High-throughput analysis of magnetic phase transition by combining table-top sputtering, photoemission electron microscopy, and Landau theory

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ABSTRACT
Owing to recent advances in material informatics, there has been increasing interest in combinatorial experimental systems for material development. We demonstrate a novel high-throughput experiment combining compact materials synthesis, synchrotron radiation measurements, and statistical data analysis. This technique focuses on not only drawing phase diagrams but also analysing phase transitions for exploring the functions of magnetic materials. In this study, a composition-gradient Fe–Co–Cr ternary thin film was prepared using a table-top sputtering system and a 3D printer. The chemical components and magnetic contrast were measured using photoemission electron microscopy through the acquisition of 1 million spectral datasets within 10 min. The ternary magnetic-phase diagram of Fe–Co–Cr obtained by statistical analysis of the magnetic circular dichroism (MCD) contrast images agreed with ferromagnetic/paramagnetic transition. The MCD histogram was fitted based on Landau theory, and the estimated critical exponent β (0.36 ± 0.028) agreed well with previous theoretical and experimental studies. This study demonstrates universal physical parameter analysis that characterises magnetic properties by a high-throughput approach combined with a simple experimental apparatus.

1. Introduction
Advances in high-throughput experiments have attracted considerable attention in materials informatics for discovering novel functional materials [1–4]. Preparation of high-throughput materials is important for the construction of experimental materials databases, and high-throughput measurements provide insights for discovering novel materials. Integrating materials synthesis, physical property measurement, and data science is also crucial for accelerating materials exploration and can lead to the discovery of novel functions and unexplored materials [5–7]. There has been significant progress in technological development in these independent areas, e.g. the automation of material synthesis [2,5–10], building material databases [11–13], and predicting physical properties by machine learning [14–16]. However, several issues remain to be addressed in high-throughput experiments. The high-throughput performance of individual parts of synthesis, measurement, and analysis needs further improvement. Moreover, the linkage of these three components is not yet complete as their sufficient integration can significantly improve the methodology of design of novel materials [9,10]. Conventional combinatorial studies have focused on drawing phase diagrams rather than extending the functional analysis [4,5]. Measurement informatics currently focuses mainly on accelerating measurement speed, overlooking the analysis of the intrinsic physical properties from the obtained dataset. Few experiments have been conducted on the origin of functions themselves, such as magnetic and electronic states, and in particular, research focusing on magnetic-phase transitions has not yet been conducted. Phase transition can be
regarded as the onset of functional appearance, and its analysis can be a useful way to search unexplored materials.

In this study, we developed a novel high-throughput experimental method by combining compact materials synthesis, physical property measurement, and statistical analysis (Figure 1). This compact instrumentation allows materials informatics research to be conducted even in small laboratories with limited resources. The fusion of the three techniques enables researchers to perform all processes from material creation to functional analysis simultaneously, thus accelerating the exploration of materials. The focus is not just on drawing phase diagrams but also on analysing phase transitions to explore the origin of the material’s function. For rapid combinatorial sample preparation, we employed an inexpensive table-top sputtering instrument with a custom 3D-printed sputter beam aperture and transmission electron microscopy (TEM) grid (Figure 1(a)). The sputter particles are collected obliquely with a beam aperture and then turned around in the shadow of the mesh of TEM grid. It enables us to deposit a Fe–Co–Cr ternary alloy thin film with a continuous composition gradient in the micro-region at once. Fe–Co–Cr was chosen as a typical 3d metal alloy system exhibiting a ferromagnetic/paramagnetic phase transition [17–19]. Moreover, Fe–Co–Cr is a promising material for application in magnetic-microelectromechanical sensor. The Fe–Co–Cr system was chosen as a model material to examine the validity of the analysis method. It is well established that the Fe-rich α phase is ferromagnetic. However, at high Cr concentrations, the Curie temperature decreases, and the alloy becomes antiferromagnetic. All-proportional solid solution alloy and easily deposited sample is adequate for this method. Therefore, the Fe–Co–Cr system is suitable for demonstrating our approach to high-throughput experiments. For complex systems with crystal grains, improving spatial resolution and adding descriptors of spatial inhomogeneity would be necessary [20]. The physical properties of the thin film were analysed using photoemission electron microscopy (PEEM) (Figure 1(b)), a powerful full-field-type microscopy technique allowing for simultaneous measurement of the chemical composition, magnetic properties, and electronic structure of a specimen. PEEM is an effective technique for analysing thin films’ magnetic properties, and several studies have reported the spin-reorientation transition of magnetic multilayers [21,22]. The X-ray absorption intensity is recorded for each pixel of the observed image. Moreover, 1 million X-ray absorption spectra (XAS) and magnetic circular dichroism (MCD) contrast images can be acquired in 10 min; that is, the efficiency of PEEM is considerably greater than that of scanning microscopes such as electron probe micro analyzer. We used these micro-spectroscopic data sets to conduct a high-throughput experiment. X-ray structure analysis was excluded in this high-throughput

