

Some New Results and Interpretation Concerning the System FeYb_2S_4

L. BEN-DOR* AND I. SHILO†

Department of Inorganic and Analytical Chemistry, Hebrew University, Jerusalem

AND I. FELNER

Racah Institute of Physics, Hebrew University, Jerusalem, Israel

Received April 26, 1978; in revised form August 25, 1978

Stoichiometric powdered FeYb_2S_4 having a cubic (special) spinel structure was prepared. The structure was based on X-ray diffraction and Mössbauer spectroscopy. The space group is $Fd\bar{3}m$ (No. 227) and the lattice constant $a_0 = 10.828 \text{ \AA}$. All the iron is divalent but only ca. 80% fills the tetrahedral $8a$ site while ca. 20% fills the octahedral $16d$ site. The ytterbium is trivalent, most of it occupying the normal octahedral $16d$ site, but ca. 16% occupies the normally empty octahedral $16c$ site, having been displaced by the iron.

Introduction

Recently Riedel *et al.* (1) published the structure of polycrystalline spinel $\text{Fe}_{1+x}\text{Yb}_{2-x}\text{S}_4$. They find all the iron in the tetrahedral site but with a valence distribution between two and three. They base their findings on both X-ray and Mössbauer data. Tomas and Guittard (2) found, first, that single crystals of so-called " FeYb_2S_4 spinel" are nonstoichiometric ($\text{Fe}_{0.76}\text{Yb}_{2.16}\text{S}_4$) and, second, that the ytterbium occupies two series of octahedral sites, viz., 1.92 atoms in the $16d$ site and 0.24 atoms in the $16c$ site. Riedel *et al.* (1) place the main emphasis on solving the oxidation state of the iron ions while the aim of Tomas *et al.* (2) was the study of the detailed structure and elucidation of the difference from the normal spinel. Following the above studies, we were able to show, using both X-ray and Mössbauer techniques, that not only the

ytterbium but also the iron ions each occupy two sites, thus forming a rather complex spinel structure.

Preparation

Stoichiometric amounts of iron, ytterbium, and sulfur were mixed well together, closed in a quartz ampoule and heated slowly to 400°C for 48 hr, then raised to 500°C for 12 hr and ultimately to 800°C for 16 hr. The resulting nonhomogeneous powder was ground thoroughly and resealed in an evacuated quartz ampoule. The material was then heated to 1000°C for 48 hr and to 1100°C for 8 hr. The resulting material was the well-known orthorhombic (3) modification of FeYb_2S_4 . After subsequent reheating at 1100°C for 48 hr and a slow raising to 1280°C (during ca. 5 hr) followed by rapid quenching in ice water a spinel modification was obtained. This material, prepared in a sealed ampoule, was shown to be stoichiometric based on atomic

* To whom correspondence should be addressed.

† In partial fulfilment of the Ph.D. degree.

absorption spectrometry for iron, contrary to the understoichiometry obtained by Tomas *et al.* (2) for crystals prepared in an open system under flow of H₂S, and similar to the powder obtained by Riedel *et al.* (1) who also worked in a closed system.

Structure Determination

X-Ray powder diffraction data were collected using a Philips diffractometer with monochromatized CuK α radiation. The scanning speed was $\frac{1}{8}^\circ/\text{min}$. The relative X-ray diffraction intensities were measured and the structural parameters refined with the aid of a FORTRAN program¹ to obtain a minimum value for the factor R defined as

$$R = \frac{\sum |I_{\text{obs}} - I_{\text{calc}}|}{\sum I_{\text{obs}}} \times 100.$$

Table I gives the observed and calculated intensities for the normal spinel and for a special spinel which shows a two-site occupancy for each of the metal ions. The R value was calculated for 12 different occupancies, and the least value, namely, $R = 9.7\%$, was obtained for Fe_{0.8}^{8a}[(Fe_{0.2}Yb_{1.68})^{16d}(Yb_{0.32})^{16c}]₄. In all cases the space group is $Fd\bar{3}m$.

