

4. An Fe^{57} Mössbauer Study of Selected Binary and Ternary Vanadium Sulfides

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Mössbauer data recorded at room temperature and 78 K for several binary and two new ternary vanadium sulfides are presented. The results are discussed in comparison with the structures and magnetic susceptibility measurements. A change in the spin state of the Fe-atoms from the Fe^{2+} high-spin state to the low-spin state is observed in the binary vanadium sulfides. This change is due to a shortening of the crystallographic c -axis which is nearly parallel to short metal-metal distances. In one ternary thallium vanadium sulfide the Fe is in the unusual trivalent low-spin state at room temperature.

Introduction. – The 3d transition-metal sulfides with metal-deficient NiAs structures are of interest because of their unusual magnetic and electric properties [1–19]. They result from the intermediate character between ionic and covalent/metallic bonding of the valence interactions. In the composition range from VS to VS_2 , the defined structures V_3S_4 and V_5S_8 are known with metal vacancies situated in alternate metal layers. The arrangement of atoms in the two structures is shown in *Fig. 1* and *2*.

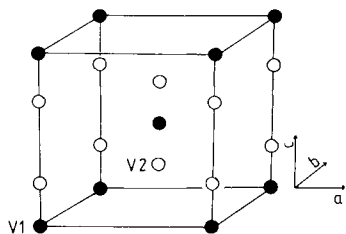


Fig. 1. The V_3S_4 structure with the $V(1)$ -atoms in the metal-deficient layers and the $V(2)$ -atoms in the filled layers. The S-atoms are omitted for clarity.

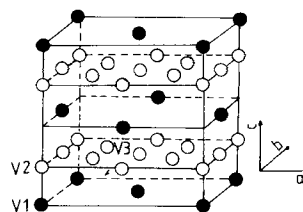


Fig. 2. The V_5S_8 structure with the $V(1)$ -atoms in the partially depleted metal layers, and the $V(2)$ - and $V(3)$ -atoms in the filled layers. The S-atoms are omitted for clarity.

Two different metal sites exist in the V_3S_4 structure. The V-atom in the metal-deficient layers is denoted as $V(1)$, the V-atom in the filled layers as $V(2)$ (*Fig. 1*). Short metal-metal distances between the two V types parallel to the c -axis allow overlap of the d orbitals and hence metallic properties in this direction. Some authors have substituted partially V

by Fe [13–19] leading to the ternary compounds $V_{3-x}Fe_xS_4$ being isomorphous to the V_3S_4 structure in the range $0 \leq x \leq 2.0$ (13). With increasing x the observed contraction of the c -axis is mostly interpreted with the stronger polarization of the Fe in the distorted VS_6 octahedra, *i.e.* due to better overlap the Fe–S bond is shorter than the V–S bond.

A *Raman* study on this series of compounds reveals that the metal-metal stretching frequency shifts to lower values with increasing x and to higher values at 70 K (15). From this observation, one may conclude that with decreasing temperature the metal-metal interaction becomes stronger. *Mössbauer* studies and neutron-diffraction investigations were used to clarify site distribution of the Fe-atoms in this composition range [13] [20]. From these data, it emerges that the Fe-atoms prefer the V(1) site up to a concentration of $x = 1.0$. Magnetic measurements in the range $V_{3-x}Fe_xS_4$ ($0 \leq x \leq 1.0$) show that these compounds order antiferromagnetically and the *Neel* point increases with increasing x reaching 140 K at the composition V_2FeS_4 ([14] [21] [22]; the value for T_N of this compound varies from 131 K to 140 K). From *Mössbauer* parameters a Fe^{2+} in the high-spin state is deduced [13] [14].

In V_5S_8 , there are three different V sites (*Fig. 2*). The V-atoms in the partially depleted layers is denoted as V(1), the V-atoms in the fully occupied layers are denoted as V(2) and V(3). Short metal-metal distances parallel to the c -axis and in the a - b plane again lead to metallic properties of this compound. With increasing x in $V_{5-x}Fe_xS_8$, mainly the c -axis is reduced (see *Table 3*).

