Ferrimagnetic Garnet Thin Films: Growth, Structure and Some Magnetic Properties

M. ORON*, I. BARLOW, W. F. TRABER

International Business Machines Corporation, Systems Development Division, San Jose, California, USA

Ferrimagnetic garnet films, mainly gadolinium iron garnet, were deposited on fused-quartz substrates and subsequently heat-treated. They were studied by optical microscopy, X-ray analysis, and electron microscopy. Magnetic properties were measured and domains observed by employing the Faraday magneto-optic effect. Structure and properties were found to depend on growth parameters established in the heat-treatment step. The role of chemical factors in promoting the observed anomalies in structure (such as precipitation of Gd_2O_3 particles) and in properties (like the unusually high compensation temperature of the thinner films) is emphasised in the discussion of results.

1. Introduction

In contrast to ferromagnetic thin films which have been studied and used extensively for the last ten years, the field of ferrimagnetic films is still in its infancy. The concept of ferrimagnetism itself is not much older than two decades. Néel [1] coined the term *ferrimagnetism* for magnetic phenomena displayed mainly by mixed, iron-containing oxides of the spinel structure, also known as ferrites. Other ferrimagnetic materials, generally of a more complicated structure, have in the meantime been discovered or deliberately synthesised.

A particularly interesting group of ferrimagnets, the so-called rare-earth garnets, was independently identified in 1956 by Bertaut and Forrat [2] and by Geller and Gilleo [3]. These materials have a cubic unit cell of space group O_h^{10} — Ia3d and chemical formula $R_3Fe_5O_{12}$, where R stands for yttrium or some of the rare-earth ions. The original ions, or their substitutes in more complicated garnets, occupy specific sites in the lattice, thus forming sublattices of different magnetic moments which interact to give rise to the observed net magnetisation. This mechanism leads to an interesting thermomagnetic property, the *compensation temperature*, at which the net magnetisation is zero because the individual magnetisations of the sublattices have equal magnitudes but opposite signs. It is evident even from this short discussion that the magnetism of garnets, and especially the compensation temperature, is strongly dependent on crystallographic parameters.

The slow development of ferrimagnetic thin films can be attributed to their much more complicated structures and properties as compared with simple metallic ferromagnets. This very reason, however, made their preparation and study more challenging and interesting. A number of reports relating to thin ferrimagnetic films have already been published [4-6].

Our work was carried out mainly on gadolinium iron garnet films ($Gd_3Fe_5O_{12}$ or, in abbreviated form, GdIG) prepared on fused-quartz substrates by chemical [7] or sputtering [8] techniques. The emphasis was on structural characterisation and possible correlation with growth conditions and magnetic properties, mainly the compensation temperature and the coercive force.

2. Experimental Procedures

2.1. Preparation

Nearly all preparation techniques of ferrimagnetic compound films involve two stages: (1) the actual deposition of materials, and (2) a postdeposition formation stage which is essen-

*Now with the Department of Electronics, Weizmann Institute of Science, Rehovot, Israel.

tially a heat-treatment. The deposition of GdIG films by sputtering was described in detail by Sawatzky and Kay [8]. Only a few of the films prepared by the above workers were examined in our study. Most of our specimens were deposited by spinning of liquid chemical solutions as described by Giess [7].

The apparatus employed for spinning was a commercial photo-resist spinner* equipped with automatic control circuitry. Most of the substrates were polished disks of fused quartz, 25.4 mm in diameter and 0.75 mm thick. Occasionally, larger or thinner substrates were used. Composition of the solutions was adjusted to correspond with the stoichiometry of the various elements in the final material. All volatile by-products were driven off the substrate in a low-temperature (about 300° C) drying process between successive coatings. The "green" film consisted of a solid mixture of amorphous material which was transformed into crystalline garnet upon heating in ambient atmosphere at higher temperatures (700 to 1100° C) for different lengths of time (4 h to 1 min). The final thickness of the GdIG films could be related to the number of coatings and the spinning parameters by optical interferometry.

2.2. Examination
Chemical stoichiometry of representative films was ascertained by X-ray fluorescence. Crystalline phases were identified by X-ray diffraction, using both diffractometer scanning and powder-camera photography. Optical microscopy was employed in the transmission and reflection modes, the latter utilising Nomarski [9] interference attachments for better resolution of topographical features.

A Faraday magneto-optic rotation attachment for the optical transmission microscope was constructed by E. B. Moore of our laboratory and used to detect magnetic domains employing polarised blue light and DC magnetic fields. This technique enabled qualitative observation of domain patterns in GdIG as initiated by Dillon [10]. Quantitative magnetic data, mainly compensation temperatures (T_{cp}) and coercivities at $T_{cp} + 10°$ C (H_{c10}) and $T_{cp} + 20°$ C (H_{c20}) were measured in a Faraday rotation hysteresigraph (60 Hz) constructed and described in detail by Beck [11].

The main effort, however, was concentrated on examining thin garnet films in the electron

*Headway Research Inc, Model EC100.

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microscope. They could be replicated using standard techniques (two-step replica, PVA, Pt/C for shadowing, and C as the final replica). However, removal of the thin, brittle films from their substrates for transmission microscopy was found to be difficult because of their strong adhesion. An attempt to chip particles out of the film [12] introduced too many artifacts.

