

Mössbauer Studies of Thiospinels.

V. The Systems $\text{Cu}_{1-x}\text{Fe}_x\text{Me}_2\text{S}_4$ ($\text{Me} = \text{Cr, Rh}$) and $\text{Cu}_{1-x}\text{Fe}_x\text{Cr}_2(\text{S}_{0.7}\text{Se}_{0.3})_4$

E. RIEDEL, R. KARL, AND R. RACKWITZ

Institut für Anorganische und Analytische Chemie, Technische Universität Berlin, D-1000 Berlin 12, Federal Republic of Germany

Received October 22, 1980; in revised form July 16, 1981

With the exception of FeRh_2S_4 , powder samples of all systems studied have been obtained as spinel phase without essential impurities. The lattice constants follow Vegard's law. From the Seebeck coefficients and the Mössbauer spectra the valence distribution $\text{Cu}_{1-x}^{1+}\text{Fe}_{2x-1}^{2+}\text{Fe}_{1-x}^{3+}[\text{Me}_{2-x}^{3+}]\text{X}_4^{2-}$ is derived for $0.5 \leq x \leq 1$, while there is only Fe^{3+} present for $0 < x \leq 0.5$. Samples with the overall composition FeRh_2S_4 contain mostly Rh_2S_3 and iron sulfide phases, but less than 20% of a spinel phase.

Introduction

Spinel compounds with compositions $\text{Cu}_{1-x}\text{Fe}_x\text{Me}_2\text{S}_4$, $\text{Me} = \text{Cr, Rh}$, have been studied several times in order to elucidate the valence characteristics of all ions involved (1-7). The system with $\text{Me} = \text{Cr}$ ("Cr system") was especially investigated, using electrical and magnetic measurements. The outcome of a few Mössbauer studies (5, 6) was not completely compatible with other data. Kondo (8) considered the Mössbauer results of his FeRh_2S_4 sample as a puzzle. Given this situation, a detailed investigation of Mössbauer spectra in conjunction with X-ray and electrical data appeared to be advisable. The data for the systems above will be compared with those for $\text{Cu}_{1-x}\text{Fe}_x\text{Cr}_2(\text{S}_{0.7}\text{Se}_{0.3})_4$ ("Se system") to check the influence of a mixed anion sublattice.

Experimental

Preparation was done by the standard

technique of heating stoichiometric mixtures of the elements (at least 99.9%) in evacuated quartz-glass ampoules. A preliminary reaction at 450-500°C was followed by two or three treatments usually at 750-850°C; a final heating cycle at 450°C in order to reduce sulfur deposition was applied whenever necessary. For samples with $x \leq 0.6$ in the Cr system the maximum temperature was 600°C. Further details can be found in (9-11).

X-Ray powder diffraction, Seebeck, and Mössbauer methods have been described earlier (9, 10, 12, 16). Mössbauer isomer shifts are relative to iron metal.

Results

Apart from FeRh_2S_4 , all samples of all systems studied could be obtained essentially free of impurities, though no system could be prepared absolutely pure over the whole range. In the Cr system, X-ray diagrams of materials with $x < 0.5$ showed very weak reflections (intensity relative to

the strongest spinel reflections $\approx 2\%$ of (Cu, Fe) S_2 phases. In the system $Cu_{1-x}Fe_xRh_2S_4$ ("Rh system"), samples with $0.6 \approx x \approx 0.9$ contain increasing amounts of Rh_2S_3 (X-ray intensity 0.5–4%). On X-ray diagrams of $FeRh_2S_4$, only some weak spinel reflections are visible besides strong reflections of Rh_2S_3 and iron sulfide phases (9, 10). These findings are compatible with (13), but not with Blasse *et al.* (14) and Kondo (8): These authors claim to have prepared a $FeRh_2S_4$ spinel with only small amounts of impurities.

In the Se system, extraneous lines with 2–4% intensity were found in diagrams of $x \leq 0.3$ and $x = 1.0$. Nevertheless, this system is the Se-richest spinel system that can be obtained reasonably pure, which is the reason why we chose this anion composition.

The lattice constants a of all three systems follow Vegard's rule (Table I). The increase from $x = 0$ to $x = 1$ is 18.7 pm (Cr system), 10 pm (Rh system), 16.6 pm (Se system). The anion shift parameters u are constant within experimental errors: $u = 0.383 \pm 0.001$ (Cr system), 0.384 ± 0.001

TABLE I
LATTICE CONSTANTS a IN THE THREE SYSTEMS
 $Cu_{1-x}Fe_xMe_2X_4$

x	a		
	Cr [pm]	Rh [pm]	Se [pm]
0.0	981.0	979.1	997.1
0.1	—	980.3	998.2
0.2	984.8	981.1	1000.8
0.3	—	982.2	1001.8
0.4	988.6	983.1	1003.5
0.45	—	—	1004.4
0.5	990.4	984.3	1005.2
0.55	—	984.6	1006.3
0.6	992.0	985.4	1007.2
0.65	—	985.4	1008.1
0.7	994.1	986.0	1009.1
0.8	995.7	987.1	1010.3
0.9	997.8	988.0	1012.2
1.0	999.8	989	1013.6

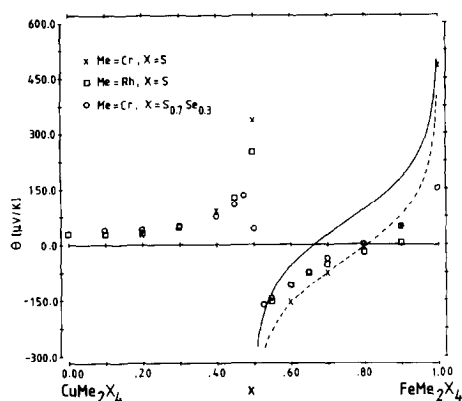


FIG. 1. Experimental and calculated Seebeck coefficients in the three systems (see text).

