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PHASE TRANSFORMATION AND SLOW RELAXATION IN FLUOSILICATES : MÖSSBAUER STUDY

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Résumé. — La transformation de phase $P\bar{3}m1 \rightarrow P2_1/C$ se manifeste dans les fluosilicates de Fe, Mg, Mn par les phénomènes suivants : (a) Apparition d'une asymétrie du gradient de champ électrique, que l'on a mesurée dans le fluosilicate de magnésium, monocristallin, en présence d'un champ magnétique de 120 kOe. (b) Variation brutale de la dissymétrie des spectres quadripolaires de poudres. (c) Absence de singularité pour l'écartement du doublet quadripolaire (sauf dans le cas du fluosilicate de manganèse).

La dissymétrie des spectres a permis d'observer les transitions à l'aide de spectres quadripolaires de poudres.

L'application à 40 K d'un champ magnétique à un monocristal de fluosilicate ferreux met en évidence un effet de relaxation électronique responsable de la dissymétrie des spectres de poudres.

Abstract. — The phase transformation $P\bar{3}m1 \rightarrow P2_1/C$ occurring in Fe, Mg, Mn fluosilicates has been characterized by the following observations : (i) removal of the axial symmetry of the electric field gradient, (ii) sharp variation of the asymmetrical shape of the quadrupole spectra of powdered samples, (iii) no noticeable variation of the quadrupole splitting (Mn-Fls excepted).

The asymmetry parameter of the gradient has been measured with a Mg-fluosilicate single crystal in a 120 kOe magnetic field. The asymmetry of the quadrupole spectra has been used to determine the transition temperatures.

By applying a magnetic field to a Fe-fluosilicate single crystal held at 40 K, we obtained experimental evidence for the presence of slow electronic relaxation which is responsible for the asymmetrical shape of the quadrupole spectra.

1. Introduction. — Much work concerning fluosilicates $MSiF_6 \cdot 6H_2O$ (« M-Fls ») has already been done (see references of [1, 2]). Optical and crystallographic studies ([3, 4]) showed the occurrence of the phase transformation $P\bar{3}m1 \rightarrow P2_1/C$ in Fe, Mn, Mg-Fls at 230 K, 230 K, 300 K respectively.

Using the Mössbauer effect, we previously observed the non axial character of the electric field gradient in the low temperature phase and measured $\eta \sim 0.3$ in these three fluosilicates [5, 6]. Applying a 120 kOe field to a Fe-Fls single crystal at room temperature, we were able to conclude that the gradient in the high temperature phase has axial symmetry [7]; it should be noted that this axial character is not required by the space group $P\bar{3}m1$ which allows a statistical disorder [4]. Therefore it remained to be shown that

the departure from axial symmetry occurs simultaneously with the phase transformation. This is done here.

Another problem was left unsolved, namely the asymmetrical shape of the quadrupole spectrum obtained with powdered samples. Here we give an explanation in terms of slow electronic relaxation. This asymmetrical shape proved to be very convenient for accurately observing the phase transformation.

2. Electric field gradient asymmetry measurements. — Mg-Fls was chosen because the transition occurs at room temperature. Small single crystals, 1 % at. ^{57}Fe doped, were grown from water solution. A 0.5 mm thick mosaic was prepared, containing within its plane the C axes of the different crystals. A 120 kOe field was applied along the γ -beam, i.e. perpendicular to the C axes. The spectra recorded at 45 °C (high-temperature phase) and 18 °C (low temperature phase) are shown on figure 1.

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FIG. 1. — Fe-Fls single crystal, submitted to a 120 kOe field applied along the C axis, at 45 °C (a) and 18 °C (b).

The 45 °C spectrum could be fairly well fitted by a theoretical spectrum of axial symmetry (Fig. 1a). The linewidths obtained by fitting four independent lines to the spectrum are given in table I. The reason why some lines are broadened might be either a slight misorientation of the crystals, or electronic relaxation effects already noticeable in the quadrupole spectra (see section 4).

