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Photomagnetic Effects in Single-Crystal Ru-Doped Lithium Ferrite

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Single crystals of $Li_{0.5}Fe_{2.5}O_4$:Ru (0.01–0.03 atoms per formula unit) are found to exhibit a light-induced change in magnetic permeability and coercive force at 77 K. A light-enhanced disaccommodation is also found in these crystals.

Magnetization measurements on a polycrystalline series of samples with the formula $Li_{0.5}Fe_{2.5-x}Ru_xO_4$ ($x = 0.00$–0.17) have shown that the Ru-ion is in a low-spin state on octahedral sites. In addition, magnetic, electrical, and optical data are given for lithium ferrite crystals doped with 0.00–0.03 Ru-atoms per formula unit, including nonphotomagnetic samples.

Introduction

It is only in recent years that a small number of materials have been known to show light-induced changes in initial magnetic permeability μ_r and coercive force H_c, namely $Y_3Fe_5O_{12}$:Si (*1*), $CdCr_2Se_4$:Ga (*2*), $FeBO_3$ (*3*), and Co-doped Ni–Zn–ferrite (*4*).

In the case of $Y_3Fe_{5-x}Si_xO_{12}$ the explanation for these so-called photomagnetic effects is given (*5*) in terms of light-induced electron transitions resulting in the redistribution of Fe^{2+}-ions, accompanied by an increase in their single-ion magnetocrystalline anisotropy.

In this paper the results of experiments on the photomagnetic effect of Ru-doped lithium ferrite crystals will be presented and the nature of the Ru-dopant in these crystals will be discussed.

Photomagnetic Effects

Photomagnetic effects have been found in single crystals of lithium ferrite, doped with Ru, with nominal composition:

$$Li_{0.5}Fe_{2.5}O_4{:}(0.01 - 0.03)\,Ru.$$

This notation is only used to denote the actual concentration of the dopant in the crystals. Lithium ferrite crystallizes in the cubic spinel structure and has an ionic distribution given by the formula $(Fe^{3+})[Li^{+}_{0.5}Fe^{3+}_{1.5}]O_4$, where () and [] denote tetrahedral and octahedral sites, respectively. It is a ferrimagnet with the moments of the tetrahedral sublattice antiparallel to those of the octahedral one.

The crystals have been grown from a fluxed melt, typically containing 163.00 g PbO, 26.50 g B_2O_3, 13.75 g Li_2CO_3, and 37.05 g Fe_2O_3, all components being analytical grade or better. The compounds are heated at 1050°C for 5 hr to allow homogenization and cooled at 1°C/hr to 600°C, where the flux is poured off. About 1.0 g RuO_2 has to be added to the melt to obtain crystals with a Ru-content of 0.03 atoms per formula unit, which seems to be the upper limit. Adding more RuO_2 to the melt results in the formation of a second phase, presumably $PbRuO_3$. Besides, homogeneously doped crystals are difficult to prepare because of the vaporization of RuO_2 during crystallization. The Ru-content has been analyzed by means of activation analysis and found to be in the range of 0.00–0.03 atoms per formula unit.

For the measurement of the initial permeability μ_r polished platelets with a thickness of 100–300 μm have been used. These are placed on top of a small pot core with inner-wound toroid as the L-part of a LC-resonance

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circuit.* By measuring the resonance frequency of this circuit (~100 kHz), changes in μ_r of about 0.5% can be detected. However, the absolute value of μ_r can only be determined qualitatively, because of the lack of a good standardizing procedure, and has been estimated to be about 5 to 10 for our samples.

The influence of illumination on the magnetic behaviour of a sample with a Ru-content of 0.03 atoms per formula unit will be described with the aid of Fig. 1. Directly after cooling in the dark to 77 K ($\mu_r \equiv \mu_{ri}$), the sample is brought to the magnetically saturated state and demagnetized by means of an alternating magnetic field ($\mu_r \equiv \mu_{r1}$). After this procedure the sample shows disaccommodation, i.e., a decrease in time of μ_r to some asymptotic value. This disaccommodation process can be repeated at will. Subsequently the sample is illuminated with unfiltered light from a 35-W halogen lamp, which causes a sharp decrease in μ_r to a steady state value μ_{rs}, typically some 40% below μ_{ri}. This situation does not change after switching off the light. Again demagnetization is able to initiate a disaccommodation process, but the value of μ_r reached immediately after demagnetization ($\mu_r \equiv \mu_{r2}$) considerably lower than that observed before illumination ($\mu_r \equiv \mu_{r1}$). Illuminating the sample for a second time, shortly after the disaccommodation has started, causes the accelerated decrease of μ_r to the same steady state value μ_{rs} as observed before.

