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MÖSSBAUER EFFECT STUDY OF NATURAL EGYPTIAN CHALCOPYRITE

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Résumé. — Des échantillons de chalcopryrite naturel de la région Umm Somuki du Désert Egyptien de l'Est ont été étudiés en utilisant l'effet Mössbauer (ME) et la diffraction de rayons X, pour identifier les phases différentes et les changements de phase des minéraux et pour étudier les propriétés physiques de ces minéraux. Le spectre Mössbauer (ME) a montré l'existence de phases α , β et γ de chalcopryrite en plus de la pyrite. Les paramètres Mössbauer ont indiqué que le Fer dans le chalcopryrite était sous forme trivalente et soumis à une liaison de covalence. Les phases α et β ont été trouvées sous forme magnétique tandis que la phase γ est paramagnétique. La température de transformation et la production de chaque phase ont été identifiées.

Abstract. — Natural chalcopryrite samples from Umm Samuki region in Eastern Egyptian Desert were studied using Mössbauer Effect (ME) and X-ray diffraction in order to identify the different phases and phase changes occurring in the ore and to investigate the physical properties of the mineral. The ME spectra showed the existence of α , β and γ phases of chalcopryrite in addition to pyrite. The ME parameters indicated that the iron in chalcopryrite was in the trivalent state and bonded covalently. The α , β -phases were found to be in a magnetic state, while the γ phase was paramagnetic. The transformation temperature and the product of each phase was identified.

1. Introduction. — The previous ME studies on natural and synthetic samples of chalcopryrite (CuFeS_2) did not give complete interpretation for the experimental results. Aramu *et al.* [1] obtained a doublet at both room and liquid nitrogen temperatures. From the values of isomer shift they suggested that chalcopryrite has the resonance structure.

For a natural chalcopryrite Raj *et al.* [2] obtained a magnetic hyperfine pattern with $H = 325$ kOe and with temperature independent quadrupole splitting which led then to assure that chalcopryrite is a covalent compound in which the iron atom is in the trivalent state. They also showed that the sample was decomposed before 300°C . Herrenberg [3] obtained a spectrum of two extra central peaks beside the six lines pattern characteristic of the magnetic phase. She did not give any interpretation about this doublet. Piekoszecosh *et al.* [4] studied a natural sample of chalcopryrite and showed that chalcopryrite is decomposed at 600 K . Greenwood *et al.* [5] and Frank [6] studied samples which showed magnetic patterns at both room and liquid nitrogen temperatures. So it was decided in the present work to carry out a complete study using X-ray diffraction and ME spectroscopy in order to identify the different phases and iron forms present in the Egyptian chalcopryrite ore, and to study the thermal decomposition and products of each phase. The

second aim is to interpret the previous results in the literature according to these different phase.

2. Experimental procedure. — Natural chalcopryrite samples were collected from Umm samuki region in the Eastern Egyptian Desert. The ME absorber, were prepared from these natural samples to give a thickness of ~ 20 mg iron/cm². The ME spectra were measured by a spectrometer of the constant acceleration type which was coupled to 512 multichannel analyser. The source was 10 mC Co^{57} in Cr matrix.

3. Results and discussion. — The ME spectra of one sample consists of a magnetic hyperfine pattern at both room and liquid nitrogen temperatures as shown in figure 1. The X-ray diffraction studies of

FIG. 1. — Mössbauer spectra of chalcopryrite (sample 1) (a) at room temperature, (b) at liquid nitrogen temperature.

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this sample showed the presence of α - and β -phases of chalcopryrite in addition to sphalerite (β -ZnS), sellite (MgF_2) and some non-iron silicate compounds. The shape of the Mössbauer — line cannot permit the separation of the two phases of chalcopryrite, i. e. the ME parameters are nearly the same.

