

High-field magnetization measurements in $\text{Sr}_2\text{CrReO}_6$ double perovskite: Evidence for orbital contribution to the magnetization

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Abstract – We have synthesized a $\text{Sr}_2\text{CrReO}_6$ double perovskite sample with the expected high Curie temperature ≈ 600 K, which shows negligible impurity phases and $\approx 15\%$ Cr/Re structural antisite disorder as shown by X-ray and neutron diffraction. High-field magnetization measurements up to 47 T show that the saturation magnetization below room temperature is much higher than the one predicted by simple models that do not take into account the Re spin-orbit coupling. The crucial role of the large Re orbital moment in the physics of $\text{Sr}_2\text{CrReO}_6$ and related compound is highlighted.

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Introduction. – Ferromagnetic oxides with Curie temperature (T_C) above room temperature can be useful in several research fields, as for example in spin electronics, where the coexistence of high spin polarization of the electrical carriers and high T_C is feasible [1]. Thus, an intense research activity has been devoted in the last years to compounds such as $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ ($T_C = 370$ K) CrO_2 ($T_C = 410$ K), and Fe_3O_4 ($T_C = 860$ K) [1]. Double perovskites ($\text{A}_2\text{BB}'\text{O}_6$, A = alkaline earth metals and B/B' = transition metals) such as $\text{Sr}_2\text{FeMoO}_6$ ($T_C = 420$ K) [2], Sr_2CrWO_6 ($T_C = 450$ K) [3], and $\text{Sr}_2\text{CrReO}_6$ ($T_C = 610$ K) [4] are also serious candidates for application in magnetoelectronic devices and have been actively studied in recent times (see ref. [5] for a review article on these materials).

Whereas the physics of FeMo-based double perovskite compounds is well understood within the model proposed by Sarma [6], where indirect exchange interactions

Fe-O-Mo-O-Fe mediated by itinerant electrons allow a ferromagnetic coupling of the Fe ions and induce a sizeable magnetic moment on the non-magnetic ion (Mo) due to hopping interactions, the physics of FeRe- and CrRe-based double perovskite compounds is more challenging. A great difference between FeMo-based and FeRe/CrRe-based double perovskites is that Re ions bear a substantial spin-orbit coupling that amounts to a Re orbital moment of the order of 1/3 of the spin moment [7,8]. Another substantial difference is that the number of potential electrons at the Re ions ($5d^1$ for Re^{+6} and $5d^2$ for Re^{+5}) is larger than for Mo ($4d^0$ for Mo^{+6} and $4d^1$ for Mo^{+5}), which can switch on on-site Coulomb repulsive interactions between electrons. Thus, in the case of FeRe/CrRe-based double perovskites, sophisticated models seem to be required to describe the observed behavior [9,10] in sharp contrast to the case of FeMo-based compounds [2].

One important magnetic property to determine in these compounds is the saturation magnetization (M_S). In the case of FeMo-based compounds such as $\text{Sr}_2\text{FeMoO}_6$,

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the maximum saturation magnetization can be simply calculated by assuming the antiparallel alignment of the high-spin ionic state of Fe^{+3} ($S=5/2$) and Mo^{+5} ($S=1/2$), which leads to $M_S = 4\mu_B/\text{f.u.}$ The experimental value of M_S becomes reduced due to the presence of B/B' anti-site disorder (misplaced B ions at B' positions and vice-versa) [11]. In this sense, Balcells *et al.* have demonstrated that the M_S of $\text{Sr}_2\text{FeMoO}_6$ is $4\mu_B/\text{f.u.}$ when the anti-site disorder tends to zero whereas it is about $2.7\mu_B/\text{f.u.}$ when the antisite disorder is 15% and eventually it would be $0\mu_B/\text{f.u.}$ with 50% antisite disorder (which means a single perovskite instead of double-perovskite) [12]. The maximum value of $4\mu_B/\text{f.u.}$ can be understood within ionic models with the possible electronic configurations $\text{Fe}^{+2}\text{-Mo}^{+6}$ ($4\mu_B$ at Fe position and $0\mu_B$ at Mo position) and $\text{Fe}^{+3}\text{-Mo}^{+5}$ ($5\mu_B$ at Fe position and $-1\mu_B$ at Mo position). The actual electronic configuration is a mixture of both as shown by Mössbauer [13] and NMR measurements [14]. The predictions of band calculations in $\text{Sr}_2\text{FeMoO}_6$ do not significantly differ from the predictions of these simple ionic models [2].

