THE INFLUENCE OF DOPANTS ON PHOTOMAGNETIC EFFECTS IN YTTRIUM-IRON GARNET

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Abstract

A survey is given of photo-induced changes in magnetic properties of yttrium-iron garnet doped with trivalent, quadrivalent and pentavalent ions. The results are compared with those in undoped YIG. Generally the presence of dopants enlarges the spread of activation energies for the relaxation processes. In many cases light-induced disaccommodation processes are also found. Some results are given for gadolinium-iron garnet and for a number of spinel ferrites.

1. Introduction

The first observation of photo-induced changes in magnetic properties was reported by Teale and Temple in 1967. These authors used the ferromagnetic-resonance technique to measure the anisotropy field of a single crystal of silicon-doped yttrium-iron garnet (YIG : Si). They found that the resonance field at low temperatures \( T < 70 \text{ K} \) could be influenced by infrared radiation. They explained the effect in terms of a redistribution of ferrous ions over octahedral sites having slightly different energies owing to different orientations of the local symmetry axis with respect to the magnetization direction. The same mechanism is responsible for photo-induced changes in optical dichroism and strain. We shall designate these phenomena as class-I effects. In all cases the experiments were performed on single crystals of silicon-doped YIG with an analysed ferrous content \( x = 0.04-0.10 \) Fe\(^{2+} \) ions per formula unit.

The so-called class-II effects were discovered by Enz and Van der Heide who observed photo-induced changes in the susceptibility and coercive force of YIG : Si. Infrared irradiation at 77 K was found to induce an irreversible decrease of \( \chi \) and an increase of \( H_c \). At temperatures above about 120 K a thermally activated relaxation occurs, which restores the original condition of the sample. Since the permeability of YIG is mainly determined by domain-wall contributions, the effect can be described in terms of an increase in domain-wall pinning. Demagnetization either after or during irradiation has no influence on the low permeability value; even if the sample is saturated magnetically during irradiation the same permeability value is obtained upon return to the demagnetized state. It follows from these experiments that the effect is due to centres which are evenly distributed throughout the bulk of the sample. These are characteristic properties of class-II effects. The microscopic basis of this class of photomagnetic effects has been described extensively in ref. 5, and we...
will summarize the conclusions of the forementioned paper only briefly. It is supposed that there occur two types of centres, labelled I and II. In the case of silicon-doped YIG the type-II centre is assumed to be an Fe$^{2+}$ ion on an octahedral site far from Si$^{4+}$ ions, whereas the type-I centre is assumed to be an Fe$^{2+}$ ion near the electron-donating silicon ion. The type-I centres, which are relatively few in number (the dopant concentrations are low), have low energy and low domain-wall-pinning strength. The type-II centres which are more abundant have a higher energy and a high pinning strength. Centres can move in the lattice by electron transport.

As the direction of the magnetization proves not to be involved in this class of photo-induced effects we are not restricted to the use of single crystals. Indeed strong photomagnetic effects have been observed in polycrystalline YIG samples. The use of polycrystalline samples has two important advantages. In the first place the purity can be higher than that of single crystals, which are always contaminated with flux constituents. Secondly, polycrystalline samples with different dopants can easily be prepared.

The purpose of this paper is to describe the effect of various dopants on photomagnetic effects in polycrystalline materials. The sample-preparation and measurement techniques are described in sec. 2. Section 3 indicates how the different types of photo-induced effects can be distinguished experimentally. Section 4 presents experimental results for YIG samples with different dopants. In sec. 5 the influence of temperature on the relaxation rate in the range between 77 K and 300 K is investigated. Finally in sec. 6 data are given on photo-induced effects in spinel ferrites.

2. Sample preparation and measurements

A widely used method of preparing spinel or garnet-type ferrites is the ball milling of oxides followed by a high-temperature solid-state reaction. To produce a garnet powder with sufficient reactivity for the sintering process the reacted powder has to be subjected to a second ball-milling treatment. This procedure inevitably leads to considerable contamination by wear of the steel balls commonly used. To produce samples of high purity we therefore prefer wet chemical methods. In most cases powders were prepared by spray-drying of sulphate solutions. FeSO$_4$ solutions were prepared from iron powder and sulphuric acid, Y$_2$(SO$_4$)$_3$ solutions from Y$_2$O$_3$ and sulphuric acid. The spray-dried sulphate powder was reacted in an oxygen atmosphere at 1200 °C. The resulting garnet powder was directly pressed into pellets under a pressure of 1 kbar. After hydrostatic pressing at 10 kbar, the pellets were sintered for 4 to 6 hours at 1430 °C in oxygen. The absence of a second phase was checked by microscopic examination of polished samples. Generally the impurity content of the sintered materials was obtained from a spectrochemical analysis. Ferrous concentrations were determined by titration with cerium sulphate.
For the magnetic measurements cores were machined from the sintered pellets, with dimensions 3 mm O.D., 2 mm I.D. and 0.5–1.0 mm height. A few windings were put around the core for permeability measurements. The field through the primary windings was normally about 10 mOe for a measurement of the initial permeability. The induced voltage was determined with a phasesensitive amplifier, allowing measurements of $\mu'$ and $\mu''$ in the frequency range 10 Hz--150 kHz. Unless otherwise indicated, all permeability values given in this report were measured at 10 kHz with a 10-mOe drive field.

For measurements of the coercive force at 50 Hz the secondary voltage induced in the core was fed into a magnetic amplifier. After integration the $B$-$H$ loop was displayed on an oscilloscope. The dynamic properties were measured with an S-curve plotter. An S-curve gives the amount of flux $\phi$ switched irreversibly by a pulse of a given fixed width $\tau$ as a function of the pulse amplitude $H_p$. From a set of S-curves the switching coefficient $S_0 = (H_p - H_0) \tau$ can be calculated. We define a dynamic coercive force $H_c(\tau)$ as the field necessary to switch half of the remanent flux. The pulse width was variable between 10 ns and 1050 ns. The maximum pulse amplitude is about 16 Oe for the shortest pulses.

