Mössbauer Studies of Thiospinels. IV. The System $FeCr_2S_4-Fe_3S_4$

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Spinel compounds of the composition $Fe_{1+x}Cr_{2-x}S_4$, with $0 \leqq x \leqq 0.5$, have been prepared in polycrystalline form. The ionic distribution $Fe^{2+}[Cr^{3+}_{2-x}Fe^{3+}_x]S^{2-}_4$ is derived from both X-ray and ^{57}Fe Mössbauer data. Room temperature Mössbauer spectra show the typical behavior of tetrahedral-site Fe^{2+} surrounded by different octahedral-site neighbors. Octahedral-site Fe^{3+} absorbs as a doublet with $\Delta \approx 0.5$ mm/s. Samples of overall composition $FeCr_2S_4$ consist mainly of a spinel $Fe^{2+}[Cr^{3+}_{2-y}Fe^{3+}_y]S^{2-}_4$, $y \approx 0.02$.

Introduction

In the group of iron-containing thiospinels, $FeCr_2S_4$, $FeIn_2S_4$, $FeYb_2S_4$, $FeRh_2S_4$, and Fe_3S_4 are the materials that attracted the most attention. After studying the solid solutions between $FeCr_2S_4$ and $FeIn_2S_4$ (*1*), $FeCr_2S_4$ and $FeYb_2S_4$ (*2*), and $FeCr_2S_4$ and $FeRh_2S_4$ (*3*), we investigated the system $FeCr_2S_4-Fe_3S_4$. $FeCr_2S_4$ is known to be an easy-to-prepare, normal spinel (*4–6* and others), whereas Fe_3S_4 is an inverse spinel which can be found in nature as greigite or synthesized by complicated techniques leading to varying products (*7–10*). Robbins *et al.* (*11*) as well as Lotgering *et al.* (*5*) have studied some compounds $Fe_{1+x}Cr_{2-x}S_4$ and concluded the ionic distribution $Fe^{2+}_{1-x}Fe^{3+}_x[Cr^{3+}_{2-x}Fe^{2+}_x]S^{2-}_4$. Gibart *et al.* (*6*) have investigated the nonstoichiometry of several $FeCr_2S_4$ samples after various heat treatments; they assumed the approximate distribution $Fe^{2+}_{0.98}Fe^{3+}_{0.02}[Cr^{3+}_{1.96}Fe^{2+}_{0.04}]S^{2-}_{3.99} \square_{0.01}$.

Experimental

Preparation. All samples were prepared in polycrystalline form by heating mixtures of the elements (99.9% or better) in evacuated silica ampoules. Two to three heat treatments of 4 to 7 days at 400–450°C, sometimes preceded by a cycle at 800°C, were applied. For details see (*3, 13*).

X-ray powder diffraction, Seebeck and room temperature ^{57}Fe Mössbauer techniques have been described earlier (*3, 13*). All Mössbauer isomer shifts are relative to metallic iron at room temperature. A Ricor cryostat was used for the acquisition of Mössbauer spectra between 77 and 300 K. The absorber temperature was regulated to ±0.5 K. The source was at room temperature.

Results

In the system $Fe_{1+x}Cr_{2-x}S_4$ only compounds with $x \leqq 0.2$ could be obtained as pure spinels. Samples with $x = 0.3$, 0.4

TABLE I

LATTICE CONSTANTS a AND SEEBECK COEFFICIENTS
Θ IN THE SYSTEM Fe$_{1+x}$Cr$_{2-x}$S$_4$

x	a (pm)	Θ (μV/K)
0.0 (FeCr$_2$S$_4$)	999.8	483
0.03	999.5	438
0.06	999.4	262
0.1	999.2	137
0.2	998.6	17
0.3	998.3	6
0.4	998.1	3
0.5	999.0	—
0.7	999.0	—

FIG. 2. Mössbauer spectra of FeCr$_2$S$_4$ at various temperatures.

