Resonant pumping of *d-d* crystal field electronic transitions as a mechanism of ultrafast optical control of the exchange interactions in iron oxides

R. V. Mikhaylovskiy[1,2a], T. J. Huisman[1], V. A. Gavrichkov[3], S. I. Polukeev[3], S. G. Ovchinnikov[3], D. Afanasiev[1,4], R. V. Pisarev[5], Th. Rasing[1], and A. V. Kimel[1]

[1]*Radboud University, Institute for Molecules and Materials, Heyendaalseweg 135, 6525 AJ Nijmegen, the Netherlands*

[2]*Department of Physics, Lancaster University, Bailrigg, Lancaster LA1 4YW, United Kingdom*

[3]*Kirensky Institute of Physics, Federal Research Center KSC SB RAS, 660036 Krasnoyarsk, Russia*

[4]*Kavli Institute of Nanoscience, Delft University of Technology, P.O. Box 5046, 2600 GA Delft, the Netherlands*

[5]*Ioffe Physical-Technical Institute, Russian Academy of Sciences, 194021 St. Petersburg, Russia*

The microscopic origin of ultrafast modification of the ratio between the symmetric (*J*) and antisymmetric (*D*) exchange interaction in antiferromagnetic iron oxides is revealed, using femtosecond laser excitation as a pump and terahertz emission spectroscopy as a probe. By tuning the photon energy of the laser pump pulse we show that the effect of light on the *D/J* ratio in two archetypical iron oxides $FeBO_3$ and $ErFeO_3$ is maximized when the photon energy is in resonance with a spin and parity forbidden *d-d* transition between the crystal-field split states of Fe^{3+} ions. The experimental findings are supported by a multi-electron model, which accounts for the resonant absorption of photons by Fe^{3+} ions. Our results reveal the importance of the parity and spin-change forbidden, and therefore often underestimated, *d-d* transitions in ultrafast optical control of magnetism.

---

[a] Email for correspondence: r.mikhaylovskiy@lancaster.ac.uk

The short-range spin-spin exchange interaction that results in long-range magnetic order is one of the important demonstrations of the quantum nature of matter. Remarkably, the strength of the exchange interaction in magnetically ordered materials expressed in terms of effective magnetic fields can reach 1000 Tesla in which the spin precession period is typically shorter than a picosecond. Controlling the exchange interaction by sub-picosecond laser pulses is thus a very appealing approach to search for a new scenario of the fastest possible control of magnetism [1].

The symmetric part of the exchange energy W_{ex} between two magnetic sublattices $\mathbf{S}_1$ and $\mathbf{S}_2$ $W_{\mathrm{ex}} = J\mathbf{S}_1\mathbf{S}_2$ is responsible for the very existence of long-range magnetic order. During recent years, the modulation of the symmetric exchange interaction by femtosecond laser pulses has been a subject of experimental and theoretical studies [2-19]. Its antisymmetric counterpart, the relativistic Dzyaloshinskii-Moriya energy $W_{\mathrm{D}} = \mathbf{D}\times[\mathbf{S}_1\times\mathbf{S}_2]$, contributes to the emergence of weak ferromagnetism [20], multiferroicity [21] and magnetic skyrmions [22]. The possibility of ultrafast optical control of the ratio between J and D has been reported for various transition metal oxides and motivated several theoretical proposals to manipulate magnetic textures through optical control [23-28]. However, presently available theoretical models fail to describe the change of exchange in realistic materials, hence there is no information which optical transitions one must pump to change D/J efficiently. In this Letter we experimentally reveal that the weak, and thus often overlooked, *d-d* transitions are responsible for the efficient modification of the D/J exchange ratio. We also suggest a multi-orbital theory that can explain the effect.

To observe the optical modification of J and/or D, one can use the fact that in a broad class of antiferromagnetic iron oxides (iron borate $\mathrm{FeBO_3}$, hematite α-$\mathrm{Fe_2O_3}$, and orthoferrites $R\mathrm{FeO_3}$, with R being a rare-earth element) the ratio D/J defines the canting angle of the two magnetic sublattices of Fe^{3+} ions. Therefore, in these materials an ultrafast change of the exchange constants J and/or D results in coherent spin motion that can be reliably separated from the heat-driven and other incoherent dynamics. Particularly, perturbation of J and/or D triggers the quasi-antiferromagnetic (q-AFM) mode of antiferromagnetic resonance [29] involving periodic oscillation of the canting angle at a THz frequency. The spin motion acts as *ac* magnetic dipole emitting coherent THz electro-magnetic waves, which were measured experimentally. The excitation of the antiferromagnetic resonance by light can be seen as an impulsive stimulated Raman process, known as inverse magnetic refraction. Microscopically, this effect involves the change of the J/D ratio [29].

