

ANALYSIS OF SELF- AND HETERODIFFUSION IN FERROMAGNETIC AND PARAMAGNETIC α -IRON

FILIPPOS VALLIANATOS

Technological Educational Institute of Crete, Branch of Chania, Chania, Greece*

(Manuscript received March 18, 1997; accepted in revised form December 11, 1997)

Abstract: Self- and heterodiffusion data in α -Fe, in ferromagnetic and paramagnetic state are analysed taking into account the anharmonic properties of the bulk material. The values obtained for the activation enthalpy, entropy and Gibbs energy are in agreement with the experimental values, given by Ceise & Herzog (1987) and Cermak et al. (1989). Using the elastic data of α -Fe, we calculate the λ parameter which in its definition contains the exchange integral for an atom at the saddle point and the equilibrium position. Furthermore, the influence of spin ordering in the activation Gibbs energy, in the Curie temperature zone, is investigated.

Key words: diffusion, paramagnetic, ferromagnetic, iron.

Introduction

Recently, several experimental studies have shown that during the transition from the ferromagnetic to paramagnetic state, the physical quantities of a magnetic mineral change not suddenly at a given temperature but gradually over a temperature interval called Curie zone (see Cermak et al. 1989).

Self-diffusion experiments shows a strong anomaly in the Arrhenius plot. This anomaly is the so-called “magnetic diffusion anomaly” (Philibert 1991). Due to the lack of experimental diffusion data in magnetic minerals, we focus our interest in the preliminary study of self and heterodiffusion in the paramagnetic and ferromagnetic state of α -Fe.

The observed anomaly may be characterized by the following features:

(a) The diffusivities in the magnetically ordered state are considerably lower than would be expected from extrapolating the Arrhenius plot measured in the paramagnetic region (Kucera et al. 1984).

(b) The observable deviation from the linear Arrhenius plot starts at a paramagnetic temperature T_p which is higher than the Curie temperature T_c .

(c) The activation enthalpy h_f^{act} of ferromagnetic state is higher than the corresponding h_p^{act} of the paramagnetic state. The variation of the actual activation enthalpy $h^{\text{act}}(T)$ from h_f^{act} to h_p^{act} is a continuous function of the temperature T . The physical basis hidden behind the latter experimental result indicates that the easiest migration occurs in the paramagnetic state and is more difficult in the ferromagnetic state. An explanation for the aforementioned experimental fact is based on the effect of the ferromagnetic spin ordering that reduces the mobility below the Curie temperature T_c . According to this model a ferromagnetic short range order already exists in paramagnetic α -iron at a temperature considerably above T_c . Therefore a smooth decrease of the diffusion coefficient is expected when approaching T_c from the high temperature range (Ruch et al. 1976).

(d) The elastic constants of many magnetic materials display anomalies near the magnetic ordering temperature T_c , suggesting that this anomalous behavior is closely connected to magnetic ordering (Satiya et al. 1985).

The aim of the present work is to study, using the so-called $cB\Omega$ model (Varotsos & Alexopoulos 1986) the influence of anharmonic properties of bulk materials (i.e. the temperature variation of the isothermal bulk modulus and the lattice parameter) to the temperature dependence of self- and heterodiffusion curves of α -iron in the transition from the ferromagnetic to paramagnetic state.

Theoretical remarks

As has been shown by Borg & Dienes (1988) the diffusion coefficient can be written as

$$D = f a^2 \nu \exp(-g^{\text{act}}/kT) \quad (1)$$

a is the lattice parameter, ν the attempt frequency, f the correlation factor, k the Boltzmann's constant and g^{act} the activation Gibbs energy for diffusion. In the case of heterodiffusion the frequency ν of the diffusing atom is determined by comparison to the frequency ν_m of an atom of the matrix material after considering the influence of their masses. To a rough approximation one can set $\nu = \nu_m (m_m/m_i)^{1/2}$; m_m, m_i the masses of matrix and diffusing atoms respectively. The activation enthalpy h^{act} and the activation entropy s^{act} are defined by the usual thermodynamic relation:

$$g^{\text{act}} = h^{\text{act}} - T s^{\text{act}} \quad (2)$$

Combining (1) and (2) it follows $D = D_0 \exp(-h^{\text{act}}/kT)$ where $D_0 = f a^2 \nu \exp(s^{\text{act}}/k)$ the preexponential factor.