![Figure 1](image-url)

Figure 1. Workflow of a high-throughput experiment combining materials synthesis, physical property measurement, and statistical analysis. (a) a 3D-printed sputter beam aperture was used to deposit a Fe–Co–Cr ternary thin film with a continuous composition gradient. (b) Photoemission electron emission microscopy (PEEM) obtained one million X-ray absorption spectra (XAS) and magnetic circular dichroism (MCD) contrast images in 10 min. (c) the MCD histogram dependence on compositional ratio was used to construct the ternary magnetic phase diagram of Fe–Co–Cr and determined the critical exponent from Landau theory.
analysis because of the pinpoint measurement. We statistically examined the chemical composition and MCD contrast images recorded in the microscopic image for data analysis (Figure 1(c)). The information in each pixel was sorted according to the chemical compositional ratio. MCD contrast histograms were prepared depending on the Fe–Co–Cr compositional ratio, and a ternary phase diagram of the MCD histograms was also prepared. Finally, we analyse the MCD histograms and magnetic-phase transitions with the aid of Landau theory, a typical model of magnetic-phase transitions based on statistical mechanics. The approach analyses the pseudo-free energy landscape from MCD image contrast data, as the MCD histogram is the probability distribution function of the magnetisation. We also demonstrated a method for extracting the critical exponent β, from the image information. β a universal parameter in phase transitions, is a fundamental constant that characterizes the magnetism of materials, and its estimation can help validate this technique.

2. Methods

We developed a compact combinatorial instrument for the rapid synthesis of Fe–Co–Cr ternary thin films with a composition gradient. The system comprises an inexpensive table-top multi-source DC magnetron sputtering instrument, a custom-manufactured sputter beam aperture for controlling the direction and diffusion of the sputtered particles, and a commercially available TEM grid. The beam aperture was 3D-printed using titanium powder: the 3D model of the jig was first designed using Autodesk MAYA and a resin jig prototype was then fabricated in Da Vinci 1.0aIO. Subsequently, the metal jig was fabricated using a metal 3D printer. The model was designed such that the three cylindrical entrance holes converged into one exit hole. As shown in Figure 2(a), the individual hole diameters were 2.3 mm, and the aperture was 4 mm thick. A TEM grid with 30 μm × 30 μm square holes was attached to the exit side of the aperture. Commercially available copper TEM grid was used (VECO, Netherlands, 400 mesh, thickness 25 μm). Fe, Co, and Cr were deposited obliquely on a SiO2/Si substrate by DC magnetron sputtering to prepare a ternary thin film with a composition gradient. The typical sputtering conditions were as follows: base pressure of 9.03 × 10−4 Pa, Ar+ pressure of 1.0 Pa, sputtering current of 25 mA, and a temperature of 300 K (room temperature). As shown in Fig. S1, the spread width of the sputter beam increases almost linearly with the height of the gap. The spread angle is estimated to be approximately 14.6°. The spread width was set to approximately 10 μm by fine-tuning the tilt and placement of the TEM grid. The height of the gap between substrate and TEM grid is suggested to be approximately 38 μm. Multicomponent layered films with a 2 nm thickness were deposited for each element; the procedure was repeated 10 times to obtain a multi-layered film with 30 total layers and a thickness of 60 nm. Subsequently, the specimen was annealed at 600°C for 1 h in situ to promote alloying. The annealing temperature and time were determined based on the diffusion coefficient of Fe–Cr (7.8 × 10−9 m2/s) and a sufficient diffusion length (1.78 μm) compared to the film thickness (60 nm) [18].

