

Structural Studies by X-Ray Diffraction and Mössbauer Spectroscopy of Cubic FeYb₂S₄ and FeLu₂S₄

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The two isostructural compounds FeYb₂S₄ and FeLu₂S₄ were studied by X-ray diffraction and Mössbauer spectroscopy. The structure was solved in the space group *Fd3m*; *Z* = 8. For the FeYb₂S₄, the S atoms occupy the (32*e*) positions. The tetrahedral (8*a*) and octahedral (16*d*) positions of the direct spinel are, respectively, occupied by 0.8 Fe²⁺ and (0.88 Yb³⁺ + 0.045 Fe²⁺). The additional octahedral (16*c*) positions are occupied by (0.12 Yb³⁺ + 0.055 Fe²⁺). For 155 reflections crystallographic *R* is 0.034. The Mössbauer spectrum results from the superposition of four doublets. Two doublets with the same isomer shift of 0.73 mm/sec are characteristic of Fe²⁺ ions in the (8*a*) position with two distorted tetrahedral symmetries simulated by two different quadrupole splittings. The third and fourth doublets correspond to Fe²⁺ ion in 16*c* and 16*d* positions. The intensity ratio between the doublets is in agreement with the distribution (Fe_{0.8}²⁺ □_{0.2}) (Yb_{1.76}³⁺ Fe_{0.09}²⁺ □_{0.15}) (Yb_{0.24}³⁺ Fe_{0.11}²⁺ □_{1.65}) which corresponds to FeYb₂S₄. The metal atoms in FeLu₂S₄ are distributed in the same way as those in FeYb₂S₄.

1. Introduction

Patrie *et al.* (1) showed that Fe(II) sulfide combines with some rare-earth sulfides *L*₂S₃, where *L* = Lu, Yb, or Sc, to give Fe*L*₂S₄ compounds. Their structure, determined from powder diagrams, has been considered as the normal spinel structure. Riedel *et al.* (2), without suspecting the normal spinel structure, explain by X-ray powder data and Mössbauer spectroscopy that the tetrahedral sites are occupied only by Fe²⁺. Recently with a study done on a single crystal, we showed that the structure of this compound is close to a normal spinel structure (3). The cubic cell contains 8(Fe_{0.76}Yb_{2.16}S₄), and parameter *a* is 10.877(2) Å (8). Iron is divalent and ytterbium trivalent. The specificity compared to the normal spinel

structure comes from the existence of partially filled tetrahedral (8*a*) and octahedral (16*d*) sites and from the existence of an additional octahedral (16*c*) site. The S atoms occupy the (32*e*) position as in the normal spinel structure (Table I). The 8*a* position is filled with iron atoms only and cannot be filled with ytterbium atoms because the coordination of this site is strictly tetrahedral. The final Fe_{0.76}Yb_{2.16}S₄ formula resulting from the refinement does not correspond to the stoichiometric reaction of one FeS with one Yb₂S₃. In fact it is difficult to conclude whether or not there are iron atoms on octahedral sites. To solve this problem, we studied the Mössbauer spectrum of this compound which allowed us to determine the occupancy of iron atoms of the different sites. From the distribution of iron atoms we

TABLE I
SITE OCCUPATION IN A NORMAL SPINEL STRUCTURE AND IN THE
DESCRIBED COMPOUND

Site	Tetrahedral 8a	Octahedral 16d	Octahedral 16c	Sulfur 32e
Direct spinel ML_2S_4	1 M^{2+}	1 L^{3+}		1 S^{2-}
$Fe_{0.76}Yb_{2.16}S_4$ Tomas and Guittard (3)	0.76 Fe^{2+}	0.96(1) Yb^{3+}	0.12(2) Yb^{3+}	1 S^{2-}

can proceed to a new refinement of the structure and determine the final atomic distribution. We complete this work with a similar study on the isomorphous cubic $FeLu_2S_4$.

2. Experimental

FeS and Yb_2S_3 (or Lu_2S_3) sulfides, mixed in stoichiometric amounts to give $FeYb_2S_4$ (or $FeLu_2S_4$), are heated under flowing H_2S up to 1250–1350°C in an induction furnace for 6 hr. Fast quenching gives the cubic form of $FeYb_2S_4$. The orthorhombic form is obtained by slow cooling (1).

Mössbauer spectra were taken with a conventional spectrometer. The room temperature source of ^{57}Co in Pd (50 mC) is moved by a linear velocity transducer (symmetrical triangular velocity signal). The absorber powder is pressed between two Mylar foils without any glue. Spectra were fitted using a least-squares routine based on convolution of Lorentzian emission and absorption lines (4). The f factors of the different tetrahedral and octahedral sites have been assumed to be identical. Our samples contained roughly the same amount of ^{57}Fe atoms: 2.2, 4.3, and 5.2 Fe/cm^2 for cubic $FeYb_2S_4$, $FeLu_2S_4$, and orthorhombic $FeYb_2S_4$, respectively.

