Strong magneto-optical effects in $ACr_2O_4$ $A$=$Fe$, Co spinel oxides generated by tetrahedrally coordinated transition metal ions

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Magneto-optical effects have been investigated over the infrared–visible spectral range in $ACr_2O_4$ ($A$ = Fe, Co) spinel oxides with non-collinear spin orders in their ground states. We found large magneto-optical Kerr rotation and ellipticity at the on-site $d$-$d$ transitions of the $A^{2+}$ ions located within the charge gap. The magneto-optical Kerr rotation of $\vartheta_{Kerr} \approx 12$ deg observed in $CoCr_2O_4$ is unprecedentedly large among magnetic semiconductors and points towards the uniqueness of tetrahedrally coordinated $Co^{2+}$ ions in generating strong magneto-optical response. Criteria of strong magneto-optical effects emerging at on-site $d$-$d$ transitions of transition metal ions are discussed.

I. INTRODUCTION

Optical rotators and isolators, produced from materials with strong Faraday effect, are important building blocks of optical fiber networks. The Faraday effect, that is the polarization rotation of light traveling through a magnetic media, is induced by the magneto-circular birefringence. The magneto-optical Kerr effect (MOKE), another manifestation of the magneto-circular birefringence and dichroism, is the polarization change upon the reflection of light from the surface of magnetic materials.$^{12}$

The MOKE provides a figure of merit for the magnetic control of light polarization due to the simplicity and small requirements towards the optical elements utilizing this phenomenon.

Principal material parameters governing the magnitude of the magneto-optical effects are the spin polarization of the photo-excited states and the strength of the spin-orbit coupling (SOI) acting on these states. In itinerant magnets, the MOKE can be enhanced in the vicinity of the plasma resonance, reaching magneto-optical Kerr rotation as large as $\vartheta_{Kerr} \approx 90$ deg found in CeSb.$^{3,4}$ In such cases the large MOKE effects usually arise from moderate values of the off-diagonal conductivity, which are highly enhanced by the strong dispersion of the reflectivity in the plasma-edge region and the magnetic field induced shift of the plasma edge.$^{3,4}$ In insulating magnets, strong magneto-optical effects have been observed in resonance with on-site $d$-$d$ or $f$-$f$ optical excitations of magnetic ions.$^{2,14}$ Fortunately to itinerant magnets, here the enhanced MOKE is mainly attributed to the strong spin-orbit coupling as the optical resonances are located in the optical gap. Recently, chromium spinon oxides and chalcogenides exhibiting large magneto-capacitance,$^{12,16}$ magneto-optical$^{10,17}$ and magneto-elastic$^{2,18}$ effects have attracted much interest.

At room temperature, FeCr$_2$O$_4$ and CoCr$_2$O$_4$ have the normal cubic spinel structure belonging to the $Fd$

$\bar{3}m$ space group.$^{19,21}$ The structural unit cell of $ACr_2O_4$ spinels contains two $A^{2+}$ ions, which constitute a diamond sublattice with tetrahedral oxygen coordination, while the $Cr^{3+}$ ions form a pyrochlore lattice. Due to the orbital degeneracy of Fe$^{2+}$ ions in the cubic spinel structure, FeCr$_2$O$_4$ undergoes a cooperative Jahn-Teller distortion at $T_{JT}=135$ K.$^{4,18,21,22}$ which reduces the crystal symmetry to tetragonal with the $I4_1/amd$ space group.$^{21}$ In contrast, in CoCr$_2$O$_4$ with no orbital degree of freedom, no measurable distortion of the cubic structure has been detected down to $T=10$ K.$^4,18$

