Magnetism of Body-Centered Cubic Fe-Ni Alloys Under Pressure: Strain-Enhanced Ferromagnetism at the Phase Transitions

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Abstract  We investigated the magnetism of body-centered cubic (bcc) FeNi alloys (Fe92Ni8, Fe87Ni13, and Fe84Ni16) as a function of pressure at room temperature through the bcc to hexagonal closed packed (hcp) phase transition. In each case, the fully saturated magnetic remanence attained maxima, 3–6 times higher than the initial value, at the hysteretic bcc → hcp and hcp → bcc transition boundaries upon compression and decompression. Magnetization maxima generally shifted to lower pressures with increasing Ni, concurrent with the phase transition. In Fe84Ni16, X-ray magnetic circular dichroism (XMCD) at the K-edge of Fe measured in a 2.5 T field together with X-ray absorption spectroscopy indicate that the magnetism defined by XMCD divided by the proportion of bcc also attains a maximum in the transition regions, similar to the magnetic remanance measurements. Enhanced remanence is attributed to a lattice mismatch between bcc-Fe and hcp-Fe phases together with defect-riddled martensite. This mechanism also explains why the remanence of bcc FeNi is 2–4 times stronger at full decompression than initially, which bears on the interpretation of paleointensity records of meteorites containing bcc FeNi alloys (kamacite). Only techniques that probe magnetic states carried out in fully saturating external fields detect magnetic signals in bcc-Fe residing in the hcp stability region, thereby explaining the discrepancy among the experimental results. How far in pressure bcc-Fe persists into the hcp stability field, especially at elevated temperatures, remains open.

1. Introduction

Iron-nickel alloys crystallize in a body-centered cubic (bcc) structure, called kamacite, when Ni concentrations are below ~20%. Above ~20% Ni, unmixing occurs, and above 25%–30% Ni, FeNi alloys possess face-centered cubic (fcc) lattices. At room temperature, bcc-Fe converts to a hexagonal closed packed (hcp) structure at ~13 GPa (Takahashi & Bassett, 1964). Huang et al. (1988) found that the bcc to hcp phase transition decreases in pressure with increasing Ni, being ~11 and ~8 GPa for Ni concentrations of 10% and 25%, respectively. Using a monochromatic synchrotron radiation X-ray source, Akahama et al. (2020) found that the onset pressure of the bcc to hcp transition decreases 0.2 GPa per at% Ni from 0% to 15% Ni, and then remained constant with increasing amounts of Ni. The reverse transition (hcp to bcc) pressure upon decompression likewise decreased with increasing Ni concentration yet was shifted ca. 6 GPa below the bcc to hcp transition pressures (Akahama et al., 2020). The transition from bcc to hcp occurs via a diffusionless, martensic mechanism that does not involve movement of atoms over distances larger than the lattice dimensions (Bassett & Huang, 1987; Huang et al., 1988). Mao et al. (1967) argued that the hcp structure develops from the bcc structure through a minor distortion of the bcc structure.

Solid inner cores of the terrestrial planets contain FeNi alloys in a hexagonal close-packed structure (Hirose et al., 2013). Nickel concentrations can attain 60% (mostly <10%) in iron meteorites (Chabot et al., 2007), which once formed the cores of differentiated proto-planets (Albertsen et al., 1983; Goldstein et al., 2009). An important open question is how high in pressure can ferromagnetism persist in iron within planets? Answering this question seemingly depends on the technique used to quantify the magnetic signal.

Mössbauer experiments generally conclude that hcp-Fe is paramagnetic (Cort et al., 1982; Nasu et al., 2002; Pipkorn et al., 1964; Taylor et al., 1982, 1991; Williamson et al., 1972), which has been corroborated by studies using X-ray circular dichroism (Baudelet et al., 2005; Mathon et al., 2004). On...
the other hand, X-ray emission spectroscopy shows finite magnetism to 30–40 GPa, well within the hcp-Fe stability field (Monza et al., 2011; Rueff et al., 2008). Iron particles immersed in a fluid inside a diamond anvil cell moved in response to an applied field gradient at 17 GPa and 260°C suggesting a ferromagnetic or paramagnetic state for hcp-Fe (Gilder and Glen, 1998). Magnetic remanence measured at 21.5 GPa argues for ferromagnetism in hcp-Fe (Wei & Gilder, 2013). Some theoretical treatments predict antiferromagnetic ordering of hcp-Fe (Ono et al., 2010; Steinle-Neumann et al., 2004), causing further confusion.

