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Hardware, methodology and applications of 2⁺D backscatter Mössbauer spectroscopy with simultaneous x-ray and γ -ray detection

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Abstract

A unique method is presented for the acquisition and analysis of ⁵⁷Fe backscatter Mössbauer spectra with simultaneous detection of the resonant 14.4 keV γ -rays and the characteristic 6.4 keV x-rays, using a custom-built multi-parameter analyser constructed on the basis of commercial analogue to digital converters and high-speed digital latches. The system allows for the simultaneous registration of Doppler-modulation velocities and photon energies, with up to 4096 and 8192 digital channels respectively. This arrangement is in contrast to most related systems, which detect at a single narrow energy window per detector. Samples of arbitrary atomic structure, morphology and surface topography can be studied without altering the setup or the analysis procedure, provided that the samples are at least micrometre sized. The hardware and software that are used to acquire data with minimal dead time are described and the custom and self-contained methods for post-measurement energy discrimination, background correction and velocity-axis folding are discussed. The data are fit using a general Hamiltonian model for the nuclear energy levels of ⁵⁷Fe and a quantum mechanical description of the angular momentum coupling is utilised, with consideration of the crystalline and chemical disorder of the sample under examination. Three examples of distinct magnetic systems, with thicknesses ranging from 5 μ m to 6 mm, that were studied using this method are presented, these are: an amorphous CoFeB-based ribbon with ultra-soft coercivity for high-frequency applications, magnetically hard Nd-Fe-B thick films on Si substrates, examined in both as-deposited and annealed states, and a sample from the nickel-rich iron meteorite NWA 6259 that contains the atomically ordered, elevated coercivity, *L*1₀ phase of FeNi, tetrataenite.

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The wide applicability and usefulness of this method is thus demonstrated on three distinct sample morphologies that required little to no surface preparation prior to examination.

Supplementary material for this article is available [online](#)

Keywords: backscatter Mössbauer spectroscopy, conversion x-ray Mössbauer spectroscopy, multi-parameter analysis, energy-resolved detection, iron fluorescence, full-Hamiltonian fitting, atomic crystalline order

1. Introduction

The underlying theory of the Mössbauer effect and the details of the Mössbauer spectroscopy (MS) technique are presented in detail in the literature [1, 2], we reiterate some of the theoretical aspects in the supplementary material. The basic process in the case of ^{57}Fe involves the Doppler-modulation of 14.4 keV photons emitted by a radioactive ^{57}Co source as it decays to ^{57}Fe , to measure hyperfine shifts in the nuclear energy levels of the naturally occurring ^{57}Fe in a sample, see figure 1, with the practical implementation varying depending on the specific application. The narrow natural linewidths ($\Gamma_0 \approx 5$ neV) of the nuclear energy levels lead to a startling relative sensitivity of the technique approaching 10^{12} .

In classic transmission MS (TMS), the absorption of the 14.4 keV photons constitutes the signal, with a number of troughs in the signal where the Doppler-shifted energy of the photon from the oscillating source matches the hyperfine split nuclear energy sub-levels of the ^{57}Fe nuclei in the sample. Backscatter MS (BSMS) records the emission from the ^{57}Fe nuclei in the sample in the backwards direction after they have been excited by the γ -ray from the source. Re-emission of the 14.4 keV γ -ray can be measured, but the ^{57}Fe nuclei can also eject inner-shell electrons through internal conversion processes [3, §9.5] and the accompanying characteristic x-rays, illustrated in figure 2. In fact, for ^{57}Fe , 90% of excited nuclei decay by internal conversion [4]. Measurement of conversion electron MS (CEMS) or conversion x-ray MS (CXMS) are both common alternatives to traditional Mössbauer, advantages include the ability to measure otherwise prohibitively thick samples and surface sensitivity, particularly in the case of CEMS. The surface sensitivity of CEMS does require some degree of surface preparation of the sample to obtain proper results, limiting the applicability of this version of MS. Simultaneous measurement of the backscattered γ -rays and x-rays has most notably been performed by Klingelhöfer and the MIMOS group [5], with their spectrometer being used to investigate paint composition in ancient Greek pottery [6] and the composition of rocks on Mars (*in situ*) [7], among other interesting applications. Simultaneous CEMS, CXMS and TMS has also been performed, requiring a unique setup to accommodate the three detectors [8].

In this work, rather than recording specific decay products at discrete energies, we record the entire fluorescence spectrum of the ^{57}Fe nuclei in the sample, as a function of the Doppler-modulation velocity, resulting in a 2D data

matrix. The continuous energy range recorded includes the characteristic x-rays and γ -rays, as well as the plethora of non-resonant photons. This 2D approach was first described by Maltsev *et al* [9] and first used in the backscatter geometry very recently by Jahns *et al* [10]. Recording the entire fluorescence spectrum allows for optimal post-acquisition energy discrimination and background correction, as well as a degree of surface sensitivity, without the sample-preparation requirements of CEMS, while the use of a single detector renders the alteration of the geometry to elucidate the hyperfine field direction trivial. The apparatus and the steps employed in the data analysis are described in detail in the following section. Three distinct examples of the technique in action are described to showcase its effectiveness and wide applicability, conferring far more accessibility to this type of materials probe than previously available.

2. Methods

2.1. Apparatus geometry

In our novel system, described in detail in this section, data are collected in the backscatter geometry [11] with the source and the detector on the same side of the absorber as in figure 3.

The absolute signal intensity collected in the backscatter geometry is reduced relative to that measured in the transmission geometry due to the multitude of de-excitation routes for the ^{57}Fe nuclei and their spatially isotropic fluorescence. As an illustrative example, when natural α -Fe is probed in the transmission geometry at normal incidence, a maximum relative intensity of the MS signal of about 27% can be readily achieved. This value may be compared to a maximum conversion of about 20% when α -Fe is probed in the backscatter geometry with an incidence angle of the source photons w.r.t. the surface normal of $A_\gamma \approx 45^\circ$. However, the multiple advantages conferred by virtue of having information in the complete 2D (energy and velocity) variable space should not be understated. One advantage is the ability to correct the background signal using photons that have been detected with off-resonance energies. In a typical acquisition scenario, the off-resonance photons can be a few times more numerous than their resonant counterparts (in unenriched and dilute specimens), allowing for a substantially more accurate subtraction of the background as a function of the velocity. The shape of the background depends primarily on the variation of the steric angles

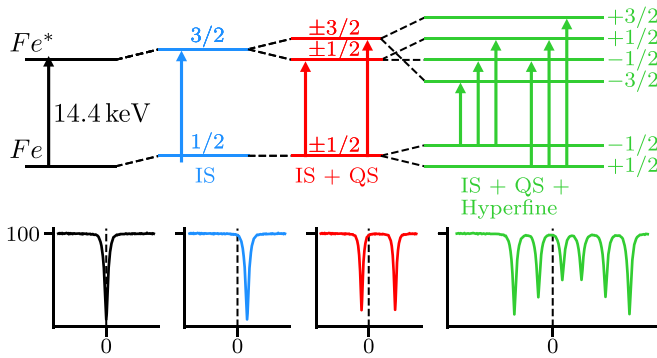


Figure 1. Typical hyperfine splitting of ^{57}Fe MS, with splitting greatly exaggerated. Reproduced with permission from [12].

