

Magnetic phase transitions and iron valence in the double perovskite $\text{Sr}_2\text{FeOsO}_6$

Peter Adler · Vadim Ksenofontov ·
Avijit Kumar Paul · Manfred Reehuis ·
Binghai Yan · Martin Jansen · Claudia Felser

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Abstract The insulating and antiferromagnetic double perovskite $\text{Sr}_2\text{FeOsO}_6$ has been studied by ^{57}Fe Mössbauer spectroscopy between 5 and 295 K. The iron atoms are essentially in the Fe^{3+} high spin ($t_{2g}^3e_g^2$) and thus the osmium atoms in the Os^{5+} (t_{2g}^3) state. Two magnetic phase transitions, which according to neutron diffraction studies occur below $T_N = 140$ K and $T_2 = 67$ K, give rise to magnetic hyperfine patterns, which differ considerably in the hyperfine fields and thus, in the corresponding ordered magnetic moments. The evolution of hyperfine field distributions, average values of the hyperfine fields, and magnetic moments with temperature suggests that the magnetic state formed below T_N is strongly frustrated. The frustration is released by a magneto-structural transition which below T_2 leads to a different spin sequence along the c -direction of the tetragonal crystal structure.

Keywords Double perovskites · Magnetic properties · Spin frustration · 57-iron Mössbauer spectroscopy

Proceedings of the 32nd International Conference on the Applications of the Mössbauer Effect (ICAME 2013) held in Opatija, Croatia, 1–6 September 2013.

P. Adler (✉) · A. K. Paul · B. Yan · M. Jansen · C. Felser
Max-Planck-Institut für Chemische Physik fester Stoffe, 01187 Dresden, Germany
e-mail: adler@cphys.mpg.de

V. Ksenofontov · C. Felser
Institut für Anorganische Chemie, Johannes Gutenberg-Universität, 55128 Mainz, Germany

A. K. Paul · M. Jansen
Max-Planck-Institut für Festkörperforschung, 70569 Stuttgart, Germany

M. Reehuis
Helmholtz-Zentrum für Materialien und Energie, 14109 Berlin, Germany

1 Introduction

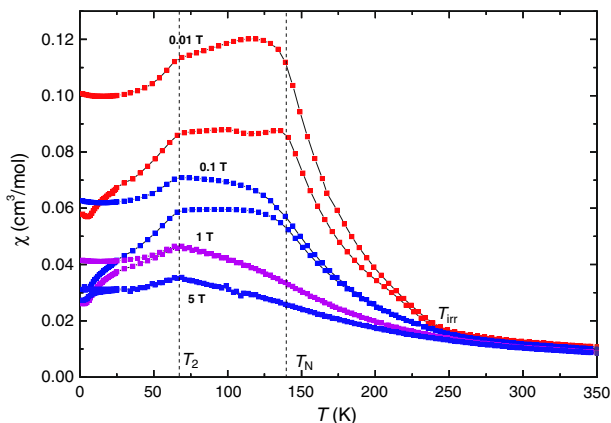
Since the discovery of large tunnelling magnetoresistance (TMR) effects in the half-metallic ferromagnetic double perovskites $\text{Sr}_2\text{FeMoO}_6$ [1] and $\text{Sr}_2\text{FeReO}_6$ [2] there has been renewed interest in the magnetic and electronic properties of other transition metal (TM) double perovskites with the general formula $A_2BB'O_6$. In the double perovskite structure the TM sites are atomically ordered and every B site is connected via the intervening oxygen atoms only with B' sites and vice versa. In particular materials with a combination of an electronically strongly correlated $3d$ element on the B and a weaker correlated $4d$ or $5d$ element on the B' site may allow a tuning of properties via adjustment of interactions like double-exchange, superexchange, and spin-orbit coupling. For iron-based double perovskites the availability of ^{57}Fe Mössbauer spectroscopy is particularly appealing as it is a sensitive probe for the local magnetic order, the valence states of iron, structural distortions and antisite disorder which is frequently present in such materials.

