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# Interstitial modification of rare-earth intermetallics

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Interstitial modification of  $R_2Fe_{17}Z_x$  is studied with  $R=Y, Sm$ , and  $Z=N, C, B, Si$ , and  $S$ . Equilibrium interstitial concentrations are calculated using a lattice gas model. For gas–solid reaction a low solubility is obtained at high temperatures, whereas a solid–solid reaction is predicted to yield  $R_2Fe_{17}Z_{1.5}$  in the high-temperature limit. Theoretical results are compared with data on  $Sm_2Fe_{17}C_x$  produced by solid–solid reaction at 500 °C. Volume expansions up to 4.8% were obtained, which corresponds to  $x \approx 2$ . The concentrations of interstitial boron and silicon are much lower.

## I. INTRODUCTION

Since the discovery that nitrogen and carbon can be introduced into  $Sm_2Fe_{17}$  from a gas phase to form new interstitial compounds  $Sm_2Fe_{17}Z_{3-5}$  with useful hard magnetic properties,<sup>1</sup> extensive studies of the structure, intrinsic magnetic properties, hysteresis and electronic structure of the new nitrides and carbides have been published.<sup>1-9</sup>

Unlike highly mobile hydrogen, nitrogen and carbon in  $Sm_2Fe_{17}$  occupy exclusively the large octahedral  $9e$  interstices coordinated by two rare-earth and four iron atoms. From the point of view of iron magnetization, the dramatic effect of the interstitial atoms is a large increase in Curie temperature (from 389 to 749 K for  $Sm_2Fe_{17}N_3$ ), due to the dilation of the lattice. Furthermore, the interstitial atoms modify the crystal field at the rare earth sites, which explains the strong uniaxial anisotropy of the nitride in contrast to the easy-plane anisotropy of pure  $Sm_2Fe_{17}$ .<sup>1,2</sup>

Questions arise whether the interstitial modification is restricted to H, C, and N only, and if there are other ways to conduct the reaction. Here, we calculate the the pressure and temperature dependence of the equilibrium interstitial concentration for reactions of the intermetallic with (i) an atomic gas, (ii) a molecular gas, and (iii) a solid, and compare the theoretical results with measurements on  $R_2Fe_{17}$  interstitially modified by solid–solid reactions with carbon. We also report gas–solid or solid–solid reactions involving boron, silicon, and sulphur

For any of these reactions, the equilibrium state is achieved by solid-state diffusion from the surface of the intermetallic. The effective particle size may be reduced by microcracks or diffusion along grain boundaries<sup>10</sup> but the gas–solid reaction time is essentially determined by the bulk diffusion of the interstitial atoms in the intermetallic

lattice.<sup>11</sup> The concentration profiles are found by solving the diffusion equation  $(\partial c/\partial t) = D\nabla^2 c$  subject to the boundary condition  $c(r_s, t) = c_0$  at the particle surface. The temperature dependence of the diffusion constant is given by the Arrhenius equation  $D = D_0 e^{-E_a/kT}$ . Short-time thermopiezic analysis (TPA) measurements have been used to determine the diffusion parameters  $D_0 = 1.0 \text{ mm}^2/\text{s}$  and  $E_a = 133 \text{ kJ/mole}$  for nitrogen in  $Sm_2Fe_{17}$  (see Ref. 11); both values can be regarded as typical for gases in metals.<sup>12</sup>

For spherical particles the diffusion problem can be solved analytically,<sup>13</sup> and we obtain the local concentration

$$c(r, t) = c_0 \left[ 1 + \frac{2R}{\pi r} \sum_{m=1}^{\infty} \frac{(-1)^m}{m} \sin \frac{m\pi r}{R} \exp\left(-\frac{m^2 \pi^2 D t}{R^2}\right) \right], \quad (1)$$

where  $R$  is the radius of the particle and  $c_0$  is the equilibrium interstitial concentration, determined below. Figure 1 shows the profiles  $c(r)$  for two different average concentrations. Equation (1) yields smooth, bathtub-like profiles for intermediate concentrations,  $c < c_0$ .