contain impurities in low concentrations (X-ray intensities of extraneous lines are around 3% of the intensity of the strongest spinel line). Samples with larger x contain a spinel phase as well as higher amounts of iron and chromium sulfides. In the range 0 $\leq x \leq$ 0.4, the lattice constants a decrease linearly within experimental error (Table I; in correspondence to values by Robbins *et al.* (*11*)). The anion shift parameter u is constant, $\bar{u}$ = 0.384 ± 0.001 (Fig. 1). Due to the small differences in the scattering powers of Fe^{2+}, Fe^{3+}, and Cr^{3+}, no meaningful data about the cation distribution could be derived from X-ray intensities. The Seebeck coefficients Θ show a drastic decrease with x (Table I).
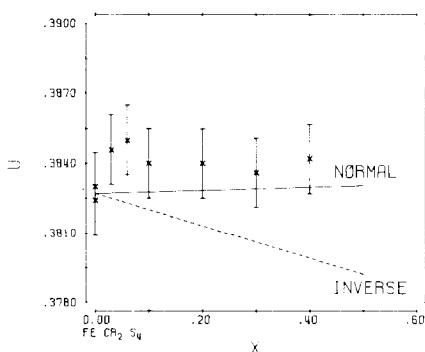
Mössbauer spectra of FeCr$_2$S$_4$ at various temperatures show different kinds of absorptions (Fig. 2 and Table II). Above T_C, a predominant singlet or weakly split doublet and a weak additional doublet appear. The quadrupole splitting Δ of the weak doublet increases rapidly with decreasing temperature. There have been numerous Mössbauer studies of FeCr$_2$S$_4$ (e.g. (*4–6, 14–18*) and references therein), but usually no additional absorption is mentioned, though visible, e.g. in Refs. (*16, 18*). Lotgering *et al.* (*5*) examined the half-widths of several spectra; their (similar) spectrum was said to be broadened due to a slight Fe excess. The

FIG. 1. Experimental (x) and calculated anion shift parameters u in the system Fe$_{1+x}$Cr$_{2-x}$S$_4$ (see text).

TABLE II

MÖSSBAUER PARAMETERS OF FeCr$_2$S$_4$

T (K)	δ/Fe (mm/s)	H_{int} (T)	Δ (mm/s)	Γ (mm/s)	PA
RT	0.591	—	0–0.02	0.26	0.93
	0.584	—	0.702	0.27	0.06
	0.38	—	0.55	0.28	0.01
240	0.643	—	0.05	0.28	0.94
	0.629	—	1.06	0.26	0.06
160	0.700	16.9	0.13	0.27	0.98
	0.294	24.5	0	0.31	0.02
90	0.726	20.6	0.40	0.28	0.98
	0.327	32.1	0	0.30	0.02
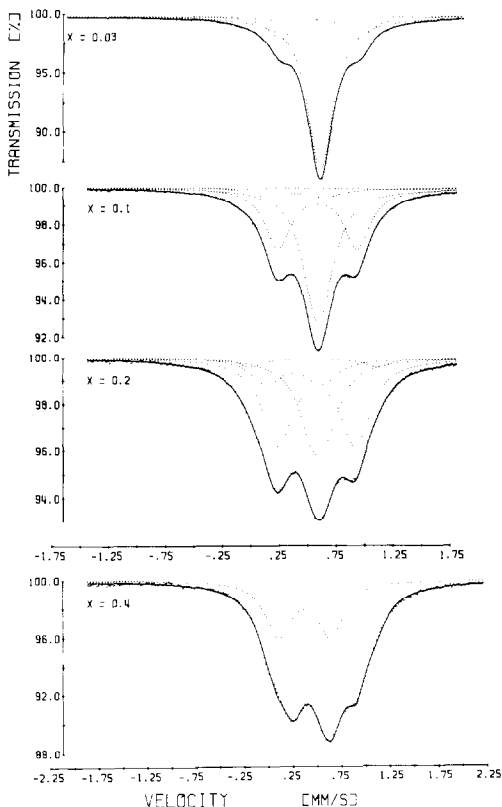
FIG. 3. Room temperature Mössbauer spectra in the system $Fe_{1+x}Cr_{2-x}S_4$ ($x = 0.4$: only D4 is shown).

asymmetry (low-velocity components more intense) increasing with x. The reason is a doublet, "D4," of $\delta \approx 0.38$ mm/s and $\Delta \approx 0.5$ mm/s, the intensity of which is proportional to x. There is evidence for its existence in the whole range $0 \leq x \leq 0.4$ from the goodness-of-fit criterion, but it can be fitted independently for $x > 0.1$ only. The intensity asymmetry in the spectrum of $Fe_{1.06}Cr_{1.94}S_4$ has been mentioned by Lotgering et al. (5) already. The main doublets are numbered D1, D2, D3 according to increasing Δ. There is no marked change with x in δ and Δ of all doublets with the exception of the increasing Δ of D1. The mean shifts $\bar{\delta}(Fe_T^{2+})$ (averaged over D1–D3) and $\bar{\delta}$ (averaged over all absorptions) decrease linearly in the range $0 \leq x \leq 0.3$. The average splitting of D1–D3, $\bar{\Delta}(Fe_T^{2+})$, increases rapidly, then slowly, with x. The additional absorptions in the $FeCr_2S_4$ spectrum (see Table II) correspond to D2 and D4 of the mixed crystals. Their intensity (partial absorption area, PA) varies from sample to sample: $PA(D2)$ can be as large as 0.10; single crystals[1] yielded values between 0.1 and 0.2.

