

# Germanium diffusion in aluminium: connection between point defect parameters with bulk properties

Ganniari-Papageorgiou, E. , Fitzpatrick, M.E. and Chroneos, A.

**Author post-print (accepted) deposited by Coventry University's Repository**

**Original citation & hyperlink:**

Ganniari-Papageorgiou, E. , Fitzpatrick, M.E. and Chroneos, A. (2015) Germanium diffusion in aluminium: connection between point defect parameters with bulk properties. Journal of Materials Science: Materials in Electronics, volume 26 (11): 8421-8424  
<http://dx.doi.org/10.1007/s10854-015-3510-5>

DOI 10.1007/s10854-015-3510-5

ISSN 0957-4522

ESSN 1573-482X

Publisher: Springer

The final publication is available at Springer via <http://dx.doi.org/10.1007/s10854-015-3510-5>

**Copyright © and Moral Rights are retained by the author(s) and/ or other copyright owners. A copy can be downloaded for personal non-commercial research or study, without prior permission or charge. This item cannot be reproduced or quoted extensively from without first obtaining permission in writing from the copyright holder(s). The content must not be changed in any way or sold commercially in any format or medium without the formal permission of the copyright holders.**

**This document is the author's post-print version, incorporating any revisions agreed during the peer-review process. Some differences between the published version and this version may remain and you are advised to consult the published version if you wish to cite from it.**

# Germanium diffusion in aluminium: connection between point defect parameters with bulk properties

E. Ganniari-Papageorgiou,<sup>1</sup> M. E. Fitzpatrick,<sup>1</sup> and A. Chroneos<sup>1,2,a)</sup>

<sup>1</sup>*Faculty of Engineering and Computing, Coventry University, Priory Street, Coventry CV1 5FB, United Kingdom*

<sup>2</sup>*Department of Materials, Imperial College London, London SW7 2BP, United Kingdom*

## Abstract

The understanding of dopant diffusion and its temperature dependence is technologically important in metals. As a model system we consider germanium diffusion in aluminium. This is an appropriate system as germanium does not form intermetallic compounds in aluminium and therefore it simplifies the investigation of its diffusion behavior. Here we use experimental elastic and expansivity data to derive the germanium diffusion coefficient in aluminium in the framework of the so-called cBΩ model, between 673 K to 883 K. This model is a powerful way to study point defect parameters in metals as it connects them to bulk properties, which are more easily accessible. The calculated diffusivities are in excellent agreement with the experimental data.

**Keywords:** Aluminium alloys; Ge diffusion

<sup>a)</sup>Electronic mail: [ab8104@coventry.ac.uk](mailto:ab8104@coventry.ac.uk)

## 1. Introduction

Diffusion is a fundamentally important process that can impact materials properties and technological applications [1-3]. Silicon (Si) and germanium (Ge) alloying elements in aluminium (Al) are important as they do not form stable or metastable intermetallic compounds [4]. When the Si or Ge concentration is beyond the solid solubility limit they form diamond-structured precipitates in the Al matrix [4]. The ternary Al- (Si, Ge) alloys can be appropriate for age hardening alloys as the maximum strengthening by a minimum amount of alloying elements and volume fraction of particles can be significant [5,6]. The diffusion of solutes in Al- (Si, Ge) alloys is important in developing understanding of the precipitation kinetics [5].

The linking of the defect Gibbs energy ( $g^i$ ) and the bulk properties in solids is an important issue in materials physics [7-10]. The Varotsos and Alexopoulos [11-13]  $cB\Omega$  model proposed that  $g^i$  is proportional to the isothermal bulk modulus  $B$  and the mean volume per atom  $\Omega$  through a constant  $c$ . The  $cB\Omega$  model is valuable as it can lead to the calculation of numerous defect parameters provided there is some experimental input incorporating bulk properties. It has been previously employed to describe the diffusion and point defect processes in numerous systems including metals, semiconductors and oxides [14-19]. In particular the  $cB\Omega$  model successfully described point defect processes in systems including alkali and silver halides,  $PbF_2$ ,  $ZnO$ , diamond,  $LiH$ , silicon (Si) olivine, and  $AgI$  [11-21]. An example of recent systematic work is the application of the  $cB\Omega$  model to investigate the diffusion processes in germanium (Ge) [22-24] with the calculated diffusivities being in excellent agreement with experiment [25-29].

