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 “non-magnetic” W atom.

DOI: 10.1103/PhysRevB.72.132402

PACS number(s): 75.25.+z, 75.30.–m, 75.50.–y

The double perovskites of the composition $A_2BB'O_6$ (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. 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$_6$. Furthermore, this compound also has been predicted half-metallic by band-structure calculations. The double perovskite with the highest $T_C$ known so far is Sr$_2$CrReO$_6$ with $T_C$=635 K. 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.

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 $\mu_B$ 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 $-0.3$ $\mu_B$ and a small orbital contribution was found. This observation is in agreement with a generalized double exchange or kinetic energy driven exchange model proposed by Sarma et al. 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. We recently showed that this model also can be applied to the A$_2$CrWO$_6$ system. 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. 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...
The remarkable point is that half-metallicity is preserved even if potential linear muffin-tin orbital method band-structure calculations using an all-electron full-the simple ionic model described above is supported by orbital and spin moment is found to be \( \frac{\mu}{H_20841} \) pound Sr\(_2\)CrReO\(_6\). Details see the theoretical results of this method for the compound Sr\(_2\)FeMoO\(_6\). Spin-orbit coupling is included in all calculations. For more details see the theoretical results of this method for the compound Sr\(_2\)CrReO\(_6\).\

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 \( m_3 = -0.31 \mu_B \) and the ratio of the orbital and spin moment is found to be \( |m_1/m_3| = 0.32 \). The number of W 5d holes deduced from the band-structure calculations is \( n_6 = 6.3 \). 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\(_2\)CrWO\(_6\) is in contrast to that for Sr\(_2\)CrReO\(_6\), where spin-orbit coupling destroys the half-metallic nature. We explain this difference between Sr\(_2\)CrWO\(_6\) and Sr\(_2\)CrReO\(_6\) 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\(_2\)CrWO\(_6\) and Ca\(_2\)CrWO\(_6\) by XMCMD.\

The sample preparation is described elsewhere.3 In short, the polycrystalline samples contain small amounts of the parasitic phases W and A\(_2\)WO\(_6\) (with A=Sr, Ca). It is important to note that we found no magnetic W impurity phases, which could possibly influence the XMCMD measurements. From superconducting quantum interference device measurements we obtained \( T_C = 443 \) K for Sr\(_2\)CrWO\(_6\) and \( T_C = 160 \) K for Ca\(_2\)CrWO\(_6\).\

The XMCMD 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 XMCMD 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 XMCMD 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\(_2\)CrWO\(_6\) sample \( (T < T_C) \) and at room temperature for the Sr\(_2\)CrWO\(_6\) 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 \( L_1/L_2 \) 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(e\(_g\)) and 2p3/2 to 5d(e\(_g\)) transitions.\

We first discuss the XANES spectra of Sr\(_2\)CrWO\(_6\) and Ca\(_2\)CrWO\(_6\) 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\(_2\)CrWO\(_6\)) 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\(_2\)FeMoO\(_6\). 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 XMCMD signal. This is clear evidence for the existence of a magnetic moment at the W 5d shell. While the XMCMD spectra at the L\(_2\) edge in Sr and Ca compounds appear to be very similar, there are distinct differences between the L\(_3\) XMCMD curves of Sr\(_2\)CrWO\(_6\) and Ca\(_2\)CrWO\(_6\). It is first very interesting to note that the XMCMD at the L\(_3\) edge in Ca\(_2\)CrWO\(_6\) is nearly two times larger than in Sr\(_2\)CrWO\(_6\). Second, for Ca\(_2\)CrWO\(_6\) the first minimum is significantly stronger than for Sr\(_2\)CrWO\(_6\), whereas for Sr\(_2\)CrWO\(_6\) 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 XMCMD 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
probed orbital and spin resolved density of states is not identical.\textsuperscript{18}

In Table I we list the magnetic moments at the W site derived from the XMCD measurements using the standard sum rules\textsuperscript{13,14} and compare them to theoretical values. For completeness, we include also data previously published by other groups on similar compounds.\textsuperscript{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 5$d$ magnetic spin moment of W $m_S = -0.33 \mu_B$/f.u. derived for Sr$_2$CrWO$_6$ 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 $m_S = -0.22 \mu_B$/f.u. and also a reduced orbital moment for Ca$_2$CrWO$_6$ compared to Sr$_2$CrWO$_6$. 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$_2$CrWO$_6$ 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 $f = 1$, i.e., for the undistorted cubic structure.\textsuperscript{3} The only exception from this rule is Ca$_2$FeReO$_6$.\textsuperscript{20} Due to the monoclinic distortion in Ca$_2$CrWO$_6$, 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 5$d$ 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$_2$CrWO$_6$. We note that a large magnetic moment is theoretically predicted for the Re site in Sr$_2$CrReO$_6$. 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.\textsuperscript{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\textsuperscript{8} and our experiment here show that in double perovskites with similar $T_C$,

![FIG. 2. (Color online) XANES spectra and derived XMCD spectra for Sr$_2$CrWO$_6$ (upper panel) and Ca$_2$CrWO$_6$ (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$_2$CrWO$_6$ and by a factor of 3 for Ca$_2$CrWO$_6$ for clarity.](image)

| 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        | $m_S(\mu_B$/f.u.) | $m_L(\mu_B$/f.u.) | $|m_L|/m_S|$ |
| Experiment      |        |        |        |
| Ca$_2$CrWO$_6$  | $-0.22\pm0.02$ | $0.10\pm0.01$ | $0.44\pm0.03$ |
| Sr$_2$CrWO$_6$  | $-0.33\pm0.02$ | $0.12\pm0.02$ | $0.35\pm0.01$ |
| Ca$_2$FeMoO$_6$ (Ref. 8) | $-0.32\pm0.05$ | $-0.05\pm0.05$ | $0.15$ |
| Theoretical     |        |        |        |
| Ca$_2$CrWO$_6$  | $-0.25$ | $0.06$ | $0.25$ |
| Sr$_2$CrWO$_6$  | $-0.31$ | $0.10$ | $0.32$ |
| Ca$_2$FeMoO$_6$ (Ref. 21) | $-0.24$ | $0.02$ | $0.09$ |
| Sr$_2$CrReO$_6$ (Ref. 7) | $-0.85$ | $0.18$ | $0.21$ |
also similar magnetic moments are found at the nonmagnetic site (Mo in Sr$_2$FeMoO$_6$ and W in Sr$_2$CrWO$_6$, 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$_2$CrWO$_6$, 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 5$d$ shell of the nonmagnetic ion W in the double perovskite system A$_2$CrWO$_6$ with A=Sr, Ca. Our experimental results are in good agreement with those of our band-structure calculations. The smaller W 5$d$ magnetic moment found for the Ca$_2$CrWO$_6$ compound is attributed to an enhanced localization of the W 5$d$ 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.

This work was supported by the Deutsche Forschungsgemeinschaft, by the BMBF (project 13N8279), and by the ESRF (HE-1658).

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