The discrepancy among the experimental and theoretical results leaves open the magnetic state of hcp-Fe. This is why Wei et al. (2017) measured Mössbauer spectra and the stepwise acquisition of saturation isothermal remanent magnetization (SIRM) on the same sample of polycrystalline, multidomain iron metal powder in a diamond anvil cell across the bcc to hcp phase transition at room temperature. A good correlation was found between the area of the Mössbauer sextet components and SIRM within the bcc stability field. However, above ~15 GPa, sextet peaks were no longer detectable whereas magnetic remanence persisted. Magnetic remanence intensity divided by the percentage of remaining bcc-Fe, deduced from the fractional area of the sextet, attained maxima at pressures near the boundaries of the hysteretic transition. The maxima were attributed to strain-related magnetostriction effects originating from distorted bcc-hcp iron.

In this contribution, we again confront two different experimental methods on the same sample using the same pressure medium to understand how both techniques detect the magnetic response through the phase transition in kamacitic, FeNi alloys. We present magnetic remanence experiments on bcc FeNi alloys (Fe92Ni8, Fe87Ni13, and Fe84Ni16). For Fe84Ni16, we made X-ray magnetic circular dichroism (XMCD) measurements at the Fe K-edge together with X-ray absorption spectroscopy.

2. Experimental Procedure and Results

2.1. Sample Characterization

Three compositionally distinct FeNi alloys were synthesized by weighing Fe (Sigma-Aldrich, >97% purity) and Ni (Goodfellow, 99.5% purity) powder, mixing them together in alumina crucibles, melting the mixture in a vertical gas mixing furnace (GERO) at 1,600°C in an argon atmosphere for 1 h, and then quenching the melt in a distilled water bath in air. Electron microprobe (CAMECA SX100) analyses yielded Ni weight percentages of 8.4 ± 0.7, 12.7 ± 0.9, and 16.4 ± 0.8 for the three synthesized alloys, which are referred to as Fe92Ni8, Fe87Ni13, and Fe84Ni16, respectively. Powder diffraction using an X-ray source wavelength of 0.709 Å (Mo kα1) identifies solely bcc structures in all three alloys (Figure 1a). Curie temperatures, measured with a Mag-Instruments, variable field translation balance in a 36 mT field, are 723°C, 674°C, and 625°C for Fe92Ni8, Fe87Ni13, and Fe84Ni16, respectively, consistent with theoretically determined Curie temperatures of the bcc-Fe-Ni alloys (Figure 1b) (Chuang et al., 1986). The thermomagnetic curves exhibit no deflections at lower temperatures, which contradicts potential contributions of parasitic magnetic phases like pure nickel (Figure 1b). Back-scattered electron microprobe images reveal small islands of a less dense (darker) phase that was identified as wüstite from the chemical compositions (Figures 1c and 1d). Magnetic hysteresis loops measured at room temperature with a PMC Micromag 3900 vibrating sample magnetometer define low (<10 mT) bulk coercivities and low (<0.1) remanence ratios, characteristic of multidomain material (Figure 1b).

2.2. Magnetic Remanence

In each experiment concerning magnetic remanence (LMU-Munich) several FeNi alloy grains, <80 μm/grain in the long axis direction, were loaded with silica gel and ruby spheres into a circular chamber in a rhenium gasket situated within a pressure cell consisting of nonmagnetic BeCu metal and moissanite anvils with culets 400 μm in diameter. Further details on the cell can be found in Gilder and Le Goff (2008). The gasket’s initial thickness of 250 μm was precompressed to 150–180 μm, and then a hole 150–200 μm in diameter was drilled by electrolysis in the center of the indentation, which served as the sample chamber. Ruby fluorescence spectroscopy was used for pressure measurements (Coherent Cube 405 nm laser, Princeton Instruments (PIXIS) charged coupled device, 150 mm, ARC SpectraPro spectrometer) before and after
each experiment. The laser was focused on individual rubies lying near the center and at the edge of the sample chamber to obtain maximum and minimum pressure values to estimate pressure gradients. Both the average and peak pressures are provided in Table 1; all plots and analyses presented herein use the average pressures.