When cooling the sample down to 18 °C (Fig. 1b), significant line broadenings were observed in the low-temperature phase, which may be attributed to the presence of several sites which are non-equivalent in presence of the applied field (these sites have been already observed at low temperature [6]). The measured line broadenings $\Delta G = \Gamma(18\text{ °C}) - \Gamma(45\text{ °C})$ are given in table I.

TABLE I

Measured line widths in the spectra of figure 1
(expressed in mm/s)

Temperatures	Line 1	Line 2	Line 3	Line 4
18 °C	0.458	0.374	0.430	0.368
45 °C	0.388	0.336	0.374	0.306
ΔG	0.07	0.04	0.06	0.06
	± 0.01	± 0.01	± 0.01	± 0.01

To explain these line broadenings ΔG , three mechanisms associated with the crystallographic change may be invoked :

- (i) possible tilt of the OZ axes of the gradient with respect to the c -axis,
- (ii) asymmetry of the gradient characterized by an asymmetry parameter η ,
- (iii) anisotropy of the hyperfine field created by the magnetization of Fe^{2+} .

(We neglect the change in line widths observed in the paramagnetic spectra, in section 4.)

These three factors have been systematically investigated by simulating the corresponding spectra by computer; the following conclusions have been obtained :

α) The tilt effect acts independently of the other two effects : $\Delta G = \Delta G(\text{tilt}) + \Delta G(\eta + \text{anisotropy})$. Consequently only one parameter is involved in the tilt effect, namely the tilt angle $\varepsilon = \widehat{OZ, C}$.

β) The tilt effect significantly broadens only lines 1 and 2; the dependence of ΔG upon ε has been drawn on figure 2.

FIG. 2. — Calculated linewidths from computer simulated spectra, as a function of η : $|H_{ix}| - |H_{iy}| = 0(\dots)$; $+3(---)$; $+6(++)$. The full line is obtained when the tilt effect is included. The shaded area represent the incertitude on ΔG .

γ) The η effect is the most important.

δ) The effects of η and the hyperfine field anisotropy are strongly correlated. Figure 2 shows that the contribution of a given anisotropy of the hyperfine field has the opposite effect on the width of lines 3, 4 and 1, 2.

We obtained good agreement between the experimental and computed ΔG values (Fig. 2) using the following set of values :

$$\eta = 0.21, \quad |H_{ix}| - |H_{iy}| = \Delta H_i = 6 \text{ kOe}, \quad \varepsilon = 2.5^\circ.$$

The value given for the hyperfine field anisotropy, $\Delta H_i = +6$ kOe compares well with the expectation values $+4.4$ kOe and $+3.3$ kOe deduced from the crystal-field data of ref. [1] and [2] respectively. The measured value of the average hyperfine field,

$$(H_{ix} + H_{iy})/2 = H_{\text{exp.}} - H_{\text{app}} + H_{\text{source}} \simeq \\ \simeq 106 - 120 + 4 = -10 \text{ kOe}$$

agrees with the expectation value -9.7 kOe obtained from both crystal-field data.

Another way to interpret the low-temperature phase spectrum was to use the previously described six-site model [6] (including the (ii) and (iii) effects, but neglecting the tilt effect). With this we obtained a rough fit (Fig. 1b) for which the fitted value of η was 0.26 (by neglecting the anisotropy of the hyperfine field, the fit was even poorer, and gave $\eta = 0.27$).

Taking into account the uncertainties concerning both the measured ΔG , and the estimated ΔH and ε values, we finally obtain for the asymmetry parameter

$$\eta = 0.20 \pm 0.03 \text{ (18 } ^\circ\text{C)}$$

to be compared to

$$\eta = 0 \text{ (45 } ^\circ\text{C)}$$

(The former value might be slightly modified if relaxation effects could be included.)

