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Rubidium chalcogenido diferrates(III) containing dimers $[\text{Fe}_2\text{Q}_6]^{6-}$ of edge-sharing tetrahedra ($\text{Q} = \text{O}, \text{S}, \text{Se}$)

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Abstract: The two isotopic rubidium chalcogenido diferrates $\text{Rb}_{12}[\text{Fe}_2\text{Q}_6](\text{Q}_2)_3$ ($\text{Q} = \text{S}/\text{Se}$), which both form needles with green-metallic lustre, were synthesized from Rb_2S , elemental iron, rubidium and sulfur ($\text{Q} = \text{S}$) or from the pure elements ($\text{Q} = \text{Se}$) at maximum temperatures of 500–800°C. Their triclinic crystal structures were determined by means of X-ray single crystal data (space group $\bar{P}1$, $a = 863.960(10)/903.2(3)$, $b = 942.790(10)/982.1(3)$, $c = 1182.70(2)/1227.4(4)$ pm, $\alpha = 77.4740(10)/77.262(6)$, $\beta = 71.5250(10)/71.462(6)$, $\gamma = 63.7560(10)/63.462(5)^\circ$, $Z = 1$, $R1 = 0.0308/0.0658$ for $\text{Q} = \text{S}/\text{Se}$). The structures contain isolated dinuclear anions $[\text{Fe}^{\text{III}}_2\text{Q}_6]^{6-}$ composed of two edge-sharing $[\text{FeQ}_4]$ tetrahedra ($d_{\text{Fe-Q}} = 223.4\text{--}232.3/236.2\text{--}244.8$ pm), which are also found in the two polymorphs of the pure alkali diferrates $\text{Rb}_6[\text{Fe}_2\text{Q}_6]$. The diferrate ions are arranged in layers running in the a/b plane around $z = 0$. Inbetween (around $z \approx \frac{1}{2}$), two crystallographically different disulfide/diselenide ions Q_2^{2-} ($d_{\text{Q-Q}} = 211.1\text{--}213.4/237.9\text{--}241.1$ pm), which are arranged in slightly puckered 3^6 nets, are intercalated. The intra-anionic distances and angles, the Rb coordination numbers and the molar volumes of these two ‘double-salts’ are in accordance with their corresponding reference compounds, $\text{Rb}_6[\text{Fe}_2\text{Q}_6]$ and Rb_2Q_2 . In addition, the two polymorphs of $\text{Rb}_6[\text{Fe}_2\text{Se}_6]$, which are both isotopic with the sulfido analogous ($\text{Cs}_6[\text{Ga}_2\text{Se}_6]$ -type, monoclinic, space group $P2_1/c$, $a = 827.84(5)$, $b = 1329.51(7)$, $c = 1074.10(6)$ pm, $\beta = 127.130(5)^\circ$, $R1 = 0.0443$ and $\text{Ba}_6[\text{Al}_2\text{Sb}_6]$ -type, orthorhombic, space group Cmce , $a = 1963.70(3)$, $b = 718.98(3)$, $c = 1348.40(7)$ pm, $R1 = 0.0264$) were prepared and characterized to complete the series of alkali diferrates(III) with oxido, sulfido and selenido ligands. The electronic band structures of the three Rb salts

$\text{Rb}_6[\text{Fe}_2\text{Q}_6]$, which have been calculated within the GGA + U approach applying an AFM spin ordering in the dimers and appropriate Hubbard parameters, allow a comparison of the chemical bonding characteristics (e.g. covalency) and the magnetic properties (magnetic moments) within the series of chalcogenido ligands. An analysis of the spin densities enables a comparative consideration of the mechanisms crucial for the magnetic ordering in chalcogenido ferrates. Ultimately, the electronic structure of the new compound $\text{Rb}_{12}[\text{Fe}_2\text{S}_6](\text{S}_2)_3$ nicely compares with those of the S_2 -free reference compound $\text{Rb}_6[\text{Fe}_2\text{S}_6]$.

Keywords: diferrates; rubidium; selenido ferrates; sulfido ferrates.

1 Introduction

The alkali chalcogenido ferrates of sodium to cesium exhibit a rich structural chemistry marked by a wide range of connectivities of $[\text{FeQ}_4]$ tetrahedra [1–4]. The chemical bonding inside the chalcogenido ferrate anions just as the magnetic ordering distinguished by extraordinary high Néel temperatures, are subjects of long-lasting but still ongoing discussions (cf. [4–6] and references therein). Compounds of this family are model systems for metalloproteins and the superconducting Fe arsenides, to name only a few examples. Among these numerous alkali oxido, sulfido and selenido ferrates, the diferrates $\text{A}_6[\text{Fe}_2\text{Q}_6]$ containing anions with two edge-sharing tetrahedra are interesting in many respects: In being dimers with two Fe(III) ions, the systems are the most simple species exhibiting an AFM ordering. As magnetic ordering is one of the most fascinating features of the whole structure family, the diferrates allow to study the mechanism of a 90° magnetic superexchange and thus to get a deeper insight in the basis for all complex magnetic systems, e.g. spin-ladder compounds etc. Additionally, the ‘molecular’ (not extended) structure allows a comparison with coordination compounds exhibiting similar building blocks [7] and therewith also with the biologically relevant $2\text{Fe}\text{--}2\text{S}$ systems [8, 9].

In view of this significance, the present work does not only report on the synthesis and the structures of the new

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‘double-salts’ $\text{Rb}_{12}[\text{Fe}_2\text{Q}_6](\text{Q}_2)_3$ ($\text{Q}=\text{S}, \text{Se}$) and the missing link in the diferrate family, $\text{Rb}_6[\text{Fe}_2\text{Se}_6]$, but also contains a basic bond theoretical study of the O/S/Se series of rubidium chalcogenido diferrates $\text{Rb}_6[\text{Fe}_2\text{Q}_6]$.

2 Experimental

2.1 Preparation and phase analysis

The title compounds were synthesized in corundum crucibles sealed in steel autoclaves under an argon atmosphere at maximum temperatures (T_{max}) of 500–800°C. Due to the different starting materials and preparation procedures, the temperature programs and individual sample compositions are described below, separately for sulfur and selenium containing samples.

After the preparations, representative parts of the reguli were ground and sealed in capillaries with a diameter of 0.3 mm. X-ray powder diagrams were collected on transmission powder diffractometer systems [Stoe STADI-P with linear PSD or Dectris Mythen 1K strip detector, MoK_α or CuK_α (Se samples) radiation, graphite monochromator]. For the phase analysis, the measured powder diagrams were compared to the calculated (program LAZY-PULVERIX [10]) reflections of the target compounds and other known phases in the systems Rb-Fe-(S/Se) .

Starting materials for the synthesis of the sulfido ferrate $\text{Rb}_{12}[\text{Fe}_2\text{S}_6](\text{S}_2)_3$ were dried iron filings, elemental sulfur and rubidium sulfide Rb_2S , which was obtained by carefully reacting a solution of elemental rubidium (Alkalimetallhandels-gesellschaft Maassen, Bonn, approx. 3 g) in liquid ammonia with stoichiometric amounts of elemental sulfur, following a protocol adapted from the synthesis of the corresponding potassium salts after Brauer [11]. $\text{Rb}_{12}[\text{Fe}_2\text{S}_6](\text{S}_2)_3$ has been obtained in X-ray pure form from samples of overall composition Rb_3FeS_3 consisting e.g. of 745.8 mg (3.67 mmol) of Rb_2S , 136.2 mg (2.44 mmol) Fe and 117.7 mg (3.67 mmol) S, at a maximum temperature of 500°C. The sample tube was heated up to 200°C with a rate of 50 K h^{-1} , followed by a ramp with 50 K h^{-1} to T_{max} . Subsequently, the sample was cooled to r.t. with a rate of 20 K h^{-1} . Only slightly elevated maximum temperatures of 600°C resulted in the exclusive formation of the monoclinic form of $\text{Rb}_6[\text{Fe}_2\text{S}_6]$. An increase of the Rb and S content, i.e. a composition closer to that of the target compound (e.g. Rb_9FeS_9), yielded only the orthorhombic form of $\text{Rb}_6[\text{Fe}_2\text{S}_6]$ [4] together with the tetramer $\text{Rb}_8[\text{Fe}_4\text{S}_{10}]$ [4]. Samples richer in Rb_2S , e.g. of overall composition

$\text{Rb}_7\text{Fe}_3\text{S}_8$ ($T_{\text{max}}=800^\circ\text{C}$), provided $\text{Rb}_{12}[\text{Fe}_2\text{S}_6](\text{S}_2)_3$ together with different amounts of the two polymorphs of the diferrate.

The three selenido ferrates were synthesized from stoichiometric amounts of the pure elements rubidium, iron filings and selenium (shots, ABCR GmbH, Karlsruhe). To delay and tone down the exothermic reaction of elemental rubidium and selenium, a ‘crucible in crucible’ technique was applied: Iron and rubidium were filled into an outer corundum crucible with an inner diameter of 10 mm. An inner zirconia crucible (9.8 mm outer diameter) with several slits at the bottom was loaded with selenium and placed above the Rb/Fe mixture, avoiding the initial contact between the elements. The two fitted sample tubes were slowly heated up to 260°C with a rate of 12 K h^{-1} . The reaction starts at the melting point of Se (221°C), when liquid selenium drops down into the Rb/Fe mixture. The reaction was completed by quickly ($\dot{T}=250 \text{ K h}^{-1}$) heating the sample to $T_{\text{max}}=800^\circ\text{C}$. Subsequently, the product was slowly ($\dot{T}=30 \text{ K h}^{-1}$) cooled to 300°C and finally to r.t. with rates up to 100 K h^{-1} .

