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ORIGIN OF THE ASYMMETRIES IN THE QUADRUPOLE SPLIT MÖSSBAUER SPECTRA OF $FeCO_3$ /SIDERITE/

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ABSTRACT

Mössbauer measurements on polycrystalline $FeCO_3$ /siderite/ often reveal asymmetric quadrupole doublets differing even in the sign of the asymmetry. Possible reasons for this phenomenon are discussed and it is concluded that oxidization plays an important role in these anomalies. Relaxation effects can not be observed at room temperature. The magnitude of the Goldanskii-Karyagin effect in siderite is estimated.

KIVONAT

Polikristályos $FeCO_3$-on (szideriten) végzett Mössbauer-mérések olyan kvadrupól-dubletteket mutatnak, amelyek gyakran az aszimmetriának még az előjelében is különböznek. Megvizsgáljuk e jelenség lehetséges okait, és arra a következtetésre jutunk, hogy az oxidáció jelentős szerepet játszik ezekben az anomáliákban. Relaxációs effektusokat szobahőmérsékleten nem lehet megfigyelni. Megbecsüljük a Goldanszkij-Karjagin effektus nagyságát szideritben.

РЕЗЮМЕ

В мессбауэровских спектрах поликристаллического $FeCO_3$ (сидерит) часто появляются асимметрические квадрупольные дублеты с различным знаком асиметрии. Обсуждаются возможные причины этого явления и авторы приходят к выводу, что окисление играет большую роль в появлении аномалий. При комнатной температуре релаксационные явления не наблюдаются. Оценивается величина эффекта Гольданского-Карягина для сидерита.

INTRODUCTION

In recent years, much interest has been paid to the Mössbauer spectra of $FeCO_3$ the mineral form of which is siderite. The interest is explained partly by the fact that several authors have observed different asymmetries in the quadrupole doublet of polycrystalline samples at about room temperature [1 - 5]. The asymmetries have been explained variously as due to relaxation of the atomic spins [5], to the Goldanskii-Karyagin effect /GKE/ [1 - 4], or to a preferred orientation of the microcrystals [3, 4].

It is thought, however, that some of these explanations have failed to take into account other asymmetry-causing effects. The aim of this paper is to discuss different possible origins of the asymmetry and to give an estimate of the value of the GKE in $FeCO_3$.

EXPERIMENTAL

The measurements were carried out on several constant-acceleration spectrometers coupled 512- and 1024-channel analysers. ^{57}Co sources diffused into Cr and Pd were used.

In the first measurement runs [3] natural samples of different origins were investigated to determine the effect of the presumably different impurities. As we could not find any significant difference between the spectra of

different samples, we continued our measurements only on samples of Dobsina. Since it was concluded from our first measurements that most of the asymmetry was caused by a preferred orientation of the microcrystals, special care was taken in the preparation of the samples. In order to avoid preferred orientations, samples were mixed with carbon powder, MgO or Mg-glass and in some cases suspended in silicone vacuum grease or paraffin. In every case the siderite powder was ground in an agate mortar. The samples were handled so that they were not subjected to shocks, press or vibrations that might produce microcrystalline orientation. Samples of different particle sizes were also investigated.

The spectra were analysed by a least squares fitting program [6]. Where there was a high negative asymmetry a Fourier analysis [7] was also performed.

Some typical spectra showing quite different asymmetries are presented in Figs. 1, 2 and 3. The results of the measurements are listed in Table 1.

The most important features of the spectra can be summarized as follows:

1./ A high negative asymmetry appeares only if the σ -line is broadened.

2./ A sample with its plane perpendicular to the gamma-beam generally yields about 5-10 % higher asymmetry than the same sample at 45°. A rotation in the plane of the sample does not result in any change.

3./ The asymmetry generally decreases with the time. /See Fig.4./

4./ The initial asymmetry is mostly positive.

