DEFECT AND IMPURITY RELATED EFFECTS IN SUBSTITUTED
EPITAXIAL YIG CRYSTALS

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ABSTRACT

Epitaxial magnetic garnet films, being of exceptional quality single crystals, play an important role in technology and physics of magnetic materials. The coercivity, reflecting the interaction between domain walls and defects, is a measure of the perfection of garnet films. Major growth defects (grain boundaries, inclusions, dislocations, etc.) are eliminated from these films. Surface irregularities, 20 to 200 nm in amplitude and 2 to 20 μm effective wavelength, and a highly stressed transient layer at the film/substrate interface can contribute up to several Oe to the observed coercivity. Microstructural inhomogeneities, smaller than the domain wall width, observed by high resolution electron microscope give rise to a coercivity of magnetostatic origin. Garnets substituted with cations of valence different from 3+ have a high magnetic anisotropy, a high optical absorption, semiconductor-like electrical properties and a high coercivity due to the presence of non-S-state Fe2+ or Fe4+ charge compensating ions.

1. INTRODUCTION

The natural garnet crystals are mixed silicates with the chemical formula of A3B2Si3O12. Their crystal structure was described as early as 1928 as cubic belonging to the space group of Ia3d(Oh 1). The elementary cell of the garnet crystal lattice contains 8 formula units, i.e. 160 ions. However the description of this structure and the understanding of many structure-sensitive physical properties are feasible if we imagine the garnet as composed of cations surrounded by polyhedra formed by 4 (tetrahedral), 6 (octahedral) and 8 (dodecahedral) oxygen anions, as shown in Fig. 1 [1]. The fantastic variety of the garnet crystals is based on this structure offering a possibility to substitute various size and/or various valency cations in the various polyhedra.

The Y3Fe2Fe3O12 (YIG) is the prototype magnetic garnet and its technological application is as old as its discovery. From that time the widening of the possibilities of garnets for use as microwave, optical and/or magnetic components went hand in hand with the understanding of fundamental problems of magnetism based on garnets as model materials.

With the development of thin films of substituted YIG, grown by liquid phase epitaxy on non-magnetic GGG for bubble memory needs, the technology and the physics have a unique possibility to work with the most perfect single crystalline magnetic materials. For successful production of large capacity bubble memory chips all the common crystalline defects had to be eliminated because the magnetic domains have to propagate along extended paths without any defect hindering the motion [2]. The most general definition of a defect is a deviation from the translational symmetry. A finite crystal can never be totally defect-free and even the lack of grain boundaries, inclusions, dislocations and other major defects may or may not indicate perfection. Films always have surfaces and interfaces and defects on a scale much smaller than the domain wall width can play a decisive role influencing physical properties. In the following the role of the surfaces, microstructure and electronic point defects on the magnetic and electrical properties of magnetic garnet films will be analyzed.

2. COERCIVITY OF MAGNETIC GARNET FILMS

A very important parameter in any application of magnetic materials is the coercivity. In an ideally soft infinite defect-free magnetic material the domain walls (DW) start to move immediately on the application of an external magnetic field. Defects represent energy barriers to the motion of the domain walls (Fig. 2) and the field necessary to displace a DW over the largest potential energy barrier is the coercive force Hc. In other words, the coercivity is the critical field for...
the start of the DW motion in the field of the defects. In this way \( H_c \), as the measure of the interaction between a DW and a defect, can be chosen as a very convenient characteristic of the perfection of a magnetic material [3]. The theoretical treatment of the coercive force for a general case is extremely difficult. However, in epitaxial garnet films the simplest case of domain walls, the 180° Bloch wall and a simple stripe domain structure, is realized. The magnetization changes by DW displacement. In this case, in equilibrium the increment of the energy gained by a DW of length \( L \) and height \( h \) moving in the field \( H \) through the distance \( \Delta x \) must be equal to, or greater than, the change in the specific DW energy \( \gamma_w \)

\[
2 HW_{m}L \Delta x \geq \Delta (\gamma_w HL)
\]

and the coercivity is given by

\[
H_c = (2W_{m}H)^{-1} \frac{d(\gamma_w HL)}{dx}
\]

where \( \gamma_w = 4(\mathcal{A}K_u)^{1/2} \), \( M_u \) is the saturation magnetization, \( K_u \) the anisotropy energy and \( \mathcal{A} \) the exchange energy. From (2) it can be seen that any change in \( K \) or \( A \) affecting \( d\gamma_w/dx \), i.e. any local change of anisotropy and/or exchange energy, or any change in the DW volume can be a source of coercivity. The anisotropy of the epitaxial garnets is composed of the original cubic magnetocrystalline anisotropy and growth-induced and a stress-induced uniaxial contribution.