A significant temperature variation is expected for the thermodynamic parameters near the Curie temperature, due

* Mailing address: 111 Homirov St., Moschato 18 345, Athens, Greece,
E-mail: fvallian@ee.teiath.gr

to the influence of spin ordering. In a first approximation we may write:

$$\begin{aligned} g^{\text{act}} &= g_p^{\text{act}} + \delta g^{\text{act}} \\ h^{\text{act}} &= h_p^{\text{act}} + \delta h^{\text{act}} \\ s^{\text{act}} &= s_p^{\text{act}} + \delta s^{\text{act}} \end{aligned} \quad (3)$$

where the subscript "p" denotes the paramagnetic contribution and δg^{act} , δh^{act} , δs^{act} are the excess activation Gibbs energy, enthalpy and entropy respectively. Substituted equations (3), in (1) and (2) an equation is derived which describes the diffusion coefficient D in the ferromagnetic state:

$$\begin{aligned} D &= f a^2 v \exp(s_p^{\text{act}}/k) \exp(-h_p^{\text{act}}/kT) \exp(-\delta g^{\text{act}}/kT) = \\ &= D_{\text{op}} \exp(-h_p^{\text{act}}/kT) \exp(-\delta g^{\text{act}}/kT) \end{aligned} \quad (4)$$

where D_{op} is the proexponential factor in the paramagnetic state.

Equation (4) has been developed in a model proposed by Ruch et al. (1976) and based on the assumption that the ferromagnetic ordering is a similar process to atomic ordering in order-disorder alloys. Using the theory of order-disorder alloys Kucera et al. (1984) proposed that the excess activation Gibbs energy can be expressed in the form:

$$\delta g^{\text{act}} = h_p^{\text{act}} \lambda R^2 \quad (5)$$

where λ is a temperature independent parameter related to the exchange integral at the equilibrium point and at the saddle point; $R(T)$ is a long range magnetic order parameter.

Equations (4) and (5) suggest that the diffusion coefficient D in the ferromagnetic state can be expressed as a function of the activation enthalpy for diffusion in the paramagnetic state (Geise & Herzing 1987):

$$D = D_{\text{op}} \exp\left(\frac{-h_p^{\text{act}}(1 + \lambda R^2(T))}{kT}\right) \quad (6)$$

For low temperatures $R(T) \rightarrow 1$ and hence the quantity $h_f = h_p^{\text{act}}(1 + \lambda)$ is by definition the activation enthalpy h_f for diffusion in the fully ordered (ferromagnetic) state (Cermak et al. 1989).

On the other hand Varotsos & Alexopoulos (1986) have proposed the so-called $cB\Omega$ model in order to study the curved Arrhenius diffusion plots. They suggested that the Gibbs energy g^{act} is given by the expression:

$$g^{\text{act}} = c^{\text{act}} B\Omega \quad (7)$$

where c^{act} is a dimensionless constant, independent of temperature and pressure; B is the isothermal bulk modulus and Ω the mean atomic volume.

The main physical idea hidden behind equation (7) is that there exist two families of parameters associated with the formation and migration of defects in solids. These two families of formation parameters result when comparing a real (i.e. containing defects) solid with either an isobaric perfect crystal (i.e. without defects) or an isochoric one (Varotsos & Alexopoulos 1986). The difference between the corresponding pa-

rameters comes mainly from the anharmonicity of the solid (Valianatos et al. 1995). We clarify that equation (7) is based on the following two assumptions which can be well justified on microscopic grounds (see Varotsos & Alexopoulos 1986):

(a) the isochoric defect entropy does not change significantly with temperature (in contrast to the usual isobaric defect entropy which may increase significantly with temperature);

(b) the isothermal compressibility of the activation volume has a value which is, at most, a few times larger than the bulk compressibility.