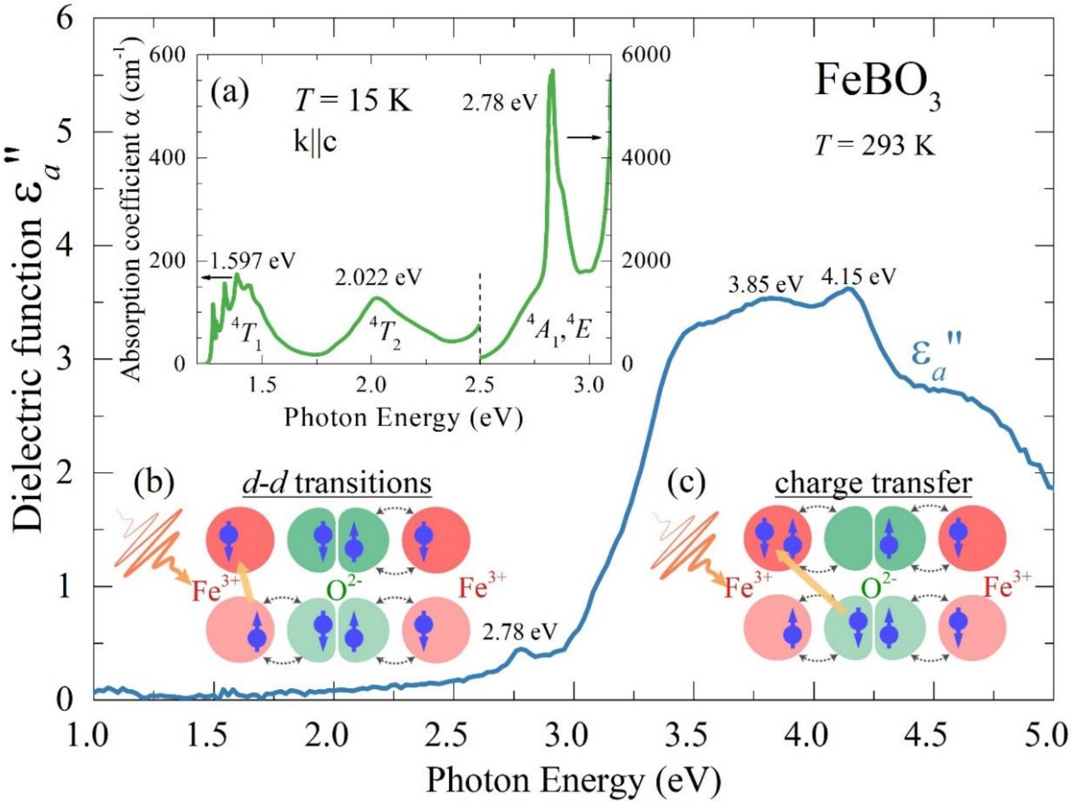

Fig. 1. (Color online). Main panel: The imaginary part of the FeBO$_3$ dielectric function as a function of photon energy measured using a spectroscopic ellipsometer. The response is dominated by strong charge transfer transitions above 3 eV. Insets: (a). Absorption coefficient of antiferromagnetic iron oxide FeBO$_3$. Absorption was measured for light propagating along the optical axis. Absorption bands due to the *d-d* transitions from the $^6A_1$ ground state to the $^4T_1$, $^4T_2$, $^4A_1$, ^4E excited states are indicated. (b). Modulation of the superexchange interaction due to the pumping of the *d-d* transitions involving a spin flip from S = 5/2 in the ground state to S = 3/2 in the excited states. (c). Schematics showing the modulation of the superexchange interaction by a laser induced charge transfer.

The optical absorption of the iron oxides is defined by charge-transfer *electric dipole* transitions between the oxygen *p* orbitals and the *d* orbitals of the Fe^{3+} ions and *d-d* transitions of the single Fe^{3+} ion (see Fig. 1 and Refs. 30-32). The virtual hopping of the electrons between Fe^{3+} and O^{2-} ions gives rise to superexchange interaction resulting in the antiferromagnetic ordering ($J > 0$). Therefore, it is natural to assume that the laser pulse excites the charge-transfer transitions, thereby modifying the hopping and consequently the exchange coupling between the neighboring Fe^{3+} ions. This scenario is illustrated in Fig. 1c and has been discussed earlier for manganites [33] and ferromagnetic/antiferromagnetic heterostructures [34,35].

The weak and broad *d*-*d* absorption bands arise due to the inter-orbital transitions between the 3*d*-states split by the crystal field (see Fig. 1 for FeBO$_3$ and Refs. 30,31 for other iron oxides). These transitions are forbidden in the electric-dipole approximation. However, they become partially allowed due to mixing of *p*-*d* atomic states of opposite parity by phonons and/or due to the inversion symmetry breaking at the position of the magnetic ion. Moreover, these electronic excitations between the $3d^5$ states of the Fe^{3+} ion require a spin-change from $S = 5/2$ to $S = 3/2$ that is also forbidden for optical transitions in the electric-dipole approximation. However, this restriction is removed by accounting for the spin-orbit coupling. A femtosecond optical pulse can excite these transitions resonantly and drive electrons into a new orbital configuration with a different spin value, thereby perturbing the superexchange (Fig. 1b). Even though most pump-probe experiments use pump pulses with a photon energy of 1.55 eV very close to the *d*-*d* absorption bands in iron oxides, the inter-orbital transitions in magnetic cations in ultrafast light-spin interactions has so far got very limited attention [36-38] and their role in the control of the *D/J* exchange ratio still remains unclear.