If the volume of the DW does not change during its motion then

\[
H_c = (2W_{m})^{-1} \frac{d\gamma_w}{dx}
\]

i.e. the coercivity is inversely proportional to the magnetization, a fact often neglected in interpreting coercivity data. In most cases this condition is not fulfilled and the DW wall volume changes along the crystal, largely due to non-magnetic inclusions. However, in the case of thin films one has to take into account another source of volume change: the change of the thickness, in other words the role of surface irregularities.

3. SURFACE IRREGULARITIES

The surface morphology of the garnet films is determined by the kinetics of the growth, the composition of the flux melt and the growth conditions. Epitaxial garnet crystals have very good as-grown surfaces, an important point in optical applications where surface scattering should be minimal. The coercivity can be a measure of the perfection of the surface of a magnetic material because an inhomogeneous surface profile gives rise to a coercivity contribution via the volume changes of the DW. Let's assume a quasi-sinusoidal one-dimensional surface profile when the volume of the DW moving in the \( x \)-direction changes along \( z \), as shown in Fig. 3.

\[
h = h(x) = h_0 + \Delta h \sin \left( \frac{2\pi x}{\Lambda} \right)
\]

where \( \Delta h \) is the amplitude of the surface roughness and \( \Lambda \) is the effective wavelength.

Following the statistical theory of Trauble and Kronmuller [4,5] and assuming for the defect density the maximum possible number of defects, i.e. \( p = 1/\Lambda^2 \), the surface coercivity is given by

\[
H_s = \gamma_w (\pi/\mathcal{W}) (\Delta h/hA) (L/2\Lambda)^{3/2} \left[ \ln(w_w/2\Delta_0) \right]^{1/2}
\]

where \( \mathcal{W} \) is the stripe domain width and \( \Delta_0 \) is the DW width. The coercivity contribution is proportional to the relative thickness change \( \Delta h/h \) and inversely proportional to the wavelength of the surface roughness. The first factor is very important in the case of thinner films. It was observed that the best epitaxial garnet films have a surface roughness amplitude of about 2 nm, i.e. the (111) kink film surface is nearly as flat as possible. The effective wavelength for the best films is in the range of 15 to 20 \( \mu m \). The surface roughness of the GaSe substituted YIG films is always higher than that of the Ga:YIG films with the same thickness and magnetic properties. For the worst films \( \Delta h = 20 nm \), \( \Lambda = 2 \mu m \) and these films have a high overall defect density. The minimum coercivity contribution for a 5 \( \mu m \) thick "typical bubble garnet film" with \( H_c < 0.5 \text{ Oe} \) is about 0.1 \text{ Oe}. However, for some films with \( H_c = 40 - 50 \text{ Oe} \), \( H_s \) can be the dominant contribution to the coercivity [3]. The reason for the surface roughness is not the constitutional supercooling and we have only indications to relate the observed effects to melt composition and growth conditions.
4. THE FILM/SUBSTRATE INTERFACE

The CaGe substituted epitaxial garnets have a pronounced tendency for higher coercivity. In these films two distinct coercivities were detected [6]. The lower term was related to the "bulk" coercivity of the film, the higher to the contribution of the film/substrate interface, as illustrated in Fig. 4.

A transient layer at the substrate/film interface is formed during the initial rapid growth of the epitaxial films and its volume fraction depends on growth conditions. CaGe substituted garnets are especially sensitive to melt composition changes [6]. If the volume fraction of the transient layer is large enough its contribution to $H_c$ will be significant. The volume fraction of a transient layer for the same film thickness is inversely proportional to $h$, thus creating an illusion of the $h^{-1}$ dependence of $H_c$.

On dipping the substrate into a melt, the initial stoichiometry is different from that of the crystal to be grown in the steady state. Initially a layer similar in composition to the melt will be formed, having a high chemical and crystallographic disorder and high inhomogeneous internal stresses. These stresses are an important source of the coercivity, as was shown by Kersten [7]. The stress $\sigma$, due to a local lattice mismatch $\Delta a/a$, is given by

$$\sigma = \frac{E}{(1-\nu)} \Delta a/a,$$

where $E=220$ GPa/m² is the Young modulus and $\nu=0.29$ is the Poisson ratio. This stress couples to the magnetostriction $\lambda$ and gives rise to an inhomogeneous anisotropy and wall energy contribution. For a statistical distribution of small internal stresses ($K_u>>\lambda\sigma$) in a volume ratio of $v$ the coercivity is given by