The stepwise acquisition of isothermal remanent magnetization was measured at each pressure step (Figure 2). Static (direct current) fields were applied in the plane orthogonal to the compression direction of the moissanite pistons. Pole pieces of the electromagnet were constructed so they could enter the housing of the pressure cell and approach the sample region as close as possible. The distance between the pole pieces was held constant for each field application in order to ensure linearity between applied current and desired field, which was calibrated with a Hall probe. The initial step was to apply a 370 mT magnetic field in the −y-axis direction, where the x-y-axis lies in the plane of the sample parallel to the culet plane, and the z-axis is perpendicular to the culet plane. Once the field on the electromagnet was reduced back to 0 mT, we removed the cell from the electromagnet and then placed the cell into the 4.2-cm diameter bore of a three-axis, superconducting (SQUID) magnetometer (2G Enterprises Inc.) to measure the magnetic remanence vector. This first data point is considered as the starting point of the experiment and labeled as 0 mT. We then flip the polarity of the field on the electromagnet and then stepwise increase the applied field intensity in the +y-axis direction. The remanence is measured with the magnetometer at each applied field increment until reaching 370 mT. An identical experimental procedure using the same cell with an empty
Table 1
Experimental Data for bcc Fe-Ni Alloys From This Study

|       |       |       |       |       |       |
|-------|-------|-------|-------|-------|-------|
| $P_{\text{ave}}$ (GPa) | $P_{\text{max}}$ (GPa) | SIRM ($\times 10^9$ Am$^2$) | Bcr (mT) | $S_{\text{corr}}$ ($\times 10^{-3}$) | SIRM$_{\text{norm}}$ | h/d |
|-------|-------|-------|-------|-------|-------|-------|
| Fe$_{92}$Ni$_8$ |       |       |       |       |       |       |
| 0.4   | 0.4   | 11.1  | 20.2  | 0.89  | 1.0  | 0.9  |
| 5.4   | 5.7   | 12.9  | 21.5  | 0.98  | 1.1  | 0.8  |
| 8.0   | 8.3   | 19.6  | 22.3  | 1.12  | 1.4  | 0.6  |
| 10.1  | 10.5  | 30.4  | 17.8  | 1.30  | 1.9  | 0.5  |
| 13.5  | 14.3  | 81.6  | 23.0  | 1.53  | 4.3  | 0.4  |
| 17.0  | 18.1  | 99.9  | 26.8  | 1.77  | 4.5  | 0.3  |
| 19.8  | 21.2  | 73.9  | 27.2  | 1.92  | 3.1  | 0.3  |
| 23.0  | 24.8  | 41.4  | 30.5  | 2.08  | 1.6  | 0.3  |
| 20.6  | 22.3  | 42.9  | 29.7  | 2.08  | 1.7  | 0.3  |
| 17.0  | 18.5  | 46.4  | 29.3  | 2.09  | 1.8  | 0.3  |
| 12.3  | 13.9  | 75.3  | 26.9  | 2.08  | 2.9  | 0.3  |
| 9.5   | 10.6  | 117.4 | 25.1  | 2.08  | 4.5  | 0.3  |
| 6.5   | 7.4   | 82.7  | 17.9  | 2.08  | 3.2  | 0.3  |
| 3.9   | 4.4   | 46.0  | 12.8  | 2.08  | 1.8  | 0.3  |
| 0.0   | 0.0   | 45.6  | 14.2  | 2.10  | 1.8  | 0.3  |
|       |       |       |       |       |       |       |
| Fe$_{87}$Ni$_{13}$ |       |       |       |       |       |       |
| 0.2   | 0.2   | 8.4   | 27.5  | 0.89  | 1.0  | 0.9  |
| 3.9   | 3.9   | 11.9  | 27.4  | 0.94  | 1.3  | 0.8  |
| 7.7   | 7.9   | 18.0  | 17.5  | 1.32  | 1.4  | 0.5  |
| 11.7  | 12.3  | 50.5  | 17.4  | 1.80  | 3.0  | 0.3  |
| 15.4  | 17.4  | 67.6  | 27.1  | 2.11  | 3.4  | 0.2  |
| 19.4  | 23.0  | 48.0  | 27.9  | 2.13  | 2.4  | 0.2  |
| 14.6  | 18.5  | 49.4  | 30.9  | 2.13  | 2.5  | 0.2  |
| 11.1  | 14.5  | 58.6  | 28.4  | 2.13  | 2.9  | 0.2  |
| 8.6   | 11.6  | 75.3  | 24.8  | 2.13  | 3.7  | 0.2  |
| 4.7   | 6.4   | 79.2  | 18.9  | 2.13  | 3.9  | 0.2  |
| 0.0   | 0.0   | 59.3  | 12.9  | 2.10  | 3.0  | 0.2  |
|       |       |       |       |       |       |       |
| Fe$_{84}$Ni$_{16}$ |       |       |       |       |       |       |
| 0.2   | 0.2   | 10.8  | 22.8  | 0.85  | 1.0  | 1.0  |
| 4.7   | 5.3   | 13.0  | 27.3  | 0.91  | 1.1  | 0.9  |
| 7.5   | 8.1   | 16.1  | 24.6  | 1.13  | 1.1  | 0.6  |
| 11.7  | 12.3  | 53.4  | 25.7  | 1.42  | 3.0  | 0.5  |
| 14.8  | 16.1  | 67.7  | 35.1  | 1.68  | 3.2  | 0.3  |
| 18.5  | 20.5  | 23.7  | 33.1  | 2.11  | 0.9  | 0.2  |
| 20.4  | 23.3  | 18.4  | 23.6  | 2.02  | 0.7  | 0.3  |
| 24.1  | 26.8  | 14.6  | 23.6  | 2.00  | 0.6  | 0.3  |
| 21.1  | 24.8  | 20.4  | 24.0  | 2.01  | 0.8  | 0.3  |
| 18.1  | 21.2  | 23.0  | 22.5  | 2.14  | 0.8  | 0.2  |
| 14.9  | 17.2  | 29.6  | 29.4  | 2.03  | 1.1  | 0.3  |
| 10.8  | 13.0  | 65.5  | 33.2  | 2.08  | 2.5  | 0.3  |
| 7.8   | 9.2   | 112.9 | 30.1  | 2.02  | 4.4  | 0.3  |
| 5.8   | 6.8   | 103.6 | 28.4  | 2.05  | 4.0  | 0.3  |
The gasket (no sample) is subsequently subtracted from the backfield curves measured with the loaded cell (with sample). We then change the pressure and repeat the process on the same sample-cell configuration. As the pressure is regulated by manually turning screws, it is difficult to prescribe specific pressures, so they vary among experiments.