Recently we have synthesized $\text{Sr}_2\text{FeOsO}_6$ which crystallizes in the tetragonal space group $I4/m$ and is an antiferromagnetic semiconductor with two magnetic phase transitions near $T_N \sim 140$ K and $T_2 \sim 67$ K, respectively [3]. This is in contrast to the metallic Re analogue $\text{Sr}_2\text{FeReO}_6$ and to the semiconducting Cr analogue $\text{Sr}_2\text{CrOsO}_6$ [4] which has attracted considerable interest as it turned out to be a ferrimagnetic insulator with an exceptionally large Curie temperature T_C of 725 K. Its insulating ground state is attributed to a completely filled minority spin Os $t_{2g}(t_{2g}^3)$ band which is separated from the empty minority spin Cr t_{2g} and majority spin states by an energy gap [4, 5]. There is still no consensus about the nature of the interactions which are responsible for achieving such high T_C 's in an insulating double perovskite [6, 7]. In the spin structure of $\text{Sr}_2\text{CrOsO}_6$ all nearest neighbour Cr^{3+} and Os^{5+} moments are ferrimagnetically aligned which leads to ferromagnetic alignment of all Cr^{3+} moments. Our recent neutron diffraction studies have shown that, similarly, ferrimagnetic layers of Fe^{3+} and Os^{5+} sites occur in the spin structures of $\text{Sr}_2\text{FeOsO}_6$ [8]. However, the spins align in two different ways along the c -direction of the tetragonal crystal structure which leads to an overall cancellation of the magnetic moments. Two magnetic phase transitions are clearly verified by neutron powder diffraction and ^{57}Fe Mössbauer experiments on $\text{Sr}_2\text{FeOsO}_6$ [8]. In this contribution we will present the temperature dependent ^{57}Fe Mössbauer spectra in detail in order to unravel the nature of the unusual magnetic phase transitions in $\text{Sr}_2\text{FeOsO}_6$.

2 Experimental

The synthesis, basic structural, and physical characterization of $\text{Sr}_2\text{FeOsO}_6$ as well as the determination of the spin structures have been described elsewhere [3, 8]. ^{57}Fe Mössbauer spectra of powdered samples have been measured between 5 and 295 K with a conventional Mössbauer spectrometer ($^{57}\text{Co}/\text{Rh}$ source) operating in the constant acceleration mode. The sample was placed into an Oxford flow cryostat. The data were analyzed with the program Recoil [9] using, depending on the spectra, a Voigt based fitting algorithm for obtaining hyperfine field distributions, Lorentzian lines, or an exact lineshape analysis. All isomer shifts are referred to α -iron.

Fig. 1 Magnetic susceptibilities of $\text{Sr}_2\text{FeOsO}_6$ obtained at various magnetic fields [3]. The *dashed lines* indicate the magnetic phase transitions as determined from the neutron diffraction data [8]