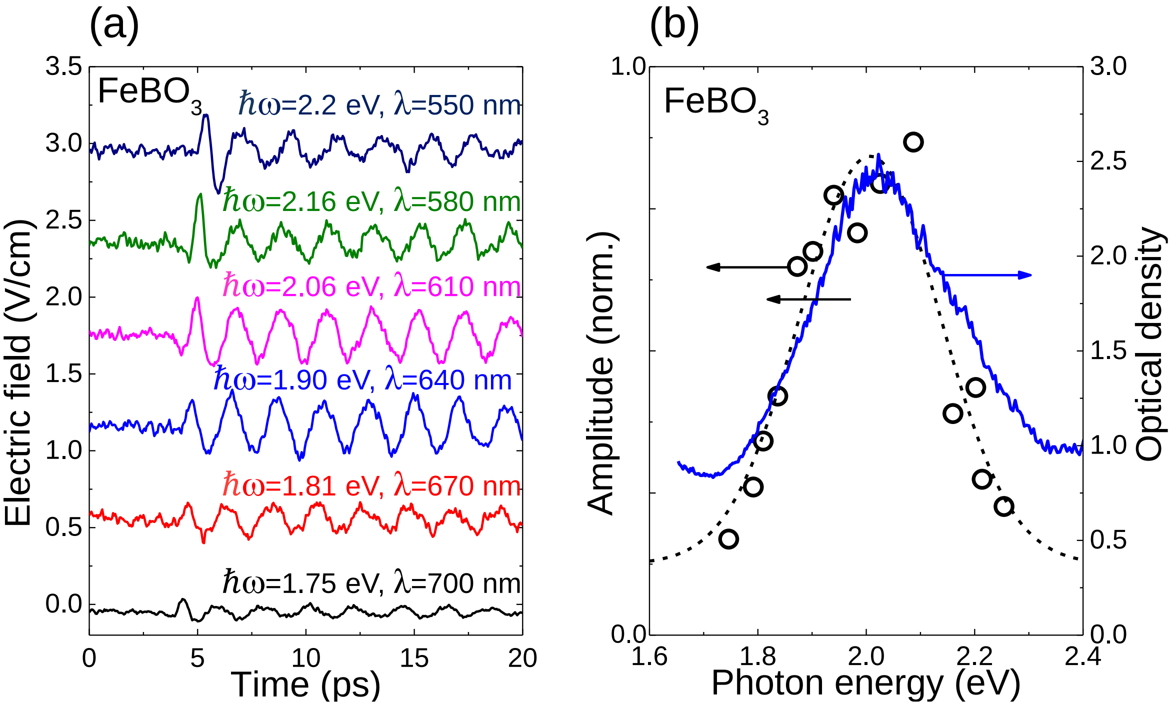

Fig. 2. (Color online). (a). Waveforms of the THz electric field emitted from FeBO$_3$ excited by femtosecond pulses of different photon energy (wavelength). The slight change in the signal delay is due to the inequality of the optical paths for different wavelengths. (b). Amplitude of the THz waveforms as a function of the pump photon energy (open circles) shown together with the measured optical density of the same sample (solid line). The amplitude is normalized with respect to the pump power, which varied for different wavelengths. Dashed line is a guide to the eye.

Spectral measurements with wavelength-tuneable laser pulses can provide an efficient way for unveiling the microscopic mechanisms responsible for the modification of the exchange interaction. To establish a spectroscopic correlation between the observed effects and the absorption bands, we employed THz emission spectroscopy [39], with tuneable photon energy of the pump laser pulse [40]. The measured THz signal is directly related to the magnetization dynamics by linear Maxwell equations [41]. The samples were brought into a single domain state by an in-plane bias magnetic field of ~0.1 Tesla.

Initially we studied a rhombohedral calcite-type single crystal of iron borate $FeBO_3$. The 370 µm thick sample was cut perpendicularly to the *z*-axis, i.e. with the antiferromagnetic vector and weak ferromagnetic moment in the basal *xy*-plane. Fig 2a shows the time traces of the electric field emitted from the photo-excited sample for different pump pulse photon energies. In order to maximize the detected signal, the measurements were done at the low temperature of 10 K. As one can see, the signals consist of quasi-monochromatic oscillations at a frequency of about 450 GHz, matching the frequency of the q-AFM mode of $FeBO_3$. The observed waveforms do not depend neither on the polarization of the pump light, nor on the crystal orientation, while their sign does change when changing the polarity of the applied magnetic field. The signals have all the properties attesting the excitation of the q-AFM by modulation of the superexchange interaction [29]. By fitting the experimental data with decaying sinusoidal functions we retrieved the amplitude of the q-AFM mode, which is plotted in Fig. 2b as a function of the pump photon energy. The amplitude shows a clear resonant behavior in the vicinity of the $^6A_1 \rightarrow {}^4T_2$ transition, with a central energy at ~2 eV (see Fig. 1a). To further support this observation, we measured the optical transmission as a function of photon energy for this particular sample. The resulting optical density perfectly matches the dependence of the q-AFM amplitude (see Fig. 2b), confirming that the optical excitation of the q-AFM mode and hence the modulation of the D/J exchange ratio is due to the resonant pumping of the $^6A_1 \rightarrow {}^4T_2$ transition.