In contrast to $V_{3-x}Fe_xS_4$, the introduction of Fe in V_5S_8 lowers the *Neel* point with increasing x and zero temperature is reached at about $x = 0.55$ [14]. From *Mössbauer* studies, one Fe^{2+} in the low-spin state is deduced [14]. At room temperature, the spin state is neither pure low-spin Fe^{3+} nor high-spin Fe^{2+} , but a mixed valence state with a very fast fluctuating rate [11].

During our investigations of channel structures of the types TlV_5S_8 [23] [24] and $Tl_xV_6S_8$ [24–26], we have prepared $Tl_{0.96}V_4FeS_8$ and $Tl_{0.77}V_5FeS_8$. In TlV_5S_8 occur three different V sites. It seems likely, therefore, that different kinds of interactions between V and S and between V and V may occur within the same material (structure details in [23]). To interpret the results of magnetic susceptibility and from *Mössbauer* resonance data and to characterize the final products, it was necessary to investigate also the starting materials by the *Mössbauer* technique. We prepared samples of the series $V_{5-x}Fe_xS_8$ ($x = 0.5$ and 1.0) and $V_{3-x}Fe_xS_4$ ($x = 0.5$ and 1.0) to reinvestigate the *Mössbauer* parameters of these compounds and to obtain a consistent data set.

Since in the previous work only few experimental details are specified, it is not unambiguous to compare the various published data sets. Most of the spectra were displayed as raw data only. The differences in the isomer shifts quoted are beyond the error margin. Not all hyperfine parameters of these materials have been reported so far.

Experimental. – The samples of the $V_{3-x}Fe_xS_4$ series were synthesized by direct reaction of the elements. The mixtures were sealed in evacuated ampoules and heated for 7 d at 1073 K. In a second step, the samples were annealed at 1193 K for 14 d. After this treatment, the samples were ground and homogenized at 1223 K for 7 d. The products were slowly cooled down to r.t. to avoid a high degree of defects. The samples of the $V_{5-x}Fe_xS_8$ series were synthesized at lower temp. because of the higher S partial pressure. In a first step, the mixtures were sintered at 673 K and subsequently heated to 1073 K for 7 d. In a second step, the ground samples were homogenized at about 973 K for 5 to 10 d. The thallium-vanadium-iron chalcogenides were prepared by reacting weighted amounts of the samples described above with Tl metal (details in [28]). The authenticity and homogeneity of all samples was checked by X-ray powder diffractometry or with *Guinier* photographs. Chemical analyses were carried out with

standard atomic-absorption spectrometry. *Mössbauer* spectra were recorded with a conventional constant acceleration spectrometer using a ^{57}Co in Pd source (about 30 mCi). All spectra were calibrated against natural Fe at 300 K. Magnetic susceptibility data were obtained with a *Faraday* balance in the temp. range between 4.2 K and 300 K at various fields up to 0.81 T. The balance was calibrated with $\text{CoHg}(\text{SCN})_4$ [29].

Results and Discussion. – An important aspect of interpreting the bonding properties of such compounds is the inconsistency of the models assumed for the bonding in these compounds. The magnetic behaviour is best described by the coexistence of itinerant

Table 1. *The Derived Mössbauer Data*^{a)}. The significant standard deviation is given in parenthesis.

Compound	T[K]	IS	QS	Γ	Rel. area
$\text{V}_{2.5}\text{Fe}_{0.5}\text{S}_4$	300	0.645(1)	0.657(2)	0.225(2)	1.01
	78	0.354(1)	0.402(2)	0.242(2)	–
V_2FeS_4	300	0.445(1)	0.584(1)	0.268(2)	1.5
	300	0.547(1)	0.537(1)	0.330(2)	4.2
	78	0.345(2)	0.311(1)	0.376(4)	1.42
	300	0.552(1)	0.271(1)	0.249(2)	–
$\text{V}_{4.5}\text{Fe}_{0.5}\text{S}_8$	78	0.266(1)	0.294(1)	0.211(1)	–
	300	0.520(1)	0.348(1)	0.325(2)	1.06
V_4FeS_8	78	0.292(1)	0.297(1)	0.182(4)	–
	300	0.635(2)	0.626(2)	0.239(2)	–
$\text{Ti}_{0.77}\text{V}_3\text{FeS}_8$	300	0.635(2)	0.626(2)	0.239(2)	–
$\text{Ti}_{0.95}\text{V}_4\text{FeS}_8$	300	0.412(1)	0.453(1)	0.234(1)	1.17

^{a)} The isomer shift (IS), the quadrupole splitting (QS), and the line width at half height (Γ) are given in mm s^{-1} relative to metallic Fe. For asymmetric doublets, the peak area ratio (rel. area) was calculated by numerical integration.

