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Review

On the atomic diffusion mechanism and diffusivity of nitrogen atoms in Sm_2Fe_{17}

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Abstract

An atomic diffusion mechanism (voidal diffusion) of nitrogen atoms in Sm_2Fe_{17} is proposed which clearly explains the low values of diffusivity observed. The nitrogen atoms are located inside 9(*e*) octahedra which share Sm corners but no faces. Migration of nitrogen atoms 9(*e*) sites cannot occur by direct jumping. The most probable way for nitrogen atoms to migrate is by jumping from a 9(*e*) site into a thermodynamically unstable tetrahedral 18(*g*) site and subsequently into a new 9(*e*) site. In such a migration path a nitrogen atom has to surmount an enormous energy barrier representing the energy needed to overcome the strong bonding with its nearest neighbours (Fe and especially Sm atoms) and more importantly the strain energy needed to break out through the octahedral face (Fe(*f*)–Sm(*c*)–Fe(*h*)) and in through the tetrahedral face (Fe(*h*)–Sm(*c*)–Fe(*h*)). Although the 18(*g*) sites cannot accommodate any nitrogen atoms under equilibrium conditions, their presence plays a key role in the diffusion of nitrogen atoms. The present atomic diffusion mechanism predicts that the anisotropic ratio of the planar (D_{xx}) to the axial (D_{zz}) diffusivity should be equal to about 0.3. It also predicts that atoms such as hydrogen, which can occupy the 18(*g*) tetrahedra under equilibrium conditions, can jump inside the "circular tunnel" formed by the adjacent 18(*g*) tetrahedra, resulting in an increase in the planar diffusivity D_{xx}, and consequently the anisotropic ratio D_{xx}/D_{zz} can reach values as large as 1.07 (essentially isotropic behaviour).

1. Introduction

$Sm_2Fe_{17}N_3$ exhibits good intrinsic magnetic properties [1, 2] and can be used to prepare permanent magnets [3–5]. The reaction between Sm_2Fe_{17} and N_2 gas is diffusion controlled and the $Sm_2Fe_{17}N_x$ produced is thermodynamically metastable. The diffusion of nitrogen atoms producing $Sm_2Fe_{17}N_x$ and the decomposition of $Sm_2Fe_{17}N_x$ into undesirable SmN and α-Fe are two competitive processes. One would like to increase the diffusivity by increasing the temperature, but at the same time the temperature has to be kept as low as possible in order to avoid thermal decomposition. The obvious solution of increasing the nitrogenation temperature has been applied to achieve very good results but always with the sacrifice of some $Sm_2Fe_{17}N_3$. An even more improved diffusivity by other means is still desired. Such an increase will not be realized unless the diffusivity is studied not only macroscopically [6–8] but also atomistically (in the actual form of atomic vibrations in the lattice).

The present study represents an attempt to gain insight to the diffusivity of nitrogen atoms Sm_2Fe_{17} at the atomic level, with the hope of stimulating interest in more studies in this direction. An atomic diffusion mechanism is proposed and the factors determining the diffusivity are examined closely. Both parts of the well-known temperature dependence of the diffusivity, $D=D_0 \exp(-\Delta H/RT)$, *i.e.* the pre-exponential factor D_0 and the activation enthalpy ΔH, are analysed in the framework of existing theories of diffusion. Such an analysis clearly interprets the low values of diffusivity observed and suggests possible ways to enhance the diffusivity. The anisotropy of the diffusivity is also examined closely and the anisotropic ratios expected for nitrogen (or carbon) and hydrogen are derived and values estimated. Possible ways of increasing the diffusivity are proposed.

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2. Atomic diffusion mechanisms

There are at least three distinct atomic diffusion mechanisms [9–25]: "vacancy diffusion", "ring diffusion" and "interstitial diffusion". The last of these involves the migration of interstitial atoms and can be divided into three different types: (1) the "interstitialcy"[15–17] mechanism, where an interstitial atom pushes a neighbouring atom into another interstitial site, itself occupying the normal site vacated; (2) the "direct interstitial" (or simply "interstitial") [23–25] mechanism, where an interstitial atom migrates along interstitial sites normally occupied (under equilibrium conditions) by the same interstitial atoms; (3) the "indirect interstitial" or "voidal diffusion" [20–22] mechanism, where an interstitial atom migrates by utilization of interstitial sites (voids) normally not occupied by the same interstitial atoms. As will be shown later, the diffusion of nitrogen atoms in Sm_2Fe_{17} resembles the case of the "voidal diffusion" mechanism [26, 27].

3. Mathematical formulation of the diffusivity

In general the diffusivity is a second-rank tensor ($\boldsymbol{D}_{ij}$) and can be described along a set of principal axes, the diagonal elements (principal diffusivities) of which are labelled as D_{xx}, D_{yy} and D_{zz}. The atomic process responsible for diffusion is generally accepted to be the brownian motion resulting from thermal agitation. The atoms are visualized as undergoing a sequence of random displacements from one lattice site to a neighbouring one, spending only a finite time on any lattice site, in this way pursuing an endless path or "random walk" [18, 28–31] throughout the crystal. In the case where the jumping atoms do not experience any drift due to chemical inhomogeneities, it was shown by Einstein [28] that the diffusivity of an atom is proportional to the average square of the net displacement ($\overline{X^2}$, $\overline{Y^2}$, $\overline{Z^2}$) of each atom after a time (τ) measured along a given direction:

$$D_{xx}=\frac{1}{2\tau}\overline{X^2},\qquad D_{yy}=\frac{1}{2\tau}\overline{Y^2},\qquad D_{zz}=\frac{1}{2\tau}\overline{Z^2}\tag{1}$$

In the case of the "ring", "direct interstitial" and "voidal" diffusion mechanisms there is no correlation in the directions of successive jumps (50% probability of an atom jumping forwards and equally 50% probability of jumping backwards) and the diffusing atom does not experience any drift (correlation effects). In this case the Einstein relations can be expressed in terms of the individual atomic displacements (x_j, y_j, z_j):

$$\overline{X^2}=\overline{\sum_{j=1}^{N}x_j^2},\qquad \overline{Y^2}=\overline{\sum_{j=1}^{N}y_j^2},\qquad \overline{Z^2}=\overline{\sum_{j=1}^{N}z_j^2}\tag{2}$$

where the total number of jumps after time τ is $N=\Gamma\tau$, Γ being the average number of jumps made by an atom per unit time. Suppose that an atom has a choice of m directions in which it can jump. Let x_i be the x component of the corresponding jump vector and let Γ_i be the rate at which atoms make jumps in direction i, so that $\Gamma=\Sigma_{i=1}^{m}\Gamma_i$. Then one can express (2) as

$$\overline{\sum_{j=1}^{N}x_j^2}=N\overline{x_j^2}=\frac{N}{\Gamma}\sum_{i=1}^{m}\Gamma_ix_i^2=\tau\sum_{i=1}^{m}\Gamma_ix_i^2\tag{3}$$

By combining (1)–(3), the general formulae for the diffusivities (D_{xx}, D_{yy}, D_{zz}) along the three principal axes are derived:

$$D_{xx}=\tfrac{1}{2}\sum_{i=1}^{m}\Gamma_ix_i^2,\quad D_{yy}=\tfrac{1}{2}\sum_{i=1}^{m}\Gamma_iy_i^2,\quad D_{zz}=\tfrac{1}{2}\sum_{i=1}^{m}\Gamma_iz_i^2\tag{4}$$

In the case of diffusion mechanisms where the directions of successive jumps are correlated (the probabilities of an atom jumping forwards and backwards are not equal), such as the "vacancy" and "interstitialcy" mechanisms [12–19], the diffusing atom experiences a drift which has to be taken into account. It turns out that for cubic crystals the correction for the diffusivity relationships (4) is only a numerical factor (f) with possible values lying between zero and unity [12, 14, 16]: $D_{xx}=\frac{1}{2}f\Sigma_{i=1}^{m}\Gamma_ix_i^2$ (similarly along the y and z directions). In the case of anisotropic crystals the correction due to correlation phenomena is not as simple [17–19] but can be computed for each individual case.

For self-diffusion in cubic crystals the Γ_i are all equal, but not necessarily in anisotropic crystals. The crystal symmetry requires the diffusivity in cubic crystals to be isotropic ($D_{xx}=D_{yy}=D_{zz}=\frac{1}{6}f\Gamma d^2$, where d is the jumping distance). Symmetry considerations suggest that in anisotropic crystals the diffusivities should behave correspondingly. For example, in tetragonal and hexagonal (rhombohedral) crystals the diffusivities along the planar axes should be equal ($D_{xx}=D_{yy}$) but different from that along the z axis ($D_{xx}=D_{yy}\neq D_{zz}$).

It now becomes clear that in order to gain some insight to the behaviour of the diffusivities, the Γ_i and x_i, y_i and z_i parameters need to be known. The latter (x_i, y_i, z_i) contribute to the pre-exponential (D_0) term of the well-known temperature dependence of the diffusivity, $D=D_0\exp(-\Delta H/RT)$ (where ΔH is the activation enthalpy), and can be determined precisely if the exact atomic diffusion mechanism and hence the diffusion path is known. The former (Γ_i) make the greatest contribution to the diffusivity and are associated (as will be shown later) with the exponential term (through ΔH) as well as with D_0 (through the entropy factor). The Γ_i are very difficult to determine but can be approximated and formulated mathematically by applying various theories.