To test whether the observed resonant behavior is present in other iron oxides, we repeated similar THz emission measurements on $ErFeO_3$, belonging to the orthorhombic crystal family of rare-earth orthoferrites. In this material we also observed THz emission corresponding to the q-AFM mode [29]. As an example, Fig. 3 shows the photon energy dependence of the amplitude of the q-AFM mode of the $ErFeO_3$ sample. The optical density of the sample is also shown in Fig. 3. Very similar to $FeBO_3$ the amplitude peaks at the photon energy corresponding to the $^6A_1 \rightarrow {}^4T_2$ absorption band. At the same time, there is no clear evidence for contribution of *f-f* transitions between Er^{3+} localized states (seen as narrow peaks just below 1.9 eV in Fig. 3) to the perturbation of the *D/J* ratio. However, THz emission efficiency seems to be centered at a slightly higher photon energy compared to the *d-d* absorption band. It may indicate some influence of the *f-f* transitions or it may also be due to the velocity mismatch between THz and optical waves at the different frequencies.

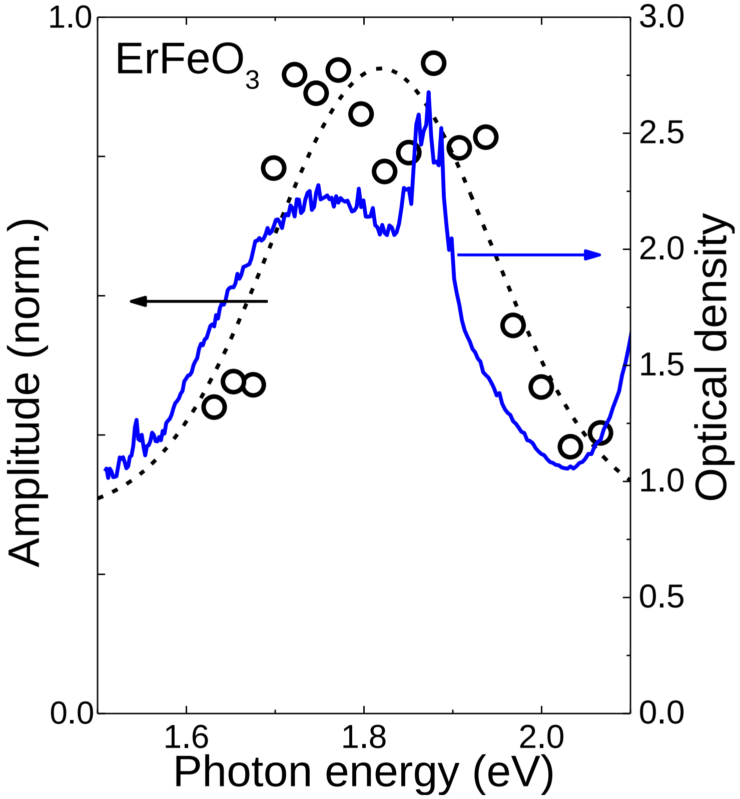

Fig. 3. (Color online). Amplitude of the THz waveforms as a function of the pump photon energy (open circles) shown along with the measured optical density of the $ErFeO_3$ sample (solid line). The amplitude is normalized as in Fig. 2. Dashed line is a guide to the eye. The narrow feature at ~1.87 eV is due to *f-f* transitions in Er^{3+} ions. This measurement was performed at room temperature.

Using a β-barium borate (BBO) single crystal the photon energy of the fundamental laser pulse at 1.55 eV was doubled to 3.1 eV in order to pump the samples in the region of the strong absorption close to their charge-transfer gap (Fig. 1). However, we observed no THz emission from all samples in this case. Although this result stands against a charge-transfer based mechanism of the superexchange modulation (Fig. 1c), one has to bear in mind that due to the strong absorption of more than 10^3 cm^{-1} at 3.1 eV, the penetration depth of the laser pulse is only ~1 μm, which is much less than that in the transparency region (~70 μm). Therefore, the THz signal is emitted from a significantly thinner part of the sample than in the 1.7-2.3 eV range. Most probably it falls below the noise level and thus requires more detailed study. Nonetheless, we can confidently state that the pumping of *d-d* transitions positioned below the charge transfer transitions dominates in the optical modulation of the *D/J* exchange ratio in the iron oxides.