A suprisingly successful peeling technique was finally worked out, whereby the film on its substrate was immersed in dilute hydrofluoric acid for 1 to 2 sec after scoring into suitable size squares. Immediately afterwards, the sample was dipped into cold distilled water, upon which the thin garnet film floated on to the water surface. After ample washing, the electron microscope specimens were collected on carbon-coated grids and examined in the electron microscope (Philips EM 100) immediately. This procedure, when carefully carried out, introduced almost no artifacts.

3. Results
Cracks formed in all films of GdIG deposited on fused-quartz substrates. Typical transmission micrographs taken with blue plane polarised light are shown in fig. 1. In 1a a magnetic DC field normal to the film surface was applied. The direction of the field was reversed but the magnitude unchanged in 1b. From the relative brightness changes of respective areas in the two micrographs, deductions can be made as to the magnetic domain structure of the film. It is evident that, in some cases, whole cracked islands act as single domains, whereas other islands seem to break up into several domains, or even group up to form one large domain.

Optical microscopy did not reveal the grain-structure of these films and its possible correspondence to the magnetic domain structure. Electron microscope replicas similarly failed to resolve this problem. It was therefore necessary to employ transmission electron microscopy. For that purpose one-coating films were spun (less than 1000 Å thick) and examined as described in section 2.2. Fig. 2 is a typical transmission micrograph of such a film. An abundance of extinction contours caused by the stress condition of the thin film was found to be characteristic of most garnet films examined. At points of high symmetry, the dark extinction bands intersect because of the saucer-shape of the foil [13]. This phenomenon is demonstrated by selected

(a)   (b)

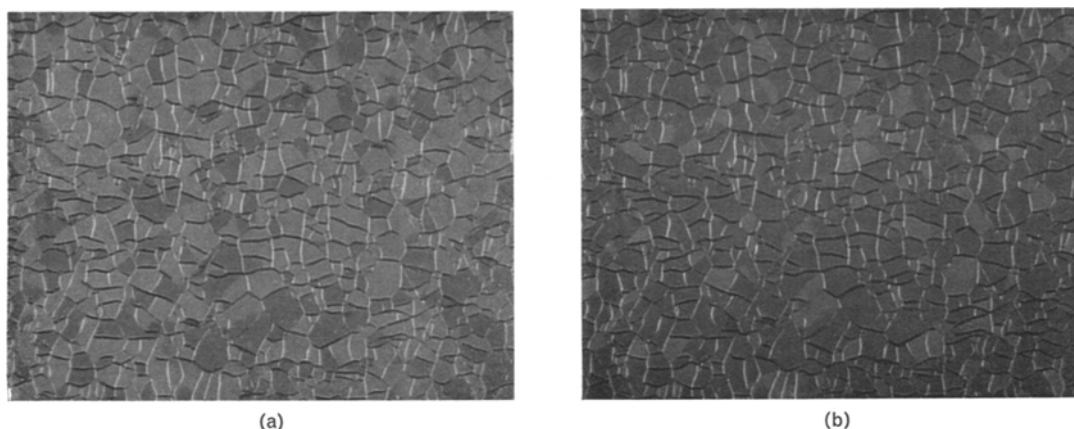*Figure 1* Optical transmission micrographs of typical GdIG film on fused-quartz substrate (× 145, blue plane polarised light), with (a) magnetic DC field normal to film; (b) same as (a) but with field direction reversed.
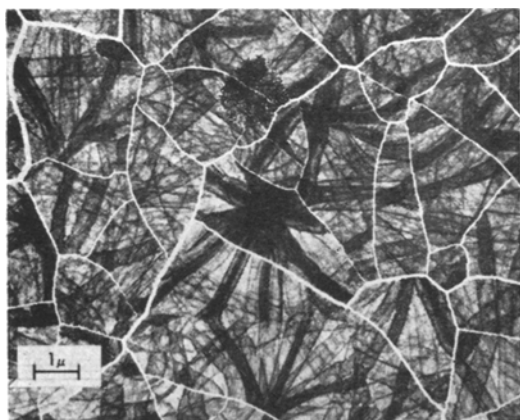

Figure 2 Electron transmission micrograph of 1000 Å thick GdIG film after slow heat-treatment at 750° C for 2 h.

area diffraction as shown in fig. 3. The diffraction pattern corresponds to a perfect $\{100\}$ plane orientation of that area extending beyond one cracked island.

The pattern of extinction contours is helpful in determining the grain-structure of the film, since contours are not continuous across grain-boundaries [14]. Fig. 4 shows a clear example of a grain-boundary in the thin garnet film; the corresponding diffraction pattern (4b) reveals that the two adjacent grains have a common [100] axis but are twisted relative to each other. The whole film shows a strong $\{100\}$ preferred orientation and relatively large grains (up to 10 μm) which extend beyond the cracked islands.

In other words, the majority of the cracks are transgranular.

Fig. 2 shows another important feature exhibited by most of the thin films examined: namely, second-phase inclusions or precipitates. Selected area diffraction (fig. 5) of a typical precipitate revealed that the inclusions were highly-strained particles of gadolinium oxide (Gd_2O_3) with their $\{100\}$ planes parallel to the substrate. All precipitates exhibited this orientation in the more than twenty films examined. However, the $\{100\}$ orientation of the GdIG matrix was not universal, although predominant; some of the films showed GdIG grains of $\{110\}$ and $\{111\}$ orientation. The oxide precipitates, so distinctly evident in the transmission electron micrographs, could also be correlated with corrugated surface areas in some of the electron microscope replicas (fig. 6). They could not, however, be detected by X-ray diffraction because the films examined were too thin.