Discussion

In the mixed crystal series between the normal spinel $Fe^{2+}[Cr_2^{3+}]S_4^{2-}$ and the inverse spinel $Fe^{3+}[Fe^{2+}Fe^{3+}]S_4^{2-}$ the ionic distribution must be between the limits $Fe^{2+}[Cr_{2-x}^{3+}Fe_x^{3+}]S_4^{2-}$ ("normal distribution") and $Fe_{1-x}^{2+}Fe_x^{3+}[Cr_{2-x}^{3+}Fe_x^{2+}]S_4^{2-}$ ("inverse distribution"). In the analogous system $Fe_{1+x}Cr_{2-x}O_4$, inversion starts around $x \approx 0.4$ (19). Robbins et al. (11) measured the magnetic moments μ of $Fe_{1+x}Cr_{2-x}S_4$, $0 \leq x \leq 0.5$. They calculated the theoretical increase of μ with x for both distributions. From the comparison with their experimental data (Fig. 4), especially from the values

detailed investigation of Gibart et al. (6) will be discussed later.

Below T_C, the outer two lines of a weak sextet with large internal field H_{int} in addition to the main sextet are visible in Mössbauer spectra of $FeCr_2S_4$. The position of the inner lines cannot be determined; for the fitting process $\Delta = 0$ was assumed. Similar absorptions were reported by Gibart et al. (6) and Lotgering et al. (5) (for $Fe_{1.06}Cr_{1.94}S_4$).

The spectra of the mixed crystal samples (Fig. 3, Table III) resemble those of the series $FeCr_{2-x}Rh_xS_4$ (3) though the quadrupole splittings are smaller here. They consist of several overlapping doublets of similar isomer shifts δ, but exhibit an intensity

TABLE III

ROOM TEMPERATURE MÖSSBAUER DATA IN THE SYSTEM $Fe_{1+x}Cr_{2-x}S_4$

	x					
	0.03	0.06	0.1	0.2	0.3	0.4
δ (mm/s)	0.590	0.589	0.587	0.59f	0.59f	0.59
	0.589	0.586	0.580	0.574	0.58	0.58
	—	0.54f	0.54f	0.54	0.53	0.54
	0.38	0.40f	0.39	0.37	0.38	0.37
Δ (mm/s)	0.02	0.02	0.05	0.10	0.16	0.13
	0.703	0.697	0.695	0.68	0.65	0.65
	—	1.15	1.26	1.11	1.10	1.13
	0.50f	0.50f	0.49	0.49	0.51	0.53
Γ (mm/s)	0.27	0.28	0.30	0.31	0.38	0.40
	0.24	0.23	0.28	0.32	0.30	0.30
	—	0.31	0.28f	0.28f	0.28f	0.28f
	0.32f	0.32f	0.33f	0.33	0.31f	0.34
PA	0.79	0.67	0.51	0.31	0.29	0.27
	0.17	0.25	0.41	0.49	0.36	0.34
	—	0.02	0.01	0.05	0.09	0.08
	0.036	0.056	0.075	0.15	0.26	0.31
$\bar{\delta}$ (mm/s)	0.581	0.575	0.567	0.547	0.522	0.513
$\bar{\delta}(Fe_T^{2+})$ (mm/s)	0.590	0.587	0.583	0.577	0.574	0.576
$\bar{\Delta}(Fe_T^{2+})$ (mm/s)	0.159	0.221	0.346	0.48	0.51	0.52

Note. f = fixed during fitting procedure.

for x = 0.4, 0.5, they concluded the inverse distribution corresponding to the octahedral-site preference of Fe^{2+}. From the values in the impurity-free low-x range, however, a normal distribution cannot be excluded.
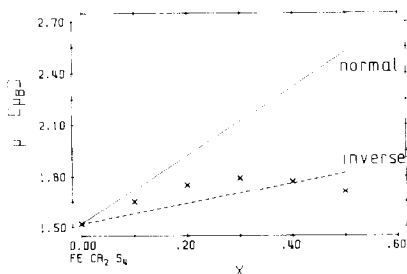

FIG. 4. Experimental (x) and calculated magnetic moments μ in the system $Fe_{1+x}Cr_{2-x}S_4$ (Robbins et al. (*11*)).