Table II lists a few of these possible structures. In all cases the sulfur occupies the 32e site and its parameter is 0.253. This table clearly shows that the Yb occupancy is more sensitive to intensity values than the iron occupancy (cf. 2, 4 with 4, 5). The Mössbauer data (see below) show that about 20% of the iron atoms move from the tetrahedral to the octahedral site but only the X-ray data can unambiguously show that the iron atoms which are displaced enter the 16d rather than the 16c site (cf. 3 and 5), and it is the ytterbium which partially fills the 16c site.

¹ A FORTRAN program for calculating X-ray powder diffraction patterns (1963) by Dr. K. Smith, University of California.

TABLE I
X-RAY DATA FOR FeYb₂S₄ ($a_0 = 10.828 \text{ \AA}$)

d_{obs}	d_{calc}	hkl	I_{obs}	I_{calc}^a	I_{calc}^b
6.252	6.251	111	38.1	51.9	39.1
3.826	3.828	220	4.6	5.8	5.4
3.265	3.265	311	76.8	100	76.2
3.124	3.126	222	50.0	29.0	47.0
2.707	2.707	400	82.9	57.5	92.8
2.484	2.484	331	12.5	18.4	11.0
2.209	2.210	422	1.8	2.6	2.4
2.084	2.084	511, 333	33.3	30.8	32.1
1.915	1.914	440	100	69.4	100
1.831	1.830	531	12.7	15.5	11.4
1.651	1.652	533	10.0	14.4	10.9
1.633	1.632	622	17.9	15.6	25.0
1.564	1.563	444	19.5	14.9	23.8
1.516	1.516	551, 711	7.0	8.6	6.4
1.410	1.409	731, 553	13.7	25.4	18.4
1.354	1.353	800	9.8	11.1	16.0
1.250	1.250	751, 555	8.0	13.3	10.3
1.243	1.242	662	8.3	6.5	10.4
1.212	1.210	840	27.1	19.7	31.2

^a Normal spinel, $R = 31\%$.

^b Special spinel, $R = 9.7\%$.

Thus the most probable structure is formulated in No. 5. The position of the atoms and the interatomic distances are given in Tables III and IV.

Mössbauer Data

Mössbauer studies of the 14.4-keV γ ray of ⁵⁷Fe in FeYb₂S₄ were performed at 295°K using a ⁵⁷Co/Rh source. Least-squares computer calculations fit the experimental spectra nicely (Fig. 1). The actual spectrum is identical with that observed by Riedel *et al.* (1); however, the appearance of two quadrupole hyperfine interactions was not considered or explained by them. The values for the isomer shift (I.S.) measured here are: $\delta_1 = 0.66 \pm 0.01 \text{ mm/sec}$; $\delta_2 = 0.86 \pm 0.02 \text{ mm/sec}$ relative to the source, as compared with 0.61 mm/sec observed by Riedel *et al.* (1) and the electric field gradients, eqQ , are 6.5 and 24.3 MHz/sec, respectively ($0.56 \pm$

TABLE II
 OCCUPATION OF METAL SITES IN VARIOUS SPINELS—FeYb₂S₄

	8 <i>a</i> (tetra)	16 <i>d</i> (octa)	16 <i>c</i> (octa)	R (%)
1. <i>n</i> -FeYb ₂ S ₄	Fe	2Yb ^o	—	31
2. Fe[Yb _{1.44} (Yb _{0.56})]S ₄	Fe	1.44 Yb	0.56 Yb	28
3. Fe _{0.8} [Yb _{1.68} (Yb _{0.32} Fe _{0.2})]S ₄	0.8 Fe	1.68 Yb	0.32 Yb, 0.2 Fe	14.8
4. Fe[Yb _{1.68} (Yb _{0.32})]S ₄	Fe	1.68 Yb	0.32 Yb	11.5
5. Fe _{0.8} [Fe _{0.2} Yb _{1.68} (Yb _{0.32})]S ₄	0.8 Fe	0.2 Fe, 1.68 Yb	0.32 Yb	9.7

0.08 and 2.10 ± 0.05 mm/sec as compared to 0.45 and 0.78 mm/sec (1)).

