ILEEMS of thin α-Fe_2O_3 films prepared by RF sputtering

C. Van Cromphaut · V. G. de Resende · E. De Grave · L. Presmanes · I. Pasquet · P. Thaillades

Abstract Thin α-Fe_2O_3 films on semi-quartz substrates have been prepared by radio frequency (RF) sputtering of a magnetite target in a pure argon gas flow with a bias power applied. The films were studied by X-ray diffraction and Integral Low-Energy Electron Mössbauer Spectroscopy (ILEEMS), the latter in the temperature range of 80 to 330 K. In ILEEMS electrons of ~10 eV are detected and therefore it is an ideal instrument to study thin films with thicknesses below 500 nm. The first ILEEMS measurements on α-Fe_2O_3 films are reported and focus on the behaviour of the Morin transition, i.e., the reorientation of Fe^{3+} spins from the [111] crystallographic direction at low temperature, to the (111) basal plane at high temperature. Some films (~400 nm) show the presence of both a weak- and antiferromagnetic hematite phase for all temperatures between 140 and 330 K. Others of about ~100 nm thick only have a weak ferromagnetic phase for temperatures between 140 and 330 K of which the hyperfine field distribution shows two maxima, related to two distinct phases. Both phases stay in some films almost equal in intensity in the spectrum for the whole measured temperature range. In others a significant evolution in the spectral areas of both weak ferromagnetic phases as function of the temperature is observed.

Keywords Mössbauer spectroscopy · ILEEMS · Hematite · Thin film

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1 Introduction

The last decades, thin films and iron oxide thin films in particular, have been the topic of numerous research reports. Iron oxide thin films are indeed excellent candidates for the production of catalysts, sensors, non-linear optical and magnetic devices [1]. ^{57}Fe Mössbauer spectroscopy (MS) offers several advantages for studies of iron-containing compounds. It is specific for iron and the results (i.e., the various Mössbauer parameters) are extremely sensitive to the electronic, magnetic and structural features of the involved Fe-bearing phases, thus generally allowing phase identification and quantitative phase analysis of mixtures of iron oxides that are difficult to distinguish from each other in the respective XRD patterns.

Several researchers have tried to study iron oxide films with conversion electron Mössbauer spectroscopy (CEMS) [2–4], but the probing depth of CEMS being larger than 500 nm makes the technique less favorable to examine very thin layers. Integral Low-Energy Electron Mössbauer Spectroscopy (ILEEMS) [5], in which electrons of ~10 eV are detected, is a surface sensitive variant of MS and is an excellent tool to examine the magnetic properties of very thin iron oxide films (20–500 nm). In this contribution, two α-Fe_2O_3 thin films have been characterized by ILEEMS in order to determine certain magnetic aspects of these hematite films.

2 Experimental

Two iron oxide films with thickness of ~400 (A200) and ~100 nm (A100), respectively, have been prepared by RF magnetron sputtering on quartz glass substrates using an Alcatel SCR650 apparatus equipped with an RF generator (13.65 MHz). The sputtering was carried out in a pure argon gas flow and the working pressure was kept at a value of 0.5 Pa. During the deposition process, the amount of oxygen in the growing oxide layer is sometimes lowered in comparison to the ceramic target [6]. After the deposition stage the samples were annealed at a temperature of 650°C in order to obtain the stoichiometry of the hematite structure.

The crystallographic structures of the films were examined by X-ray diffraction (XRD) Grazing-angle patterns with incidence of 1° and θ-2θ patterns were collected by a Siemens D5000 diffractometer in the range 23° to 65° at a step of 0.030° 2-theta, and a count time of 30 s per step. The morphology and microstructure of the films were examined by atomic force microscopy (AFM) performed on a Veeco D3000 system.

ILEEMS was applied in the temperature range between 80 K and 330 K. ILEEM spectra at several selected temperatures between 330 K and 140 K were obtained. The spectra were collected with a spectrometer operating in constant acceleration mode with triangular reference signal. A ^{57}Co(Rh) source was used. The measurements were run for several days until a background of at least 1.5×10^5 counts per channel was reached. Isomer shift values quoted hereafter are with respect to α-Fe at room temperature (RT).