The crystal data of $FeYb_2S_4$ were previously described (3). In the case of $FeLu_2S_4$ a rectangular single crystal of dimensions $0.07 \times 0.07 \times 0.02$ mm³ was used for the data collection. The linear absorption coefficient

is 357 cm⁻¹, giving a maximum $\mu R = 1.25$ and an average $\mu R = 0.95$. The cell parameter $a = 10.808(2)$ Å was obtained from least-squares refinements with crystal setting data for 18 reflections measured on a four-circle diffractometer (PW Phillips) using $MoK\alpha$ radiation ($\lambda = 0.70926$ Å). The step-scanning technique was used (5); 915 reflections were collected on four octants to a maximum value of 41° and the intensities were averaged. The reflections which may be affected by Renninger effect have been eliminated (Program Mulref (9)). Lorentz polarization and absorption corrections (Program FACIES (12)) were applied to the data; 187 reflections with $F_o^2 \geq 2\sigma(F_o^2)$ were used. The scattering factors corrected of the anomalous diffusion are taken from the International Tables for X-Ray Crystallography (6).

3. Discussion

$FeYb_2S_4$

Figure 1 shows the good fit between experimental and calculated room temperature Mössbauer spectra of cubic $FeYb_2S_4$ and $FeLu_2S_4$. Least-squares refinement allows one to deduce hyperfine parameters and the normalized intensities α_i of the four i sites necessary to obtain a satisfying reproduction of the experimental Mössbauer spectrum.

It is useful to interpret the $FeYb_2S_4$ cubic compound Mössbauer spectrum and to compare it with that of the $FeYb_2S_4$ ortho-

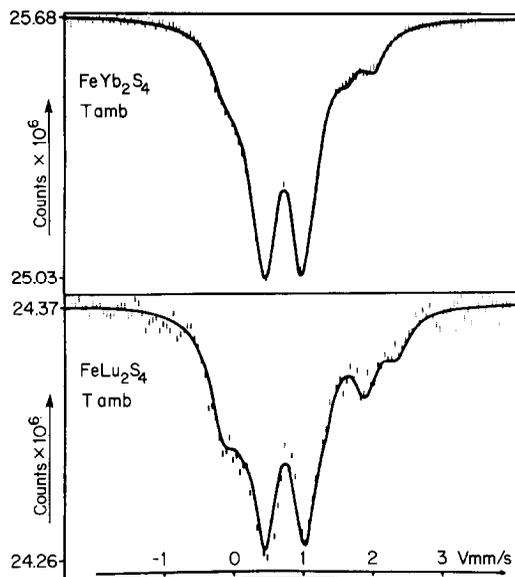


FIG. 1. Experimental and calculated room temperature Mössbauer spectra of cubic FeYb₂S₄ and FeLu₂S₄.

rhombic form at room temperature. This last spectrum is a doublet characterized by the hyperfine parameters

$\delta = 0.91 \text{ mm/sec} \pm \text{v.s. iron metal (isomer shift)}$,

$\epsilon = 1.12 \text{ mm/sec} \pm (\text{quadrupole interaction,}$

$$\epsilon = \frac{eQV_{zz}}{4} \left(1 + \frac{\eta^2}{3} \right)^{1/2},$$

where V_{zz} and η are the principal component and the asymmetric parameter of the electric field gradient at the iron nucleus characterized by its nuclear moment Q .

These values agree fairly well with those obtained by Riedel *et al.* (2). They confirm that the iron atoms occupy the octahedral site of the orthorhombic compound.

The low value of ϵ shows that the ${}^5T_{2g}$ electronic level of the iron atom in the octahedral site is split into three orbital singlets by the orthorhombic component of the crystal field.

For the cubic compound FeYb₂S₄ Table II shows that the α_3 and α_4 sites have hyperfine parameters similar to those of the orthorhombic FeYb₂S₄. Therefore those two sites correspond to the 16c and 16d octahedral positions which would then contain 0.055 and 0.045 iron atoms. The largest isomer shift corresponds to the longest Fe-S distance of the 16c site. The isomer shifts δ_3 and δ_4 of Fe²⁺ in octahedral S coordination are in agreement with spinel FeIn₂S₄ ($\delta = 0.85 \text{ mm/sec}$ (11)). The first two sites α_1 and α_2 with the same isomer shift are related to the tetrahedral 8a position occupied only by 0.8 iron atom. Our values of δ_1 and δ_2 isomer shift show that the Fe-S bonds in Fe(8a) tetrahedra are less covalent than the Fe-S