from which the source and detector ‘see’ the sample surface as the drive oscillates. A second advantage is the depth sensitivity provided by the different mean free paths of the resonant γ -rays and characteristic x-rays: Fleischer *et al* found that the maximum experimentally resolvable depth of resonant photons emitted from an Fe foil was below 50 μm for the 14.4 keV γ -rays and was roughly 20 μm for the 6.4 keV x-rays [7], corresponding to 3–5 times the photon absorption length at the specific energy. As this depth sensitivity cannot be accurately computed analytically, for any realistic sample containing multiple fluorescent and scattering species, comprehensive Monte Carlo simulations should be performed for each specific material and measurement geometry that is being investigated. The resolution varies substantially as a function of the angle of incidence of the primary photons and can reach individual micrometres. When compared with CEMS and its depth-selective version (which can and has been performed with the same acquisition electronics and a different detector in our setup), depth sensitivity can be as high as 10 s of nanometres. While these two electron-based techniques have profound requirements for surface roughness, CXMS and BSMS have no substantial requirements for sample surface preparation. Often macroscopically rough and completely untreated surfaces can be measured successfully, as well as surfaces covered by passivation layers or with polymer protection films. Finally, in contrast to TMS, thick (e.g. $t \geq 0.1$ mm for α -Fe) undiluted samples can be probed (to a certain depth) because the source γ -rays do not need to pass through the absorber.

For calibration, we use an unenriched α -Fe slab. The measured linewidths for transmission spectra were $\Gamma = 0.141$ mm s $^{-1}$ and $\Gamma = 0.172$ mm s $^{-1}$ for the inner four and outer two peaks respectively, close to the natural linewidth. When the same sample was measured for calibration in the backscatter geometry, linewidths of $\Gamma = 0.156$ mm s $^{-1}$ and $\Gamma = 0.188$ mm s $^{-1}$ were obtained for the inner four and outer two peaks, respectively. The linewidths are broader in the backscatter case primarily due to the increased steric angle from which the source and detector ‘see’ the sample. The 14.4 keV energy band is always used for the calibration spectrum in BSMS. Throughout the methods section, the data used as examples are various calibration spectra from α -Fe. Unless very short (minutes) times for the acquisition of calibration

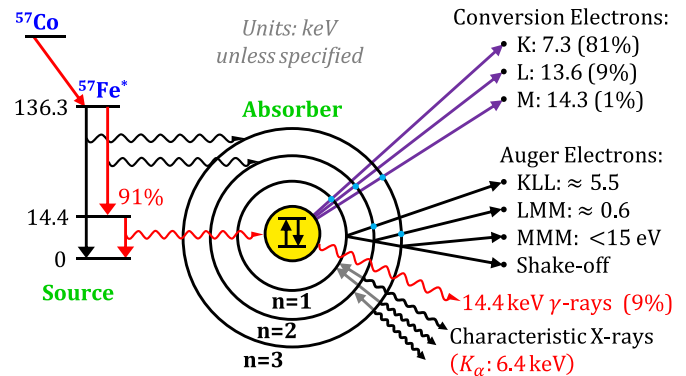


Figure 2. Production of 14.4 keV γ -rays from a ^{57}Co nucleus with absorber products illustrated. Reproduced from [13]. CC BY 4.0.

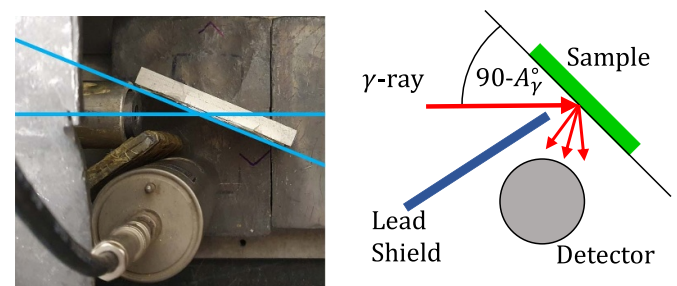


Figure 3. Typical backscatter geometry of the Mössbauer apparatus describe here, where we defined A_γ as the angle of incidence w.r.t. the surface normal. Minimal (graded) Pb shielding is used to allow for the reduction of the sample-detector distance.

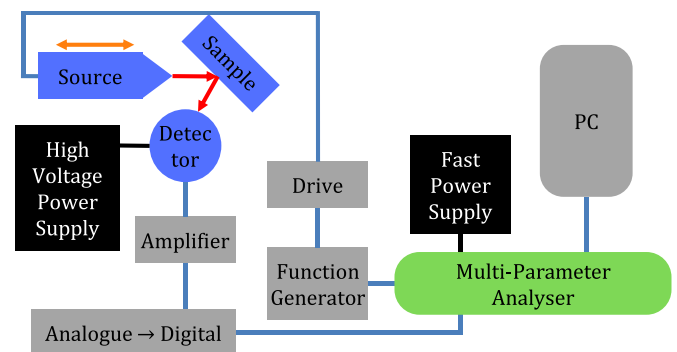


Figure 4. A block diagram showing the key components of the backscatter setup.

spectra are desirable, such as on the surface of Mars [5], the use of highly-enriched ^{57}Fe is not advisable for calibration as additional broadening due to secondary absorption and Compton scattering, among other effects, becomes non-negligible.

2.2. Data Acquisition

In this section, the setup apparatus for data acquisition will be briefly described. A block diagram for the system is shown in figure 4. A source consisting of ^{57}Co embedded in a Rh

matrix produces the γ -rays used to probe the first energy-level transition of ^{57}Fe . This source is engineered to maximise the phonon-free fraction and minimise the magnetic field and electric field gradient at the source nucleus [14]. ^{57}Co decays to excited $^{57}\text{Fe}^*$ by electron capture with a half-life of $\tau_{1/2} = 272$ d and $^{57}\text{Fe}^*$ then de-excites to its ground state, emitting the aforementioned 14.4 keV γ -ray in the process and exhibiting the Mössbauer effect [4]. In our apparatus the radioactivity of the source was $A \approx 2$ GBq when purchased, but after roughly five years this has fallen to $A \approx 0.02$ GBq, meaning significantly more time is required to obtain sufficient statistics, until the source is replaced.

The Mössbauer drive system consists of a function generator (FG) and a reciprocating linear motor on which the source is mounted. The FG produces an $f \approx 25$ Hz triangular wave signal that drives the transducer with constant acceleration within the linear permanent magnet motor. A positional feedback loop is incorporated that corrects discrepancies between the FG signal and the actual motion of the drive, see figure 5(c). The FG has ‘start’ and ‘channel’ digital signals which reset or increment a counter chip in the multi-parameter analyser (MPA), respectively. The FG can utilise up to 4096 digital discretisation channels without impacting the MPA’s dead time, but typically only 512 channels are used, as high-resolution velocity is rarely worth the memory space and processing time [15]. The source oscillates at around 10 mm s^{-1} for ^{57}Fe MS.