(Rh system), 0.381 ± 0.001 (Se system). The octahedral sites are occupied exclusively by Cr^{3+} or Rh^{3+} respectively.

The Seebeck coefficients Θ of all systems show the same characteristic behaviour with only gradual differences (Fig. 1). These results correspond to the values by Haacke and Beegle (4) and Lotgering *et al.* (6) for the Cr system.

Mössbauer spectra of all systems were run at various temperatures between 77 and 473 K (cf. Table II). The Cr system is described first:

(a) In the range $x \leq 0.5$, the spectra consist of only one type of absorption: one weakly split doublet ($\Delta \approx 0.1$ mm/s) above T_C , one symmetric sextet ($H_{int} \approx 250$ T at room temperature) below T_C (Fig. 2). To be accurate, the sextet has to be considered as the sum of several overlapping sextets of slightly decreasing internal fields and intensities leading to slightly asymmetric shape especially of the outer lines ("outer-lines effect"). The necessary number of components was determined by the usual goodness-of-fit criteria. Of course, these spectra exhibit a distribution of hyperfine fields with a range of isomer shifts.

In the range $0.5 < x < 1.0$, the spectra contain different components. Below T_C , two well-distinguished sextets are visible

TABLE II

MÖSSBAUER PARAMETERS IN THE SYSTEM $\text{Cu}_{1-x}\text{Fe}_x\text{Cr}_2\text{S}_4$ FOR VARIOUS TEMPERATURES: NUMBER OF LINES (E.G., SEXTETS) FITTED, ISOMER SHIFT δ , INTERNAL FIELD H_{int} , QUADRUPOLE SPLITTING Δ , HALF-WIDTH Γ , PARTIAL ABSORPTION AREA PA , MEAN ISOMER SHIFT $\bar{\delta}$, MEAN QUADRUPOLE SPLITTING $\bar{\Delta}$

x	T [K]	No. lines fitted	δ [mm/s]	H_{int} [T]	Δ [mm/s]	Γ [mm/s]	PA	$\bar{\delta}$ [mm/s]	$\bar{\Delta}$ [mm/s]
0.2	353	1 db	0.264	—	0.08	0.33	1.	0.264	0.08
	RT	4 sx	0.308	25.5	—	0.22	0.28	0.313	—
0.4	RT	3 sx	0.306	25.3	—	0.26	0.48	0.309	—
0.5	373	1 db	0.256	—	0.13	0.33	1.	0.256	0.13
	353	1 db	0.267	—	0.13	0.33	1.	0.267	0.13
	RT	4 sx	0.310	25.6	—	0.23	0.53	0.310	—
	220	3 sx	0.363	33.1	—	0.29	0.72	0.362	—
0.6	77	2 sx	0.434	38.5	—	0.30	0.39	0.436	—
	473	4 sg	—	—	—	0.28	—	0.265	—
	413	5 sg	—	—	—	0.28	—	0.306	—
	353	6 sg	—	—	—	0.28	—	0.349	—
	333	6 sg	—	—	—	0.28	—	0.360	—
	RT	6 sx	0.313	21.9	—	0.35	0.20	0.397	—
				0.572	5.5	—	0.42	0.18	—
	273	6 sx	0.354	28.4	—	0.34	0.30	0.415	—
				0.593	9.2	—	0.37	0.16	—
	190	5 sx	0.417	35.2	—	0.25	0.18	0.489	—
0.7	90	5 sx	0.456	37.2	—	0.26	0.33	0.504	—
			0.687	20.6	—	0.60	0.15	—	—
	RT	3 db	—	—	—	0.24	—	0.458	0.236
	273	6 sx	0.361	28.4	—	0.36	0.13	0.498	—
0.8			0.608	11.1	—	0.58	0.34	—	—
	240	6 sx	0.404	31.2	—	0.40	0.20	0.530	—
			0.632	14.8	—	0.54	0.30	—	—
	RT	3 db	—	—	—	0.26	—	0.502	0.243
0.9	RT	3 db	—	—	—	0.25	—	0.548	0.233
	273	3 db	—	—	—	0.25	—	0.577	0.275
	240	3 db	—	—	—	0.26	—	0.601	0.301
	220	3 db	—	—	—	0.26	—	0.599	0.344
0.94	RT	5 sg	—	—	—	0.27	—	0.563	—
0.97	RT	4 sg	—	—	—	0.29	—	0.578	—

Note: sg—singlet; db—doublet; sx—sextet. The values δ , H_{int} , Δ , Γ and PA are for the component with the largest (and the smallest, where applicable) splitting.

for $x = 0.6, 0.7$ (Fig. 3). The outer lines effect of the strongly split sextet increases with x and temperature. The partial area of the inner sextet increases with x . The discrepancy between calculated and observed absorptions apparent in the spectra of $x = 0.7$ show the insufficiency of the first approximation-type fitting procedure but does not influence the conclusions drawn later

on. Spectra of $x = 0.8, 0.9$ below T_C showed very complicated absorption patterns, presumably because of relaxation effects, so that no attempts were made to fit those spectra. Above T_C , a separation into two different kinds of absorptions is no longer possible (Fig. 4), though the spectra are obviously not of the simple single-line type. At least five hyperfine components (e.g.,