However, the theoretical predictions of these ionic models and density-functional theory (DFT) calculations are completely different in the case of $\text{Sr}_2\text{CrReO}_6$. In the ionic model, Cr ions having a $3d^3$ configuration should have a moment of $3\mu_B$ antiferromagnetically coupled to the neighboring Re ions with configuration $5d^2$ or $2\mu_B$, which produces a total saturation magnetization of $1\mu_B/\text{f.u.}$ The DFT calculations by Vaitheeswaran *et al.* also give a total saturation magnetization of $1\mu_B/\text{f.u.}$ if the spin-orbit coupling on Re ions is not taken into account [10]. However, if the spin-orbit coupling is included, the DFT calculation gives a total saturation magnetization around $1.3\mu_B/\text{f.u.}$, primarily due to the appearance of a sizeable orbital magnetic moment on Re ions [10]. Thus, the saturation magnetization in $\text{Sr}_2\text{CrReO}_6$ is 30% larger in the DFT calculations compared to the ionic model. In this letter we aim to shed light on the actual saturation magnetization of bulk $\text{Sr}_2\text{CrReO}_6$.

Experimental details. – The polycrystalline $\text{Sr}_2\text{CrReO}_6$ sample has been synthesized with the solid-state technique. Stoichiometric amounts of SrCO_3 , ReO_3 and Re (ReO_3/Re ratio is 5/1), and Cr_2O_3 were mixed and pressed into pellets. The pellets were heated at 1375°C during 2h in an atmosphere of $\text{Ar}/(\text{Ar}/\text{H}_2)$ in proportions 90/(9.8/0.2) with heating and cooling rates of $7^\circ\text{C}/\text{min}$. Scanning electron microscopy (SEM) was carried out using a field emission HITACHI S-4700 microscope. Quantitative chemical analysis has been performed by means of X-ray fluorescence using an ARL-advant XP wavelength sequential analyzer. X-ray diffraction was performed at room temperature with a D-Max Rigaku system with rotating anode. Neutron diffraction experiments in the temperature range 5K–710K were performed on the D1A instrument at the Institute Laue-Langevin

(Grenoble, France). Magnetization measurements up to 5 T in the temperature range 5K–800K were performed by using a SQUID magnetometer by Quantum Design. High-field magnetization measurements in the temperature range 4.2K–300K were performed at the pulsed-field facility of the IFW Dresden (Dresden, Germany), where magnetic fields up to 50 T are generated by a solenoid [15]. The magnetic field increases sinusoidally to a maximum field in 10ms then decreases sinusoidally to zero field in 10ms, followed by a small reverse field that allows the measurement of the sample coercivity. The sample magnetization is measured through the signal induced in a pick-up coil system described elsewhere [15].

Experimental results. – SEM images with secondary electrons show micrometric grains. Images taken with backscattered electrons, which tend to portray compositional information, demonstrate homogeneous composition. Stoichiometry analyses performed with the X-ray fluorescence equipment with wavelength sequential analyser indicates that the Cr/Sr ratio is 0.51 and the Re/Sr ratio is 0.48, which is very close to the expected 0.5 ratios and permits to conclude that the sample stoichiometry is the nominal one. The room temperature X-ray diffraction pattern reveals a main phase, $\text{Sr}_2\text{CrReO}_6$, with tiny impurities of Re and $\text{Sr}_{11}\text{Re}_4\text{O}_{24}$. Quantification of the patterns give 99.3(3)%, 0.05(1)% and 0.65(8)% for the double perovskite, metallic Re and $\text{Sr}_{11}\text{Re}_4\text{O}_{24}$ phases, respectively. The introduction of these tiny impurities is even not required for the successful fit of the neutron diffraction data at all temperatures. The nominal double-perovskite sample stoichiometry was used for the fits of X-ray and neutron diffraction.