The backfield curves provide two magnetic parameters at each pressure step. First, the coercivity of remanence (Bcr) is defined as the magnetic field in mT that cancels out the remanent magnetization. This is the applied field where the magnetic moment equals 0 Am$^2$ on the backfield curves (Figure 2). Provided that the sample becomes fully saturated at higher magnetic fields, one can calculate the saturation isothermal remanent magnetization (SIRM, in units of Am$^2$). The data in Figure 2 are consistent with a fully saturated sample, as the backfield curves are flat at the highest field steps; we averaged the moments from the last three field increments of the backfield curves to calculate SIRM.

In the experiments reported here, pressure was progressively raised from 0 to 19.3–24.1 GPa and then progressively decompressed back to ambient conditions. Figure 3a plots the absolute change in SIRM for the three samples. The curves show a high degree of similarity with an increase in SIRM up to 13–18 GPa followed by a decrease at higher pressures. The maximum peak in magnetization intensity upon compression occurs at lower pressures as Ni concentrations increase. Although magnetizations decrease at higher pressures into the hcp stability field, a finite magnetization clearly persists. Upon decompression, magnetization intensities increase with decreasing pressure until a maximum is reached in the 6–10 GPa range, where after the intensities decrease until full decompression. The peaks in magnetization upon decompression generally occur at lower pressures proportional to the Ni concentration; the intensity peaks are higher upon decompression than upon compression.