It seems likely that the change in η occurs at the transition temperature of Mg-Fls (26 °C on heating, 23-20 °C on cooling, according to section 4). This result certainly holds for all fluosilicates undergoing to $P\bar{3}m1 \leftrightarrow P2_1/C$ transition.

3. Quadrupole splitting measurements. — We measured the quadrupole splitting (ΔE_Q) from powder spectra in the close vicinity of the transformation temperature. In the case of Mn-Fls a slight change was observed, showing an hysteresis loop and a large temperature range where high and low temperature phases are both present (Fig. 3a). The transition temperatures are :

$$\begin{cases} 230\text{-}240 \text{ K on heating,} \\ 230\text{-}210 \text{ K on cooling.} \end{cases}$$

In the case of Mg-Fls and Fe-Fls no change was observed within the accuracy of ± 0.01 mm/s (Fig. 3b, 3c). This invariability of ΔE_Q has to be discussed.

When the Fe^{2+} ion is involved, a crystallographic transition usually produces a sizeable change in ΔE_Q . The only known exception, to our knowledge, is that of $(\text{CH}_3\text{NH}_3)_2\text{FeCl}_4$ [8]. Since ΔE_Q is given by :

$$\Delta E_Q = (1/2) e^2 q_{zz} Q \sqrt{1 + \eta^2/3},$$

FIG. 3. — Quadrupole splitting as a function of temperature : Mn-Fls (a), Mg-Fls (b), Fe-Fls (c). Full lines have been deduced from results in a larger temperature range.

the invariability of ΔE_Q requires that the changes in η and q_{zz} cancel each other. This cancellation must be expected in the case of a well isolated ground singlet [9].

Since the electronic level scheme of Fe^{2+} is well known [1, 2] we performed crystal-field calculations of ΔE_Q by using a computational method given in ref. [1]. The dropping of the non-axial terms of ref. [1] yielded a calculated decrease in ΔE_Q of 0.006 mm/s (0.003 mm/s by using the non-axial term given in ref. [2]). On the other hand, a change in the axial term would strongly change ΔE_Q . Consequently, the essential feature of the transition is the introduction of non-axial terms in the crystalline potential, while the axial terms remain the same.

We also measured the isomer shift and observed no change within an accuracy of ± 0.005 mm/s.

4. Asymmetry of the powder quadrupole spectra. —

Asymmetrical spectra were obtained above 4.2 K with powdered samples of Fe, Mg, Mn-Fls, and more generally with all fluosilicates belonging to the $P2_1/C$ or $P\bar{3}m1$ space groups. Typical spectra are shown on figure 4. (A weak contribution of Fe^{3+} is generally also observed.)

The spectra were fitted by two lorentzian lines of different widths; the measured intensities of the lines remained almost equal at all temperatures. Typical fitted values are given in table II.

We systematically measured the difference between the widths of the two lines ($\Delta\Gamma$), as a function of temperature. The same behaviour was exhibited by all fluosilicates :

TABLE II

Least-square fit parameters of powder spectra

Matrix	T (K)	$I.S.$ (mm/s)	ΔE_Q (mm/s)	Γ_1 (mm/s)	Γ_2 (mm/s)	$\Delta\Gamma$ (mm/s)	S_1 (%)	S_2 (%)
Fe-Fls	4.2	1.17	3.60	0.288	0.280	0.008	50.2 %	49.8 %
	245	1.09	3.49	0.36	0.31	0.05	53 %	47 %
	Room	1.06	3.41	0.31	0.28	0.03	52 %	48 %
Mg-Fls	4.2	1.19	3.59	0.298	0.294	0.004	49.7 %	50.3 %
	20 °C	1.04	3.31	0.27	0.25	0.02	50.5 %	49.5 %
	29° C	1.04	3.28	0.28	0.25	0.04	50.7 %	49.3 %
Mn-Fls	4.2	1.19	3.61	0.336	0.326	0.010	49 %	51 %
	235	1.09	3.47	0.37	0.29	0.08	50 %	50 %
	Room	1.06	3.34	0.29	0.25	0.04	47.5 %	52.5 %
Co-Fls	4.2	1.18	3.59	0.346	0.342	0.004	50.5 %	49.5 %
	255	1.08	3.41	0.38	0.34	0.04	52 %	48 %

The source was $^{57}\text{Co}/\text{Cu}$; S are relative intensities.