The absorber must be placed as close as possible to the detector to maximise the solid angle of the absorber’s isotropic emissions incident on the detector window, figure 3. This proximity has bearing on the necessary background and geometry corrections, as will be discussed in section 2.3. Thin Pb shielding is used between the source and detector, with suitably thick chevroned Pb bricks surrounding the entire apparatus.

A Xe/CO₂ proportional counter is used as the detector [16], operated at a high voltage between 1.5 kV and 2.0 kV, depending on whether maximum efficiency or maximum resolution is desired. The Townsend Avalanche of electrons [17], following an initial ionisation by a photon, provides a built-in amplification of the electronic signal, which allows the detection of individual photons. The magnitude of the current pulse thus produced is proportional to the energy of the ionising photons. This detector type has a relative energy resolution of 10%–15%, confirmed by fitting the fluorescence spectrum of a calibration sample, see figure 6(a).

The current pulses from the detector are first amplified by a charge-sensitive pre-amplifier with a gain of 30 dB before being further amplified by a variable-gain shaping-amplifier (with a typical gain of between 10 dB and 20 dB and shaping time between 0.1 μs and 1 μs). These pulses are then digitised by a fast analogue-to-digital converter (ADC) with a maximum resolution of 8192 digital channels (13 binary bits), but resolution this high is not necessary given the energy resolution of the detector and typically only the most significant 10 bits (1024 channels) are used to reduce the dead time from the $\Sigma\Delta$ -integration in the analogue-to-digital conversion process. The ADC provides analogue upper and lower

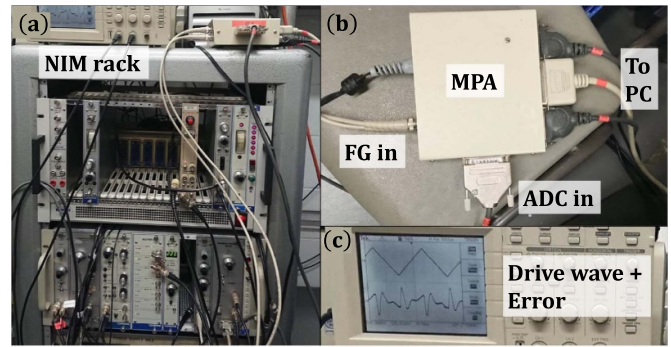


Figure 5. The electronics: Nuclear instruments module (NIM) rack which powers the drive units, amplifiers and ADCs for two setups; an overhead view of the MPA showing the connections and an oscilloscope that tracks the triangular wave from the FG and feedback signal from the drive.

discrimination thresholds on the energy, which is key to minimising the dead time by bypassing the cascade of low-energy excitations and high-energy cosmic or ^{40}K -related photons. The digitised pulse height, proportional to photon energy, is then passed on to the MPA.

The custom-built MPA is at the heart of the setup and consists of a timer-counter chip and an array of high-speed digital latches arranged into 8-bit blocks. The aforementioned FG signals control the counter, with the 512-channel digital velocity value stored in 9 bits. The 10-bit signal from the ADC, encoding the photon energy, is similarly stored. The MPA interfaces with the PC via three IEEE-1284 standard cables, each nominally capable of 8-bit parallel data transmission (up to five of these can be accommodated in principle, providing 40-bit maximal depth). An additional three or four bits are reserved for legacy hardware reasons with these types of connectors. Through low-level (Assembly) coding, the reserved bits can be utilised for data transmission, providing a theoretical 60-bit maximal depth.

The system is controlled by a computer with an Intel Pentium 4 processor (2.8 GHz) running Windows 98: the MPA latches are controlled by custom-written Assembly and C code, running on CPU interrupts (which precede the operating system interrupts), this feature is not readily achievable on modern computer operating systems. Data are read from the MPA using three IEEE-1284 connectors plugged into three (again, up to five) ‘Extended Capability Ports’ on the PC, which offer bi-directional parallel data transfer and direct memory access. Data for each detector event are read directly into the CPU’s L1-cache prior to being buffered in DRAM and are finally written to the hard drive. A rough outline of the data flow is illustrated in figure 7. The described combination of equipment allows for a tested maximum acquisition speed of order 100 kHz with 4 K velocity and 8 K energy resolution, respectively.

The front-end interface is written in LabViewTM and runs concurrently with the data acquisition. The data contain the time of detection, the drive velocity at the time of detection and the photon energy, for each photon that enters the detector. The data are read from the hard drive and each detection event

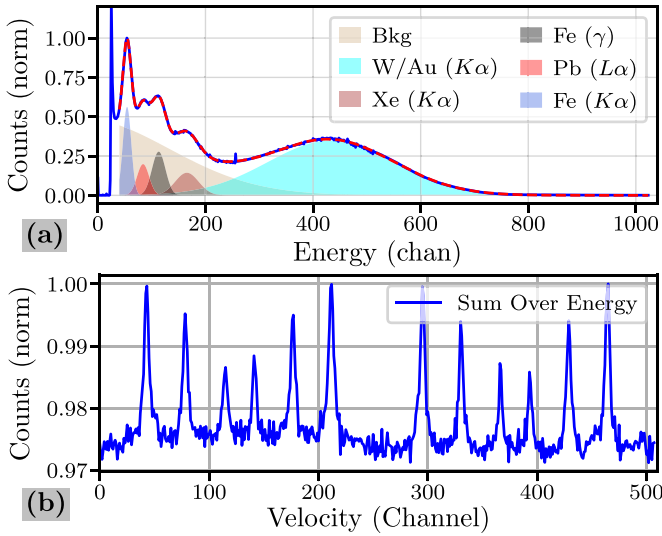


Figure 6. (a) The raw data summed over the velocity axis (fluorescence spectrum) with contributions fit using Gaussian profiles, before the geometry was optimised to remove Pb. (b) The data summed over the energy axis, clearly showing the resonant peaks and systematic background before any processing has been performed.

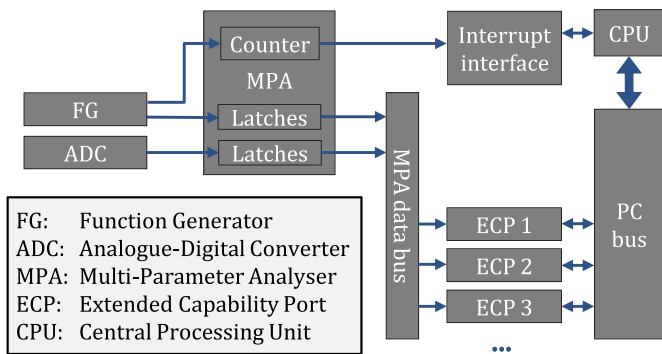


Figure 7. Bus diagram showing the flow of post-digitisation data in the setup.

is binned by its energy and velocity values, resulting in a typically 1024×512 matrix, or histogram. The raw data (figure 8), as well as the averages over the energy and velocity axes of the matrix (figure 6), are displayed in real time to ensure that the discrimination thresholds are set optimally, to determine when sufficient data have been collected and to allow a user determination of the signal-to-noise ratio (SNR) as data acquisition progresses.