Knowing the composition of the sulfido compound, the corresponding selenido ferrate $\text{Rb}_{12}[\text{Fe}_2\text{Se}_6](\text{Se}_2)_3$ has been successfully obtained from stoichiometric samples [Rb: 366 mg (4.28 mmol); Fe: 40 mg (0.72 mmol); Se: 342 mg (4.33 mmol)] applying the above described ‘crucible-in-crucible’ technique and temperature program. The sample consists mainly of the target compound, which forms dark-green shiny crystals with conchoidal fracture. The second product, the orthorhombic form of $\text{Rb}_6[\text{Fe}_2\text{Se}_6]$, can be distinguished optically in forming xenomorphic crystals with bronze sheen. Accordingly, the powder pattern is virtually completely explained by the reflections of $\text{Rb}_{12}[\text{Fe}_2\text{Se}_6](\text{Se}_2)_3$, calculated using the crystal data of Tables 1 and 2. Traces of the orthorhombic form of $\text{Rb}_6[\text{Fe}_2\text{Se}_6]$ could be identified as the additional by-product. The monoclinic form of $\text{Rb}_6[\text{Fe}_2\text{Se}_6]$ has been obtained, together with the known mixed-valent phase $\text{Rb}_3[\text{Fe}_2\text{Se}_4]$ [12], during attempts to synthesize selenido cluster ferrates (in analogy to the S and Te cluster compounds [13, 14]) from a sample of composition $\text{Rb}_7[\text{Fe}_4\text{Se}_8]$ [Rb: 312 mg (3.65 mmol); Fe: 116 mg (2.08 mmol); Se: 330 mg (4.18 mmol)].

2.2 Crystal structure determination

For the single crystal structure analysis, selected crystals were fixed in glass capillaries ($\varnothing < 0.1 \text{ mm}$) under dried paraffine oil and centered on diffractometers equipped with a microsource and a CCD area detector (Bruker APEX

Table 1: Atomic coordinates and equivalent isotropic displacement parameters (pm^2) for the crystal structures of (from top to bottom) $\text{Rb}_{12}[\text{Fe}_2\text{S}_6](\text{S}_2)_3$, $\text{Rb}_{12}[\text{Fe}_2\text{Se}_6](\text{Se}_2)_3$ and the monoclinic and orthorhombic polymorphs of $\text{Rb}_6[\text{Fe}_2\text{Se}_6]$.

Atoms	Wyck. pos.	x	y	z	U_{equiv}
Rb(1)	2i	0.23960(4)	0.30787(3)	0.33786(2)	260.1(7)
Rb(2)	2i	0.23637(4)	0.65181(3)	0.43329(3)	268.6(7)
Rb(3)	2i	0.72189(4)	0.00811(3)	0.38491(3)	272.1(7)
Rb(4)	2i	0.00112(4)	0.76161(4)	0.08494(3)	290.7(7)
Rb(5)	2i	0.79288(4)	0.42604(4)	0.20432(3)	334.0(8)
Rb(6)	2i	0.57837(4)	0.07310(4)	0.83793(3)	334.3(8)
Fe	2i	0.47629(5)	0.35322(4)	0.04462(3)	138.8(7)
S(1)	2i	0.39745(9)	0.56871(8)	0.14753(6)	174(1)
S(2)	2i	0.23375(9)	0.31732(8)	0.05149(6)	219(1)
S(3)	2i	0.67767(9)	0.13739(8)	0.11842(7)	259(2)
S(4)	2i	0.41532(10)	0.28003(10)	0.57403(8)	325(2)
S(5)	2i	0.13428(10)	0.37238(9)	0.62992(7)	270(2)
S(6)	2i	0.05546(10)	0.04604(9)	0.41389(7)	262(2)
Rb(1)	2i	0.2524(2)	0.30058(18)	0.33671(13)	308(4)
Rb(2)	2i	0.2308(2)	0.65062(18)	0.43623(13)	303(4)
Rb(3)	2i	0.7269(2)	0.00327(18)	0.38411(14)	330(4)
Rb(4)	2i	0.0055(2)	0.7592(2)	0.08183(14)	357(4)
Rb(5)	2i	0.7923(2)	0.4261(2)	0.20679(15)	390(5)
Rb(6)	2i	0.5740(2)	0.07658(19)	0.84056(14)	398(5)
Fe	2i	0.4759(3)	0.3542(2)	0.04414(17)	196(5)
Se(1)	2i	0.3963(2)	0.56951(17)	0.15147(12)	230(4)
Se(2)	2i	0.2298(2)	0.31818(18)	0.05267(14)	274(4)
Se(3)	2i	0.6810(2)	0.13316(18)	0.11831(14)	302(4)
Se(4)	2i	0.4275(2)	0.2730(2)	0.57346(17)	385(5)
Se(5)	2i	0.1237(2)	0.37550(19)	0.63344(15)	322(4)
Se(6)	2i	0.0588(2)	0.04973(19)	0.40566(14)	311(4)
Rb(1)	4e	0.35073(18)	0.42282(10)	0.10691(14)	587(4)
Rb(2)	4e	0.38572(17)	0.13135(8)	0.01832(13)	484(3)
Rb(3)	4e	0.86975(17)	0.31023(9)	0.08043(15)	548(3)
Fe	4e	0.0615(2)	0.05604(10)	0.15126(17)	346(3)
Se(1)	4e	0.14966(16)	0.60999(7)	0.62023(12)	430(3)
Se(2)	4e	0.12081(16)	0.55111(8)	0.24307(13)	437(3)
Se(3)	4e	0.34681(16)	0.16595(8)	0.30427(13)	418(3)
Rb(1)	8f	0	0.13921(9)	0.32080(5)	389(2)
Rb(2)	16g	0.17738(2)	0.34570(7)	0.12617(4)	387(2)
Fe	8d	0.07889(4)	0	0	242(2)
Se(1)	8f	0	0.21984(9)	0.07251(5)	297(2)
Se(2)	16g	0.35209(3)	0.35098(7)	0.12074(4)	365(2)

II Quazar) or a sealed tube and an image plate detector (Stoe IPDS-2).

The reflections on the diffraction images of needle shaped crystals of $\text{Rb}_{12}[\text{Fe}_2\text{S}_6](\text{S}_2)_3$ could be indexed using a triclinic lattice, so that $P\bar{1}$ and $P1$ are the only possible space groups. The structure was solved using Direct Methods (program SHELXS-2013 [17]) in the centrosymmetric space group $P\bar{1}$. The solution already yielded all atomic positions. After standardization (program STRUCTURE

TIDY [18]), the atomic positional and anisotropic displacement parameters smoothly refined to a final value for $R1$ of 0.0308 using the program SHELXL-2013 [17]. The structure of the isotypic selenido ferrate could easily be refined from the crystal data of the sulfido analogue.

The monoclinic form of the diferrate $\text{Rb}_6[\text{Fe}_2\text{Se}_6]$ crystallizes in the $\text{Cs}_6[\text{Ga}_2\text{Se}_6]$ -type structure [19]. The structure could thus be refined starting from the parameters of the respective isotypic sulfido ferrate in a few least squares cycles to an $R1$ value of 0.0443. The diffraction images of crystals of the second form of $\text{Rb}_6[\text{Fe}_2\text{Se}_6]$ exhibit orthorhombic symmetry with the integral extinction condition of a C -centered lattice and the additional zonal extinction ‘reflections $h0l$ only present for $h, l=2n$ ’ and ‘ $hk0$: $h, k=2n$ ’. The resulting space group choices, $Cmce$ and $Aba2$, as well as the values of the lattice parameters indicated isotopy to $\text{Cs}_6[\text{Fe}_2\text{Se}_6]$ [20] and the orthorhombic form of $\text{Rb}_6[\text{Fe}_2\text{S}_6]$ [4] ($\text{Ba}_6[\text{Al}_2\text{Sb}_6]$ -type structure [21]). The refinement of the atom positions and ADP parameters converged to a conclusively low $R1$ value of 0.0264.

The crystal data and the results of these anisotropic structure refinements are collected in the Tables 1 and 2 (see also [22]).

2.3 ^{57}Fe Mössbauer spectroscopy

Zero-field ^{57}Fe Mössbauer spectra of $\text{Rb}_6[\text{Fe}_2\text{O}_6]$ and $\text{K}_6[\text{Fe}_2\text{O}_6]$ (synthesis and structure determination cf. [23]) were recorded at r.t. and 77 K in a constant acceleration modus with a triangular velocity profile [accelerator, control unit and multichannel analyser, 1024 data channels] using a commercial Wissel spectrometer, a $^{57}\text{Co}/\text{Rh}$ source and a $\text{NaI}(\text{Tl})$ scintillation counter. The samples were placed in airtight PMMA containers with thin-walled windows (area 1 cm^2). The experimental spectra were approximated in least-squares fits with Lorentz functions in the thin absorber approximation (program package NORMOS-90 [24]). The isomer shift refers to $\alpha\text{-Fe}$ ($\delta^{\alpha\text{-Fe}} = 0.11 \pm 0.01\text{ mm/s} + \delta^{\text{Fe/Rh}}$). As an example, the r.t. spectrum of $\text{Rb}_6[\text{Fe}_2\text{O}_6]$ is depicted in Fig. 1.

2.4 Band structure calculations

DFT calculations of the electronic band structure were performed for $\text{Rb}_{12}[\text{Fe}_2\text{S}_6](\text{S}_2)_3$, the orthorhombic modifications of $\text{Rb}_6[\text{Fe}_2\text{S}_6]$ [4] and $\text{Rb}_6[\text{Fe}_2\text{Se}_6]$ and the corresponding oxide $\text{Rb}_6[\text{Fe}_2\text{O}_6]$ [23] using the FP-LAPW method (program WIEN2K [25]). The exchange-correlation contribution was described by the generalized

Table 2: Crystallographic data and details of the data collection and structure determination for $\text{Rb}_{12}[\text{Fe}_2\text{Q}_6](\text{Q}_2)_3$ ($\text{Q}=\text{S}, \text{Se}$) and the two polymorphs of $\text{Rb}_6[\text{Fe}_2\text{Se}_6]$.