All of the above findings were observed on one series of thin ($<$ 1000 Å) spun films formed by heat treating at 750° C for 2 h. Different solutions were used, employing various starting materials; some were even doped with gallium and other rare-earths. Yet no basic difference in their morphology could be detected. Since the occurrence of oxide precipitates could be attributed to nonstoichiometry, great care has been executed in perfecting the preparatory and analytical procedures so that less than 1 % deviation from stoichiometry could be achieved. When even this failed to prevent precipitation of
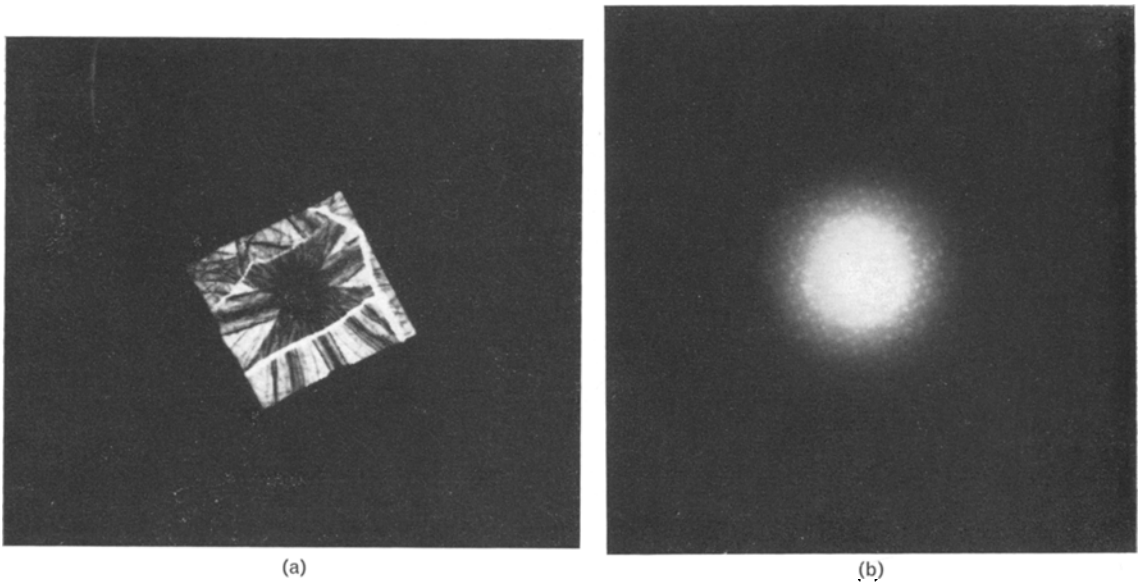
Figure 3 Selected-area electron diffraction of crossed contours spot corresponding to area of high crystalline symmetry: (a) transmission micrograph; (b) diffraction pattern.
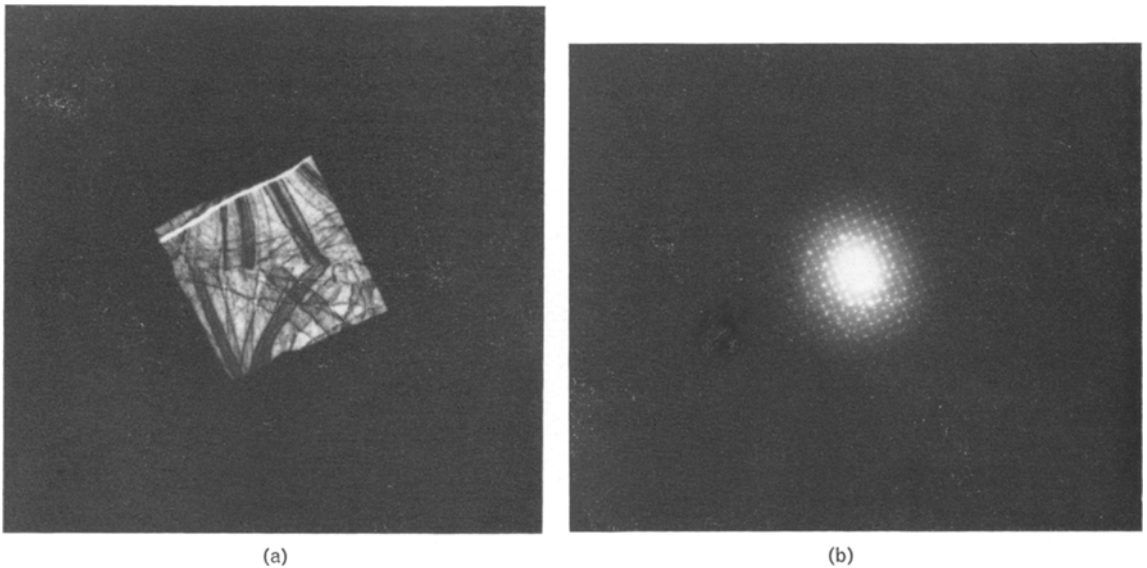

Figure 4 Selected-area electron diffraction of grain-boundary: section (a) transmission micrograph, and (b) diffraction pattern.

Gd_2O_3 which was also detected in sputtered samples, the effect of heat-treatment parameters had to be examined.