For a measurement of the photo-induced change in permeability we generally used the following procedure. After cooling in the dark by immersion of the sample in liquid nitrogen, the sample is a.c. demagnetized, and the permeability value obtained about 5 seconds after demagnetization is called $\mu_{\text{dark}}$. Subsequently the sample is irradiated with the unfiltered light of an incandescent lamp. When a saturation value has been reached, the lamp is switched off, and the permeability value obtained in this way is denoted by $\mu_{\text{irr}}$. Finally the sample is demagnetized again and after 5 seconds $\mu_{\text{dem}}$ is measured.

3. Characterization of photo-induced effects

In this section we survey the behaviour of the permeability for different types of photo-induced effects. Figure 1 shows the change in permeability as a function of time under different experimental conditions. The first case to be considered is the "pure" photomagnetic effect of class II. At the temperature $T_1$ (fig. 1a) the permeability does not change with time in the dark and demagnetization at the time $t_1$ has no influence. After a light source has been switched on at $t_2$ the permeability decreases from the value $a$ to $b$. If $T_1$ is sufficiently low, $\mu$ remains at the value $b$ after the light source is switched off at the time $t_3$. Demagnetization at $t_4$ has no influence. At a higher temperature $T_2$ we find a similar behaviour until the light is switched off, except that the $\mu$-values $c$ and $d$ are in general higher than the corresponding values $a$ and $b$, and $d$ depends on the light intensity. However, after we have switched off the light at $t_3$ we find a thermal relaxation back to the value $c$.

The second case to be considered is of the after-effect type (class-I effects).
A well-known example is the disaccommodation (D.A.). After demagnetization the domain-wall configuration is such that it does not represent a situation of minimum energy. If the thermal energy is sufficient a spontaneous relaxation occurs (fig. 1b). Often there is a broad spectrum of activation energies, and as a result the permeability falls linearly with the logarithm of the time that has elapsed since the demagnetization.

Apart from the thermally induced disaccommodation discussed above, light-induced D.A. (fig. 1c) may occur in which local changes take place in the wall itself, causing a change in the depth of the potential well.

Characteristic of D.A. processes is that demagnetization removes the decrease of permeability. In practice we have often found combinations of photomagnetic and D.A. effects.

4. Photo-induced effects in yttrium–iron garnet

4.1. Undoped YIG

Marked photo-induced effects were observed in undoped YIG at 77 K. It has been shown \(^8\) that even in YIG of very high purity an amount of about 0.01 ferrous ions per formula unit is present. The Fe\(^{2+}\) ions are probably compensated by oxygen vacancies. At 77 K the photo-induced permeability change
is irreversible. Magnetic saturation or demagnetization have no influence in this case, which means that we have an example of a pure class-II effect. The magnitude of the change in $\mu$ can be influenced by changing the Fe$^{2+}$ concentration. This can be accomplished by annealing treatments at high temperatures, e.g. at $1200 \, ^\circ\mathrm{C}$ under a defined oxygen partial pressure. The samples are rapidly cooled from the annealing temperature to room temperature in order to freeze-in the high-temperature equilibrium concentration. At the annealing temperature oxygen vacancies are formed which are compensated by ferrous ions. The Fe$^{2+}$ concentration increases with decreasing oxygen pressure. As a result the magnitude of the photomagnetic effect at 77 K increases with decreasing oxygen pressure during firing $^8)$. We also investigated a number of undoped YIG single crystals. In some crystals photomagnetic effects were observed, in others they were absent. We attributed these differences to variations in impurity content, e.g. Pb$^{2+}$ from the flux, and to deviations from stoichiometry. Often an annealing treatment at about 430 $^\circ\mathrm{C}$ in a hydrogen atmosphere can induce a photomagnetic effect. The diffusion of hydrogen into the lattice can be followed by measuring the infrared absorption near 3550 cm$^{-1}$. This absorption is due to OH vibrations. The complexity of the spectrum indicates that the hydrogen is present at many inequivalent sites. The appearance of the photomagnetic effect after this hydrogen treatment can be explained if it is assumed that the OH' ions are compensated by Fe$^{2+}$ ions. We found that the induced permeability changes after irradiation at 77 K are a mixture of class I and of class II. We did not succeed in correlating the magnitude of the induced photomagnetic effect with the integrated absorption of the OH' groups.

A photo-induced permeability change of class II was clearly evident in a single crystal of YIG grown hydrothermally from a KOH solution. Table I gives the permeability for an irregularly shaped platelet at 77 K, before and after illumination. From the absorption constant at 3550 cm$^{-1}$ the OH concentration in this crystal was estimated $^9)$ to be $\chi(\text{OH}) \approx 0.03$. Finally, measurements were made on a number of single-crystalline samples grown from a PbO–PbF$_2$–B$_2$O$_3$ flux

### TABLE I

Photomagnetic effect for a hydrothermally grown YIG single crystal measured at 77 K

<table>
<thead>
<tr>
<th>crystal</th>
<th>permeability *) $; 10 , \text{kHz}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>dark</td>
</tr>
<tr>
<td>YIG : OH</td>
<td>115</td>
</tr>
</tbody>
</table>

*) Because of the irregular shape of the sample these values contain an unknown proportionality constant.
### TABLE II

