

Mössbauer Studies of Thiospinels. III. The System $\text{FeCr}_2\text{S}_4 - \text{FeIn}_2\text{S}_4$

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Polycrystalline samples of spinel compounds $\text{FeCr}_{2-x}\text{In}_x\text{S}_4$ have been obtained in the range $0 \leq x \leq 2$. The nonlinear changes of the cell parameters are explained by the nonlinear behavior of the inversion parameter λ according to the ionic distribution $\text{Fe}_{1-\lambda}^{2+}\text{In}_\lambda^{3+}[\text{Cr}_{2-x}^{3+}\text{Fe}_\lambda^{2+}\text{In}_{2-\lambda}^{3+}]\text{S}_4^{2-}$. Room temperature ^{57}Fe -Mössbauer spectra exhibit two sets of absorptions for tetrahedrally and octahedrally coordinated Fe, respectively, each consisting of several overlapping doublets of similar isomer shifts but varying quadrupole splittings. The partial intensity of octahedral-site Fe is in agreement with λ . The spectra can be understood by accounting for the influence of variable octahedral-site neighbors on tetrahedral-site iron.

Introduction

The normal spinel FeCr_2S_4 and the inverse spinel FeIn_2S_4 are among the most important representatives of the family of iron-containing thiospinels ((1-10) and references cited therein). Investigations of the solid solution between these spinels are scarce (11, 12). In our continuing investigation of thiospinels, we now present a detailed study of the system $\text{FeCr}_{2-x}\text{In}_x\text{S}_4$ using X-ray and ^{57}Fe -Mössbauer techniques.

Experimental

Preparation. The polycrystalline samples were prepared in evacuated silica ampoules from mixtures of the elements (99.9% or better) and In_2S_3 (puriss., Fluka). Two to three heating cycles at 900°C ($x \leq 0.1$) to 1080°C ($x \geq 0.5$), followed by a cycle at 450°C to reduce sulfur deposition, were necessary. With regard to sulfur deposits, for $0.6 \leq x \leq 0.9$, only the application of a

slight sulfur excess in the starting materials led to stoichiometric products; thereby the volume of the ampoule could be taken into account. Indium-rich samples were put in an Alsint-tube inside the silica ampoule to avoid contact reactions with the silica. For further details see (13, 14).

X-ray powder diffraction, Seebeck, and Mössbauer methods have been described previously (13, 14). Mössbauer isomer shifts are relative to metallic iron.

Results

Spinel compounds in the system $\text{FeCr}_{2-x}\text{In}_x\text{S}_4$ could be prepared in the whole composition range $0 \leq x \leq 2$. However, not all compounds with $x > 0.5$ can be considered as single-phase products: Usually the X-ray reflection intensity of impurities relative to the strongest spinel reflection is about 1-2%. For FeIn_2S_4 , about 1.2% impurity intensity was the best result, obtained for a sample that had been quenched from 900°C . The positions of the

extraneous lines are independent of x ; only some could be attributed to In_2S_3 and Fe_{1-y}S phases.

Though the spinel FeIn_2S_4 had been prepared several times (4–10), neither impurity problems nor the occurrence of contact reaction with the silica wall have been mentioned.

The lattice constants a do not obey Vegard's law (Table I, Fig. 1). The deviation is slightly (about 0.5 pm) negative for $0 < x < 0.7$ and markedly (about 2 pm) positive for $0.7 < x < 2$. Brossard *et al.* (12) found a linear relationship between a and x .

The cation distribution parameter λ , according to the formula $\text{Fe}_{1-\lambda}^{2+}\text{In}_\lambda^{3+}[\text{Cr}_{2-x}^{3+}\text{Fe}_\lambda^{2+}\text{In}_{x-\lambda}^{3+}]\text{S}_4^{2-}$, as calculated from X-ray reflection intensities, reflects the nonlinear transition of Fe^{2+} from tetrahedral to octahedral sites (Fig. 2). Mimura *et al.* (11) characterized the spinel FeCrInS_4 ($x = 1$) as inverse ($\lambda = 1$). The anion shift parameter u does not show a marked change with x (Fig. 1). Especially, the value for FeIn_2S_4 ($x = 2$) exhibits a

TABLE I
LATTICE PARAMETERS a AND SEEBECK
COEFFICIENTS Θ OF $\text{FeCr}_{2-x}\text{In}_x\text{S}_4$ AT ROOM
TEMPERATURE^a

x	a (pm)	Θ ($\mu\text{V}/\text{K}$)
0.0 (FeCr_2S_4)	999.8	483
0.03	1000.6	316
0.1	1002.6	271
0.2	1005.5	230
0.35	1010.1	—
0.5	1014.8	183
0.6	1017.9	167
0.7	1021.4	—
0.9	1028.5	181
1.0 (FeCrInS_4)	1032.3	216
1.2	1038.7	213
1.35	1043.1	—
1.5	1048.9	302
1.8	1055.9	390
2.0 (FeIn_2S_4)	1061.2	360

^a The error of a is ± 0.2 pm.

