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Field-induced magnetostructural phase transition in double perovskite Ca_2FeReO_6 studied via x-ray magnetic circular dichroism

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Spin and orbital contributions to the magnetic moment of rhenium have been studied across the magnetostructural transition in Ca_2FeReO_6 double perovskite employing x-ray magnetic circular dichroism (XMCD) at the Re $L_{2,3}$ edges. Temperature-dependent measurements performed in pulsed magnetic field varying from 6.8 to 30 T revealed that the two phases of this compound are characterized by a different spin-orbit coupling. At $T=10$ K, the average orbital-to-spin moment ratio of the Re sublattice increases in the application of 30 T magnetic field by ~5%, while at $T=250$ K it is field independent and amounts to $|m_L/m_S|=0.362(6)$. The field and temperature dependences of the rhenium XMCD and bulk magnetization are explained within the scenario of a field-induced phase coexistence and transition between two monoclinic phases of diverse magnetocrystalline coupling.

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Ordered double perovskites $A_2BB'O_6$ ($A=$ alkaline earth metals, $B=3d$ transition metal, and $B'=3d,4d$, or $5d$ transition metal) have recently attracted a substantial attention owing to their large spin polarization of the electrical carriers and high Curie temperature.[1,2] These properties are strongly desired in order to realize reasonable magnetoresistance (MR) effects at room temperature enabling the application of the materials in spin electronics devices. Thus, the most promising series ($BB'=$FeMo, FeRe, CrRe, and CrOs) are being intensively studied in order to find the material with an optimal performance in terms of the application in magnetoelectronics.[3] Among the intriguing characteristics of these compounds, quite remarkable are the differences in magnetic properties of $4d$- and $5d$-based analogs, e.g., A_2FeMoO_6 and A_2FeReO_6, despite in their almost identical crystal structure.[4,5] The Re-based double perovskites show strong magnetostructural coupling as well as an unexpected increase in the Curie temperature with decreasing B-O-B' angle[4,6–9] and, thus, a reduction in the effective d-electron hopping integral,[10] in contrast to their Mo-based counterparts and other transition-metal oxides. The differences are attributed to the interplay between structural degrees of freedom with unquenched Re orbital moment,[11–16] giving rise to a competition between the octahedral ligand field and the strong spin-orbit coupling in the $5d$ orbitals.

The strongest crystallographic distortion is observed for Ca_2FeReO_6 (CFRO), which is an insulator at low temperature, revealing very high $T_C=538$ K.[17] It undergoes a structural and metal-insulator (MI) phase transition at $T_S\sim150$ K.[6] Neutron-diffraction experiments[7–9] showed a correlation between the structural deformations of the ReO_6 octahedra and the preferential occupancy of the Re $5d$ orbitals in CFRO. Granado *et al.* suggested that the two phases coexist at low temperatures and that their relative population depends on temperature and magnetic field,[8] while Oikawa *et al.* did not observe any phase separation over a wide temperature range.[9] Photoemission spectroscopy confirms the insulating nature of the low-temperature phase, revealing a narrow gap ($\Delta\sim50$ meV), but also a wide temperature range $T\sim100-200$ K, of the MI transition.[18] Azimonte *et al.* reported a significant difference in the surface sensitive magnetization profiles of bulk and the Fe sublattice attributed to magnetic hardening of grain boundaries due to larger amount of antisite defects; but the lack of significant temperature evolution suggests that the MI transition is related to bulk properties.[19] Recent high-field magnetoresistance and magnetostriction experiments suggested that the relative amount of the two phases is field dependent.[20] It was concluded that the large negative magnetoresistance (MR $>2000\%$ at $T\sim100$ K) observed in CFRO resembles the competing behavior in manganite perovskites of phases with different conductance even though the origin of such competition is different.

The purpose of this experiment was to investigate the role played by the Re orbital moment in the mechanism of the structural phase transition in CFRO and how it impacts the changes observed in magnetocrystalline anisotropy. To achieve this goal, we studied the magnetic field and temperature evolution of the orbital and spin moments of rhenium derived from bulk sensitive x-ray magnetic circular dichroism (XMCD) spectra by means of sum rules.[21,22] The main challenge was to acquire the spectra at high enough magnetic field (at least $B=20$ T) in a wide temperature range to induce a substantial change in the relative phase fraction. Such high magnetic field installations have been made available at synchrotron facilities only recently. First results of their application can be found in Refs. 23–26. This Rapid Communication aims to prove that XMCD spectroscopy can successfully be combined with pulsed magnetic field generation providing an element selective method for determining the spin and orbital behaviors under extreme magnetic fields.

