Magnetic and magnetoelectric properties of AFeF$_5$ ($A = $ Ca, Sr) spin-chain compounds

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Abstract
Fluorides in general are characterized by big variety of crystal structures, whereas those containing transition metals also often show sizable magnetic properties. The tendency of fluorine to form linear chain structures in many cases results in low-dimensional magnetism. Despite the plethora of magnetic phenomena in fluorides, their magnetoelectric properties are less studied than those of oxides. In the present work we theoretically study the magnetic and magnetoelectric properties of spin-chain compounds CaFeF$_5$ and SrFeF$_5$. The density functional theory is employed for determination of magnetic exchange constants, which are then used in Monte Carlo calculations. The symmetry analysis reveals that CaFeF$_5$ does not show magnetoelectric properties, whereas SrFeF$_5$ is a multiferroic.

Keywords: CaFeF$_5$, SrFeF$_5$, low-dimensional magnetism, spin chains, multiferroic, magnetoelectric, fluorides

1. Introduction
Multiferroics and specifically magnetoelectrics continue to be one of the focal points in condensed matter physics due to promising practical applications. Combination of magnetic and electric properties in a single material opens up new opportunities for creating various sensors, logical elements, or spin electronic devices [1]. However, interacting magnetic and electric subsystems are also of fundamental interest. In magnetism low-dimensional systems continue to serve as playground to explore exotic quantum phenomena such as spin liquids, Bose-Einstein condensation, or spin-Peierls transition [2]. Such quantum phenomena can be easily tuned, changed, or completely destroyed by small external influences. Vast experimental data on magnetoelectric compounds allows concluding that interaction of magnetic and electric subsystems is frequent for both simple or more complex magnetic orderings. Therefore, exploiting the electric subsystem as a means for tuning the magnetic subsystems via, e.g., application of external electric field, can significantly extend the plethora of magnetic phenomena in low-dimensional systems or potentially result in new effects.

Fluoride compounds offer unique opportunities for low-dimensional magnetic systems, because fluorine exhibits strong preference for linear bridging modes, which can provide the necessary topology. A great number of fluoride inorganic compounds have been synthesized and studied to date, ranging from 0D to 3D connectivity of MF$_x$ polyhedra surrounding the metal $M$ [3,4]. Even when the magnetic network has three-dimensional character, the magnetic interactions are often anisotropic leading to low-dimensional magnetism.

Many fluoride compounds have already been shown to exhibit multiferroic properties and the available experimental data were summarized in a recent review [5], however most of the compounds are the, so-called, type-I multiferroics with magnetic and electric subsystems ordering independently [6]. Therefore, from our point of view searching for new fluoride type-II multiferroic compounds, which have stronger magnetoelectric coupling than type-I compounds, can be fruitful because (i) fluorides have diverse compositions and crystal structures, (ii) in many cases the exchange coupling in them is high, and (iii) low-dimensional magnetism in combination with magnetoelectric phenomena can potentially result in new physics.

In this work we theoretically study the magnetic and possible magnetoelectric phenomena in spin-chain compounds CaFeF$_5$ and SrFeF$_5$. We find the magnetic exchange constants using the density functional theory, which are then used in Monte Carlo calculations. Supplemented with the symmetry analysis, the study reveals the magnetic and magnetoelectric properties of these fluorides.

2. Methods

We performed density functional theory (DFT) calculations using the Vienna Ab-initio Simulation Package (VASP) [7] and the projected augmented wave method [8]. The generalized gradient approximation (GGA) of exchange correlation corrected by means of the GGA+U formalism for the Fe atoms with $U_{eff} = U - J = 3$ eV was used within the Dudarev approach [9]. The energy cutoff was 500 eV, whereas the Brillouin zone integration was done using the Monkhorst-Pack scheme.