Wert [24] and Zener [13] applied Eyring's [32, 33] general quantum mechanical "theory of reaction rates" to solid state diffusion. They treated diffusion as a one-body model by means of classical statistical mechanics. Wert [24] showed that the average rate at which atoms make jumps in a particular direction is given by

$$\Gamma_i = \nu \exp\left(-\frac{\Delta G}{\kappa T}\right) = \nu \exp\left(\frac{\Delta S}{\kappa}\right) \exp\left(-\frac{\Delta H}{\kappa T}\right) = \nu^* \exp\left(-\frac{\Delta H}{\kappa T}\right) \qquad (5)$$

where $\nu = (1/2\pi)(K/m)^{1/2}$ is the normal (Einstein) frequency (harmonic approximation; K is the force constant and m is the mass of the diffusing atom) for small oscillations of the diffusing atom around the equilibrium point in the direction of the saddle point, ΔG is the isothermal (at absolute temperature T) work done to move a defect (one atom) from the original equilibrium configuration to the saddle point configuration, ΔS and ΔH are the entropy and enthalpy of activation respectively and κ is the Boltzmann constant.

Although in the elementary process only one atom jumps, diffusion is a many-body process, because the jumping atom interacts with its surrounding atoms. Vineyard [34] extended the classical reaction rate theory to cover the many-body aspects of the diffusion process, retaining the harmonic approximations around the equilibrium and saddle point configurations (both were assumed to be in an equilibrium state) and neglecting quantum effects (T greater than the Debye temperature). In doing so, he defined an $(N-1)$-dimensional hypersurface S which passes through a saddle point located between two equilibrium positions, the original position A and the one after the jump at B. The hypersurface S is perpendicular to the contours of constant potential energy of the entire N-dimensional configuration space of the crystal (the crystal contains $N/3$ atoms, so there are N degrees of freedom) and any representative point around A reaching S with a finite velocity crosses over into the region around B. After introducing the configurational partition functions and harmonic approximations for small vibrations around the equilibrium point and saddle point, an expression for the average rate at which atoms make jumps in a particular direction is derived:

$$\Gamma_i = \frac{\prod_j^N \nu_j}{\prod_j^{N-1} \nu_j'} \exp\left(-\frac{\Delta H}{\kappa T}\right) = \nu^* \exp\left(-\frac{\Delta H}{\kappa T}\right) \qquad (6)$$

where ν_j and ν_j' are the normal frequencies for vibrations about the equilibrium point (A) and saddle point within the constraining hypersurface S. ΔH is the activation enthalpy. Therefore the effective frequency (ν^*) appearing in the pre-exponential term of Γ_i does not simply involve an Einstein frequency (ν) multiplied by an entropy term ($\nu^* = \nu \exp(\Delta S/\kappa)$) as it appeared in the one-body analysis in eqn. (5), but instead is the ratio of the product of the N normal frequencies of the system at the starting point of the transition to the $N-1$ normal frequencies of the system constrained in the saddle point configuration. It can be shown [34] that eqn. (6) can be written in the form

$$\Gamma_i = \frac{C}{(m^*)^{1/2}} \exp\left(-\frac{\Delta H}{\kappa T}\right)$$

where C depends on the force constants (acting on an atom to restore its position) at the equilibrium and saddle point configurations and m^* is the effective mass for motion in the Nth mode and depends on the masses of the atoms involved and the direction cosines of the diffusing atoms at the saddle point. Strong bonding between the diffusing atom and its surrounding atoms leads to a large value of C. In the case of an interstitial atom diffusing through a plane of atoms in a direction perpendicular to the plane, the effective mass (m^*) is expected to be equal to the mass of the diffusing atom. Otherwise m^* will be greater, since usually the masses of the non-diffusing atoms are greater. Therefore the frequency ν^* is expected to be larger for small, strongly bound atoms, with their diffusing direction at the saddle point being perpendicular to the plane of barrier atoms.

The effective frequency appearing in eqn. (6) involves an entropic part and can be written [34] in the form

$$\nu^* = \tilde{\nu} \exp\left(\frac{\Delta S}{\kappa}\right) \qquad (7)$$

with

$$\tilde{\nu} = \frac{\prod_j^N \nu_j}{\prod_j^{N-1} \nu_j^0}, \qquad \Delta S = \kappa \ln\left(\frac{\prod_j^{N-1} \nu_j^0}{\prod_j^{N-1} \nu_j'}\right)$$

where ν_j^0 is the frequency of the jth normal mode for the system constrained to lie on a hypersurface S_0 defined as having the same shape as the hypersurface S; it passes through equilibrium point A and the normal to S_0 at A is along the line of force leading to the saddle point. The other frequencies have been defined in eqn. (6). Therefore Vineyard's eqn. (6) can be written as

$$\Gamma_i = \tilde{\nu} \exp\left(\frac{\Delta S}{\kappa}\right) \exp\left(-\frac{\Delta H}{\kappa T}\right) \qquad (8)$$

which is in the same form as that (eqn. (5)) proposed by Wert [24] and Zener [13]; however, the frequency factor ($\tilde{\nu}$) is not a simple Einstein frequency but takes into account all bodies and degrees of freedom in principle (see eqn. (7)).

Rice and coworkers [35–39] have also examined the many-body aspects of diffusion in a dynamic model which does not assume an equilibrium state at the top of the barrier. Rice stated that the assumption of equilibrium is not reasonable, because the atom on top of the barrier does not have sufficient time available to attain thermal equilibrium with the lattice. Later, Franklin [40] and Glyde [41] showed that the two theories of Vineyard and Rice are essentially equivalent. In this dynamic model Rice described the motion of an atom along the direction q_i connecting its original lattice site with the jump lattice site as a superposition of many normal modes of motion. In this motion the amplitude of the vibration of the diffusing atom must exceed a critical amplitude (q_0) in order to overcome the restoring force tending to pull the atom back to its original equilibrium lattice position. At the same time two other physical conditions need to be met. Firstly, the direction of the vibration has to fall in the solid angle corresponding to the location of the jump lattice site. Secondly, the neighbouring shell of atoms must be in an out-of-phase motion (with a critical amplitude q_{j0}) in order to create a hole of sufficient cross-sectional area and allow the diffusing atom to jump through. Rice was able to give a clear description of the energy barriers involved in diffusion. He expressed the total energy barrier as $\Delta E = U_0 + \Sigma_j U_j + \Sigma_{k>i} \Delta G_{kl} + \Delta G_f$, where $U_o = q_0^2/\Sigma\alpha_{1i}^2$ and $U_j = q_{j0}^2/\Sigma\alpha_{ji}^2$ are the energies related to the assumed critical amplitudes q_0 and q_{j0} respectively. α_{1i} is the contribution of the ith normal mode to the motion along the direction q_1. α_{ji} are constants weighting the contribution of the ith normal mode to the motion of atom j. ΔG_{kl} is the potential mean free energy $(\Delta G_{kl} = \Delta H_{kl} - T\,\Delta S_{kl})$ and depends on the difference in energy required to move an atom with and without normal mode constraints. To a low order of approximation ΔG_{kl} may be thought of as the difference between the local strain energy and the energy required to move each atom independently to its final configuration. ΔG_f is the free energy for defect formation $(\Delta G_f = \Delta H_f - T\,\Delta S_f)$, *e.g.* for vacancy or interstitial formation. In the case of the diffusion of already existing interstitials ΔG_f is equal to zero. The necessity of choosing q_0 in the dynamic model introduces indirectly the irreversible nature of motions assumed in diffusion and which was studied by Pigogine and Bak [42] and Rice and Frish [43].

The harmonic approximations assumed in the models described above may not be reasonable in view of the fact that atoms in diffusion undergo relatively long displacements. The effects of anharmonicity and the deformed force constants in the strained saddle point configuration were studied by Rice and Frish [43] and more extensively by Franklin [44–47]. Anharmonicity of the vibrations plays a dominant role in the irreversibility of the basic dynamic process. Generally, when the "energy well" is deep, anharmonicity would be expected to play a minor role. However, the pre-exponential factor in the diffusion coefficient is a measure of the coupling between the diffusing atom and its neighbours and depends on the shape of the potential, especially the anharmonic portion.

Quantum effects have a significance for light atoms at low temperatures. These have been studied by LeClaire [48], Flynn [49] and Franklin [45, 47].

4. Diffusion of nitrogen atoms in Sm_2Fe_{17}

4.1. *The proposed atomic diffusion mechanism*

The nitrogen-free Sm_2Fe_{17} intermetallic compound is thermodynamically stable from room temperature up to the peritectic temperature of 1250 °C, where it undergoes a peritectic phase transformation to form "Fe + liquid". The diffusion of Fe and Sm atoms occurring in this temperature range does not disturb the stable equilibrium and in fact the rhombohedral structure remains unchanged. On the other hand, in the presence of nitrogen $(Sm_2Fe_{17}N_x)$ the compound is thermodynamically metastable and any diffusion of Fe or Sm atoms results in instability of the compound and the formation of thermodynamically stable phases of SmN and α-Fe. The conditions during diffusion of nitrogen atoms in Sm_2Fe_{17} need to be such that the metastable equilibrium is maintained in order to avoid decomposition into SmN and α-Fe.