Compound		Rb ₁₂ [Fe ₂ S ₆](S ₂) ₃	Rb ₁₂ [Fe ₂ Se ₆](Se ₂) ₃	Rb ₆ [Fe ₂ Se ₆]	
Structure type			New	Cs ₆ [Ga ₂ Se ₆]	Ba ₆ [Al ₂ Sb ₆]
Pearson symbol			<i>aP</i> 26	<i>mP</i> 28	<i>oS</i> 56
Crystal system			Triclinic	Monoclinic	Orthorhombic
Space group			<i>P</i> $\bar{1}$, no. 2	<i>P</i> 2 ₁ / <i>c</i> , no. 14	<i>Cmce</i> , no. 64
Temperature		r.t.	100 K	r.t.	r.t.
Lattice parameters, pm, deg	<i>a</i>	863.960(10)	903.2(3)	827.84(5)	1963.70(3)
	<i>b</i>	942.790(10)	982.1(3)	1329.51(7)	718.98(3)
	<i>c</i>	1182.70(2)	1227.4(4)	1074.10(6)	1348.40(7)
	α	77.4740(10)	77.262(6)	—	—
	β	71.5250(10)	71.462(6)	127.130(5)	—
	γ	63.7560(10)	63.462(5)	—	—
Volume of the u.c., 10 ⁶ pm ³		816.17(2)	919.6(5)	942.51(10)	1903.75(13)
Z			1	2	4
Density (X-ray), gcm ^{−3}		3.10	3.77	3.87	3.83
Diffractometer		Bruker AXS CCD		IPDS-2	
Mo- <i>K</i> _α radiation					
Absorption coefficient $\mu_{\text{Mo}-K_{\alpha}}$, mm ^{−1}		19.43	28.44	28.49	28.20
θ Range, deg		1.8–35.6	1.8–27.5	2.8–26.7	2.1–26.8
No. of reflections collected		25760	6457	10090	7569
No. of independent reflections		6111	4028	2004	1056
<i>R</i> _{int}		0.0467	0.0608	0.0880	0.0463
Corrections		Lorentz, polarisation, absorption			
		(Multi-Scan [15])		(Xshape [16])	
Structure solution		SHELXS-2013 [17]		—	
Structure refinement		SHELXL-2013 [17]			
No. of free parameter		118	119	65	37
Goodness-of-fit on <i>F</i> ²		1.036	0.920	0.951	1.111
<i>R</i> Values [for refl. with <i>I</i> ≥ 2σ(<i>I</i>)]	<i>R</i> 1	0.0308	0.0658	0.0443	0.0264
	<i>wR</i> 2	0.0550	0.1290	0.0934	0.0521
<i>R</i> Values (all data)	<i>R</i> 1	0.0542	0.1556	0.0781	0.0335
	<i>wR</i> 2	0.0586	0.1481	0.1038	0.0539
Residual elect. density, e [−] × 10 ^{−6} pm ^{−3}		+1.7/−1.0	+1.5/−1.8	+0.9/−0.9	+0.5/−0.6

Fig. 1: Zero-field room-temperature ^{57}Fe Mössbauer spectrum of $\text{Rb}_6[\text{Fe}_2\text{O}_6]$.

gradient approximation (GGA) of Perdew, Burke and Ernzerhof [26]. Muffin-tin radii were chosen as 116 pm (2.2 a.u.) for Rb, 111 pm (2.1 a.u.) for Fe, O, S, Se and 105 pm (1.98 a.u.) for the sulfur atoms of the disulfide groups. Cutoff energies used were $E_{\text{max}}^{\text{pot}}=190 \text{ eV}$ (potential) and $E_{\text{max}}^{\text{wf}}=116 \text{ eV}$ (interstitial PW). In the spin-polarized

GGA + *U* calculation the additional Coulomb potential (Hubbard parameter U_{eff}) used for the strongly correlated Fe *d* electrons was 4.2 eV for $\text{Q}=\text{O}$ and 2.0 eV for S or Se [27–29] and the SIC (self-interaction correction) [30, 31] double counting correction method has been applied. Due to the magnetic ordering observed in several reference compounds, e.g. $\text{Na}_6[\text{Fe}_2\text{Se}_6]$, $\text{Na}_6[\text{Fe}_2\text{S}_6]$, $\text{Cs}_6[\text{Fe}_2\text{S}_6]$ [32, 33] and $\text{Rb}_6[\text{Mn}_2\text{O}_6]$ [34], an antiferromagnetic spin ordering was applied for the two iron cations of each dimer. For this AFM treatment of the Fe spins, all crystal structures were transformed into appropriate subgroups, *P*1 (for $\text{Rb}_{12}[\text{Fe}_2\text{S}_6](\text{S}_2)_3$, instead of $P\bar{1}$), *C*222₁ (for $\text{Rb}_6[\text{Fe}_2(\text{S}/\text{Se})_6]$, instead of *Cmce*) and *Cm* (for $\text{Rb}_6[\text{Fe}_2\text{O}_6]$, instead of *C*2/*m*), respectively. Electron and spin densities were calculated and visualized using the programs XCRYSDEN [35] and DRAWxTL [36]. A Bader analysis of the electron density distribution was performed to evaluate the

Fig. 2: ORTEP representations (80% probability ellipsoids [40]) of the sulfido ferrate (a) and the disulfide (b, c) anions together with the Rb coordination of selected sulfur ligands in the crystal structure of $\text{Rb}_{12}[\text{Fe}_2\text{S}_6](\text{S}_2)_3$ (bond labels cf. Table 3).

charge distribution between the atoms [37] and the bond critical points including their height (ρ_{BCP}) and Laplacian ($\nabla^2\rho_{\text{BCP}}$) using the program CRITIC2 [38, 39]. Further parameters and selected results of the calculations are summarized in Table 6. The total (tDOS) and selected partial Fe and S density of states (pDOS) are depicted in the Figs. 7 and 8.

3 Results and discussion

3.1 Syntheses

The new sulfido diferrate disulfide $\text{Rb}_{12}[\text{Fe}_2\text{S}_6](\text{S}_2)_3$ and its isotopic selenido compound have been obtained in the course of a systematic synthetic study on ternary compounds in the Rb–Fe–Q systems from samples containing elemental iron and sulfur with (previously prepared) Rb_2S as rubidium source or by directly weighing in the pure elements Rb, Fe and Se applying a ‘crucible-in-crucible’ technique at maximum temperatures between 500 and 800°C (cf. Experimental Section 2.1 for details). The selenium compound $\text{Rb}_{12}[\text{Fe}_2\text{Se}_6](\text{Se}_2)_3$ was obtained in nearly pure phase from stoichiometric samples. By-products formed are the pure diferrates $\text{Rb}_6[\text{Fe}_2\text{Q}_6]$, where the two polymorphs of the selenium phase have not yet been described and their crystal structure refinements are hence included herein. Due to the band gaps of 1.2–1.5 eV, which are attributed to $L \rightarrow M$ -CT transitions (cf. Section 3.5), the crystals of all compounds exhibit dark-metallic greenish or bronze lustre.

3.2 Crystal structure of the diferrate dichalcogenides $\text{Rb}_{12}[\text{Fe}_2\text{Q}_6](\text{Q}_2)_3$

The two isotopic compounds $\text{Rb}_{12}[\text{Fe}_2\text{S}_6](\text{S}_2)_3$ and $\text{Rb}_{12}[\text{Fe}_2\text{Se}_6](\text{Se}_2)_3$ crystallize with a new triclinic structure type. They both contain chalcogenido ferrate(III) anions $[\text{Fe}_2\text{Q}_6]^{6-}$ built up from two edge-sharing $[\text{FeQ}_4]$ tetrahedra. Additionally, three disulfide/diselenide anions $[\text{Q}_2]^{2-}$ per ferrate dimer are present. The centrosymmetric dimers $[\text{Fe}_2\text{Q}_6]^{6-}$ of the sulfido compound, together with the Rb coordination of one of the crystallographically different sulfur atoms, are depicted in an ORTEP representation in Fig. 2a. The corresponding bond lengths are collected in Table 3. As expected and likewise observed for all ferrates $[\text{Fe}_2\text{Q}_6]^{6-}$, the two terminal chalcogenido ligands $\text{Q}(2)$ and $\text{Q}(3)$ exhibit shorter Fe–Q bonds ($d_{\text{Fe-S}}^{\text{a/b}} = 223.4/224.0$ pm; $d_{\text{Fe-Se}}^{\text{a/b}} = 236.2/236.9$ pm) than the bridging ligands in the central four-membered ring of the anions ($d_{\text{Fe-S}}^{\text{c/d}} = 230.4/232.3$ pm; $d_{\text{Fe-Se}}^{\text{c/d}} = 242.4/244.8$ pm). The Fe–Fe distances of 289.9/300.2 pm (for $\text{Q} = \text{S/Se}$) are decreased in comparison with those in the two polymorphs of $\text{Rb}_6[\text{Fe}_2\text{S}_6]$ [4] and $\text{Rb}_6[\text{Fe}_2\text{Se}_6]$ (cf. Section 3.3). The angles $\text{Q}^t\text{–Fe–Q}^t$ between the terminal Fe–Q bonds (109.7–112.3/109.3–112.0° for S/Se) are slightly larger than the tetrahedral angle. In contrast, the corresponding angles in the central four-membered ring are reduced to 102.4 ($\text{Q} = \text{S}$) and 103.9° ($\text{Q} = \text{Se}$). The angles $\text{Fe–Q}^{\text{br}}\text{–Fe}$ at the μ_2 -ligands, which are crucial for the magnetic coupling, amount to 77.6 and 76.1° for the S and the Se compound, respectively.