The crystal structure relaxation was done using the stopping criterion for absolute values of forces on atoms of $10^{-3}$ eV/Å. For the determination of exchange constants spin polarized
collinear calculations were used and the Hamiltonian was fitted to relative total energies of different collinear magnetic structures. The obtained exchange constants were used in classical Monte Carlo (MC) simulations of the Hamiltonian

\[ H = \sum_{ij} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \sum_j \left( D_{xx} S_{xj}^2 + D_{yy} S_{yj}^2 + D_{zz} S_{zj}^2 \right), \] (1)

where \( \mathbf{S} \) are classical vectors of unit length and \( D_{\alpha} \) (\( \alpha = x, y, z \)) are anisotropy constants. In the Hamiltonian Eq. (1) we account only for the anisotropy terms \( D_{\alpha} \neq 0 \), which we consider being the same for all spins, pursuing a minimal model to characterize the magnetic structure. The Metropolis scheme was used for MC simulations and the size of the simulation box was chosen large enough as to not influence significantly the results (typically larger than \( 15 \times 15 \times 15 \) unit cells). After each change of temperature the system was allowed to relax for \( 5 \times 10^3 \) Monte Carlo steps per spin (MCS), whereas the statistical information was subsequently gathered over the next \( 10^4 \) MCS. The crystal and magnetic structures in this work were visualized using the software VESTA [10].

3. Crystal structure and magnetic exchange interactions

The compounds with the general chemical formula \( A^{2+} M^{3+} F_5 \) (\( A = \text{Ca, Sr, Ba}; M = \text{transition metal} \)) present many examples of 1D chain structures, which contain isolated \((MF_5)_n\) chains of octahedra. The arrangement of infinite chains depends on the ionic radii of both \( A^{2+} \) and \( M^{3+} \) and several structural types have been found [11]. \( \text{CaFeF}_5 \) and \( \text{CaCrF}_5 \) present two structural types, in which the \( MF_5 \) octahedra are linked via opposite \((\text{trans-})\)corners and the main difference is in the positions of \( Ca^{2+} \) ions. Several other fluorides, e.g., \( \text{CaVF}_5 \) and \( \text{CaTiF}_5 \), crystallize in the structure of \( \text{CaCrF}_5 \), whereas the structure of \( \text{CaFeF}_5 \) is also shared by, e.g., \( \text{CdCrF}_5 \) and \( \text{CdGaF}_5 \) [11].

In contrast to the \( \text{CaFeF}_5 \) and \( \text{CaCrF}_5 \) structures, in which the chains of \( Fe^{3+} \) ions are almost or completely linear (177.8° and 180°, respectively), the \( \text{SrFeF}_5\)-type structure contains helicoidal \((\text{FeF}_5)_n\) chains, and the octahedra are connected by corners in the \( \text{cis}-\)position [12]. Two octahedral chains with opposite rotations are present in the structure. To this structural type belong also \( \text{SrVF}_5, \text{SrCoF}_5, \) and \( \text{SrTiF}_5 \).

The crystal structures of \( \text{CaFeF}_5 \) and \( \text{SrFeF}_5 \) are shown in Figs. 1(a,d). Tables A.1 and A.2 present the lattice parameters and atomic positions obtained by DFT calculations in comparison with the experimental results taken from literature. Overall we obtain good correspondence with the experimental results with lattice parameters difference of not more than 1.5% [12] [13].

We restrict the DFT calculations of magnetic exchange constants \( J_i \) of \( \text{CaFeF}_5 \) to eleventh nearest neighbor (NN). The exchange paths in \( \text{CaFeF}_5 \) are shown in Figs. 1(b,c). Thus, the largest distance between the \( Fe^{3+} \) ions, for which the exchange...
constant is determined corresponds to next nearest neighbors (NNN) within the chains. The obtained values of $J_i$ ordered with respect to increasing distance between the spins are given in Table 1. It can be found that $J_1$ and $J_{11}$ are the only intra-chain interactions representing NN and NNN exchanges within the chains, respectively, whereas all other interactions are between different chains. The dominant exchange interaction is NN within a chain ($J_1$), while the NNN interaction $J_{11}$ is almost two orders of magnitude smaller. The strongest interchain interaction $J_5$ is roughly 30 times smaller than $J_1$. Moreover, given a strong tendency for ... up-down-up-down..., ordering with the chains, some interchain interactions introduce frustration in the system, e.g., the interactions $J_7$ and $J_9$ cannot be simultaneously satisfied. Overall, CaFeF$_5$ can be characterized as having a strong NN antiferromagnetic intrachain interaction, weak NNN antiferromagnetic exchange within the chains, and weak interchain magnetic coupling.