The first assumption leads to the conclusion that c^{act} is independent of temperature and the second one that c^{act} is independent of pressure. A detailed discussion on the range of the validity of these assumptions is given in a review by Varotsos & Alexopoulos (1982). We recall that the reliability of equation (7) has already been checked for point defects in many solids (Varotsos & Alexopoulos 1986; Vallianatos & Eftaxias 1992; Vallianatos & Eftaxias 1995).

According to this model the diffusion coefficient is given:

$$D = f a^2 v_m (m_m/m_i)^{1/2} \exp(-c^{\text{act}} B\Omega / kT) \quad (8)$$

The latter equation suggests that the plot of $\ln D$ versus $B\Omega/kT$ (instead of the usual plot $\ln D$ versus $1/T$), in the case of one diffusion mechanism, should be a straight line, with a slope equal to $-c^{\text{act}}$.

By recalling that the corresponding entropies s^{act} are given by:

$$s^{\text{act}} = - \left. \frac{\partial g^{\text{act}}}{\partial T} \right|_p$$

(the subscript "p" indicates a derivative under constant pressure), the introduction of equation (7) into the relation (2) lead to the following expressions:

$$h^{\text{act}} = c^{\text{act}} (B\Omega - T d(B\Omega) / dT) \quad (9a)$$

$$s^{\text{act}} = -c^{\text{act}} d(B\Omega) / dT \quad (9b)$$

Equations (9) indicate that the ratio

$$F = \frac{s^{\text{act}}}{h^{\text{act}}} = \frac{-d(B\Omega) / dT}{B\Omega - T d(B\Omega) / dT} \quad (10)$$

is a quantity which is a function of temperature and is solely governed by the bulk properties of the matrix material and not on the diffusing atom.

We point out that the activation entropy can be estimated using the proexponential factor (see equation 3) and recalling that $s^{\text{act}} = F h^{\text{act}}$ we lead to:

$$\ln [D_0(m_i / m_m)^{1/2}] = \ln (fa^2 v_m) + (F/k) h^{\text{act}} \quad (11)$$

Assuming that the quantity $fa^2 v_m$ is almost temperature independent (Mirani et al. 1975) equation (11) suggests that the plot of $\ln [D_0(m_i / m_m)^{1/2}]$ versus h^{act} , for different diffusing atoms should be a straight line, the slope of which is solely governed by the bulk quantities.