At low temperatures both spinel oxides show non-collinear ferrimagnetic order.$^{11}$ According to neutron scattering measurements on CoCr$_2$O$_4$, the ferrimagnetic structure arising below $T_C \approx 93$ K is followed by an incommensurate transverse conical spin re-ordering on both the Co and Cr sublattices at $T_S=20$ K, which becomes commensurate at $T_{lock-in}=13$ K.$^{22}$ Below its ferrimagnetic ordering at $T_C \approx 70$ K, FeCr$_2$O$_4$ was also reported to develop a conical spin order at $T_S=35$ K.$^{22}$ Although the details of this magnetic structure have not been investigated yet. In FeCr$_2$O$_4$, the ferrimagnetic transition is accompanied by further reduction of the symmetry to orthorhombic due to magneto-elastic effects.$^{2,18,22}$

In this work, we study the MOKE in CoCr$_2$O$_4$ and FeCr$_2$O$_4$ and report large magneto-optical Kerr rotation emerging at the on-site $d$-$d$ transitions of the tetrahedrally coordinated magnetic $A^{2+}$ ions. To the best of our knowledge, the magneto-optical Kerr rotation of $\vartheta_{Kerr} \approx 12$ deg observed in CoCr$_2$O$_4$ for photon energies close to 0.78 eV (close to be 1.55 $\mu$m widely used in telecommunication) is the highest ever observed in magnetic semiconductors and insulators.
II. EXPERIMENTAL DETAILS

Single crystals of CoCr$_2$O$_4$ used in the present study were grown by the chemical vapour transport method as presented in Ref. 14. FeCr$_2$O$_4$ single crystals were obtained by the floating zone technique. FeO and Cr$_2$O$_3$ were mixed and sintered in argon atmosphere for 12 h at 1200°C temperature, then after regrinding, the resultant was pressed in rod shape and further heated in Ar+1%H$_2$ atmosphere for 12 h at 1300°C. Single crystals of FeCr$_2$O$_4$ were formed in Ar+0.1%H$_2$ atmosphere at pressure of 2 atm in a halogen-incandescent lamp floating zone furnace (SC-N35HD, NEC).

Temperature dependent reflectivity spectra were measured and diagonal component of the optical conductivity was calculated via Kramers-Kronig transformation as reported in a previous study. The complex Kerr rotation, $\Phi_{\text{Kerr}}$, was measured at nearly normal incidence on the (001) surface of the crystals by a broadband dual-channel magneto-optical spectrometer as described in earlier papers. Magnetic fields of $\mu_0 H = \pm 0.3$ T were applied along the propagation vector of the incident light by permanent magnets ensuring the polar MOKE geometry. The off-diagonal component of the optical conductivity $\sigma_{xy}$ was evaluated using the diagonal optical conductivity $\sigma_{xx}$ and the complex Kerr rotation, i.e. the Kerr rotation $\vartheta_{\text{Kerr}}$ and the Kerr ellipticity $\eta_{\text{Kerr}}$, according to the relation: 3 28

$$\Phi_{\text{Kerr}} = \vartheta_{\text{Kerr}} + i \eta_{\text{Kerr}} = \frac{\sigma_{xy}}{\sigma_{xx} \sqrt{1 + \frac{i \sigma_{xy}}{\omega}}} \quad (1)$$

Temperature dependent magnetization was measured with a SQUID magnetometer (MPMS-5S, Quantum Design) in $\mu_0 H = 0.3$ T, in accord with the MOKE experiments.

III. RESULTS AND DISCUSSION

A. Magneto-optical Kerr rotation spectra

The temperature dependence of the complex Kerr rotation spectra of CoCr$_2$O$_4$ and FeCr$_2$O$_4$ in the near infrared–visible region are respectively shown in Figs. 1 and 2. In the ferrimagnetic state of the materials, strong MOKE is found in the energy range of the $d$-$d$ excitations of the magnetic $A^{2+}$ ions. The assignment and the fine structure of the transitions are reproduced from Refs. 29 and 10 in the inset of the figures. In the ferrimagnetic phase, strong and sharp peaks emerge in the Kerr rotation spectra at the low-energy sides of each $d$-$d$ transitions of both materials. The low-energy side peak of the Co$^{2+}$ ions located at about 0.78 eV, reaches the value of $\vartheta_{\text{Kerr}} = 12$ deg at $T = 10$ K. This excitation exhibits a similarly strong ellipticity signal with a dispersive line shape. For further analysis of the spectral features off-diagonal optical conductivity spectra were calculated according to Eq. 1.