The magnetic exchange paths of SrFeF$_5$, shown in Figs. 4(e,f), are determined up to the twelfth nearest neighbor. The calculated values of $J_i$ are given in Table 2. It can be found that the chains are composed of alternating Fe$_1$ and Fe$_2$ octahedra with alternating NN exchange constants $J_1$ and $J_2$, whose values are comparable to that in CaFeF$_5$, whereas $J_2/J_1 \approx 1.38$. The NNN intrachain interaction is $J_3$, whereas interaction $J_4$ can be considered as next nearest neighbor along the chain. The exchange interactions $J_i$ with $i = 5-12$ are interchain couplings. Similar to the case of CaFeF$_5$, the dominant exchange interactions in SrFeF$_5$ are NN intrachain couplings, whereas further neighbor exchanges within chains are significantly smaller. However, in contrast to CaFeF$_5$, interchain interactions in SrFeF$_5$ are relatively stronger.

### 4. Magnetic properties

The magnetic exchange constants obtained with the help of DFT calculations were used in Monte Carlo simulations. We have not calculated the magnetic anisotropy terms in Eq. 1 and used tentative values of $D_\alpha (\alpha = x, y, z)$ in our MC studies. In the following we assume that the axes $x$ and $y$ are parallel to the axes $a$ and $b$, respectively, and, the axis $z$ is perpendicular to both the $a$ and $b$ axes. In our MC calculations of CaFeF$_5$ we used $D_a = -0.1$, $D_b = 0.1$, and $D_z = 0$ meV. Figure 2(a) shows the temperature dependencies of magnetic susceptibility $\chi$ of CaFeF$_5$ studied along various directions. It can be found that $\chi$ experiences a broad plateau characteristic of 1D magnetic chains structure. The fitting of $\chi$ in the range of temperatures from 500 to 1000 K gives the Curie-Weiss temperature $\theta_{CW} = -219$ K, whereas from the inset in Fig. 2(a) it follows that CaFeF$_5$ experiences an antiferromagnetic phase transition at $T_N = 23$ K. Overall the results of calculations are in good agreement with the experimental data on magnetic properties of CaFeF$_5$, which give the Curie-Weiss and Neel temperatures of -202 K and 21 K, respectively [14]. The analysis of magnetic structure resulting from MC calculations shown in Fig. 2(b) below $T_N$ reveals that it is characterized by the wave vector $\vec{k} = (1/2, 0, 0)$. Thus, the magnetic cell is twice the crystallographic one (i.e. doubled along the $a$ axis) and the spins are directed along the easy axis.

Figure 3 shows the magnetic susceptibility of SrFeF$_5$ obtained from MC calculations, in which we used the anisotropy constants $D_a = -0.05$, $D_b = 0.05$, and $D_z = 0$ meV. Similar to CaFeF$_5$ the magnetic susceptibility shows a broad maximum characteristic of a 1D magnetism. The Curie-Weiss temperature obtained by fitting the data in the temperature range 500 – 1000 K gives the Curie-Weiss temperature $\theta_{CW} = -166$ K. In the inset of Fig. 3 one can discern two magnetic phase transitions at $T_{N1} = 35$ and $T_{N2} = 28$ K, corresponding to anomalies in the temperature dependence of $\chi_x$ and $\chi_y$. The analysis of magnetic structure reveals that the first phase transition at $T_{N1}$ is connected with the appearance of sinusoidally modulated structure with spins along the easy axis ($x$ axis in our case), whereas at the second phase transitions at $T_{N2}$ additional component along the $z$ axis appears resulting in cycloidal magnetic structure. The modulation wave vector is $\vec{k}_{inc} \approx (0.22, 0, 0.32)$. The plane of rotation of spins in the low-temperature magnetic structure is governed by the magnetic anisotropy, which in our model is determined by the ten-