Photomagnetic effects for YIG crystals grown under oxygen or argon pressure

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Pressure</th>
<th>$4\pi \chi'$; 10 kHz</th>
<th>Dynamic $H_c$ (Oe); pulse length 340 ns</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$300 ; K$</td>
<td>$77 ; K$</td>
</tr>
<tr>
<td>1</td>
<td>6 atm O$_2$</td>
<td>137 *)</td>
<td>100 *)</td>
</tr>
<tr>
<td>2</td>
<td>10 atm O$_2$</td>
<td>60 *)</td>
<td>129 *)</td>
</tr>
<tr>
<td>3</td>
<td>10 atm O$_2$</td>
<td>157 *)</td>
<td>154 *)</td>
</tr>
<tr>
<td>4</td>
<td>15 atm O$_2$</td>
<td>37</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>15 atm O$_2$</td>
<td>36</td>
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</tr>
<tr>
<td>6</td>
<td>20 atm O$_2$</td>
<td>95</td>
<td>31</td>
</tr>
<tr>
<td>7</td>
<td>6 atm Ar</td>
<td>20</td>
<td>3</td>
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<td>10 atm Ar</td>
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<td>8·6</td>
</tr>
<tr>
<td>9</td>
<td>15 atm Ar</td>
<td>23</td>
<td>3·6</td>
</tr>
<tr>
<td>10</td>
<td>20 atm Ar</td>
<td>6</td>
<td>3</td>
</tr>
</tbody>
</table>

under elevated pressures of either oxygen or argon). It was hoped that growing under oxygen pressure would lead to a reduction in oxygen-vacancy concentration. However, there are indications that fluorine is incorporated in the lattice, effectively leading to an increased ferrous-ion concentration. The crystals grown under argon pressure were used as a check. The results of magnetic measurements collected in table II are far from clear. The only consistent trend seems to be the marked reduction of permeability in the argon-grown crystals. We see no clear correlation with oxygen or argon pressure, except perhaps that crystals seem to be of better quality when grown in oxygen in the 6–10-atm range. The last column of table II, labelled “dark”, shows that a considerable relaxation of the change in coercive force occurs after 10 minutes in the dark.

4.2. YIG doped with quadrivalent ions

Instead of varying the Fe$^{2+}$ concentration by annealing under reduced oxygen pressure, we can also dope the garnet with quadrivalent ions such as Si, Ti, Ge, etc. It is well known, however, that the introduction of Si or Ge in a concentration of $x \gtrsim 0.01$ causes magnetic losses. Generally two loss peaks are reported with activation energies of about 0.38 eV and 0.08 eV. In our investigations of polycrystalline YIG samples doped with Si, Ge or Zr we also found these peaks. Moreover in a sample of composition $Y_{2.7}La_{0.3}Si_{0.015}Fe_{4.985}O_{12}$ we found a third peak with $E_a \approx 0.17$ eV. Measurements of dielectric losses in YIG : Si also showed the presence of at least two different peaks in $\varepsilon''/\varepsilon'$ ($\varepsilon$ being the dielectric constant). At $x(Si) > 0.005$ a loss peak was observed with a magnitude proportional to the silicon and ferrous contents, at lower silicon concentrations a different peak appeared.

Because of the magnetic losses the permeability of samples with $x \gtrsim 0.01$ at 77 K is so low that it is impossible to observe photo-induced changes. Moreover, for the higher dopers a strong disaccommodation appears.

Photo-induced effects of class II were only observable, therefore, in samples with $x(Si) \lesssim 0.01$. It has been shown, however, that the ferrous content in this dopant range depends largely upon the concentration of intrinsic defects. Figure 2 shows some experimental results measured on polycrystalline YIG samples. Data obtained on samples doped with Ti or Zr will not be discussed separately since the results are comparable with those of silicon-doped YIG. The magnitude of the photomagnetic effect is expressed in terms of the wall stiffness, i.e. the reciprocal value of the susceptibility $4\pi\chi$. In fig. 2 the change in stiffness $\Delta(4\pi\chi)^{-1}$ is plotted as a function of the analysed ferrous content. Here

$$\Delta(4\pi\chi)^{-1} = (4\pi\chi_{tr})^{-1} - (4\pi\chi_{dark})^{-1},$$
where $4\pi\chi_{\text{dark}}$ is the susceptibility at 77 K after cooling in the dark and $4\pi\chi_{\text{irr}}$ is the susceptibility at 77 K after irradiation until a saturation value is reached.

Similar data were published recently by Wurlitzer and Cibura [17]. Starting from the low-dope side of this plot the stiffness change is expected to increase due to the increasing number of type-I centres. The vanishing of the photomagnetic effect at the high-dope side can be explained by assuming that the number of available sites for type-II centres, i.e. Fe$^{2+}$ ions far from the donor ion, becomes too low. It is remarked in ref. 17 that the vanishing of the photomagnetic effect could also be explained by the marked relaxation at the higher dopant concentrations, which causes a breakdown of the susceptibility. This problem can be avoided however, if we measure the coercive force instead of the permeability. We have investigated this on a series of single crystals doped with Si or Ge. Before we give the results, one example will be discussed in more detail. A chemical analysis showed that one of the Ge-doped crystals was contaminated with 0.022 Pb, 0.002 Ca, 0.019 Ge, 0.008 Si and 0.010 Fe$^{2+}$ per formula unit. At room temperature the permeability showed a wide dispersion, e.g. $\mu = 5$ at 100 kHz, $\mu = 39$ at 1 kHz, $\mu = 110$ at 20 Hz. After cooling to 77 K in the dark the permeability was $\mu = 5.2$ at 10 kHz and $\mu = 2.8$ after irradiation. After subsequent demagnetization the latter value increases to 3.1. At 77 K a sample with a slightly higher Ge content gave $\mu \approx 2.8$ and after irradiation $\mu \approx 1$. Because of the experimental inaccuracy of these low permeability values it is very difficult to compare the changes in stiffness. In these cases more information can be obtained from measurements of the dynamic
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Fig. 3. S curves of Ge-doped YIG at 77 K before (drawn curves) and after irradiation (dashed curves). Fraction of flux $\Phi/\Phi_{\text{rem}}$ switched irreversibly by a field pulse is plotted as a function of field-pulse amplitude $H_p$ with pulse duration in nanoseconds as parameter.