A single phase polycrystalline sample of Ca_2FeReO_6 was prepared by solid-state reaction technique, showing negligible amount of antisite disorder as described in Ref. 27. The bulk sensitive XMCD measurements were performed using transmission detection employing the energy dispersive acquisition technique available at the ID24 beamline of the European Synchrotron Radiation Facility (ESRF).[24] A set of rhenium L_2- and L_3-edge spectra was recorded in the temperature range from 10 to 250 K, under magnetic field ranging from 6.8 to 30 T, generated by a minipulsed field setup.[26] The spectra were recorded at 64 points of B-T space from a ~1-mm-thick pellet optimized for unitary transmission at the Re L_3 edge by mixing appropriate amounts of CFRO and boron nitride powders. The spectra were acquired during the central 75 μs of each magnetic pulse and averaged over a number of 10–20 and 50–100 pairs of opposite field pulses at the L_2 and L_3 absorption edges, respectively. The same sequence was applied to the opposite x-ray helicity direction in order to minimize systematic errors.[28] Energy calibration and edge step normalization were accomplished by a comparison of the x-ray absorption spectra measured on the dispersive and the standard transmission setups. The latter was acquired from the same pellet at the BM29 beamline of ESRF.[29] The measured L_3/L_2 edge step ratio was equal to 2.15. The energy resolution of the dispersive setup at the Re L_2- and L_3-edge was estimated at 2.5 and 3.0 eV, respectively, while the degree of circular polarization used for the XMCD amplitude normalization was similar at both absorption edges and estimated at $P_c \sim 75(3)\%$.

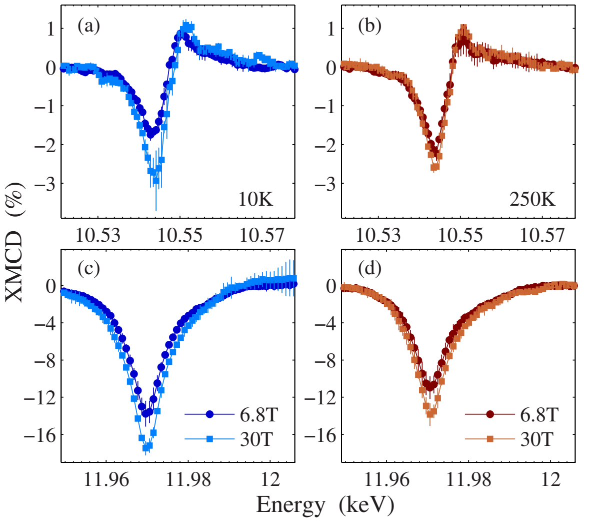

FIG. 1. (Color online) [(a) and (b)] Re L_3 and [(c) and (d)] L_2 XMCD spectra acquired under 6.8 T (filled circles) and 30 T (filled squares) magnetic field at [(a) and (c)] $T=10$ K and [(b) and (d)] 250 K. Systematic errors are denoted by vertical bars.

Figure 1 shows the XMCD spectra measured at four extreme points of the B-T space available during the experiment. The Re L_3-edge spectra reveal differential-like shape with a negative peak at the edge energy and a small positive peak ~3 eV higher followed by a long tail. The Re L_2-edge spectra consist of a single broad asymmetric negative peak. Its amplitude is much stronger than that of L_3-edge signal, in agreement with theoretical predictions of predominant $m_l=1$ orbitals occupation.[11,14] The amplitude of the spectra measured at $T=10$ K and $B=30$ T is slightly higher than the one reported in Ref. 14, where the spectra measured at $B=2$ T were normalized to the expected saturation magnetization of $M=3\mu_B$/f.u. However, the intensity excess is consistent with bulk magnetization of $M=3.13\mu_B$/f.u. at 30 T reported in Ref. 30.