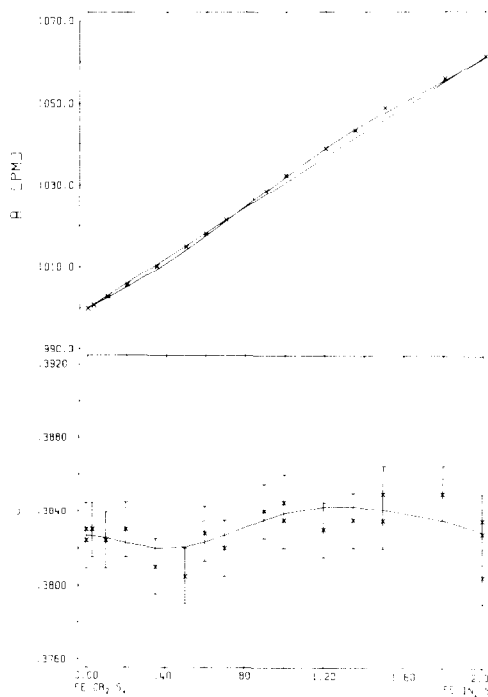


FIG. 1. Experimental (\times) and calculated lattice constants a and anion shift parameters u in the system $\text{FeCr}_{2-x}\text{In}_x\text{S}_4$ (Vegard's straight line included).

large experimental error as it is strongly influenced by the intensity of very weak X-ray reflections.

All samples have p-type semiconducting properties. The Seebeck coefficient Θ has

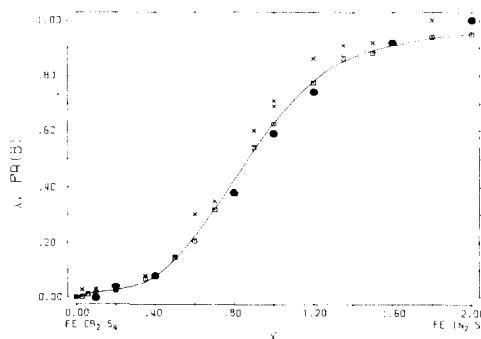


FIG. 2. X-Ray cation distribution parameter λ (\times) and partial Mössbauer area of group B, $PA(B)$ (\square), in the system $\text{Fe}_{1-x}\text{In}_x[\text{Cr}_{2-x}\text{Fe}_x\text{In}_{x-\lambda}]\text{S}_4$ (\bullet), $PA(B)$ from Brossard *et al.* (12)).