TABLE II

ROOM TEMPERATURE HYPERFINE PARAMETERS (ISOMER SHIFT δ VERSUS IRON METAL, QUADRUPOLE INTERACTION ϵ) AND NORMALIZED INTENSITIES OF IRON SITES IN CUBIC FeYb₂S₄ AND FeLu₂S₄ ($\sum \alpha_i = \alpha_1 + \alpha_2 + 2(\alpha_3 + \alpha_4) = 1$)

$T = 300^\circ\text{K}$	δ (mm/sec)	ϵ (mm/sec)	α_i	Position
Cubic	0.74 ± 0.01	0.25 ± 0.01	$\alpha_1 = 0.58 \pm 0.01$	8 a
	0.73 ± 0.01	0.44 ± 0.01	$\alpha_2 = 0.22 \pm 0.01$	
FeYb ₂ S ₄	0.94 ± 0.05	1.1 ± 0.1	$\alpha_3 = 0.055 \pm 0.020$	16 c
	0.84 ± 0.05	0.8 ± 0.1	$\alpha_4 = 0.045 \pm 0.020$	16 d
Cubic	0.74 ± 0.01	0.28 ± 0.02	$\alpha_1 = 0.57 \pm 0.01$	8 a
	0.73 ± 0.01	0.59 ± 0.02	$\alpha_2 = 0.14 \pm 0.01$	8 a
FeLu ₂ S ₄	1.06 ± 0.05	1.3 ± 0.1	$\alpha_3 = 0.05 \pm 0.020$	16 c
	0.89 ± 0.05	1.0 ± 0.1	$\alpha_4 = 0.095 \pm 0.020$	16 d

bonds in FeCr_2S_4 ($\delta = 0.58$ mm/sec (10)). In fact, these two doublets with different values of quadrupole splitting simulate mainly statistical distribution of vacancies, Yb^{3+} , and Fe^{2+} ions on 16c and 16d sites.

In order to obtain more information on the electric field gradient of these different 8a and 16c, 16d positions it should be useful to perform Mössbauer spectra at lower temperatures where a magnetic order appears: so we should be able to find the sign of V_{zz} and the asymmetry parameter η of the electric field gradient as well as the angle between the 0z direction and the spins. Unfortunately a tentative experiment at 4.2°K where the compound FeYb_2S_4 orders magnetically was difficult to interpret because of the unfavorable signal to noise ratio.

The repartition of iron atoms of the cubic FeYb_2S_4 obtained by Mössbauer spectrometry is then: 0.80Fe^{2+} in 8a position, 0.11Fe^{2+} in 16c position, and 0.09Fe^{2+} in 16d position (Table II). Now, using the 155 reflections already measured (3) a new refinement of this structure in order to determine the repartition of ytterbium and iron atoms remains to be made. One ytterbium atom and 0.1 iron atom are distributed among two 16c and 16d octahedral positions. We used the diffusion table corresponding to

$$\frac{1\text{Yb}^{3+} + 0.1\text{Fe}^{2+}}{1.1}$$

The S atoms are in the (32e) position. A least-squares refinement of the x coordinate of S atoms, of the isotropic temperature factors, and of all the cation occupation factors leads to an R factor of 0.04. During the refinement the occupation factors of iron atoms of the 8a tetrahedral position remains equal to 0.8. More particularly 0.88(2) and 0.12(1) ytterbium atoms occupy every 16d and 16c position. The sum of electrons of those sites corresponds to 2 Yb + 0.2 Fe.

Assuming the occupation of ytterbium atoms, let us verify those of iron atoms determined by Mössbauer spectroscopy following this repartition: ($0.88\text{Yb}^{3+} + 0.04\text{Fe}^{2+}$) and ($0.12\text{Yb}^{3+} + 0.05\text{Fe}^{2+}$) occupy 16d and 16c positions. The sum of occupation factors of ytterbium atoms is constrained to remain equal to 2 and that of iron atoms to 0.2. The isotropic temperature factor of the iron atom is constrained to remain equal to that of the ytterbium atom occupying the same site. Then the atomic scattering factors of pure element are given for atoms. During the refinement the occupation factors vary little and converge to the values indicated in Table IIIa. The suppression of the constraints gives the same results. The introduction of anisotropic temperature factors for the atoms occupying the 16d, 16c, and 32e sites lowers the R factor to 0.034. One difference Fourier map shows only peaks which do not get over $0.5\text{e}\text{\AA}^{-3}$.

