ESRF	**Experiment title:** Diffractometric determination of the interface stress in ferro- and paramagnetic nanocrystalline Gd	**Experiment number:** SI-788
Beamline: ID31	**Date of experiment:** from: 01 July 2002, 7:00 to: 02 July 2002, 7:00	**Date of report:** 25 August 2003
Shifts: 3	**Local contact(s):** Dr. Michela Brunelli	*Received at ESRF:*

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Report:

The goal of Experiment Si-788 was to obtain a value for the area-averaged interface (i.e. grain-boundary) stress $\langle f \rangle_A$ in nanocrystalline Gd from a measurement of the volume-averaged (and, therefore, residual-strain-free) lattice parameters. A previous, indirect measurement of $\langle f \rangle_A$ suggested an anomalously large value for the interface stress, offering an explanation for the measured dependence of the Curie transition temperature T_C of Gd on the average crystallite size [1]. Because $\langle f \rangle_A$ induces a change Δv in the volume of the unit cell v_0 according to

$$\frac{\Delta v}{v_0} = -\frac{4}{3}\frac{\langle f \rangle_A}{B^*}\left(\frac{1}{L_{\text{area}}}\right), \tag{1}$$

where B^* denotes the (polycrystalline) bulk modulus and L_{area} the area-weighted average crystallite size, it is possible to extract the average interface stress from a careful measurement of lattice parameters as a function of L_{area}. Since such measurements can be performed both below and above the Curie temperature, we hoped not only to obtain a direct measure of the true value of $\langle f \rangle_A$ in our samples, but also to determine whether ferromagnetic ordering (and the resulting magnetostriction) exerts any influence on the interface stress.

Samples of nanocrystalline Gd were prepared by inert-gas condensation/compaction in the form of disks (ϕ 8 mm) having a thickness of 0.3–0.5 mm. The disks were cut into narrow strips and sealed in glass capillaries (ϕ 0.7 mm), which were then mounted in the high-resolution powder diffractometer of beamline ID31. A streaming-LN$_2$ cryostat was employed to perform *in situ* measurements below room temperature, whereas elevated temperatures were reached with the help of a hot-air blower mounted just below the rotating capillary. Wide-angle diffraction scans were recorded from -4° to 16° (2θ) with x-ray photons of $\lambda = 0.24900\,\text{Å}$ ($E = 49.79\,\text{keV}$) while moving the nine-channel detector at 1°/min. The instrumental broadening at this wavelength was determined by fitting the profiles of Bragg peaks produced by a coarse-grained standard sample ($Na_2Ca_3Al_2F_{14}$) provided by the beamline.

Seven samples with average crystallite sizes ranging from $L_{\text{area}} = 4\,\text{nm}$ to 65 nm were investigated at 100 K, room temperature (~ 295 K) and 70°C (343 K). Since the Curie temperature of coarse-grained Gd is 292 K and the T_C of Gd is known to decrease with L_{area}, reaching 266 K at 5 nm [1], we expect the samples to be ferromagnetic at 100 K and paramagnetic at the two higher temperatures.

According to Eq. (1), we can determine the area-averaged interface stress $\langle f \rangle_A$ from measurements of the relative volume change of the unit cell, $\Delta v/v_0$, as a function of the area-weighted average crystallite size L_{area}. The latter can be extracted from an analysis of Bragg-peak profiles [2], while the volume change can be obtained at a given temperature by comparing the values of the lattice parameters a and c of the hexagonal unit cell to the literature values for single-crystalline Gd ($a = 363.6\,\text{pm}$, $c = 578.26\,\text{pm}$ at room temperature [3]); values for v_0 at 100 K and 343 K were estimated using thermal-expansion data for polycrystalline Gd [4]. We determined both the lattice parameters and the crystallite size by performing a full-pattern profile fit of each diffraction scan using the commercially available program FORMFIT [5]. This program performs a Rietveld-like refinement of (i) the parameters of the pseudo-Voigt function that is used to approximate the profiles of individual Bragg peaks and (ii) the lattice parameters, which fix the centers of the individual peak fits. The peak-profile function is convoluted with the instrumental broadening, with the microstrain and with an assumed lognormal crystallite-size distribution, thus permitting simultaneous refinement of the lattice parameters a and c, the volume-weighted crystallite size L_{vol}, the standard deviation σ of the lognormal distribution and the microstrain e. From the values of L_{vol} and σ we calculated the area-weighted crystallite size L_{area} according to $L_{\text{area}} = [(8/9)\exp(-\ln^2\sigma)]L_{\text{vol}}$, an expression that is valid for a lognormal distribution of spherical-shaped crystallites [2].