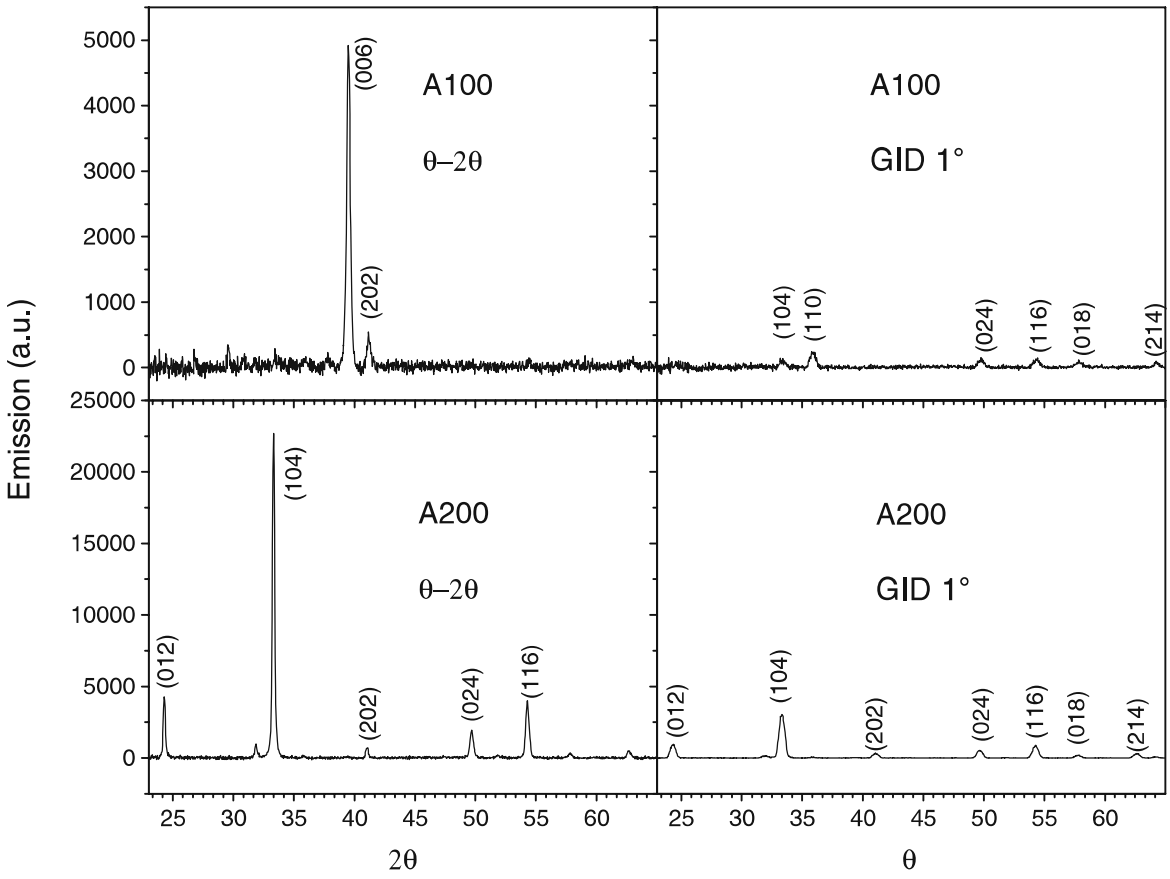

Fig. 1 θ-2θ (*left*) and glancing incidence at 1° (*right*) patterns of the thin films A100 and A200

3 Results and discussion

All diffraction peaks observed in the XRD patterns of the two films (Fig. 1) can be ascribed to hematite. For film A100, the (006) reflection, which for hematite powder is commonly less than 5% of the intensity of the most intense (104) peak, is the dominating the θ-2θ pattern. The same peak, however, is completely absent in the 1° grazing incidence pattern. This indicates a very strong orientation of the film, namely, a large amount of the grains have the (001) plane parallel with the surface of the film. A similar effect is observed in the XRD patterns of the other film, but here the film is mainly (104) oriented. As the films were deposited on glass, such a strong orientation was not expected.