### Table 1: Calculated magnetic exchange constants for CaFeF$_5$ and respective Fe – Fe distances.

| $J$ (meV) | $J_1$ | $J_2$ | $J_3$ | $J_4$ | $J_5$ | $J_6$ |
|---|---|---|---|---|---|---|
| Fe – Fe, Å | 6.437 | 6.549 | 7.506 | 7.540 | 7.599 |
| J, meV | 0.78 | -0.2 | 0.14 | 0.01 | 0.25 |

### Table 2: Calculated magnetic exchange constants for SrFeF$_5$ and respective Fe – Fe distances.

| $J$ (meV) | $J_1$ | $J_2$ | $J_3$ | $J_4$ | $J_5$ | $J_6$ |
|---|---|---|---|---|---|---|
| Fe – Fe, Å | 3.666 | 3.891 | 4.486 | 4.692 | 5.044 | 5.094 |
| J, meV | 15.5 | 21.4 | 0.05 | 0.38 | 0.34 | -0.91 |
| Fe – Fe, Å | 5.114 | 5.840 | 5.983 | 6.092 | 6.329 | 6.336 |
| J, meV | 1.35 | -0.89 | 0.16 | 2.06 | -1.01 | 1.53 |
Figure 2: (Color online) (a) Magnetic susceptibility χ₁ (blue), χ₃ (green), and χₓ (red) of CaFeF₃ measured along different directions. The inset shows the data below 80 K. (b) Magnetic structure of CaFeF₃ below 80 K.

Figure 3: (Color online) Magnetic susceptibility χ₁ (blue), χ₃ (green), and χₓ (red) of SrFeF₃ measured along different directions. The inset shows the data below 80 K.

5. Possible magnetoelectric properties and discussion

As found in the previous section, the magnetic structure of CaFeF₃ below the Neel temperature is characterized by the wave vector \( \vec{k} = (1/2, 0, 0) \), which is the Y-point of the Brillouin zone of the space group P2₁/c. The analysis of possible magnetic structures induced by a single exchange multiplet in this point [15], shows that they cannot induce electric polarization, because they do not break inversion symmetry. This conclusion is also in accord with the absence of modulated magnetic ordering because the irreducible representations (IR) in the Y-point of the Brillouin zone satisfy the Lifshitz criterion [16].

Monte Carlo calculations reveal that the magnetic ordering wave vector in SrFeF₃ is \( \vec{k}_{0ac} \approx (0.22, 0, 0.32) \). This modulation vector is close to the commensurate vector \( \vec{k}_c = (1/4, 0, 1/3) \), which is the F-point of the Brillouin zone and which is realized in our MC calculations assuming stronger single-ion anisotropy constants \( D_α \). The phenomenological treatment of magnetic phase transitions in SrFeF₃ can be performed based on the instability with the wave vector \( \vec{k}_c \), whereas the incommensurate modulation can be described by Lifshitz invariants. Indeed, the F-point lies in the interior of the Brillouin zone and the two two-dimensional IR’s F₁ and F₂ in this point do not satisfy the Lifshitz criterion. Thus, the crystal symmetry permits the invariants responsible for long-wavelength modulation of magnetic order in the ac plane

\[
\frac{\partial a_2}{\partial x} - \frac{\partial a_1}{\partial z} = a_1 \frac{\partial a_2}{\partial z} - a_2 \frac{\partial a_1}{\partial x},
\]