B. Diagonal and off-diagonal optical conductivity spectra

Figures 3 and 4 show the off-diagonal optical conductivity spectra along with the real part of the diagonal optical conductivity for CoCr$_2$O$_4$ and FeCr$_2$O$_4$, respectively. The diagonal optical conductivity spectrum sums up the contributions from transitions excited by right and left ($\Delta J_z = \pm 1$) circularly polarized photons as well as non circular contributions ($\Delta J_z = 0$). In contrast, the off-diagonal optical conductivity corresponds to the difference between the contributions coming from left and right circularly polarized photons, hence it can have both positive or negative signs.

The temperature dependence of the off-diagonal optical conductivity has similar evolution for both compounds. Below $T_C$ magnitude of the signal gradually increases with decreasing temperature and saturates at about 30 K roughly following the temperature dependence of the magnetization. 10 24 30 Lifetime of the excited states also increases towards lower temperatures as clearly manifested in the decrease of the line widths in both the diagonal and off-diagonal conductivity spectra. In CoCr$_2$O$_4$, there are two bands of excitations centered around 0.8 eV and 2 eV, which are assigned respectively to the $e^4t_2^3$ $4A_2 \rightarrow e^4t_2^3$ $4T_2$ and $e^4t_2^3$ $4A_2 \rightarrow e^4t_2^3$ $4T_1$ on-site electronic transitions of the Co$^{2+}$ ions with tetrahedral coordination. Here we note, that although the low energy $4A_2 \rightarrow 4T_2$ transition is electric-dipole forbidden (as $A_2 \otimes T_2 = T_1$ does not contain the $T_2$ irreducible representation, which is connected to the electric dipole allowed transitions), the spin-orbit coupling eventually turns it electric-dipole allowed. This is owing to the fact that the SOI splits both the $4T_1$ and $4T_2$ multiplets to the same electronic states. As a further demonstration, the spectral weight in the diagonal spectra ($\omega_0 \int \omega \sigma_{xx}(\omega) d\omega$), of the $4A_2 \rightarrow 4T_2$ transition allowed by SOI is smaller by a factor of 5 than that of the $4A_2 \rightarrow 4T_1$ band. Besides their different magnitudes, there is a sign difference between the off-diagonal conductivity of the two $d$-$d$ bands as it has been predicted for the irreducible representations of the different excited ($4T_1$ and $4T_2$) states in the framework of the crystal field theory. 29

In FeCr$_2$O$_4$, similarly to FeCr$_2$S$_4$, there is a single branch of excitation is centered at about 0.4 eV 17. This
excitation has been assigned to the $e^{3t_2^3}5E \rightarrow e^{2t_2^4}5T_2$ transitions of the tetrahedrally coordinated Fe$^{2+}$ ions.

C. Temperature dependence of the magneto-optical effect

Figure 5 shows the strength of the magneto-optical effect in FeCr$_2$O$_4$ and CoCr$_2$O$_4$ as a function of temperature, represented by integrals of the real and imaginary parts of the optical conductivity spectra over the spectral window of our study. Since the off-diagonal conductivity changes sign throughout the spectral range, the absolute value of its real and imaginary parts were integrated ($\int |\sigma_{xy}(E)| dE$) as an overall measure of the magneto-optical effect in the two compounds. For comparison, the temperature dependence of the magnetization is also plotted in the two cases. The magneto-optical effect emerges below the magnetic ordering temperature and it roughly grows as the magnetization, though considerable deviations between them are discerned well below $T_C$. This may come from the fact that the magneto-optical signal in our case specifically probes one component of the local magnetization of the Co or Fe ions, while the overall magnetization has contributions from the Cr ions as well. The non-monotonous behavior of the magnetization implies different temperature dependences of the $A$ and $Cr$ sublattice magnetizations. On the other hand the magneto-optical signal, which measures the sublattice magnetization of the $A$ ions, monotonously increases.
D. Fine structure of the d-d transitions