Importantly, in a previous study the  $cB\Omega$  model was used to calculate self-diffusion in Al [19]. In the present study we use the  $cB\Omega$  model to derive relations for

the association of the Ge diffusion in Al with the isothermal bulk modulus and the mean volume per atom.

## 2. Methodology

In a crystalline solid where a single diffusion mechanism is dominant, self- and/or dopant-diffusion can be described by the activation Gibbs energy ( $g^{\text{act}}$ ), which is the sum of the Gibbs formation ( $g^{\text{f}}$ ) and the Gibbs migration ( $g^{\text{m}}$ ) processes. Eqs. 1 and 2 define the activation entropy  $s^{\text{act}}$  and the activation enthalpy  $h^{\text{act}}$  respectively [14,15]:

$$s^{\text{act}} = - \left. \frac{dg^{\text{act}}}{dT} \right|_P \quad (1)$$

$$h^{\text{act}} = g^{\text{act}} + Ts^{\text{act}} \quad (2)$$

The diffusion coefficient ( $D$ ) is defined by:

$$D = f a_0^2 \nu e^{-\frac{g^{\text{act}}}{k_B T}} \quad (3)$$

Where  $f$  is the diffusion correlation factor depending on the diffusion mechanism and the structure,  $a_0$  is the lattice constant,  $\nu$  is the attempt frequency and  $k_B$  is Boltzmann's constant.

In the  $cB\Omega$  model the defect Gibbs energy  $g^{\text{i}}$  is connected to the bulk properties of the material via the relation [11-13]:

$$g^{\text{i}} = c^{\text{i}} B \Omega \quad (4)$$

From Eqs. (3) and (4) we obtain:

$$D = f a_0^2 \nu e^{-\frac{c^{\text{act}} B \Omega}{k_B T}} \quad (5)$$

For an experimentally-determined diffusivity  $D_1$  value at  $T_1$  the  $c^{\text{act}}$  can be calculated considering that the pre-exponential factor  $f a_0^2 \nu$  can be determined and that the  $B$  and  $\Omega$  values are usually known. The calculation of the pre-exponential

factor relies on the diffusion correlation factor (that is in turn dependent upon the diffusion mechanism and the crystal structure) and the attempt frequency [15]. Following the calculation of  $c^{act}$  the diffusivity  $D_i$  at any temperature  $T_i$  can be derived using Eq. 5 [14,15]. As a first approximation  $c^{act}$  is a constant that is temperature- and pressure-independent [15]. Importantly, the cB $\Omega$  model encapsulates anharmonic effects, which are exhibited by the temperature decrease in B and by the thermal expansivity [19].

### **3. Results and discussion**

#### **A. Background**

Al can be considered as a model system as there exists comprehensive defect data collected over more than five decades [30-34]. In a previous study Varotsos and Alexopoulos [19] employed the cB $\Omega$  model for self-diffusion in Al indicating that it can be described with a single diffusion mechanism and a  $c^{act} = 0.17357$  in the temperature range 673-916 K.

In the present study the expansivity and the isothermal bulk modulus data as embedded to the ratio  $\frac{B\Omega}{k_B T}$  were adopted from the previous study of Varotsos and Alexopoulos [19]. These values are given in Tables 1 alongside the experimental Ge diffusion coefficients reported by Thürer *et al.* [4]. The linear behaviour of  $\ln D$  versus  $\frac{B\Omega}{k_B T}$  (refer to Figure 1) testifies the validity of the cB $\Omega$  mode and that a single diffusion mechanism is operating.

#### **B. Single experimental measurement method**

In previous work Thürer *et al.* [4] determined that Ge diffusion in Al can be described via the Arrhenius relation:

$$D_{exp} = 3.39e^{-\frac{1.24 \text{ eV}}{k_B T}} \cdot 10^{-5} \text{ m}^2 \text{ s}^{-1} \quad (6)$$