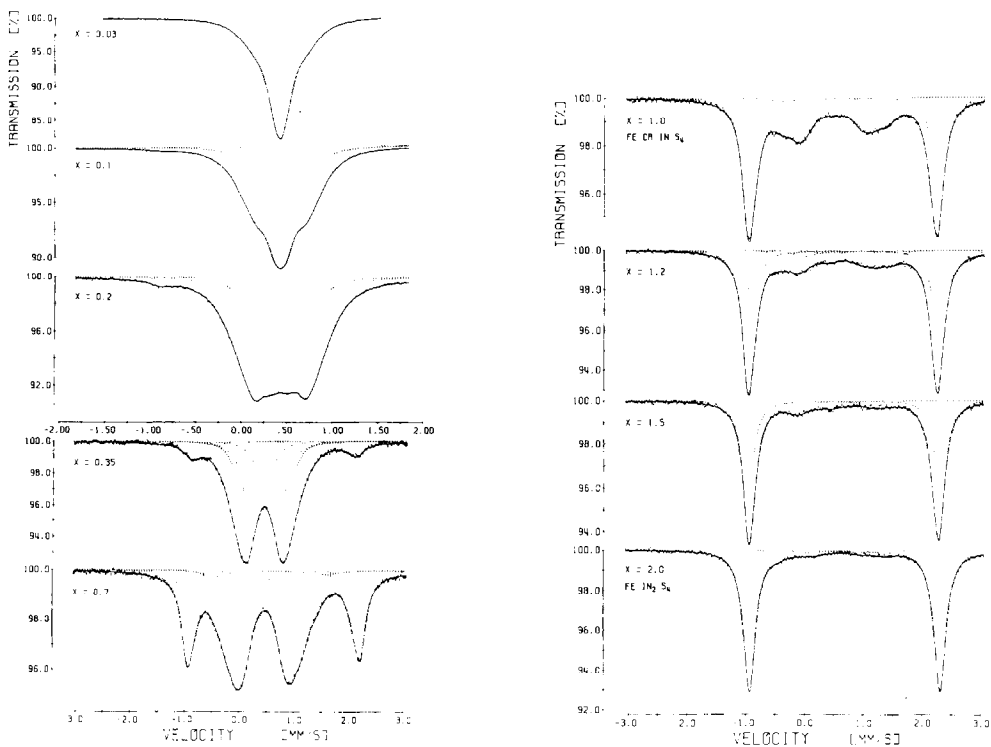


FIG. 3. Fitted Mössbauer spectra of $\text{FeCr}_{2-x}\text{In}_x\text{S}_4$ at room temperature (295 K).

the smallest values in the range $0.5 \leq x \leq 0.9$ (Table I).

The room temperature (295 K) Mössbauer spectrum of FeCr_2S_4 (13) consists mainly of a single absorption line. The spectra for $0.03 \leq x \leq 2$ (Fig. 3) contain several overlapping doublets. Two groups of doublets can be distinguished (Table II): Group A comprises doublets with isomer shifts $\delta < 0.76$ mm/s and quadrupole splittings $\Delta < 2.0$ mm/s. Doublets with $\delta \geq 0.78$ mm/s and $\Delta > 2.9$ mm/s belong to group B. It is obvious that the absorptions of group A and B are caused by tetrahedrally and octahedrally coordinated Fe atoms, respectively, according to the general spinel formula $A[B_2]X_4$. Thus the partial Mössbauer absorption area of group B, $PA(B)$, should be equivalent to the X-ray inversion parameter λ (Fig. 2). The correspondence is good with the ex-

ception of slight differences for $x > 0.5$. The direct comparison of λ and $PA(B)$ is only justified under the condition that there is no difference in recoil-free fractions f_0 , f_T between the two crystallographic sites. Sawatzky *et al.* (20) reported $f_0/f_T = 0.94$ for Fe_3O_4 . The differences between λ and $PA(B)$ found here are compatible with such a ratio F_0/f_T .

Brossard *et al.* (12) published similar PA values but denied the existence of octahedral iron atoms, Fe_O , for $x < 0.2$. The weak A-type absorptions for large x , especially for $x = 2$ (FeIn_2S_4), can be due to iron-containing impurities, at least partially. On the other hand, the fact that Hill *et al.* (10) found about 5% inversion in their X-ray single-crystal study of FeIn_2S_4 suggests that the A-type doublets indeed arise from Fe_T .

TABLE II
EXPERIMENTAL MÖSSBAUER DATA

x	No. of doublets fitted		Mean isomer shift ^a			Mean quadrupole splitting			Linewidth, Γ (mm/s)	Partial absorption area, $P(A/B)$
	group A	group B	$\delta(A)/\text{Fe}$ (mm/s)	$\delta(B)/\text{Fe}$ (mm/s)	δ/Fe (mm/s)	$\Delta(A)$ (mm/s)	$\Delta(B)$ (mm/s)			
0.0 (FeCr_2S_4)	2	—	0.590	—	0.590	?	—	0.26	0	
0.03	3	—	0.593	—	0.593	0.17	—	0.30	0	
0.06	3	1	0.596	0.78	0.598	0.28	3.03(2)	0.28-0.34	0.010(2)	
0.1	4	1	0.596	0.78	0.599	0.39	2.97(2)	0.28-0.32	0.013(2)	
0.2	4	1	0.597	0.780	0.601	0.55	2.99(2)	0.24-0.4	0.023(2)	
0.35	6	1	0.615	0.791	0.627	0.79	2.99(1)	0.31-0.33	0.070(4)	
0.5	6	1	0.628	0.793	0.652	0.95	3.036(5)	0.31-0.33	0.146(4)	
0.6	6	1	0.630	0.797	0.664	1.02	3.060(5)	0.31	0.205(4)	
0.7	5	2	0.640	0.804	0.692	1.08	3.066(5)	0.22-0.36	0.316(5)	
0.9	5	2	0.650	0.813	0.737	1.23	3.131(5)	0.22-0.34	0.541(5)	
1.0 (FeCrInS_4)	4	2	0.651	0.818	0.750	1.26	3.162(5)	0.25-0.4	0.625(5)	
1.2	4	2	0.669	0.827	0.791	1.23	3.187(5)	0.24-0.4	0.773(5)	
1.35	3	2	0.695	0.834	0.815	1.18	3.208(5)	0.22-0.4	0.862(5)	
1.5	2	2	?	0.842	?	?	3.202(5)	0.22-0.5	0.88	
1.8	2	2	?	0.853	?	?	3.228(2)	0.23-0.5	0.94	
2.0 (FeIn_2S_4)	2	1	?	0.864	?	?	3.237(2)	0.24-0.4	0.95	

