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June 1998

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# Rare Earth Nitride and Carbide Hard Magnets

L. H. Lewis, Chairman

## Immobilization diffusion in $R_2Fe_{17}$ nitrides

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The diffusion of nitrogen in  $R_2Fe_{17}$  intermetallics is investigated by an approach which reconciles the solid-solution and immobilization theories of nitrogen diffusion. It turns out that two-sublattice diffusions may yield sharp concentration profiles but leave the phase structure of the nitride unchanged. Beside the reaction time and a local relaxation time there exists a global relaxation time which governs the smoothing of concentration gradients. Due to the large number of unknown energy parameters involved it is difficult to make quantitative predictions, but in general the diffusion behavior depends on factors such as the use of  $N_2$  or  $NH_3$  as a nitrogen source. © 1998 American Institute of Physics. [S0021-8979(98)42411-3]

### I. INTRODUCTION

Since the discovery of interstitial permanent magnets such as  $Sm_2Fe_{17}N_3$ ,<sup>1</sup> the diffusion of nitrogen and carbon in  $R_2Fe_{17}$  intermetallics has attracted much attention.<sup>2-12</sup> The knowledge of the diffusion mechanism is necessary to predict the extrinsic properties of the interstitial magnets. A particular problem is that soft regions associated with incomplete nitrogeneration destroy coercivity by acting as nucleation centers, so that the nitrogen concentration in the material has to be homogeneous.<sup>2,3</sup>

In recent years, there has been considerable controversy about the phase structure of interstitial nitrides. According to the solid-solution theory, the reaction of molecular nitrogen with  $Sm_2Fe_{17}$  yields homogeneous solid solutions  $Sm_2Fe_{17}N_x$  with intermediate nitrogen contents.<sup>2,3,5,8,10,13</sup> By contrast, the two-phase theory states that the nitrides  $R_2Fe_{17}N_x$  are a mixture of nitrated ( $x \approx 3$ ) and unnitrated ( $x \approx 0$ ) phases without intermediate nitrogen contents.<sup>6,11,12</sup> Figure 1 illustrates the difference between solid solutions and compounds.

It is important to note that phase segregation is caused by *attractive interactions* between interstitial atoms, whereas the on-site interaction between the interstitial atoms and the host lattice changes leaves the phase structure unchanged.<sup>8,10,14</sup> In fact, phase transitions of gases in metals are caused by long-range elastic interactions, which yield a critical temperature  $T_0$  below which phase segregation occurs. By contrast, electronic interactions in metals are short ranged and largely repulsive.<sup>8,10,14</sup>

The nitrogen atoms diffuse inwards from the surface of the  $R_2Fe_{17}$  particles, which has given rise to the qualitative concept of core-shell diffusion.<sup>15</sup> A key question is whether the nitrogen concentration profiles  $0 \leq c(r,t) \leq 1$  of partly

nitrated particles are smooth or steplike (Fig. 2). The one-sublattice diffusion equation  $\partial c / \partial t = D \nabla^2 c$ , where  $D = D_0 \times \exp(-E_a/k_B T)$ , yields smooth nitrogen profiles.<sup>2,8,10</sup> Based on this model, an activation energy  $E_a = 133$  kJ/mole was obtained from thermopiezic measurements on  $Sm_2Fe_{17}$  in  $N_2$ . Both this activation energy and the diffusion parameter  $D_0 = 1.02$  mm<sup>2</sup>/s are typical for  $2p$  atoms in transition metals.<sup>2,3,8,10</sup> Note that experimental diffusion constants vary between from 59 to 163 kJ/mole.<sup>4,7,8,16</sup>

In the two-phase regime the diffusion constant depends on  $c$  and  $T$ . The mean-field result  $D = D_0 \exp(-E_a/k_B T) \times [1 - 4c(1-c)T_0/T]$  shows that there exist negative diffusion constants below  $T_0$ , which describe the creation of sharp phase boundaries.<sup>10</sup> Note the width of the ‘‘sharp’’ transition regions is as large as about  $1 \mu m$ ,<sup>12</sup> which can hardly be interpreted as critical fluctuations in the vicinity of the unknown critical temperature  $T_0$ .