We can compare these results with those of pure Fe (Fe$^{100}$Ni$^{0}$) powder from Wei and Gilder (2013) as the sample type and pressure medium are very similar to those for the kamacitic FeNi experiments in this study. Because magnetization is mass dependent, and given that the masses of samples are unknown in our experiments, relative values are used for SIRM for cross correlation purposes ($S_{\text{corr}} = 8.36 \times 10^{-4} (h/d)^{0.66}$; correction made to the SIRM data to account for the change in demagnetizing factor due to the increasing degree of oblateness. SIRM$_{\text{norm}}$ is the SIRM normalized by the initial value after accounting for $S_{\text{corr}}$, e.g., $[(S_{\text{corr}}/S_{\text{corr}})_{p}]/(S_{\text{corr}}/S_{\text{corr}})_{i}]$).
fect stemming from charge ordering, etc. Sample geometry remains fairly constant on the decompression path with respect to the highest pressure step; changes in magnetic remanence going down-pressure can therefore be directly compared with respect to the highest-pressure step independent of a correction factor. Although the increase in magnetization is higher for pure Fe, the dual peaks upon compression and decompression are comparable, plus the peaks for purer Fe phases occur at higher pressures than for Ni-richer phases.

Figure 2. Backfield magnetization acquisition curves for (a) and (b) Fe$_{92}$Ni$_{08}$, (c) and (d) Fe$_{87}$Ni$_{13}$, and (e) and (f) Fe$_{84}$Ni$_{16}$. Each point on every curve represents an independent measurement made in a null magnetic field inside a cryogenic magnetometer after applying, then annulling, the indicated magnetic field outside the magnetometer before each measurement. The figures on the left show the up-pressure curves and on the right, down-pressure.
X-ray absorption fine structure (XAFS) arises from the absorption of X-rays by atoms in relation to their chemical and physical states; thus, XAFS spectra are sensitive to oxidation state, coordination chemistry, atomic distances, etc. (Newville, 2014). A circularly polarized X-ray beam can further probe the magnetic moment of the atom, which is why X-ray magnetic circular dichroism (XMCD) and XAFS data are often collected on the same sample in high-pressure experiments. XAFS and XMCD at the Fe K-edge were measured on beamline ID12 at the European Synchrotron Radiation Facility in Grenoble, France. The high-pressure, low-temperature, and high-field end-station equipped with superconducting magnet (B up to 6 T) was used to record XMCD spectra; a multipurpose end station was used to record the XAFS spectra during the experiment (Rogalev & Wilhelm, 2015; Wilhelm et al., 2016). The ability to apply very high fields during the experiment makes beamline ID12 specifically useful, as one goal of our study was to understand how applied field intensity might influence the results.

The beam was focused using identical X-ray refractive lenses in front of each experimental station. The spectra were recorded using total fluorescence yield collected via a Si photodiode mounted in backscattering geometry. To reduce possible elastic scattering contribution, Mn88Ni12 foils were inserted in front of the photodiode of the multipurpose (40 μm) and of the high-field (20 μm) experimental stations. For 3d transition metals, the K-edge XMCD signal corresponds to the magnetism associated with the angular momentum of the 4p-orbital electrons. As the latter originates from coupling with spin polarized 3d states, XMCD at K-edge can be expected to reflect the overall magnetism carried by Fe. By combining XAFS and XMCD, we can simultaneously detect structural changes and the magnetism of Fe atoms (Mathon et al., 2004; Monza et al., 2011).

The experiments used a membrane type cell with diamonds whose culets were 600 μm in diameter. To reduce absorption, the diamond facing the incoming X-ray beam was partially perforated down to 100-μm thickness. A 200 μm hole bored in a work hardened rhenium gasket (h = 80 μm) was loaded with Fe84Ni16 together with Si gel and rubies, identical to the SIRM experiments; rubies were placed on the side with the solid, nonperforated diamond. We used Fe84Ni16 due to its lower bcc-hcp transition pressure (∼9–10 GPa, Huang et al., 1988 and ∼12 GPa, Akahama et al., 2020) than that for Fe100Ni0, as the highest pressure attainable by the partially perforated diamond was uncertain. We first measured the XAFS and XMCD at the K-edge of Fe in the diamond cell at ambient P and T as a function of applied field strength in order to know

**Figure 3.** (a) Saturation isothermal remanent magnetization (SIRM) as function of pressure for Fe82Ni18, Fe87Ni13, and Fe84Ni16. (b) Normalized SIRM curves of the same data as in (a) together with the data from Fe100Ni0 (Wei & Gilder, 2013) after accounting for the change in shape of the samples. Dashed lines indicate decompression path.
the field intensity required to attain saturation (Figure 4a). Accordingly, 2.5 T fields were used in the subsequent XMCD experiments to ensure full saturation. This agrees with our vibrating sample magnetometer measurements on Fe foil, which saturated at 1.3–1.5 T perpendicular to the long axis of the foil (Figure 4a). Both the XAFS spectral features and the XMCD signal at the Fe K-edge of Fe$_{84}$Ni$_{16}$ are typical of bcc-Fe.

