Huge magneto-optical effects in half-metallic double perovskites

R. Vidya,* P. Ravindran, A. Kjekshus, and H. Fjellvåg

Department of Chemistry, University of Oslo, Box 1033, Blindern, N-0315, Oslo, Norway

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Using generalized-gradient-corrected full-potential density-functional calculations we have studied the magneto-optical properties of double perovskites $A_2BB'O_6$, $A=$Ca, Sr, and Ba; $B=$Fe; and $B'$=Mo, W, and Re. Sr$_2$FeWO$_6$ has the maximum polar Kerr rotation of 3.87° and specific Faraday rotation of 4.5 $\times$ 10$^5$ deg cm$^{-1}$. All other compounds have Kerr rotation more than 1°, except Ca$_2$FeMoO$_6$ which has maximum Kerr rotation of 0.5°. Our electronic structure studies show that all these compounds are half-metallic in the ferromagnetic configuration. The large Kerr rotation is found to be due to the combined effects of relatively large exchange splitting from Fe, large spin-orbit coupling due to 4$d$ or 5$d$ elements, large offdiagonal conductivity, and half-metallicity.

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Materials with large magneto-optical (MO) effects have attracted a lot of attention in both basic and applied research. The motivation stems from desire to develop erasable MO memories and high density disks with MO readout. However, it is still a challenging problem to find a material with large MO rotation and also possessing a collection of necessary magnetic properties.

The interaction of electromagnetic radiation with magnetized matter manifests itself as MO effects. The MO effect due to reflection is called MO Kerr effect (MOKE) and that due to transmission is called MO Faraday effect. Plane-polarized light, when reflected from a metal surface or transmitted through a thin film that has nonzero magnetization will become elliptically polarized with ellipticity ($\epsilon_R$ in reflection mode and $\epsilon_F$ in transmission mode). The major axis is rotated by the angle $\theta$ ($\theta_R$ in reflection mode and $\theta_F$ in transmission mode) relative to the polarization axis of the incident beam. The MOKE is of three major types, polar, longitudinal, and equatorial. The polar Kerr effect for which the direction of the macroscopic magnetization of the ferromagnetic material and the propagation direction of plane polarized incident beam are perpendicular to the plane of the surface, is the most interesting case and used in practical applications. Digital information, which is suitably stored in the surface, is the most interesting case and used in practical applications. Digital information, which is suitably stored in the surface, is the most interesting case and used in practical applications.

Using the ab initio simulation package (VASP), All the studied compounds except SFWO are experimentally found to be ferrimagnetic metals or half-metals with antiparallel spin alignment between Fe and $B'$ moments. SFWO is found to be an antiferromagnetic insulator with $T_N=37$ K. Readers are referred to Refs. 5–10 for a detailed crystal and magnetic structure informations.
The full-potential linear muffin-tin orbital (FPLMTO) calculations presented in this paper are all electron, and no shape approximation to the charge density or potential has been used. The basis set is comprised of augmented linear muffin-tin orbitals. The calculations are based on the generalized-gradient-corrected density-functional theory as proposed by Perdew et al. The SO coupling term is included directly in the Hamiltonian matrix elements for the part inside the muffin-tin spheres, hence for spin-polarized cases the size of the secular matrix is doubled. We used a multibasis in order to ensure a well-converged wave function. As experimental polar Kerr rotation is measured by applying an external magnetic field in order to bring about the perpendicular anisotropy, we calculated the MO spectra in the ferromagnetic configuration. For ferromagnetic calculations, the easy magnetization axis is considered along [001]. For the total-energy study the \(k\)-space integration is done using a minimum of 192 \(k\) points in the irreducible part of first Brillouin zone (IBZ) and for the optical and MO studies a minimum of 420 \(k\) points were used in IBZ, depending on the crystal structure.