In the ideal condition where no diffusion of Fe or Sm atoms occurs (low temperature range) and the metastability is not disturbed, the migration of nitrogen atoms has to be occurring, as will be shown later, only by the interstitial mechanism of the "voidal diffusion" type. The latter term was used by Azároff [21, 22] to describe the role of the crystal structure in diffusion, particularly in close-packed structures. The basic concept in this mechanism is that existing unoccupied voids (polyhedra enclosing unoccupied lattice sites of the space group under consideration) are linked together to form networks (diffusion paths) resembling continuous "chains" (voids linked by shared edges or shared corners) or "tunnels" (voids linked by shared triangular faces). The diffusion path chosen by the diffusing atoms has to be the one of least resistance. Jumping of an atom from void to void takes place through the saddle point configuration. Saddle point configurations at the centre of a shared face are more favourable than those at the centre of a shared edge mainly because of strain energy considerations.

In the case of Sm_2Fe_{17} (Fig. 1) there are four kinds of voids (polyhedra enclosing unoccupied lattice sites of the $R\bar{3}m$ space group). These voids are the 9(*e*) octahedra, 18(*g*) tetrahedra, 3(*b*) dodecahedra and 3(*a*) dodecahedra. Among them, only the 9(*e*) octahedra can be occupied by nitrogen atoms under equilibrium conditions (metastable equilibrium) [2, 50]. The 9(*e*) octahedra provide both the size and chemical environment for nitrogen atoms to be accommodated. On the other hand, the sizes of the 18(*g*), 3(*b*) and 3(*a*) voids are too small to accommodate nitrogen atoms under equilibrium [2]. Nevertheless, this does not preclude that some of these voids could serve as instant mediators along the nitrogen diffusion path. Such a possibility will be examined below.

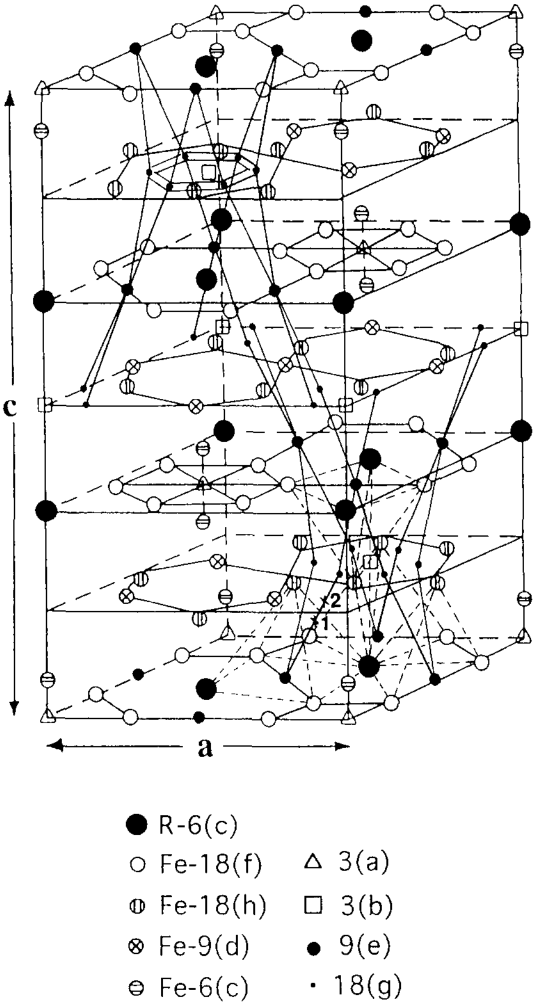

Fig. 1. Schematic representation of the hexagonal cell of the R_2Fe_{17}($R\bar{3}m$) structure and the atomic jump network (straight lines connecting the 9(*e*) and 18(*g*) sites) of the nitrogen atoms during voidal diffusion. Double lines connecting the 18(*g*) sites represent the "circular tunnel" through where hydrogen and possibly nitrogen atoms can be tunnelled. The saddle point configurations SPC1 and SPC2 are also marked by "×".

It is known that the starting and finishing points of the diffusion path are the 9(*e*) octahedra, but what is the precise trajectory of the nitrogen atoms along this diffusion path? This trajectory has to be the one where a nitrogen atom encounters the smallest energy barrier along its way. The easiest way would be if the 9(*e*) octahedra shared faces to form "tunnels" and a nitrogen atom could migrate by direct jumps through these faces. In this case the energy barrier for nitrogen migration would be associated with the energy required for the nitrogen atom to overcome the bonding with its neighbours (2 × Sm(*c*), 2 × Fe(*f*) and 2 × Fe(*h*)) and the strain energy needed to break through the shared face (Sm(*c*)–Fe(*f*)–Fe(*h*) triangle). Unfortunately, in the case of Sm_2Fe_{17} the disposition of the 9(*e*) octahedra is not nearly as favourable (Fig. 1). The 9(*e*) octahedra do not share faces or edges but only share corners (Sm(*c*)). Direct jumping of a nitrogen atom would require energy to not only overcome the neighbour bonding but more importantly to break through the centre of two unshared Sm(*c*)–Fe(*f*) edges located in the same plane. Considering the fact that the *c* plane (where the 9(*e*) sites are located) is essentially close packed (Fig. 2), the interatomic distance between Sm(*c*) and Fe(*f*) is short (3.068 Å) and the strain energy required for a nitrogen atom to break through is huge, making direct jumping impossible. Furthermore, such a jump would cause an irreversible displacement of the Sm and Fe atoms, leading to instability of the compound. If an "interstitialcy" mechanism [15–17] was operating, a nitrogen atom would cause the temporary displacement of the shared Sm atom (pushed into a 9(*e*) site) before its settlement into a neighbouring 9(*e*) site. This would require codiffusion of the nitrogen and Sm atoms, leading to destabilization of the compound to form SmN and α-Fe. In addition, the 9(*e*) site does not favour its occupation by the large Sm atoms. Such an "interstitialcy" mechanism is likely to be one of the

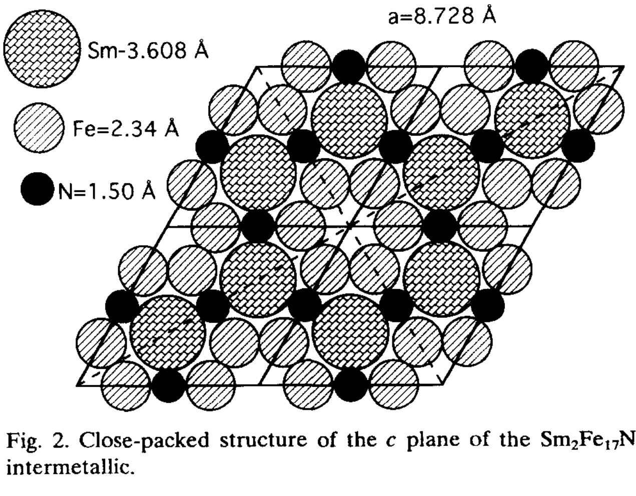

Fig. 2. Close-packed structure of the *c* plane of the $Sm_2Fe_{17}N_3$ intermetallic.

mechanisms operating at temperatures where decomposition of the $Sm_2Fe_{17}N_x$ occurs.

The fact is that diffusion occurs and therefore there must be an indirect way for nitrogen jumping between the 9(*e*) octahedra. It becomes clear that if vacancy formation is prohibited (to retain equilibrium), the existing vacant lattice sites (empty 3(*a*), 3(*b*) and 18(*g*) polyhedra) should be considered as serving as temporary stations along the nitrogen diffusion path. The question is which of them could do so in an energy-efficient way and without disturbing the equilibrium. Each of these polyhedra will be considered below in order to assess their possible role in the diffusion of nitrogen atoms.

The 3(*a*) dodecahedra are located on the same *c* plane as the 9(*e*) octahedra and share Fe(*f*) corners to form continuous "chains". Jumping of a nitrogen atom from a 9(*e*) octahedron to a 3(*a*) dodecahedron would only be possible if this Fe(*f*) corner became vacant. This would imply the diffusion of Fe atoms (by "vacancy" or "interstitialcy" mechanisms), which would lead to instability of the compound. In addition, the size of the 3(*a*) dodecahedron is extremely small (Fe(*c*)–Fe(*c*) = 2.346 Å), precluding even its instant visitation by nitrogen atoms [2].

The 3(*b*) dodecahedra are located out of the *c* plane and share Sm(*c*)–Fe(*h*) edges with the 9(*e*) octahedra to form continuous "chains". Jumping of a nitrogen atom from a 9(*e*) octahedron to a 3(*b*) dodecahedron would require energy not only to overcome the neighbour bonding but more importantly to break through the shared Sm(*c*)–Fe(*h*) edge (saddle point configuration). Owing to the fact that the Sm(*c*)–Fe(*h*) distance is short (3.089 Å) and to the small size of the 3(*b*) dodecahedron (Sm(*c*)–Sm(*c*) = 3.901 Å), the probability of such a jump is extremely small.

