Magnetic moments of W 5d in Ca$_2$CrWO$_6$ and Sr$_2$CrWO$_6$ double perovskites

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We have investigated the magnetic moment of the W ion in the ferrimagnetic double perovskites Sr$_2$CrWO$_6$ and Ca$_2$CrWO$_6$ by x-ray magnetic circular dichroism at the W $L_{2,3}$ edges. In both compounds a finite negative spin and positive orbital magnetic moment was detected. The experimental results are in good agreement with band-structure calculations for (Sr/Ca)$_2$CrWO$_6$ using the full-potential linear muffin-tin orbital method. It is remarkable that the magnetic ordering temperature, T_C, is correlated with the magnetic moment at the "nonmagnetic" W atom.

The double perovskites of the composition A$_2$BB′O$_6$ (with A an alkaline earth, B a magnetic transition metal ion, and B′ a nonmagnetic ion) are interesting materials, both due to their rich physics and their promising properties for applications in spintronics. Recently, the double perovskites have attracted renewed interest when a large room-temperature magnetoresistance was observed in Sr$_2$FeMoO$_6$ with a Curie temperature T_C=420 K.[1] Furthermore, band-structure calculations indicated that the ferromagnetic double perovskites not only have large T_C but also are half-metals. This immediately suggests their application as a source of spin-polarized charge carriers in spintronic devices. In addition to Sr$_2$FeMoO$_6$, ferrimagnetism with a T_C up to 458 K has been found in ceramic and thin film samples of the compound Sr$_2$CrWO$_6$.[2,3] Furthermore, this compound also has been predicted half-metallic by band-structure calculations.[3,4] The double perovskite with the highest T_C known so far is Sr$_2$CrReO$_6$ with T_C=635 K.[5,6] However, according to new results of density functional theory this compound is not fully half-metallic due to a strong spin-orbit coupling of Re.[7]

For clarifying the nature of magnetic exchange in the double perovskites, the knowledge on the local magnetic moments on the B and B′ site is important. For Sr$_2$FeMoO$_6$, recent x-ray magnetic circular dichroism (XMCD) measurements showed a spin moment of about 3 μ_B for Fe^{3+} ion at the B site. Interestingly, for the nonmagnetic Mo^{5+} ion at the B′ site an *antiparallel aligned* spin moment of about −0.3 μ_B and a small orbital contribution was found.[8] This observation is in agreement with a generalized double exchange or kinetic energy driven exchange model proposed by Sarma *et al.*[9] to explain the strong ferromagnetic exchange in double perovskites despite the large distance between the

magnetic ions (e.g., 8.82 Å for Sr$_2$CrWO$_6$). Subsequently, extensions of this model have been used to explain ferromagnetism in magnetic semiconductors and organic ferromagnets.[10,11] We recently showed that this model also can be applied to the A$_2$CrWO$_6$ system.[3] In the following we shortly describe the kinetic energy driven exchange model: For the magnetic ion Cr^{3+} Hund's splitting is much larger than the crystal field splitting, and the majority spin t_{2g} band is filled. In contrast, at the "nonmagnetic" site W^{5+} the crystal field splitting is large and Hund's splitting small. As the majority spin bands at the magnetic site are occupied, kinetic energy gain can only be obtained by hybridization and the hopping of the minority spin electrons from the nonmagnetic site into the empty minority spin bands of the magnetic ion. By shifting electrons from the majority spin band of the nonmagnetic site into the minority spin band, the system can gain energy. As a result, the charge carriers become strongly polarized, in the extreme case even half-metallic. Further, at the nonmagnetic site a negative spin magnetic moment develops. An evident check of the validity of this model is the investigation of the magnetic moment on the nonmagnetic B′ site. We note that in this simple model magnetic order is established by a purely electronic mechanism. In more sophisticated theories antisite disorder or breathing distortions are necessary to stabilize ferrimagnetism.[12] The relevance of such structural degrees of freedom still has to be investigated experimentally.