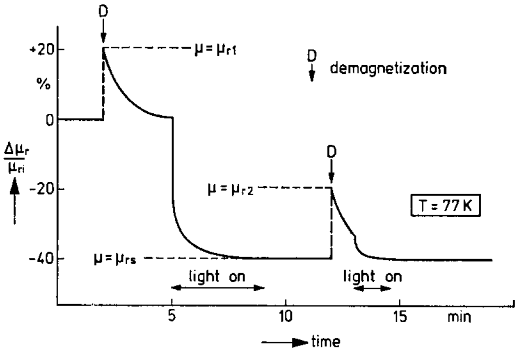

FIG. 1. Effect of illumination with unfiltered light on the initial permeability μ_r of a single crystal of $Li_{0.5}Fe_{2.5}O_4$:0.03 Ru at 77°K. $\Delta\mu_r = \mu_r - \mu_{ri}$ is the change in μ_r with respect to the value μ_{ri} measured immediately after cooling in the dark to 77°K. μ_{r1} and μ_{r2} are the values of μ_r measured immediately after demagnetization; μ_{rs} is the stationary value reached after prolonged illumination.

To explain these effects, it should be remembered that a sample is divided into magnetic domains, separated by a region where the magnetization gradually changes, the domain wall. As in other spinel ferrites, μ_r depends to a large extent on domain wall motion: anisotropic centres within the domain wall have a major influence on μ_r. Demagnetization, however, will radically change the existing domain configuration and it, therefore, provides us with a method of tracing changes in μ_r which are dependent on the exact position of the domain walls in the sample.

The disaccommodation process in Fig. 1 belongs to the latter category. It is a well-known phenomenon in spinel ferrites and has been attributed to the spontaneous redistribution of certain ions within the domain walls (*6*). At 77 K such a relaxation will be caused by ions which can be effectively transported by electronic transitions, such as Fe^{2+}—ions. Apparently disaccommodation can still be initiated after the first illumination. It can also be accelerated by light, as is evident from the second illumination in Fig. 1. This acceleration might also occur during the first illumination. In this case it can not be detected separately, because it is accompanied by a decrease in μ_r which is insensitive to demagnetization (the latter change will be discussed later on). In principle, illumination might be expected to affect any relaxation phenomenon caused by spontaneous electronic transitions. Up till now such an accelerated disaccommodation has been found in Sr-doped YIG (*7*), Ga-doped YIG (*8*), and In-doped YIG (*8*).

The decrease in μ_r during the first illumination in Fig. 1 consists to a large extent of a change which will be called a permanent photomagnetic effect because it is insensitive to demagnetization. This permanent effect is found as the light-induced difference in μ_r as measured immediately after demagnetization (μ_{r1}–μ_{r2} in Fig. 1). It is independent of the position of the domain walls, as is demon-

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* This apparatus has been designed by P. J. Rijnierse, Philips Research Laboratories.

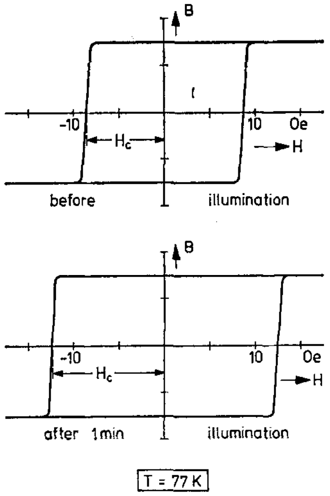

FIG. 2. Effect of illumination with unfiltered light on the hysteresis loop—in particular the coercive force H_c—of a single crystal of $Li_{0.5}Fe_{2.5}O_4$:0.03 Ru at 77°K.

strated by illuminating a sample which is in the magnetically saturated state: the same change (μ_{r1}–μ_{r2}) is found as described before. The permanent effect in Ru-doped lithium ferrite crystals is of the same order of magnitude as that in polycrystalline YIG. In both cases a change $\Delta(\mu)^{-1}$ of about 0.10 is found in the magnetic stiffness, i.e., the reciprocal magnetic permeability $(\mu)^{-1}$.