\[
\frac{\partial b_2}{\partial x} - \frac{\partial b_1}{\partial z} = b_1 \frac{\partial b_2}{\partial z} - b_2 \frac{\partial b_1}{\partial x},
\]

where \((a₁, a₂)\) and \((b₁, b₂)\) are magnetic order parameters transforming according to IR’s F₁ and F₂, respectively. Depending on the orientation of spins in the low-temperature magnetic structure of SrFeF₃ (e.g. cycloidal, proper screw, or more complex magnetic ordering) at least two magnetic order parameters describe the magnetic structure, which transform either by the same single IR F₁ or F₂ or by two different IR’s F₁ and F₂. In both cases the magnetoelectric interactions

\[
(a₁b₁ + a₂b₂)P_x,
\]

\[
(a₁a₂' - a₂a₁')P_y,
\]

\[
(b₁b₂' - b₂b₁')P_z,
\]

where the order parameters \((a₁, a₂)\) and \((a₁', a₂')\) transform according to F₁, while \((b₁, b₂)\) and \((b₁', b₂')\) according to F₂, should result in appearance of electric polarization \(P_\alpha\). Thus, SrFeF₃ is
predicted to be multiferroic below the magnetic ordering temperature $T_{N2}$, where two magnetic order parameters condense. This picture of magnetoically induced electric polarization is similar to that in many other multiferroics [17, 18, 19].

Both studied compounds, CaFeF$_3$ and SrFeF$_3$, contain spin chains with strong NN intrachain interactions, weaker NNN intrachain couplings and relatively smaller interchain interactions. In SrFeF$_3$ the interchain couplings are relatively stronger compared with intrachain one, than in CaFeF$_3$, which is probably determined by the helicoidal arrangements of spin chains in SrFeF$_3$ and, thus, shorter interchain distances. In both cases, within the chains the spins order in ...-up-down-up-down-... fashion, whereas relative ordering of chains is determined by a big number of interchain exchange constants. Our calculations show that in CaFeF$_3$ this results in magnetic ordering with \( \vec{k} = (1/2, 0, 0) \), which does not permit magnetoelectric properties, whereas in SrFeF$_3$ a modulated magnetic structure is realized resulting in multiferroic behavior. In both cases the magnetic wave vector is a result of combined action of many exchange parameters. Given possible inaccuracy in determination of exchange constants by DFT calculations the real magnetic structures in CaFeF$_3$ and SrFeF$_3$ can be characterized by wave vectors other than those found in the present work. However, since the space group P2$_1$/c is non-symmetric, analysis shows that only the magnetic structures induced by the Y-point instability should not give rise to magnetoelectric properties, whereas all other Brillouin zone boundary points (A, B, C, and Z), which are compatible with the ...-up-down-up-down-... spin ordering of the chains, contain IR’s not satisfying the Lifshitz criterion and, thus, inducing improper electric polarization [16]. It has to be noted, that in CaFeF$_3$ the energy of the obtained magnetic structure with \( \vec{k} = (1/2, 0, 0) \) is very close to that of magnetic structure with \( \vec{k} = 0 \), in which the spins of of Fe$^{3+}$ ions located at positions \((x, y, z), (1 - x, 1 - y, 1 - z), (1 - x, 1/2 + y, 1/2 - z)\), and \((x, 1/2 - y, 1/2 + z)\) are ordered in \((+ - + -)\) fashion. Such magnetic ordering breaks inversion symmetry and results in appearance of linear magnetoelectric effect below $T_S$. Neutron diffraction experiments are necessary to clarify the magnetic structures in the studied fluorides.

6. Conclusions

We have studied the spin-chain fluorides CaFeF$_3$ and SrFeF$_3$ by means of density functional theory and Monte Carlo calculations, as well as by symmetry analysis. The chains in both compounds are characterized by strong NN exchange couplings and weak NNN interactions. The interchain interactions are much weaker than the NN intrachain couplings, which gives rise to low-dimensional magnetic behavior. Our results indicate that the magnetic structure of CaFeF$_3$ does not result in magnetoelectric effects, whereas SrFeF$_3$ is multiferroic in the low-temperature incommensurate magnetically ordered phase.