In fig. 1(a) we show the room temperature X-ray diffraction pattern with the corresponding Rietveld refinement [16]. The fit is the best for a cubic double-perovskite structure of the compound, as previously reported by us [17] although Kato *et al.* [18] have reported a tiny tetragonal distortion at room temperature ($1 - a\sqrt{2}/c = -0.00096$), which is hardly distinguishable from the cubic structure. In our sample, we find a measurable tetragonal distortion only below 250K, the value of $1 - a\sqrt{2}/c$ at 200K being 0.00115. The most important parameter for the subsequent discussion is the amount of antisite disorder (Cr/Re disorder), which has been found to be $\approx 14\%$. The amount of antisite disorder is determined in the fit through the evaluation of the intensity of the full diffraction pattern, which contains several Bragg reflections that are influenced by this parameter. Some of these reflections in the cubic cell are (111), (113), and (331). In the inset of fig. 1(a) a close-up view of the data corresponding to the (111) Bragg reflection is shown together with simulations of the expected intensity of this reflection for different antisite concentrations and keeping fixed the rest of the fitting parameters. This figure nicely illustrates that the (111) Bragg reflection (and other reflections) is significantly sensitive to the antisite concentration, which allows

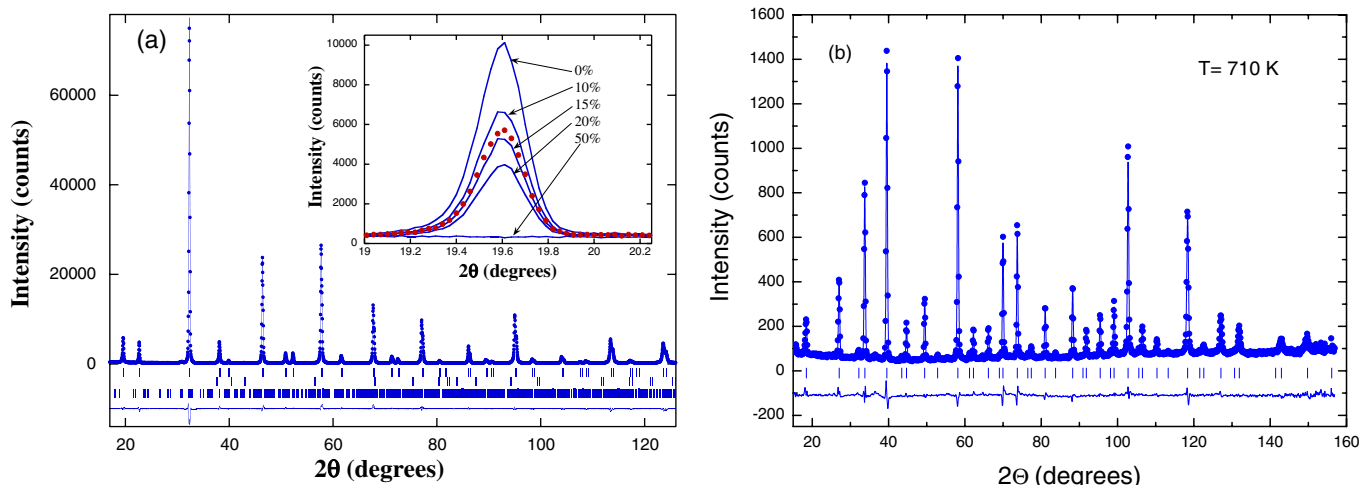


Fig. 1: (a) Rietveld refinement of the θ - 2θ X-ray diffraction data ($\lambda = 1.54 \text{ \AA}$) at room temperature. Experimental data (points) and fit (line) are plotted together with the difference (line at the bottom). Allowed reflections are marked in between. The first, second and third rows correspond, respectively, to the double-perovskite Sr₂CrReO₆ phase and the two impurity phases. The main peaks for the latter two phases are hardly noticed in the plot due to the small intensity. See table 1 for information on several fit parameters. Inset: zoom of the experimental data in the 2θ region 19° - 20.2° with corresponding simulations for AS concentration indicated in the figure (see text for details). (b) Data corresponding to the θ - 2θ neutron diffraction pattern ($\lambda = 1.39 \text{ \AA}$) taken at $T = 710 \text{ K}$ with the corresponding Rietveld refinement and residues. See table 2 for information on several fit parameters.