Most of the evidence available for  $Sm_2Fe_{17}N_x$  produced from  $N_2$  gas favors a gas-solid solution at typical nitrogeneration temperatures of about 500 °C. In particular, intermediate lattice parameters have been observed by x-ray diffraction analysis,<sup>3</sup> samples with intermediate nitrogen contents ex-

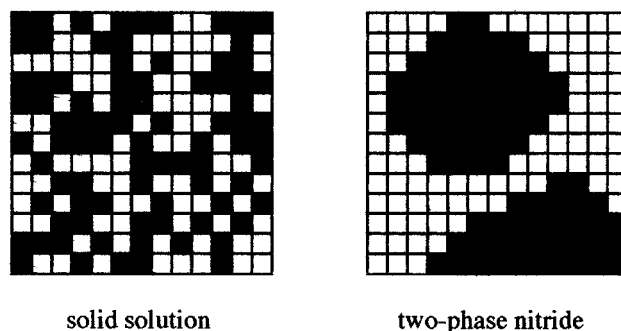


FIG. 1. Interstitial modification of a square lattice of interstitial sites. Black and white squares denote filled and empty interstitial sites, respectively.

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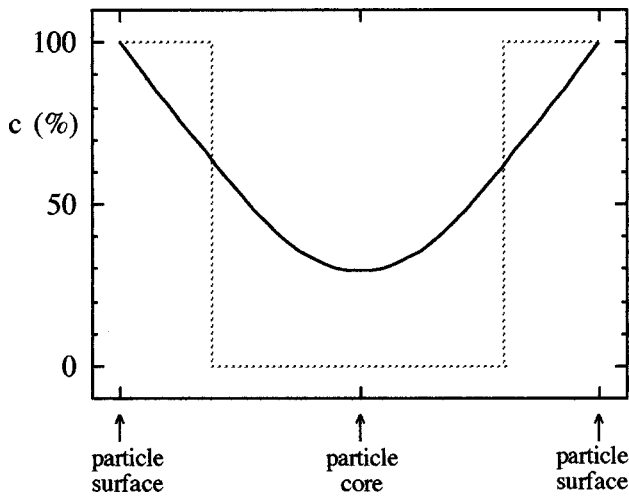


FIG. 2. Nitrogen concentration profiles for spherical particles: (solid line) ideal one-sublattice diffusion and (dotted line) sharp interface.

hibit intermediate Curie temperatures,<sup>5</sup> homogenization of partly nitrated grains yields intermediate nitrogen concentrations,<sup>13</sup> electron micrographs show smoothly varying nitrogen concentrations,<sup>9</sup> and domain-size observations<sup>17</sup> can be explained by intermediate anisotropy constants only.

However, in practice it is difficult to distinguish solid solutions from two-phase nitrides,<sup>10,18</sup> and the solid-solution character of  $R_2Fe_{17}N_x$  has been questioned by several authors.<sup>6,11,12</sup> Zhang *et al.* have argued that nitrogen diffusion in  $R_2Fe_{17}$  compounds is realized by more than two sublattices of interstitial sites.<sup>11,12</sup> Starting from the known crystal structure, they postulated the existence of trapping (*t*) and free (*f*) sites. It is assumed that the *f*-sites act as an easy diffusion pathway for the nitrogen atoms, which immobilize on the *t* sites. In the limit of ideal immobilization, where the on-site energy  $U_t$  goes to minus infinity, the immobilization mechanism yields sharp diffusion boundaries.<sup>19</sup> However, this limit amounts to an infinite heat of reaction, whereas experimental reaction energies  $U_t$  are merely of order  $-57$  kJ/mole.<sup>2</sup>

In this theoretical study, we investigate the possibility of immobilization diffusion and relate the diffusion behavior to the site and saddle-point energies of the nitrogen atoms. In particular, we answer the question whether immobilization diffusion leads to phase segregation.