2.3. Data pre-processing

Within each energy channel, the middle 20 velocity values are used to normalise the data. These central values correspond to the minimum velocity of the source (bottom of the triangular wave), where the Doppler-shifted energies are far from the resonant energies, which are observed at intermediate velocities. This normalisation thereby emphasises the resonant MS signal. The minimum velocity region is illustrated

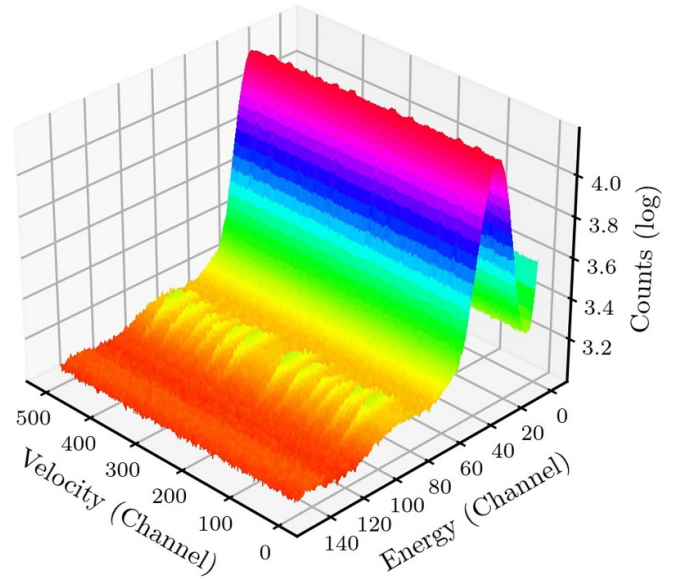


Figure 8. The 3D view of the raw data which is displayed concurrently to acquisition, showing the low-energy region (150/1024 channels). The x-ray and γ -ray peaks are clearly visible, as well as the velocity resonances, for this calibration sample.

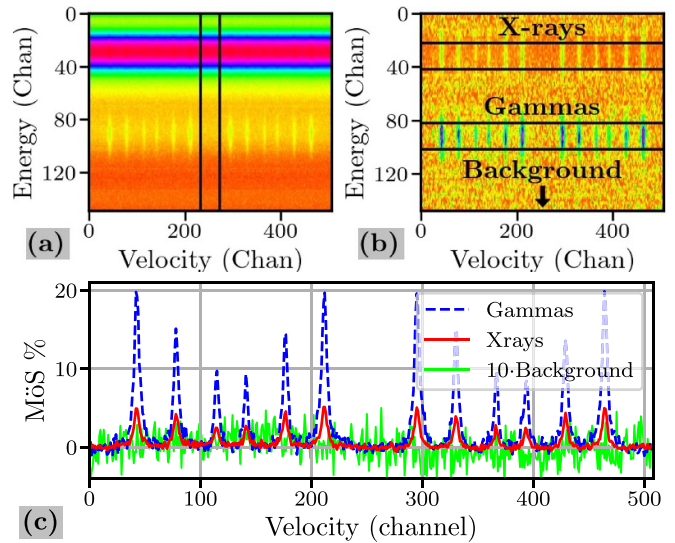


Figure 9. (a) The raw data in the low-energy region with the minimum velocity, off-resonance channels denoted. (b) The normalised data with the x-ray, γ -ray and background energy regions denoted. (c) The three spectra obtained from the energy discrimination process.

in figure 9(a). The data after normalisation are shown in figure 9(b).

To isolate the resonant signals of the characteristic x-rays and γ -rays from the non-resonant background, the energy discrimination bands are manually optimised such that the SNR is maximised; these bands are illustrated in figure 9(b). As a general rule of thumb, the bands extend ± 10 energy channels either side of the resonant peaks at 6.4 keV and 14.4 keV, but can depend on the sample peculiarities. In particular, Cr, Mn, Co, Ni and Cu emit $K\alpha$ x-rays with energies in the range

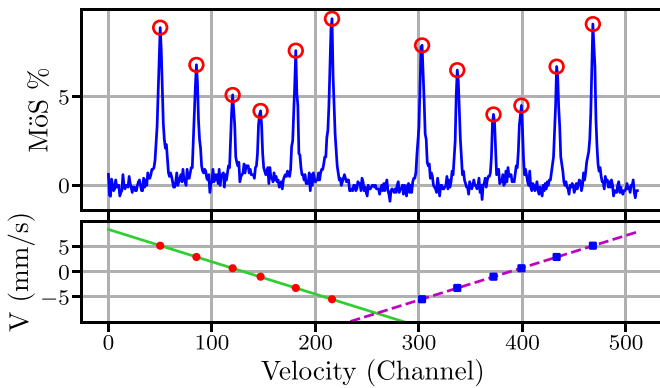


Figure 10. Calibration spectrum and determination of the folding point in the velocity axis by identifying the intersection of lines fit to the positive and negative acceleration regions.

5–8 keV, while the rare-earth elements emit L x-rays in the similar energy range 5–9 keV. Therefore specimens under examination which contain any of the aforementioned elements may benefit from more aggressive energy discrimination. In addition, the L_{α} absorption edge of Pb is at 10.5 keV, a value that lies between the two resonant energies. It is therefore imperative to optimise the geometry of the setup such that the Pb shielding does not overly contaminate the resultant spectrum. Lastly, as the detector contains Xe gas with an anode wire of Au and W, fluorescence from these elements will also be produced, but at energies that are higher than those relevant for MS, see figure 6(a).

A background contribution is present in the overall signal that varies quasi-sinusoidally with velocity. This background signal is due to the relative motion of the source: when the source is closer to the absorber, more photons hit the absorber and at steeper angles. This trend can clearly be seen in figure 9(c), where the isolated background signal is fit with a second-order sinusoid and subtracted from the resonant data. This very natural and effective method of removing the background signal would not be possible without recording the entire energy range and isolating relevant regions.

The velocity channels are converted to units of mm s^{-1} using data obtained from a calibration sample of natural α -Fe. The theoretical peak positions for α -Fe are well known; fitting two straight lines to the measured peak positions as a function of the predicted positions yields the conversion, see figure 10. Unique slopes must be used for the positive and negative acceleration components of the source motion because physically different bipolar transistors control these aspects. In this manner the centre point, or folding axis, of the velocity axis is determined with resolution better than one discrete channel and the positive and negative acceleration spectra can be averaged without spuriously broadening the peaks. The calibration must be repeated whenever the source environment is altered in any way.