Table 2. *Mössbauer Data of Some Fe-Containing Chalcogenides for Comparison*

Compound	IS [mm s^{-1}]	QS [mm s^{-1}]	Spin (S)	T [K]	Ref.
FeS	0.77	–	2	293	[33]
$\text{V}_3\text{S}_4:\text{Fe}$	0.54	–	2	293	[14]
$\text{V}_3\text{S}_4:\text{Fe}$	0.83	–	2	4.2	[14]
V_2FeS_4	0.57	–	2	293	[14]
V_2FeS_4	0.83	–	2	4.2	[14]
$\text{V}_5\text{S}_8:\text{Fe}$	0.94	–	0	293	[14]
$\text{V}_5\text{S}_8:\text{Fe}$	1.14	–	0	4.2	[14]
$\text{V}_5\text{S}_8:\text{Fe}$	0.58	0.28	?	293	[11]
$\text{V}_5\text{S}_8:\text{Fe}$	0.64	0.67	0	4.2	[11]
V_4FeS_8	0.89	–	0	293	[14]
V_4FeS_8	0.71	–	0	4.2	[14]
Fe_{1-x}S	0.67	0.24	2	293	[30]
FeS_2 (Pyrite)	0.314	0.614	0	300	[35]
FeS_2 (Marcasite)	0.277	0.506	0	300	[35]
Fe_3S_4	0.70	0.30	2	293	[33]
$\text{Fe}_{0.1}\text{Ta}_{0.9}\text{S}_2$	0.50	0.24	0	293	[37]
$\text{Fe}_{0.1}\text{V}_{0.9}\text{S}_2$	0.40	–	0	4.2	[34]
FeTi_2S_4	0.78	0.22	2	293	[30]
FeMo_2S_4	0.80	0.79	2	293	[30]
$\text{Fe}_{0.01}\text{Co}_{0.99}\text{S}_2$	0.20	0.32	0	298	[31]
$\text{Fe}_{0.01}\text{Co}_{0.99}\text{S}_2$	0.29	0.33	0	100	[31]
$\text{BaVS}_3:\text{Fe}$	0.45	1.36	$\frac{1}{2}$	293	[11]
$\text{BaVS}_3:\text{Fe}$	0.60	1.51	$\frac{1}{2}$	20	[11]

Table 3. *Lattice Parameters of the Compounds $V_{3-x}Fe_x$ ($x = 0.5$ and 1.0) and $V_{5-x}Fe_xS_8$ ($x = 0.5$ and 1.0)^{a)}. The lattice parameters of the pure sulfides are given for comparison. The significant standard deviation is given in parenthesis.*

Compound	Axial dimensions [Å]	Angle β [°]
V_3S_4	a = 5.867(2) b = 3.282(1) c = 11.362(2)	92.05
$V_{2.5}Fe_{0.5}S_4$	a = 5.859(6) b = 3.296(3) c = 11.350(11)	91.92(2)
V_2FeS_4	a = 5.857(10) b = 3.293(6) c = 11.197(18)	92.02(2)
V_5S_8	a = 11.375(5) b = 6.648(2) c = 11.299(6)	91.50
$V_{4.5}Fe_{0.5}S_8$	a = 11.393(6) b = 6.657(3) c = 11.300(6)	91.42(2)
V_4FeS_8	a = 11.361(9) b = 6.644(5) c = 11.171(8)	91.24(2)

^{a)} The data for the pure sulfides are taken from [2].

(delocalized) electrons, which are characterized by the temperature-independent paramagnetism (TIP) and localized electrons which obey the *Curie-Weiss* law. Electrical conductivity of the compounds discussed here, however, is characteristic for a metal. Furthermore, the parameters derived from the *Mössbauer* experiments are interpreted in terms of Fe cations embedded in a continuum of S anions. The treatment of the observations in the *Mössbauer* and magnetic experiments within the crystal-field theory is, consequently, a simplification of the real bonding properties in these compounds which are not represented adequately by the extreme models of ionic or metallic interactions.

