Laser-induced shift of the Morin point in antiferromagnetic DyFeO$_3$

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Abstract: Imaging domain structure of antiferromagnetic DyFeO$_3$ reveals that intense laser excitation can control the temperature of the Morin transition from collinear to non-collinear spin state. Excitation of the antiferromagnet with femtosecond laser pulses with the central wavelength of 800 nm leads to a shift of the transition temperature over 1 K to higher values as if the light effectively cools the irradiated area down.

It is suggested that the optical control of the Morin point can be a result of photo-ionization of Dy$^{3+}$ ions.

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OCIS codes: (210.3820) Magneto-optical materials; (210.4770) Optical recording; (320.2250) Femtosecond phenomena.

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1. **Introduction**

Manipulation of magnetic order with the help of light is a counter-intuitive research subject and an issue of intense debates in many areas of science ranging from the physics of spintronics [1], magnonics [2], multiferroics [3] to organic chemistry [5]. The development of lasers which are able to generate sub-100 fs intense pulses has made optical control of magnetism especially appealing. In particular, it led to the seminal observation of subpicosecond demagnetization in ferromagnetic nickel by a 60-fs laser pulse [6] and triggered the field of ultrafast magnetism. This has been continuously fueled by intriguing observations and caused no shortage of controversy in the scientific community [7,8]. The action of electric field on electronic charges, being the largest perturbation in physics of light-matter interaction, conserves the spin of electron and an efficient control of magnetic properties of media with light is therefore counter-intuitive.

Despite this fact, several effective mechanisms of such a control have been demonstrated up to date and antiferromagnetic rare-earth orthoferrites played in these studies an important role. Due to strong temperature-dependent magnetic anisotropy many rare-earth orthoferrites possess temperature driven spin-reorientation phase transitions. Therefore, even laser-induced heating is able to induce spin reorientation in these antiferromagnets [9, 10]. Rare-earth orthoferrites are also materials with a strong spin-orbit interaction in the excited state and optically induced population of the excited states can effectively change the spin-orbit interaction [11–13]. Such a photo-induced spin-orbit interaction can be seen as a modification of magnetic anisotropy and thus it is equivalent to an action of effective magnetic field experienced by the spins. Phenomenologically, the opto-magnetic fields can be described in terms of the inverse Faraday and Cotton-Mouton effects [14]. Recently, it was suggested that laser excitation of the charge-transfer transitions in the rare-earth orthoferrites can effectively lead to optical modification of the spin-spin exchange interactions in these materials [15]. Phenomenologically, this observation can be seen as the inverse magnetorefractive effect [16, 17]. All these studies show that light can effectively manipulate spins, controlling spin-orbit and spin-spin interactions responsible...
for spin order. Obviously, such a photo-induced change of the strength of the fundamental interactions should also affect critical temperatures of phase transition in the orthoferrites. Despite a large number of publications on spin dynamics induced in rare-earth orthoferrites by intense pulses in the visible and THz spectral range, an effect of intense optical excitation on the critical temperatures of the orthoferrites has not been discussed until now. In the present manuscript we address this problem and report about an effect of intense laser radiation on the critical temperature of the spin reorientation phase transition in antiferromagnetic dielectric DyFeO₃. It is argued that if an intense optical pumping ionizes Dy³⁺ ions bringing them into the Dy⁴⁺ state, it should lead to a substantial change of the effective exchange interaction between the spins of the Dy and Fe ions, affect the magnetic anisotropy experienced by the Fe-ions, change the temperature dependence of the magnetic anisotropy and thus shift the Morin point at which the spin reorientation occurs.

2. Studied sample and experimental technique

Dysprosium orthoferrite DyFeO₃ possess rather unique magnetic and magnetooptical properties which make this material attractive for optical studies of magnetic phenomena, in general, and phase transitions, in particular. Rare-earth orthoferrites are antiferromagnets with the Neel temperature of 650 K [18]. The four iron ions Fe³⁺ form two antiferromagnetically coupled magnetic sublattices M₁ and M₂, such that |M₁| = |M₂|. DyFeO₃ is characterized by a very strong temperature dependence of magnetic anisotropy that leads to a spontaneous first-order Morin phase transition at Tₘ=38 K [18]. Below the Morin point, the spins are in collinear antiferromagnetic phase with magnetic moments of the two sublattices M₁ and M₂ aligned along the y-axis, so that M₁ + M₂ = 0. Above Tₘ, the magnetic moments of the sublattices get aligned along the x axis. Moreover, due to the Dzyaloshinskii–Moriya interaction the spins of the two sublattices acquire a canting over an angle of about 0.5 degrees, giving rise to a small spontaneous magnetization M = M₁ + M₂ ≠ 0 along the z axis. Without any magnetic field the crystal splits into two types of domains with the magnetization parallel and antiparallel to the z axis, respectively. Phenomenologically, the phase transition is explained as a result of interplay between two contributions to the magnetic anisotropy experienced by the Fe³⁺ spins [19]. The first contribution in the vicinity of Tₘ almost does not depend on temperature. It originates from the spin-orbit interaction and the effect of the crystal lattice on the orbitals of Fe³⁺ ions. The second contribution originates from the spin-spin exchange interaction between 3d-electrons of the Fe³⁺ and 4f-electrons of the Dy³⁺ ions. This contribution is strongly temperature dependent as a result of thermally induced repopulation of 4f states of the Dy³⁺ ions.