The cell was then loaded in the multipurpose end station and XAFS spectra were recorded at several pressures upon compression and decompression (Table 2). Following Mathon et al. (2004), we took the first derivative of the XAFS spectra and measured the peak amplitudes of the derivative signal at around 7,118, 7,135, 7,205, and 7217 eV to reflect the proportion of the bcc phase in the cell relative to the 0 GPa peak heights. Similarly, peaks of the XMCD spectra between 7100 and 7122 eV were used to track the magnetism of Fe (Figure 4b). XAFS and XMCD for Fe$_{84}$Ni$_{16}$ were then measured at the highest pressure 13.8 GPa and during decompression at 6.9 and 4.2 GPa. XMCD peaks were smaller under pressure, but a signal was still observable at 13.8 GPa indicating that the magnetism of Fe did not fully disappear at that pressure.

### 3. Discussion

Figure 5a presents the relative amount of bcc-Fe in the cell as a function of pressure according to the XAFS data with the average uncertainties ($1\sigma$) at each pressure listed in Table 2. The bcc signal begins declining at 10.8 GPa, with 15% bcc-Fe remaining by 13.8 GPa, in good agreement with room T experiments on Fe$_{90}$Ni$_{10}$ by Huang et al. (1988). Linear extrapolation suggests no bcc remains by 14.6 GPa. The hysteretic nature of the transition shown here is consistent with published reports (Barge & Boehler, 1990; Bassett & Huang, 1987; Mao et al., 1967; Taylor et al., 1991; Wang & Ingalls, 1998). We assume that the XMCD signal at 0 GPa stems solely from ferromagnetic bcc Fe$_{84}$Ni$_{16}$, thus the relative strength of the XMCD signal represents the magnetic contribution from bcc Fe$_{84}$Ni$_{16}$ (Figure 5a). Uncertainties on XMCD are hard to estimate as the signal is derived from a single peak at each pressure. The XMCD contribution relative to bcc phase fraction for Fe$_{84}$Ni$_{16}$, albeit limited, are consistently higher (above) the XAFS data at each pressure step.
The XMCD experiments agree with the magnetic remanence data in two fundamental ways. First, magnetism persists in a finite pressure range above the discontinuous part of the bcc → hcp transition. Second, the relative proportion of XMCD/bcc-Fe and SIRM/bcc-Fe indicates the relative contribution of bcc-Fe to the magnetic signal observed by each technique (Figure 5b), and although the XMCD data are sparse, the relative pattern from both XMCD and SIRM is compatible in suggesting the magnetization efficiency (magnetization per bcc-Fe) is higher at 13.8 GPa versus the starting (0 GPa) conditions and is further heightened at the boundary of the hcp-out to bcc-in transition upon decompression. The fact that all four FeNi alloys presented herein consistently display SIRM peaks at the boundaries of the bcc → hcp and hcp → bcc transitions, and that the peaks generally shift to lower pressures with increasing Ni concentration, suggest that the enhanced remanence is an intrinsic property of FeNi alloy.

Whether magnetism persists above the bcc → hcp phase transition and whether the moment collapse precedes or coincides with the structural transition are controversial questions with scattered answers from XAFS/XMCD studies (Baudelet et al., 2005; Iota et al., 2007; Ishimatsu et al., 2007; Mathon et al., 2004; Monza et al., 2011). We suggest that differences in the applied fields used in the XMCD experiments can explain the discrepancies among the results. XMCD experiments performed in permanent fields ranging from 0.3 to 0.6 T using 4–5-μm thick iron foil samples (Baudelet et al., 2005; Iota et al., 2007; Mathon et al., 2004), or Fe powder compressed to 3 μm in thickness (Ishimatsu et al., 2007), found sharp magnetic transitions with no trace of ferromagnetism in the hcp stability region. On the other hand, K-edge XMCD experiments on Fe nanoparticles by Monza et al. (2011) in a 1.3 T field found a ferromagnetic signal that persisted to 40 GPa, well into the hcp region, consistent with our results.