However, Riedel *et al.* consider only two overlapping doublets with an identical I.S. and only slightly differing in *eqQ* values. Our data, on the other hand, show two doublets with similar I.S. but widely varying in electric field gradient.

The value of I.S. suggests beyond doubt that all the iron is divalent. Now while *eqQ*₍₁₎ (0.56 mm/sec) corresponds to a tetrahedral (8*a*) site and is by far the largest occupancy, still $19 \pm 3\%$ of the iron occupies an octahedral site and its *eqQ*₍₂₎ is nearly identical with that observed for the low-temperature orthorhombic modification of FeYb₂S₄ where all the iron is in octahedral coordination. The data for the iron in orthorhombic FeYb₂S₄ are: $\delta = 0.92 \pm 0.03$ mm/sec and *eqQ* = 2.03 ± 0.05 . Only when the X-ray data are studied is it found that the octahedral iron atoms occupy the 16*d* and not the 16*c* site. Mössbauer experiments on the Yb atom failed to be conclusive. The *eqQ* values obtained are due to the asymmetric electric

environment acting on the Fe²⁺ ions in both sites.

Magnetic Susceptibility

The magnetic susceptibility was measured with an alpha magnetometer in the temperature range 77 to 320°K and field strength of ca. 7.6 kOe. The absolute value was determined by the use of Co[Hg(SCN)₄] as standard. In the temperature range 4.2 to 70°K and field strengths of 2.5, 5, and 10 kOe the magnetization was measured using a commercial PAR Foner magnetometer, model 155. The Curie-Wiess law is well obeyed in the temperature range studied. The Curie constants *C*_M obtained are 8.6 and 8.8 emu/mole and the values for θ are -30 and -60°K, respectively, for the two temperature regions. The theoretical *C*_M when calculated from the individual contributions of Fe²⁺ (*S* = 2) and Yb³⁺ (*J* = $\frac{1}{2}$) is

 TABLE III
 POSITION OF ATOMS IN FeYb₂S₄—SPECIAL SPINEL

		<i>x</i>	<i>y</i>	<i>z</i>
Fe(1)	8 <i>a</i>	0.125	0.125	0.125
Fe(2)	16 <i>d</i>	0.5	0.5	0.5
Yb(1)	16 <i>d</i>	0.5	0.5	0.5
Yb(2)	16 <i>c</i>	0.0	0.0	0.0
S	32 <i>e</i>	0.253	0.253	0.253

 TABLE IV
 INTERATOMIC DISTANCES (Å)

Fe(1)–S	2.326
Fe(2)–S	2.675
Yb(1)–S	2.675
Yb(2)–S	2.740
Fe(1)–Fe(1)	2.707
Fe(1)–Fe(2)	2.344
Fe(1)–Yb(2)	2.344
Fe(2)–Fe(2)	2.707
Yb(2)–Fe(2)	2.707
Yb(2)–Yb(2)	3.828
S–S	2.643