In the following, we will give an interpretation of our *Mössbauer* data set presented in *Table 1*. A set of *Mössbauer* reference data from the literature is given in *Table 2*. Since we will discuss *Mössbauer* parameters in connection with lattice constants and metal atom distances, some crystallographic information is compiled in *Table 3*. The lattice parameters are refined values obtained from a least-squares fitting routine with data from *Guinier* photographs.

The Compounds $V_{3-x}Fe_xS_4$ ($x = 0.5$ and 1.0). The value for the isomer shift (IS) of 0.645 mm s^{-1} for $V_{2.5}Fe_{0.5}S_4$ at 300 K is intermediate between Fe^{2+} in the high-spin state with $S = 2$, and Fe^{2+} in the low-spin state with $S = 0$ in an octahedral environment. Following *Fatseas et al.* [30], only an IS of up to 0.5 mm s^{-1} is a distinct indication for a Fe^{2+} in the low-spin state in predominantly ionic compounds. From structural considerations, however, the relatively low value for the IS compared with high-spin compounds like FeS and $FeTi_2S_4$ (*Table 2*) may be caused by a higher degree of covalency relative to FeS as indicated by the short metal-metal distances parallel to the *c*-axis. The value for the quadrupole splitting (QS) of 0.657 mm s^{-1} is high compared with the values given in *Table 2*.

Since we can not separate the lattice and electronic contributions to the QS, we are not able to interpret the QS in detail. But it seems likely that the octahedral environment is more distorted in the present compounds than in the materials listed in *Table 2*.

At 78 K the IS is decreased to 0.354 mm s^{-1} indicating a change in the spin state of the Fe-atom. A *Raman* study of $V_{3-x}Fe_xS_4$ compounds showed a change in the metal-metal vibration frequency with decreasing temperature [15]. This change may be due to a slight change in the metal-metal distances and, therefore, a change in the environment of the Fe-atom is expected. The decrease of the QS with temperature confirm the assumption of a change of the environment around the Fe-atom.

The observation of only one type of Fe is consistent with the fact that Fe prefers the metal sites in the partially depleted metal layers at this composition [20].

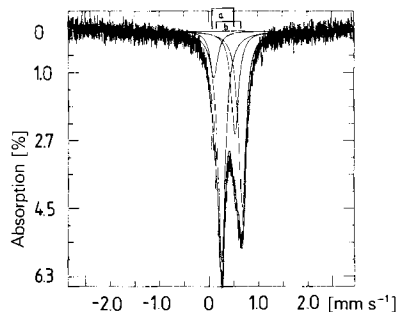


Fig. 3. The room-temperature Mössbauer spectrum of V_2FeS_4 . For details see text.

The room-temperature spectrum of V_2FeS_4 (*Fig. 3*) exhibits two doublets – *a* and *b* – due to two different Fe sites in the structure. The presence of a second crystalline phase is excluded from *Guinier* powder photographs. The stronger doublet *b* shows an IS of 0.547 mm s^{-1} and a QS of 0.537 mm s^{-1} in agreement with [14]. The decrease of IS and QS compared to the values for $V_{2.5}Fe_{0.5}S_4$ again is consistent with a shortening of the crystallographic *c*-axis. The trigonal distortion of the octahedra is reduced, and, therefore, the QS is smaller than in $V_{2.5}Fe_{0.5}S_4$. The IS is very low for an Fe-atom Fe^{2+} in the high-spin state. Magnetic measurements reveal a reduction of the effective magnetic moment to $\mu_{\text{eff}} = 3.35 \mu_B$ per Fe-atom in the temperature range 300–140 K compared to a literature value of $3.40 \mu_B$ [22]. The reduction of μ_B compared with the spin only value $4.91 \mu_B$ (the V-atoms in the full layers are nonmagnetic) could be interpreted as an admixture of Fe d-states to the V d-states. At higher temperatures the d systems are decoupled and the effective magnetic moment lies closer to the spin-only value [22]. The IS of the smaller doublet is in agreement with a Fe^{2+} low-spin state. Such a twin doublet structure is reported for the Fe-rich compound $V_{1.5}Fe_{1.5}S_4$ with an IS of about 0.60 mm s^{-1} and a QS of about 0.42 mm s^{-1} [13], which we were unable to reproduce at that composition.