## II. IMMOBILIZATION DIFFUSION

As a rule,  $R_2Fe_{17}$  intermetallics containing light rare earths crystallize in the rhombohedral  $Th_2Zn_{17}$  structure, whereas heavy rare earths tend to form the hexagonal  $Th_2Ni_{17}$  structure. The two structures derive from the  $CaCu_5$  structure but differ by the stacking of the  $CaCu_5$ -type layers. In the rhombohedral structure, the majority of the nitrogen atoms occupies the large octahedral  $9e$  sites (*t* sites), whereas the equilibrium occupancy of the  $18g$  or  $3b$  sites (*f* sites) is small.<sup>1,2,10,20</sup> Since there are three *t* sites per formula unit, the nominal composition of the nitrides is often written as  $R_2Fe_{17}N_3$ .

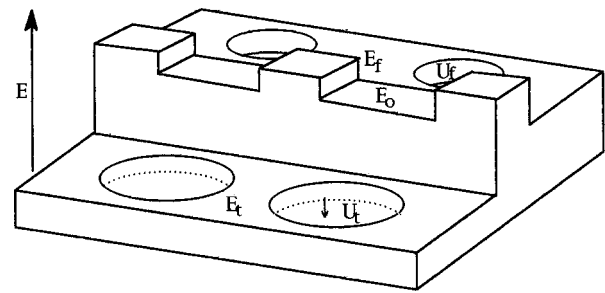


FIG. 3. Schematic energy landscape of the two-sublattice diffusion model. Note that  $E_0$  is not necessarily larger than  $E_f$  and  $E_t$ .

In the limit of strong immobilization, the nitrogen uptake is determined by the differential equation  $dL/dt \approx D_f \langle c_f \rangle / \langle c_t \rangle L$ , where  $L$  is the thickness of the fully nitrated shell and  $D_f$  is the diffusion constant of the *f*-type nitrogen atoms. The averages  $\langle c_t \rangle \approx 1$  and  $\langle c_f \rangle \ll 1$  are the equilibrium nitrogen concentrations on the respective sites. The solution of this equation,  $L = \sqrt{2D_f \langle c_f \rangle t / c_0}$ , is reminiscent of the diffusion length  $L_0 = \sqrt{Dt}$  and yields the reaction time  $t_R \approx R^2 / D \langle c_f \rangle$ .

In reality,  $U_t$  is finite and we have to start from the two-sublattice diffusion equation

$$\frac{\partial c_t}{\partial t} = D_t \nabla^2 c_t - W_{ft} c_t + W_{tf} c_f, \quad (1a)$$

$$\frac{\partial c_f}{\partial t} = D_f \nabla^2 c_f - W_{tf} c_f + W_{ft} c_t, \quad (1b)$$

where the intrasublattice diffusion constants  $D_i$  ( $i=f,t$ ) are

$$D_i = D_0 \exp\left(\frac{U_i}{k_B T} - \frac{E_i}{k_B T}\right). \quad (2)$$

The intersublattice transition rates  $W_{ft} = W(t \rightarrow f)$  and  $W_{tf} = W(f \rightarrow t)$  are given by

$$W_{ft} = \Gamma_0 \exp\left(\frac{U_t}{k_B T} - \frac{E_0}{k_B T}\right), \quad (3a)$$

$$W_{tf} = \Gamma_0 \exp\left(\frac{U_f}{k_B T} - \frac{E_0}{k_B T}\right). \quad (3b)$$

In Eqs. (1) and (2),  $U_f$  and  $U_t$  are the nitrogen on-site energies,  $E_f$  and  $E_t$  are intrasublattice saddle-point energies, and  $E_0$  is the energy of the intersublattice saddle point connecting neighboring *f* and *t* sites (Fig. 3). In a fair approximation,  $\Gamma_0 = D_0 / a_{\text{eff}}$ , where  $a_{\text{eff}} \approx 3 \text{ \AA}$  is an effective jumping distance.