As a prior experiment, we examined two standard Fe-Cr binary thin films with and without annealing. Specimens were prepared as a homogeneous film without using the beam aperture and TEM grid. XRD analysis confirmed that the Fe (110) and Cr (110) double peaks merge into a single Fe-Cr (110) peak upon annealing, suggesting that Fe and Cr are intermixing and alloying during annealing (Figure 2(b)).

For Fe–Co–Cr alloys, chemical maps and magnetic contrast images were measured using a spectroscopic PEEM instrument (Elimitec, SPELEEM, Germany) installed at BL17SU of SPring-8 [23–25]. Before the XAS/MCD-PEEM measurement, we applied an AC demagnetisation field parallel to SR incidence in an attempt to align the magnetisation of the specimen along the SR incidence. Before SR measurement, the surface was sputtered with Ar+ ions at 1 kV acceleration voltage, 15 mA of emission current, P = 2.0 × 10−5 Torr for approximately 90 min, with gentle annealing at 400 C in the preparation chamber. The XAS and MCD signals were acquired in the same field of view, and the photon energy was continuously scanned at the L absorption edges of Fe, Co, and Cr. The energy scan ranges for Fe, Co, and Cr were 700–730, 770–805, and 570–600 eV, respectively, with a step size of approximately 0.14 eV. XAS was obtained by measuring total electron yields using PEEM. PEEM measurement was carried out at room temperature (300 K). The composition ratio was determined from the XAS absorption and photoionisation cross-section of each element [26,27]. The edge height of the $L_3$ absorption peak was normalised by the photoionisation cross-section. The chemical composition ratio of the three elements was obtained by the ratio of the normalised intensities using the following formula:

$$I_{\text{nom}}^{\text{Fe}} = I_{\text{XAS}}^{\text{Fe}} / C_{\text{Fe}}$$

$$\text{Comp}_{\text{Fe}} = I_{\text{nom}}^{\text{Fe}} / (I_{\text{nom}}^{\text{Fe}} + I_{\text{nom}}^{\text{Co}} + I_{\text{nom}}^{\text{Cr}})$$

where $I_{\text{XAS}}^{\text{Fe}}$ is the edge height of the $L_3$ peak of Fe, $C_{\text{Fe}}$ is the photoionisation cross-section of Fe, $I_{\text{nom}}^{\text{Fe}}$, $I_{\text{nom}}^{\text{Co}}$, $I_{\text{nom}}^{\text{Cr}}$ are the normalised intensities of each element, and $\text{Comp}_{\text{Fe}}$ is the resulting composition ratio of Fe. The compositions of Co and Cr were
determined in the same manner. Figure 2(c) shows the XAS spectra of Fe, Co and Cr. We could confirm the absence of oxidisation of Fe and Co by these edge shapes [24]. The XAS spectrum of Cr is consistent with that of Cr$_2$O$_3$, suggesting that the surface Cr is oxidized. Cr and Cr$_2$O$_3$ are both antiferromagnetic, and their Neél temperatures are almost the same at 307 K and 308 K, respectively. Furthermore, as the collective motion of magnetic moments characterizes magnetism, the influence of the surface oxide layer on the analysis of the ferromagnetic/paramagnetic transition should be relatively small. The MCD contrast was determined by the asymmetry caused by the difference in the helicity of circularly polarised X-rays. The field of view was set to a diameter of 100 μm so that the entire island with a composition gradient was in the viewing field. The resolution of the charge-coupled device (CCD) camera was 1024 × 1024 pixels with 16-bit greyscale, and the exposure time was 3 s per image. Thus, micro-spectroscopic data of approximately 200 images (energy points) were acquired in 10 min. The signal-to-noise (S/N) ratio of a single-pixel spectrum is at most 10%, and the S/N ratio can be improved by integrating the pixel information (Figure 2(d)). Although a typical regions of interest (ROI) contains 10,000 pixels, 100 pixels is enough to obtain sufficient S/N for compositional analysis. Regarding the high-throughputness of our experiment, sample preparation and transport takes about 12 h and 24 h, respectively. Usually, multiple samples are prepared just before beamtime. Sample introduction into the vacuum chamber and alignment of lens setting takes several hours. The total time, preparation, setup, and measurement, is about 72 h. Compared to a typical experiment, while it depends on the ROI setup, a whole-image segmented by ROIs, containing the
minimum amount of pixels to perform a compositional analysis, corresponds to roughly 10,000 samples prepared individually. The estimated time to prepare and measure these samples is about 7,000 days. In the present study, the data was segmented into 41 ROIs with sufficient margin. If 41 samples were individually prepared, exchanged, and measured, it will take about 30 days in total. As a result, the practical efficiency of our method was improved by a factor of about 10. We prepared semi-automatic macros using the Python (version 3.8) modules, namely NumPy (version 1.18) and Pandas (version 1.1), to load the PEEM data, evaluate the composition ratio, analyse the MCD signal, and set the ROIs.