Table 1: Data (lattice parameter, temperature factor, cation occupancy, and fit reliability factors) obtained from the Rietveld refinement of the θ - 2θ X-ray diffraction pattern taken at room temperature and shown in fig. 1(a).

Space group	$Fm\bar{3}m$
a (\AA)	7.8152(1)
Sr at $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$	
B (\AA^2)	0.86(2)
Cr at $(0 \ 0 \ 0)$	
B (\AA^2)	0.39(3)
Occ. Cr/Re	86/14
Re at $(\frac{1}{2} \ 0 \ 0)$	
B (\AA^2)	0.06(3)
Occ. Cr/Re	14/86
O at $(x \ 0 \ 0)$	
x	0.2505(4)
B (\AA^2)	0.74(5)
R_{wp}	7.9
R_{Bragg}	4.2

reliable estimates of the amount of antisites. In order to have an independent measurement of the amount of antisite disorder, we have measured the neutron diffraction in the paramagnetic phase of this compound. In fig. 1(b) the experimental neutron diffraction data at $T = 710 \text{ K}$ and the corresponding fit is shown. The parameters extracted from the neutron fit at $T = 710 \text{ K}$ are included in table 2.

The obtained value at $T = 710 \text{ K}$ for the antisite disorder is $\approx 15.6\%$, in good agreement with the X-ray diffraction data. Similarly, the fit at $T = 2 \text{ K}$ produces antisite disorder of $\approx 16\%$. If we make the average of the antisite disorder content obtained from the X-ray and neutron diffraction fits, we can conclude that it is $\approx 15\%$ in our sample.

The main objective of the present investigation is to accurately determine the saturation magnetization of our sample. As a consequence, it is important to quantify the hypothetical contribution from ferromagnetic impurities. In fig. 2 we show magnetization isotherms of our Sr₂CrReO₆ sample in the paramagnetic phase. The curves are essentially linear in the whole field range as expected from the paramagnetic state with the exception of a very small non-linear contribution at low fields that can be ascribed to vanishing small ferromagnetic impurities. If, at all temperatures in the paramagnetic phase, we carry out a linear fit of the high-field data (0.5 to 2 T) we can estimate the magnetization coming from ferromagnetic impurities from the extrapolation of the linear fits to zero magnetic field. From this extrapolation we obtain the average magnetization value of 0.005 emu/gr for the ferromagnetic impurities, which is 2000 times smaller than the saturation magnetization expected for Sr₂CrReO₆. This allows us to rule out any significant influence of such ferromagnetic impurities in the saturation magnetization of our compound. In the inset of fig. 2 we show the magnetization data *vs.* temperature under an applied magnetic field of 1 T, which shows the onset of the ferromagnetic state at $T_C \approx 600 \text{ K}$, as previously observed [4,17].

Table 2: Data (lattice parameter, anisotropic and isotropic temperature factors, cation occupancy, cation-oxygen distances and angle, and fit reliability factors) obtained from the Rietveld refinement of the θ - 2θ neutron diffraction patterns taken at $T = 710$ K and shown in fig. 1(b).

Space group	$Fm\bar{3}m$
a (Å)	7.85309(14)
Sr at $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$	
$\beta_{11} = \beta_{22} = \beta_{33}$	0.0053(1)
B (Å ²)	1.3(1)
Cr at $(0 \ 0 \ 0)$	
$\beta_{11} = \beta_{22} = \beta_{33}$	0.0014(1)
B (Å ²)	0.3(1)
Occ. Cr/Re	84.4/15.6
Re at $(\frac{1}{2} \ 0 \ 0)$	
$\beta_{11} = \beta_{22} = \beta_{33}$	0.0014(1)
B (Å ²)	0.3(1)
Occ. Cr/Re	15.6/84.4
O at $(\frac{1}{2} \ 0 \ 0)$	
β_{11}	0.0024(2)
$\beta_{22} = \beta_{33}$	0.0067(1)
B (Å ²)	1.3(1)
Cr-O (Å)	1.976(3)
Re-O (Å)	1.951(3)
Cr-O-Re (°)	180.00(15)
AS (%)	15.6
Bragg R -factor	6.2
Chi ²	3.1