Similar to the cation coordination in the two forms of $\text{Rb}_6[\text{Fe}_2(\text{S/Se})_6]$, the μ_2 -chalcogenido ligands are

Table 3: Selected interatomic distances (pm) in the crystal structures of the chalcogenido diferrates $\text{Rb}_{12}[\text{Fe}_2\text{Q}_6](\text{Q}_2)_3$ ($\text{Q} = \text{S}, \text{Se}$).

Atoms	Distance for		CN Atoms	Distance for		CN Atoms	Distance for		CN
	Q=S	Q=Se		Q=S	Q=Se		Q=S	Q=Se	
Rb(1) –Q(5)	328.23(8)	344.4(3)	Rb(2) –Q(6)	327.60(8)	341.8(2)	Rb(3) –Q(6)	318.45(8)	332.3(2)	6
–Q(6)	332.22(7)	344.0(2)	–Q(4)	331.62(8)	344.9(3)	–Q(3)	320.16(8)	331.6(2)	
–Q(2)	338.46(8)	351.9(3)	–Q(6)	332.10(8)	349.3(3)	–Q(5)	326.13(8)	337.5(3)	
–Q(5)	339.98(8)	358.9(3)	–Q(1)	334.31(7)	345.4(2)	–Q(4)	330.64(8)	344.6(3)	
–Q(1)	340.50(7)	351.8(2)	–Q(5)	335.02(8)	347.2(2)	–Q(6)	333.61(8)	351.5(3)	
–Q(4)	349.18(9)	363.5(3)	–Q(4)	342.85(9)	360.6(3)	–Q(4)	336.43(9)	344.6(3)	
–Q(3)	372.13(8)	381.2(3)	–Q(5)	361.97(8)	369.1(3)				
Rb(4) –Q(1)	333.09(7)	346.5(3)	Rb(5) –Q(1)	330.62(7)	344.4(3)	Rb(6) –Q(3)	343.69(8)	358.4(2)	7
–Q(2)	334.76(7)	347.1(2)	–Q(5)	336.25(8)	348.8(3)	–Q(2)	344.48(8)	360.3(2)	
–Q(5)	336.09(8)	347.5(2)	–Q(2)	343.70(7)	356.4(3)	–Q(2)	349.85(8)	361.4(3)	
–Q(3)	339.21(8)	350.4(2)	–Q(2)	344.02(7)	359.4(2)	–Q(1)	351.80(7)	362.8(2)	
–Q(3)	341.60(8)	354.3(3)	–Q(4)	368.0(1)	384.9(3)	–Q(6)	353.23(8)	364.3(3)	
–Q(2)	380.93(8)	392.1(3)	–Q(3)	369.66(8)	388.9(3)	–Q(4)	363.96(9)	373.0(3)	
			–Q(6)	408.03(8)	415.0(3)	–Q(3)	390.43(8)	403.4(3)	
Fe –Q(3)	223.40(7)	236.2(3) a							
–Q(2)	224.04(7)	236.9(3) b							
–Q(1)	230.42(7)	242.4(2) c							
–Q(1)	232.29(8)	244.8(3) d	4						
–Fe	289.88(7)	300.2(4)							
Q(1) –Fe	230.42(7)	242.4(2) c	Q(2) –Fe	224.04(7)	236.9(3) b	Q(3) –Fe	223.40(7)	236.2(3) a	
–Fe	232.29(8)	244.8(3) d	–Rb(4)	334.76(7)	347.1(2)	–Rb(3)	320.16(8)	331.6(2)	
–Rb(5)	330.62(7)	344.4(3)	–Rb(1)	338.46(8)	351.9(3)	–Rb(4)	339.20(8)	350.4(2)	
–Rb(4)	333.09(7)	346.5(3)	–Rb(5)	343.70(7)	356.4(3)	–Rb(4)	341.59(8)	354.3(3)	
–Rb(2)	334.31(7)	345.4(2)	–Rb(5)	344.01(7)	359.4(2)	–Rb(6)	343.69(8)	358.4(2)	
–Rb(1)	340.50(7)	351.8(2)	–Rb(6)	344.49(8)	360.3(2)	–Rb(5)	369.66(8)	388.9(3)	
–Rb(6)	351.79(7)	362.8(2)	–Rb(6)	349.84(8)	361.4(3)	–Rb(1)	372.13(8)	381.2(3)	
			–Rb(4)	380.93(8)	392.1(3)	–Rb(6)	390.43(8)	403.4(3)	1+7
Q(4) –Q(5)	211.1(1)	237.9(3) e	Q(5) –Q(4)	211.1(1)	237.9(3) e	Q(6) –Q(6)	213.35(14)	241.1(3) f	
–Rb(3)	330.64(8)	344.6(3)	–Rb(3)	326.13(8)	337.5(3)	–Rb(3)	318.44(8)	332.3(2)	
–Rb(2)	331.62(8)	344.9(3)	–Rb(1)	328.23(8)	358.9(3)	–Rb(2)	327.60(8)	341.8(2)	
–Rb(3)	336.43(9)	344.6(3)	–Rb(2)	335.02(8)	347.2(2)	–Rb(2)	332.11(8)	349.3(3)	
–Rb(2)	342.85(9)	344.9(3)	–Rb(4)	336.09(8)	347.5(2)	–Rb(1)	332.22(7)	344.0(2)	
–Rb(1)	349.18(9)	363.5(3)	–Rb(5)	336.26(8)	348.8(3)	–Rb(3)	333.60(8)	351.5(3)	
–Rb(6)	363.96(9)	373.0(3)	–Rb(1)	339.98(8)	358.9(3)	–Rb(6)	353.23(8)	364.3(3)	
–Rb(5)	368.0(1)	384.9(3)	–Rb(2)	361.97(8)	347.2(2)	–Rb(5)	408.03(8)	415.0(3)	1+7

coordinated by five Rb (in addition to the two iron ions) and the terminal μ_1 atoms are adjacent to seven Rb cations (+1 Fe). The shortest Q–Rb distances towards the cations enclosing the metalate ions amount to 320.2/331.6 pm (Table 3) and are thus somewhat shorter than the sum of Shannon's radii of 336/350 pm [41].

The second type of anions in the double salts are the disulfide/diselenide ions $[(\text{S}/\text{Se})_2]^{2-}$. The three dichalcogenide ions per formula unit and diferrate moiety have three crystallographically different positions [Q(4)–Q(6)], whereby Q(4)/Q(5) form dumbbells (Fig. 2b). The remaining dumbbell is built up by two connected Q(6) atoms and thus exhibits inversion symmetry (Fig. 2c).

The Q–Q bond lengths with values of 211.1/213.4 (S) and 237.9/241.1 pm (Se, Table 3) are in the expected range of S–S and Se–Se single bonds (Rb_2S_2 : $d_{\text{S-S}} = 211.3$ pm and Rb_2Se_2 : $d_{\text{Se-Se}} = 246.8$ pm, [42]). The S–S bond lengths are also comparable to those observed in the potassium orthoferrate disulfide $\text{K}_9[\text{FeS}_4](\text{S}_2)(\text{S})$ ($d_{\text{S-S}} = 213.9$ pm, [4]). Whereas the disulfide dumbbells in this potassium compound are surrounded by 11 K^+ counter ions, they are overall coordinated by 10 larger cations in the new rubidium salts, resulting in a 1 Q + 7 Rb coordination for all three S/Se atoms (Fig. 2b and c).

The diferrate anions are arranged in layers running in the a/b plane of the triclinic unit cell (cf. the projections

Fig. 3: Unit cell of the crystal structure of $\text{Rb}_{12}[\text{Fe}_2\text{S}_6](\text{S}_2)_3$. (a) One diferrate and an adjacent disulfide layer running $\perp$ to the a/b plane; (b–d) projections of the unit cell along $[100]$ (b), $[010]$ (c) and $[110]$ (d). (Green balls: S; grey polyhedra: $[\text{FeS}_4]$ tetrahedra; [36]).

in Fig. 3). In these sheets, the diferrate moieties are hexagonally close packed (each anion is surrounded by six others), a motif which is also the basis of the anion packing in the pure diferrates (Section 3.3), with the main axis of the dimers pointing approx. along $[010]$. Consistently, the a and b lattice parameters are of similar lengths, whereby the b axis is somewhat increased compared to a , and the γ angle does not differ too much from 60° . These layers are stacked perpendicular to the a/b plane. In the triclinic unit cell the positions of the anions are shifted only slightly from one to the next unit cell/layer, so that no simple repetition unit results for the overall stacking sequence (Fig. 3b–d).

Inbetween these diferrate layers, puckered 3^6 nets of $[\text{Q}_2]^{2-}$ dumbbells are interspersed (at height $z \approx \frac{1}{2}$).

Figure 3a shows the arrangement of the dichalcogenide net in its position relative to the adjacent ferrate layers. The 3^6 net (yellow lines in Fig. 3a–d) is formed by a

puckered 6^3 net of $[\text{Q}(4)–\text{Q}(5)]$ dumbbells tilted relative to the plane, and $[\text{Q}(6)_2]$ dumbbells, which are oriented fairly perpendicular to the plane and center the six-membered rings of the 6^3 net. From this structure description, the 1:3 proportion of the ferrate dimers and the $[\text{Q}_2]$ dumbbells becomes obvious.

The position and coordination (red lines) of the rubidium cations in the crystal structure are visualized in Fig. 4. The Rb cations are coordinated by six $[\text{Rb}(3/4)]$, 6+1 $[\text{Rb}(5)]$ and seven $[\text{Rb}(1/2/6)]$ S/Se atoms. The shortest distances of 318.5 pm (Rb–S) and 332.3 pm (Rb–Se) are Rb– $[\text{Q}_2]$ contacts (Table 3). They are thus somewhat shorter than all remaining Rb–Q distances and are also significantly decreased with respect to the sum of Shannon's radii for Rb^+ and $(\text{S/Se})^{2-}$ of 336/350 pm (for CN = 6).