Fig. 4. Photo-induced change in the dynamic coercive force at 77 K, for a pulse width $\tau = 660$ ns in doped YIG single crystals, as a function of the Fe$^{2+}$ concentration. The increase in coercive force upon irradiation is easily obtained in this way, whereas the permeability measurements were difficult to perform. The change in $H_c$ increases with decreasing pulse length. The results are summarized in fig. 4, where the change in coercive force for a pulse width of 660 ns, measured at 77 K, is plotted against the analysed ferrous content of the single crystals. Here again the photo-induced effect decreases at the higher concentrations. We therefore conclude that the decrease of the photomagnetic effect is indeed due to a decrease of the number of available type-II sites. These data can be compared with the following results of Teale and Weatherley\textsuperscript{18}). In single crystals with an estimated Fe$^{2+}$ concentration of 0.002, irradiation produced changes in the anisotropy field which
could be ascribed to a class-II effect. In samples with \( x(Fe^{2+}) \approx 0.016 \) the class-II effect was only weakly observable together with a strong effect of class I. This agrees with our observation that samples with \( x(Fe^{2+}) \gtrsim 0.02 \) showed disaccommodation-type effects.

Apart from YIG crystals with Si or Ge dopants we also investigated YIG with Ru, Sn, La, Lu, Bi. None of these single crystals showed photomagnetic effects at 77 K.

4.3. YIG : V

We investigated polycrystalline samples of YIG with 0.05 and 0.10 vanadium atoms per formula unit. The vanadium replaces iron on octahedral sites \(^{19}\). When V is substituted in YIG together with charge-compensating ions like Ca\(^{2+}\), then it is present as V\(^{5+}\). However, without charge compensation there is also a fair probability that the vanadium ions are trivalent. We measured the saturation magnetization of our samples, but the experimental error was too great to allow any conclusions about the valency.

At 77 K both samples showed irreversible changes in \( \mu \) and \( H_c \) after irradiation (table III). An interesting feature of these V-doped garnets is shown in fig. 5. The permeability curve exhibits a strong secondary maximum at 82 K. The sample with \( x(V) = 0.10 \) shows a similar curve with a maximum at about 84 K. V\(^{3+}\) on a trigonally distorted octahedral site has a \( 3E \) ground state. Like Co\(^{2+}\), this ion therefore is expected to give a positive contribution to the cubic anisotropy constant \( K_1 \). The observed secondary maximum in the permeability–temperature curve could therefore be due to a compensation point in \( K_1 \). Close to the compensation temperature we expect a considerable rotational contribution to the permeability. If the photomagnetic effects of class II are mainly affected by the domain-wall permeability, we do not expect that they

<table>
<thead>
<tr>
<th>dopant</th>
<th>( x )</th>
<th>( 4\pi\chi ) ; 10 kHz</th>
<th>( H_c ) * (Oe)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>dark</td>
<td>irr.</td>
</tr>
<tr>
<td>V</td>
<td>0.05</td>
<td>76</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>0.10</td>
<td>22</td>
<td>11</td>
</tr>
<tr>
<td>Ga</td>
<td>0.05</td>
<td>24</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>0.25</td>
<td>20</td>
<td>6</td>
</tr>
</tbody>
</table>

* \( H_c \) measured at 50 Hz; values in parentheses are dynamic coercive forces, measured with a pulse width \( \tau = 180 \) ns.
will be strongly influenced by the compensation point. Indeed the change in $\chi^{-1}$ upon irradiation is approximately constant between 70 K and 110 K. At temperatures above 130 K the photomagnetic effect rapidly relaxes.

According to Lotgering\textsuperscript{20}) there are indications that the equilibrium $\text{Fe}^{3+} + \text{V}^{3+} \rightleftharpoons \text{V}^{4+} + \text{Fe}^{2+}$ lies at the right-hand side. In that case the origin of the secondary maximum could be related to the $\text{Fe}^{2+}$ ions instead of to $\text{V}^{3+}$ ions.

4.4. YIG: Ga

At concentrations $x(\text{Ga}) < 1$, $\text{Ga}^{3+}$ ions substitute preferentially on tetrahedral iron sites\textsuperscript{19}). The only influence on the magnetic properties to be expected is a decrease of the saturation magnetization. We prepared polycrystalline samples with $x(\text{Ga}) = 0.05$ and 0.25. A chemical analysis revealed that the $\text{Fe}^{2+}$ content of these samples was $x(\text{Fe}^{2+}) \approx 0.01$. At temperatures below 160 K we found photo-induced changes in permeability and coercive force of class II (cf. table III). Figure 6 gives an example of the behaviour of the sample with $x(\text{Ga}) = 0.05$ at three different temperatures. The curve for $T = 77$ K shows a photomagnetic effect of class II. At 152 K part of the susceptibility decrease is due to a relaxing class-II effect, while another part is of the disaccommodation type. Above 160 K the relaxation time for the class-II effect is so short that we only observe a photo-induced D.A. This photo-induced D.A. is observable up to relatively high temperatures, namely for $x(\text{Ga}) = 0.05$ to $T \approx 240$ K and for $x(\text{Ga}) = 0.10$ to $T \approx 264$ K.