The experimental data plotted in Fig. 1 show no sign of a dependence of $\Delta v/v_0$ on the magnetic ordering in the samples, as the data points measured at all three temperatures appear to lie along a common curve. The fact that this curve is exponential rather than linear, as expected for a constant value of $\langle f \rangle_A$, indicates either that the value of the interface stress depends on the average crystallite size, or that the samples differ from each other not only in the value of L_{area}. Given the bulk modulus B^* of polycrystalline Gd (37.9 GPa), we estimate an upper bound of $\langle f \rangle_A \approx 2\,\text{N/m}$ from the slope of the fit curve at $L_{\text{area}} = 100\,\text{nm}$, whereas the slope at a crystallite size of $10\,\text{nm}$ yields $\langle f \rangle_A \approx 0.2\,\text{N/m}$. Even the larger of these two values for the average interface stress is well below the level of $5.5\,\text{N/m}$ needed to explain the crystallite-size dependence of T_C that is observed in nanocrystalline Gd [1]. Thus, we conclude that the Curie-temperature depression measured in nanocrystalline Gd cannot result entirely from the volume contraction induced by the interface stress of the grain boundaries. Likewise, it is probable that observations of a drastic dependence of T_C on the thickness of Gd thin films [6] cannot be explained entirely by the *surface* stress, as the latter is generally a factor of only 2 or 3 larger than $\langle f \rangle_A$.

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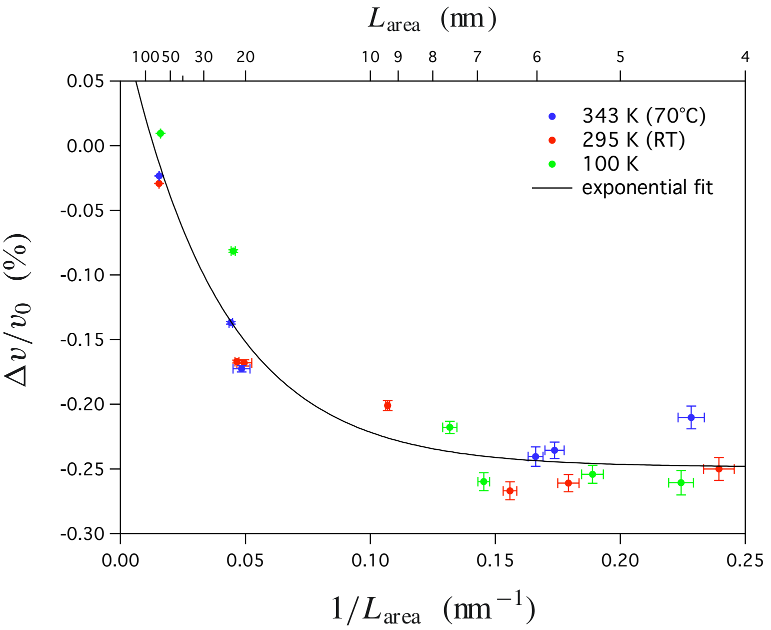

Fig. 1: Relative volume change $\Delta v/v_0$ plotted as a function of the area-weighted average crystallite size L_{area} in nanocrystalline Gd, measured at 100 K, room temperature and 70°C.

The solid curve is a global fit of an exponential function to the data points. From the slope of the fit at $L_{\text{area}} = 100\,\text{nm}$ and Eq. (1), we estimate an apparent interface stress of $2\,\text{N/m}$, dropping to $\sim 0.2\,\text{N/m}$ at crystallite sizes below $10\,\text{nm}$.