We turn to the discussion of the fine structure describing both the diagonal and off-diagonal optical conductivity spectra in comparison with the results reported for on compounds substitutionally doped with Co$^{2+}$ or Fe$^{2+}$ in tetrahedral or octahedral sites. In general, there are sharp, distinct features emerging at the low-energy sides of each bands, with significant temperature dependence. This sharp and well separated feature is the most prominent for the low-energy side of the $T_2$ multiplet of CoCr$_2$O$_4$ as well discerned in the temperature dependence of both $\sigma_{zz}$ and $\sigma_{xy}$ in Fig. 4. At the higher-energy side of these multiplets there are additional transitions with much larger line width and less significant temperature dependence. Usually, the parallel analysis of the diagonal and off-diagonal spectra supports an unambiguous assignment of optical excitations. While the diagonal spectra contains the sum of all transitions, namely $\Delta J_z = 0$ and $\Delta J_z \pm 1$ transitions the off-diagonal contains only the $\Delta J_z = \pm 1$ transitions with different signs. However, the fine structure of the d-d bands due to strong overlap between these broad transitions do not allow precise assignment of the excitations.

Width of the d-d bands are $\delta E \approx 0.3$ eV and $\delta E \approx 0.5$ eV for the $^4A_2 \rightarrow ^5T_2$ and $^4A_2 \rightarrow ^4T_1$ transitions of the Co$^{2+}$ ion, respectively, while $\delta E \approx 0.4$ eV for the $^5E \rightarrow ^5T_2$ transitions of the Fe$^{2+}$ ion. On the other hand, bandwidths reported for the d-d transitions of Co$^{2+}$ and Fe$^{2+}$ ions in general are in the range of $\delta E \approx 0.1-0.3$ eV. The observed large bandwidths cannot be explained exclusively by the effect of first-order spin-orbit coupling, since the free ion spin-orbit interaction parameters are only $\zeta_0=410$ cm$^{-1}$ $\approx 50$ meV for the $^5T_2$ multiplet of Fe$^{2+}$ and $\zeta_0=533$ cm$^{-1}$ $\approx 70$ meV for both the $^4T_2$ and $^4T_1$ multiplets of Co$^{2+}$. Moreover, strength of the SOI should be further reduced in crystals due to hybridization with the ligand orbitals. The hypothesis of the $d-d$ bands, which correspond to the free-ion spin-orbit interaction parameters, are indicated in Figs. 6 and 7 by the highlighted yellow regions.

In dilute systems with few tetrahedrally coordinated $A^{2+}$ ions, the increased bandwidth is explained by two main factors: i) the second order spin-orbit interaction, which slightly further splits the orbital degeneracy of the $d$ states and ii) the emergence of phonon sidebands at the high-energy side of the zero phonon $d-d$ multiplets due to the dynamic Jahn-Teller effect. The dynamic Jahn-Teller effect is an interplay between the purely orbital excitations of an ion (zero-phonon line, ZPL) and the vibrational modes of the surrounding lattice. Due to the hybridization of these excitations, part of the spectral weight is transferred from the ZPL to the phonon sidebands (see Fig. 8). In most dilute systems, multiplets of the $A^{2+}$ ion are mostly coupled to phonon modes with one dimensional representation (typically to the $A_1$ breathing mode of the ligand cage). The normalized intensity of the $n$-th sideband is well described by a Poisson distribution:

$$I_n = e^{-S} \frac{S^n}{n!},$$

where $S = \frac{E_R}{\hbar \omega}$ is the strength of the electron-phonon coupling, $E_R$ is the energy shift of the highest intensity side band, $\hbar \omega$ is the energy of the coupled phonon mode and $I_0 = e^{-S}$ is the intensity of the ZPL. The expectation number of the phonons coupled to the electronic excitation equals to the strength of the coupling ($S = \langle n \rangle$). Therefore, in dilute systems, the local vibrations of the ligands surrounding the $A^{2+}$ ions give sharp phonon sidebands to the optical spectra, which is schematically illustrated in Fig. 8(b).