$$H_c^{F_T} = \frac{\nu A^2}{(K_u M_B)},$$

and for high stresses ($K_u<<\lambda\sigma$):

$$H_c^{F_T} = \nu \lambda \sigma.$$

For "device quality" epitaxial garnets the thickness of the transient layer is about 0.1 µm and for small stresses, $H_c^{F_T} = 0.1$ Oe. However, for a thicker transient layer, $H_c^{F_T}$ is about 4 Oe, in the range of the observed $H_{c2}$. For a local misfit of $10^{-3}$ nm, the stress-induced anisotropy is comparable to the growth induced anisotropy, and it can even cause a change in the sign of the anisotropy energy at the interface. A $-1.5\times10^{-2}$ nm misfit leads to stresses near to the breaking strength of the garnet.

5. MISFIT STRESSES AND MECHANICAL PROPERTIES

Any stress in a magnetic material, when coupled to the magnetostriction, gives rise to stress-induced anisotropy $K_\sigma$ and a coercivity contribution which, according to Kersten's mechanism [7], is given by

$$K_\sigma = (3/2) \lambda \sigma,$$

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For a perfect epitaxy a perfect lattice fit between the film and the substrate is necessary, i.e. $\Delta a = a_f - a_s = 0$. If the film is in compression ($\Delta a > 0$) then the relaxation of the misfit stress is taking place by faceted hillock formation and a decrease of the growth induced anisotropy energy by $K^\text{A} < 0$ due to $\lambda^2 < 0$ in the rare-earth garnets [2] is realized.

The more frequent case is when the film is in tension, i.e. $\Delta a = a_f - a_s < 0$. The trouble is that when reaching the critical stress the film will be easily cracked. The condition for crack formation is that the tension due to the misfit exceed the fracture toughness of the garnet. Garnets are rigid and hard materials. Surprisingly, not too much is known about their mechanical properties, in spite of the fact that this is very important for the technology of cutting, polishing, and dicing of garnet crystals. During these processes the crystal is affected in a way similar to that during measurements of the Vickers-hardness with a diamond pyramid illustrated in Fig. 5. Cracking starts at load levels of about 10 g. The mechanical properties of GGG crystals have been described in [8] and typical microhardness, fracture toughness, and surface energy data are summarized in Table 1 for (111) oriented Ca$_2^+$ doped Gd$_4$Ga$_5$O$_{12}$ (GGG) single crystals, for Ca$_3$Ge$_3$Ga$_2$O$_{12}$ (CaGeGaG) with (100), (110) and (111) orientation, and for (111) oriented epitaxial magnetic garnet films of different composition and different lattice mismatch $\Delta a/a$.

### Table 1. Microhardness ($H$), critical fracture toughness ($K_c$), and surface energy ($\gamma$) of garnet single crystals and epitaxial films depending on thickness ($h$) and lattice mismatch ($\Delta a/a$).

<table>
<thead>
<tr>
<th>Garnet</th>
<th>$H$, GPa$^{-2}$</th>
<th>$K_c$, mN$^{-3/2}$</th>
<th>$\gamma$, Jm$^{-2}$</th>
<th>$\Delta a/a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GGG (111), 0 Ca$_2^+$</td>
<td>13.25</td>
<td>1.09</td>
<td>2.7</td>
<td>+1.34x10^{-3}</td>
</tr>
<tr>
<td>GGG 10 ppm</td>
<td>13.54</td>
<td>1.20</td>
<td>3.3</td>
<td></td>
</tr>
<tr>
<td>GGG 20 ppm</td>
<td>14.00</td>
<td>1.26</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>CaGeGaG (100)</td>
<td>12.72</td>
<td>1.58</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>(110)</td>
<td>11.60</td>
<td>1.00</td>
<td>6.2</td>
<td></td>
</tr>
<tr>
<td>(111)</td>
<td>11.49</td>
<td>0.78</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>EuErGaIG h=9.2 μm</td>
<td>11.02</td>
<td>1.53</td>
<td>5.3</td>
<td>+1.34x10^{-3}</td>
</tr>
<tr>
<td>SmCaGeYIG 5.6</td>
<td>11.08</td>
<td>0.56</td>
<td>0.7</td>
<td>-0.69x10^{-3}</td>
</tr>
<tr>
<td>SmGaYIG 6.0</td>
<td>11.96</td>
<td>0.78</td>
<td>1.4</td>
<td>-0.70x10^{-3}</td>
</tr>
<tr>
<td>EuTmGaIG 1.5</td>
<td>11.31</td>
<td>0.93</td>
<td>2.0</td>
<td>-0.77x10^{-3}</td>
</tr>
</tbody>
</table>

The crack formation in the garnets is typical of the brittle fracture. Propagating radial cracks are formed first, followed by conchoidal fracture, which would be more desirable from the point of view of the machining of these crystals. Unfortunately, the cracking of the (111) planes is the easiest. Epitaxial films due to lower melting point, complex composition and defects, are expected to be less brittle. However, the basic mechanical properties are not expected to change. Measurements performed on various epitaxial garnet films have shown that the overall hardline of the films is, in fact, lower than that of the substrate, and the fracture toughness and surface energy of the films are related to misfit stresses and to the thickness of the films, as shown in Table 1.