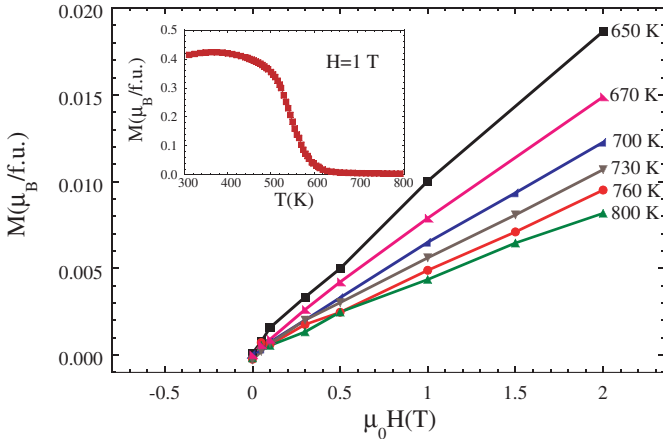


Fig. 2: Magnetization isotherms in the paramagnetic phase (lines are visual guides). The inset shows the magnetization *vs.* temperature measurement under 1 T applied magnetic field.

In order to measure the saturation magnetization in Re-based double perovskites, very high magnetic fields are required. This is evident from all previously reported magnetization hysteresis loops in Re-based

double perovskites, typically measured only up to 5 T [4,5,17,19–22]. The reason for this magnetically hard behavior (with large coercive and saturation fields) in Re-based double perovskites is thought to be the strong spin-orbit coupling on Re ions inducing high magnetic anisotropy [5,22]. In fig. 3 we show the magnetization results in $\text{Sr}_2\text{CrReO}_6$ obtained under pulsed magnetic fields up to 47 T, which allow for the first time a realistic evaluation of the saturation magnetization in a Re-based double perovskite. In fig. 3(a) the magnetization measurement under pulsed magnetic fields at 4.2 K is shown and compared with the data taken in a SQUID magnetometer at 5 K. The first piece of information extracted from this figure is that the standard measurements of the magnetization up to a few tesla are not sufficient to give precise values of the saturation magnetization in this compound. Whereas the magnetization is $\approx 0.85 \mu_B/\text{f.u.}$ at 5 T, the saturation magnetization is $\approx 0.95 \mu_B/\text{f.u.}$, this value being reached under applied magnetic fields beyond 20 T. The second piece of information drawn from this figure is the high value of the saturation magnetization, which is much higher than that expected in the ionic model if we take into account the amount of antisite disorder in our sample (15%). As explained before, the expected saturation magnetization in the ionic model or in models that do not include spin-orbit coupling is $1 \mu_B/\text{f.u.}$ in $\text{Sr}_2\text{CrReO}_6$ if we do not consider the influence of antisite disorder [10]. Nevertheless, the influence of antisite disorder is crucial in the saturation magnetization of double perovskites. The simplest model to describe such an influence is the assumption of a linear decrease of the saturation magnetization with the number of antisites and eventually the disappearance of spontaneous magnetization for the maximum level of antisites (50%). This leads to the mathematical expression $M_S = M_{ST} * (1 - 2 * AS) \mu_B/\text{f.u.}$, where M_{ST} is the theoretical saturation magnetization without the presence of antisites, and AS is the amount of antisites (ranging between 0 and 0.5). This assumption works fine in the case of $\text{Sr}_2\text{FeMoO}_6$ as explained in the introduction. The basis of this model is the existence of strong AFM exchange interactions between misplaced Fe atoms and their neighboring Fe atoms in regular sites, as discussed in ref. [5] and [23]. In $\text{Sr}_2\text{FeMoO}_6$ M_{ST} is $4 \mu_B/\text{f.u.}$ and the experimental value of MS with 15% antisite disorder is about $2.7 \mu_B/\text{f.u.}$, in close agreement with the prediction of this simple model: $2.8 \mu_B/\text{f.u.}$ [5,12]. Since the superexchange rules for Cr^{3+} and Cr^{4+} nearest neighbours in octahedral coordination foresee an AFM coupling [24] one can assume the same model in the case of $\text{Sr}_2\text{CrReO}_6$. Then, we expect the following dependence of the saturation magnetization in the ionic model: $M_S = 1 - 2 * AS \mu_B/\text{f.u.}$. For our sample, with $AS = 0.15$, we expect MS to be $0.7 \mu_B/\text{f.u.}$, which is a value much smaller than the experimental one, $0.95 \mu_B/\text{f.u.}$. The difference is significant (36%), which gives confidence to conclude that the saturation magnetization predicted by the ionic model is much lower than the real one. If we use the prediction