For this purpose a 10×10 cm fused-quartz substrate was spun and cut into small samples before firing; heat-treatment parameters such as rates of heating and cooling, maximum tempera-

ture, and duration of heating were systematically varied. Electron microscopy of these specimens suggests a correlation between the occurrence of Gd_2O_3 precipitates and heat-treatment parameters; longer heat-treatments at higher temperatures tend to enhance precipitation.
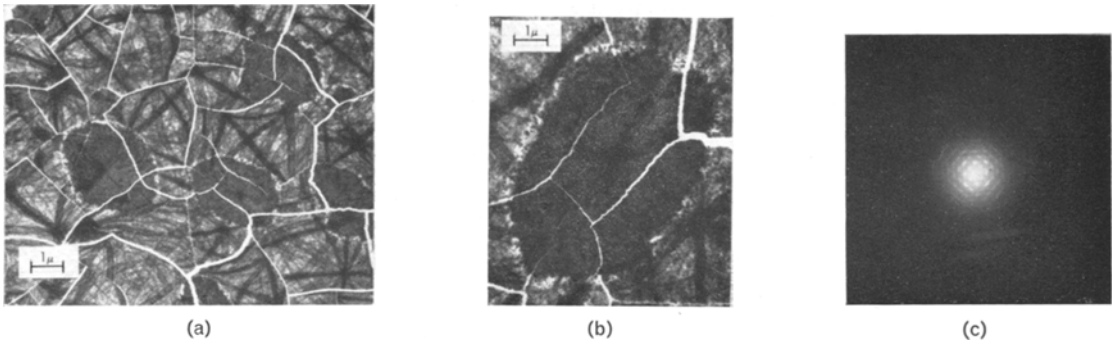
The morphology of the films was found to

Figure 5 Electron microscopy of Gd_2O_3 precipitates in **GdIG** films: (a) transmission micrograph of precipitates in matrix; (b) transmission micrograph of a single precipitate; (c) electron diffraction pattern of precipitate.
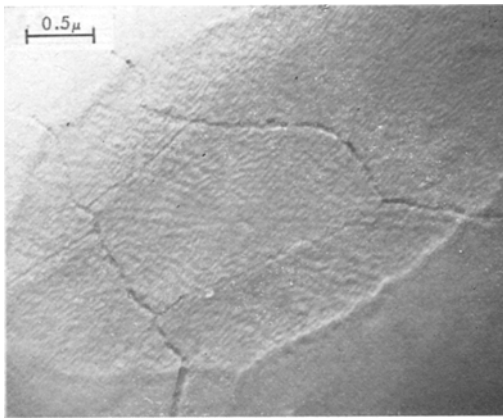

Figure 6 Electron micrograph of **GdIG** film replica showing contour of Gd_2O_3 precipitate.

depend strongly on the rate and duration of heating. Films that were inserted abruptly into hot furnaces (from 750° to 1100° C) kept there for a relatively short period (30 min to 1 min, respectively), and pulled out immediately, invariably exhibited a fine random grain-structure with no evidence of extinction contours. A typical electron micrograph of such a film is shown in fig. 7. To confirm this finding, two samples were loaded into the furnace; one was heated slowly and cooled slowly in the furnace, the other inserted at the maximum temperature (800° C) and pulled out after the duration of the treatment (20 min). The resulting structures are shown in fig. 8.

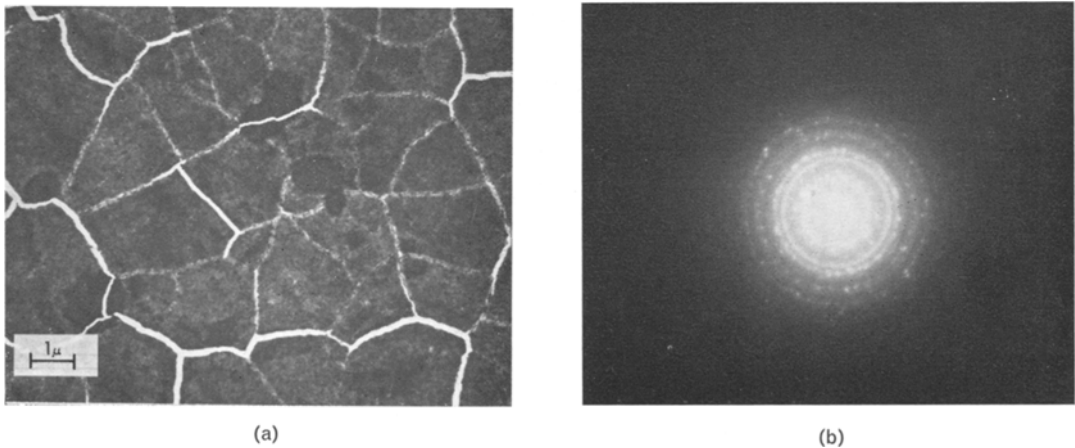As stated, all of the above samples were coated only once by spinning and, therefore, were