Epitaxial garnet films have no distinct cleavage planes, they always break normal to the (111) surface because a crack is always perpendicular to the direction of the largest stress. These stresses are due to lattice parameter mismatch and have an in-plane orientation. According to x-ray topography the cracks run parallel to the <110> and <211> directions in the (111) plane of the garnet films.

For a given misfit there is a critical thickness for crack propagation. According to the Griffith-model of brittle fracture, as was shown in [9], the critical length $\delta_c$ for the propagation of a crack is given by the critical stress equation:

$$\sigma_c = \frac{2EY}{\delta_c}$$

and the misfit stress given by (6). From (6) and (10) the critical length, i.e. the critical thickness, can be determined:

$$\delta_c = \frac{2(1-\nu)Y}{(1-\nu^2)(1+E(\Delta a/a)^2)}$$

The critical thickness is important for the growth of thick films and for the processing of the films. It can happen that the film thickness is just below the critical value for cracking, but the deposition of further layers during microelectronic fabrication steps puts the film into stress conditions, exceeding fracture limits. Therefore, for bubble memories and, especially, for the thicker magnetooptic films, the specification of the affordable maximum lattice parameter
misfit is desirable. For a 5 \( \mu m \) thick garnet film \((\Delta a/\Delta)\) can be no larger than \(1.8 \times 10^{-3}\), for \(h=50 \mu m\) \((\Delta a/\Delta)\) must be less than \(5 \times 10^{-4}\).

Measurement of the local domain wall nucleation field \(H_k\) around cracks and scratches in garnet films, assuming a rotation process of magnetization for nucleation, were used to determine the local stress-induced anisotropy and the value of the local stresses around these defects. For a 5 \( \mu m \) thick film the magnetoelastic interaction between DWs and cracks gives a localized stress of 0.3 GHNm\(^{-2}\). It is in very good agreement with the value of 0.28 GHNm\(^{-2}\) predicted from (9) for the critical stress of cracking.

6. MICROSTRUCTURAL INHOMOGENEITIES

It was observed during subsequent growth of large numbers of epitaxial garnet crystals, that while the overall quality of the films didn't change, the coercivity of the CaGe-containing garnets was increasing. The observed coercivity could not be explained based on the defect density observed in the usual way of microscopic characterization. Transmission electron microscopic investigation revealed the existence of characteristic microstructural patterns in epitaxial garnet films [3]. A quasi-periodic network of stress pattern with periodicity of about 40-50 nm, identified as due to spinodal decomposition of the garnet phase around the nominal composition, was observed in some CaGeSm:YIG samples. The stress pattern associated with the composition modulation is equivalent to a modulated anisotropy, i.e. the spatial modulation of the DW energy. The coercivity due to periodic internal stresses, according to [10], is given by

\[
H_k^2 = p[3/2 \lambda c]/M_s ,
\]

with the structure factor \(p\) depending on the ratio of the DW width and the period of the stress. Stresses whose period is of the order of the DW width give maximum contribution to \(H_k\). For a \(H_k\) of 1 Oe in a typical 5 \( \mu m \) bubble film a lattice parameter fluctuation of \(\Delta a/\Delta a=10^{-5}\) is sufficient.

In other samples of YIG with multiple substitution small precipitates of the size of \(<0.1\) \( \mu m \) and density of \(10^{15}-10^{17} cm^{-3}\) were present. EDS-STEM microanalysis has shown a variation in the chemical composition of the defects. A lattice resolution STEM image around a primary phase precipitation is shown in Fig. 6 [11]. These high density defects, although smaller than the DW width, can give a substantial contribution to the observed coercivity due to the magneto static interaction between DWs and defects, as was shown in [12].