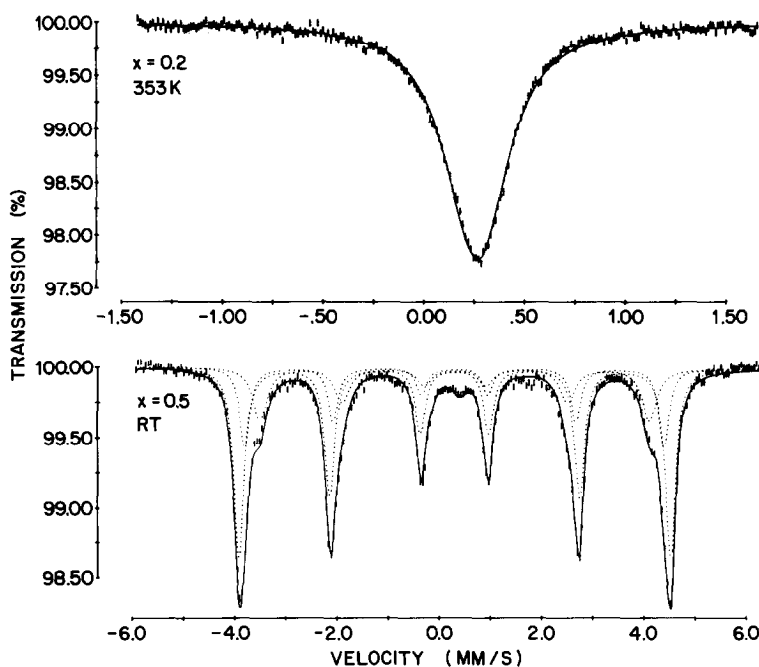


FIG. 2. Mössbauer spectra for $x = 0.2, 0.5$ in the system $\text{Cu}_{1-x}\text{Fe}_x\text{Cr}_2\text{S}_4$.

two doublets, one singlet) are necessary to obtain a satisfactory fit for $0.7 \leq x \leq 0.9$, at least four components are needed for $x = 0.6$. The components shown in Fig. 4 only serve the mathematical representation of the shape of the spectra, but do not imply the existence of a respective number of different kinds of iron atoms. Fig. 5 illustrates the temperature dependence in the paramagnetic region: The decreasing overall width with increasing temperature can be taken as evidence for the presence of overlapping doublets with temperature dependent quadrupole splittings; see also the values for the average quadrupole splittings $\bar{\Delta}$ of $x = 0.9$ in Table II.

The mean isomer shifts $\bar{\delta}$ at room temperature show a characteristic behavior (Fig. 6). While $\bar{\delta}$ remains constant for $x \leq 0.5$ ($\bar{\delta} = 0.311$ mm/s), it increases nonlinearly to $\bar{\delta} = 0.591$ mm/s at $x = 1$. Mössbauer spectra of the Cr system have been described in the literature earlier. Above T_C , Haacke and Nozik (5) found only one nar-

row Mössbauer line for all samples, the isomer shift of which increased linearly from 0.21 mm/s for $x = 0.3$ to 0.58 mm/s for $x = 1$. Below T_C , they found one sextet for $x \leq 0.5$, but two superimposed sextets for $x > 0.5$ which were interpreted as separate Fe^{2+} and Fe^{3+} patterns. Lotgering *et al.* (6) reported one absorption line with a quadrupole splitting smaller than 0.1 mm/s for $x = 0.5$ above T_C .

(b) In the Rh system, magnetically split Mössbauer spectra could be obtained for $x < 0.6$ only because of lower Curie temperatures. All results are consistent with those for the Cr system, only the numerical values of the parameters differ slightly (Table III). Spectra for $x \leq 0.5$ are equivalent. Although there are not two well-resolved sextets visible in the spectrum of $x = 0.55$ below T_C , the mathematical analysis shows the presence of a weakly split sextet ($PA = 0.19$) in addition to the predominant sextet. Spectra for $x > 0.5$ above T_C (Fig. 7) exhibit the same features as the Cr system (see also

