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Letter

Structural analysis of the hard ferromagnetic phase observed in quenched Nd–Fe alloys of hyper-eutectic composition

D. Givord, J. P. Nozières, M. F. Rossignol* and D. W. Taylor*
Laboratoire Louis Néel, CNRS, BP 166X, 38042 Grenoble Cédex (France)

I. R. Harris
School of Metallurgy and Materials, University of Birmingham, P.O. Box 363, Birmingham (U.K.)

D. Fruchart and S. Miraglia
Laboratoire de Cristallographie, CNRS, BP 166X, 38042 Grenoble Cédex (France)

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Recently, a new hard ferromagnetic phase has been reported in quenched $Nd_{100-x}Fe_x$ with hyper-eutectic compositions ($x<25$) [1–3]. This phase, labelled A_1 in the literature, has a coercivity of between 2 and 5 kOe at room temperature (depending on the quenching rate) and a Curie temperature of 245 °C. It is not possible to obtain this phase as a pure phase, and therefore only indirect analysis of its properties can be carried out. Recently, the analysis of the basic magnetic properties of this phase (*i.e.* magnetization and anisotropy) has been performed and an estimation of its composition has been deduced from the combination of Mössbauer spectroscopy and magnetic measurements [4]. In this paper we have carried out a structural analysis of this ill-defined phase by means of neutron diffraction and transmission electron microscopy (TEM).

Alloys of nominal composition $R_{100-x}Fe_x$ (R≡Nd, Pr; $6.5<x<20$) have been prepared both by induction and arc melting under an Ar atmosphere followed by casting in a water-cooled copper mould. The purities of the starting materials are Nd 99.9% and Fe 99.98%. The typical microstructure associated with a Nd–Fe alloy is shown in Fig. 1. This is formed of primary Nd dendrites embedded in a fine globular eutectic matrix composed of pure Nd and an iron-rich phase. Thermo-magnetic measurements were performed on all the alloys in a superconducting coil magnetometer under a field of 100 Oe. In each case only one anomaly was observed at $T=245$ °C (Fig. 2). This anomaly is characteristic of a ferromagnetic alignment and can be

*Also at the School of Metallurgy and Materials, University of Birmingham, P.O. Box 363, Birmingham, U.K.

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Fig. 1. Optical micrograph of a quenched $Nd_{93.5}Fe_{6.5}$ alloy.

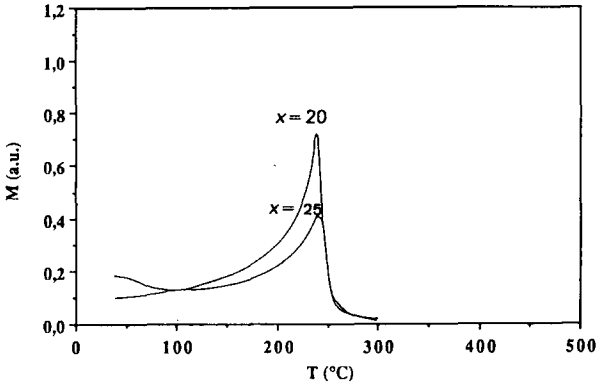


Fig. 2. Thermomagnetic measurements of cast $Nd_{100-x}Fe_x$ alloys. For hypo-eutectic alloys ($x \geq 25$) some Nd_2Fe_{17} ($T_c = 55$ °C) is observed.

attributed to the A_1 phase, thus confirming that it corresponds to the Fe-rich phase present in the alloys. After a 600 °C anneal the A_1 phase transforms into the stable Nd_5Fe_{17} phase (via the metastable Nd_2Fe_{17} phase) [5, 6]. An exothermal peak is associated with this solid state transformation revealing that A_1 is metastable [5].