5./ The resonance lines are rather narrow /about

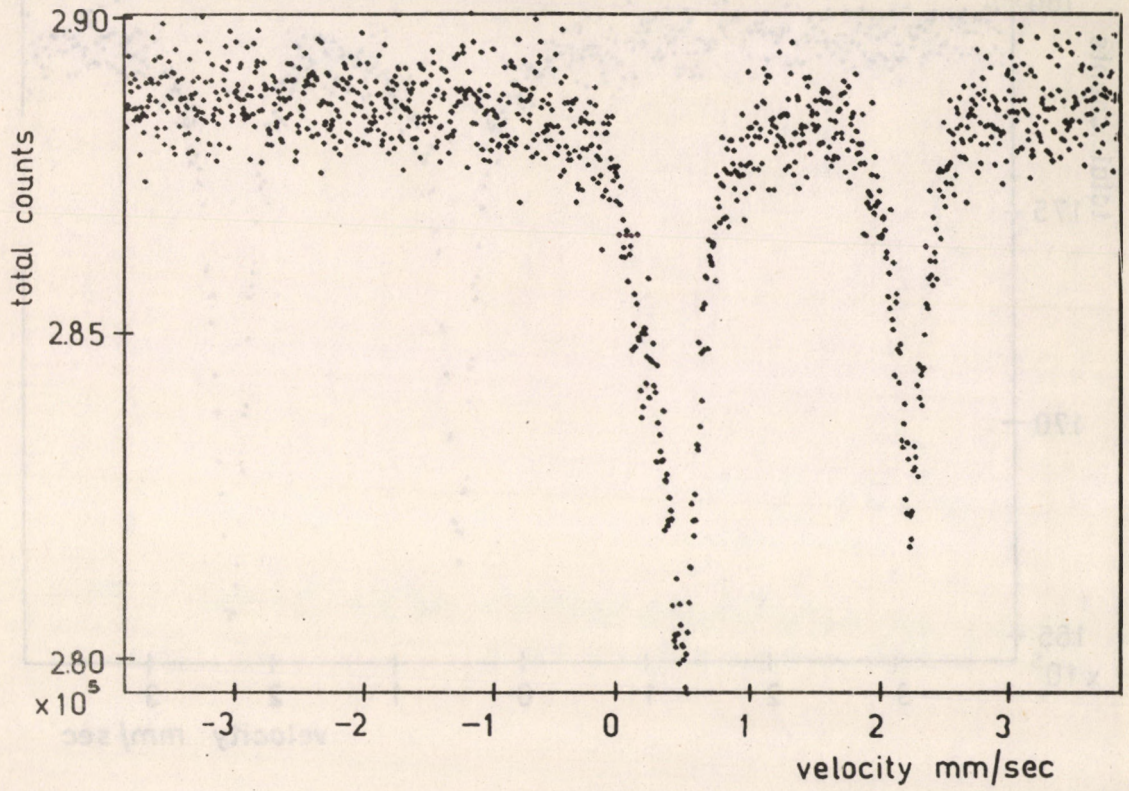
2.90
2.85
2.80
total counts
x 10^5
-3
-2
-1
0
1
2
3
velocity mm/sec

Fig. 1.