These experiments indicate that the activation energy for the relaxation process slightly increases when $\text{Fe}^{3+}$ is partly replaced by $\text{Ga}^{3+}$, but at the same time class-I effects appear.
4.5. YIG : In

\( \text{In}^{3+} \) substitutes almost exclusively on octahedral iron sites \(^{19}\). We investigated samples with In concentrations between \(0.05 \leq x \leq 0.40\) \(^*\). All samples had a high density (volume porosity \(< 0.5\%\)) and were, according to X-ray powder diagrams, free of second phases. A chemical analysis showed that the \(\text{Fe}^{2+}\) content in all of these specimens was \(x(\text{Fe}^{2+}) \approx 0.003\).

It was found that the In influences the light-induced changes in magnetic properties. At 77 K all samples show a strong photomagnetic effect of class II (table IV). At higher temperatures the situation is more complicated, depending on the indium concentration. In fig. 7 we have plotted the change of the wall stiffness after irradiation to the saturation value at different temperatures versus the indium concentration. For equal intensities of the light source, an increase in the In content causes an increase of the maximum temperature at which a photo-induced change in the stiffness can be observed. Since \(\text{In}^{3+}\) is a diamagnetic ion no direct influence on the magnetic properties of YIG is to be expected. In accordance with this neither the absolute magnitude of \(\chi\) nor the induced change \(\Delta(\chi^{-1})\) at 77 K are significantly influenced by a change in the dopant concentration. The influence of the indium content on the relaxation rate of the photomagnetic effect seems to be an increase in the spread in activation energies. We will investigate this behaviour more closely in sec. 5.

\(^*\) These samples were obtained from G. Winkler, Philips Forschungslaboratorium Hamburg.
TABLE IV

Light-induced effects in $Y_3Fe_{5-x}In_xO_{12}$ at 77 K

<table>
<thead>
<tr>
<th>$x$</th>
<th>$4\pi\chi$ (10 kHz)</th>
<th>$10^3 \cdot \Delta(4\pi\chi)^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>dark</td>
<td>irr.</td>
</tr>
<tr>
<td>0.05</td>
<td>80</td>
<td>8</td>
</tr>
<tr>
<td>0.15</td>
<td>71</td>
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<tr>
<td>0.20</td>
<td>74</td>
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</tr>
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<td>0.25</td>
<td>102</td>
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<tr>
<td></td>
<td>static $H_c$ (Oe); 50 Hz</td>
<td>$\Delta H_c$</td>
</tr>
<tr>
<td></td>
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<td>irr.</td>
</tr>
<tr>
<td>0.05</td>
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<td>1.36</td>
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<td>0.15</td>
<td>1.22</td>
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<td>1.22</td>
<td>1.46</td>
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<td>0.25</td>
<td>0.74</td>
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<td></td>
<td>switching coefficient $S_0$ ($\mu$s Oe)</td>
<td>dynamic $H_c$ (Oe); pulse length 180 ns</td>
</tr>
<tr>
<td></td>
<td>dark</td>
<td>irr.</td>
</tr>
<tr>
<td>0</td>
<td>0.17</td>
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<td>0.37</td>
</tr>
<tr>
<td>0.25</td>
<td>0.31</td>
<td>0.35</td>
</tr>
</tbody>
</table>

4.6. [Ca, V, In] YIG and related compositions

During the study of ferrimagnetic linewidths in polycrystalline garnets, numerous substituted yttrium–iron garnets were prepared by Winkler and coworkers, using standard ceramic techniques. Garnets of the following compositions were investigated:

- $Y_3-2xCa_{2x}\{Fe_{2-y}In_y\}(Fe_{3-x}V_x)O_{12}$;
- $Y_3-xCa_x\{Fe_{2-y}In_y\}(Fe_{3-x}M_x)O_{12}$, with $M = Si, Ge$;
- $Y_3-2xCa_xTh_x\{Fe_{2-y}In_y\}(Fe_3)O_{12}$.

In polycrystalline garnets the resonance linewidth is determined mainly by the magnetocrystalline anisotropy and by the porosity. The introduction of $Ca^{2+}$...
ions, compensated by tetravalent or pentavalent ions, leads to single-phase garnet materials of practically theoretical density.

Due to an increased rotational contribution several of these compositions have permeability values of $\approx 1000$ at room temperature. In many of the samples we observed photo-induced effects. However, in agreement with our earlier observation that only the contributions due to domain walls are lowered by irradiation, the relative change in permeability is small in these materials. A few examples are given in table V. From these data it is seen that the behaviour of the permeability of these compounds is more complicated than in the case of pure YIG. At 77 K many of the samples show some spontaneous disaccommodation. This is illustrated in fig. 8 for a sample of composition

$$\left\{Y_{2.7}Ca_{0.3}\right\}\left[Fe_{1.3}In_{0.5}\right]\left(Fe_{2.7}Ge_{0.3}\right)O_{12}.$$

After demagnetization the permeability decreases linearly with the logarithm of time, with a slope $(\Delta\mu/\Delta \log t) = 10 \text{ min}^{-1}$ (fig. 9, curve A). Such behaviour is to be expected when there is a wide spread in relaxation times. Irradiation causes a rapid decrease in $\mu$. However, demagnetization partly destroys this decrease, showing that we are dealing with a mixture of class-I and class-II effects. After this demagnetization process there is again a spontaneous disaccommodation. It is remarkable, however, that the slope of $\mu$ vs the logarithm of time is about twice as large as before irradiation: $(\Delta\mu/\Delta \log t) = 21 \text{ min}^{-1}$ (fig. 9, curve C), indicating a change in relaxation times. The sample remains in this state with a rapid D.A. as long as it is kept at the low temperature. This means that the starting conditions for the D.A. are changed by the irradiation.
TABLE V
Photomagnetic effects at 77 K in substituted YIG

