Photomagnetism in $\text{Ca}^{2+}\text{Fe}^{4+}$-doped yttrium iron garnet

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The temperature and time dependence of the initial susceptibility of the optical magnetization curve has been measured on epitaxial films of nominally pure yttrium iron garnet (YIG) and Ca:YIG, during illumination with white light after cooling in the dark. Depending on sample composition, the maximum temperature for the occurrence of the light-induced effects on the susceptibility is 100 K < $T$ < 150 K. The change to the low-susceptibility state by light excitation is a three-step process. The first process is characterized by time constants of the order of minutes, during the second process the susceptibility does not change, and finally, at 93 K after 4 h of illumination by 15 mW/cm$^2$ light intensity the susceptibility of Ca$_{0.11}$YIG is observed to decrease to a saturation value in less than an hour. After turning off the light the susceptibility remains constant for about an hour, then increases with a similar time dependence. No light-induced effects were detected in YIG over the same range of temperature, time, or light intensity. The results are interpreted in terms of light excitation of holes from the tetrahedral Fe$^{4+}$ sites nearest to the Ca$^{2+}$ impurity first to orientationally inequivalent sites on the same coordination sphere, then to nonmagnetic centers with intermediate energies, and finally to the next-nearest tetrahedral Fe$^{4+}$ sites of higher anisotropy energy. The energy difference between the two states is measured to be in the 3–10-meV range.

**INTRODUCTION**

At low temperature the magnetic permeability of Si$^{4+}$-doped yttrium iron garnet (YIG) can be influenced by light due to photodetachment and redistribution of electrons between inequivalent Fe$^{3+}$ and Fe$^{4+}$ states, with a time constant of about 1–3 min.$^{1–3}$ Similar effects are expected for electronic transitions between Fe$^{3+}$ and Fe$^{4+}$ ions in a Ca$^{2+}$:YIG. Measurements of light-induced effects on the electrical properties of Ca$^{2+}$:Ge$^{4+}$:YIG, with [Ca] > [Ge], have shown that at $T$ < 150 K, after several hours of illumination, the conductivity increases by 6–7 orders of magnitude.$^{4,5}$ The question immediately arises, whether and how this effect is reflected in the magnetic properties. At the same time, the case of Ca:YIG seems to be more simple than that of Si:YIG. Si is substituted onto the magnetic tetrahedral sublattice, perturbing the environment of both the Fe$^{2+}$ and Fe$^{3+}$ ions, while the dodecahedral Ca$^{2+}$ leaves the magnetic sublattices unchanged, and only the effects of charge-compensating Fe$^{4+}$ ions will affect the Fe$^{4+}$ states.

**EXPERIMENTS**

Epitaxial films of Y$_3$Fe$_2$O$_{12}$ (YIG), Ca$_{0.99}$Ge$_{0.09}$:YIG, and Ca$_{0.11}$:YIG, grown on (111)-oriented Gd$_3$Ga$_2$O$_{12}$ substrates, have been investigated. Magnetic and ferromagnetic resonance (FMR) measurements on the same films were reported earlier.$^6$ The composition of the films has been determined by electron-probe microanalysis.

The temperature and time dependencies of the initial magnetic susceptibility have been measured in an optical magnetometer. Either the initial slope of the magnetization curve, $\Delta M/\Delta H$, was measured in an increasing dc bias field or the differential susceptibility, $dM/dH$, was measured with lock-in detection of the photodetector's output at the frequency of a small modulating 400-Hz ac field of constant amplitude, superimposed on the increasing bias magnetic field. Both the dc and ac magnetic fields were oriented normal to the (111) film plane. The sample was cooled to the actual measurement temperature in darkness and the time dependence of the initial susceptibility was measured from the start of the illumination. White light with a maximum intensity on the order of tens of mW/cm$^2$ was used for illumination.

**RESULTS**

Depending on the sample composition, there is a maximum temperature ($T_m$) for the occurrence of the light-induced effects on the susceptibility. For a Ca$_{0.99}$Ge$_{0.09}$:YIG film $T_m$ = 150 K. The process occurs in three steps. Initially, a rapid decrease of the susceptibility with a time constant on the order of minutes is observed, as shown in Fig. 1, followed by a process when the susceptibility remains constant for several hours, and finally it decreases to its saturation value. The relative change of the susceptibility under the effect of the light is larger at lower temperatures.