All ILEEMS spectra of both films show a similar appearance and examples (RT, 240 K and 180 K) are plotted in Fig. 2. The obvious asymmetry in peak depths of the outer lines indicates the presence of a superposition of two sub-sextets. For A200 these sextets were interpreted assuming discrete, symmetrical sextet components with Lorentzian line shapes. The isomer shift and line width parameters, assuming a line width of the inner lines Γ and a line broadening parameter $\Delta\Gamma$, were coupled. The A100 spectra could not be computer-analyzed as superpositions of antiferromagnetic (AF) and weakly ferromagnetic (WF) hematite sextets. Instead, adequate and consistent fittings were obtained in terms of single model-independent

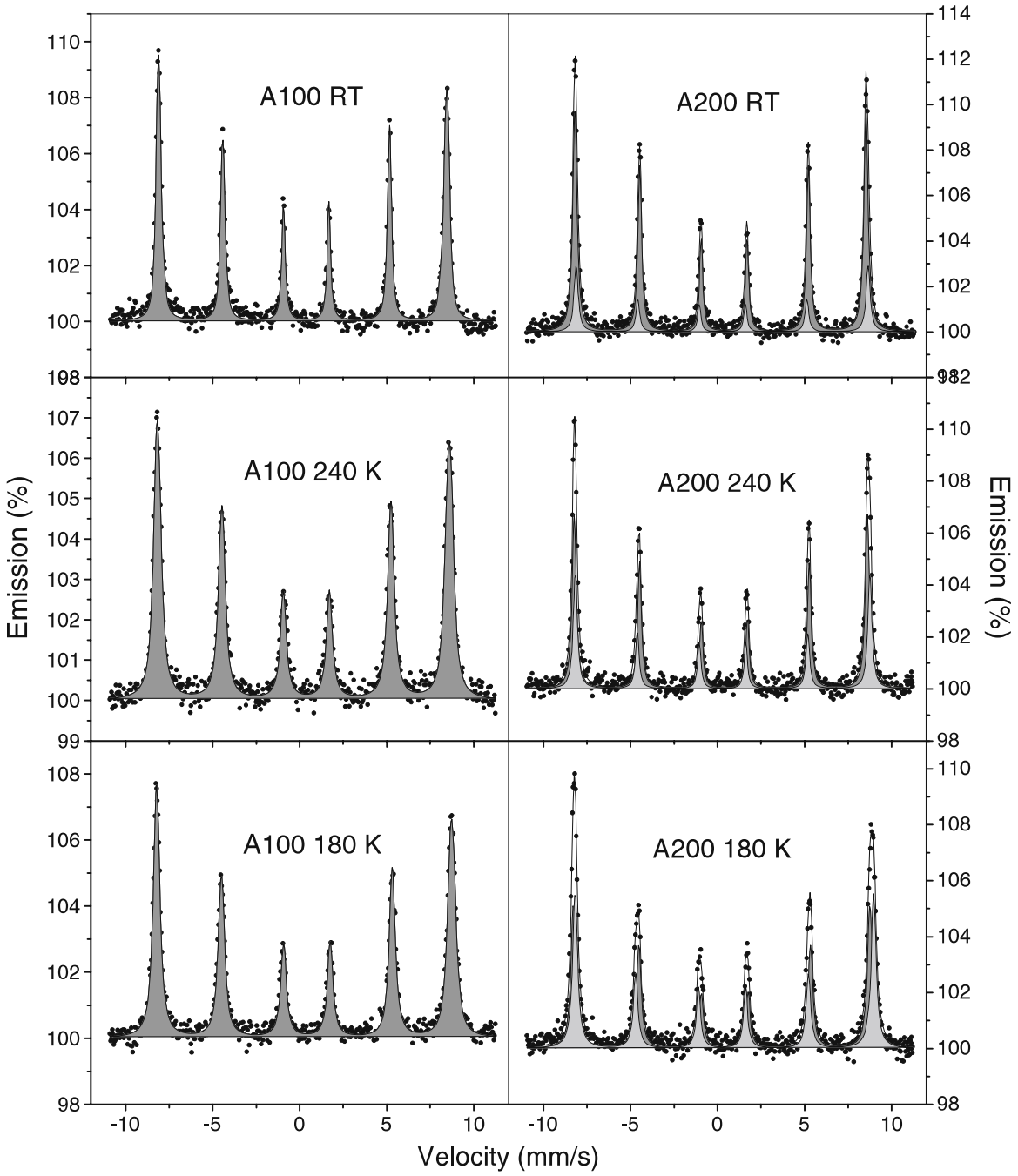

Fig. 2 ILEEMS spectra at RT (*top*), 240 K (*middle*) and 180 K (*bottom*) of thin films A100 (*left*) and A200 (*right*)

distributions of hyperfine-parameter values. The A100 numerical data quoted hereafter refer to maximum-probability values. The hyperfine field, to which the isomer and quadrupole shift values were correlated, was allowed to vary between 490 and 550 K in steps of 2 kOe.

The resulting hyperfine parameters are listed in Table 1. Both films behave differently when the temperature is lowered. For A200 an antiferromagnetic phase is already found at RT, which is quite surprising since for bulk hematite an AF state is observed only at temperatures lower than ~260 K. On lowering the temperature, the contribution of the AF phase increases at the expense of the WF phase (Fig. 3).