\{Y_{2.7}\text{Ca}_{0.3}\} [Fe_{2-y}\text{In}_y] (Fe_{2.7}\text{Ge}_{0.3})O_{12}

<table>
<thead>
<tr>
<th>y</th>
<th>4\pi\chi,; 10 kHz</th>
<th>dynamic (H_c) (Oe); pulse length 180 ns</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>dark</td>
<td>irr.</td>
</tr>
<tr>
<td>0.5</td>
<td>263</td>
<td>146</td>
</tr>
<tr>
<td>0.7</td>
<td>306</td>
<td>204</td>
</tr>
</tbody>
</table>

\{Y_{2.4}\text{Ca}_{0.6}\} [Fe_{2-y}\text{In}_y] (Fe_{2.7}\text{V}_{0.3})O_{12}

<table>
<thead>
<tr>
<th>y</th>
<th>4\pi\chi,; 10 kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>dark</td>
</tr>
<tr>
<td>0.55</td>
<td>182</td>
</tr>
<tr>
<td>0.7</td>
<td>228</td>
</tr>
</tbody>
</table>

\{Y_{3-2x}\text{Ca}_x\text{Th}_x\} [Fe_{2-y}\text{In}_y] \text{(Fe}_3\text{)O}_{12}

<table>
<thead>
<tr>
<th>x</th>
<th>y</th>
<th>4\pi\chi,; 10 kHz</th>
<th>dynamic (H_c) (Oe); pulse length 180 ns</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>dark</td>
<td>irr.</td>
</tr>
<tr>
<td>0.1</td>
<td>0</td>
<td>22</td>
<td>15</td>
</tr>
<tr>
<td>0.3</td>
<td>0</td>
<td>34</td>
<td>22</td>
</tr>
<tr>
<td>0.6</td>
<td>0</td>
<td>22</td>
<td>17</td>
</tr>
<tr>
<td>0.3</td>
<td>0.4</td>
<td>206</td>
<td>139</td>
</tr>
</tbody>
</table>

In terms of our model for the photomagnetic effect this behaviour could be translated into a change of the distribution of distances between the \(\text{Fe}^{2+}\) ion and the electron-donating ion \(^5\).
Fig. 8. Photo-induced effect at 77 K for a polycrystalline sample of
\( \{Y_{2.7}Ca_{0.3}\} [Fe_{1.5}In_{0.5}](Fe_{2.7}Ge_{0.3})O_{12} \).

Fig. 9. Permeability vs the logarithm of time at 77 K for a sample of
\( \{Y_{2.7}Ca_{0.3}\} [Fe_{1.5}In_{0.5}](Fe_{2.7}Ge_{0.3})O_{12} \).
Data from the curve shown in fig. 8. Curve A: Disaccommodation after cooling in the dark and demagnetization. Curve B: During illumination. Curve C: Disaccommodation after illumination and subsequent demagnetization.

4.7. YIG: Mn

We prepared polycrystalline YIG samples with manganese in concentrations from 0.01 to 0.10 per formula unit. Table VI gives some data obtained from measurements on sintered cores of these materials. The samples with 0.05 and 0.10 Mn only show class-I effects. The sample with \( x(Mn) = 0.01 \), however, also shows a photomagnetic effect of class II. For this sample we found in addi-
TABLE VI

Influence of irradiation at 77 K on the susceptibility of $Y_3Fe_{5-x}Mn_xO_{12}$

<table>
<thead>
<tr>
<th>$x$</th>
<th>$4\pi\chi$; 10 kHz</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>dark</td>
</tr>
<tr>
<td>0.01</td>
<td>125</td>
</tr>
<tr>
<td>0.05</td>
<td>69</td>
</tr>
<tr>
<td>0.10</td>
<td>48</td>
</tr>
</tbody>
</table>

Fig. 10. Susceptibility at 77 K for a sample of $Y_3Fe_{4.99}Mn_{0.01}O_{12}$ as a function of time.

tion a slight increase in the dynamic coercive force upon irradiation at 77 K: in the dark $H_c(20) = 11.6$ Oe, after irradiation $H_c(20) = 12.0$ Oe. An interesting aspect of this material is the rapid relaxation of the photomagnetic effect at 77 K (fig. 10). The presence of manganese seems to have a profound influence on the recombination processes. It is possible that Mn plays an active role in the photomagnetic effect. The equilibrium $Fe^{2+} + Mn^{3+} \approx Fe^{3+} + Mn^{2+}$ probably lies at the right-hand side. For the samples with 0.05 or 0.10 Mn this means that all oxygen vacancies in the garnet are compensated by Mn$^{2+}$ ions and the remainder of the dopant will be present as Mn$^{3+}$. Since the concentration of oxygen vacancies is of the order of $x \approx 0.004 - 0.010$ per formula unit 8), the sample with 0.01 Mn forms a borderline case, small amounts of Fe$^{2+}$ being present together with 0.01 Mn$^{2+}$. Upon irradiation at 77 K electrons can be photo-detached from Mn$^{2+}$ and/or Fe$^{2+}$. The number of sites available for type-II centres is much smaller in these Mn-doped samples, however, so that most of the electrons trapped at Fe$^{3+}$ sites will relax rapidly. The appearance of class-I effects in samples with higher manganese content seems to be an effect common to all cases of YIG doped with trivalent ions studied so far.
4.8. Photo-induced effects in gadolinium-iron garnet

Samples of Gd$_3$Fe$_5$O$_{12}$ (GdIG) were prepared by the same procedure as used for YIG. Sintering at 1450 °C produced dense samples with no second phase. The susceptibility at room temperature was very low due to the compensation point in the magnetization. At 77 K we found $4\pi\chi = 100$ immediately after demagnetization. Due to a D.A. process the susceptibility decreased in about 15 minutes to 85. Irradiation caused a rapid decrease to 60; subsequent demagnetization produced an increase to $4\pi\chi = 87$.