Subscripts 1 and 2 refer to the low and high energy lines respectively.

FIG. 4. — Quadrupole spectra of Fe-Fls (powder) : 4.2 K (a), 245 K (b).

- (i) $\Delta\Gamma$ is negligible at 4.2 K.
- (ii) $\Delta\Gamma$ increases progressively in the range 0-100 K.
- (iii) Above about 100 K, $\Delta\Gamma$ decreases slowly.
- (iv) A jump occurs at the temperature where the transition $\text{P}2_1/\text{C} \rightarrow \text{P}\bar{3}\text{m}1$ has been observed by X-ray measurements.

This behaviour is shown in figure 5 where results are also given for the $\text{Fe}_{0.6}\text{Zn}_{0.4}$ -Fls which undergoes the same transition nearby 270 K.

In addition, the intensity of the low-velocity line was measured as a function of temperature (*scanning* method, using a constant-velocity drive) : a jump was observed at the transition temperature.

From both $\Delta\Gamma$ data and scan measurements, the transition temperature was carefully studied in all three fluosilicates (Fig. 6); a thermal hysteresis was observed, and the following transition temperatures were obtained :

FIG. 5. — $\Delta\Gamma$ as a function of temperature for several fluosilicates.

$$\begin{aligned}
 &\text{Fe-Fls} \left\{ \begin{array}{l} 225 \text{ K on heating } (\pm 1 \text{ K}) \\ 223 \text{ to } 220 \text{ K on cooling } (\pm 1 \text{ K}) , \end{array} \right. \\
 &\text{Mg-Fls} \left\{ \begin{array}{l} 299 \text{ K on heating } (\pm 1 \text{ K}) \\ 296 \text{ to } 293 \text{ K on cooling } (\pm 1 \text{ K}) . \end{array} \right.
 \end{aligned}$$

FIG. 6. — Line intensity of the low energy line (scanning) and $\Delta\Gamma$ measurements in the region of the crystallographic transition.

In the case of Mn-Fls, the $\Delta\Gamma$ data were too scattered to give the transition temperature; the scan (Fig. 6c) was in qualitative agreement with the ΔE_Q data.

In addition, we noticed that the measured $\Delta\Gamma$ might depend on the sample preparation. The results given for Fe-Fls concern a powder obtained by grinding a single crystal; powders prepared directly

gave larger $\Delta\Gamma$ values. It might be possible that the amount of Fe^{3+} has some influence on $\Delta\Gamma$, but we have no experimental evidence for this.

We studied also the special case of Co-Fls which undergoes the crystallographic change $R\bar{3} \rightarrow P2_1/C$ [10] near 270 K. The quadrupole interaction ΔE_Q changes from 2.0 to 3.5 mm/s [11], while the sign of the q_{zz} component remains unchanged [1]. We obtained quadrupole spectra typical of a random orientation (contrary to ref. [11]) since the room temperature spectrum is symmetrical. In the low-temperature phase, we observed an asymmetrical spectrum (Fig. 7) similar to Fe-Fls spectra, in agreement with the similarity of the electronic level scheme.

By thermal scanning of the low-energy line, we observed a very large hysteresis (Fig. 8) and determined the following transition temperatures :

$$\begin{cases} 270\text{-}280 \text{ K on heating} \\ 255\text{-}245 \text{ K on cooling} . \end{cases}$$

FIG. 7. — Quadrupole spectra of Co-Fls (powder) : 300 K (a), 270 K by heating (b), 260 K (c).