Photomagnetic samples also show a permanent increase in the coercive force H_c of about 50%. This has been found by measuring the influence on the hysteresis loop of a toroidal sample at 77 K, as shown in Fig. 2. In both cases (μ_r- and H_c-effect), the original situation can be restored by heating the sample to room temperature. These data suggest a similar model as that for YIG (*5*): an energetically unfavourable redistribution of anisotropic centres throughout the sample is frozen in at low temperatures, but is able to relax at higher temperatures. Since permanent effects are only found in crystals containing at least 0.01 Ru-atoms per formula unit, it seems that the Ru-atom plays an important role in them. Unfortunately, it is difficult to determine experimentally how the dopant is substituted in these crystals (lattice site, spin state, valence state), because the Ru can only be incorporated to a maximum content of 0.03 atoms per formula unit. Therefore, the substitution of Ru in polycrystalline lithium ferrite has been studied.

Properties of Polycrystalline Ru-Doped Lithium Ferrite

Samples with the chemical formula $Li_{0.5}Fe_{2.5-x}Ru_xO_4$ have been prepared according to standard ceramic techniques. The starting materials Li_2CO_3, Fe_2O_3, and RuO_2 are weighed in the stoichiometric ratio, except for the RuO_2, to which an excess of 10% (by weight) is added to compensate for vaporization losses. The compounds are ground and fired at 700°C for 10 hr in a mixture of dry O_2 and CO_2 to prevent vaporization of Li_2O. After regrinding they are fired at 1200°C in dry O_2 for 10 hr. X-Ray powder diffraction has shown the product to be a single-phase spinel for values of x up to 0.17. The actual Ru-content has been determined by means of activation analysis.

Measurements of the saturation magnetization σ in fields up to 18 kOe have been made on a null coil pendulum magnetometer of the type described by Enz *et al.* (*9*), from liquid helium temperature up to Curie temperature, and measurements of the susceptibility χ were made up to 1200 K. The results are shown in Fig. 3 and reveal normal ferrimagnetic behaviour. σ at 0 K is found by extrapolation and a correction (smaller than 1 emu) is made for samples with a value of x higher than 0.05, because they do not saturate in the fields

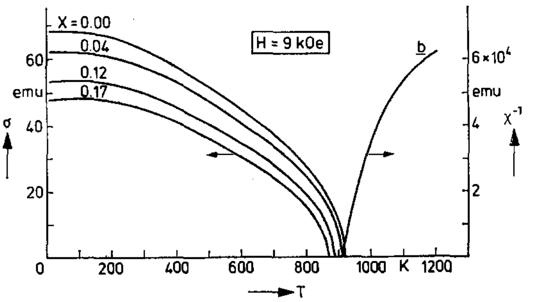

FIG. 3. The temperature dependence of the saturation magnetization σ (below the Curie temperature T_c) and the reciprocal susceptibility χ^{-1} (above T_c) of polycrystalline $Li_{0.5}Fe_{2.5-x}Ru_xO_4$, for different values of x.

applied. This gives $\sigma = 68$ emu for $x = 0$, which corresponds well to the value reported in literature (*10*). Subsequently the change of the saturation magnetization at 0 K with respect to the nonsubstituted $Li_{0.5}Fe_{2.5}O_4$ is calculated as Δn_B in Bohr magnetons (μ_B), according to $\Delta n_B = (M/5585)\Delta\sigma$, where $M =$ molecular weight (*10*). Δn_B is expected to be proportional to x with a constant of proportionality $d\Delta n_B/dx$ which is simply related to the type of substitution. From a theoretical point of view, four different values of this constant are possible and can be derived as follows.