The coercive force increases slightly upon illumination: at 50 Hz and 77 K we found $H_c$ (dark) = 0.54 Oe, $H_c$ (irr) = 0.57 Oe, while the dynamic coercive force with $\tau = 180$ ns was $H_c$ (dark) = 4.31 Oe, $H_c$ (irr) = 4.41 Oe.

We therefore conclude that the photo-induced changes in GdIG are predominantly of the class-I type.

5. The temperature dependence of the photomagnetic effect

In this section we will take a closer look at the temperature dependence of the permeability and coercive force after irradiation. It has been shown that the photomagnetic changes in undoped YIG $^{22}$) can be described approximately by a two-centre process, e.g.

$$[\text{Fe}^{2+} \ldots \text{V}_0] \rightleftharpoons \text{Fe}^{2+} + \text{V}_0.$$

Such a dissociation leads to a rate equation of the form

$$\frac{dn}{dt} = -\alpha n^2 + \beta I (n_0 - n),$$

where $n$ is the number of dissociated centres and $n_0$ the number of undissociated centres at the time $t = 0$, $I$ the intensity of the light, $\alpha$ a temperature-dependent relaxation-rate coefficient, and $\beta$ a wavelength-dependent sensitivity $^5$). The recombination process is thought to be thermally activated, with:

$$\alpha = \alpha_0 \exp \left(-\frac{E_a}{kT}\right).$$

We can calculate the activation energy $E_a$ from a measurement of the recombination as a function of temperature. To describe the experimental results we need a relation between the concentration $n$ and the measured magnetic properties, e.g. $\Delta H_c$ or $\Delta (\chi^{-1}) = \chi^{-1} \text{irr} - \chi^{-1} \text{dark}$. For concentrations below a critical concentration $n_c$ we have

$$\Delta (\chi^{-1}) \propto \Delta H_c \propto n, \quad n < n_c;$$

for higher concentrations we have

$$\Delta (\chi^{-1}) \propto \Delta H_c \propto n^{1/2}, \quad n > n_c.$$
For undoped YIG these equations proved to give a satisfactory description of the experiments \(^{22}\). For \(t \geq 0\) the solution of eq. (1) is

\[
n(t) = \frac{2n_0}{1 + z \coth (\frac{1}{2} \beta I z t)} ,
\]

with

\[
z = \left( 1 + \frac{4 \alpha n_0}{\beta I} \right)^{1/2} .
\]

An analysis of \(n(t)\) is rather complicated, however, since the factor \(\beta\) increases rapidly in the wavelength region where the absorption constant increases \(^{16}\). In practice this means that we have to work with an inhomogeneous intensity distribution in our samples. We preferred to irradiate until a saturation value was reached and then analyse the relaxation curve. From eq. (4) it follows that the saturation concentration \(n_s\) of the dissociated centres is given by

\[
n_s = \frac{2n_0}{1 + z} .
\]

After switching off the light the relaxation is described by

\[
n(t) = \frac{n_s}{1 + \alpha n_s t} .
\]

The initial slope of the relaxation curve is

\[
\left( \frac{dn}{dt} \right)_{t=0} = -\alpha n_s^2 .
\]

To analyse the susceptibility behaviour it is convenient to define the quantity

\[
q = -\frac{1}{\Delta(\chi^{-1})} \left( \frac{d}{dt} \Delta(\chi^{-1}) \right)_{t=0}
\]

\[
= \frac{\chi_{\text{dark}}}{(\chi_{\text{dark}} - \chi_{\text{irr}}) \chi_{\text{irr}}} \left( \frac{d\chi_{\text{irr}}}{dt} \right)_{t=0}
\]

where \(\Delta(\chi^{-1})\) is the change in \(\chi^{-1}\) after irradiation until the saturation value is reached:

\[
\Delta(\chi^{-1}) = \chi_{\text{irr}}^{-1} - \chi_{\text{dark}}^{-1},
\]

and \((d\chi/dt)_0\) is the initial slope of the \(\chi\) curve after switching off the light source. Substituting eq. (7) together with (3a) or (3b) we find

\[
q = \alpha n_s \quad \text{or} \quad q = \frac{1}{2} \alpha n_s .
\]
R. METSELAAR and M. A. H. HUYBERTS

\[ q = \frac{x_{\text{dark}}}{x_{\text{dark}} - x_{\text{irr}}} \left( \frac{dx_{\text{irr}}}{dt} \right)_{t=0} \]

as a function of \( T^{-1} \) for a sample of \( \text{Y}_3\text{Fe}_{4.75}\text{In}_{0.25}\text{O}_{12} \); \( q \) is a measure for the relaxation time of the photomagnetic effect.

We can distinguish two limiting cases:

1. When \( \alpha n_0 \ll \beta I \), we have \( z = 1 \) or \( n_s \approx n_0 \); this will be the case at low temperatures. With eq. (3a) we then get \( q = \alpha n_0 \); with eq. (3b) we get \( q = \frac{1}{2} \alpha n_0 \). In both cases the temperature dependence of \( q \) is given by

\[ \ln q \propto -(E_a/kT). \quad (10) \]

2. When \( \alpha n_0 \gg \beta I \), we can write

\[ z \approx 2 \left( \alpha n_0 / \beta I \right)^{1/2} \quad \text{or} \quad n_s \approx \left( \beta I n_0 / \alpha \right)^{1/2}. \]

This will be the high-temperature limit. Irrespective of whether eq. (3a) or (3b) holds, the temperature dependence of \( q \) will be

\[ \ln q \propto -(E_a/2kT). \quad (11) \]

Figure 11 shows the results of such an analysis for a YIG sample with \( x(\text{In}) = 0.25 \); similar curves are obtained for the other In-doped samples. From the slope of this curve in the temperature region 77–180 K we find

![Figure 11. The quantity](image-url)
$E_a \approx 0.08$ eV if we assume that we are dealing with the low-temperature limiting case (eq. (10)). For the region around 250 K we find $E_a \approx 0.6$ eV for the same limiting case. It is more probable, however, that at this temperature the slope is given by $E_a/2k$ (eq. (11)), i.e. $E_a$ would be $\approx 1.2$ eV. For the samples with a lower indium concentration the spread in activation energies is somewhat smaller. Measurements of the changes in dynamic coercive force instead of the susceptibility give similar results.