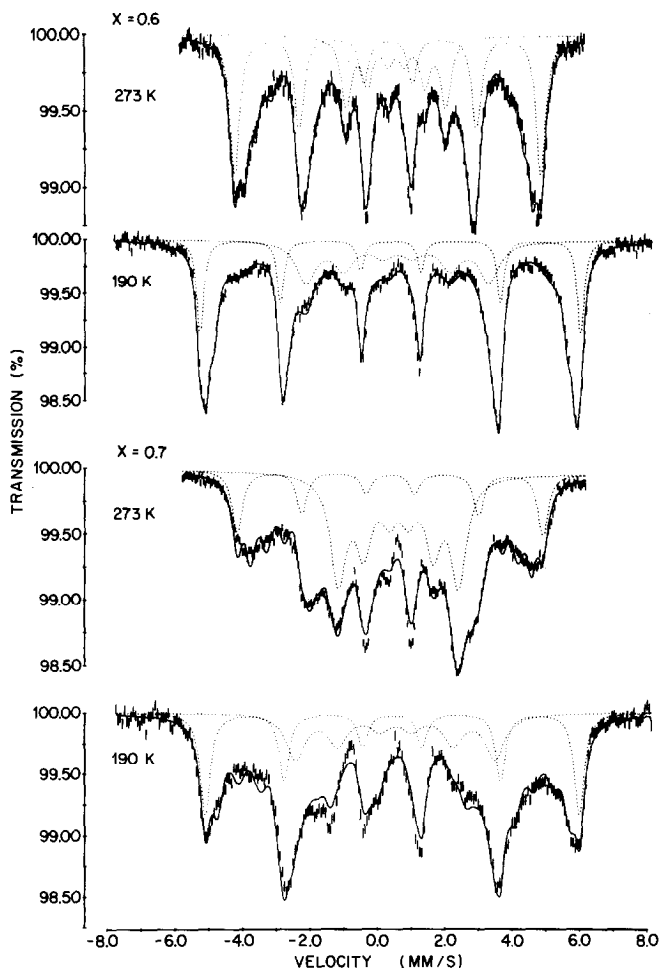


FIG. 3. Magnetically split Mössbauer spectra for $x = 0.6, 0.7$ in the system $\text{Cu}_{1-x}\text{Fe}_x\text{Cr}_2\text{S}_4$ (only components of maximal and minimal splitting are shown).

the similar behavior of $\bar{\delta}$ in Fig. 6).

Two different components are apparent in the room temperature Mössbauer spectrum of a sample with the overall composition FeRh_2S_4 (Table IV). It consists mainly ($PA \approx 0.83$) of a broad asymmetric sextet (parameters of the components: $\delta = 0.74 \dots 0.81$ mm/s, $H_{\text{int}} = 28.4 \dots 23.4$ T). Additional absorptions ($PA \approx 0.17$) exist in the center of the spectrum (main contribution: a doublet with $\delta \approx 0.30$ mm/s, $\Delta \approx 0.49$ mm/s); they could not be characterized more distinctly because they overlap largely with the inner sextet lines. Kondo

(8) reported a superposition of one central broad line and a hyperfine split spectrum; this fact was taken as evidence for the existence of two different states of which the magnetic one was considered as a puzzle.

(c) The Mössbauer spectra in the Se system resemble those in the two other systems. Room temperature spectra in the region $x < 0.6$ are magnetically split. Spectra for $0.5 \leq x \leq 1.0$ above T_C are shown in Fig. 8; the overall splitting increases continuously from $x = 0.5$ (broad single absorption line) to $x = 1$. All spectra for $0.5 < x \leq 1.0$ obviously consist of overlapping doublets

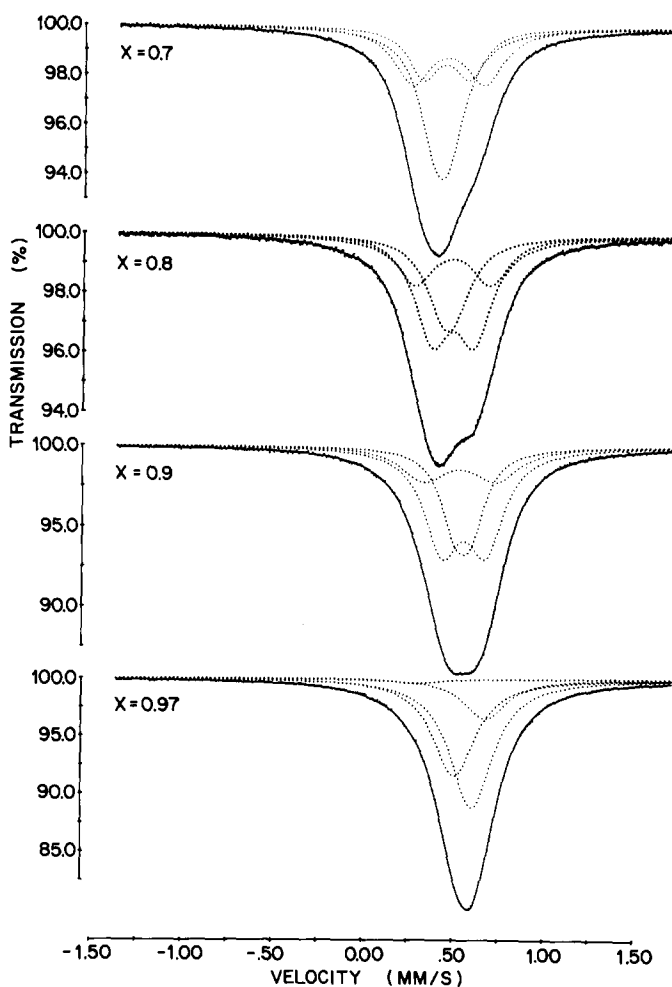


FIG. 4. Room temperature Mössbauer spectra for $0.7 \leq x \leq 0.97$ in the system $\text{Cu}_{1-x}\text{Fe}_x\text{Cr}_2\text{S}_4$.

(see e.g., the spectrum $x = 1.0$). The change of the average shift $\bar{\delta}$ is identical with the behavior presented in Fig. 6 for the other systems: constant value of 0.27 mm/s for $x \leq 0.5$, nonlinear increase to 0.594 mm/s for $x = 1$.