Because of the metallic nature, a dominant contribution to the optical tensor comes from intraband transitions in the lower-energy region. The intraband contribution to the diagonal components of the conductivity is normally described by the Drude formula,

\[
\sigma_D(\omega) = \frac{\omega_p^2}{4\pi(\tau - i\omega)},
\]

where \(\omega_p\) is the unscreened plasma frequency and \(\tau\) is the relaxation time which characterizes the scattering of charge carriers, depends on the amount of vacancies and other defects, and therefore varies from sample to sample. Our experience show that if we use \(\tau\) around 0.3 eV we get good agreement with the experimental spectra. So, we have used \(\tau\) as a parameter with the value 0.3 eV for all our calculations. The \(\omega_p\) depends on the concentration of charge carriers. The extraction of Drude parameters from the experimental data requires a free-electronlike region in the optical spectra which does not exist for the compounds studied here. As the experimental determination of Drude parameters is intrinsically difficult, we have chosen an alternative path. We have calculated the spin resolved unscreened plasma frequency by the Drude formula,

\[
\sigma_\text{Drude}(\omega) = \frac{\omega_p^2}{4\pi(\tau - i\omega)}. 
\]

For the total-energy study the \(k\)-points in the first Brillouin zone (IBZ) were used in IBZ, depending on \(m\).

Damping \(\gamma\) and dielectric function \(\varepsilon_\text{Drude}(\omega)\) can be written as

\[
\varepsilon_\text{Drude}(\omega) = 1 + \frac{4\pi\tau}{\omega}(\sigma_{xx} + i\sigma_{xy}).
\]

where \(\sigma_{xx}\) and \(\sigma_{xy}\) are the diagonal and off-diagonal components, respectively, of the conductivity tensor. In terms of conductivities they are given as

\[
\sigma_{xx} = \frac{\omega_p^2}{4\pi(\tau - i\omega)}, \quad \sigma_{xy} = \frac{\omega_p^2}{4\pi(\tau - i\omega)}.
\]

A detailed description of optical and MO calculation is given in Refs. 15 and 16.

The ferromagnetic calculations of all the compounds converge to be ferrimagnetic, viz., the magnetic moments of Fe and B' are antiparallel to each other. The magnetic moment of Fe is found to be around 3.5 \(\mu_B\) with prominent densities from 4 to 8 eV. Below \(E_g\) for Sr2Fe2O6, \(E_g\) is 0.59, 1.36, and 0.56 eV, respectively. The site-projected density of states for the above-mentioned compounds is shown in Fig. 1. In all the three compounds Sr is completely ionized, hence electrons are in the conduction band from 4 to 8 eV. Below \(E_F\), the major-spin channel is mainly occupied by Fe 3d orbitals and O 2p orbitals. In particular, Fe \(e_g\) orbitals are closer to \(E_F\) (from \(-2\) to 0 eV) and Fe \(t_{2g}\) orbitals are present from \(-8\) to \(-2\) eV with prominent densities from \(-4\) to \(-2\) eV. The \(B'\) orbitals are antibonding in the majority-spin channel with \(t_{2g}\) orbitals above \(E_F\) (from 0.25 to 2 eV) and \(e_g\) orbitals are higher-lying (from 4 to 7 eV). The W antibonding \(t_{2g}\) orbitals in SFWO are present between 1–2 eV, making its \(E_g\) larger.
TABLE I. Magnitude of energy gap ($E_g$) in majority-spin channel, maximum Kerr rotation $\theta_{K\text{max}}$, maximum specific Faraday rotation $\theta_{F\text{max}}$, and maximum figure of merit (FOM; in Kerr configuration) for $A_2FeB'O_6$ (where $A=$Ca, Sr, and Ba; $B'=\text{Mo, W, and Re}$). The values in the parenthesis indicate the energy (in eV) at which the maximum occurs.

| Composition       | $E_g$ (eV) | $|\theta_{K\text{max}}|$ (deg) | $|\theta_{F\text{max}}|$ (10$^4$ deg cm$^{-1}$) | FOM (deg) |
|-------------------|-----------|-------------------------------|---------------------------------|----------|
| Ca$_2$FeMoO$_6$   | 1.02      | 0.50 (1.25)                   | 1.73 (3.20)                     | 0.23 (2.06) |
| Ca$_2$FeWO$_6$    | 1.09      | 1.32 (1.89)                   | 2.28 (1.00)                     | 0.50 (1.90) |
| Ca$_2$FeReO$_6$   | 0.19      | 1.04 (1.43)                   | 3.15 (2.48)                     | 0.62 (1.10) |
| Sr$_2$FeMoO$_6$   | 0.59      | 1.21 (1.96)                   | 1.04 (1.91)                     | 0.44 (1.92) |
| Sr$_2$FeWO$_6$    | 1.36      | 3.87 (1.55)                   | 4.50 (1.48)                     | 1.63 (1.50) |
| Sr$_2$FeReO$_6$   | 0.56      | 1.84 (1.72)                   | 3.67 (4.83)                     | 0.90 (1.80) |
| Ba$_2$FeMoO$_6$   | 0.93      | 1.46 (0.87)                   | 2.05 (3.25)                     | 0.62 (1.60) |
| Ba$_2$FeWO$_6$    | 1.80      | 1.70 (2.83)                   | 4.43 (3.15)                     | 0.69 (2.60) |
| Ba$_2$FeReO$_6$   | 0.53      | 1.51 (1.54)                   | 3.10 (2.90)                     | 0.65 (1.54) |