The MCD contrast data were correlated with the Fe–Co–Cr composition (divided with a step size of 5 at %) determined from the XAS intensity at the corresponding area. Then, each MCD data cluster was converted into a histogram indicating the distribution of the number of pixels as a function of MCD intensity. The magnetic phase (ferromagnetic or paramagnetic) for each composition was determined from the number of peaks appearing in the histogram. The obtained MCD histograms were quantitatively organised on a Fe–Co–Cr ternary-phase diagram. Finally, the MCD histograms were analysed using the Landau theory, and the critical exponent $\beta$ was extracted. The Landau theory can describe the pseudo-free energy of the system by a simple fourth-order polynomial of an order parameter, which is magnetisation in the case of a magnetic material. Since the specimen may practically have a remanent magnetisation, we left the first-order term as the internal magnetic field for fitting.

3. Results and discussion

Figure 3(a-c) depicts the chemical composition maps obtained by PEEM, which show that the chemical composition of Fe, Co, and Cr spatially and continuously changes. The line profiles of the compositional distribution of Fe, Co, and Cr are shown in the lower parts of Figure 3(a-c) respectively. The composition of each element varies continuously in a linear fashion, confirming that the composition distribution is adequately prepared. A ternary composition map of Fe–Co–Cr obtained by superimposing the three images is displayed in Figure 3(d). The overlapped region at the centre shows the alloying of the three elements. Figure 3(e) depicts the MCD image of Fe obtained at the same area as the composition map, indicating a clear magnetic contrast in the centre and upper-right region of the sample. In the superimposed composition and MCD images, the appearance and disappearance of magnetic contrast align with variations in the chemical compositional ratio of Fe–Co–Cr (Figure 3(f)). The MCD contrast appears in regions of intermediate concentration of all three elements and regions of high Co concentration. However, the contrast disappears in regions of high Cr and Fe concentrations. This suggests that a ferromagnetic/paramagnetic-phase transition occurs depending on the Fe–Co–Cr composition. We confirm the reproducibility of the appearance and disappearance of the MCD contrast in five adjacent island thin films (Figure S2.) The origin of the fan-shaped magnetic domain structure cannot be fully explained from these data alone. The magnetic domain structure is determined by a delicate balance between magnetostatic energy and exchange energy. The formation of in-plane magnetic domain structures suggests that the magnetostatic energy is dominant. As the stripes lie parallel to the compositional contours, composition-dependent magnetic moments can contribute to the magnetostatic energy. Therefore, the magnetostatic energy due to compositional gradient may be considered a promising candidate that explains the origins of the fan-shaped magnetic domain structure. This result also indicates that the compositional gradient of the sample is obtained in a reproducible manner. We obtained these magnetic-phase transition data in approximately 30 min with the proposed high-throughput measurement system.

Next, the ternary-phase diagram of the MCD histogram is depicted in Figure 4(a), which was obtained simultaneously by the statistical analysis of MCD contrast depending on the Fe–Co–Cr compositional ratio. We divided the image into 40 ROIs according to compositional ratio with steps of 5 at%. Figure S3 shows the spatial distribution of ROIs, which indicates that a reasonably continuous compositional distribution is formed. As shown in Figure 3(e) and S3 (b), a clear black-and-white MCD contrast appears with a width of approximately 5 μm in the ferromagnetic region of Fe$_{35}$Co$_{30}$Cr$_{35}$. The MCD contrast gradually decreases and fine gray dots appear when the paramagnetic transition area of Fe$_{35}$Co$_{25}$Cr$_{40}$ and Fe$_{30}$Co$_{35}$Cr$_{35}$ is approached. After the transition to paramagnetism of Fe$_{30}$Co$_{30}$Cr$_{40}$, the MCD contrast disappears and the image is completely gray. A quantitative examination of the origin of the shape of the magnetic domain structure is challenging. However, in the region of ferromagnetic/paramagnetic transition, the width of ferromagnetic domain gradually narrows down as the magnetic moment decays. As shown in Figure 3(e) , small submicron-sized gray magnetic domains appear diffusely near the boundary, and wide gray domain appears after the paramagnetic transition. This clearly indicates the transition of the specimen from the ferromagnetic to paramagnetic state. One histogram typically contains MCD information corresponding to approximately 10,000 pixels, which is a sufficient amount of data for statistical
analysis. Thus, we could draw most of the ternary-phase diagram at once, and the missing data at the edges of the phase diagram were filled by improving the design of the sputter beam aperture.