Discussion

The electrical and magnetic properties of the system $\text{Cu}_{1-x}\text{Fe}_x\text{Cr}_2\text{S}_4$ have been explained by Lotgering *et al.* (6) on the basis of a model developed by Lotgering and van Stapele (15) for thio- and selenospinel in

general ("LSt-model"). The model postulates the valence distribution $\text{Cu}^{1+}[\text{Me}_{1+\delta}^{3+}\text{Me}_{1-\delta}^{4+}]\text{S}_4^{2-}\text{S}_6^{-1}$ for $x = 0$ (S^{-1} represents a hole in the valence band), and $\text{Cu}_{0.5}^{1+}\text{Fe}_{0.5}^{3+}[\text{Me}_2^{3+}]\text{S}_4^{2-}$ for $x = 0.5$. For $0.5 \leq x \leq 1.0$ follows the distribution $\text{Cu}_{1-x}^{1+}\text{Fe}_{2x-1}^{2+}\text{Fe}_{1-x}^{3+}[\text{Me}_2^{3+}]\text{S}_4^{2-}$.

First we discuss whether the Mössbauer spectra are consistent with the LSt-model.

Especially from their low-temperature Mössbauer measurements, Haacke and Nozik (5) have already concluded that indeed only Fe^{3+} exists for $x \leq 0.5$, while both Fe^{3+} and Fe^{2+} exist for $0.5 < x < 1$.

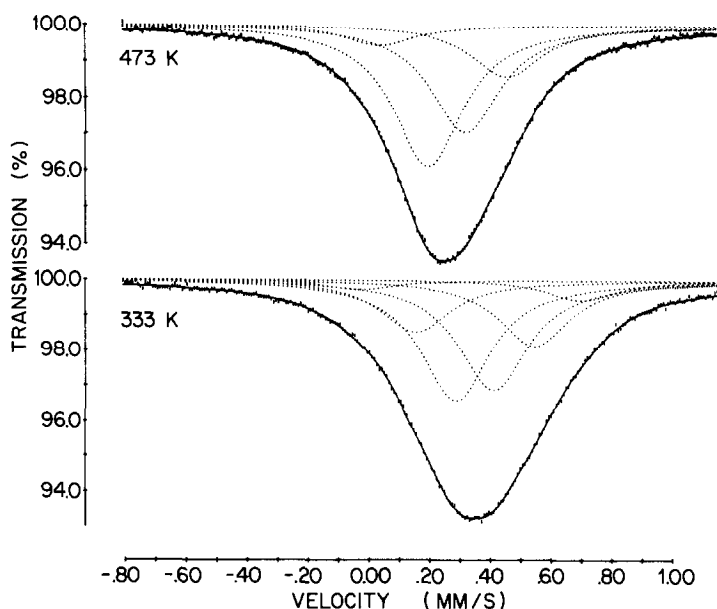


FIG. 5. Mössbauer spectra for $\text{Cu}_{0.4}\text{Fe}_{0.6}\text{Cr}_2\text{S}_4$ at elevated temperatures.

However, the linear increase of $\bar{\delta}$ they reported between $x = 0.3$ and $x = 1.0$, is in contrast with the iron valences predicted by the model. Our room temperature $\bar{\delta}$ data exhibit a characteristic nonlinear change which is completely consistent with the

LSt-model (Fig. 6). The essentially constant, low values for $\bar{\delta}$ in the range 0.27–0.33 mm/s are evidence for the exclusive existence of Fe^{3+} for $x \leq 0.5$. The large values H_{int} below T_C confirm this interpretation; the slight inhomogeneity of H_{int}

TABLE III
MÖSSBAUER PARAMETERS^a IN THE SYSTEM $\text{Cu}_{1-x}\text{Fe}_x\text{Rh}_2\text{S}_4$

x	T [K]	No. lines fitted	δ	H_{int}	Δ	Γ	PA	$\bar{\delta}$	$\bar{\Delta}$
0.2	RT	1 db	0.334	—	0.088	0.22	1.	0.334	0.088
0.4	RT	1 db	0.330	—	0.086	0.25	1.	0.330	0.086
0.5	RT	1 db	0.328	—	0.068	0.26	1.	0.328	0.068
	160	1 db	0.423	—	0.065	0.27	1.	0.423	0.065
0.55	90	4 sx	0.446	25.6	—	0.26	0.47	0.437	—
	RT	3 sg	—	—	—	0.28	—	0.350	—
	80	7 sx	0.457	23.6	—	0.37	0.13	0.454	—
0.6	RT	4 sg	—	—	—	0.70	0.19	—	—
	120	5 sg	—	—	—	0.30	—	0.379	—
0.7	RT	3 db	—	—	—	0.38	—	0.494	—
0.8	RT	3 db	—	—	—	0.29	—	0.426	0.332
0.9	RT	3 db	—	—	—	0.28	—	0.459	0.449
0.9	RT	4 db	—	—	—	0.27	—	0.487	0.474

^a Symbols as in Table II.

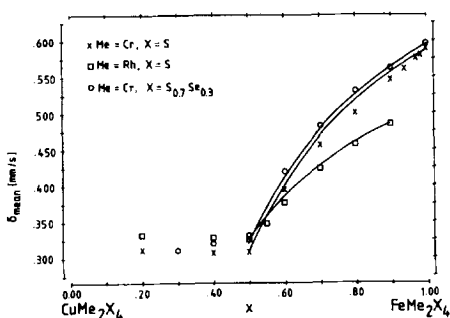


Fig. 6. Experimental (\times , \square , \circ) and calculated mean isomer shifts in the systems $\text{Cu}_{1-x}\text{Fe}_x\text{Me}_2\text{S}_4$ at room temperature.

leading to the outer lines effect is probably due to inhomogeneous distribution of atoms on tetrahedral sites.