The fact that the A_1 phase is found to be such a fine eutectic and that the phase itself is unstable on annealing, hence preventing the possibility of large pure A_1 grains, means that methods such as scanning electron microscopy (SEM) analysis are inefficient for compositional and structural analysis. In addition, X-ray analysis performed on such alloys reveals only the characteristic rays of the free crystallized Nd. This result can be explained by the large predominance of the rare earth in the scattering for alloys of

such composition. However, the Fermi length of Fe is larger than that of Nd (0.954×10^{-12} cm compared with 0.769×10^{-12} cm), hence the use of neutron diffraction is *a priori* more adequate to observe the A_1 diffraction pattern. A neutron diffraction study has been performed at the Institute Laue-Langevin (ILL) (Grenoble) on the D20 diffractometer using neutrons of wavelength 1.295 Å with a flux density of 1.7 10^6 cm^{-2} s^{-1}. The neutron diffraction pattern of a quenched $Nd_{80}Fe_{20}$ alloy is reported in Fig. 3. The bulk of the rays are those characteristic of hexagonal Nd metal but, in addition, a diffuse contribution can be seen for $23°<2\theta<40°$, indicated by an arrow in Fig. 3. This diffuse contribution can be divided into approximately two separate peaks or humps centred at $2\theta=32°$ and $2\theta=37°$ respectively. The associated diffusion vectors **Q** ($\mathbf{Q}=4\pi\cdot\sin\theta/\lambda$) are 2.67 $Å^{-1}$ and 3.1 $Å^{-1}$ respectively. These two values can be directly related to the position of the diffusion peaks observed in amorphous rare-earth transition metal alloys (R–M). The value $\mathbf{Q}=3.1$ $Å^{-1}$ corresponds to the first diffusion peak associated with the M–M pairs ($\mathbf{Q}=3.16$ $Å^{-1}$ for such pairs). The diffusion vector $\mathbf{Q}=2.67$ $Å^{-1}$ is inbetween the values associated with the first diffusion peaks of the R–R pairs ($\mathbf{Q}=2.26$ $Å^{-1}$) and the R–M pairs ($\mathbf{Q}=2.75$ $Å^{-1}$); hence the contribution at $2\theta=32°$ should be a combination of the two. From the width of these peaks, a correlation length of approximately 25 Å is deduced from the Sherrer formula $L=0.89\lambda/\Delta2\theta\cos\theta$, where $\Delta2\theta$ is the half-height width of the peaks. Such a diffusion pattern strongly suggests the existence in the alloy of an amorphous or nano-crystallized Nd–Fe phase.

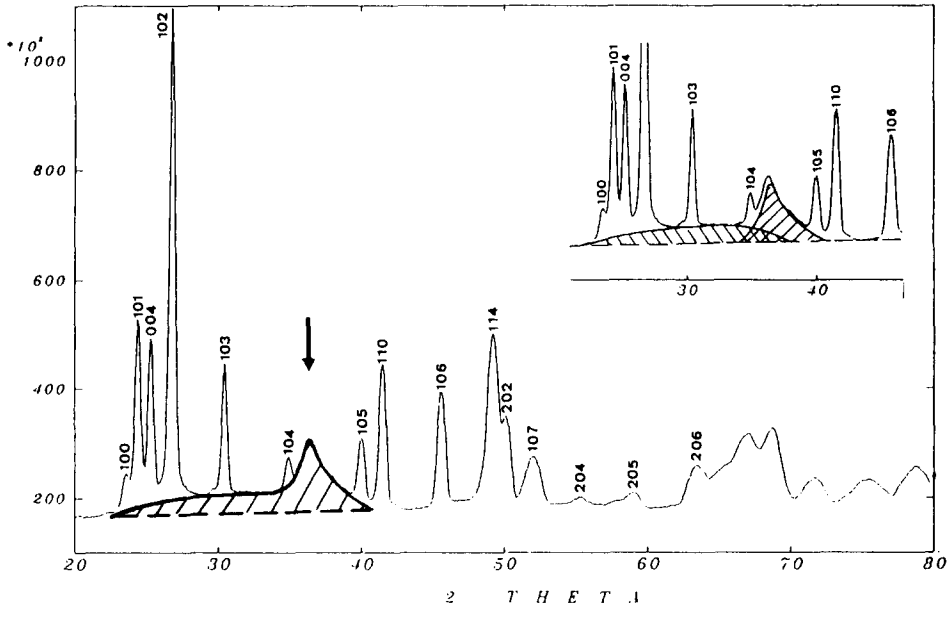


Fig. 3. Neutron diffraction pattern of a quenched $Nd_{80}Fe_{20}$ alloy.