TABLE IIIa

FINAL ATOMIC COORDINATES ($\times 10^4$), OCCUPANCY FACTORS, AND MEAN SQUARE VIBRATION AMPLITUDES U_{ij} ($\times 10^4$) OF CUBIC FeYb_2S_4 ^a

Fe	Yb	S	Position	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
0.80(0.01)			8a	1250	1250	1250	158	158	158	0	0	0
0.045(0.010)	0.88(0.01)		16d	5000	5000	5000	94	94	94	-15	-15	-15
0.055(0.010)	0.12(0.01)		16c	0	0	0	125	125	125	42	42	42
		1	32e	2531(1)	2531(1)	2531(1)	107	107	107	-3	-3	-3

^a Standard deviations in terms of the last digit are in parentheses.

TABLE IIIb

FINAL ATOMIC COORDINATES ($\times 10^4$), OCCUPANCY FACTORS, AND MEAN SQUARE VIBRATION AMPLITUDES U_{ij} ($\times 10^4$) OF CUBIC FeLu₂S₄^a

Fe	Lu	S	Position	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
0.71(0.02)			8 a	1250	1250	1250	105	105	105	0	0	0
0.095(0.010)	0.84(0.01)		16 d	5000	5000	5000	110	110	110	-17	-17	-17
0.050(0.010)	0.16(0.01)		16 c	0	0	0	148	148	148	-22	-22	-22
		1	32 e	2528(1)	2528(1)	2528(1)	143	143	143	-13	-13	-13

^a Standard deviations in terms of the last digit are in parentheses.*FeLu₂S₄*

The Mössbauer spectrum of the FeLu₂S₄ cubic compound is interpreted as the cubic FeYb₂S₄. We come to an analogous distribution of iron atoms. Every 8a, 16c, and 16d site is occupied by 0.71, 0.05, and 0.095 iron atoms.

The scrutiny of structure factors of the two FeLu₂S₄ and FeYb₂S₄ cubic compounds shows a great similarity; therefore, we suppose they have the same structure. A least-squares refinement of x S-atom coordinate, of occupation factors of the three metallic sites, and of anisotropic thermal parameters, in the same way as that used to study the FeYb₂S₄ cubic compound, leads to an R factor of 0.022. The final results are given in Tables IIIb and IV.

4. Conclusion

In these compounds, iron is divalent and the rare-earth atom, ytterbium or lutetium, is trivalent.

In FeYb₂S₄, 0.80 iron atom lies on every tetrahedral 8a position and the two octahedral 16d and 16c sites are partially filled with, respectively, (0.88 Yb³⁺ + 0.04₅ Fe²⁺) and (0.12 Yb³⁺ + 0.55 Fe²⁺). Accordingly the formula is (Fe_{0.8²⁺} □_{0.2})Yb_{1.76³⁺}Fe_{0.09²⁺} □_{0.15}) (Yb_{0.24³⁺}Fe_{0.11²⁺} □_{1.65})S₄.

In the FeLu₂S₄ compound the 8a tetrahedral site is partially filled with 0.71 iron atom only and the two octahedral 16d and 16c sites by, respectively, (0.84 Lu³⁺ + 0.09₅ Fe²⁺) and (0.16 Lu³⁺ + 0.05 Fe²⁺). That gives the formula (Fe_{0.71²⁺} □_{0.29}) (Lu_{1.68³⁺}Fe_{0.19²⁺} □_{0.13}) (Lu_{0.32³⁺}Fe_{0.10²⁺} □_{1.58})S₄.

Thus we get the formulas FeYb₂S₄ and FeLu₂S₄ given by the preparation of compounds. The tetrahedral 8a sites are occupied only by iron atoms. The remaining iron atoms and the rare-earth atoms are in statistical disorder on the octahedral 16c and 16d positions. This type of mixed site was previously mentioned (7). The occupancy of the octahedral 16c site is possible because

TABLE 4

INTERATOMIC DISTANCES WITH STANDARD DEVIATIONS OF CUBIC FeYb₂S₄ AND FeLu₂S₄

	Tetrahedral position 8a	Octahedral position 16c	Octahedral position 16d
FeYb ₂ S ₄	Fe-S = 2.413(1) Å	Yb-S = 2.753(1) Å Fe-S = 2.686(1) Å	Yb-S = 2.686(1) Å Fe-S = 2.686(1) Å
FeLu ₂ S ₄	Fe-S = 2.392(1) Å	Lu-S = 2.732(1) Å Fe-S = 2.672(1) Å	Lu-S = 2.672(1) Å Fe-S = 2.672(1) Å

the tetrahedral $8a$ positions are only partially filled. In fact, this structure may be considered as a modification of a normal spinel with a supplementary $16c$ site or as a rock-salt structure with a tetrahedral $8a$ position. It is probably possible to obtain other atomic distributions corresponding to different experimental conditions like those in FeSc_2S_4 (8).

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