Figure 7 **GdIG** thin film (1000 Å) after insertion into 750° C furnace for 30 min and immediate withdrawal: (a) transmission micrograph; (b) electron diffraction micrograph.
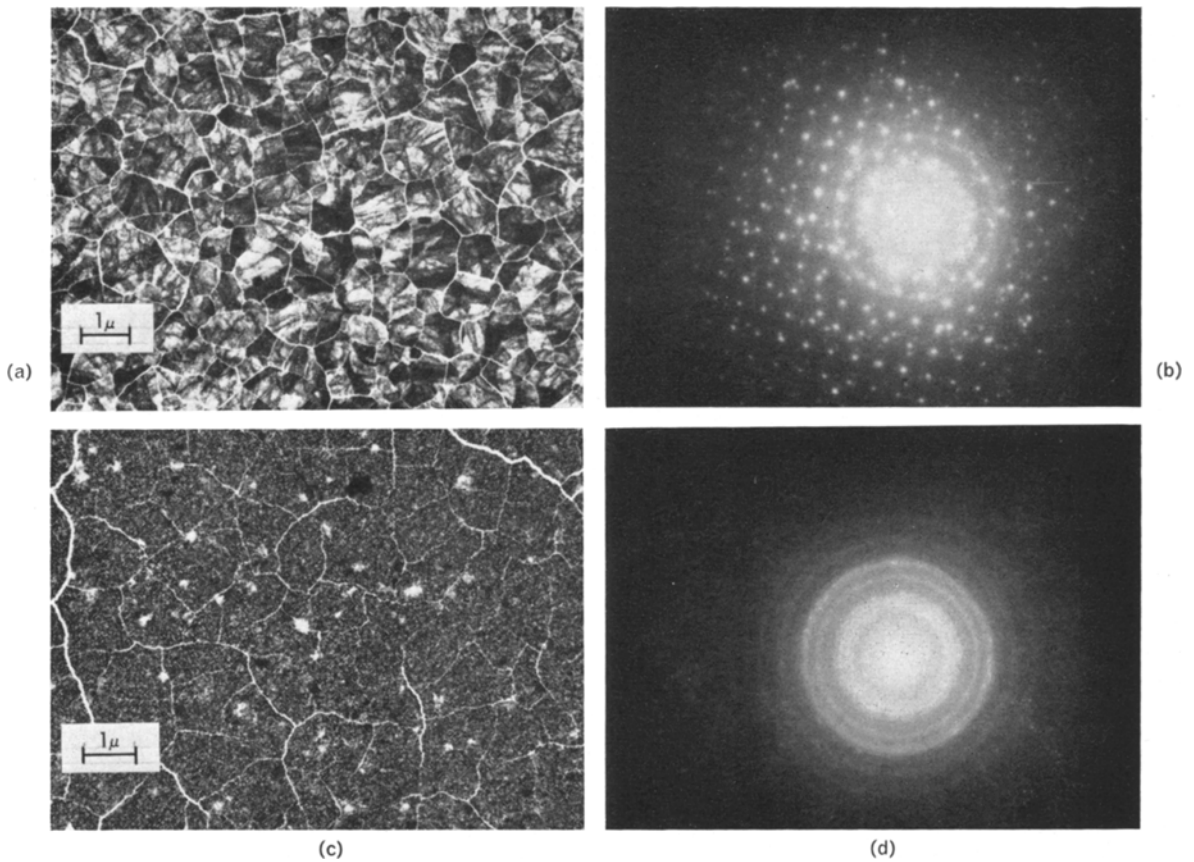
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Figure 8 Two sections of a GdIG thin film heated at different rates to 800° C and kept there for 20 min: (a) slow heating and cooling; (b) diffraction pattern of a 3 × 3 μm area in (a); (c) immediate insertion into and withdrawal from furnace; (d) diffraction pattern of 3 × 3 μm area in specimen shown in (c).

rather thin compared with the films used in the study of magnetic properties. They typically displayed very high coercive forces ($H_{c10} >$ 1500 Oe) and relatively high compensation temperatures. Because of these high coercivities, it was practically impossible to study their domain structure, since the switching fields in the Faraday attachment could not match the high coercivity values. A general result of the magnetic measurements was that compensation temperatures of films treated at higher temperatures tended to be higher than those of lower temperature treatments (e.g. $T_{cp} = 5°$ C for 750° C heat-treatment; $T_{cp} = 13°$ C for 900° C heat-treatment; and $T_{cp} = 25°$ C for the 1100° C heat-treatment.

In order to correlate the "normal" magnetic properties of the thicker films with the electron microscope findings on the thinner ones, it was necessary to detect somehow whether the struc-
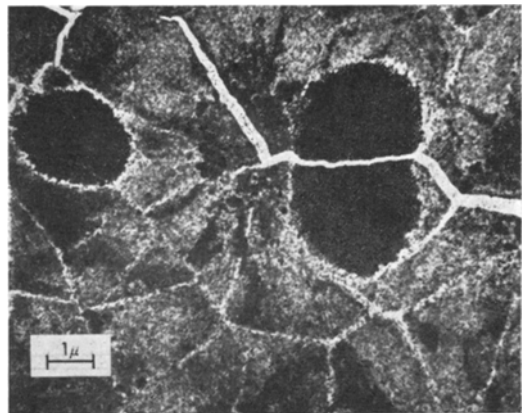

Figure 9 Electron transmission micrograph of a GdIG film (originally 1 μm thick) which has been thinned down by etching in HF acid. (Note occurrence of precipitates.)

tural features discovered by electron transmission were also valid for the "normal" films. This was

accomplished by very prolonged etching of films in concentrated hydrofluoric acid until some of their edges were thin enough for transmission. Fig. 9 is a typical transmission micrograph exhibiting again the occurrence of Gd_2O_3 precipitates. This was the only valid result obtained by prolonged etching of thicker films; the severe etching was too destructive, preventing a study of other features.