From this equation we can calculate  $D_1$ . To be able to derive  $D_i$  at any temperature using the single experimental measurement (SEM) method (refer to Eq. 5 and the previous section) it is necessary to calculate the pre-exponential factor  $f a_0^2 \nu$ . Here we consider that  $f$  is equal to 0.78, which corresponds to monovacancy diffusion in fcc metals [35]: this can be justified by the study of Thürer *et al.* [4] which determined that the mechanisms of Ge and self-diffusion in Al are the same, with the Ge-vacancy interaction being weak. The lattice constant  $a_0 = 4.124 \text{ \AA}$  [33]. For Ge diffusion in Al the attempt frequency can be approximated by [36]:

$$\nu = \nu_D \sqrt{\frac{m_{Al}}{m_{Ge}}} \quad (7)$$

Where  $\nu_D$  is the Debye frequency, and  $m_{Al}$  and  $m_{Ge}$  are the corresponding masses for Al and Ge respectively. The Debye frequency was reported to be  $\nu_D = 6.8 \times 10^{14} \text{ s}^{-1}$  [33] (derived from the Debye temperature 328 K [37]). Therefore,  $\nu = 4.144 \times 10^{14} \text{ s}^{-1}$  and the pre-exponential factor is  $5.497 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$ .

From Eq. 6 at  $T = 883 \text{ K}$ ,  $D_1 = 2.84 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$ . Using the corresponding  $\frac{B\Omega}{k_B T} = 82.79$  (refer to Table 1 and [19]),  $c^{act} = 0.2027$ . Therefore, using the single experimental measurement method the diffusion of Ge in Al can be described within the cB $\Omega$  model with:

$$D_{cB\Omega}^{SEM} = 5.497e^{-\frac{0.2027B\Omega}{k_B T}} \cdot 10^{-5} \text{ m}^2 \text{ s}^{-1} \quad (8)$$

With this relation the Ge diffusivities with respect to temperature can be deduced. Figure 2 is the Arrhenius plot for Ge diffusion coefficients in Al determined by experiment [4] and deduced by the cB $\Omega$  model. It can be seen that the single experimental measurement method adequately describes Ge diffusion in Al at high temperatures but it diverts from experiment at the lower temperature range. For

example, for  $T = 673$  K (the lowest temperature considered here) there is a difference of 86.9% (refer also to Table 1). Nonetheless the application of the  $cB\Omega$  model in Ge-doped Al even with the single experimental method can lead to the calculation of diffusivity that will be within a reasonable (within an order of magnitude) agreement to experiment. These diffusivity values, however, will not be appropriate to derive the activation energy of diffusion in the system given that the slope in the Arrhenius plot will be different to the experimentally-determined one.

### C. Mean value method

As discussed in previous studies the method of the single experimental measurement (refer to [14,15] and references therein) is not unique and methods such as the so-called compensation law [38,39] and the “mean value” method (MV) [40-42] have been used to calculate  $c^{act}$ . In the single experimental measurement method the calculated value of  $c^{act}$  will be affected on the errors in the pre-exponential factor,  $B$ ,  $\Omega$ , and  $D_1$  values, and these can be significant when a single experimental values set is considered. To validate the present results and avoid the dependence of  $c^{act}$  on the experimental uncertainties the mean value method is also considered here [38-43]. As mentioned previously the linear behaviour of  $\ln D$  versus  $\frac{B\Omega}{k_B T}$  shows the validity of the  $cB\Omega$  model and additionally the  $c^{act}$  is the slope (refer to Eq. 5). The Ge diffusion coefficients in Al are associated to the isothermal bulk modulus and the mean volume per atom via:

$$D_{cB\Omega}^{MV} = 4.582e^{-\frac{0.1448B\Omega}{k_B T}} \cdot 10^{-7} m^2 s^{-1} \quad (9)$$

Figure 2 shows that the mean value method is in excellent agreement with the experimental [4] Ge diffusion coefficients in Al. Having established the validity of the  $cB\Omega$  model for Ge diffusion in Al other defect properties including migration and

formation entropies which are difficult to determine experimentally can be calculated for a wide temperature range.

#### **4. Conclusions**

1. We have demonstrated that the cB $\Omega$  model is applicable to Ge diffusion in Al. The efficacy of the cB $\Omega$  model, particularly using the mean value method, to describe Ge diffusion in Al encourages its application to metallic systems and alloys for which there is limited experimental data.