The calculated Kerr spectra are compared with the available experimental spectra for $A_2FeMoO_6$ (where $A=$Ca, Sr, and Ba). The magnitude of the calculated Kerr rotation peaks for CFMO and SFMO agrees very well with that of experiment (at 101 K), but for BFMO theoretical calculations overestimate the magnitude. The position of theoretical MOKE peaks are somewhat shifted in relation to the experimental ones. In general, the peaks of calculated optical conductivities and polar Kerr spectra are displaced toward higher energies with respect to experimental spectra. This may be due to the fact that DFT overestimates the $3d$-band width which in turn affects the optical and MO spectra peaks to shift toward higher energy. This can be artificially corrected by increasing lattice parameters which gives narrower bands or

FIG. 1. Site-projected density of states for Sr$_2$FeB'O$_6$ where $B'=\text{Mo, W, and Re}$.

FIG. 2. Polar Kerr rotation ($\theta_k$) and Kerr ellipticity ($\epsilon_k$) spectra for Ca$_2$FeB'O$_6$ where $B'=\text{Mo, W, and Re}$. Experimental data for CFMO are from Ref. 17.

compared to the other two compounds, whereas the Re $t_{2g}$ orbitals are just above $E_F$ (from 0.25 to 1.4 eV). In both spin channels O $2p$ orbitals are present from −8 to −2 eV. The $B' d$ orbitals are well hybridized with O $2p$ orbitals so that the bonding states are well-localized (from −8 to −6 eV) and antibonding states are above $E_F$. The states present at $E_F$ in the minority-spin channel is due to the hybridized Fe and $B' t_{2g}$ orbitals. A more detailed analysis of magnetic and electronic properties will be given elsewhere.21
by performing GW-corrected calculations of MO spectra. However, it has to be mentioned that the experimental peak positions are sample-dependent\footnote{see for example the Pt-MnSb case in Ref. 24} and appear to depend on stoichiometry, homogeneity, impurities, etc., whereas the magnitude depends on sample preparation, annealing, etc. One month after polishing samples exhibit a marked aging effect compared to the sample just after polishing.\footnote{Expt. 1} The magnitude is enhanced by a factor of 1.5 and the center (or zero-crossing) shifts toward the longer wavelength side.\footnote{Expt. 2} Moreover, we can see that the experimental Kerr rotation peaks for $A_2FeMoO_6$ are almost doubled at 101 K compared to that at room temperature. It has to be mentioned that we have calculated the MO properties for single crystals at low temperature and hence it is more appropriate to compare our results with the experimental spectra measured at low temperatures for single crystals.

In an attempt to understand the reason for huge MO effects on the studied compounds, we show reflectivity and conductivity spectra for $A_2FeB'O_6$ where $B'=$Mo, W, and Re. Experimental data for SFMO are taken from Ref. 17 (Expt. 1) and Ref. 22 (Expt. 2).

It is remarkable that the real part of diagonal conductivity of SFMO is in reasonable agreement with the available experimental spectra.

**FIG. 3.** Polar Kerr rotation ($\theta_K$) and Kerr ellipticity ($\varepsilon_K$) spectra for $Sr_2FeB'O_6$ where $B'$=Mo, W, and Re. Experimental data for SFMO are taken from Ref. 17 (Expt. 1) and Ref. 22 (Expt. 2).

**FIG. 4.** Polar Kerr rotation ($\theta_K$) and Kerr ellipticity ($\varepsilon_K$) spectra for $Ba_2FeB'O_6$ where $B'$=Mo, W, and Re. Experimental data for BFMO is taken from Ref. 17.