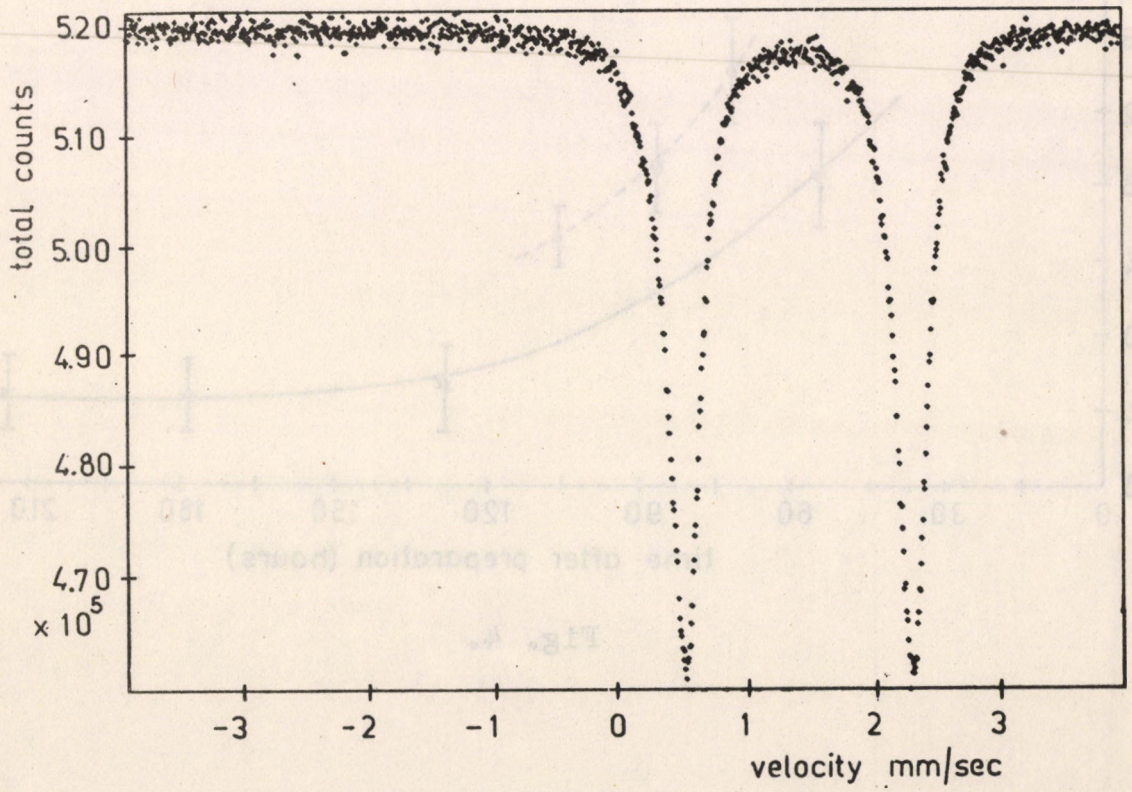
5.20
5.10
5.00
4.90
4.80
4.70
total counts
x 10^5
-3
-2
-1
0
1
2
3
velocity mm/sec

Fig. 2.

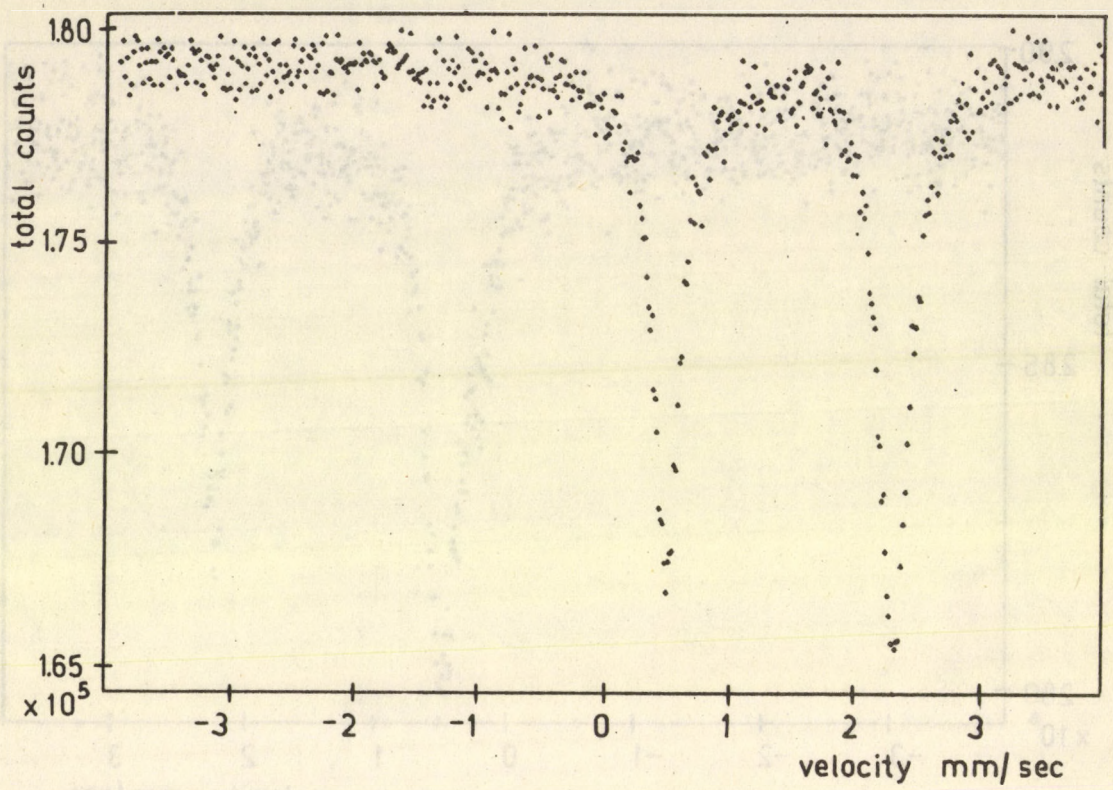
1.80
1.75
1.70
1.65
x 10^5
total counts
-3
-2
-1
0
1
2
3
velocity mm/sec

Fig. 3.