4. Discussion

Cracking of garnet films, deposited on fused-quartz substrates and heat-treated at high temperatures, can be most easily explained by the considerable difference between the thermal expansion coefficients of the two materials ($5 \times 10^{-7}/^{\circ}$ C for fused quartz and about $100 \times 10^{-7}/^{\circ}$ C for GdIG). Almost all the cracking takes place in the crystalline phase. Nucleation of the crystalline phase, which is believed to be garnet whenever the composition of the amorphous material is stoichiometric, starts at temperatures higher than 600° C, as has been confirmed by Giess' kinetic study [15]. In some cases crystallisation is actually accompanied by cracking, as can be seen from fig. 10. However, the volumetric change associated with the phase transformation cannot be the only cause for the high tensile stresses which finally lead to fracture through cracking. This has been most convincingly demonstrated by Moore and by Sawatzky who succeeded in depositing crack-free films on substrates with matched coefficients of thermal expansion.

The transgranular mode of fracture, as observed by transmission microscopy and optical micrographs like fig. 10b is contrary to the accepted view that fracture in ceramics is intragranular [16]. This in itself is, therefore, an important finding.

As in any phase transformation, the morphology of the final film is determined by the laws of nucleation and growth (fig. 10). At relatively low temperatures, nucleation seems to originate at preferred sites provided by the substrate. The orientation of the initial nuclei will be such that growth of crystals with their low index planes parallel to the substrate is favoured, minimising the free energy of transformation [17,18]. Whenever the rate of heating is slow and followed by a prolonged heat-treatment, the initial nuclei will proceed to grow until all the material is transformed into a film of relatively large and well-oriented grains, as is indeed evidenced by figs. 2, 3, and 8a.

However, if the film is heated rapidly to high temperatures, nucleation occurs primarily during the transformation stage, because the relatively high superheating provides sufficient activation energy for the formation of a large number of randomly oriented nuclei. If the heat-treatment is carried out only for short periods at these high temperatures, the growth stage is short and does not yet involve recrystallisation phenomena. The resultant morphology will be one of a random, fine-grain structure as demonstrated in figs. 7 and 8c.

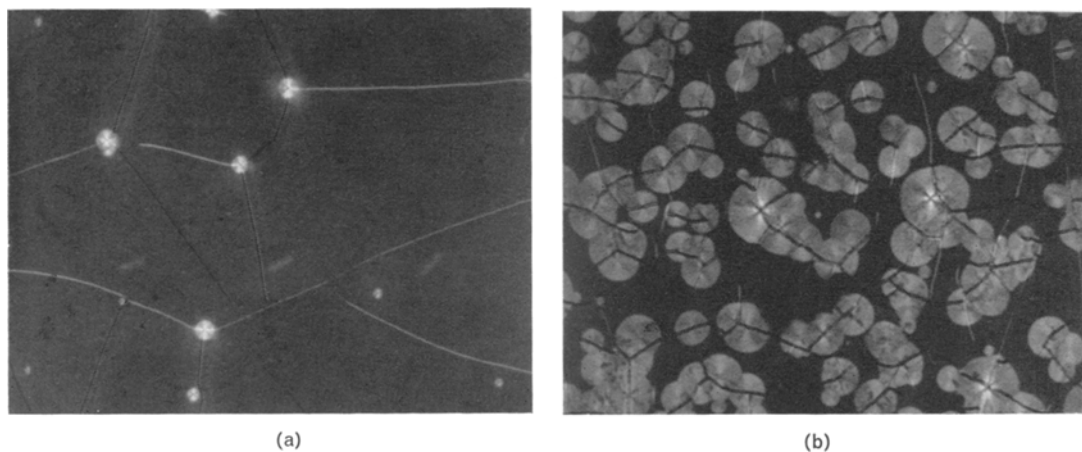It should be noted that the cracking of films

(a)   (b)

Figure 10 Optical transmission micrographs of GdIG film ($\times$ 520, blue plane polarised light): (a) after 4 h at 650° C, and (b) after an additional hour at 700° C.

by no means relieves them of all the strains and stresses accumulated in the formation process. The extinction contours displayed by the well-oriented films show that they are still deformed even after release from the substrate. In this respect, garnet films do not differ from other materially more simple films which are known to be highly stressed [19]. The significance of the high strain level in reference to the magnetic properties of GdIG films has been discussed at length by Sawatzky and Kay [8]. Employing the general finding that compensation temperatures are a function of hydrostatic stress [20], they attributed the observed increase in compensation temperature of their thinner films to increased stress conditions which were reflected in changes of the lattice parameter.