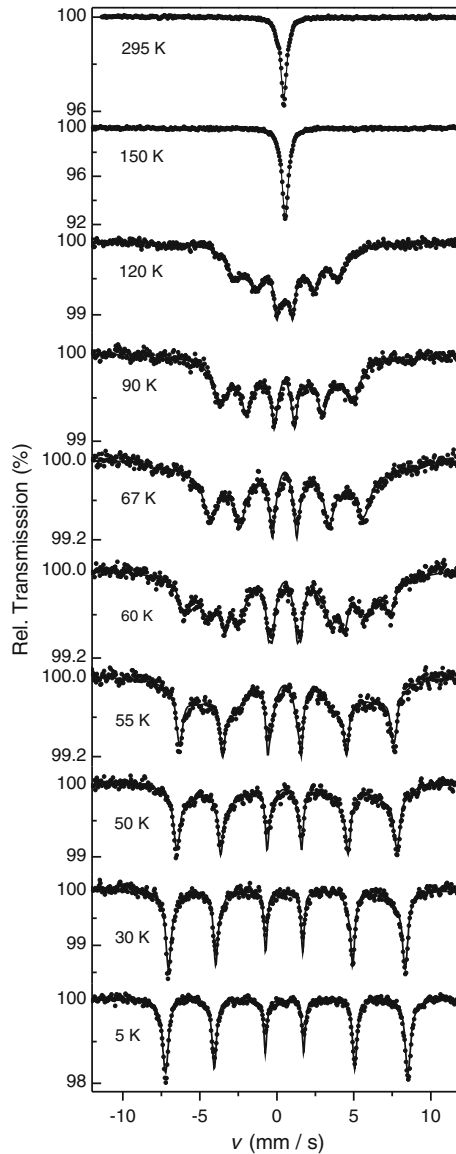


3 Results and discussion

For comparison with the Mössbauer spectra we first show the magnetic susceptibilities of $\text{Sr}_2\text{FeOsO}_6$ obtained at different magnetic fields under zero-field cooling (ZFC) and field-cooling (FC) conditions (Fig. 1). The shape of the susceptibility curves $\chi(T)$ changes considerably with increasing field strength. At the lowest field of 0.01 T the ZFC $\chi(T)$ curve shows a broad hump with downturns below $T_N = 140$ K and $T_2 = 67$ K, respectively. Specific heat measurements confirmed that the anomalies near these temperatures correspond to phase transitions [3]. In the high temperature range above 250 K a Curie-Weiss like behavior with positive Θ -parameter was found ($\Theta = +80$ K at 1 T). Below $T_{\text{irr}} \sim 250$ K a sudden increase in $\chi(T)$ occurs and the $\chi(T)$ curves recorded under ZFC and FC conditions start to deviate from each other. The transition near T_N appears to be suppressed successively with increasing magnetic field and T_{irr} is shifted to lower temperatures. On the other hand, the transition at T_2 becomes sharper. The shapes of the $\chi(T)$ curves suggest that overall antiferromagnetic ordering occurs, but the magnetism is determined by competing ferro- and antiferromagnetic interactions, which possibly lead to magnetic frustration effects.

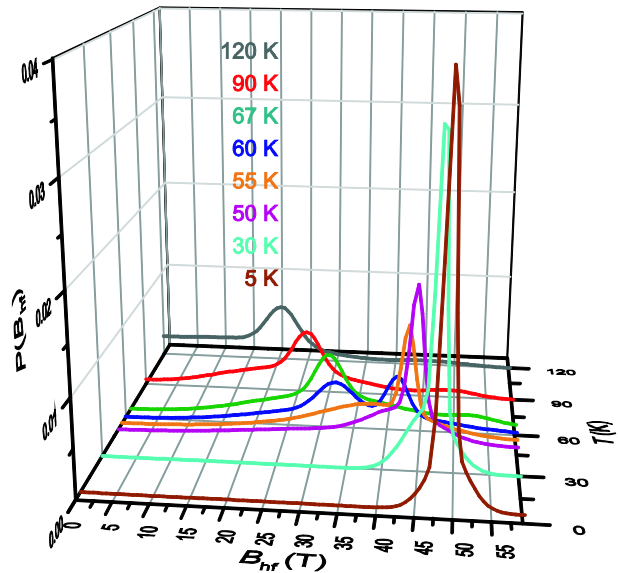
The ^{57}Fe Mössbauer spectra recorded between 5 and 295 K without magnetic field (Fig. 2) confirm that two magnetic phase transitions occur. At 295 K and 150 K essentially a single line spectrum is found, which evidences that $\text{Sr}_2\text{FeOsO}_6$ is paramagnetic in this temperature range. Any magnetic clusters below 250 K, the formation of which, may be indicated by the shape of the $\chi(T)$ curve, must be rapidly relaxing on the Mössbauer time scale. The absence of an apparent quadrupole splitting is in agreement with the nearly cubic crystal structure in the paramagnetic phase ($cla = 1.006$ at 295 K) [8]. A weak shoulder in the low velocity region of the single line, being most apparent at 295 K, can be taken into account by an additional single line subspectrum with an isomer shift $IS = 0.00(7)$ mm/s and an area fraction of 5(3) %. The small IS value suggests that the signal corresponds to Fe^{4+} arising from a minor SrFeO_3 impurity which is chemically reasonable as the sample was annealed at an oxygen pressure of 120 MPa [3]. Between 67 and 150 K the Mössbauer spectra are indicative of a single but quite broad hyperfine pattern. We have modeled the spectra by a distribution of hyperfine fields B_{hf} with two

Fig. 2 Mössbauer spectra of $\text{Sr}_2\text{FeOsO}_6$ measured without external field in the temperature range 5–295 K



components, a broad one with a width ΔB_{hf} of ~ 10 T and a more narrow one. At 60 K an additional even narrower hyperfine sextet with increased hyperfine splitting occurs, which is taken into account by a further component in the B_{hf} distribution. Fitting the spectrum at 60 K with two independent phases leads to equal isomer shifts within the error limits. Accordingly, all spectra were evaluated with a single IS and also a with a single quadrupole splitting parameter ε . Down to 30 K phase coexistence is observed in the Mössbauer spectra, but the signals corresponding to the residual AF1 phase are broad. The evolution of the B_{hf} distribution with temperature is shown in Fig. 3. The spectrum at 5 K can be fitted by a hyperfine