2.4. Model

Our *ab initio* mathematical model for fitting the Mössbauer data is derived from a full Hamiltonian description of the

nuclear sub-levels with coupling to the multipole field of the incoming γ -rays from the source, with pseudo-Voigt profiles used to account for various sources of broadening. The detailed derivation of the model and its implications are discussed in the supplementary materials. In the usual case of a homogeneously magnetised absorber, the formula used to represent the observed intensity I of the Mössbauer signal can be denoted by the function:

$$I = C_1 \cdot SC(v, \Gamma, \sigma, \mu, \delta, Q, B_{\text{hf}}, \Theta) + C_2.$$

In the above equation, Γ , σ and μ are the Lorentzian width, Gaussian width and mixing ratio of the pseudo-Voigt profiles, respectively, encompassing the various sources of peak width such as the natural linewidth and crystal disorder. δ , Q and B_{hf} are the isomer shift, effective quadrupole moment and magnetic hyperfine field at the nucleus, respectively. Θ is the polar angle describing the direction of emission of the source γ -rays, $\vec{k}_{\gamma}$, with respect to the magnetic hyperfine field B_{hf} . C_1 and C_2 are scaling constants.

The parameter Θ is key to investigating the magnetic orientation within a sample. In an ^{57}Fe MS sextet, the relative areas of peaks 2 and 5 vary with Θ as $x = 4 \sin^2(\Theta)/(1 + \cos^2(\Theta))$, where the peak intensity ratios are 3: x :1:1: x :3. For magnetically isotropic absorbers, the model is integrated with respect to Θ and $x = 2$. For more detail on how the relative areas of the peaks yield information about magnetic orientation, refer to the supplementary material.

For single crystals with substantial structural and chemical disorder, it does not make sense to use a single value for the hyperfine parameters as the ^{57}Fe nuclei will exist in a variety of distinct local environments. In this case a ‘ B_{hf} -broadened’ or ‘ Q -broadened’ model is used, where the spectrum is represented as a sum of contributions with the hyperfine parameter in question chosen from a continuous Gaussian distribution of values, with the width of the distribution dependent on the degree of atomic disorder [18]. The B_{hf} -broadened model results in a peak broadening that is proportional to the velocity of the source, while the broadening due to a distribution of Q values is constant, allowing one to visually decide which approach is more suitable (or indeed use both).

2.4.1. Regression. When the data have been fully pre-processed, the constituent x-ray and γ -ray spectra are considered individually and the appropriate fitting model is chosen from those described in section 2.4. The model is fit to the data using a least-squares non-linear regression algorithm for the input parameters. The experimentalist’s algorithm of choice can be used, but we prefer a basic iterative grid-search for most cases, where we can specify strict boundaries for the parameters and fit them individually in order of physical relevance. The steps in the algorithm are given in the supplementary material.

3. Examples of application

In this section, the earlier-described Mössbauer data collection and analysis approach has been applied to three unique forms

of magnetic material: an amorphous CoFeB-based ribbon, Nd-Fe-B thick films and a slab of an iron-nickel meteorite. These samples have been chosen as they are examples of form factors which are either better suited to BSMS and CXMS or simply impossible to measure in the transmission geometry. When measuring in the backscatter geometry, only one side of a planar sample is accessible at a time and it is important to know to what depth the sample is probed. The 50 μm and 20 μm values mentioned in section 2.1 were estimated by Fleischer *et al* [7] as the maximum escape depths for 14.4 keV and 6.4 keV photons, with good SNR and distinct shapes of the Mössbauer spectra, originating from an Fe foil surface layer and an Fe-containing substrate layer respectively, at normal incidence. Although the materials investigated all have a similar density and mass-energy absorption length to pure Fe, the presence of additional fluorescence contributions in conjunction with disorder in the local Fe environments degrades the signal. Thus the resolvable depth of information collected from these samples is assumed to be 50% less than that estimated by Fleischer. For the average (close to the most probable) depth probed, we assume the values to be halved again so the depths probed by the γ -rays and x-rays are approximately 13 μm and 5 μm at normal incidence. These values can then naively be reduced by the cosine of the angle of incidence with respect to the surface normal. More accurate estimates can, in principal, be obtained via Monte Carlo simulations of the photon absorption and detection processes for arbitrary angle of incidence. Here we have not performed these as no publicly available code exists and the examples referenced by Fleischer *et al* [7] are only for normal incidence.

3.1. Amorphous CoFeB-Based Ribbon

Power conversion electronics typically involve magnetic-core inductors that are operated at high frequencies, up to 500 kHz. In order to minimise losses, ultra-soft magnetic materials with minimal coercivity but appreciable saturation magnetisation are desired. One such class of materials recently shown to satisfy these conditions is melt-spun amorphous CoFeB-based alloys [19]. An example composition of this material was studied using the BSMS technique.

3.1.1. Sample description. The sample studied was a melt-spun ribbon of dimension 12 μm thick by approximately 2 mm wide, of nominal composition $\text{Co}_{75.5}\text{Fe}_{4.5}\text{B}_{20}$. This material was produced by injecting a molten arc-melted precursor onto a rapidly rotating Cu wheel (outer rim velocity $v \approx 80 \text{ m s}^{-1}$). As the wheel side (WS) of the resultant amorphous ribbon, in contact with the Cu wheel, cools via conduction much more rapidly than the free side (FS) cools in contact with the quenching atmosphere, the FS can, in principal, more readily facilitate partial crystallisation of the alloy. In preparation for MS, a mosaic sample was assembled out of $l \approx 2 \text{ cm}$ long segments of ribbon that were taped together using transparent adhesive tape. The sample was placed in the beam path such that the long axes of the ribbon segments were oriented perpendicular

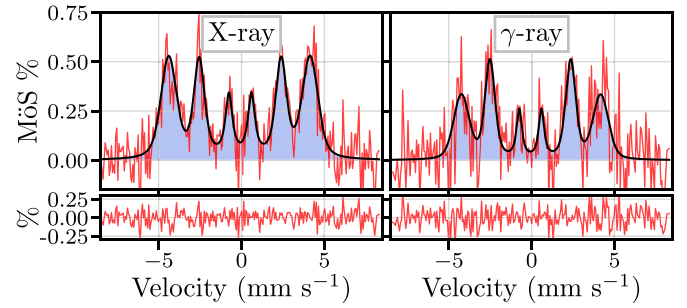


Figure 11. Mössbauer spectra from the amorphous CoFeB ribbon segments. Note that the broadened peaks are caused by the spread of hyperfine parameters due to the atomic disorder, and the different relative peak ratios are due to the different magnetic orientations in the bulk versus near the surface.

to the incoming photons and the short axes were oriented in the source-sample-detector plane.

Transmission Mössbauer data as well as backscatter Mössbauer data from both sides of the ribbon segments were collected, and processed as described in section 2, all spectra are shown in the supplementary material.