Note. The error is ± 1 in the last digit unless otherwise stated in parentheses. ? = no accurate values obtainable.

^a Relative to Fe.

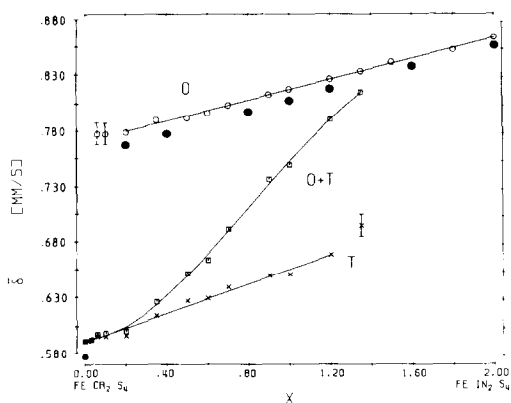


FIG. 4. Mean isomer shifts δ in the system $\text{FeCr}_{2-x}\text{In}_x\text{S}_4$ (●, Brossard *et al.* (12)).

Regarding the Fe_0 absorptions, they are represented by one narrow doublet for $x < 0.7$, but two narrow doublets of quite similar values δ and Δ for $x \geq 0.7$. The mean isomer shift, $\delta(\text{B})$, increases linearly with x (Fig. 4). For hypothetical Fe_0 in FeCr_2S_4 the value $\delta = 0.772$ mm/s follows from linear-regression analysis and extrapolation. The mean quadrupole splitting, $\Delta(\text{B})$,

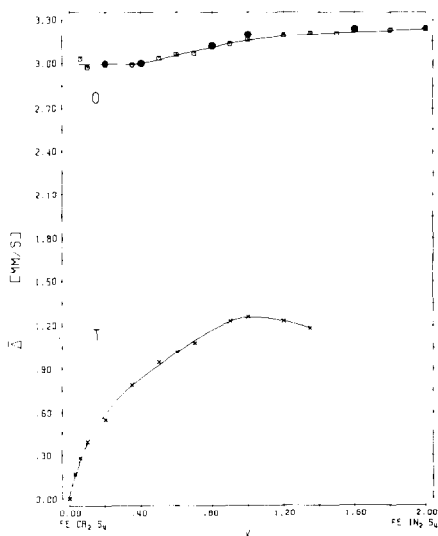


FIG. 5. Mean quadrupole splittings Δ in the system $\text{FeCr}_{2-x}\text{In}_x\text{S}_4$ (●, Brossard *et al.* (12)).

shows a nonlinear increase with x (Fig. 5).

The A-type absorptions caused by tetrahedral iron, Fe_T , resemble the Mössbauer spectra of the spinel system $\text{Fe}[\text{Cr}_{2-x}\text{Rh}_x]\text{S}_4$ (13). They consist of several doublets of not too different isomer shifts, but varying quadrupole splittings. The increase of $\delta(\text{A})$ with x is linear (Fig. 4). Regression analysis renders $\delta = 0.590$ mm/s for FeCr_2S_4 and $\delta = 0.720$ mm/s for Fe_T in FeIn_2S_4 (extrapolated). The slope is steeper than it is for $\delta(\text{B})$. The mean quadrupole splitting $\Delta(\text{A})$ has a maximum at $x = 1$ (Fig. 5).