As indicated in Figure 4a, >1.5 T fields are necessary to fully saturate FeNi alloy along the z-axis, perpendicular to the culet plane of the cell, as opposed to ca. 0.3 T parallel to it. The 2.5 T fields used in our XMCD experiments sufficiently saturated the Fe₈₄Ni₁₆ powder along the z-axis direction (Figure 4a), while the experiments by Monza et al. (2011) were close to saturation. This also explains why the SIRM method is a robust indicator of the magnetic state of the samples, since the external field is applied parallel to the long axis (x-y) dimension of the sample chamber, where 0.37 T fields were more than enough to achieve full saturation (Figures 2 and 4a), and the remanent magnetization is measured in the same direction (Wei & Gilder, 2013). Lack of saturating fields can likely explain why Mössbauer spectra fail to resolve persistent ferromagnetism in Fe₁₀₀Ni₀ and Fe₉₀Ni₁₀ above the bcc-out to hcp-in transition (Cort...
et al., 1982; Nasu et al., 2002; Papandrew et al., 2006; Taylor et al., 1991), whereas SIRM is still measurable (Wei et al., 2017).

Degree of hydrostaticity related to the pressure medium and/or sample synthesis/origin may play a role in explaining the incongruous experimental results, yet we argue that such effects will be secondary. In our study, the samples were characterized by SEM and Curie temperature measurements (Figure 1); such data do not exist in most high-pressure studies on the bcc-hcp transition, so it is difficult to describe how sample genesis influences the measurements. Pressure cycling experiments on the magnetic properties of magnetite showed no dependency on the origin or texture of the sample (natural vs. synthetic) (Biał o et al., 2019).

Our results raise two important points: (1) magnetic remanence is clearly enhanced at the transition boundaries and (2) magnetic remanence is measurable well into the hcp stability region (e.g., the region traditionally considered as hcp-only). The transformation process from one phase to the other is non-diffusive and martensitic (Giles et al., 1971) that follows the Burgers path (Dewaele et al., 2015; Dupé et al., 2013; Merkel et al., 2004). The X-ray diffraction and transmission electron microscope observations of Dewaele et al. (2015) concerning the deformation and phase transformation of Fe under pressure can readily explain the results. Dewaele et al. (2015) found that elastic stresses increased in the regions where bcc-Fe and hcp-Fe coexist, partly due to the lattice parameter mismatch between the two phases and partly due to interaction stress between bcc and hcp grains. Moreover, X-ray diffraction peak broadening suggests elastic microstresses can be attributed to a considerable increase in dislocation density.

Our SIRM data suggest that strained bcc-Fe has a higher remanent magnetization than unstrained bcc-Fe. On the up-pressure path, both dislocation density and elastic stresses at the bcc-hcp interface increase until the proportion of bcc and hcp components become approximately equivalent, which results in the peak in SIRM. At higher pressures, hcp increases relative to bcc, and the magnetization decreases, although the persistence of defects in the remaining, defect-riddled bcc-Fe allows ferromagnetism to persist into the hcp-Fe region. This “martensitic” bcc-Fe can persist locally in the hcp stability field until all trace of martensite is fully removed (Zarkevich & Johnson, 2015). Going down in pressure, elastic stresses again increase at the hcp-bcc interface as bcc-Fe returns, until the proportion of hcp-bcc becomes equivalent, producing the remanent magnetization peak in the down-pressure path. The down-pressure peak is higher than the up-pressure peak as the concentration of defects is higher. Going further down-pressure, the remanence decreases with the decreasing presence of hcp-Fe. Remanence remains higher upon full decompression due to the defect state of bcc-Fe, whereas the initial conditions had significantly lower defect concentrations.

We previously argued that the persistence of magnetism at pressures >18 GPa was due to a distorted hcp phase (Wei & Gilder, 2013; Wei et al., 2017). Indeed a recent combined X-ray emission spectroscopy and neutron diffraction study is consistent with this conclusion (Lebert et al., 2019). However, we now think it is more likely that the remanent magnetization originates from nonconverted bcc-Fe that goes undetected by XAFS, Mössbauer, XRD, etc. techniques, although we cannot completely rule out the possibility that distorted hcp has a slight magnetization.