As expected, the XMCD intensity is the strongest at low temperature and high field at both edges. The Re L_2-edge spectra reveal a similar intensity increase of ~25%, with rising magnetic field from 6.8 to 30 T in the entire temperature range. A different behavior is observed at the Re L_3-edge. The field-induced increase in dichroism intensity at $T=10$ K is much stronger (~50%) than the one observed at 250 K. Moreover, the low-field L_3-edge spectra grow in intensity with rising temperature, in contrast to the L_2-edge and bulk magnetization. The latter effect confirms that the orbital distribution of Re 5d electrons is affected by the structural phase transition and thus the spin-orbit coupling may also be affected. To shed more light on the effect, a sum-rules analysis was performed and the temperature and field variations of the orbital-to-spin moment ratio (m_L/m_S) of rhenium moment was derived. As expected by Hund's rules, the ratio is negative and the orbital moment is not quenched, which is consistent with strong spin-orbit coupling of heavy ($Z=75$) rhenium ions. However, the absolute value of $m_L/m_S \sim 0.36$ is significantly lower than 0.5 (1.0) expected for Re$^{5+(6+)}$, which indicates that the octahedral ligand field of oxygen 2p orbitals plays an important role as well. The results of the orbital-to-spin moment ratio determination over the entire B-T space studied in the experiment are shown in Fig. 2. The smallest absolute value of $|m_L/m_S|=0.348(10)$ is observed at $T=10$ K and $B=6.8$ T. A significant field-induced evolution at low temperature is revealed, $|m_L/m_S|$ increasing to 0.357(9) at $T=10$ K and $B=30$ T. A rise with temperature is observed (within error margin) in the entire field range, showing a "saturation" at the value of $|m_L/m_S| \sim 0.362(6)$ at $T=250$ K. Although the single point uncertainty of m_L/m_S is considerably large, a tendency in temperature and field dependences is unambiguous. It is clear that in the temperature range well above the phase transition, i.e., $T>200$ K, the m_L/m_S value is almost independent on the magnetic field. The results presented are interpreted within the model of two competing phases char-

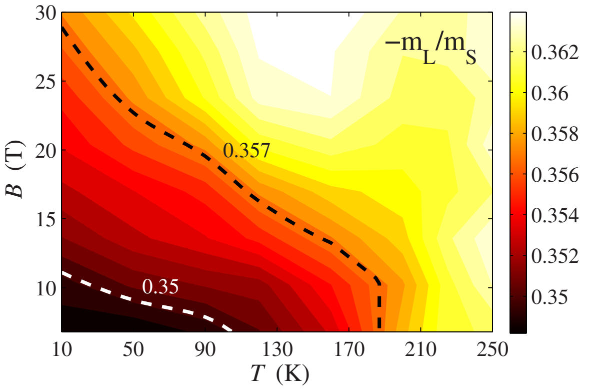

FIG. 2. (Color online) Evolution of the m_L/m_S ratio measured at 64 points of B-T space. Iso-m_L/m_S curves are presented at arbitrary values as guides for the eyes. Absolute uncertainty of the single point data after a two-dimensional smoothing is ~0.002.

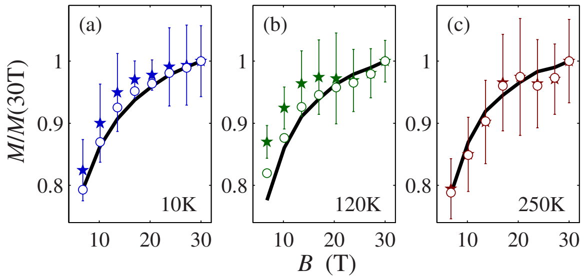

FIG. 3. (Color online) Field dependence of the Re total (filled stars) and orbital (open circles) magnetization compared to bulk (black line) at (a) $T=10$, (b) 120, and (c) 250 K. Spin moment evolution is very close to that of the total Re moment. Orbital moment error bars are omitted for clarity. Bulk magnetization data have been taken from Refs. 27 and 30.