Table 1 Mössbauer parameters of A100 and A200

Temperature (K)	Weakly ferromagnetic					Antiferromagnetic				
	H_{hf}	δ	$2\varepsilon_Q$	I_2	RA	H_{hf}	δ	$2\varepsilon_Q$	I_2	RA
A200										
140	528	0.34	−0.14	2	45.6	534	0.34	0.16	1.33	54.4
160	528	0.33	−0.17	2	44.6	533	0.33	0.13	1.33	55.4
180	528	0.32	−0.18	2	50.9	532	0.32	0.14	1.33	49.1
200	527	0.31	−0.20[a]	2	57.3	530	0.31	0.15	1.33	42.7
220	525	0.31	−0.19	2	59.6	529	0.31	0.09	1.33	40.4
240	522	0.29	−0.21	2	62.9	525	0.29	0.03	1.33	37.1
260	521	0.29	−0.22	2	68.2	523	0.29	0.03	1.33	31.8
270	522	0.28	−0.22	2	72.4	523	0.28	0.04	1.33	27.6
300	519	0.27	−0.21	2	79.2	520	0.27	−0.01	1.33	20.8
330	515	0.26	−0.21	2	95.1	519	0.26	0.02	1.33	4.9
A100										
140	523.6	0.33	−0.17	1.96	58.2	535.0	0.33	−0.11	1.96	41.8
160	524.3	0.32	−0.15	1.93	80.0	533.7	0.32	−0.09	1.93	20.0
180	522.0	0.33	−0.17	1.89	47.0	529.3	0.33	−0.13	1.89	53.0
200	519.1	0.32	−0.17	1.86	45.0	532.3	0.32	−0.13	1.86	55.0
220	515.6	0.31	−0.20	1.88	46.0	527.8	0.31	−0.14	1.88	54.0
240	514.3	0.30	−0.19	1.95	46.0	524.8	0.30	−0.16	1.95	54.0
260	509.7	0.28	−0.22	1.91	41.0	522.7	0.28	−0.18	1.91	59.0
280	512.7	0.28	−0.20	1.90	53.0	521.0	0.28	−0.19	1.90	47.0
300	510.9	0.27	−0.21	1.88	50.0	516.5	0.27	−0.19	1.88	50.0
330	509.3	0.26	−0.22	1.94	57.0	514.6	0.26	−0.19	1.94	43.0

H_{hf} hyperfine field (kOe), δ isomer shift (mm/s), $2\varepsilon_Q$ quadrupole shift (mm/s), I_2 relative spectral area of the middle lines with respect to the inner lines, RA relative area of the subspectrum (%)
[a]Parameter fixed during iteration