FIG. 8. — Thermal scanning of the $R\bar{3} \leftrightarrow P2_1/C$ transition in Co-Fls.

5. Failure of static explanations. — In order to explain an asymmetrical quadrupole doublet the presence of texture, non-equivalent sites, or the Goldanskii-Karyagin effect are usually invoked.

Texture can be ruled out because the 4.2 K spectra are quite symmetrical for all samples.

In the case of Fe-Fls, the sample was obtained by grinding pieces of a large, carefully grown single crystal [12]. The study of single crystals in a magnetic field, at low temperature, showed the presence of two crystallographically equivalent sites in each twin component [6]. The presence of these equivalent sites had also been proved by EPR measurements [13]. Consequently the possibility of having non-equivalent sites seems to be unrealistic.

Nevertheless, let us assume that non-equivalent sites are present. The asymmetrical doublet would then be explained by the spreading out of both the quadrupole interaction and the isomer shift. At 4.2 K the narrowing of the Fe-Fls lines should result from the collapse of both ΔE_Q and I.S. values. Then the behaviour of the isomer shift for non-equivalent sites would be unrealistic : no spreading at 4.2 K, spreading that increases with temperature in the range (0-100 K), and decreases above 100 K.

Finally, the Goldanskii-Karyagin effect is probably small since the fitted areas of the quadrupole lines differ by only a few percent. In any case, it cannot lead to different line-widths.

6. Proton motions. — Proton motions have been observed in NMR studies of fluosilicates [14]. Although changes in the motion frequencies have been observed at temperatures close to the transition temperature in Fe, Mn, Mg-Fls, these motions can by no means explain the observed asymmetrical doublet of the powder spectra, because of the following reasons :

(i) The frequencies deduced from NMR data, in the temperature range 0-300 K, are much too low to influence the Mössbauer lineshape (10^4 - 10^5 Hz compared to the 10^7 for the Mössbauer linewidth).

(ii) These motions occur in all fluosilicates, even in Zn and Ni-Fls for which the quadrupole spectra of powders are symmetrical.

(iii) In addition, if one assumes that the isomer shift does not depend on the proton positions, a symmetrical doublet would result [15].

In any case, these motions do exist and are likely to result in a symmetrical line broadening and in a thermal variation of the crystalline field. This effect should be similar to the conformational excitation mechanism recently described [16]. Such effects have already been reported in the case of fluosilicates [1, 17], but not extensively studied at the present time (absolute measurements of line widths are difficult when cryogenic devices are used).

7. Slow electronic relaxation : single crystal experiment in a magnetic field. — For a long time, the ferrous ion in a non-magnetic matrix was thought to exhibit fast electronic relaxation. However relaxation effects in the presence of applied fields have been recently reported [18, 19].

Therefore we have been led to carefully examine the behaviour of fluosilicates in applied fields : previous measurements had been performed in the temperature range 0-100 K on an Fe-Fls single crystal in a magnetic field [1] : when the applied field was perpendicular to *C*, the effective field was easily measured ; on the contrary, when the applied field was parallel to *C*, unexpected line broadenings were observed above 15-20 K, for which no explanation could be given ; at 4.2 K, for any direction of the applied field, narrow lines were obtained.

Here we present results of new experiments performed on an Fe-Fls single crystal platelet held at 40 K. The magnetic field and the γ -beam were along the *C* axis. Experimental spectra are shown on figure 9.

FIG. 9. — Fe-Fls single crystal at 40 K, submitted to a magnetic field parallel to the *C* axis : 0 kOe (a), 30 kOe (b), 60 kOe (c).

A large broadening of the low-energy line was observed. The spectra have been very well fitted by Lorentzian lines whose parameters are given in table III (thickness effects can be seen from the low-field values).