According to the 'double salt' character of the ferrate dichalcogenides $\text{Rb}_{12}[\text{Fe}_2\text{Q}_6](\text{Q}_2)_3$, the sum of the volumes of $\text{Rb}_6[\text{Fe}_2\text{Q}_6]$ and the tripled volumes of Rb_2Q_2 [42] are only

Fig. 4: Coordination of the six crystallographically different Rb cations in the crystal structure of $\text{Rb}_{12}[\text{Fe}_2\text{S}_6](\text{S}_2)_3$ (green balls: S; gray balls: Rb; grey polyhedra: $[\text{FeS}_4]$ tetrahedra; [36]).

1.8–2.7% larger than the observed molar volumes of the title compounds.

In contrast to the pure diferrates, which are found (although not isotypic, see below) in the whole series of

alkali salts from Na to Cs, $\text{Rb}_{12}[\text{Fe}_2\text{S}_6](\text{S}_2)_3$ and $\text{Rb}_{12}[\text{Fe}_2\text{Se}_6](\text{Se}_2)_3$ are observed with Rb^+ as counter ion only. For potassium, the orthoferrate $\text{K}_9[\text{FeS}_4](\text{S}_2)(\text{S})$ is obtained from similarly composed samples [4].

3.3 Crystal structures and polymorphism of $\text{Rb}_6[\text{Fe}_2\text{Se}_6]$

The anions and the unit cells of the two polymorphs of $\text{Rb}_6[\text{Fe}_2\text{Se}_6]$ are depicted in Fig. 5.

In the monoclinic form (Fig. 5a, b), the dimers $[\text{Fe}_2\text{Se}_6]^{6-}$ exhibit inversion symmetry only. As always, the two terminal Fe–Se(2/3) distances ($d_{\text{Fe–Se}}^{a/b} = 237.5/239.3$ pm) are shorter than the bond length to the bridging selenium ligand Se(1) ($d_{\text{Fe–Se}}^{c/d} = 241.0/243.3$ pm, Table 4 top, Fig. 5b). The Fe–Fe distance is somewhat larger than in the isotypic potassium salt [43]. The bond angles in the central planar four-membered ring are 99.4° at the metal and

Fig. 5: Unit cells (a, c) and ORTEP representations of the anions (70% probability ellipsoids [40]) (b, d) in the two polymorphs of $\text{Rb}_6[\text{Fe}_2\text{Se}_6]$ (bond labels cf. Table 4).

Table 4: Selected interatomic distances (pm) in the crystal structures of the monoclinic (above) and the orthorhombic form (below) of $\text{Rb}_2[\text{Fe}_2\text{Se}_6]$ (CN in brackets: ECoN values).

Atoms	Distance	CN	Atoms	Distance	CN	Atoms	Distance	CN	Atoms	Distance	CN
Rb(1) –Se(1)	335.4(2)		Rb(2) –Se(3)	330.8(2)		Rb(3) –Se(1)	336.8(2)		Fe –Se(2)	237.4(2)	a
–Se(2)	343.1(2)		–Se(2)	340.7(2)		–Se(1)	348.0(2)		–Se(3)	239.3(2)	b
–Se(2)	346.9(2)		–Se(2)	342.9(2)		–Se(3)	348.4(2)		–Se(1)	241.0(2)	c
–Se(3)	344.0(2)		–Se(3)	342.9(2)		–Se(2)	363.9(2)		–Se(1)	243.3(2)	d
–Se(3)	384.0(2)		–Se(1)	373.9(2)		–Se(3)	368.7(2)		–Fe	313.4(3)	
–Se(3)	403.0(2)	6 (5.00)				–Se(2)	391.0(2)	5 (4.82)			
						–Se(2)	397.6(2)	7 (5.97)			
Se(1) –Fe	241.0(2)		Se(2) –Fe	237.5(2)	a	Se(3) –Fe	239.3(2)	b			
–Fe	243.3(2)		–Rb(2)	340.7(2)		–Rb(2)	330.8(2)				
–Rb(1)	335.4(2)		–Rb(2)	342.9(2)		–Rb(2)	342.9(2)				
–Rb(3)	336.8(2)		–Rb(1)	343.1(2)		–Rb(1)	344.0(2)				
–Rb(3)	348.0(2)		–Rb(1)	346.9(2)		–Rb(3)	348.4(2)				
–Rb(2)	373.9(2)	2 + 4	–Rb(3)	363.9(2)		–Rb(3)	368.7(2)				
			–Rb(3)	391.0(2)		–Rb(1)	384.0(2)				
			–Rb(3)	397.6(2)	1 + 7	–Rb(1)	403.0(2)	1 + 7			
Rb(1) –Se(1)	334.1(1)		Rb(2) –Se(2)	343.2(1)		Fe	237.4(1)	2 × a			
–Se(2)	337.3(1)	2 ×	–Se(2)	346.2(1)		–Se(1)	242.0(1)	2 × b			
–Se(1)	339.8(1)		–Se(2)	360.4(1)		–Fe	309.8(2)				
–Se(1)	354.2(1)	5 (5.04)	–Se(2)	366.3(1)							
			–Se(1)	367.1(1)	6 (5.79)						
			–Se(2)	367.9(1)							
Se(1) –Fe	242.0(1)		Se(2) –Fe	237.4(1)	a						
–Rb(1)	334.1(1)		–Rb(1)	337.3(1)							
–Rb(1)	339.8(1)		–Rb(2)	343.2(1)							
–Rb(1)	354.2(1)		–Rb(2)	346.2(1)							
–Rb(2)	367.1(1)	2 ×	–Rb(2)	360.4(1)							
			–Rb(2)	366.3(1)	2 + 5						
			–Rb(2)	367.9(1)	1 + 6						

80.6° at the μ_2 -selenido ligand. The selenido ligands are coordinated by 2+5 (μ_2) and 1+7 (μ_1) Rb⁺ ions, the shortest Rb–Se distance is 330.8 pm and therewith slightly shorter than the sum of Shannon's radii. The coordination numbers of the Rb cations are 6 (4+2), 5 and 7 (5+2) [for Rb(1/2/3), cf. Table 4 top] and are thus fully comparable to the cation coordinations in Rb₁₂[Fe₂Se₆](Se₂)₃. The main axis of the ferrate ions [Fe₂Se₆]⁶⁻ (centered at 0, 0, 0) is oriented along the longer basis axis *c*, but is somewhat tilted against the monoclinic *b* axis (Fig. 5a). Like in the layers of Rb₁₂[Fe₂Se₆](Se₂)₃, the ferrate anions are arranged in a distorted hexagonally close packed layer running along the *a/c* plane of the unit cell. As a consequence, the monoclinic angle β is close to 120°. The adjacent equivalent layer of anions is staggered in the [100] direction, so that the double tetrahedra are positioned above the edges of the triangles of the basis layer. The stacking sequence along the monoclinic *b* axis thus resembles that of the α -U-type (|:A–D:|, Fig. 5a).

The second form of Rb₆[Fe₂Se₆] as well as the cesium salt Cs₆[Fe₂Se₆] [32] crystallize in the orthorhombic Ba₆[Al₂Sb₆]-type structure [21]. The views of the unit cells in Fig. 5a and c show the similarities between the two polymorphs of the Rb salt: As in the monoclinic form, the diferrate double tetrahedra are arranged in the *a/b* plane in hexagonal close packed layers, in which the Fe–Fe vectors are oriented parallel to the elongated *a* axis. The |:A–D:| α -U-type stacking of these layers is also similar. An alternative, crystal-chemically more obvious description of the anion packing in *o*-Rb₆[Fe₂Se₆] starts from a hexagonal rod packing of the dimers in the *b/c* plane. The stacking sequence of these layers along the third direction [100] is likewise that of the α -U-type, in this case denoted as |:A'–D':| in Fig. 5c. The Fe–Se distances in the 2/*m* symmetric anion (Fig. 5d) are comparable to the bond lengths in the potassium and the monoclinic Rb compound (terminal: 237.4 pm; bridging: 241.0/243.3 pm; Table 4). The Fe–Fe distance is slightly shorter (309.8 pm) than in the monoclinic form. The coordination number of the bridging Se ligand is the same in both polymorphs (2+5 for Fe+Rb), whereas the coordination sphere of the terminal selenido ligand is reduced to 1+6.

Similar to the situation in the two sulfido polymorphs *m/o*-Rb₆[Fe₂S₆] [4], crystal chemical arguments suggest that the monoclinic form is the l.t. and the orthorhombic form the h.t. form of Rb₆[Fe₂Se₆], because the molar volume of *m*-Rb₆[Fe₂Se₆] is one per cent smaller than for the *o*-form. The coordination number of the Rb cations is slightly reduced ($\textcircled{O}\text{ECoN}_{\text{Rb}}=5.26$) compared to the orthorhombic phase (Table 4, $\textcircled{O}\text{ECoN}_{\text{Rb}}=5.52$). [Due to the large variation of the A–Q distances in most of the cation

coordination polyhedra (c.c.p.), effective coordination numbers (ECoN, [44]) are used throughout this work to quantify and compare the cation coordinations]. The calculated lattice energy of *m*-Rb₆[Fe₂Se₆] (program GULP [45, 46]) is 32 kJ/mol smaller than the value of the orthorhombic polymorph. The isotypism of the *o*-form with the Cs salt also supports this phase relation.

3.4 Crystal chemistry of the diferrates A₆[Fe₂Q₆]

The structure types and the ranges of interatomic distances, etc. of all known alkali diferrates(III) are collected in Table 5. Four of the five structure types containing pairs of tetrahedra exhibit layers with a hexagonal close packed arrangement of the dinuclear units (red lines in Fig. 6): The two oxido ferrates (left hand side of Fig. 6) as well as the sulfido/selenido compounds (right hand side) are connected by a group-subgroup relation. In all four structure types, the layers are |:A–D:| stacked (cf. the glide planes indicated in all four sub-figures).