In our work, films of the same thickness – in fact, different samples of the same film – when heat-treated at different temperatures, exhibited different compensation points. The fact that the compensation point was higher for films heat-treated at higher temperatures for shorter periods may indicate that the shift of the compensation point was at least partly stress-induced. However, not everything can be explained by this "stress theory". For example, we have observed that films, which were floated off their substrates and thus left only with "intrinsic" stresses [19], showed a decrease in coercive force by a factor of two, but their compensation point remained practically unchanged. Fig. 11 shows such a film before and after etching in hydro-fluoric acid with the corresponding hysteresis loops. The etching has definitely relieved some of the stresses, virtually lifting areas in the film off the substrate (11b), yet it did not affect the compensation point. To explain this discrepancy,
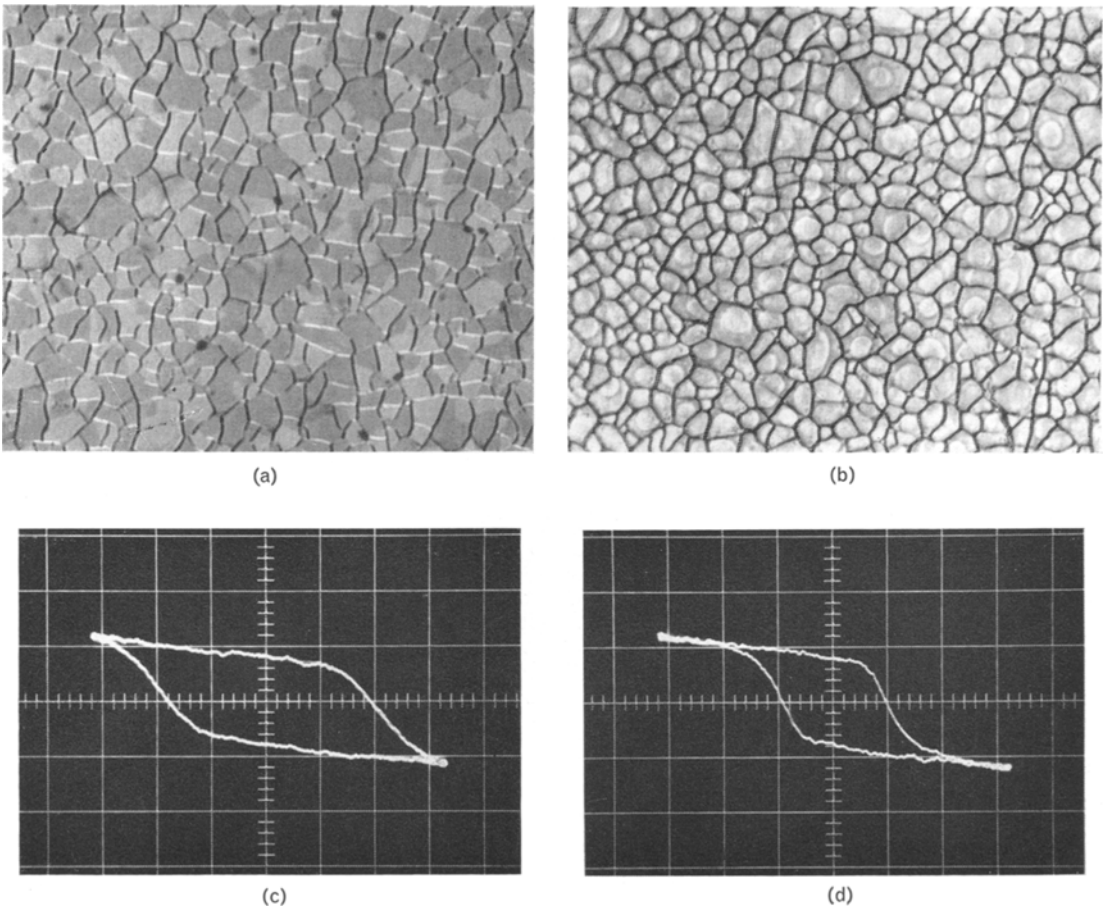

(a)   (b)

(c)   (d)

Figure 11 GdIG film (a) before and (b) after etching with HF acid (× 630), along with the corresponding hysteresis loops (c) and (d). Horizontal axis calibration: 60 Oe per division.

(a)   (b)
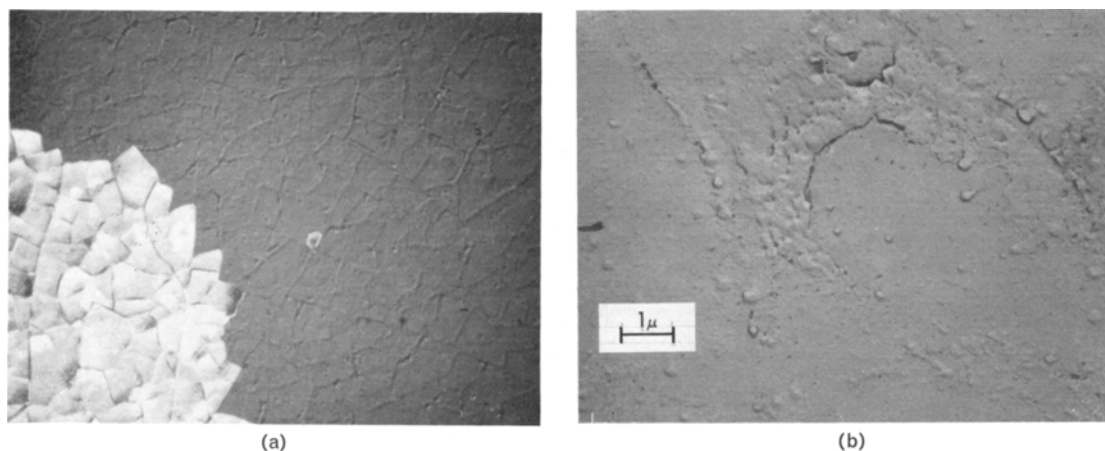
Figure 12 Fused-quartz substrate surface exposed by mechanical removal of film: (a) Nomarski reflection micrograph (× 275); (b) electron micrograph of replica.

we are almost forced to consider chemical factors.