The change of $\bar{\delta}$ for $0.5 \leq x \leq 1.0$ demonstrates the transition from pure Fe^{3+} to pure Fe^{2+} . It was calculated from the values $\bar{\delta}_{x=0.5}$ and $\bar{\delta}_{x=1}$, respectively, using the equation¹

$$\bar{\delta} = \frac{(1-x) \cdot \delta_{x=0.5} + (2x-1) \cdot \delta_{x=1}}{x}$$

where the expressions in parentheses are the stoichiometric factors for Fe^{3+} and Fe^{2+} according to the LSt-model. The calculations lead to the solid lines in Fig. 6, which sustain the nonlinearity found in the experiment.

In the magnetically split spectra of $x = 0.6, 0.7$ in the Cr system, the appearance of a separate Fe^{2+} -sextet (smallest H_{int} , highest δ : about 0.20–0.25 mm/s higher than the Fe^{3+} shift) is obvious.² Its partial area ($x = 0.6$: $PA(\text{Fe}^{2+}) = 0.18 \pm 0.02$; $x = 0.7$: $PA(\text{Fe}^{2+}) = 0.32 \pm 0.02$), however, is much smaller than the expected value 0.33 or 0.57, respectively. The direct comparison with expected values is only justified under the condition that there is no difference in recoil-free fractions between $\text{Fe}^{2+}/\text{Fe}^{3+}$

¹ For the Rh system, the value $\delta_{x=1} = 0.507$ mm/s was estimated from extrapolation.

² Though not obvious, it is present in the low-temperature spectrum of $\text{Cu}_{0.48}\text{Fe}_{0.52}\text{Rh}_2\text{S}_4$ as well.

TABLE IV
MÖSSBAUER DATA FOR THE MAIN SEXTET IN THE
“ FeRh_2S_4 ” SPECTRUM COMPARED WITH
LITERATURE DATA FOR Fe_{1-y}S ($y = 0-0.15$)

δ [mm/s]	H_{int} [T]	Δ [mm/s]	Reference
0.74 . . . 0.81	28.4 . . . 23.4	0.15 . . . 0.36	This work
0.65 . . . 0.76	30.8 . . . 27.5	0.26	(18)
0.64 . . . 0.77	31.0 . . . 22.5	0.16 . . . 0.31	(19)
0.75 . . . 0.78	30.4 . . . 22.8	0 . . . 0.23	(20)

sites. Although this is probably the case, it will not account for the entire deviation. Therefore the observed difference and the strong outer lines effect of the Fe^{3+} -sextet (it consists of components not only with differing H_{int} and intensity, but with differing δ between the Fe^{3+} and Fe^{2+} values also) indicate that Fe does not simply exist as pure Fe^{3+} and Fe^{2+} here, but rather in valence states between these extremes also. The frequency of this electron exchange between Fe^{2+} and Fe^{3+} apparently increases with temperature (increasing outer lines effect) and x (cf. the 273-K spectra in Fig. 3).

Therefore it is not surprising that the spectra in the range $0.5 < x < 1.0$ (of all systems) above T_c cannot be explained simply as one Fe^{2+} and one Fe^{3+} absorption (e.g., one doublet, one singlet). Even the assumption of several absorptions of different splittings with the δ of pure Fe^{2+} and pure Fe^{3+} taken from $x = 1.0$ and $x = 0.5$, possibly caused by inhomogeneous cationic environment (9), does not yield satisfactory fits. These results are further evidence for the electron exchange between Fe^{2+} and Fe^{3+} , but in the temperature range studied the iron atoms are not yet electronically equivalent (note the asymmetry of all spectra). Haacke and Nozik (5) have already deduced an electron exchange between Fe^{2+} and Fe^{3+} from their spectra above T_c .

The Mössbauer spectra in the system $\text{Cu}_{1-x}\text{Fe}_x\text{Cr}_2(\text{S}_{0.7}\text{Se}_{0.3})_4$ demonstrate the in-