For Ca$_{0.11}$:YIG no light-induced effects have been observed at $T$ > $T_m$ = 100 K after illumination for 7 h. At 93 K and at 8 mW/cm$^2$ light intensity no effect could be observed during 7 h of illumination. At 15 mW/cm$^2$ the excitation starts after 4 h of illumination and reaches its saturation, a value corresponding to a decrease by about 5 times in less than 1 h, as shown in Fig. 2. On increasing the light intensity at the same temperature the decrease of the susceptibility becomes steeper and it starts minutes earlier.
drastically due to the presence of $\text{Fe}^{4+}$ ions with a high spin-orbit coupling and high single-ion anisotropy.\(^6\)\(^,\)\(^8\) The coercivity and susceptibility will change due to the steep wall-energy gradient between the $\text{Fe}^{3+}$ and $\text{Fe}^{4+}$ sites.

If there are two or more inequivalent $\text{Fe}^{4+}$ sites, and the energy supplied by the light quanta is enough to induce transitions between these states, then the domain walls will move towards the new minimum-energy positions, determined by the change in the wall-energy profile. In the garnet lattice the impurity Ca ions occupy dodecahedral $Y$ sites. These sites have six tetrahedral Fe neighbors, two “near,” but orientationally inequivalent sites at a distance of 0.309 nm and four “far” sites at 0.379 nm. If the concentration of the $\text{Ca}^{2+}$ ions is not too high, the charge-compensating $\text{Fe}^{4+}$ ions will be located at nearest-neighbor tetrahedral sites, with an energy of $E_f$, forming $\text{Ca}^{2+} - \text{Fe}^{4+}$ centers due to the Coulomb attraction. Upon irradiation the extra hole can be excited to another site having a higher energy. The newly created center may be located on the same coordination sphere, or at a “far” tetrahedral site having a higher energy, $E_f > E_i$, due to local symmetry changes and the increased $\text{Ca}^{2+} - \text{Fe}^{4+}$ distance. As a consequence, the anisotropy energy, the domain-wall energy, the coercivity, and the initial susceptibility will change.

If the excitation process is assumed to be similar to that in the two-center model of magnetic aftereffect in magnetite\(^6\) or to the case of the classical photomagnet CdCr$_2$Se$_4$,\(^9\) then the simplest rate equation will have a form of

$$\frac{dn_i}{dt} = -\frac{a_i n_i^2}{n_0} + b_i (n_0 - n_i).$$

The first term describes the random recombination rate of the excited hole.\(^11\) The second gives the rate of the formation of the final, highest-energy $\text{Fe}^{4+}$ centers, $n_i$, which is proportional to the light intensity $I$ and the number of the available sites, $n_0 - n_i$, where $n_0$ is the overall number of the low energy “near” sites and $n_i$ is the number of occupied new sites. For the case of a single “far” center $i = 1$ and $n_i = n$. The decay rate of the new centers during and after illumination is assumed to be governed solely by thermal recombination, $a_i \sim \exp(-E_i/\kappa T)$. The coefficient $a_i$ depends on the trapping cross section of the new centers, and $b_i$ is a constant related to the photodetachment cross section of the low energy “near” sites.

The first, fast process of the light excitation is related to the hopping of the hole between the two nearest-neighbor tetrahedral iron sites to the Ca impurity, a process essentially equivalent to that observed in Si$^{4+}$Fe$^{2+}$YIG.\(^1\)\(^,\)\(^2\)

The final state is reached through the creation of $\text{Fe}^{4+}$ ions at “far” centers. If the measured susceptibility and/or coercivity change is proportional to the number of the newly created centers, $H_c - n$, then the time dependence of the change of $H_c$ would be proportional to $\chi^{-1}$, reflecting the time development of the new magnetic state $n(t)$, given as a solution of the second-order differential equation (2). Performing the integration, the time evolution of the new state will be given as

$$n = n_0 + (n_1 - n_2) \left[ 1 + \exp(-t/D) \right],$$

FIG. 1. Initial process of the time evolution of the initial susceptibility of $\text{Ca}_{0.11}\text{Ge}_{0.89}$:YIG upon excitation with white light of 10 mW/cm$^2$ intensity, at $T = 91$ K ( ), 123 K ( ), 140 K ( ), and 170 K ( ).