## II. EQUILIBRIUM CONCENTRATIONS

With increasing time, the concentration  $c(r, t)$  in Eq. (1) approaches its equilibrium value  $c_0$ . The weight of experimental evidence on  $Sm_2Fe_{17}N_x$  suggests that nitrogenation at temperatures of order 500 °C yields a uniform solid solution rather than a two-phase mixture of  $\alpha$ - $Sm_2Fe_{17}N_x$  and  $\beta$ - $Sm_2Fe_{17}N_x$  (see Refs. 11 and 14). In particular, by tuning the nitrogenation conditions, it is possible to produce grains with well-defined intermediate nitrogen concentrations and sharp x-ray diffraction peaks.<sup>14</sup>

TABLE I. Results of interstitial modification reactions of  $R_2Fe_{17}$ ,  $R=Y, Sm$ , with C, B, and Si.

Material	Structure	$a$ (Å)	$c$ (Å)	$T_c^0$ (K)	$\Delta T_c$	$\Delta v/v\%$
$Sm_2Fe_{17}$	$Th_2Zn_{17}$	8.523	12.447	389	...	...
$Sm_2Fe_{17}/CH_4$	$Th_2Zn_{17}$	8.740	12.570	668	279	6.2
$Sm_2Fe_{17}/C(s)$	$Th_2Zn_{17}$	8.700	12.560	661	270	4.8
$Y_2Fe_{17}$	$Th_2Ni_{17}$	8.445	8.283	322	...	...
$Y_2Fe_{17}/B_{10}H_{14}$	$Th_2Ni_{17}$	8.445	8.283	322	0	0.2
$Y_2Fe_{17}/B(s)$	$Th_2Ni_{17}$	8.462	8.287	332	10	0.4
$Y_2Fe_{17}/SiH_4$	$Th_2Ni_{17}$	8.456	8.315	383	61	0.6

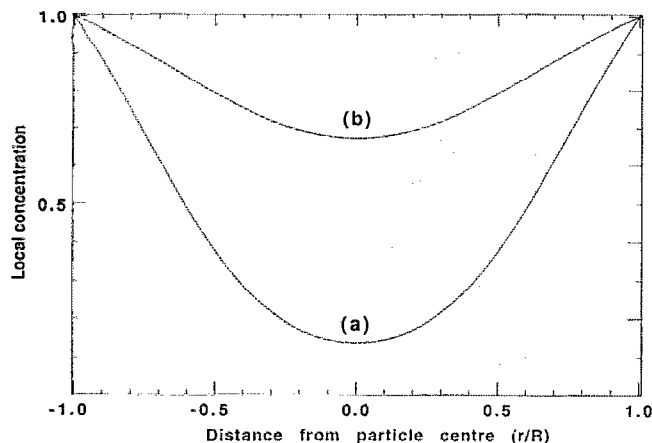


FIG. 1. Nitrogen concentration profiles for spherical particles with mean concentrations of 0.70 (solid line) and 0.90 (dashed line).

Here, we neglect the interatomic interactions and model the interstitial intermetallic system as an ideal solution.

The solubility of interstitial atoms in metals is determined by two factors. On one hand, the atoms tend to occupy interstitial sites if it is energetically favorable to do so, i.e., if the net binding energy per interstitial atom  $U_0$  is negative. On the other hand, thermal activation tends to create disorder in the gas–solid system. Here,  $U_0$  contains large chemical contributions of opposite sign as well as the energy needed to expand the lattice around the interstitial atoms. It is therefore difficult to predict its value, so it must be treated as an experimentally determined parameter.

The equilibrium concentration  $c_0$  as function of  $U_0$ ,  $P$ , and  $T$ , can be calculated from the partition function of the system using the standard methods of statistical mechanics. This procedure automatically includes the entropic contribution to the free energy, which is different according to whether the source of the interstitial atoms is an atomic gas, a molecular gas or a solid. The lattice gas model used for the calculations is illustrated in Fig. 2.

The equation of state for the atomic gas Fig. 2(a) is

$$c_0 = \left( 1 + \frac{kT}{v_0 P} e^{U_0/kT} \right)^{-1}, \quad (2)$$

where  $v_0$  is the lattice-gas cell volume, which can roughly be interpreted as the volume of the atom to be accommodated. The prefactor  $kT/v_0 P$  can also be written  $\rho_0/\rho$ .