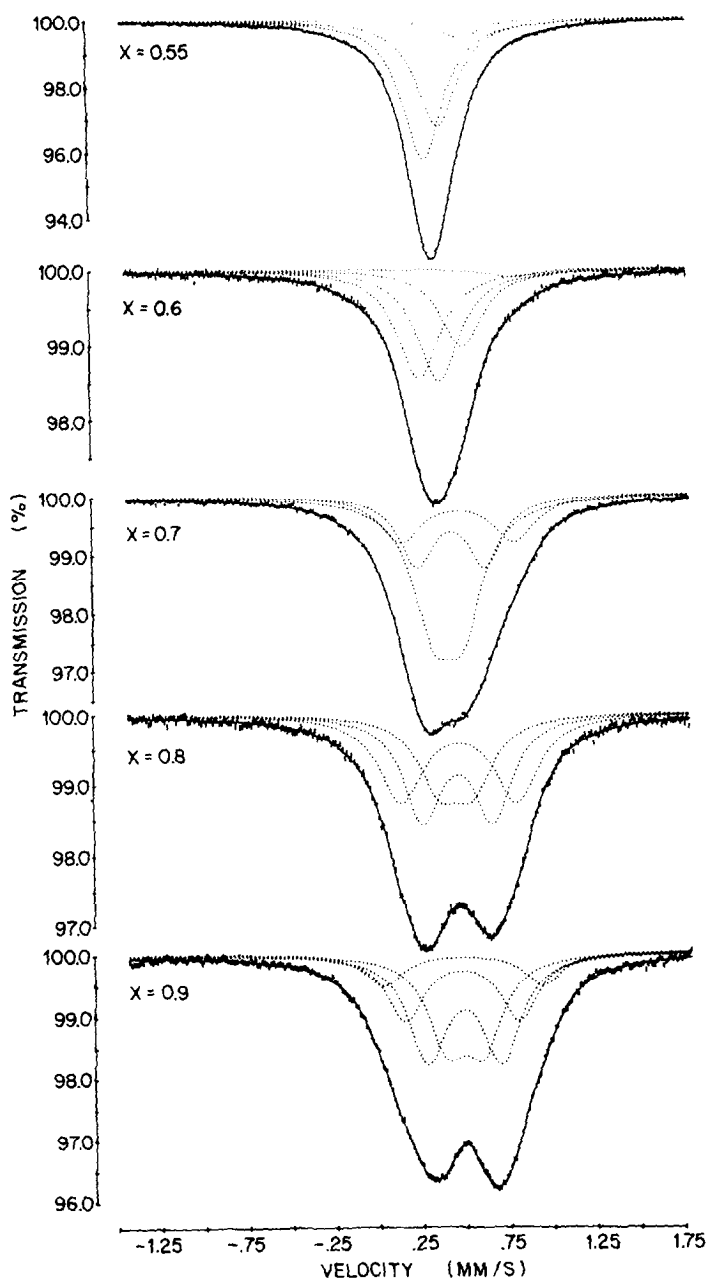


FIG. 7. Room temperature Mössbauer spectra for $x > 0.5$ in the system $\text{Cu}_{1-x}\text{Fe}_x\text{Rh}_2\text{S}_4$.

fluence of inhomogeneous anionic environment. The spectra of $x = 0.5, 1.0$ show clearly that while Fe^{3+} (spherically symmetric d^5 configuration) is relatively insensitive, Fe^{2+} is largely affected by the pres-

ence of two different anions (cf. (17, 11)). From the shape of the spectra of $x = 0.8, 0.9$ in conjunction with $x = 1.0$ it can be concluded that the anionic influence is stronger than the cationic one, which is rea-