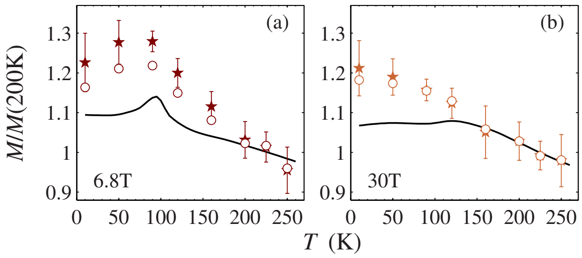

FIG. 4. (Color online) Temperature dependence of the Re total (filled stars) and orbital (open circles) magnetizations compared to bulk (black line) at (a) $B=6.8$ and at (b) 30 T. Spin moment evolution is very close to that of the total Re moment. Orbital moment error bars are omitted for clarity. Bulk magnetization data have been taken from Refs. 27 and 30.

acterized by different magnetocrystalline coupling expressed by distinct orbital-to-spin moment ratio. Below T_S, the dominating insulating phase characterized by different crystal field and therefore different splitting of the Re t_{2g} levels coexists with the metallic one. The relative abundance of the phases can be controlled by an external magnetic field, which alters the energy splitting of t_{2g} orbitals and thus affects their population. Above T_S, the metallic phase is dominating and thus the application of the external field has negligible influence on electronic properties. This is in sharp contrast with the temperature region below T_S, where the magnetic field favors the metallic phase at the expense of the insulating one observed as a strong-field effect on the value of m_L/m_S. In the same temperature range, the highest magnetoresistance effect is also observed.[20]

The comparison of the shape of bulk and the Re sublattice magnetization (total and orbital) curves clearly indicates that different microscopic magnetic properties of CFRO exist below and above T_S. The normalized $M(T)$ curves (Fig. 3) measured well above the phase-transition temperature fit nicely; but a significant difference is revealed in the vicinity and below T_S. Bulk magnetization does not show saturation in the entire probed temperature range, while the total moment of the Re one—derived from sum rules as m_S+m_L—seems to saturate at low temperature upon the application of magnetic field of ~20 T. The effect is especially pronounced at 120 K [Fig. 3(b)], where the magnetic field affects substantially the phase coexistence.[20] This apparently striking result can be naturally explained by a larger magnetization of the Re sublattice in the insulating phase than in the metallic one and taking into account that bulk magnetization is determined by the difference between the Fe and Re sublattice magnetization. As the Fe magnetization has spin origin, it is not expected to change significantly across T_S.[19] Therefore, bulk magnetization is expected to decrease below T_S due to the larger magnetization of the Re sublattice, which is antiparallel to the Fe one. Upon the application of magnetic field at or below T_S, the magnetic alignment is favored and the increase in bulk and the Re magnetization are expected. However, simultaneously, the high-temperature metallic phase is favored, which has smaller (larger) Re (bulk) magnetization. Further confirmation of this model is given by the comparison of the temperature dependence of the Re and bulk magnetizations shown in Fig. 4. The two magnetization profiles normalized at $T\sim200$ K, the temperature corresponding to a single magnetocrystalline phase, indicate a nice agreement at higher temperatures only. Below T_S, a considerable excess of 10–15 % in the normalized Re magnetization is observed with respect to bulk, reinforcing the hypothesis of higher Re sublattice magnetization in the insulating phase compared to the metallic one. Thus, we put forward that the decrease in the relative Re to bulk magnetization upon transition from insulating to metallic phase can be explained by the change in the Re t_{2g} electronic levels occupation and, consequently, in the Re sublattice magnetization.[31] This affects the hopping integral of the double-exchange-like interaction and thus has strong impact on the electronic properties of the compound studied.

In conclusion, the Re orbital-to-spin moment ratio and the evolution of magnetic moment of rhenium sublattice was derived from Re $L_{2,3}$-edge XMCD spectra and compared to bulk magnetization measurements. The temperature dependence of m_L/m_S ratio gives an unequivocal evidence that the two crystallographic phases observed in Ca_2FeReO_6 are characterized by different spin-orbit coupling. A gradual increase in the absolute m_L/m_S ratio and thus an abundance of the metallic phase is induced by a strong magnetic field below T_S. Comparison of the field and temperature dependences of the Re sublattice and bulk magnetic moments reveals that the former one is significantly higher in the insulating phase. This gives evidence that the phase transition is accompanied by the evolution in the population of Re t_{2g} levels, which confirms the charge-transfer character of the metal-insulator phase transition.

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