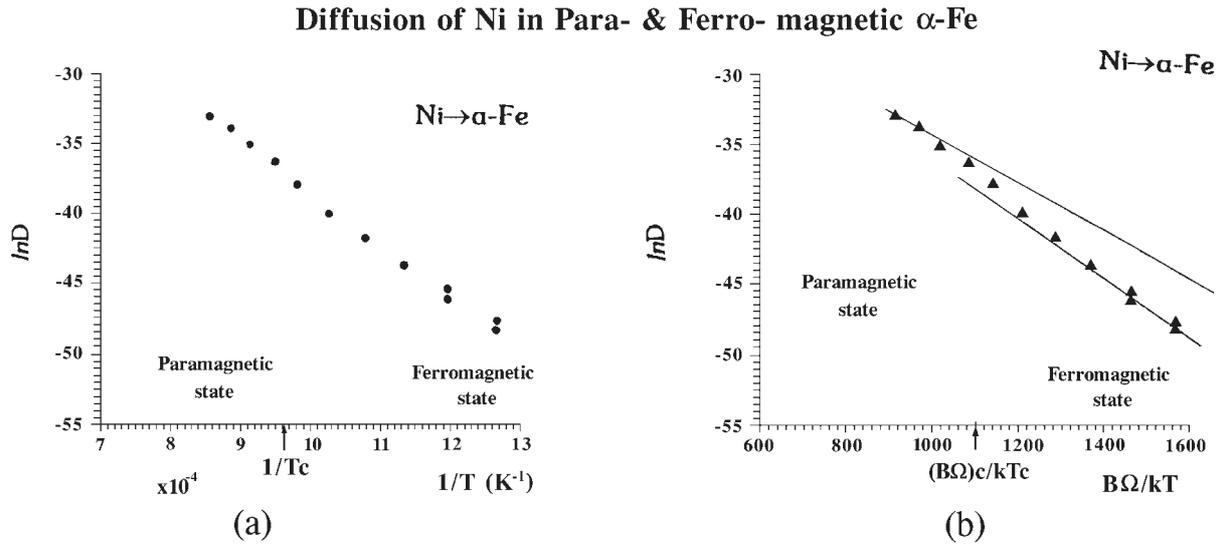


Fig. 1. (a) The Arrhenius plot of $\ln D$ vs. $1/T$ and (b) the plot of $\ln D$ vs. $B\Omega/kT$ for Ni diffusion in α iron. We point out that $T_c^{-1} = 9.6 \times 10^4 \text{ K}^{-1}$ and that $(B\Omega)_c/kT_c = 1100$.

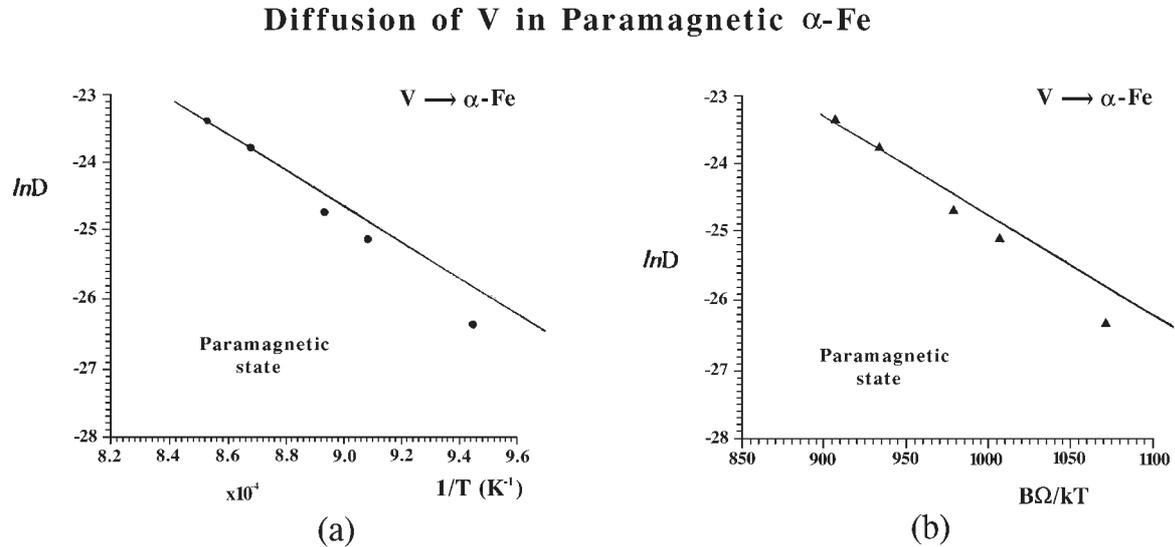


Fig. 2. (a) The Arrhenius plot of $\ln D$ vs. $1/T$ and (b) the plot of $\ln D$ vs. $B\Omega/kT$ for V diffusion in α iron for $T < T_c$.