The spectra of another sample from the same locality showed a central doublet at both room and liquid nitrogen temperatures beside the magnetic pattern which was obtained for the first sample. The broadening of the absorption peaks of the central doublet together with the asymmetry of the intensity of its lines indicate the superposition of more than one hyperfine pattern in this region. This was confirmed by the X-ray diffraction results of this sample which showed the presence of α , β , and γ -phases of chalcopryrite as well as pyrite (FeS_2) beside the non-iron compounds. These results means that the α and β -phases of chalcopryrite are in magnetic states at room temperature while the γ -phase and pyrite are in the paramagnetic state till liquid nitrogen temperature. These results indicate also that Egyptian chalcopryrite ore contains all the phases at which chalcopryrite can exist together with some pyrite. The formation of the three phases in the ore can throw some light on the geochemical conditions under which the Egyptian chalcopryrite ore was formed. Chalcopryrite should have been formed under high temperature and on cooling separation of phases may occur under favourable conditions [7].

According to Pauling and Brockway [8] the iron atom in chalcopryrite (CuFeS_2) is coordinated by tetrahedron of sulphur atoms with interatomic distances $\text{Fe-S} = 2.20 \text{ \AA}$. It is known [8-10] also

that chalcopryrite can exist in three phases : α - CuFeS_2 which is tetragonal with $a = 5.25$, $c = 10.32 \text{ \AA}$, β - CuFeS_2 which is cubic with $a = 10.60 \text{ \AA}$ and γ - CuFeS_2 which is tetragonal with $a = 10.58$, $c = 5.37 \text{ \AA}$. Magnetically α - is antiferromagnetic and β - is ferromagnetic, but no informations were given about the magnetic properties of the γ -phase. Combining the results of the present measurements with these informations, one can interpret the discrepancies in the previous results [1-6]. The zeeman pattern obtained by Raj *et al.*, Pickoszecoch *et al.*, Greenwood *et al.* and Frank was due to either α -, or β -chalcopryrite. The values of the ME parameters obtained in the present work (Table I) for these two phases are nearly in agreement with those obtained by Frank [6]. The quadrupole splitting which has a value of 0.08 mm/s at both room and liquid nitrogen temperatures is independent on temperature. This independency suggests that iron in chalcopryrite is in the trivalent state in high symmetry site. The observed value of the internal magnetic field (360 kOe) is less than those of ionic Fe^{+3} compounds ($\sim 500 \text{ kOe}$) but it is comparable with the value obtained [11] for KFeS_2 where Fe atom is in the trivalent state and bonded covalently. This is in agreement with the conclusion by Raj *et al.* [2] for the iron atom in chalcopryrite. How ever varied results [9, 12] have been obtained in attempts to determine the valency states of copper and iron in chalcopryrite. Neutron diffraction experiments [9] indicate that copper and iron are in mono and trivalent states respectively. Measurements of X-ray absorption edges [12] suggest that copper is present in two valence states, so that resonance between $\text{Cu}^+\text{Fe}^{+3}$ and $\text{Cu}^{+2}\text{Fe}^{+2}$ may be

TABLE I

Mössbauer parameters for Chalcopryrite

	Sample	Temperatures	<i>I. S.</i> mm/s	<i>Q. S.</i> mm/s	<i>H</i> kOe	Γ mm/s	Reference
(1)	α , B- CuFeS_2	R. T.	0.40 ± 0.08	0.08 ± 0.04	360 ± 5	0.56 ± 0.08	Present work
	—	L. N.	0.40 ± 0.08	0.08 ± 0.04	370 ± 5	0.64 ± 0.08	— —
(2)	α , B- CuFeS_2	R. T.	0.36 ± 0.08	0.08 ± 0.04	357 ± 5	0.72 ± 0.08	Present work
	γ - CuFeS_2		0.12 ± 0.04	0.40 ± 0.08	zero	0.48 ± 0.08	
	FeS_2		0.40 ± 0.04	0.64 ± 0.04	zero	0.48 ± 0.04	
(2)	α , B- CuFeS_2	L. N.	0.36 ± 0.08	$\text{zero} \pm 0.08$	366 ± 5	0.80 ± 0.08	— —
	γ - CuFeS_2		0.16 ± 0.04	0.48 ± 0.08	zero	0.56 ± 0.08	
	FeS_2		0.44 ± 0.04	0.56 ± 0.04	zero	0.56 ± 0.04	
	Chalcopryrite	R. T.	0.55 ± 0.03	0.60 ± 0.03	zero		1
	—	L. N.	0.87 ± 0.03	0.40 ± 0.03	zero		1
	Chalcopryrite	R. T.	0.26 ± 0.02	0.05 ± 0.02	325 ± 10		2
	—	R. T.	0.49	—	356		5
	—	L. N.	0.63	—	368		5
	—	R. T.	0.26 ± 0.02	$\text{zero} \pm 0.01$	352 ± 3	0.32	6
	—	L. N.	0.28 ± 0.02	$\text{zero} \pm 0.02$	370 ± 5	0.34	6

I. S. is relative to Fe metal.

presumed. Whereas earlier workers using cryoscopic and electrolytic method, designated that both metals are divalent.