3.1.2. Results. The x-ray and γ -ray spectra obtained from the ribbon segments are shown in figure 11. A poor SNR was expected due to the small proportion of natural abundance Fe in the composition, in tandem with the other factors described in section 2.1. The spectra collected from the WS and the FS of the ribbon segments were practically indistinguishable, suggesting that the amorphous crystal structure of the ribbon was uniform throughout the volume despite the different cooling rates of the opposing sides, this uniformity is likely due to the small thickness of the ribbon. The MS peaks are very broad due to the amorphous nature of the alloys and are well-fitted using a B_{hf} -broadened model [19, 20]. The average value for the hyperfine field returned from the regression fit is $B_{\text{hf}} = 26.3 \text{ T}$ with $\sigma B_{\text{hf}} = 0.8 \text{ T}$. This low value of B_{hf} , compared to the canonical value of $B_{\text{hf}} \approx 33 \text{ T}$ for α -Fe, reflects the structural and chemical disorder of the atomic sites occupied by the Fe nuclei in these types of ribbon.

The magnetisation orientation ($\vec{m}$) of the ribbon was anticipated to be in-plane (IP) due to shape anisotropy, exacerbated by the high moment and ultra-low coercivity. This assumption was tested using the collected MS data. As described in section 2.4, the angle Θ between the momentum direction of the incoming photons $\vec{k}_\gamma$ and the sample magnetisation $\vec{m}$, is obtained from the relative peak areas within a sextet. Angles of $\Theta_x = 57^\circ \pm 2^\circ$ and $\Theta_\gamma = 71^\circ \pm 5^\circ$ were obtained from application of the fitting procedure for the x-ray and γ -ray spectra, respectively. The angle of incidence between $\vec{k}_\gamma$ and the surface normal was determined as $A_\gamma \approx 65^\circ$ for these measurements. Assuming that the magnetism $\vec{m}$ is oriented IP and along the ribbon's long axis, Θ would be equal to 90° given the orientation of the ribbon segments in the experiment; in this case the absorption peak intensity ratios would be 3:4:1. However, the angle $\Theta_\gamma = 71^\circ \pm 5^\circ$

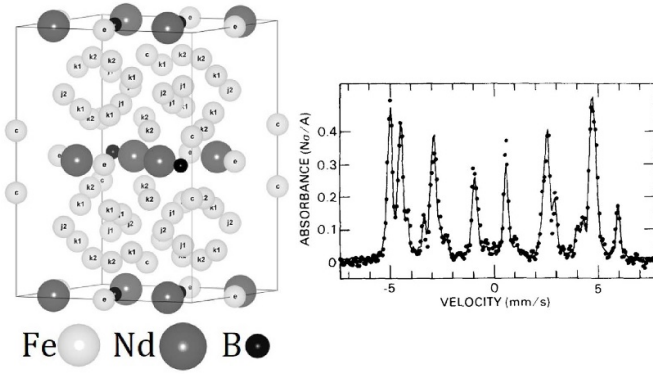


Figure 12. $\text{Nd}_2\text{Fe}_{14}\text{B}$ unit cell with various Fe sites, and the Mössbauer spectrum measured on a melt-spun bulk alloy by Pinkerton and Dunham. Reproduced with permission from [22].

determined from the γ -ray spectrum implies that $\vec{m}$ has a component, approximately 20% of the total magnitude of the magnetisation, that is aligned along the short (IP) axis of the ribbon segments. The ribbon segments were confirmed to be magnetised in the IP direction by measuring a transmission spectrum with the photons from the source normal incident on the surface, where a value of Θ close to 90° was obtained. This conclusion, that the ribbon is magnetised IP with finite components along both IP axes, is good news for the proposed application of this type of ribbon, as a finite component of $\vec{m}$ oriented away from the easy axis is anticipated to mitigate power losses during rotation of magnetisation in power conversion applications. The smaller value of $\Theta_x = 57^\circ \pm 2^\circ$, obtained from fitting the x-ray spectrum compared to that derived from analysis of the γ -ray spectrum, points to spatially inhomogeneous magnetisation in the ribbon. This result is consistent with the existence of a larger component of $\vec{m}$ along the short IP axis near to the surface of the ribbon compared to that of the bulk, or perhaps reveals some component of $\vec{m}$ in an out-of-plane (OOP) orientation near the surface. The presence of flux-closure domains near the ribbon surface, perhaps associated with the highly amorphous surface state or with strain, may underlie this observed change in the direction of $\vec{m}$ revealed by the x-ray spectrum as compared to the information provided the γ -ray spectrum.

3.2. Nd-Fe-B thick films

$\text{Nd}_2\text{Fe}_{14}\text{B}$ -based magnets have the largest energy product among all modern commercial magnets [21], resulting in their widespread use in a variety of applications. The $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase has a large, complex unit cell with six distinct Fe-occupied sites. These sites are denoted k_1 , k_2 , j_1 , j_2 , c and e with occupancies of 16, 16, 8, 8, 4 and 4, respectively.

The hyperfine parameters for Fe nuclei in $\text{Nd}_2\text{Fe}_{14}\text{B}$ have been determined on a bulk, melt-spun sample, using traditional TMS [22], see figure 12. Currently, thick films (micrometric) of $\text{Nd}_2\text{Fe}_{14}\text{B}$ are used to fabricate micron-scale magnets for use in MEMS devices [23] and are well-suited to the

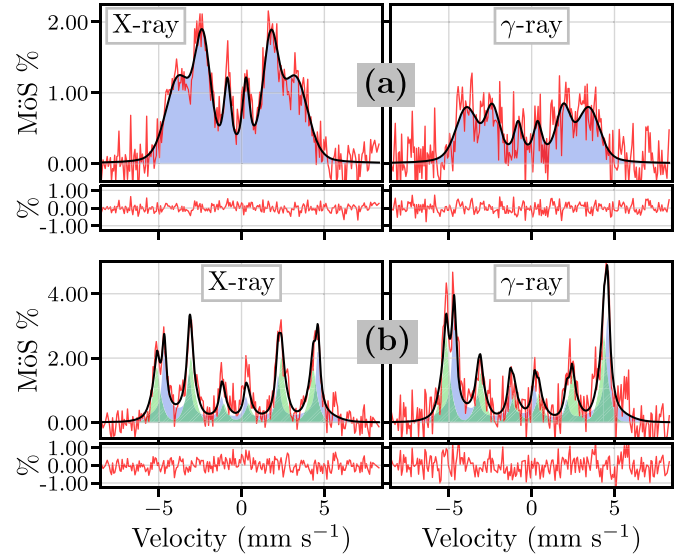


Figure 13. X-ray and γ -ray spectra from the $T_{\text{dep}} = 550^\circ\text{C}$ film, measured (a) before (fit using B_{hf} -broadened model) and (b) after annealing at $T_{\text{dep}} = 700^\circ\text{C}$ (fit using two single-crystal contributions).

depth-selective characterisation provided by simultaneous x-ray and γ -ray photon collection from MS.

3.2.1. Sample description. Mössbauer spectra were recorded from two Nd-Fe-B films of $5\ \mu\text{m}$ thickness that were in the virgin magnetic state. These films were made by triode sputtering at 550°C onto Si substrates, along with Ta buffer and capping layers of $100\ \text{nm}$ thickness. One film was studied in the as-deposited state while the other was studied after annealing at 700°C for 10 min to crystallise the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. Data were accumulated for approximately three weeks, in order to obtain adequate statistics, as the activity of the ^{57}Co source used was low. In addition to the low activity, the relative thinness of the absorbing films resulted in a low SNR, so only the two most populous Fe lattice sites were considered when fitting the data, as the contributions from the other sites could not be resolved. For the as-deposited films, the B_{hf} -distribution model was used. The annealed sample was subsequently magnetised OOP in 5.5 T and remeasured at remanence.