For undoped YIG $E_a$ also increases with increasing temperature, but not as strongly as found for the In-doped samples. For $150 K < T < 250 K$ the slope of $\varphi$ vs $T^{-1}$ corresponds to 0.2 eV, i.e. $E_a$ is 0.2 or 0.4 eV. For $77 K < T < 150 K$ we find $E_a \approx 0.02$ eV.

6. Photo-induced effects in spinel ferrites

Holtwijk et al.\textsuperscript{7}) have measured the influence of light on the switching behaviour of polycrystalline Co-substituted NiZn ferrites of composition (Ni$_{0.8}$Zn$_{0.2}$)$_{1-x}$Co$^{2+}$$_x$Co$^{3+}$$_y$Fe$_{2-y}$O$_4$. Light-induced changes were observed when the materials contained Co$^{3+}$ ions. At 203 K both the switching coefficient $S_0$ and the dynamic coercive force $H_c(\tau)$ increase upon irradiation. At 77 K, however, $H_c(\tau)$ increases but $S_0$ decreases. It is supposed that a light-induced electron transfer between Co$^{3+}$ and Co$^{2+}$ ions is responsible for the photomagnetic effect in these materials. We have performed measurements of the permeability of polycrystalline cores with compositions

$$(\text{Ni}_{0.36}\text{Zn}_{0.64})_{1.0175}\text{Co}_{0.0025}\text{Fe}_{1.96}\text{O}_{3.96} \text{ (material A)}$$

and

$$(\text{Ni}_{0.36}\text{Zn}_{0.64})_{1.0150}\text{Co}_{0.005}\text{Fe}_{1.96}\text{O}_{3.96} \text{ (material B)},$$

where Co should be present as a divalent ion. At 77 K both specimens show a spontaneous D.A. (table VII). Irradiation causes a rapid light-induced D.A.

**TABLE VII**

Susceptibility at 77 K for Co$^{2+}$ containing NiZn ferrites;

A = $(\text{Ni}_{0.36}\text{Zn}_{0.64})_{1.0175}\text{Co}_{0.0025}\text{Fe}_{1.96}\text{O}_{3.96}$

B = $(\text{Ni}_{0.36}\text{Zn}_{0.64})_{1.0150}\text{Co}_{0.005}\text{Fe}_{1.96}\text{O}_{3.96}$

<table>
<thead>
<tr>
<th>material</th>
<th>dark</th>
<th>spontaneous D.A.</th>
<th>irr.</th>
<th>demagn.</th>
<th>spontaneous D.A.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>82</td>
<td>74</td>
<td>59</td>
<td>82</td>
<td>74</td>
</tr>
<tr>
<td>B</td>
<td>112</td>
<td>95</td>
<td>78</td>
<td>108</td>
<td></td>
</tr>
</tbody>
</table>
Evidence of light-induced charge transfer between Co$^{2+}$ and Co$^{3+}$ ions in YIG has been given by Lotgering $^{23}$). As with the spinel ferrites, the photo-induced effects here are also mainly of type I.

We have also investigated samples of Ni$_{0.32}$Zn$_{0.68}$ ferrite containing 0.01 Ni$^{3+}$ or 0.05 Ni$^{3+}$. These samples did not show D.A. nor was there any effect of irradiation. Jonker of this laboratory has prepared a number of polycrystalline and single-crystalline spinel ferrites with Ti or Ru dopes, where $0 \leq x \leq 0.05$. A survey is given in table VIII. The only samples showing light-induced changes in permeability and coercive force were single crystals of LiFe$_5$O$_8$ doped with Ru. The results of these investigations will be published elsewhere $^{24}$). Evidence is given by Jonker that the Ru ions play an essential role in the observed light-induced changes in this material.

7. Conclusions

We have measured the influence of substitutions in yttrium–iron garnet on the photo-induced changes in permeability and coercive force in the temperature range 77 K to 350 K.

Small amounts of Fe$^{2+}$ ions are necessary to obtain photomagnetic effects.

<table>
<thead>
<tr>
<th>composition</th>
<th>influence of irradiation on $4\pi\chi$ at 77 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiFe$_2$O$_4$ : Ru</td>
<td>none</td>
</tr>
<tr>
<td>NiFe$_2$O$_4$ : Ti</td>
<td>possibly some light-enhanced D.A.</td>
</tr>
<tr>
<td>MgFe$_2$O$_4$ : Ti</td>
<td>none</td>
</tr>
<tr>
<td>MnFe$_2$O$_4$</td>
<td>none</td>
</tr>
<tr>
<td>LiFe$_5$O$_8$ : Ti</td>
<td>none</td>
</tr>
<tr>
<td>LiFe$_5$O$_8$ : Ru</td>
<td>photomagnetic effect in $4\pi\chi$ and $H_c$ together with light-enhanced D.A.</td>
</tr>
</tbody>
</table>

These Fe$^{2+}$ ions are present as intrinsic defects in pure YIG, or can be induced by dissolving small amounts ($x < 0.01$) of electron-donating ions, like Si, Ti, Ge or H. The introduction of trivalent diamagnetic ions, such as In or Ga, causes an increase in the range of activation energies for the relaxation processes. In many cases the presence of dopants also leads to the occurrence of light-induced disaccommodation processes. Experiments with Mn-doped YIG, and Co- or Ru-doped spinel ferrites suggest that electron transfer between ions of these elements also produces photo-induced effects.
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