Here, we report both on band-structure calculations on the system (Sr/Ca)$_2$CrWO$_6$ using the full-potential linear muffin-tin orbital method, and on XMCD measurements detecting the spin and orbital magnetic moment at the nonmagnetic W atom. Using the magneto-optical sum-rules of
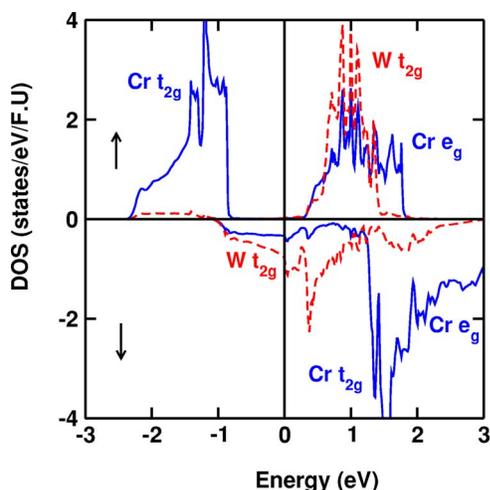
FIG. 1. (Color online) Orbital resolved density of states (DOS) of Sr_2CrWO_6 with spin-orbit coupling. The Fermi energy is indicated by zero energy level.

XMCD[13,14] spin and orbital magnetic moments can be calculated separately, thereby allowing for an experimental test of the kinetically driven exchange model and the band-structure calculations for $(Sr/Ca)_2CrWO_6$.

The half-metallicity of $(Sr/Ca)_2CrWO_6$ as derived from the simple ionic model described above is supported by band-structure calculations using an all-electron full-potential linear muffin-tin orbital method (FPLMTO).[15] One advantage in this method is that no shape approximation of the potential, wave functions, or charge density is made. Spin-orbit coupling is included in all calculations. For more details see the theoretical results of this method for the compound Sr_2CrReO_6.[7]

Our results from the band-structure calculations are presented in Fig. 1. The spin-up bands, which are plotted in the upper half of Fig. 1, show the crystal field splitting of the Cr $3d$ bands at the Fermi level whereas the hybridized Cr $3d$ and W $5d$ spin-down bands (plotted in the lower half) are located at the Fermi level. The magnetic spin moment at the W site is calculated to be $m_S=-0.31$ μ_B and the ratio of the orbital and spin moment is found to be $|m_L/m_S|=0.32$. The number of W $5d$ holes deduced from the band-structure calculations is $n_h=6.3$. Qualitatively, the band-structure calculated by FPLMTO appears to be similar to that calculated by LMTO using the atomic sphere approximation (ASA).[3] The remarkable point is that half-metallicity is preserved even if spin-orbit coupling is included. This result for Sr_2CrWO_6 is in contrast to that for Sr_2CrReO_6, where spin-orbit coupling destroys the half-metallic nature. We explain this difference between Sr_2CrWO_6 and Sr_2CrReO_6 as due to the fact that W has one $5d$ electron less than Re, causing the W t_{2g} states to shift upwards in energy, away from the Fermi level. As a result, the hybridization at the gap becomes less pronounced, and the gap is preserved. In order to validate the prediction of the band-structure calculations, we investigated the magnetic moment on the W atom of the double perovskites Sr_2CrWO_6 and Ca_2CrWO_6 by XMCD.

The sample preparation is described elsewhere.[3] In short, the polycrystalline samples contain small amounts of the parasitic phases W and A_3WO_6 (with A=Sr, Ca). It is important to note that we found no magnetic W impurity phases, which could possibly influence the XMCD measurements. From superconducting quantum interference device measurements we obtained $T_C=443$ K for Sr_2CrWO_6 and $T_C=160$ K for Ca_2CrWO_6.

The XMCD measurements on the W $L_{2,3}$ edges were performed at the European Synchrotron Radiation Facility (ESRF) at beam line ID12.[16] The spectra were recorded using the total fluorescence yield detection mode. The XMCD spectra were obtained as the direct difference between consecutive XANES scans (x-ray absorption near edge spectrum) recorded with opposite helicities of the incoming x-ray beam. To ensure that the XMCD spectra are free from any experimental artifacts the data was collected for both directions of the applied magnetic field of 7 T (parallel and antiparallel to the x-ray beam). The degree of circular polarization of the monochromatic x-ray beam was 98%. The measurements were performed at low temperature for the Ca_2CrWO_6 sample ($T<T_C$) and at room temperature for the Sr_2CrWO_6 sample ($T<T_C$).

Since the samples measured in backscattering geometry were very thick, the spectra were first normalized to the edge jump of unity and then corrected from self-absorption effects. The edge jump intensity ratio L_3/L_2 was then normalized to 2.19/1.[17] This is different from the statistical 2:1 branching ratio due to the difference in the radial matrix elements of the $2p1/2$ to $5d(L2)$ and $2p3/2$ to $5d(L3)$ transitions.