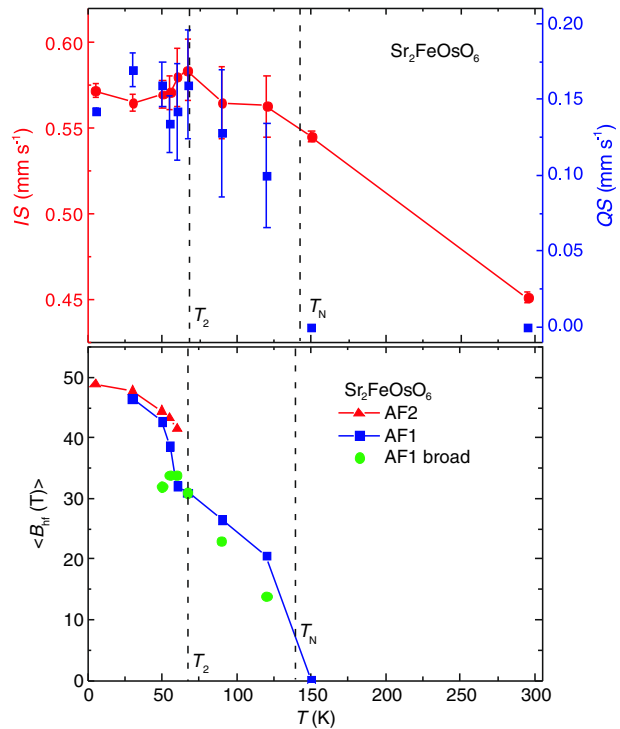
Fig. 3 Evolution of the hyperfine field distribution with temperature in the range 120 K (*back*) to 5 K (*front*) as obtained from the evaluation of the spectra depicted in Fig. 2



field distribution as well, but it is also possible to describe the spectra by a single quite sharp hyperfine sextet. The neutron diffraction data of $\text{Sr}_2\text{FeOsO}_6$ suggest that a residual fraction of about 15 % AF1 phase persists even at 2 K [8]. The absence of a separate sextet in the 5-K Mössbauer spectrum evidences that the magnetic moments of the two phases become equal at low T . This is in agreement with the evolution of the average hyperfine fields B_{hf} with temperature (Fig. 4 bottom). Below $T_N = 140$ K, B_{hf} increases only smoothly to about 30 T at 67 K. Below 67 K, where transformation into AF2 occurs, the B_{hf} value of the residual AF1 phase successively approaches the larger B_{hf} of AF2. Since $\text{Sr}_2\text{FeOsO}_6$ is a nearly cubic magnetic material the hyperfine field is essentially determined by the Fermi contact interaction and follows the ordered magnetic moment at the iron site. In fact, the total magnetic moments derived from the powder neutron diffraction data [8] show a very similar temperature dependence with moment values of $1.8 \mu_B$ at 75 K and $3.4 \mu_B$ at 2 K, respectively. Thus both, the Mössbauer and the neutron data are evidence for an unusual temperature evolution of the magnetic moment which does not follow a simple critical law. A further peculiarity is a pronounced magneto-elastic coupling which accompanies the formation of the AF1 phase below T_N and leads to an increase of the tetragonal distortion c/a from 1.006 at 295 K to 1.017 at 2 K [8]. Here, c corresponds to the pseudo-cubic unit cell. The increased structural distortion is also reflected in the Mössbauer spectra, where in contrast to the paramagnetic phase, below T_N a quadrupole interaction is observed (Fig. 4, top). Since the crystal structure is tetragonal, and the spins are aligned along c , the quadrupole splitting QS amounts to $2|\varepsilon|$, where $\varepsilon = e^2 V_{zz} Q/4$. For instance, $QS = 0.14$ mm/s at 5 K.