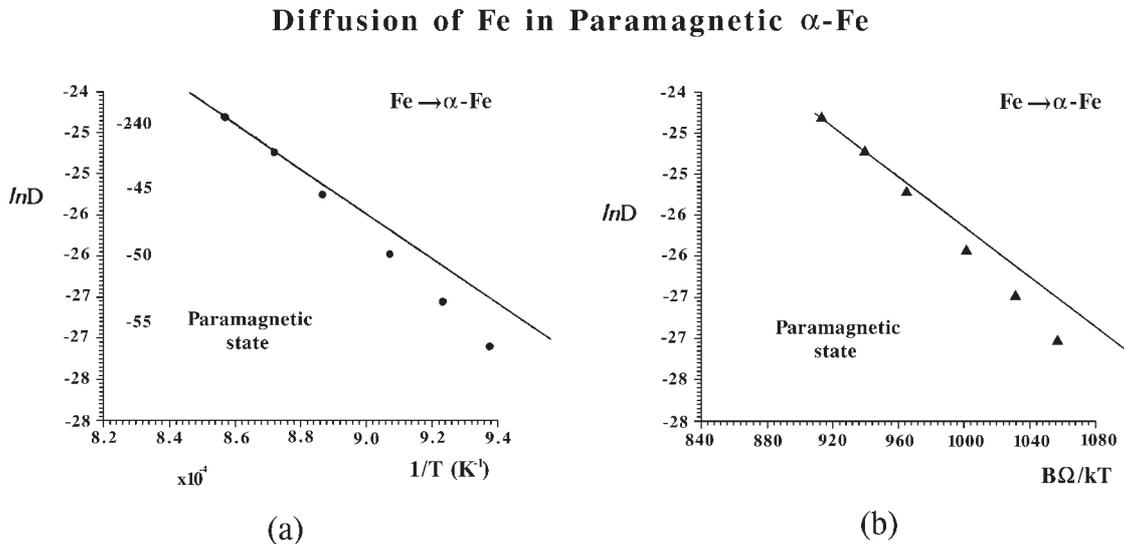


Fig. 3. (a) The Arrhenius plot of $\ln D$ vs. $1/T$ and (b) the plot of $\ln D$ vs. $B\Omega/kT$ for Fe self-diffusion in α iron for $T < T_c$.

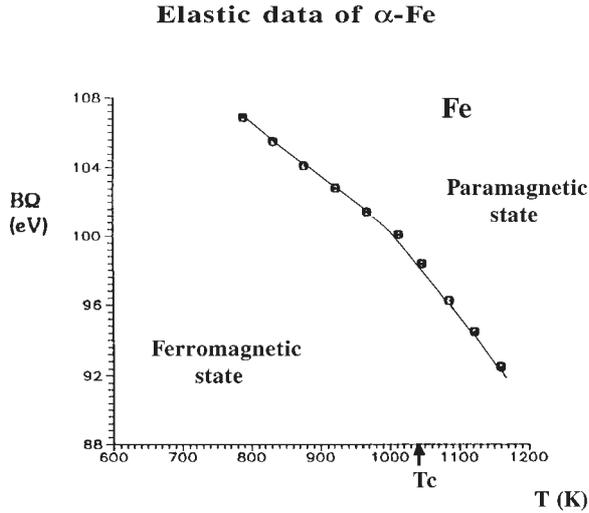


Fig. 4. Temperature dependence of the bulk quantity BQ for α -iron.

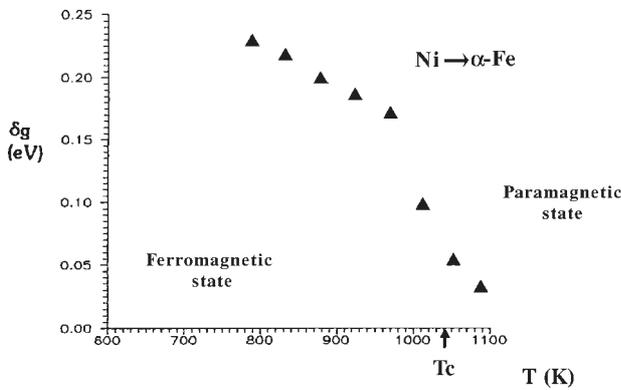


Fig. 5. Temperature dependence of the excess Gibbs activation energy in the Curie temperature zone for Ni diffusion in α -iron. The estimated values of δg are based on a linear regression of the data presented in Fig. 1.