It was shown previously [21] by electron microprobe analysis that chemical interaction at a bulk GdIG/fused-quartz interface indeed takes place. Furthermore, optical examination of substrate areas exposed by peeling off a poorly adhering film shows that the quartz has undergone some chemical reaction (fig. 12) which might be caused by diffusion across the interface. Because of its larger atomic size, gadolinium diffuses less readily than iron. The net result of this interaction might therefore be a gradient of iron composition in the film, with a more pronounced iron deficiency near the interface. In addition, at higher temperatures, silicon diffusion into the film also becomes considerable [21].

The mechanism suggested above gives an explanation of the fact that T_{cp} is a function of thickness in a series of specimens [8] or in any one tapered specimen. Moreover, it was shown by Giess [22] that, if successive coatings of a multicoating film are intentionally made to be iron- or gadolinium-rich, their compensation temperature is lowered or raised correspondingly; a phenomenon which can be explained with the aid of fig. 13.

One octant of the garnet structure $\{R_3\}[Fe_2]$ $(Fe_3)O_{12}$ was drawn (fig. 13a), representing the three types of sites designated as the $\{24c\}$ dodecahedral, the $[16a]$ octahedral and the $(24d)$ tetrahedral positions. The magnetic interaction between the c-d sublattices is positive whereas the d-a is negative, giving rise to a compensation point at the temperature where the absolute values of the two interactions are
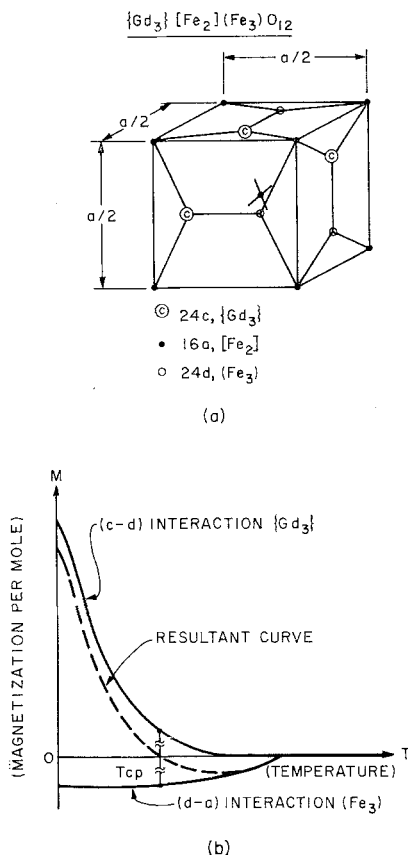

(a)

(b)

Figure 13 Simple schematic of GdIG: (a) octant of crystallographic unit cell, showing only the cation sites, and (b) qualitative magnetisation versus temperature curves.

equal (fig. 13b). Depletion of iron from the garnet tends to make the d-a interaction curve

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(representing the sum of the individual interactions per mole) less negative, thus shifting T_{cp} to a higher temperature. Substitution of iron atoms by the nonmagnetic silicon, which greatly prefers the d sites [23], enhances this situation.

An additional consequence of this iron depletion is the precipitation of Gd_2O_3 out of the relatively gadolinium-rich matrix. Gadolinium oxide seems to be a more stable phase; and the existing stress conditions probably tend to provide favourable kinetics for the precipitation of {100} Gd_2O_3 platelets parallel to the substrate and at least partially coherent with the matrix, as evidenced by their streaked electron-diffraction patterns (fig. 5c). The occurrence of precipitates and the localised stress fields associated with them not only aids in explaining the general high level of coercive forces found in the films, but also accounts for the spatial spread in coercivity values.

The precipitation of Gd_2O_3 is no doubt accompanied by a simultaneous depletion of gadolinium in the garnet matrix, especially in the thicker films where the precipitates will be correspondingly larger. But even assuming a uniform depletion of gadolinium across the thickness of the film, it is still possible to show qualitatively (fig. 14) that a gradient of compositions can be formed such that up to a certain thickness the film will be gadolinium-rich, and above that thickness it will be iron-rich. This
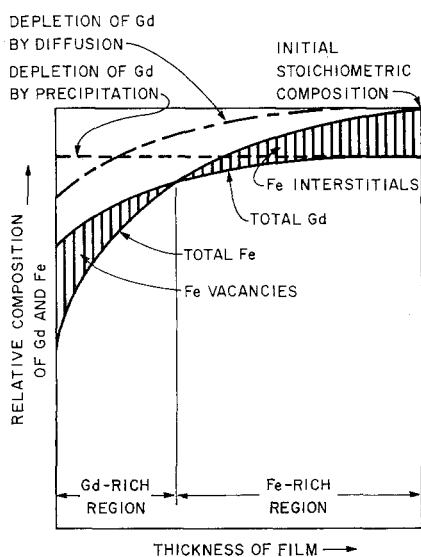
situation can very well account for the change in compensation temperature and lattice parameter with the thickness of films. For explaining the latter, we must assume that a deficiency or excess in iron is realised by creation of Fe lattice-vacancies or interstitials, correspondingly.

In this discussion we have shown that stress considerations alone cannot explain all the irregularities in the properties of GdIG films deposited on fused-silica substrates. Our findings strongly suggest that chemical interaction with the substrate and precipitation of gadolinium oxide may also contribute to the observed anomalies. The actual situation most likely results from a combination of all these factors.

Acknowledgements

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Figure 14 Qualitative diagram of composition profiles of Gd and Fe across a GdIG film.

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