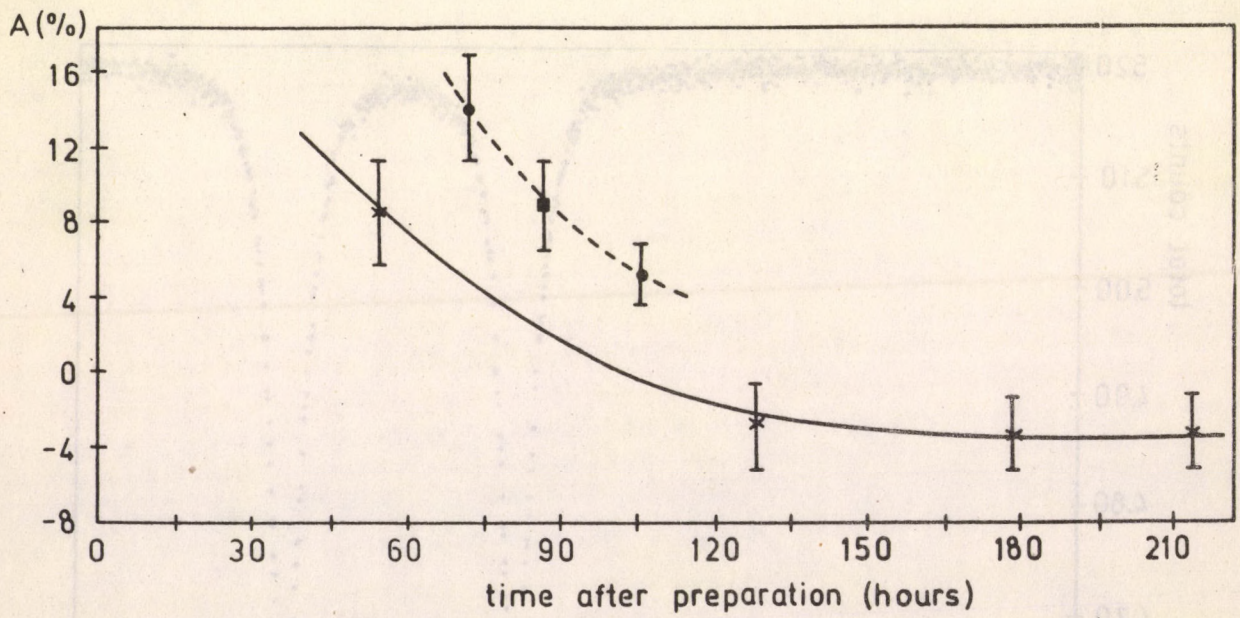
A (%)
16
12
8
4
0
-4
-8
0
30
60
90
120
150
180
210
time after preparation (hours)

Fig. 4.

Table 1.

Asymmetries and linewidths measured on several siderite samples at room temperature