With geometrical relations for the spinel lattice (*20*), the following atomic distances Me–S can be derived from a and u data (*1*):

$$Fe_T^{2+}-S = 229.8 \text{ pm},$$
$$Fe_O^{2+}-S = 253 \text{ pm},$$
$$Cr_O^{3+}-S = 242.5 \text{ pm}.$$

As there are no reliable distances Fe^{3+}–S available, these values were derived from the experimental decrease of a in this system with the assumption of either normal or inverse distribution, respectively:

$$Fe_O^{3+}-S = 238 \text{ pm},$$
$$Fe_T^{3+}-S = 216.5 \text{ pm}.$$

Using these five distances, with the experimental change of a being explained automatically, the theoretical change of u can
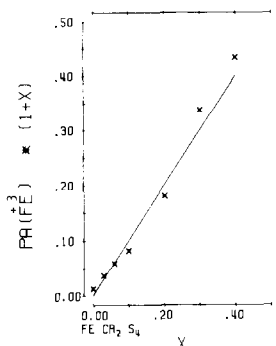
FIG. 5. Experimental (x) and calculated Mössbauer areas of Fe^{3+} in the system $Fe_{1+x}Cr_{2-x}S_4$.

be calculated for both distributions. Figure 1 shows that from this point of view the normal distribution is favored, though the contrary cannot be excluded because of the large experimental errors.

The interpretation of the Mössbauer spectra is based on the assumption that Fe_O^{2+} should absorb as a strongly split doublet ($\Delta \approx 3$ mm/s) with $\delta \geqq 0.77$ mm/s as it is the case in the whole system $FeCr_{2-x}In_xS_4$ (_1, 15_) without remarkable changes with x. It is not reasonable to expect a drastic difference in parameters of Fe_O^{2+} between $FeCr_{1.94}In_{0.06}S_4$ and $FeCr_{1.94}Fe_{0.06}S_4$. As a doublet of the above kind does not appear in any spectrum of the system $Fe_{1+x}Cr_{2-x}S_4$, the normal distribution is confirmed. Therefore it is apparent

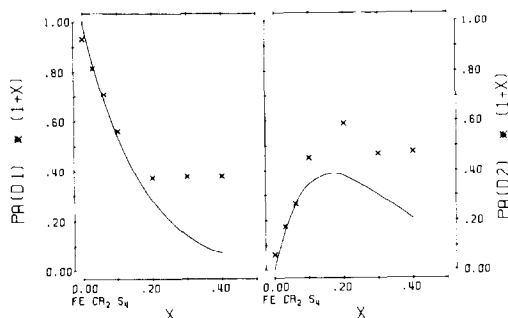that D4 represents Fe_O^{3+} while D1–D3 represent Fe_T^{2+} surrounded by different octahedral-site neighbors in the same way it was found for the systems $FeCr_{2-x}Rh_xS_4$ (_3_) and $FeCr_{2-x}In_xS_4$ (_1_).

The Mössbauer parameters of Fe_O^{3+} follow the general trend. The quadrupole splitting $\Delta \approx 0.5$ mm/s is much smaller than the ≈ 3 mm/s found for Fe_O^{2+}, but larger than that for Fe_T^{3+} (e.g., $Cu_{0.5}Fe_{0.5}^{3+}$ [CrRh]S_4: $\Delta = 0.13$ mm/s (_3_)); the isomer shift $\delta \approx 0.38$ mm/s is smaller than that for Fe^{2+} but larger than that for Fe_T^{3+} ($Cu_{0.5}Fe_{0.5}^{3+}$[CrRh]S_4: $\delta = 0.313$ mm/s). Figure 5 shows that the partial areas $PA(Fe^{3+})$ multiplied by $(1 + x)$ correspond to the theoretically expected values x.

The different doublets for Fe_T^{2+} arise in the manner described earlier (_1, 3, 13_) for the systems mentioned above. D1, D2, and D3 can be correlated to iron atoms with 0, 1, and 2 Fe^{3+} atoms in their neighborhood of 12 octahedral-site cations, respectively. Because of the strong overlap with the Fe^{3+} doublet, however, the experimental data are less accurate than for the comparable systems. Nevertheless, the basic validity of this model can be demonstrated with Fig. 6. It compares experimental partial areas with theoretical values calculated with the equation for binomial distributions assuming random distribution of cations on octahedral sites; for small x the correspondence is good to satisfactory.