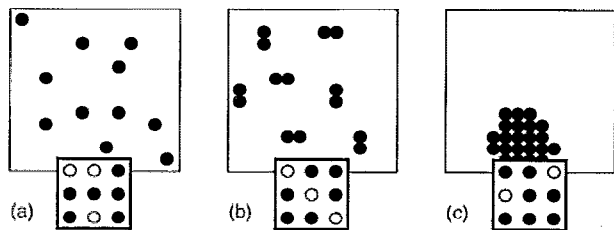


FIG. 2. Schematic illustration of the lattice gas model: (a) atomic gas, (b) molecular gas, and (c) solid reactant.

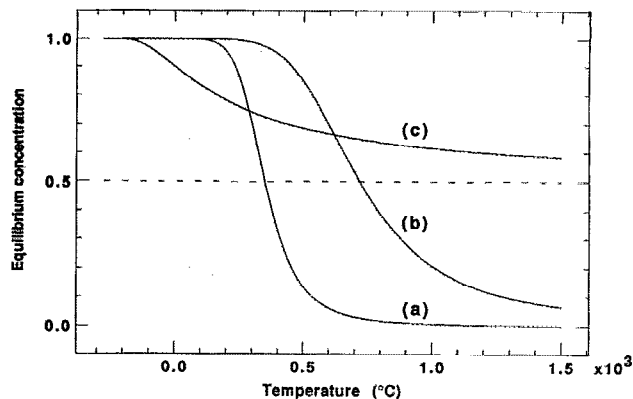


FIG. 3. Equilibrium interstitial concentrations in  $\text{Sm}_2\text{Fe}_{17}$  as function of temperature and 1 bar pressure: (a) atomic gas with  $U_0 = -50$  kJ/mole, (b) molecular gas with  $U_0 = -50$  kJ/mole, (c) solid reactant with  $U_0 = -5$  kJ/mole.

For the reaction of a binuclear molecular gas such as  $\text{N}_2$ , we obtain<sup>11,14</sup>

$$c_0 = \left( 1 + \sqrt{\frac{6kT}{v_0 P}} e^{U_0/kT} \right)^{-1}. \quad (3)$$

In the case of solid phase interstitial modification, the equilibrium concentration does not depend on pressure:

$$c_0 (1 + e^{U_0/kT})^{-1}. \quad (4)$$

The temperature dependence of the concentration at 1 bar pressure in the three cases is shown in Fig. 3. An interesting point is that the equilibrium concentration for solid–solid reactions is always greater than for gas–solid reactions, with the same value of  $U_0$ , and it shows the weakest temperature dependence. The effect is due to the lower entropy of the reagent. Artificially atomized gases and implanted ions do not establish thermal equilibrium and must be excluded. We now discuss the reactions of  $\text{R}_2\text{Fe}_{17}$  with some molecular gases and solids.

### III. EXPERIMENTAL RESULTS

#### A. Nitrogen

From isothermal absorption experiments,<sup>11</sup> a value  $U_0 = -57$  kJ/mole has been deduced for molecular nitrogen in  $\text{Sm}_2\text{Fe}_{17}$ . No convenient solid source of nitrogen has been found to compare gas–solid and solid–solid reactions.

#### B. Carbon

We previously reported interstitial modification of  $\text{Sm}_2\text{Fe}_{17}$  using a hydrocarbon gas.<sup>2</sup> Similar results can be achieved with solid graphite. To study the solid–solid reaction, finely ground reactants were mixed and heated in vacuum at about 500 °C. Depending on heating time and temperature, a lattice expansion was observed, for instance 4.8% for a 5-h heat treatment at 500 °C (Fig. 4). Below 450 °C no reaction was observed. As opposed to gas–solid interstitial modification, the lattice expansion near the surface increases with time, which might indicate that the reaction rate is limited by the carbon flux through the

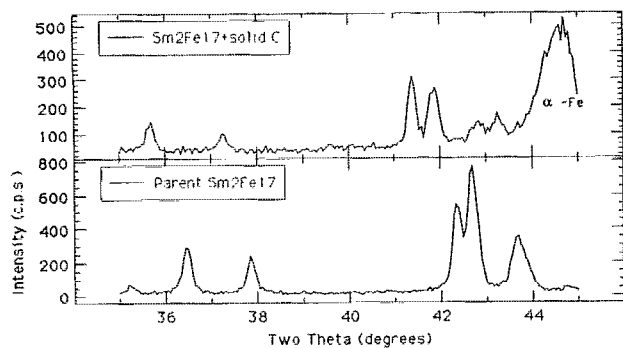


FIG. 4. X-ray diffraction pattern showing the lattice expansion in  $\text{Sm}_2\text{Fe}_{17}\text{C}_x$  heated with graphite at  $500^\circ\text{C}$ .

particle surface, possibly because of the comparatively small contact area between the intermetallic and graphite grains.