3.2.2. Results. X-ray and γ -ray spectra obtained from the film before and after annealing are shown in figure 13. The literature values for the hyperfine parameters were used as a starting point for the regression for the annealed film. For the as-deposited film, the B_{hf} -distribution model was used with a lower initial value of the hyperfine field and a larger broadening compared to the annealed film.

The good quality of the fits in figure 13(b), and the striking similarity of these data to the spectrum in figure 12, confirmed that this film was crystallised in the desired $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase. The different relative heights of the peaks noted in our data as compared to those of Pinkerton and Dunham are attributed to a different angle of incidence of the source γ -rays. The crystal

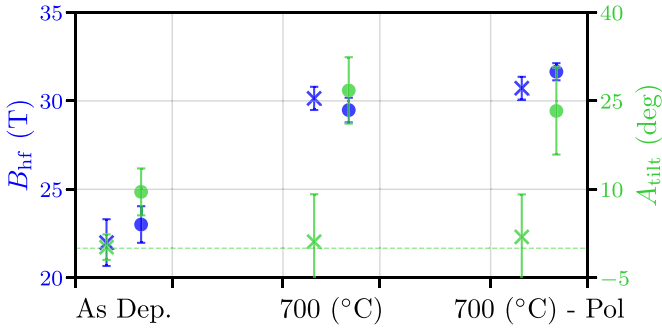


Figure 14. The hyperfine field magnitude (blue) and the tilt of the hyperfine field axis away from the film normal (green) are shown, the area-weighted average of the two primary Fe-containing sites was used for the annealed films. X denotes data from the x-ray spectra and • from the γ -ray spectra.

structure present in the as-deposited film was quite disordered with a much-reduced average B_{hf} value, see figure 13(a). After magnetisation, the annealed sample exhibited a slightly higher value for the local hyperfine field compared to that of the sample in the virgin state, as expected, but yielded otherwise identical fitting results.

The angle of incidence of the source γ -rays with respect to the surface normal was $A_\gamma \approx 67^\circ$ for these measurements. It is useful here to introduce a ‘tilt’ angle $A_{tilt} = A_\gamma - \Theta$, where again A_γ is the angle between k_γ and the surface normal, and Θ is the angle between k_γ and the magnetisation. The tilt angle A_{tilt} therefore contains information about the canting of the magnetisation away from the surface normal, a useful figure of merit for perpendicular magnetic anisotropy materials. The measured values for B_{hf} and A_{tilt} are shown in figure 14. A_{tilt} was found to be zero within experimental error for all three x-ray spectra, consistent with magnetisation that was oriented fully perpendicular near the surface of the films, regardless of whether they had been annealed or not. In contrast, analyses of the γ -ray spectra, originating from deeper within the film, revealed a tilt angle of $10^\circ \pm 4^\circ$ for the as-deposited films and a tilt angle of $27^\circ \pm 7^\circ$ for the annealed film. This result implies that some component of the magnetisation within the volume of the film was oriented IP, and this IP component is larger in the annealed film than it is in the as-deposited film. This interpretation was again reinforced by analysis of a conventional transmission spectrum recorded with incoming γ -rays normally incident on the as-deposited film. In this case a value of $\Theta = 19^\circ \pm 5^\circ$ was obtained from the fit, consistent with up to roughly 20% of the film volume possessing an IP magnetic polarisation, leaving the majority of the film with an OOP magnetic polarisation. The attainment of a finite tilt angle for the bulk of the film (derived from the γ -ray spectrum) but not for the film surface (derived from the x-ray spectrum) might be explained by the presence of flux-closure domains with an IP remnant magnetisation that formed near the substrate interface. A comparison of data collected in the transmission and backscatter geometries at different incidence angles, using the as-deposited film, is shown in the supplementary material.

Notably, OOP remnant magnetisation was detected in all samples, supporting the existence of a significant uniaxial

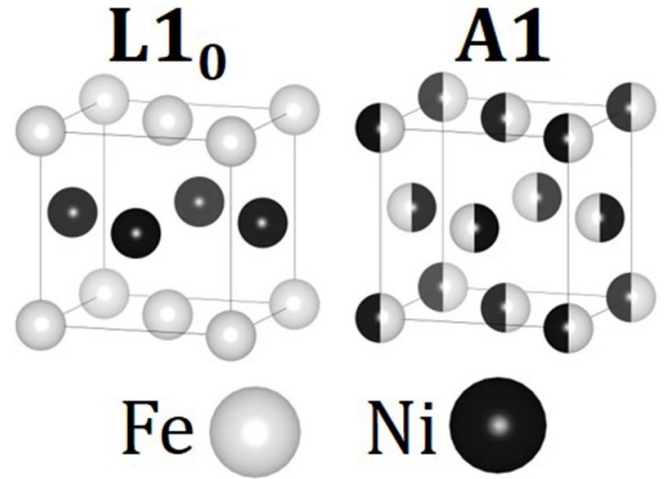


Figure 15. The atomically ordered ($L1_0$) and atomically disordered ($A1$) crystalline phases of equiatomic FeNi.

anisotropy even in as-deposited films, i.e. prior to the establishment of long-range crystalline and atomic order. This result was evidenced by the similar values of Θ obtained from the regressions of the data from all three measurements: on the as-deposited, annealed and magnetised films. Further, this result (that all films were observed to be magnetised OOP) is in agreement with magnetometry data obtained from Nd-Fe-B films that were sputter-deposited at a temperature that was just below the crystallisation temperature of the $Nd_2Fe_{14}B$ phase and were then subsequently annealed [24].

3.3. Meteoritic FeNi phase analysis

Magnetocrystalline anisotropy is a key property of technologically useful magnetic materials. To this end, FeNi is a promising candidate magnetic material which exhibits significant uniaxial anisotropy without rare-earth or heavy-metal elements, when it is crystallised in the tetragonal $L1_0$ structure (space group 123, $P4/mmm$), see figure 15 [25]. However, the disordered-fcc $A1$ parent phase (space group 225, $Fm\bar{3}m$) is very close in energy to that of the $L1_0$ phase, and the kinetics of formation of the ordered phase is very slow [26]. FeNi in the $L1_0$ phase can be synthetically produced [27–29] in ultra-thin film form but a consistent large-scale synthesis method has not yet been demonstrated.

An interesting source of $L1_0$ -type FeNi is extraterrestrial bodies, specifically very slow-cooled iron-nickel meteorites. The extremely long-term cooling that such meteorites undergo in the vacuum of space provides sufficient time to form the $L1_0$ phase [30]. To investigate this material, we obtained a sample extracted from the nickel-rich iron meteorite NWA 6259 [31] and employed the BSMS technique to non-destructively investigate the Fe-containing crystalline phases present within it.