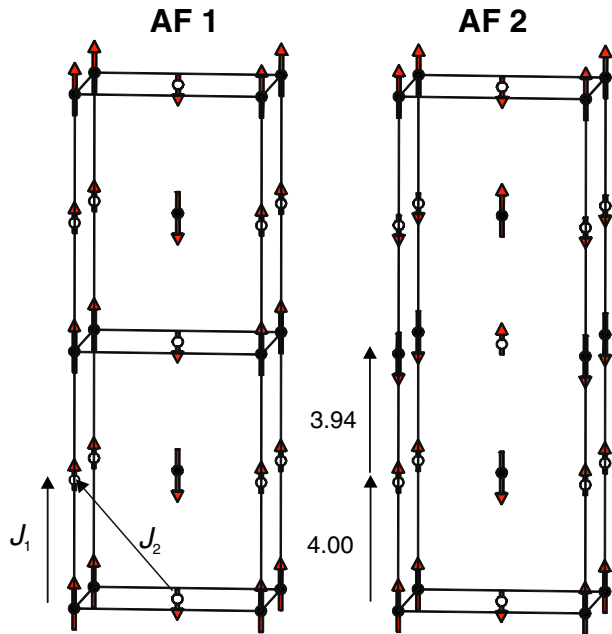
Before discussing the magnetic phase transitions in more depth, we consider the iron oxidation state based on the Mössbauer isomer shifts. The IS values of 0.45 mm/s at 295 K and 0.57 mm/s at 5 K are in the upper range of values which is typical for Fe^{3+} . This suggests that the metal ions in SrFeOsO_6 can be essentially described as Fe^{3+} ($t_{2g}^3 e_g^2$) and Os^{5+} (t_{2g}^3) sites, respectively. Also $B_{hf} = 49$ T at 5 K is in agreement

Fig. 4 Temperature dependence of isomer shifts IS (spheres) and quadrupole splittings QS (squares) and of the average hyperfine fields $\langle B_{\text{hf}} \rangle$ as derived from fits of the Mössbauer spectra. Solid lines are guides for the eye



with Fe^{3+} . The presence of Fe^{4+} in $\text{Sr}_2\text{FeOsO}_6$, which has been suggested recently [10], would give rise to much smaller IS and B_{hf} values, and thus can be discarded. It is instructive to compare the IS values of $\text{Sr}_2\text{FeOsO}_6$ with those of related iron containing double perovskites. In Sr_2FeWO_6 divalent localized $\text{Fe}^{2+}(t_{2g}^3 e_g^2)$ occurs as is apparent from $IS = 1.2$ mm/s and the concomitant large quadrupole splitting $QS \sim 2$ mm/s at 20 K [11]. Accordingly, tungsten must be in the hexavalent W^{6+} state. On the other hand, $IS = 0.71$ mm/s at 77 K suggests that $\text{Sr}_2\text{FeReO}_6$ is an intermediate valence material [12, 13], similar as the prototypical $\text{Sr}_2\text{FeMoO}_6$ [14]. Obviously, the ferromagnetic metallic state is associated with iron mixed-valency which is in agreement with the model of a double-exchange like, hybridization driven delocalization of t_{2g} minority spin electrons in a hybridized Fe-O- B' band [15, 16]. The delocalization of the minority spin t_{2g} electrons leads to additional d -electron density at the iron sites and thus to an increased IS compared to Fe^{3+} . On the other hand, in $\text{Sr}_2\text{FeOsO}_6$ IS is by about 0.15 mm/s smaller which indicates a less pronounced hybridization between Fe t_{2g} and Os t_{2g} than between Fe t_{2g} and Re t_{2g} states. Indeed, our electronic structure calculations on $\text{Sr}_2\text{FeOsO}_6$ [3] revealed an energy gap between the filled Os $t_{2g}(t_{2g}^3)$ and the empty Fe t_{2g} and Os e_g states, which is in agreement with the presence of Fe^{3+} and Os^{5+} . Thus, the Mössbauer isomer shift is a sensitive probe for the variable electronic situation at the Fe sites in iron-containing double perovskites. In the series $\text{Sr}_2\text{Fe}B'\text{O}_6$ where B' is a $5d$ transition element, the trend in IS reflects the successive stabilization of the B' t_{2g} orbitals relative to the Fe t_{2g} orbitals from W to Re to Os. In $\text{Sr}_2\text{FeReO}_6$ these orbitals are quite close in energy and thus the hybridization is largest which allows stabilization of

Fig. 5 Illustration of the spin structures of the two magnetic phases of $\text{Sr}_2\text{FeOsO}_6$ as determined from neutron powder diffraction experiments [8]. The nearest neighbour Fe-Os and next nearest neighbour Os-Os exchange interactions J_1 and J_2 along c are indicated at the left. The alternation of Fe-Os distances for AF2 is shown at the right. The distances given in Å are obtained from DFT calculations [8]



the ferromagnetic metallic state. The fact that IS for $\text{Sr}_2\text{FeOsO}_6$ is quite high for an Fe^{3+} oxide may imply that the hybridization mechanism still contributes somewhat to the balance of interactions [6]. The temperature dependence of IS follows the trend expected from the second-order Doppler shift (Fig. 4, top). As there is no major anomaly in IS near T_2 any change of the iron valence state can be excluded.