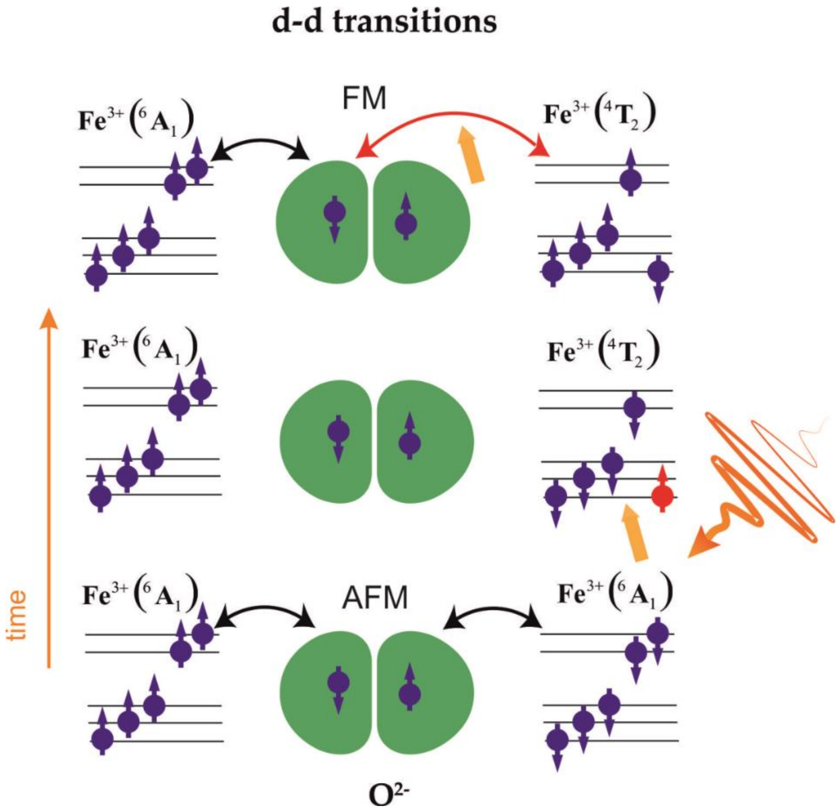

Fig.4. (Color online). Illustration of the photoinduced modulation of the superexchange interaction in an iron oxide. In the ground state (lower panel) the hopping results in the antiferromagnetic alignment of spins. The optical excitation flips one spin in an iron ion (red one, middle panel) and as a result in the excited state (upper panel) the interaction becomes ferromagnetic and more spins change their orientation.

The existing models for non-equilibrium exchange [1] neglect the possibility of laser-induced spin flips due to magnetic dipole transitions or non-local optical transitions associated with the generation of exciton-magnon pairs at the neighboring lattice sites [42]. Here we theoretically discuss how the incorporation of the excited states of the magnetic cation can result in a change of the superexchange interaction under optical pumping. We employ the formalism recently developed in Ref. 43. We consider a rare-earth free case of $FeBO_3$. In its ground state a non-zero value of the spin canting angle $\varphi_0 \approx 0.95^{\circ}$ is observed, which can be explained as a result of Dzyaloshinskii-Moriya interaction [44].

Under optical pumping, the $^4T_2$ triplet excited states with spin $S = \frac{3}{2}$ are populated. The conclusion of the multi-electron approach [43] is that the resonant occupation of some excited states of the Fe^{3+} ions under optical pumping may change the value and even the sign of the superexchange interaction between the excited ion and a neighboring ion in the ground state. For the $^4T_2$ excited term of the Fe^{3+} ion a ferromagnetic (FM) type of exchange has been found [45].

To clarify the physics of the complicated multielectron approach [43] we illustrate the optical modulation of the superexchange interaction in Fig. 4. At equilibrium the superexchange arises from electron hopping between two Fe^{3+} ions in the ground state with S=5/2 via an O^{2-} ion (see the lower part of Fig.4). One spin-up (↑) electron from the left cation virtually hops to oxygen forming a ↑↓ pair and back with the same spin projection. Another oxygen spin-up electron also virtually hops to the right cation to the spin-down (↓) electron and back. Such mechanism favours the antiferromagnetic (AFM) ordering between the neighboring Fe^{3+} ions. After a photoinduced *d-d* transition (upper part of Fig. 4) one of the electrons in the excited ion is antiparallel to the others and the spin of the excited term becomes 3/2. The virtual hopping of the spin-up electron from the left cation in the ground state to oxygen and back is the same as it was before the laser excitation, while for the right excited cation the virtual hopping of the second oxygen spin-down electron and back is possible for the spin-up cation, where four electrons of the excited $^4T_2$ term remain parallel to the spin of the left cation, so their interaction becomes ferromagnetic (FM). We should remark that this picture is just a cartoon of the complicated calculation [43,46] where the effective spin Hamiltonian including both ions in the ground and excited states is obtained by means of a perturbation theory.

Besides the qualitative picture shown in Fig.4, direct calculations [43] lead to an AFM superexchange in the ground state, and to a FM interaction J_{ij}^{ex} for Fe^{3+} ions under optical pumping at A and B absorption lines of a set of A ($^4T_1$), B ($^4T_2$) and C ($^4A_1, {}^4E$) optical *d-d* excitations [45]. The optically induced FM contributions to the superexchange J_{ij}^{ex} dominate due to the largest overlap of *2p* oxygen orbitals with excited $Fe^{3+}\left({}^4T_2\right)$ ions. When excited in the C line, the FM contribution of the interaction J_{ij}^{ex} vanishes due to a sharp drop in the overlapping for the excited $Fe^{3+}\left({}^4A_1, {}^4E\right)$ ions. The AFM state of $FeBO_3$ is maintained at equilibrium at a low concentration of excited ion pairs $Fe^{3+}\left({}^4T_2\right)$-

$\mathrm{Fe}^{3+}\left({}^{6}A_{1}\right)$ with FM exchange. We assume that the optical transition occurs instantaneously, and the lifetime of the excited Fe^{3+} ion exceeds the characteristic time of the change in the superexchange interaction *h/W* ~ 10^{-15} s, where W is the band width.