Subsequently, we analysed the MCD contrast for the ferromagnetic/paramagnetic transition. We generated a histogram as a function of MCD asymmetry for each ROI. Since the MCD signal is proportional to the inner product of the magnetic moment and the optical axis, it is useful for analysing the magnetic state of the specimen. To simplify the task, we considered the classification of ferromagnetism and paramagnetism in this study. A double-peaked MCD histogram, as depicted in Figure 4(b), corresponds to a ferromagnetic state. This is attributed to the MCD signal that is produced and appears as a positive or negative value (white and black contrast in the grey-scale image), when spontaneous magnetisation arises, although the classification depends on the angle between magnetisation and SR incident. A single-peaked MCD histogram, as depicted in Figure 4(c), can correspond to a paramagnetic state or ferromagnetic state with 90°, because the inner product becomes zero (monotonic grey contrast) in no net magnetisation or orthogonal geometry. Broad and unclear structure in MCD histograms would be influenced by fine structure of magnetic domains and the angle of magnetisation. Accordingly, the contribution of demagnetisation energy in magnetic domain structures must also be considered. However, spatial information was eliminated by ROI extraction, and we analysed the data assuming the contribution of spatial

Figure 3. Chemical compositions, MCD contrast images, and superimposed maps obtained by PEEM of the Fe–Co–Cr thin film. (a – c) Chemical composition maps and line profiles of Fe, Co, and Cr. (d) Superimposed chemical map of Fe, Co, and Cr with an overlapped region at the centre and (e) MCD image in the same area showing the magnetic contrast around the centre. (f) Superimposed image of chemical compositional ratio and MCD.
inhomogeneity is averaged out. Thus, the gray signal is not a universal feature; nevertheless, the width, hem, and shape of the MCD histogram could be a useful feature for classifying magnetic state.

This study employed two simple measures to discuss the ferromagnetic/paramagnetic states. We used the presence/absence of peak splitting in the histogram and the full width at 20% of the maximum of the histogram. These parameters of histogram analysis have been previously examined in a Fe-Cr binary alloy, which shows a typical ferromagnetic/paramagnetic transition (Figure S4) [19]. The 40 MCD histogram panels were categorised by colour (ferromagnetic: red, paramagnetic: green) and overlaid on the previously established Fe–Co–Cr ternary phase diagram (Figure 4(a)) [17–19]. Thus, the ferromagnetic and paramagnetic-phase distributions determined from the MCD histograms agree with the known phase boundaries of the ferromagnetic/paramagnetic transition. We also compared the MCD histogram to the ROI of the original PEEM image for further confirmation. We have twice confirmed the reproducibility of the magnetic-phase diagram drawing of the Fe–Co–Cr system (Figure S5). We examined Fe-Cr binary alloy using the same experimental technique and confirmed that the ferromagnetic transition occurs as the Fe concentration increases (Figure S4). Thus, we demonstrated the high-throughput measurement of a ternary magnetic-phase diagram.