Discussion

Crystallographic Properties

The cation distribution in the system $\text{Fe}^{2+}\text{Cr}_{2-x}\text{In}_x^{3+}\text{S}_4^{2-}$ could be derived from both X-ray data and Mössbauer absorption areas. The characteristic nonlinear transition of Fe^{2+} from tetrahedral to octahedral sites had been found in the comparable spinel systems $\text{Fe}^{2+}\text{V}_{2-x}^{3+}\text{Fe}_x^{3+}\text{O}_4$ (15) and $\text{Fe}^{2+}\text{Cr}_{2-x}^{3+}\text{Fe}_x^{3+}\text{O}_4$ (16) as well.

Using geometrical relations of the spinel lattice (17) and the following set of atomic distances $Me-S$ (consistent with the single-crystal data by Hill *et al.* (10)),

$$\begin{aligned} \text{Fe}_T^{2+}-S &= 229.8 \text{ pm} \\ \text{Cr}_0^{3+}-S &= 242.5 \text{ pm} \\ &\text{from } a \text{ and } u \text{ of } \text{Fe}[\text{Cr}_2]\text{S}_4; \end{aligned}$$

$$\begin{aligned} \text{In}_T^{3+}-S &= 245 \text{ pm} \\ (\text{Fe}^{2+}, \text{In}^{3+})_0-S &= 257 \text{ pm} \\ &\text{from } a \text{ and } u \text{ of } \text{In}[\text{FeIn}]\text{S}_4; \end{aligned}$$

the changes of a and u with x can be calculated. The calculations were carried out with varying values for $\text{Fe}_0^{2+}-S$ and $\text{In}_0^{3+}-S$, making use of the known average value. The best match with the experimental values (cf. Fig. 1) was achieved with

TABLE III

DATA OF MÖSSBAUER ABSORPTIONS OF TETRAHEDRAL IRON IN $\text{FeCr}_{2-x}\text{In}_x\text{S}_4$: ISOMER SHIFT δ , QUADRUPOLE SPLITTING Δ , PARTIAL AREA PA , AND THEORETICAL INTENSITY

x	δ (mm/s)	Δ (mm/s)	PA	Doublet	Surrounding	Calculated frequency
0.03	0.593	0.05	0.80	D1	(12/0)	0.834
	0.594	0.61	0.17	D2	(11/1)	0.152
	0.565	0.86	0.03	D3	(10/2) (9/3)	0.013 0.001
0.06	0.596	0.09	0.67	D1	(12/0)	0.694
	0.601	0.56	0.21	D2	(11/1)	0.258
	0.588	0.82	0.12	D3	(10/2) (9/3)	0.044 0.004
0.1	0.596	0.12	0.49	D1	(12/0)	0.540
	0.600	0.54	0.32	D2	(11/1)	0.341
	0.590	0.82	0.16	D3	(10/2)	0.099
	0.488	1.23	0.02	D4	(9/3) (other)	0.017 0.003
0.2	0.595	0.20	0.40	D1	(12/0)	0.282
	0.604	0.57	0.28	D2	(11/1)	0.377
	0.598	0.81	0.14	D3	(10/2)	0.230
	0.586	1.06	0.18	D4	(9/3) (other)	0.085 0.026

$\text{Fe}_0^{2+}\text{-S} = 253$ pm and $\text{In}_0^{3+}\text{-S} = 261$ pm. The s-shaped relation between a , u , and x (experimentally, hardly visible for u) is theoretically well founded.

Mössbauer Spectra

The spectra will be discussed in comparison with those of $\text{Fe}[\text{Cr}_{2-x}\text{Rh}_x]\text{S}_4$ (13). Both series contain Fe only as Fe^{2+} , but the In series contains Fe on both tetrahedral and octahedral sites. The isomer shifts are characteristic for thiosystems: $\delta(\text{Fe}_T^{2+}) \approx 0.58\text{--}0.72$ mm/s, $\delta(\text{Fe}_O^{2+}) \approx 0.77\text{--}0.87$ mm/s. The difference $\delta_0 - \delta_T$ is about 0.14–0.18 mm/s, comparable to the value 0.17 mm/s found for oxospinel (18).