In principle the Ru can substitute in the ferrite in many different ways, two of which are given by the substitution equations:

$$2Fe^{3+} \nearrow Ru^{3+}(4d^5) + Fe^{3+}(3d^5), \quad (1)$$

$$\searrow Ru^{4+}(4d^4) + Fe^{2+}(3d^6). \quad (2)$$

Fe^{2+} is believed to occur on octahedral sites exclusively, and both Fe^{2+} and Fe^{3+} are in the high-spin state in oxidic compounds. But the Ru-ion might occur on both tetrahedral and octahedral sites and, since it is a $4d^n$-ion, it might be in a low-spin state as well, allowing eight different possibilities for substitution. $d\Delta n_B/dx$ is calculated by adding the magnetic moments of the ions of Eq. (1) or (2) with the appropriate sign (depending on octahedral or tetrahedral substitution). Taking the spin-only values for the magnetic moment of the ions, because those including the orbital moment are unknown, four values of $d\Delta n_B/dx$ are found, namely +4, 0, −2, and −4 μ_B/Ru-atom. These values correspond to the dotted lines in Fig. 4.

The points in Fig. 4 represent the values of Δn_B which have been calculated from the experimental results as described. They correspond to the full line with slope $d\Delta n_B/dx = -4.4$ μ_B/Ru-atom. Since these points only fit the dotted line with slope −4 μ_B/Ru-atom reasonably well within experimental accuracy, it is concluded that Ru occurs preferably on octahedral sites in a low-spin state in lithium ferrite, whereas its valence state remains unknown. Of course, it can not be excluded that small amounts of Ru occur on tetrahedral sites as well. The same occurrence as found here is reported for the pseudo-perovskites $SrRuO_3$ and $LaRuO_3$ (*11*), and Ru^{3+} in YIG (*12*). However, Krishnan has reported the existence of Ru^{4+} on tetrahedral sites in $NiFe_2O_4$ (*13*). Both Ru^{3+} and Ru^{4+} are reported in literature, accentuating the question of the valence state of the Ru-ion, which can not easily be solved by means of magnetic measurements. Attempts to reproduce the photomagnetic effects in polycrystalline samples have failed, probably because the exact composition of photomagnetic crystals is still unknown and therefore difficult to duplicate.

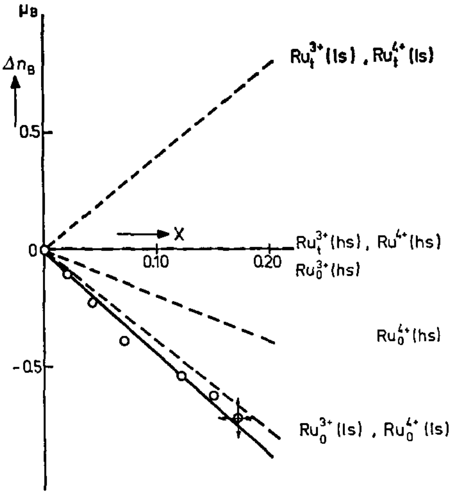

FIG. 4. The change in saturation magnetization Δn_B (expressed in Bohr magnetons μ_B) at 0°K with respect to $Li_{0.5}Fe_{2.5}O_4$ as a function of x in polycrystalline $Li_{0.5}Fe_{2.5-x}Ru_xO_4$. The full line corresponds to the experimental results, the dotted lines show the theoretically expected dependence of Δn_B on x. The indices t and o denote tetrahedral and octahedral sites; hs and ls denote high-spin and low-spin states, respectively.

Additional Experiments and Discussion

Two types of light-induced changes in magnetic permeability have been observed. One is a light-enhanced disaccommodation which can be attributed to the light-induced transport of centres of the same type as those involved in the spontaneous disaccommodation. The other is a permanent effect, similar to that observed in YIG. It can be attributed to light-induced electron redistributions between centres with different anisotropy. The presence of Ru seems to be essential for the permanent effect. Therefore it has to be established which anisotropic centres probably occur in these photomagnetic crystals.

From the magnetization measurements it is found that Ru is incorporated as either Ru^{3+} or Ru^{4+} on octahedral sites in a low-spin state. Both these ions are known to be very anisotropic (*12, 14*) and may therefore play a role as a photomagnetic centre. Information concerning the valence state of the Ru-ions may be obtained by measuring the optical absorption of Ru, substituted in a transparent, diamagnetic spinel host, in the region of 350–2500 nm. Single crystals of $ZnGa_2O_4$, doped with 0.006 Ru-atoms per formula unit show an absorption band (Fig. 5) at 7850 cm^{-1} (=1270 nm), which can be attributed to a $^3T_1 \rightarrow {}^5E, {}^1E$ transition of Ru^{4+} in a low-spin state on octahedral sites (*15*). No absorption band is found at about 16 700 cm^{-1} (=600 nm), where the $^2T_2 \rightarrow {}^2T_2, {}^2E$ and $^2T_2 \rightarrow {}^2A_2, {}^2T_1$ transitions of low-spin, octahedral Ru^{3+} are expected, according to optical measurements of Ru-doped $Gd_3Ga_5O_{12}$ (*15*). These data indicate that Ru preferentially substitutes as Ru^{4+} in spinels. However, since the Ru^{4+}-band is in the region of strong absorption of the photomagnetic crystals (Fig. 5), no direct evidence about its presence or absence can be obtained.