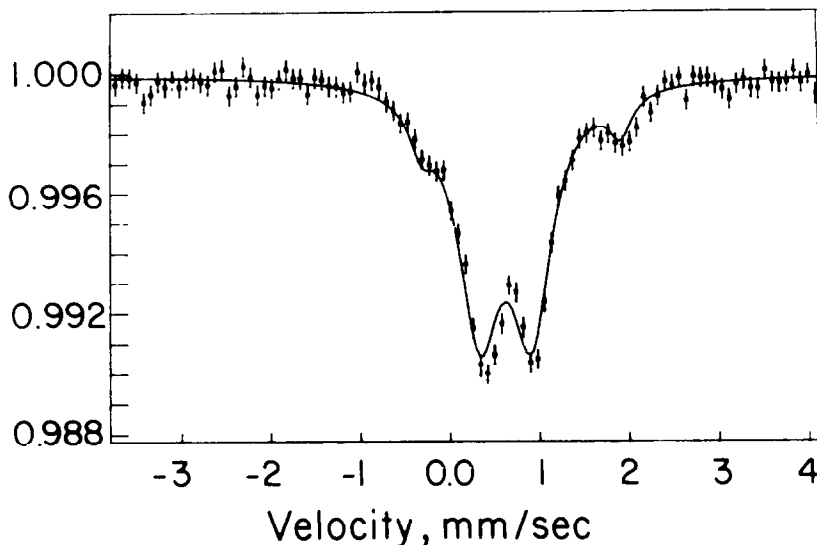


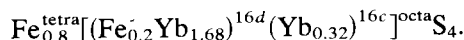
FIG. 1. Mössbauer spectra of FeYb_2S_4 (special spinel) showing good fit between the experimental data (dots) and the least-squares computer calculations (smooth curve).

8.14 emu/mole, and experimental results observed elsewhere are 8.6 (4) and 10.3 (5) emu/mole. Our value is consistent with the chemical analysis and shows nearly pure additive behavior. If one takes into account the highest possible expected C_M value for Fe^{2+} on adding the orbital to the spin contribution one arrives at 8.91 emu/mole, and thus our average result of 8.7 emu/mole clearly indicates that *some* orbital contribution cannot be ruled out. The high value (5) observed in the literature might be due to some ferromagnetic impurity. Since no magnetic ordering was observed at 4.2°K the Mössbauer experiment was carried out at room temperature only.

Conclusions

On the basis of chemical analysis and X-ray and magnetization data, it was shown that our powdered FeYb_2S_4 is stoichiometric and cubic with $a_0 = 10.828 \text{ \AA}$, in agreement with former data: 10.82 \AA (1, 5), 10.838 \AA (6, 7). From the appearance of two quadrupole doublets in weight ratio of octahedral:tetrahedral occupancy of 0.19 ± 0.03

substantiated by X-ray intensity fits, it was shown that both the iron and ytterbium ions each occupy two sites and the compound should be formulated:



As has been shown (2) this is an interesting spinel structure: whereas in the rock salt structure all octahedral sites (16d, 16c) are occupied, in the normal spinel only half of them are occupied (16d only) but here 84% of this site is occupied by ytterbium and another 10% by iron. These iron atoms eject 16% of ytterbium atoms from their normal 16d site into the normally unoccupied 16c site. The bulk of iron atoms stay in their tetrahedral 8a site (cf. Table II, 3 and 5, showing the preference of iron to the 16d rather than the 16c site).

Species	Fe	Yb, Fe	Yb
Site	8a	16d	16c
<i>n</i> -Spinel	1	2, —	—
Special spinel	0.8	1.68, 0.2	0.32

Our factor of occupancy of the tetrahedral site is 0.8, in perfect agreement with 0.76

observed by Tomas *et al.* (2). This might point to a family of spinels which are stabilized when a certain amount, ca. 20%, of the divalent ion moves into the normal octahedral site simultaneously with the ejection of the trivalent ion from this site into the normally unoccupied octahedral site. It is probable that lattice energy considerations based on both charge and ionic radii play an important role in the metal occupancy in such systems.

Acknowledgment

We are grateful to Professor J. Flahaut, Paris, for suggesting the topic and for his continual interest and advice.

References

1. E. RIEDEL, R. KARL, AND R. RACKWITZ, *Mater. Res. Bull.* **12**, 599 (1977).
2. A. TOMAS AND M. GUITTARD, *Mater. Res. Bull.* **12**, 1043 (1977).
3. M. PATRIE AND R. M. CHEVALIER, *C. R. Acad. Sci., Paris* **263**, 1061 (1966).
4. S. KAINUMA, *J. Phys. Soc. Japan* **30**, 1205 (1971).
5. L. SUCHOW AND A. A. ANDO, *J. Solid State Chem.* **2**, 156 (1970).
6. M. PATRIE, J. FLAHAUT, AND L. DOMANGE, *C. R. Acad. Sci., Paris* **257**, 2585 (1964).
7. M. GUITTARD, C. SOULEAU, AND H. FARSAM, *ibid.*, **259**, 2847 (1964).