This transition, the so-called Morin transition (MT), changes very slowly over a much broader temperature range (>200 K) as compared to common bulk samples (~60 K) [7]. At 180 K, the contributions of the two phases are equal. Therefore 180 K can be considered as the Morin transition temperature, which is much lower than for the bulk analog (~260 K). These two effects, i.e. the coexistence of AF and WF phases over a broad temperature range and a low average MT temperature are normally observed in hematite samples with small particles sizes and/or Al-for-Fe substitutions [8]. At the higher temperatures the quadrupole shift of the AF phase is close to zero and the difference between the hyperfine fields H_{hf} of the WF and AF phase is often rather small (normally ~8 kOe). These features have also been observed for (small-particle) hematite powders at temperatures where the relative area of the AF phase is small [8].

The relative spectral areas of the middle lines to the outer lines are normally close to 2:3 when the orientation of the spins in three dimensions is random. For the AF phase of film A200 this ratio is about 1.33, which is an indication for a strong spin texture effect in the film.

The calculated distributions of the hyperfine field of the ILEEMS spectra of A100 reveal the presence of two more or less distinct WF phases WF1 and WF2, both characterized by a negative quadrupole shift. After adjusting the distribution profiles with two Gaussian functions, it became clear that these phases stay about equally intense over the whole temperature range from 140 to 330 K (Fig. 3). The

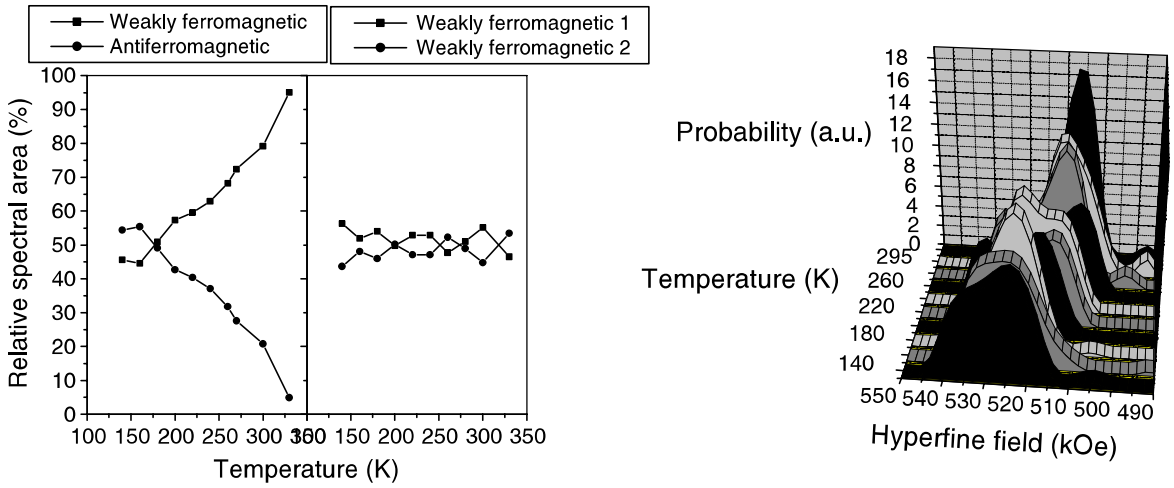

Fig. 3 Relative spectral areas (% of total spectrum) as a function of the temperature for thin film A200 (*left*) and A100 (*right*). Hyperfine field distributions derived from the ILEEMS spectra at several temperatures between 140 and 330 K of thin film A100. The distribution shows two maxima, related to two distinct weakly ferromagnetic phases