preparation		thickness ($mgFe/cm^2$)	Θ	A (%)	Γ_π (mm/sec)	Γ_σ (mm/sec)	
mixed with carbon powder (R)	1	1.2	90°	−41.6±2.1	.412±.015	.518±.015	I
	2	1.2	30°	−47.6±1.4	.431±.011	.529±.011	
mixed with carbon powder (D)	1	1.2	90°	-17.5±2.4	.434±.015	.460±.011	II
	2	1.2	45°	-17.4±2.0	.438±.011	.464±.011	
mixed with carbon powder (R)	1	1.2	90°	- 0.2±3.0	.307±.008	.351±.010	III
	2	1.2	45°	- 7.8±1.2	.309±.003	.329±.003	
mixed with MgO and suspended in paraffin (D)	1	1.7	90°	−49.4±2.1	.266±.007	.386±.006	IV
	2	1.7	45°	-56.5±1.0	.201±.005	.333±.005	
mixed with MgO 2 years before preparation of the sample (D)	1	1.7	45°a	- 1.6±1.4	.279±.002	.274±.002	V
	2	1.7	45°b	+ 0.8±0.9	.291±.001	.288±.001	
	3	1.7	90°	+ 6.7±0.5	.285±.001	.286±.001	
mixed with Mg-glass powder (D)	1	3.0	90°	+ 8.4±1.1	.287±.003	.288±.003	VI
	2	3.0	45°a	+ 5.9±0.7	.293±.002	.291±.002	
	3	3.0	45°b	+ 3.4±0.7	.295±.002	.295±.002	
mixed with Mg-glass and suspended in silicone grease (D)	1	3.0	90°	+21.3±1.8	.279±.003	.274±.005	VII
	2	3.0	45°a	+ 9.6±1.4	.302±.003	.287±.003	
	3	3.0	45°b	+ 7.9±2.3	.282±.005	.276±.006	
	4	3.0	90°	+14.7±1.2	.279±.003	.279±.003	
mixed with Mg-glass powder (D)	1	1.3	90°	- 2.9±2.2	.290±.006	.304±.006	VIII
	2	1.3	45°	- 3.1±2.4	.339±.008	.339±.008	
	3	1.3	90°	+ 2.7±2.6	.332±008	.364±.009	

preparation		thickness (mgFe/cm²)	Θ	A (%)	Γ_π (mm/sec)	Γ_σ (mm/sec)	
mixed with Mg-glass powder, particle size ∿ 10μm (D)	1	2.0	45°/a	+ 8.4±3.0	.303±.007	.277±.007	IX
	2	2.0	90°	+14.1±3.2	.314±.008	.290±.008	
	3*	2.0	90°	+ 8.5±2.8	.321±.007	.319±.008	
	4	2.0	90°	+ 5.6±1.6	.288±.004	.288±.004	
	5	2.0	45°/a	- 2.6±2.6	.285±.007	.302±.007	
	6	2.0	45°/a	- 2.9±1.9	.288±.006	.298±.006	
	7	2.0	45°/b	- 3.2±1.9	.283±.006	.294±.006	
mixed with Mg-glass powder, particle size∿1μm (D)	1	2.0	90°	+ 2.9±1.2	.293±.003	.291±.003	X
	2	2.0	45°/a	- 0.5±1.5	.291±.004	.296±.004	
	3	2.0	45°/b	+ 1.7±1.4	.291±.004	.305±.004	
	4	2.0	90°	+ 4.1±2.4	.293±.006	.290±.006	

R=Rozsnyó, D=Dobsina. a and b refer to 2 perpendicular positions in the plane of the sample. Θ is the angle between the direction of the gamma-beam and the plane of the sample.

*T = 100 K

the best linewidths measured with the corresponding sources/.

6./ The average value of the asymmetry A = I /I -1 at the sample with the least angular dependence is A = = (1.9±0.5)%

DISCUSSION

Up till now, the asymmetries observed on the quadrupole doublet of siderite at room temperature have been explained by relaxation effects, GKE, or a preferred orientation of the microcrystals. Oxidization of the sample, however, also results in an asymmetry, since a ferric impurity

may contribute to the σ-line /v = 0.30 mm/sec/, giving a negative asymmetry. The presence of a ferric impurity is supported by statements 1./, 3./ and 4./ of the above list of experimental results. The fact of oxidization might seem rather surprising in the case of mineral samples, but the light brownish colour of the crystallites in some cases indicated the presence of Fe^{3+} ions.

The low value of the linewidth can be understood if it is supposed that

a./ the lines of some oxides /occuring presumably in the form of thin surface layers/ practically coincide with the σ-line and/or

b./ the surface Fe^{2+} ions show a surface GKE and they in the course of oxidization /or some other chemical surface process/ are inactived from the point of view of the surface GKE.

Another fact revealed by the narrow linewidth is that the environment of the Fe atoms is rather homogenous, a rare occurrence in mineral samples.

The finding that the initial asymmetry is generally positive shows that no relaxation effects can be observed at room temperature. This conclusion is in contradiction with the results of Walker et al. [5] and suggests that their sample probably contained some ferric impurities.