Finally, we analysed the MCD histograms near the magnetic-phase transition using the Landau theory, a reasonable model that can describe magnetic transition using the pseudo-free energy $F$ of a system based on the mean-field approximation. Landau theory explains magnetic-phase transitions based on statistical mechanics. The stability of the system is described by a landscape of free energies, and the occurrence of stable or unstable state is described by a probability. The MCD histogram can be regarded as a probability distribution of magnetic states. Our idea is to draw the
pseudo-free energy experimentally by flipping the vertical MCD histogram upside down. The horizontal axis corresponds to the magnetization, which is an order parameter in Landau theory. The following simple fourth-order polynomial of the magnetisation \( m \) can represent the magnetic-phase transition \([28,29]\).

\[
F = -hm + Am^2 + Bm^4
\]

The second-order term \( Am^2 \) is the demagnetization energy term, and the sign of the coefficient \( A \) corresponds to the ferromagnetic/paramagnetic transition. The fourth-order coefficient \( B \) is the magnetic anisotropy energy term, and \( h \) is the magnetic field. Note that the experimental MCD histograms remained asymmetric due to the remnant magnetisation. Therefore, we left the first-order term \( hm \) as a correction term to perform the fitting. It should also be noted that the Landau theory cannot wholly treat spatial inhomogeneity in magnetic domain structures because of the mean-field approximation \([30]\). Therefore, we abandoned the spatial information in the MCD-PEEM image and statistically treated the MCD data to investigate only the presence of a ferromagnetic/paramagnetic transition. We used data with clearly separated black and white contrast for fitting the curve. As a result of fitting the MCD histograms, the coefficient \( A \) changed from \( 2.00 \times 10^{-3} \) in the ferromagnetic phase \((Fe_{25}Co_{40}Cr_{35})\) to \(-6.99 \times 10^{-3} \) in the paramagnetic phase \((Fe_{30}Co_{30}Cr_{40})\), where the change in the sign indicates a magnetic phase transition. The coefficient \( B \) ranged from \( 1.90 \times 10^{-5} \) \((Fe_{25}Co_{40}Cr_{35})\) to \( 9.43 \times 10^{-5} \) \((Fe_{30}Co_{30}Cr_{40})\). Finally, we evaluated the critical exponent \( \beta \) to validate the analytical method. Critical exponent \( \beta \) is a fundamental constant that characterizes not only magnetic-phase transitions but also phase transitions. It is a universal parameter that is independent of materials. \( \beta \) can be expressed by the following equation

\[
\sqrt{A/2B} = |T_c - T|^\beta
\]

with the experimental \( A \) and \( B \) values for \( Fe_{30}Co_{45}Cr_{15} \). The Curie temperature \( T_c \) for the corresponding composition \((210^\circC)\) was taken from a previous study \([19]\). We verified the reproducibility of the results by repeating the same experiment for several different viewing fields. The \( \beta \) value obtained by this procedure was \( 0.36 \pm 0.028 \). Comparison with \( \beta \) values determined with the three-dimensional Ising model \((0.365)\) and for \( Fe_{78}Cr_{12}Si_{8}Nb_{3}B_{1}Cu_{1} \) \((0.367–0.376)\) \([29,31–34]\) showed that our results are in good agreement. Strictly speaking, estimating the critical exponents requires scanning both the magnetic field and temperature, which is time-consuming and requires the use of liquid helium. In this analysis, however, we could estimate the critical exponent with a fair agreement with the literature from the image information. As mentioned above, there remains an issue with using the Landau theory to treat spatial inhomogeneity. The introduction of a correction term describing the inhomogeneity of the magnetic domain structure would be useful to correct the landscape of free energy \([33,34]\). In a separate study, we have treated the inhomogeneity in microstructure via informatics. We have extracted the features of the magnetic domain structures and analyzed the energy landscape in information space \([20]\).

Finally, we remark on the importance of Landau theory for exploring material functions and materials informatics. Landau theory explains the ferromagnetic/paramagnetic phase transition based on statistical physics. It provides us with the conditions (composition and temperature) exhibiting ferromagnetism and is useful for searching the functional magnetic materials. From the viewpoint of material informatics, this study draws a phase diagram using image information at once. We discussed the information recorded in each pixel to describe the pseudo-free energy and analysed the magnetic-phase transition based on Landau theory.

While \( \beta \) is a universal physical parameter, both parameters, \( A \) and \( B \), depend on the material they are the gradients of the free energy landscape in Landau theory, and they depend on temperature and composition. The parameter \( A \) describes the demagnetization energy, and \( B \) describes the magnetic anisotropy energy. Curie temperature is a function of \( A \), \( B \) and magnetic moment. The Curie temperature is a relevant physical property in determining the appearance of ferromagnetism. Various physical parameters can be extracted from Landau theory, which is essential in the search for magnetic materials.