In order to confirm these results obtained on Nd–Fe alloys, similar measurements have been performed on $Pr_{80}Fe_{20}$ alloys since the Fermi length of Pr is even lower than that of Nd (0.445×10^{-12} cm). The neutron diffraction pattern (Fig. 4) is similar to that obtained for Nd based alloys but accentuates the contribution of the diffusion peak ($\mathbf{Q} = 31.$ Å^{-1}) associated with Fe–Fe pairs.

As confirmation of the aforementioned results, TEM observations were carried out using a JEOL 4000 (400 kV) electron microscope at the University of Birmingham. For this purpose, thin lamellae were prepared by ion beam thinning under ultra high vacuum conditions. A bright field image of a quenched $Nd_{80}Fe_{20}$ alloy is shown in Fig. 5 which shows two separate zones; Zone A consisting of crystalline Nd (see diffraction pattern Fig. 6(a)) and Zone B formed of Nd and Fe including a few crystallized precipitates of Nd. The chemical composition of Zone B, determined using a spot of 500 Å diameter, is $Nd_{49}Fe_{51}$. However, Zone B can be seen to be heterogeneous, formed from an intimate mixture of bright and dark regions at a scale of approximately 100 Å. The corresponding diffraction pattern is shown in Fig. 6(b). Several rings characteristic of amorphous or nanocrystalline phase(s) can be seen. In addition to the characteristic rings of amorphous or nanocrystalline Nd, two rings can be seen at $\mathbf{Q} = 2.7$ (0.2) Å^{-1} and $\mathbf{Q} = 3.1$ (0.2) Å^{-1}. These $\mathbf{Q}$ values correspond exactly to the diffusion peaks observed by neutron diffraction except that the relative intensities are inversed, *i.e.* for the neutrons the $\mathbf{Q} = 3.1$ Å^{-1} peak is the more intense whereas with TEM the $\mathbf{Q} = 2.7$ Å^{-1} peak is the more intense. Such a property is a direct

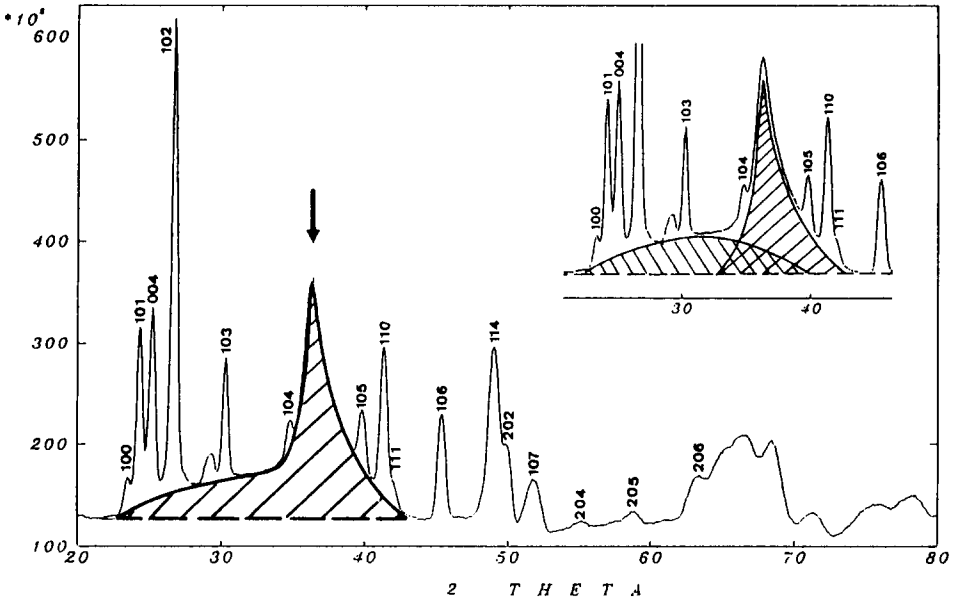


Fig. 4. Neutron diffraction pattern of a quenched $Pr_{80}Fe_{20}$ alloy.