In several ferrimagnets, such as Ti-rich titanomagnetite (Fe_{3−x}Ti_{x}O_4) or pyrrhotite (Fe_{1−x}S), pressure leads to an increase in coercivity (Gilder & Le Goff, 2008; Gilder et al., 2011), which is not the case for kamacite. This is likely due to the much larger saturation moment of FeNi compared to the other phases. For example, pressure systematically increases coercivity proportional to the Ti concentration in titanomagnetite while the saturation moment decreases with increasing Ti. The coercivity of highly strained Fe_{90}Ni_{10} manufactured by mechanical alloying only slightly increases as a function of milling time (Volk et al., 2018), on the same order of magnitude as that found here (Table 1).

It should be kept in mind that the pressure induced bcc-hcp transition will spread over a finite range of pressures, with a magnetic bcc tail persisting above the transition line (Zarkevich & Johnson, 2015). That defects can stabilize magnetism beyond typically accepted phase boundaries is not unique to FeNi alloys. For example, the persistence of ferrimagnetism below the Morin transition in hematite (Fe_{2}O_{3}) (e.g., Néel & Pauthenet, 1952) has been argued to result from the presence of defects (Dunlop, 1971; Özdemir & Dunlop, 2006). Biał o et al. (2019) demonstrated how defects and permanent strain of the crystal lattice influence the Verwey transition in magnetite (Fe_{3}O_{4}). The Verwey transition temperature increases in pressure cycled magnetite as a function of dopant concentration, whereas the transition temperature decreases when...
measured under pressure. This is because the magnetic response is highly sensitive to domain wall pinning whereas the electronic response is not. This results in a slightly differential expression of the Verwey transition temperature in response to strain.

4. Conclusions

High-pressure experiments at room temperature on Fe$_{92}$Ni$_{08}$, Fe$_{87}$Ni$_{13}$, and Fe$_{84}$Ni$_{16}$ show distinct enhancements in remanence at the bcc → hcp and hcp → bcc transition boundaries, which we attribute to strain from a lattice mismatch between the two phases (Dewaele et al., 2015). Strain from defects arising from the martensitic transition provides further enhancement of the magnetic remanence. The defect-related enhancement allows the ferrimagnetic character of bcc-Fe to persist into the hcp stability field. Most physical techniques (XMCD, Mössbauer, etc.) that are used to probe the magnetism of Fe alloys under pressure find an absence of exchange-coupled magnetism past the traditional bcc-hcp transition pressure. This is because those measurements were carried out perpendicular to the maximum dimension of the samples in relatively low fields (0.3–0.6 T), whereas >1.3 T fields are required to achieve full saturation. The two experiments (Monza et al., 2011 and the present study) employing strong (≥1.3 T) external fields conclude ferromagnetism can indeed persist well above the typically accepted transition pressures. Magnetic fields are applied parallel to the long axis of the sample in the saturation magnetization experiments (SIRM), where the sample becomes fully saturated by 0.1–0.3 T, with the remanence being measured in the same direction. This explains why the SIRM technique (Wei & Gilder, 2013; Wei et al., 2017), and others based on magnetic remanence (Gilder & Glen, 1998; Hsieh et al., 2018; Lesik et al., 2019), serve as sensitive probes of the magnetic state of material under pressure and consistently find the persistence of ferromagnetism into the hcp stability field.

The implications are important for the Earth and planetary sciences. For one, absolute or relative palaeointensity estimates from meteorites containing FeNi alloys will likely be underestimated as any creation of defects after the acquisition of remanence will yield disproportionately higher thermoremanent or anhysteretic remanent acquisition with respect to the original, relatively defect-free material. In other words, because pressure cycling increases the potential for magnetic remanence acquisition (Figure 3), shocked FeNi-bearing rocks/meteorites will acquire higher magnetic remanences when exposed to applied magnetic fields relative to the initial state when the remanence was initially acquired (preshock). This will lead to shallower slopes on an Arai or pseudo-Arai plot, thereby yielding lower than expected (relative) palaeointensity estimates (Volk & Gilder, 2016). The persistence of remanence could be important for the magnetic anomalies or magnetic field behavior originating in the interior regions, including the solid cores, of some planets or moons.

Data Availability Statement

Data from this study can be downloaded at https://data.mendeley.com/datasets/9r93pgt9rt/2 and https://data.mendeley.com/datasets/bdw8fw454/1.

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