Status Solidi A* **23**, K35 (1974).
- ⁸D. Bartdorff, G. Neumann, and P. Reimers, *Philos. Mag.* **A38**, 2, 157 (1978).
- ⁹Y. A. Chang and L. Himmel, *J. Appl. Phys.* **37**, 2, 3568 (1966).
- ¹⁰C. R. Brooks, *J. Phys. Chem. Solids* **29**, 1377 (1968).
- ¹¹*Metals Handbook: Properties and Selection of Metals*, 8th ed., edited by Taylor Lyndon (American Society for Metals, Cleveland, 1961), Vol. 1.
- ¹²N. L. Peterson, in *Diffusion in Solids, Recent Developments*, edited by A. S. Nowick and J. J. Burton (Academic, New York, 1975), p. 118.
- ¹³Y. P. Varshni, *Phys. Rev. B* **2**, 10, 3952 (1970).
- ¹⁴O. Vollmer and R. Kohlhaas, *Z. Metallk.* **59**, 273 (1968); see also *Z. Angew., Physik* **25**, 365 (1968).
- ¹⁵J. G. E. M. Backus, H. Bakker, and H. Mehrer, *Phys. Status Solidi B* **64**, 151 (1974).
- ¹⁶Nghi Q. Lam, S. J. Rothman, H. Mehrer, and L. J. Nowicki, *Phys. Status Solidi B* **57**, 225 (1973).
- ¹⁷S. J. Rothman, N. L. Peterson, and J. T. Robinson, *Phys. Status Solidi* **39**, 635 (1970).
- ¹⁸H. Mehrer, *J. Nucl. Mater. Science* **69-70**, 38 (1978).
- ¹⁹W. R. Marquardt and J. Trivisonno, *J. Phys. Chem. Solids* **26**, 273 (1965).
- ²⁰P. A. Smith and C. S. Smith, *J. Phys. Chem. Solids* **26**, 279 (1965).
- ²¹G. E. Monfort and C. A. Swenson, *J. Phys. Chem. Solids* **26**, 291 (1965).
- ²²J. N. Mundy, T. E. Miller, and R. J. Porto, *Phys. Rev. B* **3**, 2445 (1971).
- ²³J. N. Mundy, S. J. Rothman, N. Q. Lam, H. A. Hoff, and L. J. Nowicki, *Phys. Rev. B* **18**, 6566 (1978).
- ²⁴R. Lowrie and A. M. Gonas, *J. Appl. Phys.* **36**, 2189 (1965).
- ²⁵Nachire Soga, *J. Appl. Phys.* **37**, 3416 (1966).
- ²⁶G. Morizur, A. Radenac, and J. Cretenet, *High Temp. High Pressures* **8**, 113 (1976).
- ²⁷D. S. Tanhauser, L. J. Bruner, and A. W. Lawson, *Phys. Rev.* **102**, 1276 (1956); B. Dorner, in *Proceedings of the International Conference on Lattice Dynamics, Paris, 1977*, edited by M. Balkanski (Flammarion, Paris, 1978).
- ²⁸K. Maier, M. Peo, B. Saile, H. E. Schaefer, and A. Seeger, *Philos. Mag.* **A40**, 701 (1979).
- ²⁹R. Grover, I. C. Getting, and G. C. Kennedy, *Phys. Rev. B* **7**, 567 (1973).
- ³⁰J. N. Mundy, *Phys. Rev. B* **3**, 2431 (1971).
- ³¹C. A. Swenson, *J. Phys. Chem. Solids* **29**, 1337 (1968); he gives the values $B(0) = 61.6$ kbars and $(\partial B_s/\partial P)|_T = 3.6$, which differ considerably from the values reported in Ref. 29.
- ³²H. M. Gilder and D. Lazarus, *Phys. Rev. B* **11**, 4916 (1975).
- ³³A. S. Nowick and G. J. Dienes, *Phys. Status Solidi* **24**, 461 (1967).
- ³⁴R. D. Peters, M. A. Breazcale, and V. K. Pare, *Phys. Rev. B* **1**, 3245 (1970).