The amplitude of reflectivity for the sample just after polishing is more than two times larger than that of the sample one month after polishing (as seen in the experimental spectra for SFMO in Fig. 5). A dip in the reflectivity spectra in the lower energy region (around 1.7 eV) has been experimentally interpreted as due to the plasma resonance of conduction electrons in the crystal since the diagonal and offdiagonal elements of the dielectric tensor is expected to exhibit an anomaly near the plasma edge.\footnote{Expt. 3} Therefore both reflectivity and Kerr spectra are affected by this. In order to check whether the dip around 1.7 eV is really due to plasma resonance, we have also calculated the electron energy loss spectrum (EELS). The function representing characteristic energy losses (or plasmon oscillations) is proportional to the probability that a fast electron moving across a medium loses energy per unit length. Generally speaking, plasma resonances manifest themselves as rather distinct peaks in the EELS,\footnote{Expt. 4} and are thus a feature easily observed experimentally. The EELS for SFMO, SFWO, and SFRO show prominent peaks at 1.62, 1.49, and 1.14 eV, respectively. The reflectivity spectra of SFWO and SFRO also show a dip at 1.3 and 1.6 eV, respectively. Hence, the dip observed in these compounds is due to the plasma resonance. However, no experimental reflectivity spectra are available for SFWO and SFRO to compare our theoretical spectra with. As Kerr spectra show peaks for all these compounds in the energy region 1–2 eV, plasma resonance also plays an important role in the $\theta_{K\text{max}}$ values (Fig. 5).

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the Kerr rotation can be enhanced by a larger off-diagonal
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FIG. 5. Reflectivity and conductivity spectra for Sr₂FeB'O₆
where B' =Mo W, and Re. Experimental data for SFMO are taken
from Ref. 27 (Expt. 1), Ref. 28, (Expt. 2), Ref. 18 (Expt. 3), and
Ref. 29 (Expt. 4).

except that the amplitude of theoretical spectra is higher than
that of experimental spectrum in the lower energy region. As
experimental spectra are derived through Kramers-Kronig
transformation of reflectivity spectra, there is slight discrep-
ancy. The Drude component is involved in the theoretical
conductivities, which will enhance the amplitude in the
lower energy region. Around 0.5 eV, a small bump is ob-
erved which is due to Fe ε₂ to Mo τ₂g transition. The peak at
4 eV observed by experiments is shifted to 3 eV, instead a
small bump is seen at 4 eV. This peak is attributed to the
O 2p to hybridized τ₂g of Fe and Mo. In the case of SFWO,
two prominent peaks occur around 4 and 4.5 eV. The first
peak is due to O 2p to Fe τ₂g transition and the second peak
is due to O 2p to W τ₂g transition. Around five peak struc-
tures appear for SFRO. An experimental study 30 is available
for this compound up to 0.8 eV. However, no prominent
structure exists within that narrow energy region to be com-
pared with our theoretical spectrum. The lower energy peaks
at 0.6 and 0.8 eV can be attributed to the interband (Fe ε₂ to
Re τ₂g) transition. The peaks at 2 and 3.25 eV are due to
O 2p to Fe and Re hybridized τ₂g transition. The peak around
4 eV is due to O 2p to τ₂g transition. From the figure it can be
seen that the overall topology of the diagonal conductivity
for the three compounds is somewhat similar. As experimen-
talists often display ωσₓ, instead of σₓ, we also show ωσₓ in the
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The Kerr rotation peaks of all the studied compounds lie
in the energy region of infrared to visible radiation. An in-
tense search is going on for materials with MO peaks in the
lower wavelength region for use in high-density storage. 1
Among the studied compounds CFRO (−0.89° at 2.47 eV),
SFRO (−1.5° at 2.3 eV), BFWO (−1.70° at 2.83 eV), and
BFRO (−0.86° at 2.83 eV) have large peaks in the green-
violet energy region. It has to be noted that a large polar Kerr
rotation, typically greater than about 0.2° is clearly of benefit
in reading information stored in a thermo-MO thin film.1 The
strong SO coupling results in a large uniaxial anisotropy
which is one of the essential requirements for a MO storage
device. The magnitude of the uniaxial anisotropy depends on
structural anisotropy and hence noncubic systems usually
possess large magnetic anisotropy. Moreover flexibility to
substitute or dope A, B or B' elements will be useful to tune
the MO properties according to the need. In that perspective
the present compounds may be of relevance for high-density
storage applications.