We first discuss the XANES spectra of Sr_2CrWO_6 and Ca_2CrWO_6 shown in Fig. 2. As expected, a similar behavior is found for the closely related compounds. The white lines at the W $L_{2,3}$ edges have a rich fine structure which is related to the valency and crystal field.[8] The L_3 absorption edges showed a clear double peak structure with slightly less intensity of the peak at higher energy, whereas at the L_2 edge this peak is less intense and forms a high energy shoulder. This double peak structure is identified as the signature of the crystal field splitting ($\sim$3.2 eV for Sr_2CrWO_6) of the $5d$ band into t_{2g} and e_g states. Similar double peak structures have also been observed at the Mo $L_{2,3}$ absorption edges for the double perovskite Sr_2FeMoO_6,[8] however, with a more pronounced separation between the peaks and slightly different intensities at the L_3 edge.

As shown in Fig. 2, for both absorption edges we find a rather intense XMCD signal. This is clear evidence for the existence of a magnetic moment at the W $5d$ shell. While the XMCD spectra at the L_2 edge in Sr and Ca compounds appear to be very similar, there are distinct differences between the L_3 XMCD curves of Sr_2CrWO_6 and Ca_2CrWO_6. It is first very interesting to note that the XMCD at the L_3 edge in Ca_2CrWO_6 is nearly two times larger than in Sr_2CrWO_6. Second, for Ca_2CrWO_6 the first minimum is significantly stronger than for Sr_2CrWO_6, whereas for Sr_2CrWO_6 the first maximum is more pronounced. These differences can be attributed to different radii of the A site ions, which cause changes in the crystal and, in turn, the electronic and magnetic structure. Third, the observed XMCD oscillations for both compounds are strongly damped (but still present) at the L_2 edge as compared to the L_3 edge. This shows that the
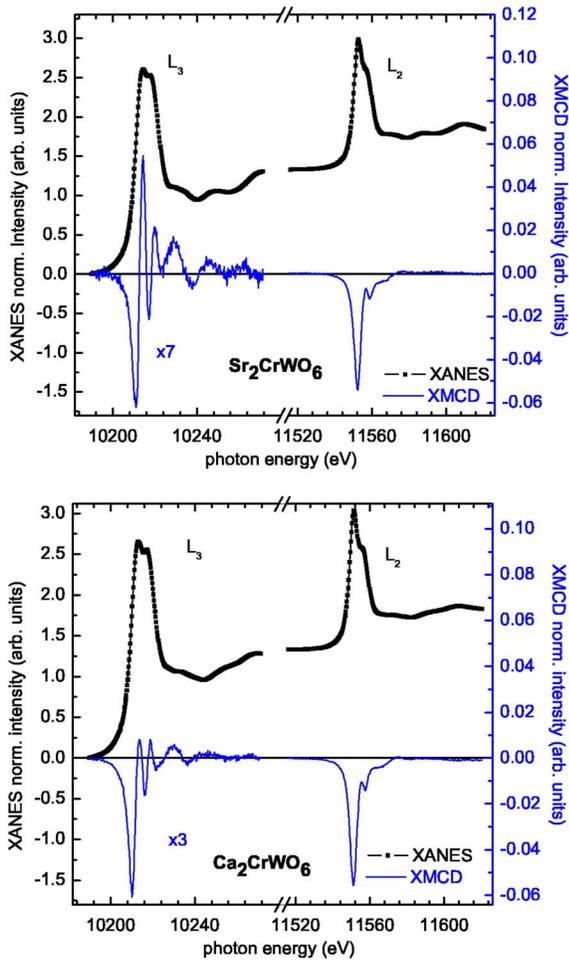
FIG. 2. (Color online) XANES spectra and derived XMCD spectra for Sr_2CrWO_6 (upper panel) and Ca_2CrWO_6 (lower panel). The XANES spectra (symbols) are corrected as described in the text. The XMCD spectra are shown as full lines. The XMCD spectrum of the W L_3 edge was multiplied by a factor of 7 for Sr_2CrWO_6 and by a factor of 3 for Ca_2CrWO_6 for clarity.

probed orbital and spin resolved density of states is not identical.[18]

In Table I we list the magnetic moments at the W site derived from the XMCD measurements using the standard sum rules[13,14] and compare them to theoretical values. For completeness, we include also data previously published by other groups on similar compounds.[7,8,21] Furthermore, the ratio $|m_L/m_S|$ is calculated, since this quantity is not affected by possible uncertainties in the calculated number of holes. Table I shows that the 5d magnetic spin moment of W m_S $=-0.33$ μ_B/f.u. derived for Sr_2CrWO_6 is in excellent agreement with the theoretically calculated value. We note that this degree of agreement is a bit fortuitous, since effects of antisite disorder and the exact oxygen content of the investigated samples have not been taken into account in the theoretical analysis. We further note that the orbital moment is only three times smaller than the spin moment. From this we can conclude that spin-orbit coupling of the delocalized t_{2g} electron at the W site is of considerable size, although not able to destroy the half metallic character of this compound.