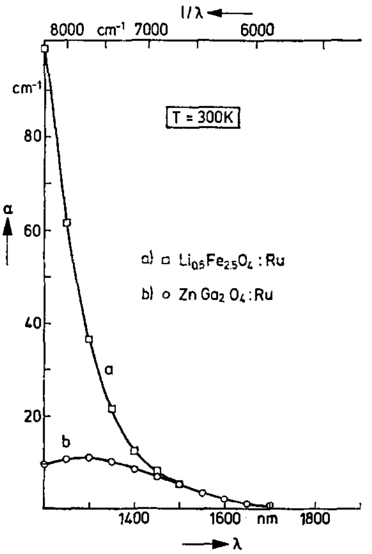

FIG. 5. The optical absorption of a single crystal of $Li_{0.5}Fe_{2.5}O_4$:0.03 Ru and the absorption band of Ru—normalized to 0.03 Ru atoms per formula unit—as measured in single crystalline $ZnGa_2O_4$:0.006 Ru as a function of wavelength (λ) at 300 K. Both spectra do not change essentially when measured at 4.2°K. The absorption coefficient α has been corrected for reflections according to Johnson and Walton (*16*).

Ru^{3+} and Ru^{4+} are not the only ions which could play a role as anisotropic centres. The Fe^{2+}-ion is also known to be anisotropic, though much less than the Ru-ions (*14*). And the occurrence of Fe^{2+}-ions in the photomagnetic crystals can not be excluded a priori, since chemical analysis has shown that undoped lithium ferrite crystals contain up to 0.01 Fe^{2+}-ions per formula unit. However, it is rather improbable that the mechanism of the permanent effect is exactly the same as that proposed for YIG with only Fe^{2+}-ions as photomagnetic centres (*5*), since both undoped and Ti-doped lithium ferrite crystals, which are expected to behave similarly because of their Fe^{2+}-content, show no photosensitivity. Therefore a better knowledge of the possible role of Fe^{2+} is necessary.

Some additional information is obtained here from optical and conductivity data of lithium ferrite crystals with Ru-concentrations between 0.00 and 0.03 atoms per formula unit. For this purpose the optical absorption coefficient at 1250 nm (α_{1250}) and the resistivity (R_0) have been measured, both at room temperature. A transition between a region of low Ru-concentrations, characterized by a high absorption ($\alpha_{1250} \sim 500$ cm^{-1}) and low resistivity ($R_0 \sim 10^2 - 10^3$ Ωcm), and a region of higher Ru-concentrations, with $\alpha_{1250} \sim 200$ cm^{-1} and $R_0 \sim 10^5$–10^9 Ω cm, has been found at a dopant level of about 0.01 atoms per formula unit. These data seem to suggest that those Fe^{2+}-ions commonly thought to be responsible for a high absorption and low resistivity in spinel ferrites, are absent in the region of higher Ru-concentrations. This may be essential for the occurrence of permanent photomagnetic effects, which are exclusively found at higher Ru-concentrations ($\geqslant$0.01 atom per formula unit).

It is tempting to speculate on possible mechanisms for the observed photosensitivity in view of the presented data, However, more experimental data are required in order to find the actual substitution mechanism and to allow a more detailed explanation of the observed effects.

Conclusion

The discovery of a photomagnetic effect which is independent of the domain wall configuration together with a light-enhanced disaccommodation in single crystals of Ru-doped $Li_{0.5}Fe_{2.5}O_4$ has been reported. Magnetization measurements of polycrystalline $Li_{0.5}Fe_{2.5-x}Ru_xO_4$ showed the Ru to be in a low-spin state on octahedral sites. Although the present data are insufficient for a detailed explanation of the observed photomagnetic effects, it is evident that Ru plays a very essential role in them.

Acknowledgments

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