In high-symmetry crystals with a regular network of $A^{2+}$ ions where several different phonons with higher
FIG. 3. (Color online) Diagonal (a,b) and the complex off-diagonal (b-f) optical conductivity spectra at various temperatures of the two transitions of CoCr$_2$O$_4$. Regions of the electronic states approximated by the free-ion spin-orbit splitting for the $^4$T$_2$ and $^4$T$_1$ multiplets are indicated by the coloured stripes around 0.8 eV and 1.9 eV, respectively. Blue and red arrows indicate the possible arrangement of the SOI and Zeemann split ZPLs for the $^4$T$_2$ multiplet.

dimensional representation may couple to the electronic excitations. In this case Eq. (2) is expanded to multi-dimensional form and the phonon sidebands are widened\[48–51\], which is illustrated in Fig. 3(c). Here we note that the intensity of the ZPL highly depends on the $S$ coupling constant. For $S = 1$ the ZPL is the strongest and the phonon sidebands are evanescent, while for large coupling the ZPL is negligible and the phonon sidebands dominate the spectrum.

Strength of the electron-phonon coupling in spinel compounds can be estimated by determining $E_R$ and $\hbar \omega$ separately. $E_R \approx 0.15$ eV is well approximated by the width of the multiplets ($2E_R = \delta E \approx 0.3$ eV), which is in general appropriate for both oxide and chalcogenide spinels.\[10\] Phonon energy of the coupled modes can be estimated by the highest energy optical phonon mode, as it is mainly composed of lattice vibrations of the lighter ligand nuclei. Therefore, for oxide spinels the highest energy optical phonon modes ($\hbar \omega \approx 74$ meV) brings a relatively small coupling constant ($S=2$).\[18\] On the other hand, in sulfur and selenium based spinels the ligands are heavier ($\hbar \omega \approx 49$ meV and $\hbar \omega \approx 37$ meV, respectively\[52\]) and the electron-phonon couplings are also higher, $S=3$ and $S=4$, respectively. In sulfide and selenide spinels the expansive 3$p$ and 4$p$ orbitals of the ligand ions have stronger hybridization with the 3$d$ orbitals of the $A^{2+}$ transition metal ions, thus the stronger electron-phonon coupling is expected, in accord with the observations.
states of the free-ion spin-orbit split multiplet is indicated by the coloured stripes. Arrows within the region marks the possible assignment for SOI-split ZPL transitions, the outside region corresponds to the phonon sidebands.

E. Criteria of strong magneto-optical effects

Based on our experimental results, we list the criteria of strong magneto-optical effects at on-site d-d transitions of transition metal ions in magnetic crystals. Besides the well-known criteria (i)-(v), we add two empirical, and material specific ones:

(i) To make the on-site d-d transitions electric-dipole allowed, the inversion symmetry at the transition metal sites needs to be broken, e.g. by the tetrahedral coordination of the sites.

(ii) Since spin forbidden transitions are usually weak, the on-site d-d transitions have to be spin allowed as well. This excludes the ions with half-filled d shell carrying spin S=5/2.

(iii) The material has to be a semiconductor with sufficiently large gap so that the d-d transitions lie within the optical band gap.

(iv) Strong spin-orbit interaction is needed to split the degeneracy of the d orbitals within the crystal-field multiplets (e and t_2 states in spinels with cubic symmetry).