These experimental spectra are quite different from those expected in the fast-relaxation assumption : by applying a 30 kOe field at 40 K, according to the crystal-field data of ref. [1], a -36 kOe hyperfine field is expected, leading to a -6 kOe effective field. Thus the expected broadening of the low energy line is 0.19 mm/s instead of the measured value,

TABLE III

Least-square fit linewidths of the Fe-FIs single crystal experiment at 40 K (see Fig. 9). Powder data are given for comparison

Applied field kOe	Γ_1 (mm/s)	Γ_2 (mm/s)	$\Delta\Gamma$ (mm/s)	S_1 (%)	S_2 (%)
0 (powder)	0.32	0.31	0.02	—	—
0 crystal	0.46 (*)	0.32	0.14 (*)	69	31
10	0.60 (*)	0.32	0.28 (*)	72.5	27.5
15	0.75	0.33	0.42	74	26
20	0.87	0.33	0.54	75	25
30	1.01	0.34	0.67	76	24
50	1.17	0.34	0.83	75	25
60	1.28	0.35	0.93	75	25

(*) Overestimated because of thickness effect on line 1.

0.65 mm/s. On the contrary, the expected broadening of the high-energy line, 0.031 mm/s is close to the measured value 0.025 mm/s.

Once more, the static explanations have failed :

(i) Any static assumption, at 40 K, would lead to line broadenings proportional to the applied field. This disagrees with the behaviour of the low-energy line width, whose main variation occurs below 30 kOe.

(ii) A misalignment of the crystal, or a texture of the local axes would not broaden the lines : the temperature of 40 K was chosen so that the effective field (hyperfine + applied) was small for any direction of the applied field (according to crystal-field data of ref. [1]).

(iii) In addition, magnetization measurements in pulsed fields [20] as well as EPR measurements on Fe^{2+} [21] showed directly that the D parameter of the spin Hamiltonian has a well-defined value. Consequently a well-defined value of the effective field is expected and broad lines should not be observed.

On the other hand, electronic relaxation effects can account for the observed spectra. The line shape agrees with Blume's theory [22] and therefore suggests a longitudinal character for the relaxation. The asymmetrical doublet in the paramagnetic state also agrees with electronic relaxation effects.

8. Discussion. — In the absence of a magnetic field, the magnetic hyperfine structure cannot be observed if electronic singlets (diamagnetic) are concerned.

This is the case of Fe^{2+} in fluosilicates at 4.2 K, according to the crystal-field determinations [20, 21] summarized on figure 10 : only the ground singlet is populated and no relaxation effects are expected, in agreement with symmetrical quadrupole spectra obtained from powders, and with narrow lines obtained from single crystals in applied fields.

At higher temperature, the thermal population of the $S_z = \pm 1$ and $S_z = \pm 2$ levels occurs. Only

FIG. 10. — Electronic levels scheme (from [1, 2, 20, 21]).

the $S_z = \pm 2$ levels are expected to give rise to a magnetic hyperfine contribution to the spectrum, since the splitting of these levels, 0.1 cm^{-1} , is not really much larger than the hyperfine coupling. If the electronic relaxation between these levels is not fast, the Blume effect can be observed, and the increase in $\Delta\Gamma$ in the temperature range 0-100 K can be attributed to the thermal population of the $S_z = \pm 2$ levels.

Above 100 K, the spin levels are almost equipopulated, and the decrease in $\Delta\Gamma$ indicates the usual increase in the spin-lattice relaxation rates.

The jump in $\Delta\Gamma$ occurring at the transition temperature can be easily explained now : the disappearance of the non-axial terms in the spin Hamiltonian results in the presence of true electronic doublets $S_z = \pm 1$ and ± 2 : the magnetic components of the electronic-nuclear coupled levels are increased (actually saturated), and finally the asymmetry due to the Blume effect is increased.