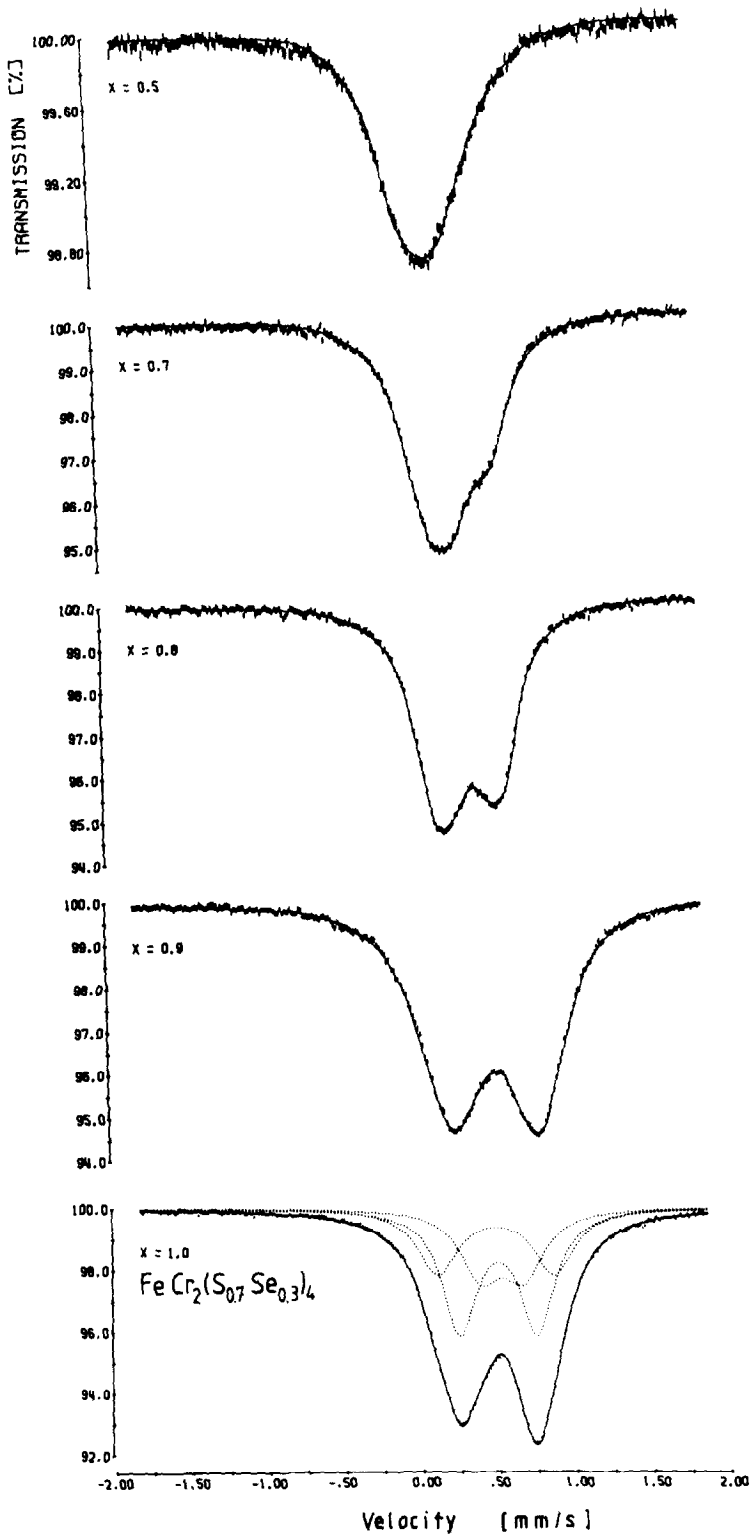


FIG. 8. Mössbauer spectra for $\text{Cu}_{1-x}\text{Fe}_x\text{Cr}_2(\text{S}_{0.7}\text{Se}_{0.3})_4$.

sonable when considering the respective distances in the lattice. The first anionic coordination sphere of an Fe_T^{2+} in $\text{FeCr}_2(\text{S}_{0.7}\text{Se}_{0.3})_4$ consists of either S_4 or S_3Se or S_2Se_2 (the Se-richer configurations are statistically negligible in the first approximation). Each of these configurations gives rise to a different quadrupole splitting of the respective iron atom (cf. Fig. 8). (17).

The Mössbauer spectrum of the "FeRh₂S₄" sample can be interpreted in correspondence with the X-ray results. The main sextet is most likely to be due to Fe_{1-y}S , $y = 0-0.15$, as can be seen in comparison with the literature data in Table IV and figures published in those references. Only the remaining, not magnetically split absorptions ($PA \approx 0.17$) can arise from spinel (and other?) phases. It is questionable whether a pure spinel FeRh_2S_4 can be prepared by the standard techniques applied so far.

It is a matter of course that the general behavior of the Seebeck coefficient is compatible with the LSt-model as this model had been established partially on the basis of those data for the system $\text{Cu}_{1-x}\text{Fe}_x\text{Cr}_2\text{S}_4$ (6). Though there is no need to repeat that discussion it is interesting to try and calculate the change of Θ for $0.5 < x < 1.0$ using the principles for semiconductors with localized d -electron states (21). The equation

$$\Theta = 198 \cdot 10g \frac{2x - 1}{1 - x} + B$$

(B-transport constant)

yielded the solid and dashed line ($B = 0$ and $-100 \mu\text{V/K}$ respectively) in Fig. 1. Only the data in the Cr system can be accurately explained by a curve of the calculated shape; the B value is unusually large, how-

ever. Nevertheless the assumption of pure tetrahedral site conduction is justified still.

References

1. R. PLUMIER AND F. K. LOTGERING, *Solid State Commun.* **8**, 477 (1970).
2. S. HARADA, *Mater. Res. Bull.* **8**, 1361 (1973).
3. P. R. LOCHER AND R. P. VAN STAPELE, *J. Phys. Chem. Solids* **31**, 2643 (1970).
4. G. HAACKE AND L. C. BEEGLE, *J. Phys. Chem. Solids* **28**, 1699 (1967); *J. Appl. Phys.* **39**, 656 (1968).
5. G. HAACKE AND A. J. NOZIK, *Solid State Commun.* **6**, 363 (1968).
6. F. K. LOTGERING, R. P. VAN STAPELE, G. H. A. M. VAN DER STEEN, AND J. S. VAN WIERINGEN, *J. Phys. Chem. Solids* **30**, 799 (1969).
7. E. M. GYORGY, M. ROBBINS, P. GIBART, W. A. REED, AND F. J. SCHNETTLER, *Amer. Inst. Phys. Conf. Proc.* 1972 **10**, 1148 (1973).
8. H. KONDO, *J. Phys. Soc. Japan* **41**, 1247 (1976).
9. E. RIEDEL AND R. KARL, *J. Solid State Chem.* **35**, 77 (1980).
10. R. KARL, Thesis, TU Berlin 1978, D 83.
11. R. RACKWITZ, Thesis, TU Berlin 1979, D 83.
12. E. RIEDEL AND R. KARL, *J. Solid State Chem.* **38**, 40 (1981).
13. R. E. TRESSLER AND V. S. STUBICAN, *Nat. Bur. Stand. Spec. Publ.* **364**, 695 (1972); *J. Amer. Ceram. Soc.* **51**, 648 (1968).
14. G. BLASSE AND D. J. SCHIPPER, *J. Inorg. Nucl. Chem.* **26**, 1467 (1964).
15. F. K. LOTGERING AND R. P. VAN STAPELE, *Solid State Commun.* **5**, 143 (1967); *J. Appl. Phys.* **39**, 417 (1968).
16. E. RIEDEL AND R. KARL, *J. Solid State Chem.* **38**, 48 (1981).
17. E. RIEDEL AND T. DÜTZMANN, *Mater. Res. Bull.* **15**, 1409 (1980).
18. K. ONO, A. ITO, AND E. HIRAHARA, *J. Phys. Soc. Japan* **17**, 1615 (1962).
19. S. HAFNER AND M. KALVIUS, *Z. Kristallogr.* **123**, 443 (1966).
20. J. A. MORICE, L. V. C. REES, AND D. T. RICKARD, *J. Inorg. Nucl. Chem.* **31**, 3797 (1969).
21. G. H. JONKER AND S. VAN HOUTEN, "Halbleiterprobleme," Band VI, p. 118. Vieweg, Braunschweig (1961).