(v) The material has to be either a ferro- or ferrimagnet, where the magnetic exchange interaction removes the degeneracy of the states with different J_z values.

(vi) Among the SOI-split multiplets of the excited states, there should be only one with higher spin degeneracy than the ground state. In this case, sum of the oscillator strengths of the remaining transitions to the |J_z|-1 excited states will have the same...
FIG. 6. (Color online) (a) Schematic illustration of the hybrid electron-lattice excitations in the presence of electron-phonon coupling. Transitions are allowed from the ground state to the phonon side bands of the excited multiplet, which increases the spectral width of the transition. (b–e) Illustration of the absorption spectra for different models: (b) Dilute systems have spiky coupling. Transitions are allowed from the ground state to the phonon side bands of the excited multiplet, which increases the oscillator strength is transferred to the phonon side-bands. In oxide spinels the $\hbar\omega$ phonon energy is larger and the $S$ coupling parameter (Eq. (2)) is smaller as compared to chalcogenide spinels. Therefore, in the former case, shown in panel (d), the ZPL is less overlapped by the phonon sidebands while in the second case, sketched in panel (e), the phonon sidebands are not just more overlapped with the ZPL, but also most of the intensity is transferred to the sidebands.

The ligand ions should be light, so the $\hbar\omega$ is high and the phonon sidebands are well separated from the ZPL. Furthermore, hybridization between the orbitals of the transition metal and the ligand ions should be small. The electron-phonon coupling should be weak, therefore only a small part of the oscillator strength is transferred to the phonon sidebands.

By a systematic analysis of the Tanabe-Sugano diagrams and taking into account the effect of spin-orbit coupling, we found a few transition-metal ions with tetrahedral environment which might have compliance with these conditions. Besides the interesting $e^24^34^12^1$ ground and the $e^24^34^12^2$ excited states combination of $\text{Co}^{2+}$, the $V^{3+}$ ion has similarly favorable electron configuration. Experimental studies on vanadium doped compounds have shown that tetrahedrally coordinated $V^{3+}$ ions usually realize $e^23^1$A$_2$ ground and the $e^24^34^12^2$ excited states, which could be optimal for strong magneto-optical effects. However, $V^{3+}$ ions, similarly to the $\text{Cr}^{3+}$ ions, dominantly occupy octahedral environments when forming regular sublattice in crystals and only enter tetrahedral sites as dopants. Thus, they are unfavored by condition (i). Tetrahedrally coordinated $\text{Mn}^{2+}$ ions carry $S=5/2$ spins, hence, a strong magneto-optical response from these ions is excluded by condition (ii). Optical excitations of $\text{Fe}^{3+}$ ions in tetrahedral coordination do not fulfill condition (iv) as observed in former works as well as in the present study. Tetrahedrally coordinated $\text{Ni}^{2+}$ and $\text{Cu}^{2+}$ ions show orbital degeneracy, which is lifted by the distortion of oxygen tetrahedra upon the cooperative Jahn-Teller transition. In the distorted state, for both ions there is no orbital degeneracy either in the ground or the excited states. Correspondingly, we expect a weak magneto-optical response for these ions. Therefore, the best candidates which can generate strong magneto-optical effects are the tetrahedrally coordinated $\text{Co}^{2+}$ ions.

IV. CONCLUSIONS

We observed strong magneto-optical Kerr effect at the on-site $d$-$d$ transitions of $\text{Co}^{2+}$ and $\text{Fe}^{2+}$ ions in the spinel oxides $\text{CoCr}_2\text{O}_4$ and $\text{FeCr}_2\text{O}_4$. The magneto-optical Kerr rotation $\vartheta_{\text{Kerr}}=12\degree$ observed in $\text{CoCr}_2\text{O}_4$ is the largest reported so far in magnetic semiconductors and insulators. We discussed the criteria of strong magneto-optical effects in insulating transition-metal oxide compounds and the unique potential of the tetrahedrally coordinated $\text{Co}^{2+}$ ions.

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