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References

[1] A. P. Pyatakov, A. K. Zvezdin, Magnetoelastic and multiferroic media, Phys.-Uspekhi. 55 (2012) 557.
[2] A. Vasiliev, O. Volkova, E. Zvereva, M. Markina, Milestones of low-d quantum magnetism, npj Quantum Materials 3 (2018) 18.
[3] P. Hagenmuller (Ed.), Inorganic Solid Fluorides: Chemistry and Physics, Academic Press, 1985.
[4] M. Leblanc, V. Maisonneuve, A. Tressaud, Crystal chemistry and selected physical properties of inorganic fluorides and oxide-fluorides, Chem. Rev. 115 (2014) 1191.
[5] J. F. Scott, R. Blinc, Multiferroic magnetoelectric fluorides: why are there so many magnetic ferroelectrics?, J. Phys.: Condens. Matter 23 (2011) 113202.
[6] D. Khomskii, Classifying multiferroics: Mechanisms and effects, Physics 2 (2009) 20.
[7] G. Kresse, J. Furthmuller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Phys. Rev. B 54 (1996) 11169.
[8] P. E. Blöchl, Projector augmented-wave method, Phys. Rev. B 50 (1994) 17953.
[9] S. L. Dudarev, G. A. Botton, S. Y. Savrasov, C. J. Humphreys, A. P. Sutton, Electron-energy-loss spectra and the structural stability of nickel oxide: An LSDA+U study, Phys. Rev. B 57 (1998) 1505.
[10] K. Momma, F. Izumi, VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data, J. Appl. Cryst. 44 (2011) 1272.
[11] D. Babel, A. Tressaud, Crystal chemistry of fluorides, in: P. Hagenmuller (Ed.), Inorganic Solid Fluorides: Chemistry and Physics, Academic Press, 1985, Ch. 3, p. 77.
[12] R. von der Mühll, F. Daut, J. Ravez, Structure cristalline de SrFeF$_3$, J. Solid State Chem. 8 (1973) 206.
[13] J. Graulich, W. Massa, D. Babel, Zur Kristallstruktur von CaFeF$_3$, Z. Anorg. Allg. Chem. 629 (2003) 365.
[14] J.-M. Dance, J.-L. Soubeyroux, L. Fournes, A. Tressaud, Magnétisme monodimensionnel dans les fluorures à chain CaCdF$_3$ et CaFeF$_3$, C. R. Acad. Sc. Paris C 288 (1979) 37.
[15] V. P. Sakhnenko, N. V. Ter-Oganessian, Exchange symmetry in description of magnetoelectrics, Phys. Solid State 54 (2012) 311.
[16] V. P. Sakhnenko, N. V. Ter-Oganessian, Improper ferroelectric antiferromagnetics, Ferroelectrics 400 (2010) 12.
[17] N. V. Ter-Oganessian, V. P. Sakhnenko, Interpretation of magnetoelectric phase states using the phraophase concept and exchange symmetry, J. Phys.: Condens. Matter 26 (2014) 036003.
[18] P. Tolédano, Pseudo-proper ferroelectricity and magnetoelectric effects in TbMnO$_3$, Phys. Rev. B 79 (2009) 094416.
[19] P. Tolédano, W. Schranz, G. Krexner, Induced ferroelectric phases in TbMn$_2$O$_5$, Phys. Rev. B 79 (2009) 144103.