Comparing the magnetic spin moment at the W atom for the two compounds, we find a reduction of the magnetic spin moment of only $m_S=-0.22$ μ_B/f.u. and also a reduced orbital moment for Ca_2CrWO_6 compared to Sr_2CrWO_6. This corresponds to the structural differences between these compounds. On replacing Sr^{2+} by the smaller ion Ca^{2+}, the tolerance factor f (Ref. 19) of the A_2CrWO_6 system deviates significantly from unity and the crystal structure changes from cubic to monoclinic. It has been pointed out recently that for all ferrimagnetic double perovskites T_C seems to be maximum for $f \simeq 1$, i.e., for the undistorted cubic structure.[3] The only exception from this rule is Ca_2FeReO_6,[20] Due to the monoclinic distortion in Ca_2CrWO_6 the B–O–B bonding angle deviates significantly from 180°. This results in a reduction of the hopping integral, i.e., in a weaker delocalization of the W 5d electron and, in turn, in a weakening of the magnetic exchange. As a direct consequence, T_C and the magnetic moment induced at the W are reduced in Ca_2CrWO_6. We note that a large magnetic moment is theoretically predicted for the Re site in Sr_2CrReO_6. However, so far no experimental verification is made by XMCD measurements.

We finally discuss our findings in the context of the model developed by Sarma *et al.*[9] as described in short above. The key point of this model is that the ferromagnetic coupling between the magnetic ions is established by (fully) spin polarized charge carriers with opposite magnetization direction originating from the nonmagnetic site. The spin magnetic moment is smeared out over several sites and bonds, however, it must lead to a finite negative spin magnetization at the nonmagnetic site. Previous experiments[8] and our experiment here show that in double perovskites with similar T_C,

TABLE I. Measured (experiment, normalized to 5 K) and calculated (theoretical) magnetic moments per formula unit (f.u.) at the nonmagnetic ions (W, Mo, Re) for different double perovskites at 5 K.

	Material	$m_S(\mu_B/\mathrm{f.u.})$	$m_L(\mu_B/\mathrm{f.u.})$	$|m_L/m_S|$
Experiment	Ca_2CrWO_6	-0.22 ± 0.02	0.10 ± 0.01	0.44 ± 0.03
	Sr_2CrWO_6	-0.33 ± 0.02	0.12 ± 0.02	0.35 ± 0.01
	Sr_2FeMoO_6 (Ref. 8)	-0.32 ± 0.05	-0.05 ± 0.05	0.15
Theoretical	Ca_2CrWO_6	-0.25	0.06	0.25
	Sr_2CrWO_6	-0.31	0.10	0.32
	Sr_2FeMoO_6 (Ref. 21)	-0.24	0.02	0.09
	Sr_2CrReO_6 (Ref. 7)	-0.85	0.18	0.21

also similar magnetic moments are found at the nonmagnetic site (Mo in Sr_2FeMoO_6 and W in Sr_2CrWO_6, see Table I). As soon as the kinetic exchange is reduced due to lattice distortions, the spin magnetic moment decreases as shown in the case of Ca_2CrWO_6, at the same time also T_C decreases. In this sense, the magnetic coupling, the degree of delocalization, and the magnetic moment at the nonmagnetic site are consequences of the kinetic energy driven exchange model. However at this stage, it is difficult to quantify these relations or establish a theory to calculate T_C. It would be also important to confirm the half-metallicity of the double perovskites in question by additional methods as spin-resolved photoemission spectroscopy or tunneling magnetoresistance effects.

In summary, we have performed XMCD measurements of the magnetic moment at the $5d$ shell of the nonmagnetic ion W in the double perovskite system A_2CrWO_6 with A=Sr, Ca. Our experimental results are in good agreement with those of our band-structure calculations. The smaller W $5d$ magnetic moment found for the Ca_2CrWO_6 compound is attributed to an enhanced localization of the W $5d$ electron due to a monoclinic distortion. Our results suggest that there is a correlation between the magnitude of the magnetic moment at the nonmagnetic ion and the magnetic ordering temperature T_C in the double perovskites. We believe that this correlation can provide important clues on how to construct an accurate theory for the magnetic ordering temperature in double perovskites.

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