At 78 K the compound is antiferromagnetic. A multiline spectrum is expected due to the internal magnetic field. As it can be seen from *Fig. 4*, however, no magnetic splitting is observed. The fit procedure leads to a single doublet with an IS of 0.345 mm s^{-1} indicative of Fe^{2+} in the low-spin state. The highly asymmetric doublet and the wide line, however, may be an indication of the onset of the hyperfine splitting.

The reduction of the IS compared to $V_{2.5}Fe_{0.5}S_4$ at 78 K might be again due to the shortening of the *c*-axis with temperature and a resulting increase in overlap. This should result in a lower value for the QS as compared to $V_{2.5}Fe_{0.5}S_4$ (see *Table 1*).

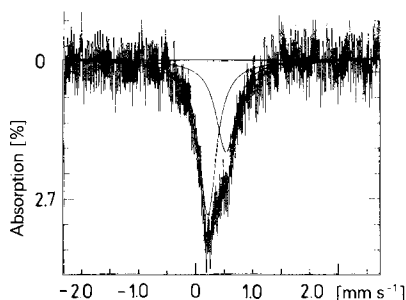


Fig. 4. The Mössbauer spectrum of V_2FeS_4 recorded at 78 K. For details see text.

Our results and those in [13] [14] are remarkably different. The difference between the room-temperature value for the IS and the value at 4.2 K is 0.26 mm s^{-1} for V_2FeS_4 [14] being too large to be explained by second-order *Doppler* shift, which reaches above the characteristic *Debye* temperature θ_D the classical limit of $7.3 \cdot 10^{-4} \text{ mm s}^{-1} \text{ K}^{-1}$. If we assume a maximum value for the *Doppler* shift of about 0.15 mm s^{-1} , the value for the IS at 4.2 K should be 0.72 mm s^{-1} . The observed IS of 0.83 mm s^{-1} at 4.2 K seems to be too high for a Fe^{2+} in the low-spin state and a Fe^{2+} in the high-spin state contradicts the magnetic measurements.

The Compounds $V_{5-x}Fe_xS_8$ ($x = 0.5$ and 1.0). The IS of about 0.552 mm s^{-1} at 300 K is at the lower limit for Fe^{2+} in the high-spin state in $V_{4.5}Fe_{0.5}S_8$. This low value is attributed to short metal-metal distances parallel to the crystallographic *c*-axis and in the *a-b* plane. The QS is of the same order as the values given in *Table 2* for Fe^{2+} in the high-spin state. The IS at 78 K of 0.27 mm s^{-1} is an indication for a Fe^{2+} in the low-spin state and in agreement with the magnetic measurements [11], which show that the magnetic susceptibility of $V_{4.55}Fe_{0.45}S_8$ is only slightly higher than the susceptibility of the pure sulfide at this temperature. The slight change of the QS is ascribed to small configuration changes of the valence state.

Massenet et al. [11] obtained an IS of 0.58 mm s^{-1} for a V_5S_8 sample doped with 2 wt.-% ^{57}Fe . This value is in good agreement with our results for $V_{4.5}Fe_{0.5}S_8$. At 4.2 K, the IS reaches 0.64 mm s^{-1} [11]. The QS is increased to 0.67 mm s^{-1} at 4.2 K from 0.28 mm s^{-1} at room temperature. This value is high for a Fe^{2+} in the low-spin state. The line width is lower than the ^{57}Fe natural line width at both temperature (0.15 mm s^{-1} at 300 K and 0.17 mm s^{-1} at 4.2 K) [11]. From magnetic measurements and the *Mössbauer* parameters, *Massenet et al.* concluded that at 4.2 K the Fe-atoms are in the Fe^{2+} low-spin state and in the temperature range 50 K to 200 K the Fe switches to a magnetic state which seems to be neither pure low-spin Fe^{3+} nor high-spin Fe^{2+} , but a mixed valence state fluctuating at a rate too fast to be distinguished by the *Mössbauer* effect [11].

Our results deviate remarkably from those published in [14]. The value for the IS of a V_5S_8 sample doped with 1 wt% ^{57}Fe are 0.94 mm s^{-1} at 300 K and 1.14 mm s^{-1} at 4.2 K. These large IS are due to high-spin Fe^{2+} at both temperatures, in disagreement with magnetic measurements [14]. The somewhat lower IS for V_4FeS_8 of 0.52 mm s^{-1} compared with the IS for the Fe-poorer sample again is ascribed to shorter metal-metal distances in this compound. This effect – decreasing of the IS with increasing covalency – is also observed in the system $Co_{1-x}Fe_xS_2$ [31].