### C. Boron, silicon, and sulfur

The irreversible volume expansion achieved with decaborane or solid boron is very small,  $<0.5\%$ . On exposure to decaborane vapour at  $575^\circ\text{C}$  the volume expands by  $1.9\%$ , but most of this can be reversed by heating in vacuum. It is therefore attributed to hydrogen. The expansion with solid boron at  $730^\circ\text{C}$  is  $0.4\%$ , and  $\alpha\text{Fe}$  appears as a secondary phase, as in the reaction with graphite.

The reversible lattice expansion achieved with silane is also small. After heating in silane for 4 h at  $500^\circ\text{C}$  the expansion was  $3.8\%$ , but again most of this is due to hydrogen. The expansion which remained after pumping cycles at  $350^\circ\text{C}$  is  $0.6\%$ . Silicon has a tendency to replace iron substitutionally, reducing the lattice parameters so it is difficult to estimate how much of it has entered the lattice interstitially. Reaction with solid silicon at  $700^\circ\text{C}$  leads to lattice expansion, and the appearance of  $\text{FeSi}$ .

Reactions with hydrogen sulfide and solid sulfur both lead to the formation of  $\text{FeS}$ . There was no evidence for interstitial sulfur.

## IV. DISCUSSION

With all four elements, the results of gas–solid and solid–solid reactions are quite similar, which is not what we were led to expect from the considerations of Sec. II. However, after the reaction of 2–17 intermetallics with hydrocarbon gases, a layer of soot can be observed on the surface. This is incompatible with the detailed balance principle of statistical mechanics, which would require permanent recombination of hydrocarbon gases from the interstitial carbon and hydrogen atoms. We conclude that the hydrocarbon gases decompose irreversibly into hydrogen and carbon at its surface, which then react independently, apart from site blocking effects, with the intermetallic lattice. The reaction with carbon is a solid–solid reaction. The hydride gases of the other elements probably also decompose to deposit a surface layer of B, Si, or S.

From Eq. (4) and Fig. 3(c), we should expect a moderate solubility for any solid if the temperature is sufficiently high, regardless of the sign of  $U_0$ . However, high temperatures cannot always be achieved without upsetting the metastable equilibrium of the interstitially modified intermetallic lattice, leading to its disproportionation to a more stable mixture of phases. A low reaction temperature may be required to preserve the integrity of  $\text{Sm}_2\text{Fe}_{17}\text{Z}_x$ .

Another way to produce  $\text{Sm}_2\text{Fe}_{17}\text{C}_x$  is to introduce carbon by melting. With this method, at most about 1.5 carbon atoms per formula unit can be introduced,  $c_0=0.5$  (Ref. 15). This agrees fairly well with our predictions, Eq. (4) and Fig. 3(c), if we assume quasi-equilibrium conditions just below the melting point of the phase. The high-temperature limit of Eq. (4) is  $c_0=0.5$ .

## V. CONCLUSIONS

Solid–solid reaction is a possible way to introduce metalloids such as carbon into intermetallic lattices. The interstitial modification using hydrocarbon or other similar hydrogen containing gases can be interpreted as a special kind of solid-phase interstitial modification.

Compared to gas-phase interstitial modification, the solid–solid reaction has three potential advantages: (i) The reaction can be conducted at temperatures where hydrocarbon gases would destroy the lattice due to the effect of hydrogen. (ii) From the thermodynamic point of view, solid–solid reaction is more favorable than gas–solid reaction, due to the large entropy of the gas. Furthermore, in the case of carbon, gas–solid reaction at temperatures of about  $500^\circ\text{C}$  is very unlikely due to the low vapor pressure of carbon. (iii) Low-temperature solid-phase interstitial modification may permit a new and simplified permanent-magnet processing route.

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