2. The mean value method is a better way to derive the diffusivities as compared to the single experimental measurement method. This stems mainly from the inaccurate calculation of the pre-exponential factor in the latter method. Density functional theory calculations will need to be employed to consider whether there is binding between Ge and vacancies in Al. This would in turn impact the pre-exponential factor.

#### **Acknowledgements**

The authors are grateful for funding from the Lloyd's Register Foundation, a charitable foundation helping to protect life and property by supporting engineering-related education, public engagement and the application of research.



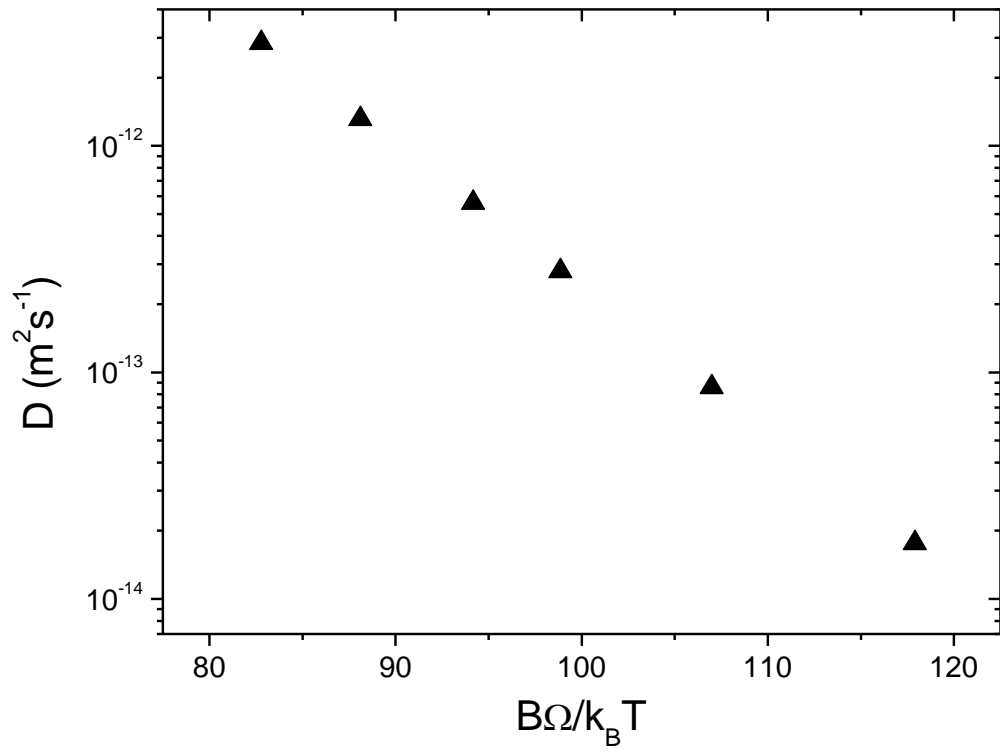
## References

1. J.A. Kilner, *Nat. Mater.* **7**, 838 (2008)
2. D. Rupasov, A. Chroneos, D. Parfitt, J.A. Kilner, R.W. Grimes, S.Ya. Istomin, E.V. Antipov, *Phys. Rev. B* **79**, 172102 (2009)
3. H. Tahini, A. Chroneos, R.W. Grimes, U. Schwingenschlögl, H. Bracht, *Appl. Phys. Lett.* **99**, 072112 (2011)
4. A. Thüerer, G. Rummel, Th. Zumkley, K. Freitag, H. Mehrer, *Phys. Stat. Sol. A* **149**, 535 (1995)
5. E. Hornbogen, A.K. Mukhopadhyay, E.A. Starke jr., *Z. Metallk.* **83**, 577 (1992)
6. E. Hornbogen, A.K. Mukhopadhyay, E.A. Starke jr., *Scripta Metall. et Mater.* **27**, 733 (1992)
7. P. Varotsos, K. Alexopoulos, *Phys. Rev. B* **30**, 7305 (1984)
8. A. Chroneos, M.E. Fitzpatrick, L.H. Tsoukalas, *J. Mater. Sci.: Mater. Electron.* **26**, 3287 (2015)
9. A. Chroneos, R.V. Vovk, *J. Mater. Sci.: Mater. Electron.* **26**, 2113 (2015)
10. J. Philibert, *Defect Diffus. Forum* **249**, 61 (2006)
11. P. Varotsos, K. Alexopoulos, *Phys. Rev. B* **15**, 4111 (1977)
12. P. Varotsos, K. Alexopoulos, *Phys. Rev. B* **15**, 2348 (1977)
13. P. Varotsos, K. Alexopoulos, *Phys. Rev. B* **22**, 3130 (1980)