The IS decreases with temperature to a value of 0.292 mm s^{-1} at 78 K, indicating a Fe^{2+} in the low-spin state. We observed in low-temperature powder photographs (taken with a

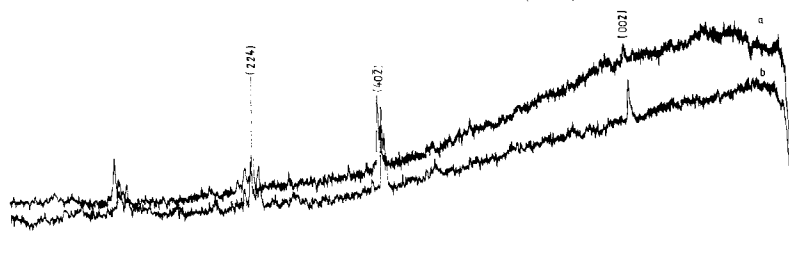


Fig. 5. The photodensitometer curves of X-ray powder photographs of V_4FeS_8 taken with a Simon camera. Only a few reflections are indexed. a) Recorded at 78 K; b) At room temperature.

Simon camera) a significant contraction of the c -axis, which is nearly parallel to short metal-metal distances (see Fig. 2 and Fig. 5). This leads us, together with the changes in relative intensities of principal reflections (see Fig. 5), to the conclusion that the low-temperature contraction of the structure qualitatively influences the whole electronic structure of the compound, which is consistent with the observed decrease in QS at 78 K. From the QS of 0.348 mm s^{-1} at 300 K and 0.297 mm s^{-1} at 78 K and their temperature dependence relative to the variation in the IS, we conclude that the Fe-atoms are in the high-spin state at 300 K and in the low-spin state at 78 K. The nearly identical values for QS for the two compounds at 78 K indicate that the lattice contribution to the QS is similar for both compounds. The slight decrease of the QS on going from V_4FeS_8 to $V_{4.5}Fe_{0.5}S_8$ at 300 K is due to the smaller distortion of the octahedral symmetry as consequence of the lower Fe content (see also Table 3).

Finally from the data for the two compounds, we conclude that the Fe-atoms in both compounds are in the same environment. From structural arguments, the most probable site is located in the partially depleted layers. Fe in the fully occupied layers should mainly affect the a - and b -axis lattice parameters and not the c -axis. We note that our results are significantly different from those in [14].

The Compound $Tl_{0.77}V_5FeS_8$. The Mössbauer spectrum of this compound is displayed in Fig. 6. From the IS of 0.635 mm s^{-1} , we deduce iron in the Fe^{2+} high-spin state. The reduction of the IS compared with that of FeS [33] may be indicative of higher covalency in $Tl_{0.77}V_5FeS_8$. From short metal-metal distances parallel to the crystallographic c -axis strong interactions are expected. These interactions may lead to a shielding of the 4s orbitals and, hence, to a decrease of the IS. The value for the QS of 0.626 mm s^{-1} is larger

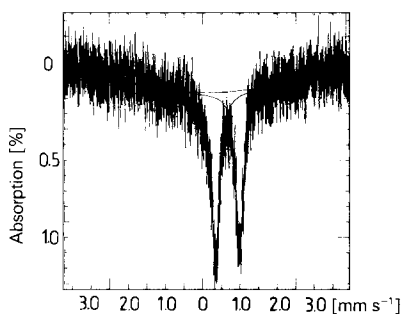


Fig. 6. The Mössbauer spectrum of $Tl_{0.77}V_5FeS_8$ recorded at 300 K. For details see text.

than the values given in *Table 2*. It should be mentioned that the octahedral environment in $Tl_{0.77}V_3FeS_8$ is much more distorted than in the compounds $V_{3-x}Fe_xS_4$ and $V_{5-x}Fe_xS_8$. The decision for Fe^{2+} in the high-spin state is supported by magnetic susceptibility measurements [32]. An effective magnetic moment of $3.03 \mu_B$ per Fe-atom is significantly lower than the spin-only value for Fe^{2+} high-spin ($\mu_{eff} = 4.90 \mu_B$), but too high for Fe^{3+} in the low-spin state ($\mu_{eff} = 1.73 \mu_B$). Fe^{2+} in the low-spin state can be excluded from the magnetic measurements. The reduction of the effective magnetic moment per Fe-atom again can be understood in terms of the participation of d electrons of the Fe-atoms in d-states in the compound.