Despite the small magnetization in the high temperature phase, DyFeO₃ exhibits a giant Faraday rotation of about 3000° cm⁻¹ which makes this material especially convenient for magnetooptical measurements. To avoid effects of the linear birefringence on the Faraday rotation [20] the studied DyFeO₃ crystal was cut perpendicular to the optical axis [4] and had the thickness of 100 μm. The optical axis is tilted over 55 degrees with respect to the z-axis. In our experiments we employed the technique of magneto-optical imaging with a possibility to excite the sample with a well defined sequence of ultrashort laser pulses. Each of the pulses had the duration of 60 fs. The details of the setup are described elsewhere [21].

Using the magneto-optical Faraday effect we visualized the magnetic domains in DyFeO₃ crystal. With the help of these measurements we studied how laser excitation, magnetic field and temperature affect the domain pattern. Figure 1 shows typical magneto-optical images of the orthoferrite measured in the vicinity of the Morin point. In the following for convenience instead of temperature T we will use new variable ΔT=T-Tₘ. In the low temperature phase the net magnetization is zero and the image is seen as a grey area, as shown in Fig. 1(a). A
typical domain pattern in the high temperature phase is shown in Fig. 1(c). The black and the white areas correspond to the domains in which the magnetization $M_z$ points “up” and “down”, respectively. In fact, this stripe-like structure of the black and white domains shows that the crystal is in the high-temperature $\Gamma_4$ phase. In the vicinity of the Morin point ($|\Delta T| \leq 0.15 \text{ K}$) one observes a co-existence of the both phases, as it shown in Fig. 1(b), which is typical for first-order phase transitions. We have not observed any pronounced temperature hysteresis of the Morin transition in DyFeO$_3$, see Fig. 1(d). This hysteresis-free behavior, in contrast to the common expectations for first-order phase transitions, is typical for the Morin transition in DyFeO$_3$ [19].

![Fig. 1. (a)-(c) Magneto-optical images of DyFeO$_3$ single crystal in zero magnetic field at three different temperatures in the vicinity of the Morin point $T_M$ ($\Delta T=T-T_M$). Grey areas at $\Delta T=-1 \text{ K}$ correspond to the collinear antiferromagnetic phase $\Gamma_1$. Black and white stripe domains detected at $\Delta T=0$ and $\Delta T=1 \text{ K}$ are ferromagnetic domains in the $\Gamma_4$ phase with magnetizations “up” and “down”, respectively. (d) Changes in the net magnetization upon warming up (red) and cooling down (blue), estimated from the images.](image)

3. **Experimental results**

We have found that if the crystal is excited with about 10 ultrashort laser pulses, the Morin temperature of the irradiated area changes. Each of these pulses had the fluence of about 20 $\mu \text{J}$ and the central wavelength of 800 nm. Figure 2 shows images of the crystal taken after the

![Fig. 2. Magneto-optical images of the photo-excited DyFeO$_3$ single crystal at different temperatures. The area excited by a sequence of at least 10 ultrashort laser pulses is shown by solid circle. In the low temperature phase ($\Delta T=T-T_M=-1 \text{ K}$) one can hardly distinguish any contrast between the laser-excited and non-excited areas. A temperature increase reveals that in the area prepared by the laser-excitation the Morin transition occurs at higher temperatures.](image)
Fig. 3. Magneto-optical images of the photo-excited DyFeO$_3$ single crystal obtained at different magnetic fields and at fixed temperature $\Delta T=T-T_M=-5$ K. Rows (a) and (b) correspond to the experiments performed in positive and negative magnetic field, respectively. Applying a positive field induces the Morin transition into a single domain state with the magnetization “up”. Applying a negative magnetic field induces the Morin transition into a single domain state with the magnetization “down”. The stripe domain pattern corresponds to the intermediate state, i.e. the state in which domains of the two competing phases $\Gamma_1$ and $\Gamma_4$ coexist [26]. In the area excited by the sequence of the laser pulses, marked by solid line, the Morin transition occurs at higher fields.

illumination. It is seen that in the low temperature phase the excitation hardly contributes to the contrast. Upon an increase of the temperature the crystal undergoes the Morin transition from the collinear to non-collinear antiferromagnetic spin state. In the area irradiated by the laser pulses the Morin transition occurs at higher temperature than in the surroundings.