The 18(*g*) tetrahedra are located out of the *c* plane and share Sm(*c*)–Fe(h) edges with the 9(*e*) tetrahedra to form continuous "chains", similarly to the situation existing for the 3(*b*) dodecahedra. However, the jumping of a nitrogen atom from a 9(*e*) octahedron to an 18(*g*) tetrahedron can be performed not necessarily through the shared Sm(*c*)–Fe(*h*) edge but in a less energy-requiring trajectory through two triangular faces (saddle point configurations): an octahedral face (Sm(*c*)–Fe(*f*)–Fe(*h*) and a tetrahedral face (Sm(*c*)–Fe(*h*)–Fe(*h*)). The size of the 18(*g*) tetrahedron is not large enough to accommodate nitrogen atoms under equilibrium conditions but is large enough for the nitrogen atoms to instantly reside before jumping to a 9(*e*) equilibrium site. In addition, the planar coordinates of the 18(*g*) sites are not fixed (one degree of freedom on the line connecting the centres of the Sm(*c*)–Sm(*c*) and Fe(*h*)–Fe(*h*) distances [2]), allowing the entering nitrogen atom flexibility to temporarily accommodate itself by adjusting to the new chemical environment inside the 18(*g*) tetrahedron. It should be noted here that six 18(*g*) tetrahedra share a common Sm(*c*)–Sm(*c*) edge and the neighbouring ones share a triangular face. The 18(*g*) voids can be thought of as forming a circular "tunnel" (toroid). The existence of this circular "tunnel" might possibly be of minor importance for the migration of nitrogen atoms because the 9(*e*) voids are preferred, but in the case of a smaller diffusing atom, *e.g.* hydrogen, it should play a major role in enhancing the diffusivity by tunnelling the hydrogen atoms and ejecting and spreading them over longer distances. This is certain to be occurring in view of the fact that hydrogen atoms can occupy the 18(*g*) sites under equilibrium conditions.

Assuming that the diffusion conditions are such that the structure remains unaltered (no decomposition), requiring the Fe and Sm atoms to be "immobile", in the sense that they are confined to vibrate only around their equilibrium lattice sites, and allowing only the nitrogen atoms to be mobile, the "voidal diffusion" of nitrogen atoms into the Sm_2Fe_{17} structure can be described as follows. A nitrogen atom located in a 9(*e*) octahedron jumps into one of the four neighbouring 18(*g*) tetrahedra (two above and two below the plane) by breaking out through the Sm(*c*)–Fe(*f*)–Fe(*h*) octahedral faces and in through the Sm(*c*)–Fe(*h*)–Fe(*h*) tetrahedral faces. In this unstable position the nitrogen atom will seek to equilibrate by jumping back to the same (50% chance) or to a new (50% chance) 9(*e*) octahedron and so on. The entire jumping network (uncorrelated random walk) of nitrogen atoms between 9(*e*) octahedra through 18(*g*) tetrahedra is shown in Fig. 1.

4.2. Mathematical formulation of the nitrogen diffusivity

In accordance with the diffusion theories described previously (Section 3), a nitrogen atom located at a 9(*e*) site will be vibrating and allowed to migrate if the following conditions are satisfied (see Figs. 1 and 3).

(1) The amplitude of vibration in the direction along the 9(*e*)–18(*g*) line and towards the Sm(*c*)–Fe(*f*)–Fe(*h*) face is large enough to overcome the restoring force acting on it due to its neighbours (2 × Fe(*f*), 2 × Fe(*h*) and 2 × Sm(*c*)). This translates to an energy barrier U_0 expected to be quite large because of the strong bonding especially between the nitrogen and Sm atoms.

(2) At the same time this barrier is overcome, the atoms forming the Sm(*c*)–Fe(*f*)–Fe(*h*) triangle (of the 9(*e*) octahedron) need to be in an out-of-phase motion and reach a critical amplitude (energy barrier U_1) in order to provide the required cross-sectional area for the nitrogen atom to attain the first saddle point configuration (SPC1). The amplitudes of these motions are expected to be small and an additional free energy (ΔG_{s1}) is needed to force the three atoms apart in

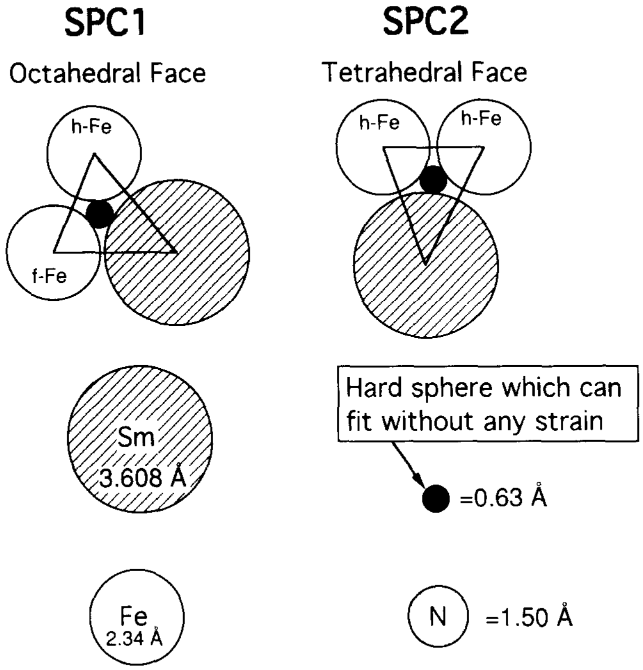

Fig. 3. Saddle point configurations SPC1 and SPC2 that must be attained if nitrogen migration is to take place. These represent the highest energy barriers for nitrogen diffusion.

order for the nitrogen atom to attain SPC1. ΔG_{s1} is expected to be very large, because the hole through the Sm(*c*)–Fe(*f*)–Fe(*h*) triangle is very small compared with the size of the nitrogen atom (Fig. 3).

(3) Once SPC1 has been attained, the migrating nitrogen atom moves out of the Sm(*c*)–Fe(*f*)–Fe(*h*) face into a space forbidden by the symmetry of the space group. The nitrogen atom is thought to be sitting on a flat energy plateau and has to move towards the 18(*g*) site. This means that an additional energy barrier has to be overcome. This is associated with the out-of-phase motion and the reaching of the critical amplitude (energy barrier U_2) of the atoms forming the Sm(*c*)–Fe(*h*)–Fe(*h*) triangle (of the 18(*g*) tetrahedron) in order to provide the required cross-sectional area for the nitrogen atom to attain the second saddle point configuration (SPC2). The amplitudes of these motions are expected to be small and an additional free energy (ΔG_{s2}) is needed to force the three atoms apart in order for the nitrogen atom to attain SPC2. ΔG_{s2} is expected to be very large, because the hole through the Sm(*c*)–Fe(*h*)–Fe(*h*) triangle is very small compared with the size of the nitrogen atom (Fig. 3).

Once the migrating nitrogen atom has attained SPC2, it moves into the 18(*g*) site (tetrahedron). As mentioned previously, the 18(*g*) site cannot accommodate the nitrogen atom in an equilibrium fashion and the atom seeks to equilibrate back to the original or to a new available 9(*e*) octahedron (Fig. 1). A representation of the energy barriers encountered by a nitrogen atom as a function of its migration path is shown in Fig. 4.

The total probability ($\mathscr{P}$) of a nitrogen atom making a successful jump from one 9(*e*) octahedron to another is the product of the probabilities of the migrating atom successfully jumping each of the individual energy barriers (Fig. 4) encountered in its path:

$$\mathscr{P}=\exp\left(-\frac{U_0+U_1+U_2+\Delta G_{s1}+\Delta G_{s2}}{RT}\right) \qquad (9)$$

The free energies ΔG_{s1} and ΔG_{s2} contain an enthalpy and an entropy contribution and can be expressed as

$$\Delta G_{s1}=\Delta H_{s1}-T\,\Delta S_{s1}, \qquad \Delta G_{s2}=\Delta H_{s2}-T\,\Delta S_{s2} \qquad (10)$$

If all the work (ΔG_s) goes into straining the lattice, the entropy contribution $\Delta S_s=(\partial\,\Delta G_s/\partial T)_p$ represents an upper limit and can be shown [23–25, 51–53] to be equal to $-\Delta H_0\;\mathrm{d}(\mu/\mu_0)/\mathrm{d}T$ where μ refers to an appropriate elastic modulus and the suffix “0” refers to the absolute zero temperature. The term $\mathrm{d}(\mu/\mu_0)/\mathrm{d}T$ is negative for most materials of interest, which prompted Zener [25] to suggest that the “activation entropy” for diffusion should always be positive irrespective of whether interstitials or vacancies are involved in the process. However, Huntington *et al.* [54] pointed out that this was a rather macroscopic approach to the entropy contribution and the local nature of the diffusion process had been neglected. They showed that the