In our single-crystal experiment, the magnetic field along the C axis mixes the electronic wave functions, within the following two limits :

(i) Zero external field (diamagnetic levels) :

$$\left\{ \begin{array}{l} (|1\rangle \pm |-1\rangle) / \sqrt{2} \\ (|2\rangle \pm |-2\rangle) / \sqrt{2} \end{array} \right.$$

(ii) Large external field (pure Zeeman levels) :

$$\left\{ \begin{array}{l} | +1 \rangle, | -1 \rangle \\ | +2 \rangle, | -2 \rangle \end{array} \right.$$

The observed increase in the width of line 1 (Fig. 9) is due to the increase in the magnetic component of the levels $S_z = \pm 1$ which are thermally populated at 40 K. This agrees with the fact that a large magnetic field was required in contrast with systems previously studied [18, 19], involving the $S_z = \pm 2$ levels, where a small field was used.

In order to illustrate this last effect, we have plotted on figure 11 the calculated $\langle S_z \rangle$ in the various spin levels, as a function of the applied field : the variation of $\Delta\Gamma$ is very similar to that of $\langle S_z \rangle$ in the $|S_z = \pm 1\rangle$ levels.

The reason why no broadened lines are obtained

FIG. 11. — Measured $\Delta\Gamma$ in the single crystal experiment of figure 9 (left hand scale, $\otimes$). Calculated $|\langle S_z \rangle|$ in the various electronic levels (right hand scale).

when the magnetic field is perpendicular to the C axis (at any temperature) is not clearly understood; it probably involves the fact that the perpendicular field disturbs the electronic level scheme in a way different from that of the parallel field.

We attempted to observe a similar effect with a fluosilicate belonging to the $R\bar{3}$ space group (the $R\bar{3}$ fluosilicates exhibit an axial quadrupole interaction of about -2 mm/s). A mosaic was made from a few platelets of $\text{Fe}_{0.3}\text{Zn}_{0.7}\text{-Fls}$ single crystals, held at 30 K and submitted to a 50 kOe applied field parallel to the C axis. Narrow lines were obtained (Fig. 12). The measured effective field, 19 kOe, was in good agreement with the value calculated by the fast relaxation assumption of ref. [1] : 19.4 kOe. (The presence of extra-lines in figure 12 has been explained in ref. [6].)

Therefore the electronic relaxation is fast in the $R\bar{3}$ fluosilicates at this temperature. This agrees with the observation of symmetrical quadrupole spectra obtained with Zn, Ni-Fls (and Co-Fls above 270 K). It is worth noting the essential difference between the $R\bar{3}$ series of fluosilicates and the other series, namely that the trigonal crystalline potential splits the orbital Γ_5 by ~ 200 cm^{-1} in the first series, and by $\sim 1\,500$ cm^{-1} in the second series (a ground state singlet is obtained in all cases). Consequently, the magnitude of the axial crystal field is likely to influence the spin-lattice relaxation.

FIG. 12. — $\text{Fe}_3\text{Zn}_7\text{-Fls}$ mosaic at 30 K, submitted to a magnetic field parallel to the C axis : 0 kOe (a), 50 kOe (b).

At the present time, the influence of the metallic ions on the relaxation rates is not definitively established, since the differences in $\Delta\Gamma$ between different fluosilicates might be attributed to sample preparation.

9. Conclusion. — The transition $P3m1 \leftrightarrow P2_1/C$ occurring in some fluosilicates has been observed by the Mössbauer effect. The relevant parameters are neither the isomer shift, nor the quadrupole splitting, but the asymmetry parameter of the E.F.G. and the asymmetrical line shape of the quadrupole spectra. The reported experiments agree well with the hypothesis of a slow electronic relaxation. A quantitative model of relaxation taking into account the various electronic level schemes has yet to be worked out. On the other hand, experiments with larger magnetic fields are planned.

Another unresolved problem is the influence of proton motions, for which further experimental data are needed.

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