Oxido ferrates of general composition A₃[FeO₃]=A₆[Fe₂O₆] are known not only as ternary phases containing a single alkali metal A^I. In the extensive work of Hoppe and coworkers, a number of salts with two different alkali cations were studied (cf. Table 5). In the structures of Na₃[FeO₃], Na₂K[FeO₃], Na₂Rb[FeO₃], NaK₂[FeO₃] and K₂Rb[FeO₃], which crystallize in three distinct structure types, zweier single chains ¹[FeO₂O_{2/2}] are formed [47–49]. In the presence of widely differing ionic radii such as in Na₅Cs[FeO₃]₂ [50], the formation of vierer single chains is observed. In these ino-ferrates, the conformation of the chains obviously adapts to the preferred coordination numbers of the counterions. The first oxido ferrate containing edge-sharing tetrahedra was reported by Hoppe as early as 1973 [51, 52, 67]. Much later the Rb and Cs salts were added [23, 53]. The Cs ferrate crystallizes in the K₆[Mn₂O₆]-type structure [53], whereas the isotypic K and Rb compounds form their own structure type [51, 68]. However, the two structure types are closely related by a direct *klassengleiche* group-subgroup relationship according to C2/*m* → P2₁/*c* (Fig. 6, left; [53, 67]). In the Cs salt, the dinuclear anions are slightly tilted against the monoclinic *b* axis, which causes a decreased coordination of the oxido ligands by the large Cs⁺ cations (μ_1 : 1+6 → 1+5/6; μ_2 : 2+5 → 2+4). As a consequence, the cation's averaged ECoN is also smaller in the cesium compound.

Most of the alkali sulfido and selenido diferrate salts A₆[Fe₂Q₆] have been synthesized and structurally characterized by the Bronger group in the last decade of the

Table 5: Comparison of the crystal structure, intra-ferrate atomic distances together with selected Mössbauer and magnetic parameters of the known alkali di- and chain-ferrates(III).

Compound	Structure type	Space group	ECoN _A (ϕ)	Distances		δ/mms^{-1}	H_{eff}^0/T	J/meV
				Fe–Q ^t	Fe–Q ^{br}			
Na ₂ [FeO ₃] ₂	[47]	P2 ₁ /n		185.6–186.2	191.6–192.4			
Na ₄ K ₂ [FeO ₃] ₂	[48]	Pnma		183.7–183.9	190.2			
Na ₂ K ₄ [FeO ₃] ₂	[49]	Pnma		182	189			
CsNa ₅ [FeO ₃] ₂	[50]	I4 ₂ d		185.2–185.5	190.3–190.			
Na ₄ Rb ₂ [FeO ₃] ₂	[48]	Cmma						
K ₄ Rb ₂ [FeO ₃] ₂	[48]	Cmma						
K ₆ [Fe ₂ O ₆]	[51, 52]	C2/m	4.89	185.3	194.1/195.5	0.147(2)	1.554	
Rb ₆ [Fe ₂ O ₆]	[23]	C2/m	4.83	184.4	194.2/194.6	0.155(3)	1.546(7)	
Cs ₆ [Fe ₂ O ₆]	[53]	P2 ₁ /c	4.34	183.6–184.1	193.6–193.8			
Na ₆ [Fe ₂ S ₆]	[32, 54, 55]	P2 ₁ /c	4.58	224.9/225.3	225.9/229.8			–12.5
K ₆ [Fe ₂ S ₆]	[4]	P2 ₁ /c	5.13	224.3/226.0	228.9/230.5			
m-Rb ₆ [Fe ₂ S ₆]	[4]	P2 ₁ /c	5.23	224.9/226.7	229.6/231.0			
o-Rb ₆ [Fe ₂ S ₆]	[4]	Cmce	5.52	225.2	230.0			
Rb ₁₂ [Fe ₂ S ₆](S ₂) ₃	^a	P $\bar{1}$		223.4/224.0	230.4/232.3			
Cs ₆ [Fe ₂ S ₆]	[32]	Cmce	5.61	225.2	229.5			–10.4
Na ₆ [Fe ₂ Se ₆]	[32, 56]	P2 ₁ /c	4.94	236.8/236.8	237.5/241.3			–11.4
K ₆ [Fe ₂ Se ₆]	[43]	P2 ₁ /c	5.18	236.4/238.1	239.9/241.7			–8.3
m-Rb ₆ [Fe ₂ Se ₆]	^a	P2 ₁ /c	5.26	237.4/239.3	241.0/243.3			
o-Rb ₆ [Fe ₂ Se ₆]	^a	Cmce	5.54	237.4	242.0			
Rb ₁₂ [Fe ₂ Se ₆](Se ₂) ₃	^a	P $\bar{1}$		236.2/236.9	242.4/244.8			
Cs ₆ [Fe ₂ Se ₆]	[20]	Cmce	5.59	237.2	241.1			
Na[FeS ₂]	[57, 58]	I222		–	222		27.0	
K[FeS ₂]	[58, 59]	C2/c		–	223.2/223.8	0.36	0.58	
Rb[FeS ₂]	[58, 59]	C2/c		–	220/222	0.21	0.51	–20.8
HT-Rb[FeS ₂]	[60]	Immm		–	222.1/222.5	0.19	0.45	19.6
Cs[FeS ₂]	[59, 61–64]	Immm		–	222.6/223.6	0.21	0.44	19.1 ^c
K[FeSe ₂]	[58, 65]	C2/c		–	236.3/236.9	0.34	0.44	21.8
Rb[FeSe ₂]	[6, 58]	C2/c		–	238.3/238.6	0.24	0.34	21.6
Cs[FeSe ₂]	[1, 65, 66]	C2/m ^b		–	235.5/236.6			

^aThis work, ^b $T > 123^\circ\text{C}$: CsFeS₂-type; ^ctriclinic form at 4.2 K.

The $K_6[Mn_2O_6]$ - (yellow box in Fig. 6) and the $Cs_6[Ga_2Se_6]$ -type (red box) structure do not only contain a similar anion, but crystallize with the same space group, and the structures are isopointal. The dinuclear anions with their center at 0,0,0 exhibit inversion symmetry. However, in $Cs_6[Ga_2Se_6]$ the anions are significantly tilted with respect to the monoclinic b axis. This causes – for the same μ_2 - Q coordination number (2+4) – an increased CN of the μ_1 chalcogenido ligands. Besides, the atomic parameters and the value of the monoclinic angle are too different to call the two structures isotypic.

Despite our extensive and systematic experimental work, tellurido ferrates $A_6[Fe_2Te_6]$ were not yet obtained, although edge-sharing $[FeTe_4]$ tetrahedra are prominent building blocks in mixed-valent cluster tellurido ferrates [13].

Due to the significance of the intra-anionic bond distances and angles for the following discussion of the chemical bonding, the reduced magnetic moments on Fe and the magnetic exchange mechanisms, the relevant interatomic distances and selected physical properties are collected in Table 5. This comparison also includes the chain ferrates $A[FeQ_2]$, for which extensive investigations (magnetic measurements, ^{57}Fe Mössbauer spectroscopy, neutron diffraction, etc.) have been performed (cf. [6] for a recent review).

Both for the dinuclear $[Fe^{III}_2Q_6]^{6-}$ and the chain anions $[Fe^{III}(S/Se)_2]^-$ in all alkali salts the intra-molecular $Fe-Q^{br}$ bond lengths and $Fe-Fe$ distances are hardly (and not systematically) influenced by the size of the alkali counter ions: For each chalcogen, the $Fe-Q$ distances in the Na–Cs salt series are very similar. The $Fe-O$ distances are 193.6–195.5 pm long and the $Fe-S$ ($Fe-Se$) bond lengths are in the narrow range 223.4–226.7 pm (237.5–243.3 pm). The respective distances in the sulfido and selenido chain ferrates are somewhat smaller, but here too lie in very narrow ranges (S: 220–224 pm; Se: 236–239 pm). Comparably, the $Fe-Fe$ distances also show no trends in the alkali series (for the dinuclear units: $Q=O$: 272.1–273.3 pm, $Q=S$: 287.6–300.5 pm, $Q=Se$: 297.4–313.4 pm). The Rb-salts of the monoclinic $Cs_6[Ga_2Se_6]$ -type polymorph, the only structure type with a 1+7 coordination of the μ_1 - Q ligands, show the largest $Fe-Fe$ distances of the mentioned distance ranges. In the chain anions, the $Fe-Fe$ distances are again shorter, also in this case with no trends arising from the A^+ counter ions ($Q=S$: 269.5–272.5 pm; $Q=Se$: 281.5/283.8 pm).

3.5 Electronic structure of $Rb_{12}[Fe_2S_6](S_2)_3$ and $Rb_6[Fe_2S_6]$

The band structures of the title compound and the more simple reference compounds $Rb_6[Fe_2Q_6]$ ($Q=O, S, Se$) were

calculated using the FP-LAPW DFT method (GGA+ U) including spin-polarization and a suitable Hubbard U parameter of $U_{eff}=4.2/2.0/2.0$ eV (for $Q=O/S/Se$) [27, 28]. In all cases, antiferromagnetic ordering of the two $Fe(III)$ ions of the dimers has been applied in the subgroups given in the Experimental section. The AFM spin ordering, where two M^{3+} ions of $S=\frac{5}{2}$ are coupled antiferromagnetically (overall $S=0$), has been experimentally verified by means of magnetic susceptibility data, ^{57}Fe Mössbauer spectroscopy and neutron diffraction studies for several alkali sulfido and selenido diferrates [1, 32, 33, 55] and oxido metallates(III) such as the manganate(III) $Rb_6[Mn_2O_6]$ [34], which is isotypic to $Rb_6[Fe_2O_6]$ [23]. For a series of model compounds for protein bound $2Fe-2(S/Se)$ clusters, DFT calculations support the singlet spin electronic structure as the ground state for oxidized $Fe^{III/II}$ dimers with sulfur or selenium ligands [8, 9]. In a comprehensive experimental and theoretical study of a series of $2Fe-2Q$ coordination compounds, the AFM spin state has also been unequivocally determined, independent of the type of the chalcogenido ligand and the differences in the magnetic exchange path [7].