It is known that for temperatures just below the Morin point the transition can be triggered by a moderate magnetic field $H>H_c$ applied along the $z$—crystallographic axis [19]. In order to trigger the field-induced Morin transition, we canted the magnetic field $H$ in the sample plane $(010)$ over 15 degrees such that the field acquired projections on all three crystallographic axes. Fig. 3 shows the images of the domain pattern obtained for the sample at the fixed temperature just below the Morin point $\Delta T=-5$ K at different magnetic fields. These measurements clearly reveal that the irradiated area, experiences belated changes upon the field increase. To summarize the experimental observation, we have plotted $H$-$T$ phase diagram of the Morin transition. It was found that the diagram in the area which has been exposed to the intense laser excitation is substantially shifted from the diagram for the unaffected area, as shown in Fig. 4. We could not reveal any dependence of the difference between the diagrams on the number of the laser pulses. Once the photo-excited state is formed the phase diagram does not change anymore. All these experiments clearly reveal an effect of intense laser excitation on the Morin temperature in DyFeO$_3$ shifting the whole phase diagram to higher temperatures. We have not revealed any correlation between the probability of appearance of the area with a changed Morin temperature on the repetition rate of the exciting pulses. The lifetime of the photo-induced state exceeds 3 hours. We could not erase the photo-induced state even by heating the sample up to 150 K.

4. Discussion

The phase transition from $\Gamma_1$ to $\Gamma_4$ phase in the orthoferrite originates from thermally induced repopulation of $4f$ states of Dy-ions. It thus reasonable to suggest that the photo-induced change of the temperature of the phase transition originates from long-living effects of light on the Dy-subsystem.

The Dy$^{3+}$ ion contains 9 electrons on the outer $4f$ shell, thus being the Kramer’s ion. The local symmetry the ion in DyFeO$_3$ is described by the point group $C_5$ so that the original ground
Fig. 4. The phase diagram revealing the ratio of the critical magnetic field $H_c$ and the critical temperature $\Delta T_M$ at the Morin transition, defined as $\Delta T_M = T_M(H_c) - T_M(0)$, for the crystal area unaffected by the photo-excitation and the area exposed to the photo-excitation. It is seen that the Morin point in the photo-excited area is clearly shifted. The inset shows changes in the net magnetization upon application of magnetic field, estimated from the images, and the way how the critical magnetic field was determined.

The ground multiplet $^6H_{15/2}$ ($L=5, S=5/2, J=15/2$), corresponding to that of the Dy$^{3+}$ ion, splits and the lowest two doublets with a good accuracy are $|\pm 15/2\rangle$ ($M_J = \pm 15/2$), $|\pm 13/2\rangle$ ($M_J = \pm 13/2$) [22]. The energy separation between these two doublets is about $E_1 = 6.5 \text{ meV}$. Since the Dy$^{3+}$ ions are located in non-centrosymmetric positions, otherwise forbidden optical transitions become allowed in electric dipole approximation, including the transition from $^6H_{15/2}$ to $^6F_{5/2}$ ($L=3, S=5/2, J=5/2$) around 1.5 eV, which perfectly matches the energy of the pumping photons.

Importantly, the light-induced shift of the Morin point was observed only under pumping by very intense laser pulses with fluence around 1 PW/cm$^2$. When dielectrics are excited by light with so large intensities, the multiphoton absorption, necessary to induce an interband transition, cannot be neglected [23]. Moreover, multiphoton process get significantly enhanced near optical resonances in the vicinity of real transitions, such as $^6H_{15/2} \rightarrow ^6F_{5/2}$. Thus it is reasonable to assume that intense pumping of the Dy$^{3+}$ ions in our experiments results in photo-ionization of the Dy$^{3+}$ ions. In real crystals due to defects and impurities there is always a possibility that the excited electrons will be caught by deep and long-living states in the band gap. In this case the dysprosium ions are effectively brought to a long-living Dy$^{4+}$ state. It is interesting to analyze how such an ionization of the dysprosium ions can affect the Morin point in DyFeO$_3$ crystals.