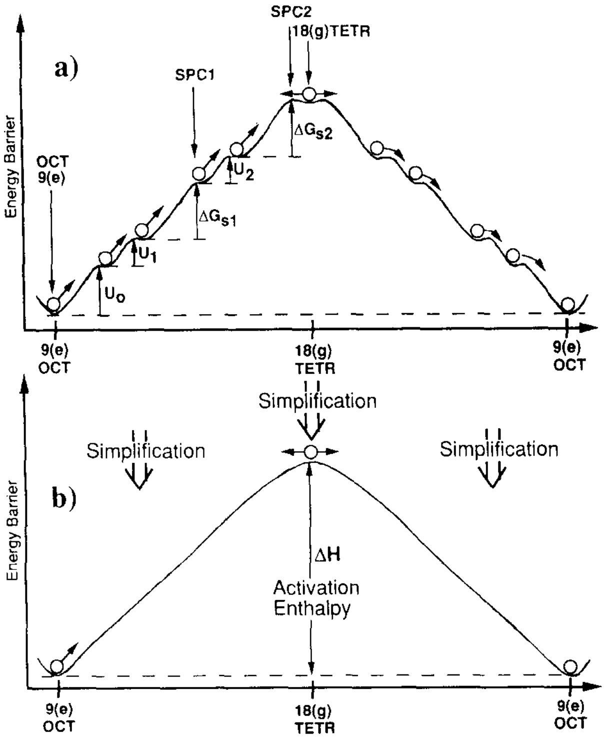

Fig. 4. (a) Individual energy barriers for nitrogen diffusion (see text) as a function of the diffusion path. (b) Simplification of the total activation enthalpy for nitrogen diffusion as expressed in $D=D_0\exp(-\Delta H/RT)$.

entropy contribution comes from three regions: the atoms in the immediate neighbourhood of the defect, the region over which the defect sets up an elastic stress field and finally the surface condition and its influence. The entropy change due to the surface condition always has the opposite sign to that in the neighbourhood of the defect and generally makes only a small contribution. Owing to the local nature of the diffusion process, only the first two contributions will be considered here.

The entropy change in the immediate neighbourhood of the defect can be expressed as

$$\Delta S_v = R\sum_i \ln\left(\frac{\nu_{i0}}{\nu_i'}\right) \tag{11}$$

where ν_{i0} are the frequencies without the defect and ν_i' are the altered frequencies with the defect. Interstitial atoms cause local crowding (especially in the SPC) and the frequencies rise, whereas vacancies cause local expansion and the frequencies drop. Therefore, according to eqn. (11), the change in entropy is negative for interstitials (this is the case for diffusion of nitrogen in Sm_2Fe_{17}) and positive for vacancies.

The entropy change in the region of the elastic stress field should be as predicted by Zener, namely $\Delta S_s = -\lambda \Delta H_0\, d(\mu/\mu_0)/dT > 0$, where λ represents a fraction since only a portion of the work goes into straining the lattice (when $\lambda = 1$, ΔS_s represents an upper limit). By taking into account the two entropy contributions, eqn. (9) can be written as

$$\mathscr{P} = \exp\left(\frac{\Delta S_{s1} + \Delta S_{v1} + \Delta S_{s2} + \Delta S_{v2}}{R}\right) \times \exp\left(-\frac{U_0 + U_1 + U_2 + \Delta H_{s1} + \Delta H_{s2}}{RT}\right) \tag{12}$$

The average rate (Γ) at which a nitrogen atom makes successful jumps in the direction along the line connecting the equilibrium 9(*e*) site with the 18(*g*) site is the product of the effective frequency of the attempted jumps ($\tilde{\nu}$) along the diffusing direction and the probability $\mathscr{P}$:

$$\Gamma = \tilde{\nu} \exp\left(\frac{\Delta S_{s1} + \Delta S_{v1} + \Delta S_{s2} + \Delta S_{v2}}{R}\right) \times \exp\left(-\frac{U_0 + U_1 + U_2 + \Delta H_{s1} + \Delta H_{s2}}{RT}\right) \tag{13}$$

The effective frequency $\tilde{\nu}$ is the frequency of the nitrogen atom around the 9(*e*) site along the 9(*e*)–18(*g*) line and is influenced by its six nearest neighbours (at least). The indices "1" and "2" indicate the situations where the diffusing nitrogen atom encounters the triangles of SPC1 and SPC2 respectively.

According to eqn. (4), the diffusion coefficients for rhombohedral crystals are $D_{xx} = D_{yy} = \frac{1}{2}\Sigma_{i=1}^4 \Gamma x_i^2$ along the planar (x, y) axes and $D_{zz} = \frac{1}{2}\Sigma_{i=1}^4 \Gamma z_i^2$ along the *c* axis (uncorrelated random walk). On the basis of the proposed diffusion mechanism these can be estimated as

$$D_{xx} = D_{yy} = \tfrac{1}{2}\Gamma\left[\left(\frac{a}{6}\right)^2 + \left(\frac{a}{6}\right)^2 + \left(\frac{2a}{6}\right)^2 + \left(\frac{2a}{6}\right)^2\right] = \tfrac{5}{36}\Gamma a^2 \tag{14}$$

$$D_{zz} = \tfrac{1}{2}\Gamma\left[\left(\frac{c}{3}\right)^2 + \left(\frac{c}{3}\right)^2 + \left(\frac{c}{3}\right)^2 + \left(\frac{c}{3}\right)^2\right] = \tfrac{2}{9}\Gamma c^2 \tag{15}$$

where "*a*" and "*c*" are the lattice parameters. Therefore the anisotropic ratio is

$$\frac{D_{xx}}{D_{zz}} = \frac{\frac{5}{36}\Gamma a^2}{\frac{2}{9}\Gamma c^2} = \frac{5}{8}\left(\frac{a}{c}\right)^2 \tag{16}$$

The ratio of the lattice parameters (a/c) for Sm_2Fe_{17} is 0.687 and therefore, according to eqn. (12), the anisotropic ratio D_{xx}/D_{zz} is 0.295. If the ratio $a/c = 0.691$ for $Sm_2Fe_{17}N_3$ is taken instead, the anisotropic ratio D_{xx}/D_{zz} becomes 0.298, which is essentially the same (within 1%) as for Sm_2Fe_{17}. Therefore it can be concluded that the diffusivity of nitrogen in the *c* plane of Sm_2Fe_{17} is about three-tenths ($\frac{3}{10}$) of that along the *c* axis.

When the diffusing atoms are able to jump inside the "circular tunnel" formed by the adjacent 18(*g*) sites, the upper limit of the diffusivity along the planar axes can be calculated as

$$D_{xx} = D_{yy} = \tfrac{1}{2}\Gamma\left[\left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2\right] = \tfrac{1}{2}\Gamma a^2 \tag{17}$$

whereas D_{zz} remains the same as in eqn. (15). In this case the upper limit of the anisotropic ratio becomes

$$\frac{D_{xx}}{D_{zz}} = \frac{\frac{1}{2}\Gamma a^2}{\frac{2}{9}\Gamma c^2} = \frac{9}{4}\left(\frac{a}{c}\right)^2 \tag{18}$$

If the values $a/c = 0.687$ and 0.692 corresponding to Sm_2Fe_{17} and $Sm_2Fe_{17}H_5$ [2] respectively are substituted in eqn. (18), the upper limit of the anisotropic ratio D_{xx}/D_{zz} is estimated to be 1.062 and 1.077 respectively. This means that the diffusivity becomes essentially isotropic. This limit is expected to be reached in the case of the diffusion of hydrogen atoms in Sm_2Fe_{17}. This is because hydrogen atoms can be tunnelled around the 18(*g*) sites, which can be occupied under equilibrium conditions, and then ejected at the more remote 9(*e*) sites ($x_i = a/2$). Nitrogen atoms are not expected to behave in this manner, although anisotropic ratios slightly above 0.3 cannot be excluded.

Let us now write the diffusivity including the expression of Γ (eqn. (13)):

$$D_{xx}=\tfrac{5}{36}a^2\tilde{\nu}\exp\left(\frac{\Delta S_{s1}+\Delta S_{v1}+\Delta S_{s2}+\Delta S_{v2}}{R}\right)\times\exp\left(-\frac{U_0+U_1+U_2+\Delta H_{s1}+\Delta H_{s2}}{RT}\right) \quad (19)$$

$$D_{zz}=\tfrac{2}{9}c^2\tilde{\nu}\exp\left(\frac{\Delta S_{s1}+\Delta S_{v1}+\Delta S_{s2}+\Delta S_{v2}}{R}\right)\times\exp\left(-\frac{U_0+U_1+U_2+\Delta H_{s1}+\Delta H_{s2}}{RT}\right) \quad (20)$$

Equations (15) and (16) can be written in the familiar form $D=D_0\exp(-\Delta H/RT)$, where

$$\begin{aligned}D_0&=\gamma\tilde{\nu}\exp\left(\frac{\Delta S_{s1}+\Delta S_{v1}+\Delta S_{s2}+\Delta S_{v2}}{R}\right)\\&=\gamma\tilde{\nu}\exp\left(\frac{(\Delta S_{s1}+\Delta S_{s2})+(\Delta S_{v1}+\Delta S_{v2})}{R}\right)\\&=\gamma\tilde{\nu}\exp\left(\frac{(\Delta S_{s1,2}+\Delta S_{v1,2})}{R}\right)\\&=\gamma\tilde{\nu}\exp\left(\frac{\Delta S}{R}\right)\end{aligned} \quad (21)$$

$$\begin{aligned}\Delta H&=U_0+(U_1+U_2)+(\Delta H_{s1}+\Delta H_{s2})\\&=U_0+U_{1,2}+\Delta H_{s1,2}\end{aligned} \quad (22)$$

with

$$\Delta S=(\Delta S_1+\Delta S_2)+(\Delta S_{v1}+\Delta S_{v2})=\Delta S_{1,2}+\Delta S_{v1,2} \quad (23)$$

$$\gamma=\tfrac{5}{36}a^2 \text{ for } D_{xx}, \qquad \gamma=\tfrac{2}{9}c^2 \text{ for } D_{zz} \quad (24)$$

ΔS and ΔH are the molar "activation entropy" and "activation enthalpy" respectively for the diffusion of nitrogen atoms in Sm_2Fe_{17}.