The Compound $Tl_{0.95}V_4FeS_8$. The value for the IS of this compound of 0.412 mm s^{-1} offers three different possible electronic configurations of the Fe-atoms: Fe^{2+} in the low-spin state with $S = 0$, Fe^{3+} in the low-spin state with $S = 1/2$, and Fe^{3+} in the high-spin state with $S = 3/2$.

In the non-substituted compound TlV_5S_8 , V has the formal oxidation state +3. If we assume that the oxidation state is not changed with substitution, trivalent Fe should be present. From magnetic measurements an effective magnetic moment of $2.05 \mu_B$ per Fe-atom is derived assuming all V-atoms to be nonmagnetic [27]. From these measurements, a Fe^{2+} in the low-spin state is excluded, because it would be in contradiction with our observations that the whole magnetic moment in $Tl_{0.96}V_5S_8$ is localized on the V-atoms [27]. Furthermore, from the effective magnetic moment, a Fe^{3+} in the high-spin state is also impossible. From the magnetic data in relation with the IS, we conclude that iron is in the Fe^{3+} low-spin state. A similar IS is observed in $Fe_{0.5}V_{0.5}S_2$ [34]. The spin-only value for Fe^{3+} in the low-spin state is $1.73 \mu_B$. The somewhat higher μ_{eff} derived here is typical for Fe^{3+} compounds due to the not perfectly quenched orbital contribution [27].

Conclusions. – We have presented *Mössbauer* data for $V_{3-x}Fe_xS_4$ ($x = 0.5$ and 1.0), $V_{5-x}Fe_xS_8$ ($x = 0.5$ and 1.0), and data for the new compounds $Tl_{0.95}V_4FeS_8$ and $Tl_{0.77}V_5FeS_8$. In the substituted vanadium sulfides the Fe-atoms are in the Fe^{2+} high-spin state at room temperature. The values for the IS reflect an increase in covalency on going from $x = 0.5$ to $x = 1.0$. This covalency is due to shortening of the crystallographic c -axis in the structures. The values for the QS are, parallel to the lattice parameters, sensitive to the distortion of the electronic environment by various substitutional modifications of the V_3S_4 structure. A change in the spin state from high-spin to low-spin is observed in both systems at lower temperatures.

In $Tl_{0.77}V_5FeS_8$ the Fe-atoms are in the high-spin state. Strong metal-metal interactions parallel to the crystallographic c -axis reduce the IS and, therefore, the effective magnetic moment. The spin state of iron in $Tl_{0.95}V_4FeS_8$ is the unusual Fe^{3+} low-spin state with $S = 1/2$.

The line width of all compounds are only slightly higher than the natural line width. The slightly asymmetric intensity ratios of the peak areas may be caused by preferred orientation of the plate-like or needle-like crystals [36]. In general, we found an agreement between *Mössbauer* parameter and structural and magnetic informations. The unusual electronic structure as reflected by our measurements in comparison with simple iron chalcogenides may have two different reasons. It could be a genuine property of the vanadium sulfides caused by the ambivalent position of V in the periodic table between ionic and covalent sulfides. On the other hand, the distortion of the structure following

the substitution of V by Fe or the possible location of Fe on interstitial sites leads to an incorrectly transmitted image of the average bulk structure by the Fe nuclei probes. The aforementioned correlation of *Mössbauer* trends with other results allows the conclusion that we determined representative bulk parameters, and that we demonstrated another peculiarity of V in the periodic behaviour of bonding in the 3d element row.