The theoretical change of the overall isomer shift $\bar{\delta}$ can be calculated for both kinds of cation distribution using the following constant values:

$\delta(Fe_T^{2+}) = 0.591$ mm/s
   (from $FeCr_2S_4$);
$\delta(Fe_O^{2+}) = 0.772$ mm/s
   (from $FeCr_{2-x}In_xS_4$ with $x \to 0$(_1_));
$\delta(Fe_T^{3+}) = 0.310$ mm/s
   (from $Cu_{0.5}Fe_{0.5}Cr_2S_4$ (_12_));
$\delta(Fe_O^{3+}) = 0.38$ mm/s
   (here).

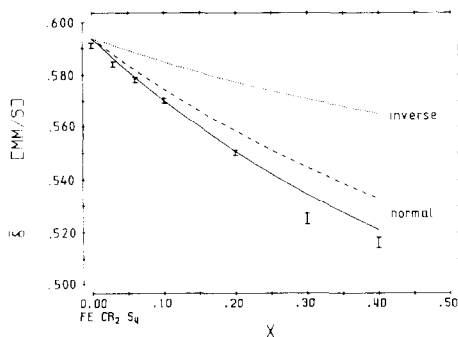FIG. 6. Experimental (x) and calculated Mössbauer areas of Fe^{2+} in the system $Fe_{1+x}Cr_{2-x}S_4$.

FIG. 7. Experimental (I) and calculated average isomer shifts in the system Fe$_{1+x}$Cr$_{2-x}$S$_4$.

The resulting dotted and dashed lines in Fig. 7 indicate normal cation distribution. The remaining discrepancy can be eliminated by accounting for the slight changes of the above values with x (13) (solid line in Fig. 7). To sum up:

—the change of the anion shift parameter u,

—the change of the average isomer shift $\bar{\delta}$,

—the absence of a strongly split Fe$_0^{2+}$ doublet,

—the presence of a doublet with parameters (δ, Δ) well compatible with Fe$_0^{3+}$,

unanimously indicate the normal cation distribution Fe^{2+}[Cr$_{2-x}^{3+}$Fe$_x^{3+}$]S$_4^{2-}$ in the range $x \leqq 0.4$.

This is in contrast with Lotgering et al. (5) who interpreted the Mössbauer spectrum of Fe$_{1.06}$Cr$_{1.94}$S$_4$ on the basis of an inverse distribution. The authors claimed that only the charge difference between Fe^{2+} and Cr^{3+} on octahedral sites could cause a marked quadrupole splitting at the tetrahedral site. The quadrupole splittings in the system FeCr$_{2-x}$Rh$_x$S$_4$ (3) contradict this argument. In conjunction with the similar doublets for $x > 0$, the additional absorptions in the spectrum of FeCr$_2$S$_4$ can only be explained by the presence of a small amount of Fe$_0^{3+}$. The existence of the weak sextet with the large H_{int} in the magnetically split spectra is

further evidence for Fe^{3+}. Therefore the samples studied here must be considered as a mixture of a spinel Fe^{2+}[Cr$_{2-y}^{3+}$Fe$_y^{3+}$]S$_4$ and y Cr$_3$S$_4$ (or something stoichiometrically equivalent), $y \approx 0.02$. The Cr$_3$S$_4$ phase might not be detectable in the X-ray diagram because of its small amount. In the single crystals y appears to be larger.

A slight Fe excess in the spinel phase has been assumed by Lotgering et al. (5) and Gibart et al. (6). Gibart et al. fitted their FeCr$_2$S$_4$ spectrum with an Fe$_T^{2+}$ singlet (δ = 0.59 mm/s), an Fe$_T^{3+}$ singlet (δ = 0.20 mm/s) and an Fe$_0^{2+}$ doublet (δ = 0.68 mm/s, Δ = 0.48 mm/s). The Δ value for Fe$_0^{2+}$ appears to be unreasonably small. We fitted our spectra with this theory also and got similar results for room temperature, but an isomer shift of 0.10 mm/s and an Fe$_0^{2+}$ doublet (δ = 0.68 the 240-K spectrum. The decreasing shift with decreasing temperature for this line is physically impossible which makes this assignment questionable. Contrarily to (5, 6), Brossard et al. (15) already concluded from the absence of a strongly split doublet characteristic for Fe$_0^{2+}$, that no Fe^{2+} exists on octahedral sites of Fe$_{1+x}$Cr$_{2-x}$S$_4$.

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