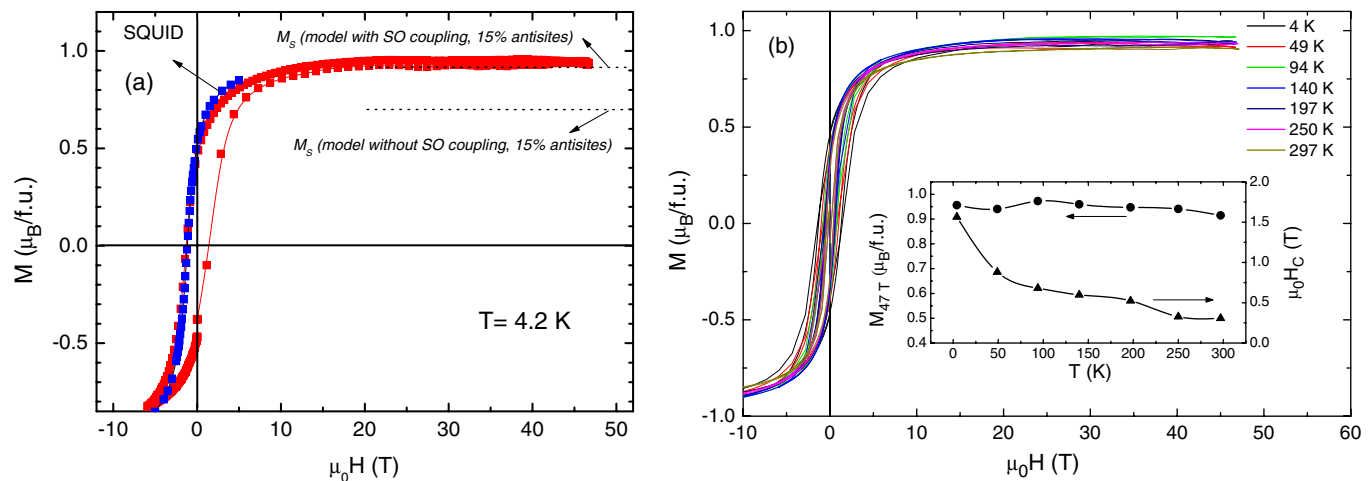


Fig. 3: (a) Magnetization *vs.* applied magnetic field at $T = 4.2\text{ K}$ measured with a SQUID magnetometer up to 5 T and with pulsed magnetic fields up to 47 T. The dashed lines show the expected saturation magnetization value with Cr/Re antisite disorder of 15% in a simple model without spin-orbit (SO) coupling as well as in a model with SO coupling. (b) Magnetization *vs.* applied magnetic field (up to 47 T) at temperatures ranging between 4.2 K and 297 K. The inset shows the saturation magnetization and the coercive field *vs.* temperature extracted from such measurements.

of the DFT calculation that takes into account the spin-orbit coupling in Re ions, the saturation magnetization for a $\text{Sr}_2\text{CrReO}_6$ sample without antisites should be $1.3 \mu_{\text{B}}/\text{f.u.}$ [10] and the following dependence with the antisite content is expected if the above-mentioned model is assumed: $M_S = 1.3 * (1 - 2 * \text{AS}) \mu_{\text{B}}/\text{f.u.}$ For a sample with $\text{AS} = 0.15$, which is our case, the prediction would be $M_S = 0.91 \mu_{\text{B}}/\text{f.u.}$, in good agreement with the experimental value. Thus, our measurements strongly suggest the necessity of incorporating the spin-orbit coupling in the description of the physics of $\text{Sr}_2\text{CrReO}_6$, including the magnetization. The Re orbital moment has been predicted and found to be parallel to the Fe spin moment and antiparallel to the Re spin moment [7,8,10], which explains why the actual saturation magnetization is larger than previously considered.