Analysis of experimental data

The experimental data used in this study for self-diffusion in α -Fe (in the temperature range 1087–1168.5 K) are taken from Geise & Herzig (1987); data for diffusion of Vanadium (in the range 1058–1607 K) and Nickel (in the range 788–1160 K) in α -Fe are from Geise & Herzig (1987) and from Cermak et al. (1989), respectively. All of them were collected using a radiotracer method. These experimental data are plotted in figures 1, 2 and 3, versus $1/T$ and BQ/kT respectively. For the estimation of the quantity BQ (Fig. 4) we use the values of the bulk modulus B and the atomic volume tabulated by Varotsos & Alexopoulos (1986). We clarify that the isothermal bulk modulus B was estimated using measurements of the adiabatic one B_s . These values are transformed to isothermal ones according to the thermodynamic formula:

$B^{-1} = B_s^{-1} + T \Omega \beta^2 C_p^{-1}$, where Ω the atomic volume, β the volume expansion coefficient and C_p the specific heat under constant pressure.

An inspection in Figs. 1–3 show a diffusion anomaly close to T_c , even in the case when one plots $\ln D$ versus BQ/kT as suggested by Varotsos & Alexopoulos (1986).

Table 1: The “ c ” values for self and heterodiffusion in α -Fe, in ferro- and paramagnetic state, estimated using a straight line fitting to the available data in the pure para- or ferromagnetic state (see text).

Diffusing atom	c_p	c_f
Ni	0.01760	0.0219
V	0.01856	---
Fe	0.01904	---

Table 2: Calculated values and experimental ones (see Geise & Herzig 1987; Cermak et al. 1989) for activation enthalpy and entropy for self and heterodiffusion in the ferro and paramagnetic state of α -iron.

Diffusing atom	Calculated atom value	Experimental value
Ni	$h_p = 2.70$ eV	from 2.27 to 2.70 eV
	$h_f = 2.87$ eV	from 2.74 to 2.96 eV
	$s_p = 10.75$ k	-----
	$s_f = 7.69$ k	-----
V	$h_p = 2.85$ eV	(2.85 ± 0.07) eV
	$s_p = 11.3$ k	-----
Fe	$h_p = 2.92$ eV	(2.93 ± 0.02) eV
	$s_p = 11.63$ k	-----

Furthermore, in the fully paramagnetic or ferromagnetic state the diffusion curves are described by straight lines. A least square fitting to a straight line (using the end points in the two pure states) leads to a slope which is equal to $-c_p^{\text{act}}$ and $-c_f^{\text{act}}$ for the paramagnetic and ferromagnetic states respectively (see Table 1). Using the quantities c_p^{act} and c_f^{act} the Gibbs activation energy, entropy and enthalpy can be deduced for any temperature in the aforementioned limiting ranges (i.e. in the pure paramagnetic or ferromagnetic state) by means of the relations (7), (9a) and (9b). The values estimated in this way are tabulated in Table 2. For the sake of comparison the available experimental data are also given. By comparing the calculated values with the experimental ones we see an agreement within the experimental limits.

The c_p^{act} value allows the determination of the Debye frequency. Applying equation (8), using the bulk quantity BQ (see Fig. 4) and assuming that $f = 0.727$ (corresponding to a normal vacancy diffusion mechanism) and $a = 2.9 \times 10^{-10}$ m, we estimate the Debye frequency $\nu_D = 2.4 \times 10^{12} \text{ s}^{-1}$ which should be compared with the value $5.6 \times 10^{13} \text{ s}^{-1}$ estimated using the Debye temperature $\Theta_D = 428$ K (Gray 1972).

We turn now to the calculation of the temperature independent parameter λ . From equation (6) we lead to $\lambda = (h_f^{\text{act}}/h_p^{\text{act}}) - 1$. Using the estimated values for the activation enthalpies, we find $\lambda = 0.062$. The experimental value lies between 0.060 and 0.088 (Cermak et al. 1989).