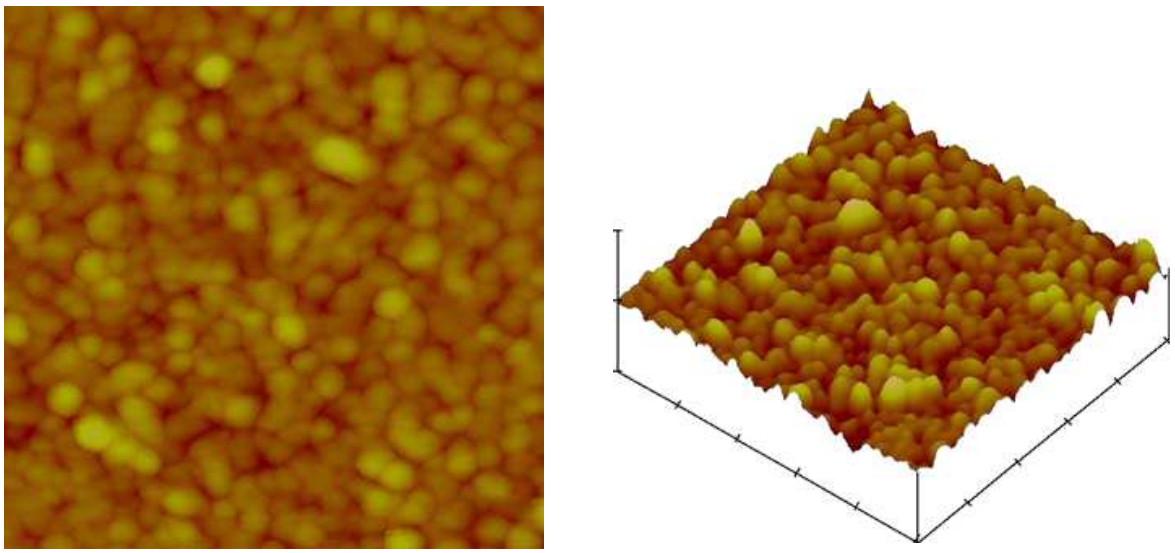

Fig. 4 AFM images of the hematite thin film A100 (1 × 1 μm), depth scale 25 nm

hyperfine field and the quadrupole shift of the WF1component are consistently lower by ~10 kOe and 0.05 mm/s, respectively, than those of the WF2 component, while the isomer shifts are nearly the same. The differences in the hyperfine parameters WF1 and WF2 are rather small and it is believed that they can be attributed to differences in defect structure, the latter affecting the symmetry distortions of the involved Fe sites. The apparent absence of a MT for A100 down to 140 K is commonly observed in hematite powders with small particle size of ~20 nm or less. However, AFM observations of the films clearly show that particle sizes of the grains in both films are larger (see Fig. 4 for A100). From Scherrer's formula, using the most intense peak of the θ-2θ pattern, the particle size of A100 and A200 was estimated to be 23 nm and 56 nm, respectively. Thus, it is likely that the grains as seen in the AFM images are conglomerates of smaller particles of about 20 nm.

Similar effects have been observed by Fujii et al. [4] for epitaxial hematite films on sapphire substrates, for which the MT temperature was found to be dependent on the orientation of the film. An (102) oriented film had a MT at 400 K, which is much higher than that of a free crystal. The authors suggested that the high MT temperature is due to anisotropic lattice strains in the film. The transition in a (001)-film could not be observed down to 2.5 K. Also Gota et al. [9] have observed the same in (001)-epitaxial hematite films (2 and 8 nm) on sapphire substrates and attributed the effect of the absence of the Morin transition in their films to a lattice expansion in the *c* plane which changes the Fe^{3+} ion special positions in the unit cell to such an extent that it makes the dipolar contribution to the magnetic anisotropy to be the dominant term, even at very low temperature. The magnetic moments stay pinned in the basal plane and the easy magnetic axis cannot turn onto the *c*–axis. These results show that this effect is not related to the film thickness and/or substrate, but rather to film orientation.

Finally, it should be mentioned that alternative procedures applied for fitting the ILEEMS spectra did not significantly affect the results concerning the presence of the two phases, their magnetic properties (weakly or antiferromagnetic), nor the results about the MT. Further studies of the films by means of positron annihilation to examine the defect structure in an attempt to support these preliminary results and interpretations are currently in progress and will be the subject of a forthcoming report. In addition more films will be prepared in which physical parameters such as the film thickness and annealing temperature will be varied in order to extend the information about the behavior of the MT in thin hematite films.

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