![Fig. 6 Two-dimensional [111] direction lattice resolution image of a garnet crystal with a primary phase precipitation (arrow). White dots correspond to octahedral site atoms.](image)

7. ELECTRONIC POINT DEFECTS AND CHARGE UNCOMPENSATED GARNETS

Epitaxial magnetic garnet crystals are mass-produced with a coercivity \(H_k<0.5\) Oe. However, a perfect YIG crystal should be an ideal soft magnetic material with much lower coercivity. One of the reasons for the increased coercivity is the presence of electronic point defects, impurity ions with a high orbital angular momentum and a high single ion anisotropy. Bubble memory garnets always contain rare earth ions to increase the growth-induced anisotropy, and these ions with a high orbital momentum, like Sm, are a source of a coercivity contribution.

However, the coercivity of substituted YIG, containing no rare earth ions at all, is always higher than that of pure YIG (-10\(^{-4}\) Oe). This effect is more evident in garnets containing non-magnetic ions in valence states different from the usual 3\(^{+}\) state of the cations in YIG. The increase of the coercivity is pronounced when the two- and four-valent ions are not fully compensated. The case of the Ca\(^{2+}\)Ge\(^{4+}\):YIG substitution was already mentioned. These charge uncompensated ions have a drastic effect on the magnetization, anisotropy, transport and optical properties of the garnets [13]. A rapid increase in the anisotropy energy at low temperatures and an increase in the ferromagnetic resonance linewidth, i.e. the magnetic losses, has been recently reported for Ca:YIG and Ge:YIG films [14].

The tetravalent dopants, like Si\(^{4+}\) or Ge\(^{4+}\), substitute for Fe\(^{3+}\) at tetrahedral sites. For charge compensation the valence of the corresponding amount of octahedral site Fe\(^{3+}\) ions changes to Fe\(^{2+}\). In the case of divalent substitution, e.g. Ca\(^{2+}\) ions, occupying dodecahedral sites, it is expected that tetrahedral site Fe\(^{3+}\) ions will be converted to Fe\(^{4+}\). The increase of the room temperature electrical conductivity by 6-7 orders of magnitude [13] and large photo- and electric field induced excitation effects have been observed in CaGe:YIG, as shown in Fig. 7 [15]. On decreasing the temperature the conductivity of the film decreases exponentially to a non-conducting state. Upon the application of light and/or a moderate electric field the conductivity increases to its room temperature value (or above it) and the high conductivity excited state can be destroyed only on heating the crystal.
These charge uncompensated garnets represent a new and intriguing class of magnetic semiconductors, and changes similar to the changes in electrical conductivity, are expected to occur in thermal properties. An increase in the thermal conductivity by several orders of magnitude should have an effect on a magnetooptical memory due to the quick spread out of the laser energy on writing. At the same time, the optical absorption of the charge uncompensated garnets is increased around 1 μm due to the transitions of Fe2+ or Fe4+ ions.

The behavior of the iron ions in valence states different from 3+ can be understood on the basis of the electronic structure. The Fe3+ ion is an S-state ion with L=0. Both Fe2+ and Fe4+ have S=2 and an orbital angular momentum of L=2. Both are in a triply degenerate T cubic ground state, have a significant spin-orbit interaction and a high single ion anisotropy contribution [14]. The localized crystal field effects around the highly anisotropic Fe2+ or Fe4+ impurity ions give rise to very large localized anisotropy fluctuations. If the anisotropy energy K and/or the exchange energy A fluctuates at discrete lattice points then, due to the resulting localized DW energy variations, the coercivity increases. According to the statistical potential theory of coercivity [4] it was shown in [5] that the resulting Hc

\[ H_c = \frac{n}{4} \left( \frac{K}{A} \right) \left( \frac{16}{15} (K^2 + A) + \frac{11}{60} (A_2 + A_3^2) \right) \]

where N is the density of the anisotropic ions, A and A are the dispersions of the fluctuating K and A. For Fe2+ and Fe4+ ions A in (13) is several orders of magnitude larger than the anisotropy of the majority Fe3+ ions. The change in the exchange energy can be neglected compared with the anisotropy effects. The intrinsic Hc contribution of \(10^{21} \text{Fe}^{2+} / \text{cm}^3\) is the order of Hc = 0.05 Oe increasing rapidly with decreasing temperature. Strong magnetic after-effect and time dependent changes are indicated to be present in these garnets due to the charge transfer processes between iron ions in different valence states corresponding to the redistribution of the anisotropic iron ions among non-equivalent sites. A light-induced increase of the coercivity by an order of magnitude was observed in CaYIG garnets at T < 200 K, i.e. in the temperature range of the photoinduced excitation effects of the electrical conductivity. The increase of the coercivity is caused by the stabilisation of DWs in deeper energy minima corresponding to higher anisotropy energy of the sites occupied as a result of valence exchange under light excitation. The temperature range of the existence of the effect indicates that the energy separation between the non-equivalent sites is of the order of ±10 meV.

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