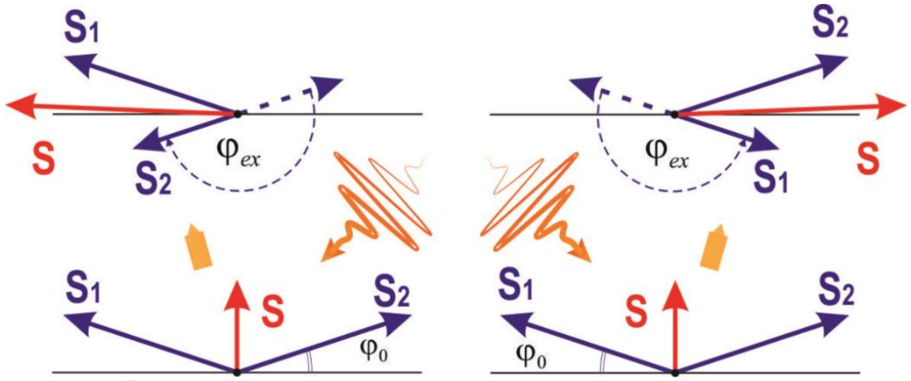

Fig.5 (Color online). Change of the relative orientation of the magnetic moments in an exchange-coupled pair of Fe^{3+} ions due to the sign change of the superexchange interaction from AFM ($J_{ij} < 0$, lower part) to FM ($J_{ij}^{ex} > 0$, upper part) induced by the laser pulse. The lower part shows the relative orientation of the spin moments $\mathbf{S}_1$ and $\mathbf{S}_2$ of the two ions in the ground state. The upper part shows the relative orientation of $\mathbf{S}_1$ and $\mathbf{S}_2$ of the two ions in which one is in the excited state. Left part of the figure corresponds to optical *d-d* transitions in the magnetic sublattice A, where S_1 =5/2, S_2=3/2 and the right part corresponds to *d-d* transitions in the sublattice B, where S_1 =3/2, S_2=5/2.

The spin-orbit interaction appears already in the first order of perturbation theory and results in a small change in the spin-canting angle. However, this last contribution is not important in the model under discussion, because the main effect is the rearrangement of spins of the two AFM sublattices shown in Fig. 5. The lower part of Fig. 5 shows four spins in the ground state, two $\mathbf{S}_1$ from the A sublattice and two $\mathbf{S}_2$ from the B sublattice. The excitation of the A sublattice ion is shown in the left part and that of the B ion in the right part. There are two major effects of the *d-d* excitations that should be taken into account. The first one is the spin change from *S*=5/2 to *S*=3/2, shown by dotted lines in the upper part of Fig. 5. The second effect is the excited spin rotation with the total spin **S** oriented left or right depending on which cation has been excited. It is evident that both sublattices are excited similarly, so the total magnetization is not changed. Nevertheless, the localized *d-d* excitation forms the excited total magnetic moment **S**. Therefore, the spin canting angle φ_{ex} at the optically excited $\mathrm{Fe}^{3+}\left({}^{4}T_{2}\right)$ state is modified as determined by the changed values of the superexchange and spin-orbit interactions:

$$\varphi_{ex} = \left(\pi - \frac{D_{ex}}{J_{ij}^{ex}} \right). \tag{1}$$

These processes are illustrated in Fig. 5. The phase shift $\sim \pi$ arises due to a spin flip at the optically excited $\mathrm{Fe}^{3+}\left({}^4T_2\right)$ center in one of the magnetic sublattices under the action of the optically-induced FM $J_{ij}^{ex} > 0$ superexchange interaction.

The most remarkable result of the optical response in $FeBO_3$ under resonant pumping of the ${}^6A_1 \leftrightarrow {}^4T_2$ transition is the sign change in the superexchange interaction from AFM $J_{ij} < 0$ to FM $J_{ij}^{ex} > 0$. Because the optical absorption in both sublattices of the AFM material is identical, the total magnetic moment under optical pumping is still close to zero and no macroscopic FM ordering arises (Fig. 5). Evidently, in the linear regime the concentration x of optically excited centers is proportional to the intensity of the optical pump, which should not be too large to avoid dielectric breakdown. Using the absorption coefficient of $FeBO_3$ (Fig. 1), the size of its unit cell [47], the pump fluence and the excitation volume, we may estimate that in our experiment $x \leq 10^{-3}$. This number is in line with our estimation of the modulation of the ratio $D/J \geq 10^{-4}$ [29].

In summary, we have shown that optical control of the exchange interaction in iron oxides can be achieved by resonant excitation of the *d*-*d* crystal field transitions in magnetic Fe^{3+} ions, involving a spin change ΔS=1. Our finding demonstrates another alternative to the currently used theoretical approaches based on the Hubbard model for the description of ultrafast light-spin interactions. It reveals novel opportunities for resonant optical control of the exchange interaction and thus opens up new perspectives for experimental and theoretical research in the field of ultrafast magnetism.