14. P. Varotsos, K. Alexopoulos, (1986) *Thermodynamics of point defects and their relation with the bulk properties*. North-Holland, Amsterdam
15. P. Varotsos, *J. Appl. Phys.* **101**, 123503 (2007)
16. P. Varotsos, *Solid State Ionics* **179**, 438 (2008)
17. B.H. Zhang, X.P. Wu, *Appl. Phys. Lett.* **100**, 051901 (2012)
18. F. Vallianatos, V. Saltas, *Phys. Chem. Minerals* **41**, 181 (2014)
19. P. Varotsos, K. Alexopoulos, *Phys. Stat. Sol. B* **110**, 9 (1982)
20. I. Sakelis, *J. Appl. Phys.* **112**, 013504 (2012)
21. E. S. Skordas, *Solid State Ionics* **261**, 26 (2014)
22. A. Chroneos, R.V. Vovk, *Mater. Sci. Semicon. Proc.* **36**, 179 (2015)
23. A. Chroneos, R.V. Vovk, *J. Mater. Sci.: Mater. Electron.* **26**, 3787 (2015)
24. A. Chroneos, Y. Panayiotatos, R.V. Vovk, *J. Mater. Sci.: Mater. Electron.* **26**, 2693 (2015)
25. H.H. Silvestri, H. Bracht, J.L. Hansen, A.N. Larsen, E.E. Haller, *Semicond. Sci. Technol.* **21**, 758 (2006)
26. S. Brotzmann, H. Bracht, J. Lundsgaard Hansen, A. Nylandsted Larsen, E. Simoen, E.E. Haller, J.S. Christensen, P. Werner, *Phys. Rev. B* **77**, 235207 (2008)
27. S. Brotzmann, H. Bracht, *J. Appl. Phys.* **103**, 033508 (2008)
28. R. Kube, H. Bracht, A. Chroneos, M. Posselt, B. Schmidt, *J. Appl. Phys.* **106**, 063534 (2009)
29. A. Chroneos, H. Bracht, *Appl. Phys. Rev.* **1**, 011301 (2014)
30. T.S. Lundy, J.F. Murdock, *J. Appl. Phys.* **33**, 1671 (1962)
31. A.S. Berger, S.T. Ockers, M.K. Chason, R.W. Siegel, *J. Nucl. Mater.* **69-70**, 734 (1978)
32. B. Grabowski, T. Hickel, J. Neugebauer, *Phys. Rev. B* **76**, 024309 (2007)
33. P. Varotsos, *J. Appl. Phys.* **105**, 083524 (2009)
34. M. Mantina, Y. Wang, R. Arroyave, L.Q. Chen, Z.K. Liu, C. Wolverton, *Phys. Rev. Lett.* **100**, 215901 (2008)
35. J.N. Mundy, *Phys. Rev. B* **3**, 2431 (1971)
36. K. Eftaxias, V. Hadjicontis, *Phys. Stat. Sol. B* **160**, K9 (1990)
37. R.C.G. Killean, E.J. Lisher, *J. Phys. C* **8**, 3510 (1975)