3.3.1. Sample description. The meteoritic sample studied had an area of 70 mm $\times$ 35 mm at its widest points and a thickness of 6 mm, too thick to conduct a TMS investigation. This

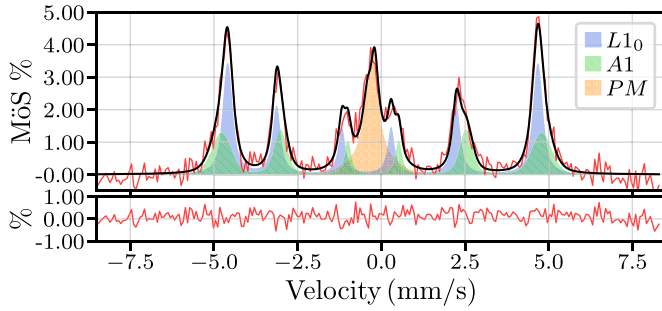


Figure 16. The x-ray MS spectrum obtained from the FeNi meteoritic sample, with $A_\gamma = 20^\circ$.

specimen had been cut with a diamond saw and mechanically polished on one side. It was mounted in the usual fashion for backscatter measurements with the polished side facing the incoming γ -rays from the MS source. The polished face was at all times protected by a layer of transparent adhesive tape.

3.3.2. Results. FeNi has a simple (compared to $\text{Nd}_2\text{Fe}_{14}\text{B}$) and well-studied structure; the theoretical hyperfine parameters for different crystal phases are known [32] and were used as a starting point for the regression of the MS data. In addition to inclusion of the spectra anticipated from tetrataenite and from the disordered FCC phase, a spectrum from a paramagnetic (at room temperature) phase, denoted ‘PM’, was included in the model as well. This latter phase contributed a tight doublet (treated as a large singlet) to the spectrum and its inclusion was necessary to fit the data [26, 33], see figure 16. For the analysis of the volume fractions of the different crystal phases, we initially considered only the x-ray spectrum, which had better SNR than that provided by the γ -ray spectrum. The relative areas within the overall spectrum corresponding to the three phase types, equivalent to their relative volume fractions, were determined as $66\% \pm 5\%$ $L1_0$, $17\% \pm 10\%$ A1 and $17\% \pm 5\%$ PM. This value for the volume fraction of the $L1_0$ phase is among the highest reported for FeNi alloys, and the highest for naturally occurring FeNi [29]. The angle between $\vec{k}_\gamma$ and B_{hf} , where B_{hf} is taken as the average for the $L1_0$ and A1 phases, was found to be $\Theta = 49^\circ \pm 5^\circ$ for this measurement, see figure 16. The angle of incidence between $\vec{k}_\gamma$ and the surface normal was $A_\gamma \approx 30^\circ$, implying that the magnetisation was tilted by at least 20° IP in the $5\text{ }\mu\text{m}$ region nearest the specimen surface.

The fits of the model to the x-ray and γ -ray MS spectra collected from the NWA 6259 specimen gave slightly different values for the relative phase contributions, consistent with a depth dependence of the composition. To investigate this possibility more systematically, measurements were repeated with different incidence angles of the incoming photons, with the results shown in figure 17.

The volume fraction of the $L1_0$ phase is found to decrease significantly as A_γ was increased, while the volume fractions of the PM and A1 phases both increased. At small values of A_γ , the source γ -rays arrive at an orientation that is nearly perpendicular to the sample surface, thus penetrating further into

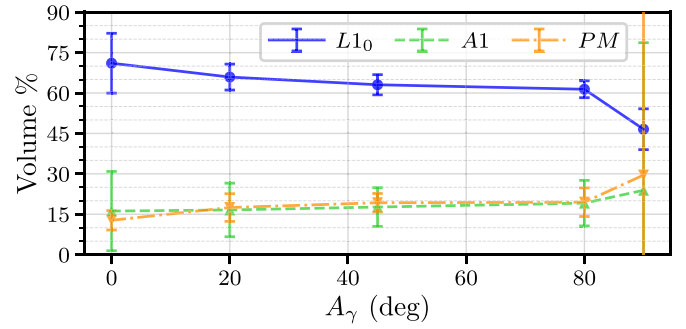


Figure 17. The dependence of the volume fractions of the different crystal phases on A_γ . The error at small angles is due to low MS sensitivity and poor SNR. The point at 90° suffers from large systematic uncertainty as only approximately half the viewing angle is exposed at grazing incidence.

the material and providing lower surface sensitivity. From the results shown in figure 17, it can be concluded that the $L1_0$ phase is less prevalent near the surface region compared to its concentration in the bulk, while the opposite is true for the PM phase, with the A1 phase exhibiting near constant prevalence as a function of depth within the specimen. This observed gradient in the contributions of the constituent phases may have been caused by the mechanical and thermal stresses near the surface arising from the specimen preparation procedures of cutting and polishing. These stresses are considered to have compromised the $L1_0$ atomic order near the surface, with the PM phase being preferentially formed over the A1 phase. This observation implies that a distinctly different crystal structure has been formed.

4. Summary

It is demonstrated here that BSMS with simultaneous recording of the entire fluorescence spectrum shows immense promise as a tool to investigate a wide range of materials properties, such as local atomic order, magnetic orientation and the presence of different Fe-containing phases. This technique provides an intrinsic depth sensitivity by virtue of the two different mean free paths of the resonant photon energies: the 14.4 keV re-emitted γ -rays and the 6.4 keV conversion x-rays. The applicability of BSMS to samples with varying thicknesses and degrees of crystalline order has been confirmed, and advantages over TMS have been established, in cases where the transmission and backscatter geometries are both feasible. Essentially any iron-containing sample can be non-destructively investigated with this approach, making this technique very attractive as a probe in modern magnetic materials science as well as in the earth and planetary sciences. Our experimental setup has been largely custom-built and programmed in-house at a fraction of the cost of a single commercial MPA. It has been shown that this multi-parallel-acquisition MS technique provides a viable alternative to other spectroscopic techniques to investigate a number of key material properties, for a variety of sample geometries.

The here-described electronics and software can and have also been utilised to perform conversion electron MS (CEMS) (see, for example, the supplementary material of Borisov *et al* [34]), where the electrons themselves are detected rather than the photons. The high speed and low dead time of the acquisition electronics are of even higher importance in this case due to the much larger number of electrons in the detector cascade.

5. Future work

A very-rarely used methodology to decrease linewidths below the natural Lorentzian ones is time-differential MS, where the 122.1 keV γ -rays emitted by the source (figure 2) are detected using a scintillation detector, signalling the occupation of the 14.4 keV energy level in the source ^{57}Fe nuclei. Subsequent detections of the resonant fluorescence photons from the sample can then be assigned a time delay value, since the occupation of the 14.4 keV energy levels in the source. When processing the data, detected photons can be discriminated based on their time delay and the energy level lifetime, thus improving the SNR [35], and this additional dimension can be readily incorporated with the modular MPA design described here.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Acknowledgments

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