We proceed finally to the estimation of the temperature dependence of the excess Gibbs activation energy δg^{act} in the Curie temperature zone, for the case of Ni diffusion in α -Fe. To estimate δg^{act} we apply the following approximation: we make a least square fitting to a straight line of the $\ln D$ versus BQ/kT for the temperature range in which a pure paramagnetic state exists (i.e. $\delta g^{\text{act}} > 0$). The straight line fitting leads to the expression $\ln D = -0.0176 (BQ/kT) - 16.704$. From there on, we use a linear extrapolation to esti-

mate the diffusion values $D^{(SL)}$ predicted by the straight line (SL) in all the temperature range. By definition $\delta g^{act} = g^{act}(T) - g_p^{act}(T) = kT \ln [D^{(SL)}/D_{exp}]$ where D_{exp} the experimentally observed diffusion values (Cermak et al. 1989). In figure 5 we give the plot of δg^{act} versus the temperature.

Conclusion

The self-diffusion data of α -Fe and the heterodiffusion data of Ni and V in α -Fe, in the ferromagnetic and paramagnetic state were analysed, by using the $cB\Omega$ model. Introducing the temperature and pressure independent constants c_p and c_f we calculate the activation enthalpy in paramagnetic and ferromagnetic state, in the examined cases.

The calculated values agree with the experimental ones reported in the literature and enable the calculation of parameter λ using only the elastic data of α -Fe in the examined magnetic states.

Furthermore, using the published experimental data we estimate the excess Gibbs activation energy δg^{act} which represents the thermodynamic influence due to spin ordering.

References

- Borg R. & Dienes G., 1988: An introduction to Solid State Diffusion. *Academic Press*, Boston.
- Cermak J., Lubbehusen M. & Mehrer H., 1989: The influence of the magnetic phase transformation on the heterodiffusion of Ni in α iron, *Z. Metallkde*, 80, 213–219.
- Geise J. & Herzing C., 1987: Impurity diffusion of Vanadium and self-diffusion in iron, *Z. Metallkde.*, 78, 291–294.
- Gray D.E., (Ed.), 1972: American Institute of Physics Handbook, 3rd ed., *Mc Graw-Hill*.
- Kucera J., Kozak L. & Mehrer H., 1984: Magnetic anomalies and self-diffusion and Co heterodiffusion in α Fe, *Phys. Stat. Sol. (a)*, 81, 497–505.
- Mirani H., Harthoom R., Zuurendonk T., Helmerhorst S. & Vries G., 1975: The influence of the ferromagnetic transition on self-diffusion in b.c.c FeSi, *Phys. Stat. Sol. (a)*, 29, 115–127.
- Philibert J., 1991: Atom movements. Diffusion and mass transport in solids. *Les Editions de Physique, Paris*, 118–120.
- Ruch L., Djordije S., Helen Y. & Girifaleo L., 1976: Analysis of diffusion in ferromagnets. *J. Phys. Chem. Solids*, 37, 649–653.
- Satija S., Comes R. & Shirone G., 1985: Neutron scattering measurements of phonons in iron above and below Tc. *Phys. Rev. B.*, 32, 3309–3311.
- Vallianatos F. & Eftaxias K., 1992: The application of $cB\Omega$ model for the calculation of variation of the activation volume for creep with depth in the earth's lower mantle, *Phys. Earth Planet. Inter.*, 71, 141–146.
- Vallianatos F. & Eftaxias K., 1994: Some thermodynamic aspects of estimation methods for activation volume, *Acta Geophys. Pol.*, XLII, 13–23.
- Vallianatos F., Eftaxias K. & Vassilikou-Dova A., 1995: A material science approach for the evaluation of the rheological state into the Earth's Lower mantle. *Radiation effects and Defects in Solids*, 137, 217–221.
- Varotsos P. & Alexopoulos K., 1982: Current methods of lattice defects analysis using Dilatometry and Self-diffusion. Critical review and proposals. *Phys. Stat. Sol. (b)*, 110, 9–31.
- Varotsos P. & Alexopoulos K., 1986: Thermodynamics of point Defects and their relation with bulk properties. *North Holland*.