Acknowledgements

We thank A. Toonen and S. Semin for technical assistance. The work at Radboud University was supported by de Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) and the European Research Council ERC Grant agreement No. 339813 (Exchange). R.V.M. thanks ERC, Grant agreement No 852050 (MAGSHAKE). V.A.G., S.I.P. and S.G.O. are thankful to the Russian Science

Foundation for the financial support under the grant 18-12-00022. The theoretical part of this research was performed by V.A.G., S.I.P. and S.G.O. under the RSF grant 18-12-00022. The contribution of R.V.P. into the experimental part was supported by the RSF grant 16-12-10456.

References

1. J. H. Mentink. Manipulating magnetism by ultrafast control of the exchange interaction. J. Phys.: Cond. Mat. **29**, 453001 (2017).

2. H.-S. Rhie, H. Dürr and W. Eberhardt. Femtosecond electron and spin dynamics in Ni/W(110) films. Phys. Rev. Lett. **90**, 247201 (2003).

3. A. Melnikov, I. Radu, U. Bovensiepen, O. Krupin, K. Starke, E. Matthias and M. Wolf. Coherent optical phonons and parametrically coupled magnons induced by femtosecond laser excitation of the Gd (0001) surface. Phys. Rev. Lett. **91**, 227403 (2003).

4. J. Wang, I. Cotoros, K. Dani, X. Liu, J. Furdyna and D. Chemla. Ultrafast enhancement of ferromagnetism via photoexcited holes in GaMnAs. Phys. Rev. Lett. **98**, 217401 (2007).

5. S. Wall, D. Prabhakaran, A. T. Boothroyd, and A. Cavalleri. Ultrafast coupling between light, coherent lattice vibrations, and the magnetic structure of semicovalent LaMnO$_3$. Phys. Rev. Lett. **103**, 097402 (2009).

6. M. Först, et al. Driving magnetic order in a manganite by ultrafast lattice excitation. Phys. Rev. B **84**, 241104 (2011).

7. R. Carley, et al. Femtosecond laser excitation drives ferromagnetic gadolinium out of magnetic equilibrium. Phys. Rev. Lett. **109**, 057401 (2012).

8. T. Li, et al. Femtosecond switching of magnetism via strongly correlated spin–charge quantum excitations. Nature **496**, 69 (2013).

9. R. R. Subkhangulov, et al. All-optical manipulation and probing of the d-f exchange interaction in EuTe. Sci. Rep. **4**, 4368 (2014).

10. J. H. Mentink and M. Eckstein. Ultrafast quenching of the exchange interaction in a Mott insulator. Phys. Rev. Lett. **113**, 057201 (2014).

11. M. Matsubara, et al. Ultrafast optical tuning of ferromagnetism via the carrier density. Nat. Comm. **6**, 6724 (2015).

12. J. H. Mentink, K. Balzer and M. Eckstein. Ultrafast and reversible control of the exchange interaction in Mott insulators. Nat. Comm. **6**, 6708 (2015).

13. B. Frietsch, et al. Disparate ultrafast dynamics of itinerant and localized magnetic moments in gadolinium metal. Nat. Comm. **6**, 8262 (2015).

14. J. O. Johansson, J.-W. Kim, E. Allwright, D. M. Rogers, N. Robertson and J.-Y. Bigot. Directly probing spin dynamics in a molecular magnet with femtosecond time-resolution. Chem. Sci. **7**, 7061 (2016).

15. S. Eich et al. Band structure evolution during the ultrafast ferromagnetic-paramagnetic phase transition in cobalt. Sci. Adv. **3**, e1602094 (2017)

16. Ph. Tengdin, et al. Critical behavior within 20 fs drives the out-of-equilibrium laser-induced magnetic phase transition in nickel. Sci. Adv. **4**, eaap9744 (2018).

17. S. F. Maehrlein, et al. Dissecting spin-phonon equilibration in ferrimagnetic insulators by ultrafast lattice excitation. Science Advances **4**, eaar5164 (2018).

18. D. Afanasiev, et al. Ultrafast spin dynamics in photodoped spin-orbit Mott insulator Sr$_2$IrO$_4$. Phys. Rev. X **9**, 021020 (2019).

19. A. Ron, et al. Ultrafast enhancement of ferromagnetic spin exchange induced by ligand-to-metal charge transfer. arXiv:1910.06376 (2019).

20. I. Dzyaloshinsky. A thermodynamic theory of “weak” ferromagnetism of antiferromagnetics. J. Phys. Chem. Solids **4**, 241 (1958).

21. I. A. Sergienko and E. Dagotto. Role of the Dzyaloshinskii-Moriya interaction in multiferroic perovskites. Phys. Rev. B **73**, 094434 (2006).

22. U. K. Rößler, A. N. Bogdanov and C. Pfleiderer. Spontaneous skyrmion ground states in magnetic metals. Nature **442**, 797 (2006).

23. C. Dutreix, E. A. Stepanov, and M. I. Katsnelson. Laser-induced topological transitions in phosphorene with inversion symmetry. Phys. Rev. B **93**, 241404(R) (2016).