Since Eq. (1) is difficult to solve, we use the approximate ansatz

$$c_i(x, t) = c_{i0} \exp(-t/\tau) \cos(2\pi x/L), \quad (4)$$

which transforms Eq. (1) into a quadratic secular equation. The diagonalization of the matrix yields two relaxation modes (Fig. 4). The *local* relaxation time  $t_L$ ,

$$t_L = \frac{a_{\text{eff}}^2}{D_0} \exp\left(\frac{E_0 - U_f}{k_B T}\right), \quad (5)$$

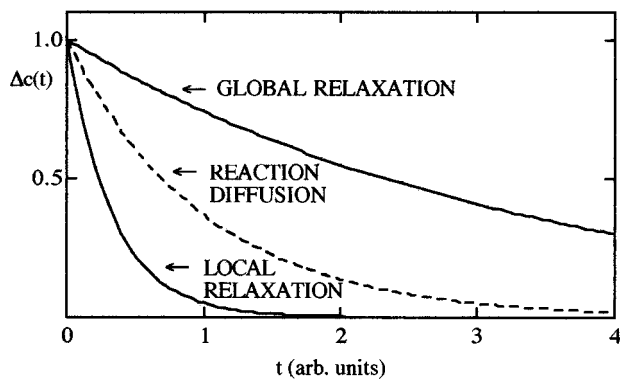


FIG. 4. Splitting of relaxation modes due to immobilization diffusion (schematic).  $\Delta c$  is the deviation from equilibrium.

describes transitions from the  $f$  sublattice to the  $t$  sublattice and is comparatively small. Note that the local character of  $t_L$  is seen from the absence of the ‘‘particle size’’  $L$  in Eq. (5).

The global relaxation time

$$t_G = \frac{L^2}{4\pi^2} \frac{\exp(-U_t/k_B T)}{\exp(-E_t/k_B T) + \exp(-E_f/k_B T)} \quad (6)$$

describes the approach towards macroscopic equilibrium and equals the time necessary to homogenize an originally step-like concentration profile. For one-sublattice solid-solution diffusion  $t_G \approx t_R$ , whereas immobilization diffusion is characterized by  $t_G > t_R$ . Since the homogenization leads to smooth nitrogen concentration profiles, the existence of sharp boundaries during immobilization diffusion does not establish a separate nitride phase. By comparison, interatomic interaction yields sharp equilibrium phase boundaries below  $T_0$ .<sup>2,3,8,10,14</sup>

### III. DISCUSSION AND CONCLUSIONS

Since Eq. (1) involves five energy values, it is not possible to predict the diffusion behavior from the known  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$  values  $U_t$  and  $E_a = E_t - U_t$ . Magnetic after effect measurements<sup>16</sup> yield a third experimental value,  $Q = E_0 - E_f/2 - E_t/2 = 62$  kJ/mole for  $\text{Nd}_2\text{Fe}_{17}\text{N}_x$ .

A possible explanation for the steplike profiles observed for  $\text{Sm}_2\text{Fe}_{17}$  heated in ammonia is that the high effective nitrogen pressure associated with the presence of  $\text{NH}_3$  enhances the concentration  $\langle c_f \rangle$  and therefore reduces  $t_R$ .<sup>8,9,21</sup> Note, however, that NMR experiments on  $\text{Sm}_2\text{Fe}_{17}$  nitrided in ammonia show a large number of defects,<sup>8,22</sup> which complicates the interpretation of the experimental results.

In general, we expect some dependence of the energy parameters on the rare earth’s atomic number. A particularly difficult situation is found in intermetallics which may occur

in either of the 2:17 structures, such as  $\text{Y}_2\text{Fe}_{17}$ . Variable<sup>23</sup> nitrogen environments observed by NMR indicate a considerable volume fraction of intermediate material, which is contradictory to the absence of intermediate nitrogen concentrations in  $\text{Y}_2\text{Fe}_{17}\text{N}_x$ . This does not exclude, however, that  $\text{Y}_2\text{Fe}_{17}\text{N}_x$  is more difficult to homogenize than  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$ .

In conclusion, we have shown that intersublattice diffusion involving nonequivalent sites leads to local and global relaxation modes. In general, both relaxation times differ from the reaction time. Depending on the site and saddle-point energies involved, smooth or steplike nitrogen concentration profiles are obtained, but the phase structure of the nitride is not affected by immobilization.

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