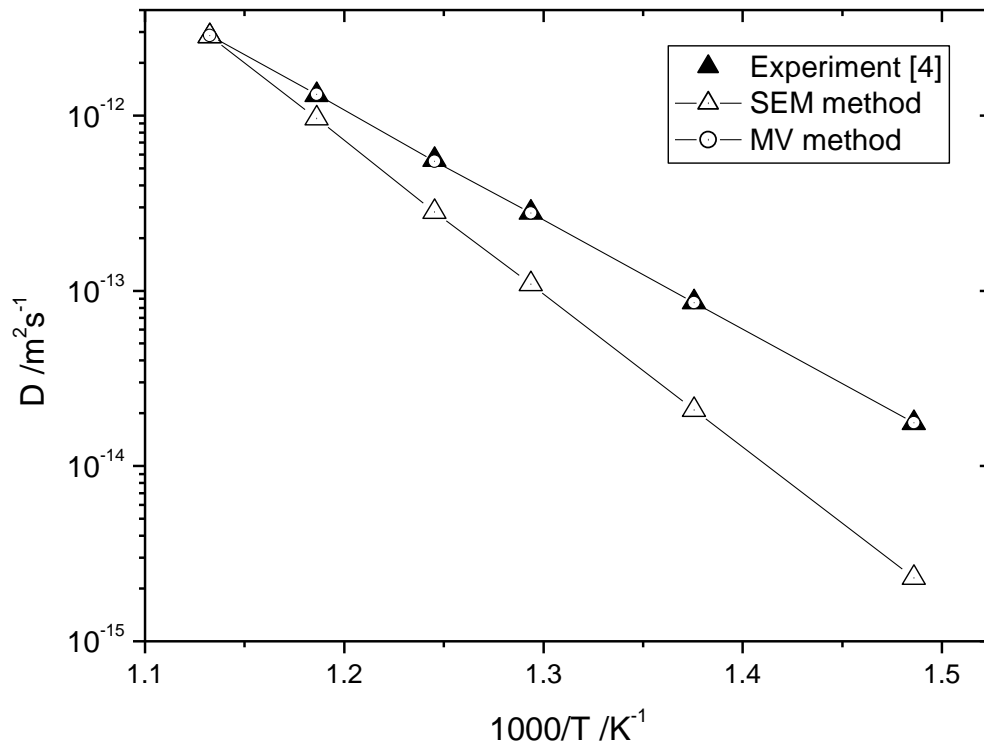
38. B.H. Zhang, X.P. Wu, J.S. Xu, R.L. Zhou, J. Appl. Phys. **108**, 053505 (2010)
39. B.H. Zhang, X.P. Wu, R.L. Zhou, Solid State Ionics **186**, 20 (2011)
40. E. Dologlou, J. Appl. Phys. **110**, 036103 (2011)
41. B.H. Zhang, X.P. Wu, Chin. Phys. B **22**, 056601 (2013)
42. B.H. Zhang, AIP Advances **4**, 017128 (2014)
43. A. Chroneos, R.V. Vovk, Solid State Ionics **274**, 1 (2015)

**Table 1.** Derived and determined [4] Ge diffusion coefficients in Al alongside the elastic and expansivity data introduced via  $\frac{B\Omega}{k_B T}$  [19] used in the cB $\Omega$  model.

T / K	$\frac{B\Omega}{k_B T}$	$D_{exp}$ / m <sup>2</sup> s <sup>-1</sup>	$D_{cB\Omega}^{SEM}$ / m <sup>2</sup> s <sup>-1</sup>	$\frac{D_{cB\Omega}^{SEM} - D_{exp}}{D_{exp}}$ (%)	$D_{cB\Omega}^{MV}$ / m <sup>2</sup> s <sup>-1</sup>	$\frac{D_{cB\Omega}^{MV} - D_{exp}}{D_{exp}}$ (%)
673	117.9	$1.76 \times 10^{-14}$	$2.30 \times 10^{-15}$	-86.9	$1.77 \times 10^{-14}$	1
727	107.0	$8.59 \times 10^{-14}$	$2.09 \times 10^{-14}$	-75.6	$8.56 \times 10^{-14}$	0
773	98.87	$2.79 \times 10^{-13}$	$1.09 \times 10^{-13}$	-61.0	$2.78 \times 10^{-13}$	0
803	94.17	$5.59 \times 10^{-13}$	$2.82 \times 10^{-13}$	-49.6	$5.48 \times 10^{-13}$	-2
843	88.11	$1.31 \times 10^{-12}$	$9.63 \times 10^{-13}$	-26.4	$1.32 \times 10^{-12}$	1
883	82.79	$2.84 \times 10^{-12}$	$2.83 \times 10^{-12}$	-0.2	$2.86 \times 10^{-12}$	1



**Figure 1.** The Ge diffusion coefficients [4] in Al with respect to  $\frac{B\Omega}{k_B T}$ .



**Figure 2.** The Arrhenius plot for Ge diffusion coefficients in Al calculated by experiment [4] and derived by the  $cB\Omega$  model using both the single experimental measurement method and the mean value method.