5. Discussion

Equations (19)–(24) reveal what is behind the pre-exponential (D_0) and exponential terms in the Arrhenius equation of the temperature dependence of the diffusivity, $D=D_0\exp(-\Delta H/RT)$. It is possible now to discuss each term individually and assess their specific contribution to the diffusivity. It becomes clear that the planar and axial diffusivities differ by a factor of about 0.3. This is a consequence of the fact that a nitrogen atom jumping from a 9(*e*) site to another 9(*e*) site travels longer distances along the *c* axis as compared with the *x* and *y* axes. Therefore the diffusivities along the planar and axial directions differ only in the pre-exponential term D_0. The exponential term (activation enthalpy) is the same for both diffusivities.

5.1. *The pre-exponential factor D_0*

The pre-exponential term D_0 contains a geometrical factor γ, a frequency factor $\tilde{\nu}$ and an entropy factor $\exp(\Delta S/R)$. The geometrical factor γ is constant for a given compound and atomic diffusion mechanism. For nitrogen diffusion along the planar axes (x,y) in Sm_2Fe_{17} ($a=8.549$ Å and $c=12.441$ Å [2]) the factor γ equals 1.015×10^{-15} cm^2. Along the *c* axis $\gamma=3.440\times10^{-15}$ cm^2.

The rest of the terms (frequency and entropy factors) are the same for both D_{xx} and D_{zz}. If one assumes that the normal lattice vibration frequencies for Sm_2Fe_{17} are of the order of 10^{13} s^{-1}, then the vibrational frequency for an interstitial nitrogen atom located in a 9(*e*) octahedron and causing local crowding is expected to be slightly higher. On the other hand, the frequency decreases as the "effective mass" increases. As was shown before (Section 3), the "effective mass" is equal to the mass of the nitrogen atom if the diffusion direction is normal to the plane of barrier atoms, *i.e.* if the direction along the 9(*e*)–18(*g*) line is normal to the planes of Fe(*f*)–Sm(*c*)–Fe(*h*) and Fe(*h*)–Sm(*c*)–Fe(*h*) barrier atoms. Since the diffusion direction forms an angle of less than 90° with these planes, the "effective mass" becomes higher, causing a slight decrease in the nitrogen frequency. Whether the final "effective frequency" $\tilde{\nu}$ will be higher or lower than 10^{13} s^{-1} will depend on the balance of the two effects mentioned above. In the present case and for practical purposes $\tilde{\nu}$ will be assumed to remain essentially unchanged at 10^{13} s^{-1}.

The entropy factor contains two kinds of entropy changes: the $\Delta S_{v1,2}$ term associated with the change in the vibrational frequencies of the atoms surrounding the nitrogen atom at SPC1 and SPC2 and the $\Delta S_{s1,2}$ term associated with the straining of the lattice. The nitrogen atom at the SPC positions causes crowding and the vibrational frequencies of the surrounding atoms increase. Assuming that the increase is the same at both SCP1 and SPC2 and also that, as a first approximation, only the three barrier atoms in each SPC are affected, the change (from eqn. (11)) in the entropy due to the change in the vibration frequencies (of $2\times3=6$ atoms) will be approximately

$$\Delta S_{v1,2}=6R\ln\left(\frac{\nu_{i0}}{\nu_i'}\right) \quad (25)$$

If one assumes that the free energies for straining the lattice are the same when the nitrogen atom goes through the first (SPC1) and second (SPC2) planes of barrier atoms, then, from Section 4.2, $\Delta S_{s1,2}=-\lambda\,\Delta H_0$

$d(\mu/\mu_0)/dT$. The factor λ can be assumed to be almost unity and ΔH_0 to be of the order of the activation enthalpy for diffusion, half of which comes from each plane of barrier atoms. The term $d(\mu/\mu_0)/dT$ is almost constant in the temperature region of interest (350–550 °C) and negative for most compounds of interest.

$\Delta S_{v1,2}$ is always negative and $\Delta S_{s1,2}$ is always positive. The total entropy change ΔS will be approximately equal to

$$\left[-6\ln\left(\frac{\nu_i'}{\nu_{i0}}\right)-\lambda\frac{\Delta H_0}{R}\frac{d(\mu/\mu_0)}{dT}\right]R$$

The contributions of each of the entropies for various values of ν_i'/ν_{i0} and $\Delta H_0/R$ (ranging from around the minimum [6, 7] and maximum [8] values of activation enthalpies reported so far in the literature) and assuming $\lambda=1$ and $d(\mu/\mu_0)/dT=-0.0001$ K^{-1} (typical value for intermetallics [55]) are given in Table 1. The difference in the absolute values of the two entropies (one negative and the other positive) determines whether the total entropy change will be positive or negative and whether the entropy factor $\exp(\Delta S/R)$ will be greater or less than unity. The entropy change ΔS takes negative values only when ν_i'/ν_{i0} is above 1.1 or 1.3, corresponding to the lower and higher values of $\Delta H_0/R$ respectively. The pre-exponential factor D_0 decreases with increasing ν_i'/ν_{i0} and increases with increasing ΔH_0. D_0 varies from 0.04 to 6 mm^2 s^{-1} along the planar axes and from 0.1 to 19 mm^2 s^{-1} along the c axis. Values of D_0 much smaller than 0.04 mm^2 s^{-1} would require high ν_i'/ν_{i0} ratios (greater than 2.0) and very low activation enthalpies for diffusion. In view of this result, the reported values of D_0 in the range 10^{-4}–10^{-3} mm^2 s^{-1} [6, 7] would require an activation entropy $\Delta S/R=-6.92$ (the most conservative value estimated from D_0 along x and y). Such a negative value would require an extremely high ν_i'/ν_{i0} ratio of about 3.7–4.1 (assuming $\Delta H_0/R=8500$–$16\,000$ K) or a negative $\Delta H_0/R=-44\,900$ K (assuming a reasonable value of ν_i'/ν_{i0} of about 1.5). Both these requirements are physically impossible and therefore the accuracy of such reported values must be questioned [8]. More precise values of D_0 (although assumed isotropic) were reported recently by Skomski and Coey [8]. They reported values of D_0 and ΔH equal to about 1.02 mm^2 s^{-1} and 133 kJ mol^{-1} K^{-1} ($\Delta H_0/R=15\,996$ K) respectively. Under the same assumptions as employed above, the ν_i'/ν_{i0} ratio can be estimated to be about 1.3 (along x, y) to 1.6 (along z), values considered to be physically reasonable.

5.2. *The activation energy for diffusion, ΔH*

The total activation energy ΔH consists of five parts as was shown in eqn. (22). Among them, $U_{1,2}$ is expected to be relatively low because of the small amplitudes of the oscillating atoms. U_0 is expected to be large because of the strong binding force between the nitrogen atom and its six nearest neighbours (especially the two Sm atoms) and the large amplitude the nitrogen atom has to attain in order to perform a successful jump. However, by far the most important contribution to the activation enthalpy comes from the energy $\Delta H_{s1,2}$ required to strain the lattice at SPC1 and SPC2. The cross-sectional area available for the nitrogen atom to break through the two triangular faces composed of two Fe atoms and one Sm atom is very small (Fig. 3). Only an atom with an atomic radius of less than 0.32 Å (assuming a hard sphere) can go through SPC1 and SPC2 freely. For the nitrogen atom with an atomic radius of 0.75 Å the three barrier atoms (2×Fe and 1×Sm) need to be displaced by about 0.43 Å (assuming isotropic displacement for all Fe and Sm atoms) in order to open a hole sufficiently large to go through. In such a situation the Fe–Fe and Fe–Sm interatomic distances have to be stretched out by about 28% and 23% respectively, corresponding to a change in the triangle area by about 56%. If one assumes that a displacement of about 0.2 Å is contributed by the

TABLE 1. Contributions to the activation entropy of diffusion

$\Delta H_0/R$ (K) ν_i'/ν_{i0}	8500					16000				
	1.0	1.1	1.3	1.5	2.0	1.0	1.1	1.3	1.5	2.0
$\Delta S_{v1,2}/R$	0	−0.572	−1.574	−2.433	−4.159	0	−0.572	−1.574	−2.433	−4.159
$\Delta S_{s1,2}/R$	0.85	0.85	0.85	0.85	0.85	1.6	1.6	1.6	1.6	1.6
$\Delta S/R$	0.85	0.278	−0.724	−1.583	−3.309	1.6	1.028	0.026	−0.833	−2.559
$\exp(\Delta S/R)$	2.34	1.32	0.48	0.21	0.037	4.95	2.80	1.03	0.43	0.077
D_0 along x, y (mm^2 s^{-1})	2.4	1.3	0.5	0.2	0.04	6	3	1	0.5	0.08
D_0 along z (mm^2 s^{-1})	8	4.5	1.7	0.7	0.13	17	10	3.5	1.5	0.27