For the two sulfido ferrates $Rb_{12}[Fe_2S_6](S_2)_3$ and $o-Rb_6[Fe_2S_6]$ the total (tDOS, gray shaded) and selected partial (pDOS) Fe (red and orange lines) and S (green/blue lines) density of states are depicted in Fig. 7. The tDOS show definite band gaps and a valence band region predominantly formed by S- p states. The conduction band is determined by the five Fe- d states of the upper Hubbard band, so that the compounds belong to the class of ‘charge transfer semiconductors’ (class 2B) in the ZSA scheme [69].

$Rb_6[Fe_2S_6]$ has 46 valence electrons per formula unit (v.e./f.u.), excluding the sulfur s states [$6(6 \times Rb) + 16(2 \times Fe) + 24(6 \times S)$]. The 23 α/β spin states each are formed by the five $^{7/4}$ v.e./f.u. of the HS- Fe^{III} ions $Fe(11)/Fe(12)$, which are primarily located around -4.6 eV, and 18/18 v.e./f.u. of the sulfide p electrons. Further details of the population of the different Fe- d states are discussed in the context of the analysis of the chemical bonding and the magnetic exchange interaction below. The DOS of $Rb_{12}[Fe_2S_6](S_2)_3$ (Fig. 7, bottom) is directly comparable and shows additional 30 S- p v.e. of the three disulfide ions (blue lines) at energies -3.7 to -4.0 eV (σ^b), -2.4 to -3.0 (π^b) and -0.8 to E_F ($\pi^{a,b}$). Due to the latter $\pi^{a,b}$ states, the band gap of the compound is slightly reduced in comparison with the pure diferrate. In agreement with the ‘double salt’ character of the title compound, the Bader charges (q_{BB}) and volumes (V_{BB}) of the Rb and Fe cations and the sulfido ligands show no significant difference in comparison with $Rb_6[Fe_2S_6]$ (first two columns of Table 6). As expected, the sulfur atoms of the disulfide

Fig. 7: Calculated total density of states (tdOS, gray) together with Fe and S partial DOS (coloured lines) of *o*-Rb₆[Fe₂S₆] (top) and Rb₁₂[Fe₂S₆](S₂)₃ (bottom) in the range between -4.9 and 3.6 eV relative to E_F .

ions exhibit a less negative Bader charge than the S ligand atoms of the ferrate anions. The S–S bonds show a high electron density at the bond critical point ($\rho_{\text{BCP}} = 0.87 \text{ e}^- 10^{-6} \text{ pm}^{-3}$ and a Laplacian of $-3.36 \times 10^{-8} \text{ pm}^{-5}$, which both nicely agree with calculated (0.89, -2.8) as well as experimental (0.83, -3.7) values obtained for the disulfide moiety in pyrite (FeS₂) [70].

3.6 Comparison of bonding and magnetism in the Rb diferrates Rb₆[Fe₂Q₆]

The results of the calculations on the three Rb-diferrates Rb₆[Fe₂Q₆] allow to compare the bonding features (covalency, electron and spin densities, magnetic moments and exchange path, etc.) among the series, i.e. from O to Se ligands. For the three Rb-salts, the calculated DOS of the majority spin are illustrated in Fig. 8. Further results of the

calculations are summarized in the last three columns of Table 6. The DOS of the three compounds show the same uniform features, with some general trends evident: From O to Se, the block of occupied Fe-*d* states (lower Hubbard band) is shifted to higher energies. Simultaneously, the energy of the upper Hubbard band and therewith the band gap decreases from 2.15 eV in the oxido down to 1.24 eV in the selenido ferrate. The smaller dispersion of all bands in the oxido salt can be ascribed to the predominantly ionic bonding.

The Fe–Q bonds in all diferrates exhibit distinct bond critical points (BCP) in the electron density map, whereas the midpoint of the Fe–Fe vector coincides with a ring critical point. As always, the height of the electron density at the BCP (ρ_{BCP}) decreases with increasing Fe–Q bond lengths and thus does not carry a valuable information for the comparison of the bonding of the three chalcogenido ligands. In contrast, the change of the character of the chemical bonding from predominantly ionic to covalent becomes evident from the strong differences of the Laplacian of the electron density at the BCP [71], which decreases from +12.9 for the Fe–O via +3.6 for the Fe–S down to $+2.6 \times 10^{-8} \text{ pm}^{-5}$ for the Fe–Se bond.

A concordant trend is the continuous decrease of the Fe Bader charges q_{Fe} from +1.61 in the oxido via +1.11 (Q=S) to +0.97 in the selenido dimer, with a simultaneous increase of the Bader volumes (V_{BB}). The calculated iron charges of the sulfur compounds are thereby in the typical range of the respective Fe(III) sulfido ferrates [4] and are clearly larger than the calculated values of mixed valent dimer [72], chain [73] or cluster [14] ferrates.

The results of the DFT band structure calculations allow to specify the nature of the observed reduction of the magnetic moments of Fe (which is not nearly as large as usually determined when using the Heisenberg model to fit the magnetic susceptibility data [5]): For all dimers, the five Fe-*d*[↑] states are fully occupied (≈ 0.9). Together with a small *s*-*d*_{*z*²} mixing (*s* occupation ≈ 0.1 , cf. the states at -3 and -3.6 eV), the resulting overall Fe[↑] electron numbers are 4.59–4.64. Contrarily, the different σ donor capabilities of the chalcogenido ligands cause distinct differences in the Fe-*d*[↓] population: Only for the sulfido and the selenido ligands, the *d* states of the *t*₂ subset (blue, green and cyan lines in Fig. 9), i.e. those *d* orbitals pointing towards the Q ligands, are twice as strongly occupied as the *e* states *d*_{*z*²} (red lines) and *d*_{*x*²−*y*²} (orange lines). The consequences of this specific further *L*→*M* donation are reduced magnetic moments, especially for the S and Se compounds (O: 3.83; S: 3.49; Se: 3.48 μ_B). The derived values for the Fermi contact contribution of the magnetic hyperfine field of 274 (Q=O), 21.2 (S) and 20.4

Table 6: Details and selected results of the calculation of the electronic structure of $\text{Rb}_{12}[\text{Fe}_2\text{S}_6](\text{S}_2)_3$ and the orthorhombic diferrates $\text{Rb}_6[\text{Fe}_2\text{Q}_6]$ ($\text{Q} = \text{O}, \text{S}, \text{Se}$).

Compound	$\text{Rb}_{12}[\text{Fe}_2\text{S}_6](\text{S}_2)_3$	$\text{Rb}_6[\text{Fe}_2\text{S}_6]$	$\text{Rb}_6[\text{Fe}_2\text{Se}_6]$	$\text{Rb}_6[\text{Fe}_2\text{O}_6]$
Crystal data	Tables 1 and 2	[4]	Tables 1 and 2	[23]
R_{mt} , pm		Rb: 116; Fe/O/S/Se: 111; S in S_2 : 105		
$R_{\text{mt}} \cdot K_{\text{max}}$	7.5	7.5	8.0	7.5
k -points/(BZ, IBZ)	432, 216		864, 126	900, 250
Monkhorst-Pack-Grid	$9 \times 8 \times 6$		$12 \times 12 \times 6$	$10 \times 9 \times 10$
DOS plot	Fig. 7, top	Fig. 7, bottom		Fig. 8
Band gap/eV	1.34	1.47	1.24	2.15
	Bond ^a			
ρ_{BCP} , $\text{e}^- 10^{-6} \text{ pm}^{-3}$	a 0.600/3.62 (223.4)	0.584/3.55 (224.8)	0.509/2.61 (237.4)	0.849/12.92 (184.5)
$\nabla^2 \rho_{\text{BCP}}$, $\text{e}^- 10^{-8} \text{ pm}^{-5}$	b 0.593/3.61 (224.0)	0.524/3.36 (229.6)	0.440/-(242.0)	0.668/9.94 (194.2)
(d , pm)	c 0.515/3.36 (230.4)	—	—	0.661/9.74 (194.6)
	d 0.497/3.23 (232.2)	—	—	—
	e 0.867/-3.36 (211.0)	—	—	—
	f 0.867/-3.36 (213.4)	—	—	—
	Ring ^b	0.195/1.30	0.170/0.95	0.24/2.24
	Fe-Fe	289.9	309.8	272.8
	Atom			
Bader charge	Rb(1) +0.783 (27.7)	+0.789 (30.5)	+0.770 (31.7)	+0.803 (25.6)
(volume, 10^6 pm^3)	Rb(2) +0.786 (28.3)	+0.785 (28.3)	+0.773 (29.8)	+0.794 (25.7)
	Rb(3) +0.769 (28.9)	—	—	+0.789 (24.8)
	Rb(4) +0.795 (30.7)	—	—	—
	Rb(5) +0.800 (30.8)	—	—	—
	Fe +1.111 (12.0)	+1.113 (11.9)	+0.968 (13.5)	+1.611 (10.3)
	Q(1) -1.100 (33.0)	-1.080 (32.6)	-0.987 (29.3)	-1.321 (18.2)
	Q(2) -1.188 (38.2)	-1.198 (39.4)	-1.145 (47.1)	-1.337 (18.0)
	Q(3) -1.193 (41.1)	—	—	—
	Q(4) -0.794 (36.9)	—	—	—
	Q(5) -0.782 (32.6)	—	—	—
	Q(6) -0.787 (36.7)	—	—	—
Magnetic moment/ μ_{B}	Fe 3.56	3.56	3.55	3.89

^aBond labels cf. Tables 3 and 4, ^bring critical point in the center of the Fe_2Q_2 rhomb.