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REFERENCES

- [1] F. Gronvold, H. Haraldsen, B. Pedersen, T. Tuft, *Rev. Chim. Miner.* **1969**, *6*, 251.
- [2] A. B. deVries, F. Jelinek, *Rev. Chim. Miner.* **1974**, *11*, 624.
- [3] Y. Kitaoka, H. Yasuoka, Y. Oka, K. Kosuge, S. Kachi, *J. Phys. Soc. Jpn.* **1979**, *46*, 1381.
- [4] B. G. Silbernagel, R. B. Levy, F. R. Gamble, *Phys. Rev. B* **1975**, *11*, 4563.
- [5] J. B. Forsyth, P. J. Brown, I. Kawada, H. Nozaki, M. Sacki, *J. Phys. C* **1979**, *12*, 4261.
- [6] H. F. Franzen, D. M. Strachan, R. G. Barnes, *J. Solid State Chem.* **1973**, *7*, 374.
- [7] H. Nozaki, Y. Ishizawa, *Phys. Lett. A* **1977**, *63*, 131.
- [8] M. Taniguchi, M. Wakihara, Y. Shirai, *Z. Anorg. Allgem. Chem.* **1980**, *461*, 234.
- [9] Y. Oka, K. Kosuge, S. Kachi, *Phys. Lett. A* **1974**, *50*, 311.
- [10] H. Nishihara, H. Yasuoka, Y. Oka, K. Kosuge, S. Kachi, *J. Phys. Soc. Jpn.* **1977**, *42*, 787.
- [11] O. Massenet, J. Mercier, A. Chang, R. Buder, A. B. H. Mohamed, *J. Phys. Chem. Solids* **1980**, *41*, 1009.
- [12] Y. Kitaoka, H. Yasuoka, *J. Phys. Soc. Jpn.* **1980**, *48*, 1949.
- [13] H. Nozaki, H. Wada, H. Yamamura, *Solid State Commun.* **1982**, *44*, 63.
- [14] Y. Oka, K. Kosuge, S. Kachi, *Mat. Res. Bull.* **1977**, *12*, 1117.
- [15] M. Ishii, H. Wada, H. Nozaki, I. Kawada, *Solid State Commun.* **1982**, *42*, 605.
- [16] H. Wada, *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2918.
- [17] H. Wada, *Bull. Chem. Soc. Jpn.* **1978**, *51*, 1368.
- [18] H. Wada, *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2130.
- [19] H. Wada, *Bull. Chem. Soc. Jpn.* **1980**, *53*, 668.
- [20] I. Kawada, H. Wada, *Physica B* **1981**, *105*, 223.
- [21] B. L. Morris, R. H. Plovnick, A. Wold, *Solid State Commun.* **1969**, *7*, 291.
- [22] S. Muranaka, T. Takada, *J. Solid State Chem.* **1975**, *14*, 291.
- [23] L. Fournes, M. Vlasse, M. Saux, *Mat. Res. Bull.* **1977**, *12*, 1.
- [24] L. Fournes, M. Vlasse, *Rev. Chim. Miner.* **1978**, *15*, 542.
- [25] M. Vlasse, L. Fournes, *Mat. Res. Bull.* **1976**, *11*, 1527.
- [26] R. Schöllhorn, Physics of Intercalation Compounds, Proceedings of an International Conference, Trieste, 1981, Italy, July 6–10.
- [27] W. Bensch, E. Amberger, J. Abart, *Solid State Commun.* **1984**, *51*, 979.
- [28] W. Bensch, E. Amberger, in preparation.
- [29] J. Abart, J. Voitländer, *Solid State Commun.* **1981**, *40*, 277.
- [30] G. A. Fatseas, J. B. Goodenough, *J. Solid State Chem.* **1980**, *33*, 219.
- [31] P. K. Gallagher, J. B. MacChesney, R. C. Sherwood, *J. Chem. Phys.* **1969**, *50*, 4417.
- [32] W. Bensch, J. Abart, E. Amberger, submitted.
- [33] D. J. Vaughan, M. S. Ridout, *J. Inorg. Nucl. Chem.* **1971**, *33*, 741.
- [34] F. J. DiSalvo, M. Eibschütz, C. Cres. D. W. Murphy, J. V. Waszczak, *Phys. Rev. B* **1979**, *19*, 3441.
- [35] N. N. Greenwood, T. C. Gibb, 'Mössbauer Spectroscopy', Chapman and Hall, London, 1971.
- [36] T. C. Gibb, R. Greatrex, N. N. Greenwood, *J. Chem. Soc. (A)* **1968**, 890.
- [37] M. Eibschütz, F. J. DiSalvo, *Phys. Rev. Lett.* **1976**, *36*, 104.