In fig. 3(b) we show the set of magnetization measurements at several temperatures. The coercive field increases from 0.31 T at room temperature up to 1.56 T at 5 K. Apart from the usual increase of the coercive field in ferromagnetic materials when decreasing the temperature due to the weakening of thermal assistance in magnetization reversal, it seems that an additional mechanism is contributing to this sizeable change. This mechanism can be the lowering of the crystal symmetry from cubic to tetragonal below room temperature in $\text{Sr}_2\text{CrReO}_6$ as previously observed by neutron diffraction [17]. Due to the strong magnetostructural coupling in Re-based double perovskites, it is very likely that this structural change contributes to the increase of the magnetic anisotropy and, as a consequence, of the coercivity, as previously found in A_2FeReO_6 [22]. On the other hand, the saturation magnetization is less dependent on temperature. It slightly increases from $0.91 \mu_{\text{B}}/\text{f.u.}$ at room temperature up to $0.95 \mu_{\text{B}}/\text{f.u.}$ at 5 K.

Discussion and conclusions. – The available data on ferromagnetic double-perovskites strongly suggest that whereas the intuitive ionic picture not including spin-orbit coupling effects is a good approximation to the description of the involved physics in the case of Mo-based compounds, this is not the case for Re-based compounds. The current magnetization measurements under high fields are a beautiful demonstration of the breakdown of the intuitive ionic picture in $\text{Sr}_2\text{CrReO}_6$. Until now, it had been taken for granted that the experimental saturation magnetization of ferromagnetic double-perovskites should meet the predictions of the ionic model, which actually does not hold true for $\text{Sr}_2\text{CrReO}_6$ and probably for other Re-based and W-based double-perovskites. This makes the physics of Re-based and W-based double-perovskites much richer than that of their Mo-based counterparts as we discuss hereafter.

One of the main differences between Re-based and Mo-based compounds is the significant orbital moment existing in Re-based compounds (of the order of 1/3 of the spin moment on Re ions) as predicted in theoretical models [9,10] and clearly demonstrated by X-ray magnetic circular dichroism measurements [7,8]. The origin of the Re orbital moment is the strong spin-orbit coupling in the heavy Re ions due to the unfilled $5d$ states. The existence of strong orbital moments in Re-based compounds opens up the possibility of strong magnetostructural effects due to the coupling between the spin and lattice degrees of freedom. Evidence for interesting magnetostructural effects has been recently given for a few Re-based compounds [5,21,25,26]. The recently reported $\text{Sr}_2\text{CrOsO}_6$ double-perovskite compound, with $T_C = 725\text{ K}$, also presents significant orbital effects [27].

In the light of the current results, we can also discuss the potentiality of Re-based compounds compared to

Mo-based compounds in the field of spin electronics. On the one hand, the spin polarization at the Fermi level of Re-based compounds is predicted to be lower than that of the Mo-based counterparts, which are thought to be half metals (100%) [2]. For example, $\text{Sr}_2\text{CrReO}_6$ is predicted to have spin polarization of 86% [10] and their performance in magnetoelectronics would decrease with respect to Mo-based compounds. However, the higher Curie temperature of Re-based compounds is still attractive for applications above room temperature. On the other hand, the orbital effects seem to be at the basis of the higher magnetic anisotropy and coercivity of Re-based compounds. Whereas, this is detrimental for low-field intergrain magnetoresistance achievable with polycrystalline samples, it can be an advantage for their integration as magnetically hard electrodes in magnetic tunnel junctions [5].

In conclusion, we have studied the magnetization up to very high magnetic field of a $\text{Sr}_2\text{CrReO}_6$ sample with $\approx 15\%$ antisite defects. The obtained result is that the saturation magnetization is much larger than that one predicted by the intuitive ionic model that does not take into account the Re orbital moment, which seems not to be valid for this compound and, in general, for Re-based double perovskites. In contrast, the existing theoretical calculations including the spin-orbit coupling at Re ions seem to describe better the experimental results. The breakdown of the ionic model is connected to the large Re orbital moment, which is significant in Re-based double perovskites, and consequently in $\text{Sr}_2\text{CrReO}_6$. Implications of these results for the physics of Re-based compounds have been discussed, in particular concerning magnetostructural effects and application of these compounds in the field of spin electronics.

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