Fig. 8: Calculated total density of states (tDOS, gray) together with Fe and O/S/Se partial DOS (coloured lines) of $\text{Rb}_6[\text{Fe}_2\text{O}_6]$, $o\text{-Rb}_6[\text{Fe}_2\text{S}_6]$ and $o\text{-Rb}_6[\text{Fe}_2\text{Se}_6]$ in the range between -5.8 and 3.9 eV relative to E_{F} .

Fig. 9: Calculated Fe-d (coloured lines) and S-p pDOS (gray, divided by 8) of $\text{Rb}_6[\text{Fe}_2\text{Se}_6]$ in the range between -4.9 and 2 eV relative to E_{F} .

T (Se) (and the trends among them) are consistent with the reliable values for the effective magnetic hyperfine fields H_{eff} obtained for the chain ferrates from Mössbauer

spectroscopic data at low temperatures (cf. Tab. 3.4). These results are in agreement with the comparative theoretical and X-ray absorption study of Atanasov et al. on an ortho ($\text{Na}_2[\text{FeS}_4]$) and a chain sulfido ferrate ($\text{K}[\text{FeS}_2]$), in which the authors observed a strong mixing of d^5 and d^6L states, i.e. a distinct $\text{S} \rightarrow \text{Fe}$ electron transfer, already in the separate $[\text{FeS}_4]^{5-}$ units [5]. They also report on a considerable occupation of the Fe 4s states, which explains the – for HS-Fe(III) ions – comparatively low Mössbauer isomer shifts of 0.15–0.36 mm/s [74]. The comparable δ values of the oxido dimers and the sulfido/selenido chain ferrates (further Mössbauer spectroscopic data are unfortunately lacking to date) are compatible with the similar Fe 4s occupation obtained from the band structure calculations. They also show, that the degree of Fe 4s population is not

connected with the covalency of the Fe–Q bond. The comparable value of 0.202 mm/s for the tetrahedral network of $\text{Rb}[\text{FeO}_2]$ also confirms, that the connectivity of the $[\text{FeQ}_4]$ tetrahedra makes no difference [75]. The strong variation of the quadrupol splitting of the ^{57}Fe Mössbauer doublet is evidently related to the deviation from the ideal tetrahedral symmetry, which is very pronounced in the dinuclear species (e.g. $\text{Rb}_6[\text{Fe}_2\text{O}_6]$: $\Delta E = 1.55 \text{ mms}^{-1}$, connected with a high calculated EFG ($V_{zz} = 7.9 \times 10^{21} \text{ V m}^{-2}$, $\eta = 0.251$). Overall, the Mössbauer spectroscopic parameters are conformant with the values found in similar molecular 2Fe-2Q dinuclear complexes [7].

The specific reduction of the magnetic moment via the t_2 subset of the Fe- d states also becomes evident from the spin density plots, which are shown in Fig. 10 for

Fig. 10: Spin densities of $\text{Rb}_6[\text{Fe}_2\text{Q}_6]$: (a) schematic diagram of the superexchange in $[\text{Fe}_2\text{Q}_6]$ dinuclear units; (b) perspective view of the spin density map of $\text{Rb}_6[\text{Fe}_2\text{Se}_6]$ at a level of $\pm 0.01 \text{ e} \cdot 10^{-6} \text{ pm}^{-3}$; (c and d) spin densities of $\text{Rb}_6[\text{Fe}_2\text{O}_6]$ and $\text{Rb}_6[\text{Fe}_2\text{Se}_6]$ in the xz plane (yellow points: BCPs).

$\text{Rb}_6[\text{Fe}_2\text{O}_6]$ and $\text{Rb}_6[\text{Fe}_2\text{Se}_6]$. The perspective view of the spin density map of $\text{Rb}_6[\text{Fe}_2\text{Se}_6]$ in Fig. 10b illustrates the strong spin distribution on the terminal Q ligands. Independent of the type of the chalcogene, the μ_2 - Q ligand's p states exhibit an 'outer' spin polarization, which is accompanied by an 'inner' reverse and more pronounced spin distribution (Fig. 10c). These features of the spin density are fully comparable with those found for GaFeO_3 and its S -substituted derivative [76], which likewise exhibit Fe– Q –Fe bridges associated with a strong antiferromagnetic exchange.

The calculated spin densities can accordingly be transferred into a simplified picture of the superexchange mechanism (Fig. 10a), which easily explains the AFM spin ordering even for the HS- d^5 electron configuration of Fe(III) (which is not compatible with the classical 90° superexchange GKA rules [77, 78]) without any need for π -bonding contribution, for which the calculated bond ellipticity values (η) of the Fe– Q bonds do not provide any indication. The magnetic superexchange via ligand polarization does not require any covalent bonding [79], but is merely established by a sufficient electron (and spin) density along the Q –Fe contact, i.e. a considerable electron density at the bond critical point. In the three compounds $\text{Rb}_6[\text{Fe}_2Q_6]$, these ρ_{BCP} values at the Fe– μ_2 - Q bridges amount to 0.66 ($Q=\text{O}$), 0.52 (S) and 0.44 (Se) $\text{e}^-10^{-6} \text{ pm}^{-3}$ and are thereby – despite the change in the bonding type – not too different.

In conclusion, the AFM band structure calculations, the comparison of anion geometries and the reliable magnetic data of the dimers $A_6[\text{Fe}_2Q_6]$ and the chain ferrates(III) $A[\text{Fe}Q_2]$ provide several arguments against a direct Fe–Fe magnetic exchange in these compounds, although this type of exchange mechanism is still discussed in recent references (e.g. for $\text{Rb}[\text{FeSe}_2]$ in [6]) and is appropriate for dinuclear coordination compounds with very short Fe–Fe distances below 270 pm [7]:

- In all alkali chalcogenido ferrates(III), the Fe–Fe distances are larger than 270 pm and the magnetic interactions are still very strong in compounds with Fe–Fe distances of about 310 pm (e.g. in $\text{K}_6[\text{Fe}_2\text{Se}_6]$ [43]).
- The spin densities of the Fe(III) cations do not show any deviation from a spherical shape along the Fe–Fe vector (cf. circles around the iron atoms in Fig. 10c and d), whereas they deviate widely from spheres in the direction towards the ligands.
- The Fe partial DOS does not show a pronounced occupation of the Fe- d_{z^2} states, which could be considered as an indication for a direct exchange.
- The reliable magnetic coupling parameters J in the sulfido compounds coherently amount to approx. -5 meV per Fe–S–Fe bridge (i.e. $\approx -10 \text{ meV}$ for the

dinuclear and $\approx -20 \text{ meV}$ for the chain ferrates). This value also corresponds to the J parameter of CuFeS_2 , where a direct Fe–Fe interaction is fully excluded due to the corner-sharing of the $[\text{FeS}_4]$ tetrahedra in the chalcopyrite structure. [In contrast, the magnetic coupling of recently reported coordination compounds with a much shorter Fe–Fe distance of 264.7 pm and – according to DFT calculations – a predominant direct Fe–Fe exchange are with -22.7 meV much larger [7]].] Similarly, the very high Néel temperature of the cristobalite-like $[\text{FeO}_2]^-$ network in $\text{Rb}[\text{FeO}_2]$ [75, 80, 81] and the comparable ^{57}Fe Mössbauer isomer shifts of $\text{Rb}[\text{FeO}_2]$ and $\text{Rb}_6[\text{Fe}_2\text{O}_6]$ demonstrate, that the AFM exchange mechanisms of edge- and corner-sharing tetrahedrally coordinated Fe(III) HS ions are not fundamentally different.

The influence of the alkali counter ion on the bond distances and angles inside the dimers and the chains is only marginal. After a critical review of the magnetic parameters (μ , H_{eff} , J) obtained from susceptibility data, this also applies for the magnetic interactions of the Fe(III) ions. Therefrom exempted are the strong changes of J' (and similarly the J'/J ratio) for the overall magnetic ordering at low temperatures from sodium to cesium salts, which are attributed to the increasing separation of the ferrate anions.

4 Summary

In the course of a systematic re-investigation of the ternary systems Rb–Fe–S/Se, the two new chalcogenido ferrates(III) $\text{Rb}_{12}[\text{Fe}_2Q_6](Q_2)_3$ ($Q=\text{S/Se}$) were prepared from Rb, Fe and either Rb_2S or elemental Se. Similarly, the missing members of the series $A_6[\text{Fe}_2\text{Se}_6]$, the two polymorphs of $\text{Rb}_6[\text{Fe}_2\text{Se}_6]$ which are isotypic to their sulfido counterparts, were prepared and structurally characterized by means of single crystal X-ray data. Like the pure diferrates $\text{Rb}_6[\text{Fe}_2Q_6]$, the new triclinic mixed diferrates/dichalcogenides contain layers of anions composed of two edge-sharing $[\text{Fe}Q_4]$ tetrahedra, in this case alternating with layers of dichalcogenide dumbbells $[Q_2]^{2-}$. GGA + U band structure calculations considering the AFM ordering in the dimers have been performed for the new compounds as well as for the pure diferrate series $A_6[\text{Fe}_2Q_6]$ ($Q=\text{O, S, Se}$). The occupation of the individual Fe- d and s states and the spin density maps corroborate the HS state of Fe(III) with only slightly reduced magnetic moments caused by a Fe– Q electron donation, particularly for S/Se

ligands. Regardless of the character of the Fe–Q bond, the strong AFM interaction is supported by a superexchange mechanism achieved by a spin polarization of the ligand's *p* states.

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