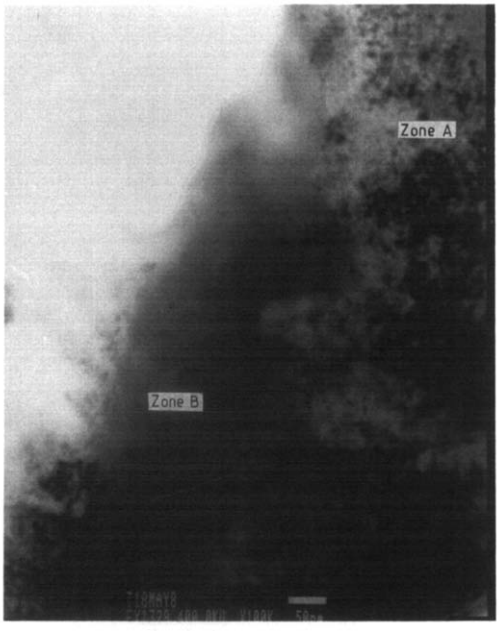
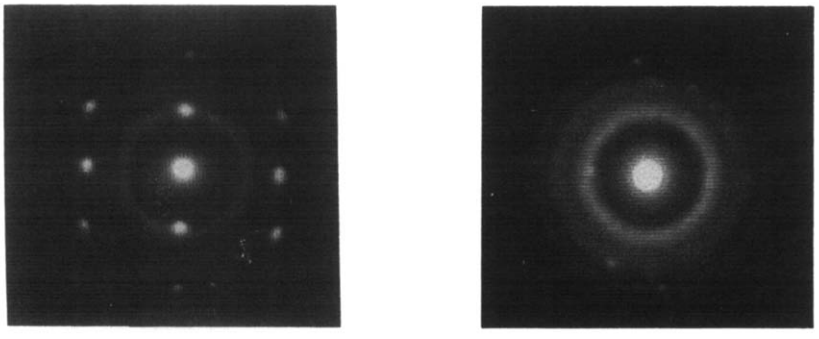


Fig. 5. Bright field image of a quenched $Nd_{80}Fe_{20}$ alloy showing pure crystalline Nd (Zone A) and a region formed of Nd and Fe plus a few crystalline Nd precipitates (Zone B).



(a) (b)

Fig. 6. Diffraction patterns corresponding to the electron microscopy images of Fig. 5 for (a) Zone A and (b) Zone B.

consequence of the diffusion cross-section of Nd and Fe inverting when using X-rays or neutrons.

As the only two phases present in as-cast Nd–Fe alloys of hyper-eutectic composition are Nd and the iron-rich A_1 phase, we can conclude from the combined previous results with neutrons and TEM that the hard ferromagnetic A_1 phase is amorphous or nanocrystalline. This is most surprising since the formation of an amorphous phase is usually associated with a rapid solid-

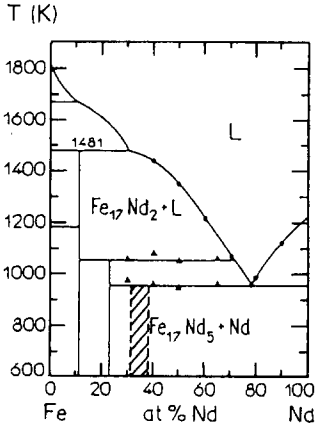


Fig. 7. Nd–Fe phase diagram including the stable Nd_5Fe_{17} phase (from ref. 7). The hatched area represents the composition range for A_1.

ification which is not the case here. This phenomenon can be explained by looking at the Nd–Fe phase diagram, Fig. 7, recently reported by Schneider *et al.* [7]. If a Nd–Fe alloy, close to the eutectic composition, is equilibrium-cooled it tends to form pure Nd on one hand and the stable Nd_5Fe_{17} (A_2) phase on the other. Therefore, when cast, certain regions of the alloy tend to become enriched in Fe, other regions in Nd. Since the atomic mobilities of these elements in one another are very low below 550 °C, the alloy solidifies in a metastable state formed from Fe-rich and Nd-rich regions rather than reaching the stable equilibrium state. It is this Fe-rich eutectic phase which is termed A_1 and exhibits hard magnetic properties.

The only information we have on the composition of A_1 has been determined indirectly by combining results from Mössbauer spectroscopy and magnetic measurements [4]. The deduced Nd–Fe ratio ranges from 1:2.2 to 1:2.6 depending on the assumptions of the Nd-moment in the phase. The hatched region on Fig. 7 corresponds to this composition range. As expected from previous reasoning the Fe concentration is lower than that in the stable Nd_5Fe_{17} phase.

Acknowledgments

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