Appendix A. Structural parameters

Tables A.1 and A.2 present the lattice parameters and atomic positions of CaFeF$_3$ and SrFeF$_3$ obtained by DFT calculations in comparison with the experimental results taken from literature.
Table A.1: Structural parameters of CaFeF$_5$ obtained experimentally ($a=5.492$ Å, $b=10.076$ Å, $c=7.599$ Å, $\beta=110.02^\circ$, sp. gr. P2$_1$/c) [13] and by DFT calculations in this work ($a=5.571$ Å, $b=10.218$ Å, $c=7.694$ Å, $\beta=109.9^\circ$)

| Atom | x   | y   | z   |
|------|-----|-----|-----|
| Fe   | exp. 0.10314 | 0.24644 | 0.3996 |
|      | DFT 0.10542  | 0.24653  | 0.4001  |
| Ca   | exp. 0.52690 | -0.01783 | 0.2540  |
|      | DFT 0.52914  | 0.98047  | 0.2548  |
| F$_1$ | exp. 0.38640 | 0.11840  | 0.4448  |
|      | DFT 0.38841  | 0.11776  | 0.4443  |
| F$_2$ | exp. 0.35480 | 0.38740  | 0.4924  |
|      | DFT 0.35781  | 0.38768  | 0.4945  |
| F$_3$ | exp. 0.12140 | 0.60360  | 0.1878  |
|      | DFT 0.12073  | 0.60462  | 0.1880  |
| F$_4$ | exp. 0.17220 | 0.86320  | 0.1413  |
|      | DFT 0.16907  | 0.86377  | 0.1405  |
| F$_5$ | exp. 0.14990 | 0.29350  | 0.1621  |
|      | DFT 0.15270  | 0.29490  | 0.1629  |

Table A.2: Structural parameters of SrFeF$_5$ obtained experimentally ($a=7.062$ Å, $b=7.289$ Å, $c=14.704$ Å, $\beta=95.4^\circ$, sp. gr. P2$_1$/c) [12] and by DFT calculations in this work ($a=7.127$ Å, $b=7.395$ Å, $c=14.891$ Å, $\beta=95.2^\circ$)

| Atom | x   | y   | z   |
|------|-----|-----|-----|
| Fe$_1$ | exp. 0.5062 | 0.6185 | 0.1614 |
|      | DFT 0.5070 | 0.6170 | 0.1611 |
| Fe$_2$ | exp. 0.8107 | 0.6832 | 0.3750 |
|      | DFT 0.8118 | 0.6846 | 0.3753 |
| Sr$_1$ | exp. 0.6896 | 0.1536 | 0.0873 |
|      | DFT 0.6847 | 0.1559 | 0.0870 |
| Sr$_2$ | exp. 0.0015 | 0.6529 | 0.1374 |
|      | DFT 0.0003 | 0.6587 | 0.1385 |
| F$_1$ | exp. 0.6977 | 0.4951 | 0.0986 |
|      | DFT 0.7001 | 0.4964 | 0.0978 |
| F$_2$ | exp. 0.3190 | 0.6978 | 0.0678 |
|      | DFT 0.3190 | 0.6920 | 0.0676 |
| F$_3$ | exp. 0.3145 | 0.6658 | 0.2414 |
|      | DFT 0.3130 | 0.6586 | 0.2417 |
| F$_4$ | exp. 0.6797 | 0.5565 | 0.2715 |
|      | DFT 0.6831 | 0.5543 | 0.2714 |
| F$_5$ | exp. 0.6548 | 0.8301 | 0.1503 |
|      | DFT 0.6526 | 0.8293 | 0.1488 |
| F$_6$ | exp. 0.9935 | 0.4878 | 0.3911 |
|      | DFT 0.9997 | 0.4935 | 0.3890 |
| F$_7$ | exp. 0.9680 | 0.8067 | 0.2936 |
|      | DFT 0.9669 | 0.8129 | 0.2941 |
| F$_8$ | exp. 0.6113 | 0.8693 | 0.3540 |
|      | DFT 0.6036 | 0.8617 | 0.3560 |
| F$_9$ | exp. 0.6531 | 0.5802 | 0.4594 |
|      | DFT 0.6545 | 0.5734 | 0.4584 |
| F$_{10}$ | exp. 0.9559 | 0.8206 | 0.4657 |
|       | DFT 0.9561 | 0.8205 | 0.4677 |