Coming now back to the magnetic phase transitions, in Fig. 5 we display the magnetic structures of $\text{Sr}_2\text{FeOsO}_6$ as determined from the neutron diffraction experiments [8]. Below $T_N = 140$ K an overall antiferromagnetic spin structure is formed, where subsequent ferrimagnetic Fe-Os layers are aligned with parallel spins along c (AF1). Below $T_2 = 67$ K this spin structure switches into another one with an alternating sequence of antiparallel and parallel pairs of Fe and Os moments (AF2). The gradual evolution of the average hyperfine fields and corresponding magnetic moments with decreasing T suggests that the magnetic order in AF1 is still incomplete. This is further supported by the evolution of the hyperfine field distribution with temperature (Fig. 3). Between 67 and 140 K, that is in the temperature region of the AF1 spin structure, the B_{hf} distribution shows a well-defined maximum, but it is broad with a width of the order 10 T. At 60 K the sextet assigned to the emerging AF2 phase has a larger B_{hf} and is already sharper than the AF1 signal, though still somewhat broadened. On lowering the temperature the AF2 sextet sharpens further and the residual AF1 signal merges with the AF2 pattern. These observations suggest the following scenario: Below T_N the ordered AF1 phase starts to form, but the coherence length of the ordered regions is still quite small. Possibly there is a distribution in the sizes of the ordered regions and therefore a distribution in Néel temperatures and spin relaxation times. This is the origin of the broad Mössbauer patterns in this temperature range. The sharper spectra in the AF2 phase suggest an enhanced coherence length of the ordered regions. While the

B_{hf} value of 49 T at 5 K approaches the range of values which is typical for Fe^{3+} ($S = 5/2$), the magnetic moment of $3.4 \mu_{\text{B}}$ at 2 K is still much smaller than the fully ordered Fe^{3+} moment of $5 \mu_{\text{B}}$. In contrast to the local Mössbauer probe, neutron diffraction averages over larger sample regions. Accordingly, the quite low magnetic moment suggests that there is still a considerable degree of spin disorder. The behaviour of $\text{Sr}_2\text{FeOsO}_6$ is to some extent comparable to that of the geometrically frustrated double perovskite Sr_2YRuO_6 where two anomalies near $T_1 = 32$ K and $T_2 = 24$ K were found [17]. It was suggested that below T_1 a partially ordered magnetic state emerges, while full magnetic order is reached below T_2 . Although we have no spectra in the direct vicinity of T_N , our ^{57}Fe Mössbauer spectra between 67 and 120 K show some resemblance with the shape of ^{99}Ru Mössbauer spectra of Sr_2YRuO_6 [18] in the vicinity of T_2 . These spectra have been analysed within two models, namely a static hyperfine field distribution model and a model considering random spin fluctuations. In Sr_2YRuO_6 there is only one fcc-like lattice with magnetically active frustrated Ru sites, whereas in $\text{Sr}_2\text{FeOsO}_6$ both Fe and Os carry magnetic moments which are located at two interpenetrating fcc-like lattices. This leads to a more complex situation with a larger number of potentially competing exchange interactions.

The irreversibilities in the magnetic susceptibility curves, the gradual evolution of magnetic moments [8] and the shape of the Mössbauer hyperfine patterns suggest frustration of the exchange interactions in the AF1 structure, which is at least partly released by switching into the AF2 spin structure. This view is corroborated by our band structure calculations on both, the AF1 and the AF2 phase [3, 8] which suggest that the AF2 spin structure is stabilized with respect to AF1 by a structural modulation which results in alternation of shorter and larger Fe - Os distances (Fig. 5). This is expected to modulate the ratio J_1/J_2 of the nearest neighbour Fe-Os and next nearest neighbor Os-Os exchange interactions and finally leads to the formation of the more relaxed AF2 structure.

4 Conclusions

Our ^{57}Fe Mössbauer studies on the insulating double perovskite $\text{Sr}_2\text{FeOsO}_6$ together with neutron diffraction and electronic structure studies [8] yield a detailed insight into the complex magnetism of this system. A subtle interplay between spin, orbital, and lattice degrees of freedom fine-tunes the balance of competing exchange interactions in $\text{Sr}_2\text{FeOsO}_6$ and leads to the formation of two antiferromagnetic spin structures below 140 K and 67 K. This in contrast to the related ferrimagnetic Cr-analogue $\text{Sr}_2\text{CrOsO}_6$. We have provided evidence that frustration effects in the AF1 structure are relaxed in the AF2 phase which is stabilized by a structural modulation.

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