$\lambda=1$, $d(\mu/\mu_0)/dT=-0.0001$ K^{-1}, $\bar{\nu}=10^{13}$ s^{-1}, $D_0=\gamma\bar{\nu}\exp(\Delta S/R)$, $\gamma=1.015\times10^{-13}$ mm^2 along x, y, $\gamma=3.440\times10^{-13}$ mm^2 along z.

vibration of the barrier atoms, the remaining 0.23 Å has to come through straining. This means that the Fe–Fe and Fe–Sm interatomic distances have to be stretched out by about 15% and 12% respectively, corresponding to a change in the triangle area by about 28%. Such strains require a very high energy, which reflects the high values of activation enthalpy for diffusion observed. The strain energy (w) per unit volume per nitrogen atom required to strain the Fe–Fe and Fe–Sm bonds within the elementary volume of the three barrier atoms (2×Fe and 1×Sm) is approximately given by $w=\frac{1}{2}E\epsilon^2$ (E is the Young modulus and ϵ is the strain). The total strain energy for both SPC1 and SPC2 is twice as much ($w_t=E\epsilon^2$), assuming that "w" is equal at each configuration. By assuming values of E and ϵ equal to 150 GPa and 0.12 respectively, w_t is estimated to be 2.16×10^9 J m^{-3} $atom^{-1}$. The elementary volume of "hard spheres" ($r_{Fe}=1.17$ Å and $r_{Sm}=1.8041$ Å) is 39.39×10^{-30} m^3. Therefore the total strain energy at SPC1 and SPC2 is estimated to be 51 kJ mol^{-1}. If ϵ is taken as 0.23, the total strain energy becomes 188 kJ mol^{-1}. These two values (51 and 188 kJ mol^{-1}) represent a lower and an upper limit of the total strain energy which is expected to account for the majority of the activation enthalpy (ΔH) for diffusion of nitrogen atoms.

Atoms with a small atomic radius (*e.g.* hydrogen) can easily pass through SPC1 and SPC2 without having to exert any considerable amount of strain. Consequently, the activation enthalpy for diffusion of hydrogen in Sm_2Fe_{17} is very low, resulting in high diffusivities. As a result, the absorption of hydrogen by Sm_2Fe_{17} is not controlled by diffusion and takes place very fast. Of course, this is not the case for the absorption of nitrogen by Sm_2Fe_{17}, where the activation enthalpy for diffusion is expected to be very high (for reasons explained above), resulting in low diffusivities, and diffusion becomes the controlling factor for the growth of $Sm_2Fe_{17}N_3$.

5.3. *Suggestions for improvement in nitrogen diffusivity*

One of the goals of the present study was to determine how the macroscopic and microscopic processes of diffusion are intrinsically related, in this way allowing one to suggest ways to improve the low values of diffusivity, which imposes the largest obstacle in the production of $Sm_2Fe_{17}N_3$ by controlling its growth.

The pre-exponential factor (D_0) can be increased only slightly by increasing the lattice parameters of the structure. This can be done by changing the composition of the Sm_2Fe_{17} compound via the partial replacement of Sm and/or Fe by other elements that cause an expansion of the lattice.

A considerable increase in the diffusivity can only be achieved by decreasing the activation enthalpy. As discussed above, the greatest energy barriers a nitrogen atom encounters along its diffusion path are due to the strong bonding with its neighbours (in the 9(e) octahedron), which does not allow long jumps (the restoring force is large), and most importantly due to the strain energy required for the migrating nitrogen atom to break through the two planes of barrier atoms. Again, one way to change the activation energy is by changing the chemical composition of the compound. The energy barrier due to the bonding of the nitrogen atom with its neighbours is not expected to change much, since the bonding of the rare earth atom with nitrogen contributes the most and is very strong for the entire series of rare earths. The most important energy barrier, namely the strain energy required for the nitrogen atom to break through the octahedral (SPC1) and tetrahedral (SPC2) faces, can be lowered if the atoms forming these faces (2×Fe and 1×Sm) are moved further apart. This can be achieved in two ways. The first way is to replace Fe and/or Sm by other elements causing an expansion of the lattice and consequently a favourable shifting of the equilibrium positions, thus creating a larger hole for the nitrogen atom to pass through. The second method is to expand the lattice not by replacing the Fe and/or Sm atoms but by introducing other interstitial elements such as carbon and/or hydrogen.

The partial replacement of Fe and/or Sm by other elements, although potentially causing an increase in the diffusivity, is not desirable because of the expected decrease in the saturation magnetization and anisotropy field of the compound, leading to weaker permanent magnets.

Expanding the lattice by introducing interstitials such as carbon and/or hydrogen seems to be the most promising way of increasing the diffusivity of nitrogen atoms. Small amounts of interstitial carbon ($Sm_2Fe_{17}C_x$, $0\leqslant x\leqslant1$) can be introduced directly during casting followed by homogenization. Carbon causes a large expansion of the lattice (especially along the planar axes) and consequently a lower activation enthalpy for nitrogen diffusion is expected. In addition, carbon increases the thermal stability of the compound and also the final low carbon Sm_2Fe_{17} carbonitride exhibits as high a saturation magnetization and anisotropy field as the pure $Sm_2Fe_{17}N_3$ itself [2]. The introduction of nitrogen atoms into Sm_2Fe_{17} in the presence of hydrogen (or ammonia) is expected and has been proven to be greatly beneficial [2, 5, 56]. Hydrogen makes two major contributions. One is the physical pulverization of the Sm_2Fe_{17} particles, constantly creating new, clean activated surfaces readily available for nitrogen atoms to saturate. The second contribution is related to the expansion of the lattice with the ultimate result of an increase in nitrogen diffusivity. Nitrogenation in the presence of hydrogen (or ammonia) is more effective when temperature cycling (instead of isothermal conditions) is employed. This is because hydrogen is absorbed (lattice expansion) in larger quantities in the lower temperature range. Temperature cycling causes absorption and desorption of hydrogen, a dynamic process expected to facilitate hydrogen replacement and the final accommodation of nitrogen atoms. One can think of the hydrogen atoms as causing an agitation among the mobile species (H and N atoms) and thus facilitating their migration. Such a codiffusion of hydrogen and nitrogen atoms may also permit the use of the 18(*g*) circular tunnel by nitrogen atoms, leading to an increase in diffusivity along the planar axes and consequently to an increase in the anisotropic D_{xx}/D_{zz} ratio.

It is our intention to proceed in the future by measuring the diffusivity of nitrogen in Sm_2Fe_{17} along both the planar and *c* axes as a function of temperature in the presence and absence of hydrogen. If the pre-exponential factor (D_0) and activation enthalpy along both directions are known precisely, then it will be possible to confirm, reject or improve the proposed atomic diffusion mechanism. For example, if the anisotropic D_{xx}/D_{zz} ratio is found to be between 0.3 and 1.07, this will suggest that nitrogen atoms can be tunnelled through the 18(*g*) circular tunnel, something that was proposed before for hydrogen atoms.

Precise diffusion experiments need to be conducted on Sm_2Fe_{17} specimens of precisely known shapes, where the mathematics of diffusion-controlled growth can be applied without any strong ambiguities. Generally Sm_2Fe_{17} particles have irregular shapes, and although average geometrical characteristics (*e.g.* diameter or surface-to-volume ratio) can be estimated (microscopy observations), geometrical details may play an important role in the diffusion of nitrogen and growth of the $Sm_2Fe_{17}N_3$ shell. In addition, when the surface-to-volume ratio increases (*e.g.* for small particles), the diffusion coefficient can be greatly affected. Therefore diffusion studies conducted on small particles [6, 8], although useful, may not be as precise. This is especially true when anisotropy is totally neglected. For that matter a textured semi-infinite slab of Sm_2Fe_{17} single-phase alloy may be the most suitable for such experiments. It is also important to point out that pretreatment of the specimen under hydrogen can change its morphology by introducing cracks which will misleadingly show increased values of the diffusivity. The temperature of the hydrogen treatment is very important, because if it exceeds the value of 510 °C (*e.g.* 600 °C in ref. 7), a portion of the alloy will be decomposed into Sm hydride and α-Fe [2, 4, 5, 57], with obvious consequences on the interpretation of the results. A few of the above observations are believed to be the reasons behind the variety of values of pre-exponential factors (D_0) and activation enthalpies (ΔH) reported so far in the literature [6–8].

The discussion on nitrogen diffusivity in Sm_2Fe_{17} can be extended to carbon diffusivity with the following remarks. The atomic radius of carbon (0.77 Å) is larger than that of nitrogen (0.75 Å). Thus the strain energy required for the attainment of SPC1 and SPC2 should be larger for carbon. The binding energy of the carbon atom (at the 9(*e*) site) with Fe as well as with Sm atoms is higher than the corresponding value for the nitrogen atom [58]. This will increase the energy barrier needed to overcome the restoring forces. Overall, the total activation enthalpy for carbon diffusion is expected to be greater than that for nitrogen diffusion.