For small x , the absorptions of Fe_T in the In system correspond with those in the Rh system completely, the only difference being the smaller quadrupole splittings here. Therefore the validity of the interpretation given for the Rh system is confirmed. The

quadrupole splitting of Fe_T is governed by the number of Cr and In atoms on the neighboring 12 octahedral sites. Numbering the doublets D1, D2, . . . , in order of increasing Δ , the relation (first approximation)

$$D1 \hat{=} \text{Fe}(12 \text{ Cr}/0 \text{ In}),$$

$$D2 \hat{=} \text{Fe}(11 \text{ Cr}/1 \text{ In}),$$

$$D3 \hat{=} \text{Fe}(10 \text{ Cr}/2 \text{ In}),$$

can be established in complete analogy. The comparison between observed partial absorption areas and theoretical frequencies of different (Cr/In) surroundings, calculated with the assumption of a random distribution of Cr and In on octahedral sites, is given in Table III and shows satisfactory agreement for $x < 0.2$, comparable to the Rh system. In this range, the amount of Fe_O is negligible. A correlation between δ and D1, D2, D3, apparent in the Rh system, cannot be seen here, presumably because

of larger experimental errors due to stronger overlap of doublets. Here again, a linear increase of Δ_{D1} with x is found, evidence for the influence of next nearest neighbors. The ratio Δ_{D2}/Δ_{D3} should be constant for both systems if the splittings are caused by the same mechanism. For the Rh system the value is $0.85/1.44 = 0.59$, which is, within experimental error, the same as $0.57/0.83 = 0.69$ for the In system. For the same reason the ratio of the maximum mean splitting $\bar{\Delta}_{\max}$ (at $x = 1.0$) to Δ_{D2} should be constant, too. For the Rh system $1.21/0.85 = 1.43$, whereas for the In system $1.26/0.57 = 2.21$. The much greater value for this system indicates that in the region $x > 0.2$ the Fe_0 content leads to larger Δ values than would be expected on the basis of the simple (Cr/In) model which holds for the low- x region only.

Brossard et al. (12) fitted their spectra assuming two kinds of configurations: one with 0, 1, 2, . . . (Fe) and 12, 11, 10, . . . (In + Cr) on octahedral sites; the other with 0, 1, 2, . . . (In) and 12, 11, 10, . . . (Fe + Cr); in other words, either Fe_0 or In_0 is considered a disturbing factor. They concluded that In_0 is more important than Fe_0 . Looking at $0 < x \leq 0.2$ (approximately $\text{Fe}[\text{Cr}_{2-x}\text{In}_x]\text{S}_4$), it can be excluded immediately that Fe_0 is the only disturbing factor. The relative influence of In_0 vs Fe_0 on the resulting Δ cannot be estimated without detailed model calculations.

Furthermore, the authors argued that the size difference between In_0^{3+} and Cr_0^{3+} is more efficient than the charge difference between Fe_0^{2+} and Cr_0^{3+} . Using the technique mentioned earlier, the value $\text{Rh}_0^{3+}-\text{S} = 238$ pm (14) can be derived from the change of a in the Rh system. The larger quadrupole splittings there despite the small size difference,

$$(\text{Cr}_0^{3+}-\text{S} - \text{Rh}_0^{3+}-\text{S}) = 4.5 \text{ pm};$$

$$(\text{In}_0^{3+}-\text{S} - \text{Cr}_0^{3+}-\text{S}) = 18.5 \text{ pm},$$

show that atomic size is not a dominant factor.

The authors report separate doublets for Fe_T with 0, 1, 2, 3, and 4 In_0 neighbors, each In_0 increasing δ by 0.01 mm/s and Δ by 0.34 mm/s. We did not find constant differences of Δ in either system; with the reasonable assumption that every quadrupole splitting is not only influenced by the kind of neighbors but by the geometrical order as well, such constant differences of Δ cannot be expected.

In contrast to the Fe_T absorptions, the Fe_0 absorptions do not exhibit drastic changes within the series $\text{FeCr}_{2-x}\text{In}_x\text{S}_4$. The inhomogeneous cationic environment gives rise to a slight asymmetry of the Fe_0 doublet only. Δ_0 is caused by the trigonal arrangement of the cation neighbors (nearest neighbors: six octahedral-site cations) and the noncubic geometry of the anion neighbors ($u \neq 0.375$); the anionic influence is related to the value of u (19). The increase of $\bar{\Delta}_0$ resembles the shape of the Fe_0 and In_T content, but not the shape of the variation of u (no minimum/maximum values), which leads to the idea that the size of $\bar{\Delta}_0$ is determined by the Fe_0 content.

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