In this study, we found an equivalence of the temperature dependence scan to a scan of the paramagnetic component in a composition-gradient Fe-Co–Cr ternary thin film, and the universal physical constants could be obtained using a simple instrument configuration. In contrast to conventional exhaustive combinatorial analyses, the technique reported herein is a relatively simple way to obtain a universal parameter from image information. Although further studies are required to establish the general validity, our proposed system is an opening point for realising further efficient and inexpensive high-throughput experiments. The currently performed ex situ – in situ combination with beamline instruments has the potential to accelerate database construction and enable efficient materials discovery.

In summary, this study involved integrating a simple combinatorial thin-film deposition
technique using a 3D-printed sputtering aperture and high-throughput measurements of both the chemical composition and magnetic contrast of a Fe–Co–Cr ternary gradient thin film by PEEM. The appearance and disappearance of MCD contrast were confirmed depending on the chemical compositional ratios. Consequently, we could compose the magnetic-phase diagram of the Fe–Co–Cr ternary system by statistical analysis of the acquired image information. The ternary diagram was also in good agreement with the established ferromagnetic/paramagnetic transition and miscibility information. Finally, the evaluation of the critical exponent $\beta$ is based on the Landau theory, and the results showed quantitatively good correspondence with previous studies. This study describes a simple and efficient high-throughput experimental method combining materials synthesis, physical property measurement, and statistical analysis for exploring material functionalities. This work focused not only on drawing the phase diagram but also on analysing the magnetic-phase transition as an integral component of exploring the material functions. Moreover, the use of a 3D printer in high-throughput combinatorial sample preparation may provide the opportunity to conduct materials informatics research for small laboratories with limited resources, and contribute to expanding the field of materials informatics.

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Author contribution statement

M.K. designed and directed the experiments. T.N. and M. Y. prepared specimens, performed PEEM measurements, and analysed the data. T.O. carried out the PEEM experiment. D.N. and A.F. contributed to the preparatory experiment and discussions. All authors discussed the results and contributed to the final manuscript.

Data availability statement

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

References

[1] Lookman T, Alexander FJ, Rajan K. Information science for materials discovery and design Ch. Switzerland: Springer; 2016.
[2] Ludwig A. Discovery of new materials using combinatorial synthesis and high-throughput characterisation of thin-film materials libraries combined with computational methods. npj Comput Mater. 2019;5:70.
[3] Ramprasad R, Batra R, Pilania G, et al. Machine learning in materials informatics: recent applications and prospects. npj Comput Mater. 2017;3:54.
[4] Kusne AG, Keller D, Anderson A, et al. High-Throughput determination of structural phase diagram and constituent phases using GRENDEL. Nanotechnology. 2015;26(44):444002.
[5] Xiang X-D, Sun X, Briceño G, et al. A combinatorial approach to materials discovery. Science. 1995;268 (5218):1738–1740. DOI:10.1126/science.268.5218.1738
[6] Priyadarshini D, Kondratyuk P, Miller JB, et al. Compact tool for deposition of composition spread alloy films. J Vac Sci Technol A. 2012;30(1):011503.
[7] Zhao J-C. Combinatorial approaches as effective tools in the study of phase diagrams and composition–structure–property relationships. Prog Mater Sci. 2006;51(5):557–631.
[8] Shiga M, Tatsumi K, Muto S, et al. Sparse modeling of EELS and EDX spectral imaging data by nonnegative matrix factorization. Ultramicroscopy. 2017;170:43–59.
[9] Kotsugi M, Mizuguchi M, Sekiya S, et al. Determination of local magnetic moment in Li$_x$FeNi using photoelectron emission microscopy (PEEM). J Phys Conf Ser. 2011;266:012095.
[10] Kotsugi M, Wakita T, Tanuchi T, et al. Direct metallographic analysis of an iron meteorite using hard x-ray photoelectron emission microscopy. IBM J Res Dev. 2011;55(4):13. DOI:10.1147/JRD.2011.2159159
[11] Thienhaus S, Naujoks D, Pfetzing-Micklich J, et al. Rapid identification of areas of interest in thin film materials libraries by combining electrical, optical, X-ray diffraction, and mechanical high-throughput measurements: a case study for the system Ni–Al. ACS Comb Sci. 2014;16(12):686–694.
[12] Iain A, Ong SP, Hau tier G, et al. Commentary: the materials project: a materials genome approach to accelerating materials innovation. APL Mater. 2013;1(1):011002. DOI:10.1063/1.4812323
[13] National institute for materials science. AtomWork-Adv. Available from: https://atomwork-adv.nims.go.jp/service.html.