As a closing remark, we want to stress the important role the 18(*g*) sites play in the diffusion of nitrogen. Although nitrogen atoms can "visit" the 18(*g*) sites, they cannot stay there under equilibrium conditions. This is in accordance with what interstitial size calculations and X-ray diffraction studies have shown [2], supported by neutron diffraction studies [50]. Although a miniscule non-equilibrium amount of nitrogen is possibly trapped at the 18(*g*) sites under certain conditions, reports [59–61] of interstitial nitrogen concentrations far exceeding the value of 3 N atoms per Sm_2Fe_{17} formula unit (by reaction of Sm_2Fe_{17} with ammonia) are believed to be greatly exaggerated as a result of the occurrence of chemical reactions of the byproducts (SmN) and the hydrogen present in the alloy with atmospheric oxygen and moisture as well as because of possible stabilization of the Fe_4N phase during the decomposition of $Sm_2Fe_{17}N_3$ [26].

References

1 J.M.D. Coey, H. Sun and Y. Otani, A new family of rare earth iron nitrides, in S.G. Sankar (ed.), *Proc. Sixth Int. Symp. on Magnetic Anisotropy and Coercivity in Rare Earth–Transition Metal Alloys, Pittsburgh, PA, October 1990*, Carnegie Mellon University, Pittsburgh, 1990, p. 36.

2 C.N. Christodoulou and T. Takeshita, *J. Alloys Comp., 198* (1993) 1–24.

3 C.N. Christodoulou and T. Takeshita, *J. Alloys Comp., 196* (1993) 161–164.

4 C.N. Christodoulou and T. Takeshita, *J. Alloys Comp., 196* (1993) 155–159.

5 C.N. Christodoulou and T. Takeshita, Sm_2Fe_{17}-nitride-based permanent magnets produced by rapid solidification, HDDR and powder metallurgy techniques, *Rep. Magnetics Working Committee, Magnetics Conf., Tokyo, December 1992, MAG-92-245*, IEEE, Tokyo, 1992, pp. 53–66.

6 J.M.D. Coey, J.F. Lawler, H. Sun and J.E.M. Allan, *J. Appl. Phys., 69* (1991) 3007.

7 H. Kaneko, T. Kurino and H. Uchida, *Proc. 7th Int. Symp. on Magnetic Anisotropy and Coercivity in Rare Earth–Transition Metal Alloys, Canberra, July 1992*, The University of Western Australia, Canberra, 1992, pp. 320–330.

8 R. Skomski and J.M.D. Coey, *J. Appl. Phys., 73* (1993) 7602.

9 L.S. Darken, *Trans. Am. Inst. Min. (Metall.) Eng., 175* (1948) 184.

10 A.D. LeClaire, in B. Chalmers (ed.), *Progress in Metal Physics,* Vol. 1, Butterworths, London, 1949, pp. 306–379.

11 C. Zener, *Acta Crystallogr., 3* (1950) 346.

12 J. Bardeen and C. Herring, in W. Shockley (ed.), *Imperfections in Nearly Perfect Crystals,* Wiley, New York, 1952, p. 261.

13 C. Zener, in W. Shockley (ed.), *Imperfections in Nearly Perfect Crystals,* Wiley, New York, 1952, p. 269.

14 K. Compaan and Y. Haven, *Trans. Faraday Soc., 52* (1956) 786.

15 C.W. McCombie and A.B. Lidiard, *Phys. Rev., 101* (1956) 1210.

16 A.D. LeClaire and A.B. Lidiard, *Philos. Mag., 1* (1956) 518.

17 K. Compaan and Y. Haven, *Trans. Faraday Soc., 54* (1958) 1498.

18 J.G. Mullen, *Phys. Rev., 124* (1961) 1723.

19 A.P. Batra, *Phys. Rev., 159* (1967) 487.

20 R. Sun, *J. Chem. Phys., 28* (1958) 290.

21 L. Azároff, *J. Appl. Phys., 32* (1961) 1658.

22 L. Azároff, *J. Appl. Phys., 32* (1961) 1663.

23 C. Wert and C. Zener, *Phys. Rev., 76* (1949) 1169.

24 C.A. Wert, *Phys. Rev., 79* (1950) 601.

25 C.A. Zener, *J. Appl. Phys., 22* (1951) 372.

26 C.N. Christodoulou and T. Takeshita, Nitrogenation of Sm_2Fe_{17}: mechanism, phases and stability, *J. Alloys Comp., 202* (1993) 173–182.

27 C.N. Christodoulou and T. Takeshita, in H. Henein and T. Oki (eds.); Macroscopic and atomic diffusion mechanism of nitrogen into Sm_2Fe_{17}, *Proc. 1st Int. Conf. on Processing Materials for Properties, Honolulu, HI, November 1993,* TMS, Warrendale, PA, 1993, pp. 293–296.

28 A. Einstein, *Ann. Phys., 17* (1905) 549.

29 H.A. Kramers, *Physica, 7* (1940) 284.

30 S. Chandrasekhar, *Rev. Mod. Phys., 15* (1943) 1.

31 A.D. LeClaire, *Philos. Mag., 3* (1958) 921.

32 H. Eyring, *J. Chem. Phys., 3* (1935) 107.

33 A.E. Stearn and H. Eyring, *J. Phys. Chem., 44* (1940) 955.

34 G.H. Vineyard, *J. Phys. Chem. Solids, 3* (1957) 121.

35 S.A. Rice, *Phys. Rev., 112* (1958) 804.

36 O.P. Manley and S.A. Rice, *Phys. Rev., 117* (1960) 632.

37 N.H. Nachtrieb, H.A. Resing and S.A. Rice, *J. Chem. Phys., 31* (1959) 135.

38 S.A. Rice and N.H. Nachtrieb, *J. Chem. Phys., 31* (1959) 139.

39 A.W. Lawson, S.A. Rice, R.D. Corneliussen and N.H. Nachtrieb, *J. Chem. Phys., 32* (1960) 447.

40 W. Franklin, *J. Phys. Chem. Solids, 28* (1967) 829.

41 H.R. Glyde, *Rev. Mod. Phys., 39* (1967) 373.

42 I. Pigogine and T.A. Bak, *J. Chem. Phys., 31* (1959) 1368.

43 S.A. Rice and H.L. Frish, *J. Chem. Phys., 32* (1960) 1026.

44 W. Franklin, *J. Phys. Chem. Solids, 28* (1969) 829.

45 W. Franklin, *Phys. Rev., 180* (1969) 682.

46 W. Franklin, *Phys. Rev. B, 2* (1970) 2906.

47 W. Franklin, *J. Chem. Phys., 57* (1972) 2659.

48 A.D. LeClaire, *Philos. Mag., 14* (1966) 1271.

49 C.P. Flynn, *Phys. Rev., 171* (1968) 682.

50 O. Isnard, S. Miraglia, J.L. Soubeyroux, D. Fruchart and J. Pannetier, *Phys. Rev. B, 45* (1992) 2920.

51 C. Zener, *Acta Crystallogr., 2* (1949) 163.

52 G.J. Dienes, *J. Appl. Phys., 21* (1950) 1189.

53 C.A. Wert, *J. Appl. Phys., 21* (1950) 1198.

54 H.B. Huntington, G.A. Shirn and E.S. Wajda, *Phys. Rev., 99* (1955) 1085.

55 Young-Won and F.H. Froes, in S.H. Whang (ed.), *Proc. 1989 Symp. on High Temperature Aluminides and Intermetallics, TMS Fall Meeting, Indianapolis, IN, October 1989,* TMS, Warrendale, PA, 1990, p. 465.

56 C.N. Christodoulou and T. Takeshita, Anisotropic Sm_2Fe_{17} powders prepared by special nitro-hydrogenation, *Proc. 3rd IUMRS Int. Conf. on Advanced Materials, Tokyo, August–September 1993,* Elsevier, Amsterdam, 1994.

57 C.N. Christodoulou and T. Takeshita, *J. Alloys Comp., 194* (1993) 113–117.

58 C.N. Christodoulou and T. Takeshita, *J. Alloys Comp., 190* (1992) 41–48.

59 K. Kobayashi, T. Iriyama, N. Imaoka, T. Suzuki, H. Kato and Y. Nakagawa, *Proc. 12th Int. Workshop on RE Magnets and Their Applications, Canberra, July 1992,* The University of Western Australia, Canberra, 1992, pp. 32–43.

60 H.H. Uchida, H. Uchida, T. Yanagisawa, S. Kise, V. Koeninger, Y. Matsumura, U. Koike, K. Kamada, T. Kurino and H. Kaneko, *Proc. 7th Int. Symp. on Magnetic Anisotropy and Coercivity in Rare Earth–Transition Metal Alloys, Canberra, July 1992,* The University of Western Australia, Canberra, 1992, pp. 342–353.

61 Y.-N. Wei, K. Sun, Y.-B. Fen, J.-X. Zhang, B.-P. Hu, Y.-Z. Wang, X.-L. Rao and G.-C. Liu, *J. Alloys. Comp., 194* (1993) 9.