24. E. A. Stepanov, C. Dutreix, and M. I. Katsnelson. Dynamical and reversible control of topological spin textures. Phys. Rev. Lett. **118**, 157201 (2017).

25. H. Fujita and M. Sato. Ultrafast generation of skyrmionic defects with vortex beams: Printing laser profiles on magnets. Phys. Rev. B **95**, 054421 (2017).

26. D. Yudin, D. R. Gulevich, and M. Titov. Light-induced anisotropic skyrmion and stripe phases in a Rashba ferromagnet. Phys. Rev. Lett. **119**, 147202 (2017).

27. T. H. Kim, P. Grünberg, S. H. Han, and B. K. Cho. Precessional switching of antiferromagnets by electric field induced Dzyaloshinskii-Moriya torque. Phys. Rev. B **97**, 184427 (2018).

28. F. Freimuth, S. Blügel, and Y. Mokrousov. Spin-orbit torques and tunable Dzyaloshinskii-Moriya interaction in Co/Cu/Co trilayers. Phys. Rev. B **98**, 024419 (2018).

29. R. V. Mikhaylovskiy, et al. Ultrafast optical modification of exchange interactions in iron oxides. Nat. Comm. **6**, 8190 (2015).

30. D. L. Wood, J. P. Remeika, and E. D. Kolb. Optical spectra of rare-earth orthoferrites. J. Appl. Phys. **41**, 5315 (1970).

31. A. M. Kalashnikova, V. V. Pavlov, R. V. Pisarev, L. N. Bezmaternykh, M. Bayer, Th. Rasing. Linear and nonlinear optical spectroscopy of gadolinium iron borate $GdFe_3(BO_3)_4$. JETP Letters **80**, 293 (2004)

32. R. V. Pisarev, A. S. Moskvin, A. M. Kalashnikova, and Th. Rasing. Charge transfer transitions in multiferroic $BiFeO_3$ and related ferrite insulators. Phys. Rev. B **79**, 235128 (2009).

33. H. B. Zhao, et al. Coherent spin precession via photoinduced antiferromagnetic interactions in $La_{0.67}Ca_{0.33}MnO_3$. Phys. Rev. Lett. **107**, 207205 (2011).

34. X. Ma, et al. Ultrafast spin exchange-coupling torque via photo-excited charge-transfer processes. Nat. Comm. **6**, 8800 (2015).

35. Z. Zheng, et al. Ultrafast modulation of exchange-coupling induced anisotropy in Fe/CoO by laser induced charge transfer. Appl. Phys. Lett. **110**, 172401 (2017).

36. R. Iida, et al. Spectral dependence of photoinduced spin precession in $DyFeO_3$. Phys. Rev. B **84**, 064402 (2011).

37. D. Talbayev, et al. Spin-dependent polaron formation dynamics in $Eu_{0.75}Y_{0.25}MnO_3$ probed by femtosecond pump-probe spectroscopy. Phys. Rev. B **91**, 064420 (2015).

38. Y. M. Sheu, Y. M. Chang, C. P. Chang, Y. H. Li, K. R. Babu, G. Y. Guo, T. Kurumaji, and Y. Tokura. Picosecond creation of switchable optomagnets from a polar antiferromagnet with giant photoinduced Kerr rotations. Phys. Rev. X **9**, 031038 (2019).

39. G. Gallot and Grischkowsky. Electro-optic detection of terahertz radiation. J. Opt. Soc. Am. B **16**, 1204 (1999).
40. R. V. Mikhaylovskiy, et al. Terahertz magnetization dynamics induced by femtosecond resonant pumping of Dy^{3+} subsystem in the multisublattice antiferromagnet $DyFeO_3$. Phys. Rev. B **92**, 094437 (2015).
41. T. J. Huisman, R. V. Mikhaylovskiy, A. Tsukamoto, Th. Rasing, A. V. Kimel. Simultaneous measurements of terahertz emission and magneto-optical Kerr effect for resolving ultrafast laser-induced demagnetization dynamics. Phys. Rev. B **92**, 104419 (2015).
42. V. V. Eremenko, N.F. Kharchenko, Y.G. Litvinenko, V.M. Naumenko, in book: Magneto-Optics and Spectroscopy of Antiferromagnets, Springer-Verlag New York, X, 276 p., 1992.
43. V. A. Gavrichkov, S. I. Polukeev, and S. G. Ovchinnikov. Contribution from optically excited many-electron states to the superexchange interaction in Mott-Hubbard insulators. Phys. Rev. B **95**, 144424 (2017).
44. S. G. Ovchinnikov and V V Rudenko. Anisotropic interactions in magnetic crystals with S-state ions. Nanostructures. Physics-Uspekhi, **57**, 1180 (2014).
45. See Supplementary file.
46. V. A. Gavrichkov, S. I. Polukeev, and S. G. Ovchinnikov. Cation spin and superexchange interaction in oxide materials below and above spin crossover under high pressure. Phys. Rev. B **101**, 094409 (2020).
47. R.Diehl. Crystal structure refinement of ferric borate, $FeBO_3$. Solid State Communications **17**, 743 (1975).