In a transmission mode, large Faraday rotation is desirable
for applications. 32 Materials with large Faraday rotation are

onal conductivity of all three compounds shows a minimum
around 1.5–2 eV where maximum of θK is observed. The
off-diagonal conductivity of SFWO and SFRO show higher
values than that of SFMO, implying that the high Kerr rota-
tion of these compounds also result from high off-diagonal
conductivity. The influence of intraband effects on the
MOKE is restricted to energies smaller than 1–2 eV.

The MOKE signal is proportional to f · M, where f is
determined by the complex refractive index at the probe fre-
frequency and M is the magnetization. 22 The refractive index
of SFMO, SFWO, and SFRO in the energy region 1–2 eV
(where θKmax occurs) is 1.56, 1.88, and 1.98, respectively.
Though the refractive index of SFWO is slightly smaller than
SFRO, its magnetic moment is 3.99μB whereas SFRO has
3.07μB. So it has larger θKmax than SFMO and SFRO. The
fact that the Kerr rotation correlates with the atomic mag-
etic moment of spin should not be surprising since the MO
effect involves spin-orbit interaction. 31 Incident photons ex-
cite the 3d valence electrons of the transition metals by al-
ter their orbital angular momenta. When the electrons fall
back from their excited states, the emitted photons are polar-
ized and characteristic of both spin orientation and magni-
tude. Thus, the SO interaction couples the momentum of the
electron with its spin and provides the link for the circularly-
polarized electromagnetic waves to couple to the magnetiza-
tion of the material. The heavier the atom, the stronger will
be the SO interaction. Thus, all the studied compounds have
large MO effects. Moreover, SFWO has maximum exchange
splitting of 3.1 eV and its band gap in the majority spin
channel is 1.36 eV. So the electrons are highly spin polarized
in the HMF state. Therefore, larger off-diagonal conduc-
tivity, refractive index, magnetic moment, SO coupling, exchange
splitting, band gap, and plasma resonance combine to give
huge MO values for all the studied compounds, and in par-
ticular to SFWO. The polar Kerr ellipticity is a measure of
how the shape of the wave has changed upon reflection and
depends only on the absolute magnitudes of the reflection
coefficients. As the reflectivities of these compounds are also
large, they also have large polar Kerr ellipticity.

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tense search is going on for materials with MO peaks in the
lower wavelength region for use in high-density storage. 1
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In a transmission mode, large Faraday rotation is desirable
for applications. 32 Materials with large Faraday rotation are
used in devices called optical isolators. Therefore we predict the specific Faraday rotation and ellipticity of $A_2FeB'\text{O}_6$ (not shown), experimental Faraday spectra are hitherto not available for comparison. In Table I we have given the maximum of specific Faraday rotation for each compound. Specific Faraday rotation of all the studied compounds is greater than $1 \times 10^3 \text{deg cm}^{-1}$. It is interesting to note that SFWO has the maximum Kerr as well as Faraday rotation among $A_2FeB'\text{O}_6$.

In order to detect the written information in a MO medium easily, and to make the signal-to-noise ratio as high as possible, the MO figure of merit (FOM) should be large. The FOM is defined as $\text{FOM} = \sqrt{R^2 + \epsilon^2}$, where $R$, is reflectivity and $\theta_k$ and $\epsilon_k$ as defined earlier. For the sake of simplicity, in Table I we have given the maximum of FOM and the corresponding energy at which it occurs. The FOM calculated for the present compounds is comparable with that of the well-known MO material PtMnSb. In spite of the fact that FOM is often used to characterize the performance of a MO medium and the factors determining FOM depend on the structure on which magnetic material is embedded, we believe that the given large FOM values may motivate more MO studies on these systems.

In conclusion, the presently studied compounds have many of the basic requirements for a MO medium, such as presence of uniaxial magnetic anisotropy, $T_C$ ranging between 300 and 600 K, large Kerr rotation, large Faraday rotation, large FOM, HMF at room temperature, long term stability, etc. For the first time, using full-potential density functional calculations, we have shown that $A_2BB'O_6$ have the huge MO effects among the oxides and can be considered as potential candidates for MO applications. The huge magneto-optical effects are found to result due to combined effects of large off-diagonal conductivity, refractive index, magnetic moment, SO coupling, exchange splitting, band gap, and plasma resonance.

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*Electronic address: vidya.ravindran@kjemi.uio.no


104415 (2002).