[14] Suzuki Y, Hino H, Kotsugi M, et al. Automated estimation of materials parameter from X-ray absorption and electron energy-loss spectra with similarity measures. npj Comput Mater. 2019;5:39.

[15] Iwasaki Y, Kusne AG, Takeuchi I. Comparison of dissimilarity measures for cluster analysis of X-ray diffraction data from combinatorial libraries. npj Comput Mater. 2017;3:4.

[16] Iwasaki Y, et al. Identification of advanced spin-driven thermoelectric materials via interpretable machine learning. npj Comput Mater. 2019;5:103.

[17] Kaneko H, Homma M, Nakamura K. New ductile permanent magnet of Fe-Cr-Co system. AIP Conf Proc. 1972;5:1088.

[18] Forcey KS, Iordanova I, Yaneva M. The diffusivity and solubility of deuterium in a high chromium martensitic steel. J Nucl Mater. 1997;240(2):118–123.

[19] Kaneko H, Homma M, Nakamura K, et al. Phase diagram of Fe-Cr-Co permanent magnet system. IEEE Trans Magn. 1977;13(3):1325–1327.

[20] Masuzawa K, Kunii S, Foggia J, et al. Analysis of the coercivity mechanism of YIG based on the extended Landau free energy model. T Magn Soc Japan. 2022;6:1–9.

[21] Kuch W. Layer-Resolved microscopy of magnetic domains in multi-layered systems. Appl Phys A. 2003;76(5):665–671.

[22] Gottlob D, Doğanay H, Nickel F, et al. Microscopic analysis of the composition driven spin-reorientation transition in Ni88-xPd12-x/001. Ultramicroscopy. 2015;159:503–507.

[23] Wang J, Kuch W, Chelaru LI, et al. Influence of exchange bias coupling on the single-crystalline FeMn ultrathin film. Appl Phys Lett. 2005;86 (12):122504. DOI:10.1063/1.1883318

[24] Kotsugi M, Mitsumata C, Maruyama H, et al. Novel magnetic domain structure in iron meteorite induced by the presence of L1 0 -FeNi. Appl Phys Express. 2009;3(1):013001. DOI:10.1143/APEX.3.013001

[25] Fukidome H, Kotsugi M, Nagashio K, et al. Orbital-Specific tunability of many-body effects in bilayer graphene by gate bias and metal contact. Sci Rep. 2014;4(1):3713. DOI:10.1038/srep03713

[26] Regan Tj, Ohldag H, Stamm C, et al. Chemical effects at metal/oxide interfaces studied by x-ray-absorption spectroscopy. Phys Rev B. 2001;64(21):214422. DOI:10.1103/PhysRevB.64.214422

[27] Yeh J-J, Lindau I. Atomic subshell photoionization cross sections and asymmetry parameters: 1 < Z < 103. Data Nucl Data Tables. 1985;32(1):1–155.

[28] Chakin PM, Lubensky TC. Principles of condensed matter physics. Cambridge: Cambridge University Press; 1995.

[29] Stanley HE. Introduction to phase transitions and critical phenomena. London: Oxford University Press; 1971.

[30] Iwano K, Mitsumata C, Ono K. 2-D magnetic domain patterns on thin films with perpendicular magnetic anisotropy. IEEE Trans Mag. 2016;52(7):7004604.

[31] Phan T-L, Thanh PQ, Chau N, et al. Influence of Cr doping on the critical behavior of Amorphous Alloy Ribbons Fe88-xCrxSi58Nb5B15Cu5, IEEE Trans Magn. 2014;50(11):1200104. DOI:10.1109/TMAG.2014.2325949

[32] Le Guillou JC, Zinn-Justin J. Critical exponents for the n-Vector model in three dimensions from field theory. Phys Rev Lett. 1977;39(2):95.

[33] Yamada T, et al. Visualization of topological defect in labyrinth magnetic domain by using persistent homology. Vac Surf Sci. 2019;62:153–160.

[34] Obayashi I, Hiraoka Y, Kimura M. Persistence diagrams with linear machine learning models. J Appl Comput Topol. 2018;1(3–4):421–449.