The disagreement in the values of the ME parameters in some previous results with ours may be due to the non-purity of the mineral in their samples since chalcopryrite is often intergrown with other copper and iron sulphides [13]. On the other hand the doublet obtained by Aramu *et al.* [1] and that obtained by Herzenberg [3] beside the magnetic pattern may be due to the γ -phase of chalcopryrite.

The spectrum due to γ -CuFeS₂ alone in our sample could be separated by measuring a sample of natural Egyptian pyrite from the same locality. Applying the peeling off method [14] and assuming equal line widths for pyrite and γ -chalcopryrite the parameters of both pyrite and γ -CuFeS₂ was determined (Table I). The ME parameters obtained for γ -chalcopryrite are $I. S. = 0.12$ mm/s and $Q. S. = 0.40$ mm/s. These values are not in agreement with those obtained by Aramu *et al.* [1]. On the other hand it is clear (Table I) that the values obtained by Aramu *et al.* are in agreement with those characteristic for pyrite. So their sample could have been pyrite. The low value of $I. S.$ obtained in this work indicates also that γ -CuFeS₂ is a covalent compound.

The sample which contains the three phases of chalcopryrite and pyrite was subjected to the thermal decomposition process. Different specimens were heated in steps of 50 °C up to 600 °C during two hours, and then annealed to the room temperature slowly. The ME spectra for some of the measured samples are shown in figure 2. It was found from the measured spectra that all components are nearly constant up to 250 °C. This means that this temperature is not sufficient to cause any chemical or phase transformations. At 300 °C a new magnetic hyperfine pattern started to appear with a decrease in the intensity of the α and β -phases. The values of the ME parameters of the new magnetic pattern ($H = 510 \pm 5$ kOe, $Q. S. = 0.32 \pm 0.08$ mm/s and $I. S. = 0.44 \pm 0.08$ mm/s) are characteristic of the iron oxide α -Fe₂O₃. So it can be suggested that at 300 °C the α , and β -phases of chalcopryrite starts to decompose to α -Fe₂O₃. At 450 °C the component due to pyrite disappeared with corresponding increase in the intensity of the next magnetic pattern, due to α -Fe₂O₃. To confirms that pyrite was decomposed to α -Fe₂O₃ at 450, the ME spectrum of a pure natural pyrite sample was measured after heating the sample to 450 °C and the same magnetic pattern was obtained. The ME spectrum of the same sample at liquid nitrogen temperature showed change in the sign of the quadrupole splitting due to Morin transition [15]. This insure that the magnetic pattern which was

FIG. 2. — Mössbauer spectra of chalcopryrite (sample 2) at different temperatures (a) at liquid nitrogen temperature, (b) at room temperature, (c) at 300 °C, (d) at 450 °C and (e) 550 °C

obtained during the decomposition of pyrite and chalcopryrite is due to the formation of α -Fe₂O₃. At 550 °C the γ -phase of chalcopryrite decomposed also to α -Fe₂O₃.

4. Conclusion. — From the above results it can be concluded that Egyptian chalcopryrite ore contains the different phases α , β , and γ -CuFeS₂, pyrite, sphalerite and sellite. The existence of these compounds can give an idea about the geochemical conditions under which chalcopryrite was formed.

The iron in chalcopryrite is in the trivalent state and is bonded covalently.

The α -phase is antiferromagnetic, the β -phase is ferromagnetic and the γ -phase is paramagnetic till liquid nitrogen temperature.

The α and β -phases of chalcopryrite decompose to α -Fe₂O₃ in the range between 300 °C to 400 °C, the γ -phase decomposes to α -Fe₂O₃ between 500 and 550 °C and pyrite decomposes to α -Fe₂O₃ at about 450 °C.

The obtained results of the different phases of chalcopryrite can remove the ambiguity in the previous results.

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