FIG. 2. Time dependence of the relative change of the initial susceptibility for $\text{Ca}_{0.11}$:YIG at $T = 93$ K. Illumination is with white light of 15 mW/cm$^2$ intensity. At $t = 0$, the light was turned off. Data are shown for three series of measurements.
where $D$ is determined by initial conditions, i.e., the light intensity $I$, the temperature through $a$, and the initial concentration of Fe$^{4+}$ in the $E_0$ states:

$$D = [bl(1 + 4an_0/bl)^{1/2}]^{-1} \quad (4)$$

and

$$n_{1,2} = -bl/2a \pm bl/2a(1 + 4an_0/bl)^{1/2} \quad (5)$$

are the two real roots of the second-order equation in the denominator of the integral of Eq. (2). For $D = 0.1$ the time development of the new state is gradual and very slow, for $D = 10$ an abrupt change to the final state distribution takes place. The steepness of the increase of $n$ is determined by the value of $D$. The smaller the $D$, the steeper the $n(t)$. This is in accordance with the observation that with an increase of the light intensity and/or decrease of the temperature, the $\chi(t)$ curve of Fig. 2 becomes steeper.

On turning off the light the domain wall may stay localized in the new states, until the former site distribution is restored by a thermal deexcitation process. If there is an $E_b$ energy barrier between the initial and final states, then a thermal energy of magnitude $E_b$ is needed to delocalize the extra charge, i.e., to deexcite it to the low-energy states. If $kT > E_b$, then on turning off the light the dark state is immediately restored; when $kT > E_b$, the decay process is very slow. For the case of Ca$_{0.11}$YIG, $T \approx 100$ K is enough to overcome $E_b$, i.e., the highest energy barrier between the two states is on the order of 100 K ($< 10$ meV). This value is in agreement with the energy difference between the two Fe$^{4+}$ states, as derived from FMR linewidth measurements on the same material and the value for the localization energy of the extra hole at a tetrahedral Fe$^{3+}$ site.

For the thermal decay of the new states, Eq. (2) leads to an $n \sim t^{-1}$ dependence, in contradistinction to the observed delayed decay of susceptibility, shown in Fig. 1. This observation makes questionable the simplified assumption of the photoexcitation process with only one type of center, in spite of the seemingly successful mathematical description. The delayed transition to the new state on illumination and its slow decay may indicate the presence of a large number of other, nonmagnetic centers, having a lower energy and/or higher trapping cross section than the magnetic "far" Fe$^{4+}$ sites. After turning on the light, and establishing the new equilibrium between the two types of the "near" sites, there is a long time interval during which no magnetic changes are observed. During this process the nonmagnetic centers may be populated. As they are nonmagnetic in nature, no change in the local magnetic anisotropy energy is expected; i.e., the susceptibility remains constant until the population of the "far" Fe$^{4+}$ centers starts to dominate. On turning off the light the rate of the decay of the different centers depends on the energy barriers between them, leading to the observed distribution. The nonmagnetic traps might be identified with hole-trapping oxygen ions, i.e., the creation of O$^-$ centers, the existence of which has already been assumed for the interpretation of the magnetization and conductivity data.

In conclusion, the change of the susceptibility of Fe$^{4+}$ doped YIG under the effect of light excitation is a three-step process. The initial, fast process at $t > 0$ is related to transitions between orientationally inequivalent tetrahedral sites within the same coordination sphere, the next process is the slow excitation of holes to nonmagnetic centers, and finally the excitation to "far" centers for which the development of states of higher anisotropy energy takes place.

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6. M. Pardavi-Horváth, P. E. Wigen, G. Vertesey, and P. DeGasperis, in International Conference of Magnetism Digest, Tokyo, 1987 [INTERMAG Digest (to be published)].
7. M. Pardavi-Horváth, A. Thavendrarajah, P. E. Wigen, and P. DeGasperis, these proceedings.
11. S. H. Yuan, M. Pardavi-Horváth, P. E. Wigen, and P. DeGasperis, these proceedings.