The unusually high angular dependence of the asymmetry is hardly explicable purely on the basis of a preferred orientation of the microcrystals, though we can not propose any other explanation. However, from our data it is obvious that the angular dependence is connected in some way with the preparation of the sample.

Finally, it seems possible to estimate the GKE of

the bulk material. As the asymmetry of least angular dependence was A = (1.9±0.5)% for a 2 mg Fe/cm^2 thick sample we may consider this value as the asymmetry belonging to the thickness 2 mg Fe/cm^2 at room temperature in $FeCO_3$. This value is in fair agreement with the value A = 3.2% which is expected from the single cristal data of Goldanskii et al. [2] but does not agree well with the later single crystal data of Vinogradov et al. [4], who themselves found the same divergence. /From their single crystal data a small negative asymmetry can be expected for the polycrystalline measurements, yet they obtained a small positive asymmetry, in correspondence with our present results./

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61.922

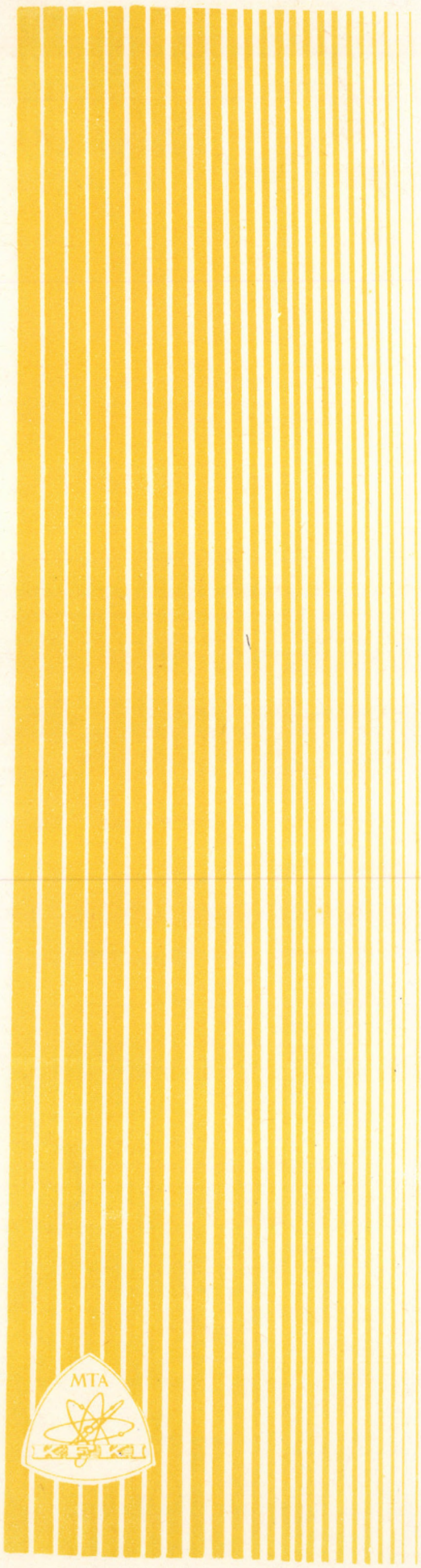
FIGURE CAPTIONS

Fig.1 The spectrum belonging to Measurement IV/1 of Table 1. $A = (-49.4 \pm 2.1)\%$. A small peak on the negative side of the σ -line was found by both the Fourier and the least squares analysis. The source was ^{57}Co in Cr.

Fig.2 The spectrum belonging to Measurement V/2 of Table 1. $A = (+0.8 \pm 0.9)\%$. The source was ^{57}Co in Cr.

Fig.3 The spectrum belonging to Measurement VII/1 of Table 1. $A = (+21.3 \pm 1.8)\%$. The source was ^{57}Co in Cr.

Fig.4 Time dependence of the asymmetry as a consequence of the gradual oxidization observed in Sample IX. of Table 1. ⊗ and the dashed line: $\theta = 90^{\circ}$, $T = 300$ K, ⊠ : $\theta = 90^{\circ}$, $T = 100$ K, x and the full line: $\theta = 45^{\circ}$, $T = 300$ K.



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