Photomagnetism in Ca²⁺Fe⁴⁺-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/cm² 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^{3+} 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^{2+} and Fe^{3+} 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^{3+} states.

EXPERIMENTS

Epitaxial films of $Y_3Fe_5O_{12}$ (YIG), $Ca_{0.99}Ge_{0.90}$:YIG, and $Ca_{0.11}$:YIG, grown on (111)-oriented $Gd_3Ga_5O_{12}$ substrates, have been investigated. Magnetic and ferromagnetic resonance (FMR) measurements on the same films were reported earlier.[6,7] 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/cm² 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 $Ca_{0.99}Ge_{0.90}$:YIG film $T_m \simeq 150 \, K$. 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 $T > T_M \simeq 100 \, K$ after illumination for 7 h. At 93 K and at 8 mW/cm² light intensity no effect could be observed during 7 h of illumination. At 15 mW/cm² 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.

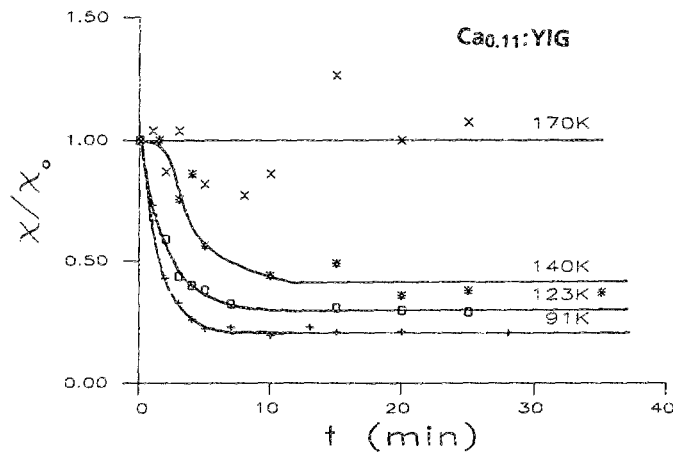[a] On leave from the Central Research Institute for Physics, Budapest, Hungary.

FIG. 1. Initial process of the time evolution of the initial susceptibility of $Ca_{0.99}Ge_{0.90}$:YIG upon excitation with white light of $10\,mW/cm^2$ intensity, at $T = 91$ K (+), 123 K ($\square$), 140 K (*), and 170 K ($\times$).

After turning off the light at the same temperature, the susceptibility remains nearly constant for about an hour, then it decreases in one step, with a decay process, similar in kinetics to the transition to the third phase of excitation.

No light-induced susceptibility effects have been detected in a nominally pure sample of epitaxial YIG film in the same range of temperature, time, or light intensity.

DISCUSSION

At low magnetic fields the garnet films have a simple stripe-domain structure. The magnetization changes by domain-wall motion. In this case the initial susceptibility χ is inversely proportional to the domain-wall coercivity H_c. The coercivity is determined by the local inhomogeneities of the domain wall energy σ_w met by the wall along its path, x, during the magnetization process, i.e.,

$$\chi^{-1} \sim H_c \sim d\sigma_w/dx, \qquad (1)$$

where $\sigma_w = (AK)^{1/2}$, A is the exchange constant, and K is the anisotropy energy. The local anisotropy can be changed
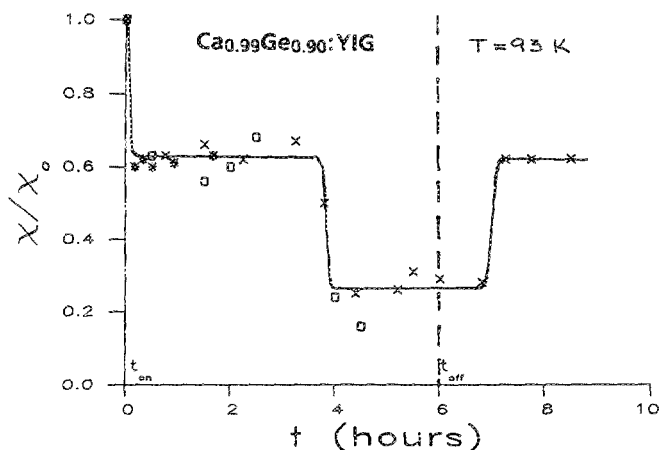

FIG. 2. Time dependence of the relative change of the initial susceptibility for $Ca_{0.11}$:YIG at $T = 93$ K. Illumination is with white light of $15\,mW/cm^2$ intensity. At t_{off} the light was turned off. Data are shown for three series of measurements.

drastically due to the presence of 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 Fe^{3+} and Fe^{4+} sites.

If there are two or more inequivalent 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 Ca^{2+} ions is not too high, the charge-compensating Fe^{4+} ions will be located at nearest-neighbor tetrahedral sites, with an energy of E_1, forming $Ca^{2+} - Fe^{4+}$ 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, $E_2 > E_1$, due to local symmetry changes and the increased Ca^{2+}-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[9] or to the case of the classical photomagnet $CdCr_2Se_4$,[10] then the simplest rate equation will have a form of

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

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 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, $a_i \sim \exp(-E_b/kT)$. The coefficient a depends on the trapping cross section of the new centers, and b 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 Fe^{4+} ions at "far" centers. If the measured susceptibility and/or coercivity change is proportional to the number of the newly created centers, $H_c \sim n$, then the time dependence of the change of H_c would be proportional to χ^{-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

$$n = n_2 + (n_1 - n_2)/[1 + \exp(-t/D)], \qquad (3)$$

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:

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

and

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

are the two real roots of the second-order equation in the denominator of the integral of Eq. (2).[12] 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 site 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 sites, 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[6] and the value for the localization energy of the extra hole at a tetrahedral Fe^{3+} site.[7]

For the thermal decay of the new states, Eq. (2) leads to an $n \sim t^{-1}$ dependence, in contradiction 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 betweeen 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.[7,11]

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 $t \geqslant 0$ 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.

ACKNOWLEDGMENTS

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