The ground multiplet of the long-living Dy$^{4+}$ state is $^7F_0$ ($L=3, S=6, J=9$). Note, that the way how the ground multiplet of the Dy$^{4+}$ ions splits in the crystal field in DyFeO$_3$ is similar to the splitting of the ground multiplet of the Tb$^{3+}$ ions in TbFeO$_3$. One can say that a photo-ionization of Dy$^{3+}$ ions makes them Tb$^{3+}$-like.

The effective exchange field $H_{ex}$ between the spins of the 3$d$-electrons of the transition ions and the 4$f$-electrons of the rare-earth ions is proportional to the Lande factor $g_L$ of the rare-earth ion [25]:

$$H_{ex} \sim \frac{g_L}{g_L - 1}. \quad (1)$$
So, the value of the $d$-$f$ exchange increases in the direction from heavier rare-earth ions to lighter. The Lande factors of the $^6H_{15/2}$ and $^7F_j$ multiplets are quite different ($g_L = 1/3$ in the case of $^6H_{15/2}$ and $g_L = 1/4$ in the case of $^7F_j$). Consequently, the photo-ionization of the Dy$^{3+}$ into Tb$^{3+}$-like ion results into an increase of the exchange field.

In the model of the Morin transition suggested in [19] the Morin temperature $T_M$ is defined by the equality:

$$K_{Dy}(T_M) = K_{Fe},$$  \hspace{1cm} (2)

where $K_{Fe}$ is the energy of magnetic anisotropy which holds the Fe$^{3+}$ spins in the $xz$-plane ($\Gamma_4$ phase). $K_{Dy}(T)$ is the temperature dependent $d$-$f$ exchange energy. It acts as an effective anisotropy on the Fe$^{3+}$ spins and tries to align the spins in the $xy$ plane, along the $y$-axis ($\Gamma_1$ phase). According to [19]:

$$K_{Dy}(T) = K_{Dy}(0) \tanh \left( \frac{E_1}{2kT} \right),$$  \hspace{1cm} (3)

where $k$ is the Boltzman constant and $K_{Dy}(0) \sim (H_{el})^2$.

If the concentration of the Dy$^{4+}$-ions induced by light is small ($x \ll 1$), one can find that:

$$K_{Dy} = (1-x) \cdot K_{Dy^{3+}} + x \cdot K_{Dy^{4+}}.$$  \hspace{1cm} (4)

Here parameters $K_{Dy^{3+}}$ and $K_{Dy^{4+}}$ account for the difference of the Lande factors of the ions. Substituting Eq. (4) into the Eq. (2) one obtains:

$$K_{Dy}(0) \left( 1 + \frac{7}{9} x \right) \tanh \left( \frac{E_1}{2kT} \right) = K_{Fe}.$$  \hspace{1cm} (5)

The very same equation can be written as:

$$\frac{1}{T_M} \frac{dT_M}{dx} \approx \frac{7}{9} \frac{\sinh \left( \frac{E_1}{T_M} \right)}{E_1}.$$  \hspace{1cm} (6)

Equation (6) shows that in order to shift the Morin point over 1 K, it is sufficient to ionize about 2 % of the dysprosium ions.

### Conclusion

Imaging magnetic domains in antiferromagnetic DyFeO$_3$ in the vicinity of the Morin point allows to reveal an effect of ultrashort intense laser pulses on the critical temperature of the phase transition in the orthoferrite. It is shown that excitation of the antiferromagnet with at least 10 femtosecond laser pulses at the central wavelength 800 nm leads to a shift of the transition temperature over 1 K to higher values as if the light can effectively cools the irradiated area down. The measurements at different temperatures and magnetic fields allowed us to reveal the whole phase diagram for the photo-excited crystal. It is suggested that the optical control of the Morin point can be a result of photo-ionization of Dy$^{3+}$ ions.

### Acknowledgments

The work was supported by the program Leading Scientist of the Russian Ministry of Education and Science (14.Z50.31.0034) and the European Research Council under the European Unions Seventh Framework Program (FP7/2007-2013)/ERC Grant Agreement No. 257280 (Femto-magnetism), the Foundation for Fundamental Research on Matter (FOM, the European Union’s Seventh Framework Program (FP7/2007-2013) Grants No. NMP3-LA-2010-246102 (IFOX). The authors thank R.V. Pisarev for providing the samples and Th. Rasing for continuous support.