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PARAMAGNETIC RELAXATION PHENOMENA IN ALUMS

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Résumé. — On a étudié l'élargissement par effet de relaxation des raies Mössbauer dans les alums. On a observé des raies de forme lorentzienne dans la plupart des alums ; la relaxation électronique est donc isotropique ; la seule exception est l'alun de Cs.

Abstract. — The relaxation broadening of the Mössbauer lines in alums has been studied. In most alums lines of Lorentzian shape were observed, consequently the electronic relaxation is isotropic. The only exception is the Cs-alum.

Electronic spin relaxation generally results in the Mössbauer spectra having complex shape. When the relaxation time (τ_R) is equal to, or somewhat smaller than the nuclear Larmor period (τ_L) then Mössbauer spectra with broadened lines are found. Relatively extensive theoretical and experimental work has been devoted to this problem [1-10]. Recently Afanasiev and Gorobchenko [11] made a thorough analysis on the fast relaxation case using the method of Gabriel [12] and Schwegler [13]. It was shown that for fast relaxation a comparatively simple description in terms of certain physical parameters could be obtained. Their theoretical calculation has shown that the shape of the absorption lines is very sensitive to the characteristics of the relaxation process, namely whether the relaxation is longitudinal, anisotropic transverse, isotropic transverse, or isotropic. In each case the relative intensity of the $-\frac{1}{2} \rightarrow \frac{1}{2}$, $\frac{1}{2} \rightarrow -\frac{1}{2}$; $-\frac{1}{2} \rightarrow -\frac{1}{2}$, $\frac{1}{2} \rightarrow \frac{1}{2}$; and $-\frac{1}{2} \rightarrow -\frac{3}{2}$, $\frac{1}{2} \rightarrow \frac{3}{2}$ transitions are different.

Isotropic relaxation (if the spin points at any direction with an equal probability) has the simplest effect on the spectra : the line-shape remains Lorentzian though the width may increase considerably. Most alums have cubic structure (Fig. 1) consequently isotropic relaxation probably occurs. For checking this supposition the Mössbauer spectra of some alums were measured and the absorption line-shapes analysed.

Those alums with the following compositions were studied : $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$, $\text{KFe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$, $\text{RbFe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$, $\text{CsFe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$,

The crystals were grown from the aqueous solutions of the components. The Mössbauer absorbers (containing

FIG. 1. — The crystal structure of alums.

BN powder as inert materials) were prepared by grinding single crystals. The samples were immersed in liquid nitrogen after preparation to avoid any loss of the structural water. The last measurement generally being performed at room temperature. A conventional constant acceleration Mössbauer spectrometer with a $^{57}\text{Co}(\text{Cr})$ source was used. The minimum width of the Mössbauer line measured with 2.5 mg Fe/cm^2 in sodiumhexacyanoferrate (II) absorber was 0.32 mm/s . The velocities are given relative to the centroid of a natural metallic iron absorber. The Mössbauer spectra of the alum absorbers were measured at 87 and 300 K.

The spectra consisted of a broadened single line for each alum sample. The measured spectra were fitted by using a program based on a conventional least squares fitting procedure extending it with the resulting formula of the theoretical calculations given in [11]. One spectrum is shown in figure 2 as an illustrative example of the quality of the fit used in the program.

Fig. 2. — The Mössbauer spectrum of $\text{CsFe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ measured at 87 K.

TABLE I

The isomer shift values (δ) of the measured alums. δ values are given relative to metallic iron. The error: ± 0.02 mm/s.

Compound	87 K	220 K	300 K
$\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$	—	—	0.42
$\text{KFe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$	0.45	0.39	0.36
$\text{RbFe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$	0.47	0.43	0.38
$\text{CsFe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$	0.46	0.37	0.35
$\text{TlFe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$	0.47	0.41	—

Table I, summarizes the isomer shift values (δ) of the alums studied. The isomer shifts were adopted as the energy difference between the centroids of the broadened lines and the spectrum of metallic iron. The δ values correspond to the existence of high spin ferric ions in these alums. The δ values differ only slightly in the various alums, consequently the ionic character of the chemical bond of the Fe^{3+} ions is not significantly affected by the monovalent ions.

The line-width values together with the calculated relaxation parameters are summarized in tables II and III. The relaxation parameter (γ) is the phenomenological relaxation constant having the meaning formulated as in [11]. Its values are related to the relaxation time and to the actual process (isotropic, longitudinal, etc.) of the electronic spin relaxation. For isotropic

relaxation the broadening (Δ_b) of the single Lorentzian line is

$$\Delta_b = (\gamma/2) (15 A_e^2 - 10 A_e A_g + 3 A_g^2),$$

where A_e and A_g are the hyperfine coupling constants of the excited and ground state, respectively.

For longitudinal relaxation the absorption line is composed of three Lorentzian lines with the following parameters:

$$\begin{aligned} & \frac{1}{2} \gamma_{zz} (3 A_e - A_g)^2, \\ & \frac{1}{2} \gamma_{zz} (A_e - A_g)^2, \\ & \frac{1}{2} \gamma_{zz} (A_e + A_g)^2. \end{aligned}$$

The relative intensities are $\frac{1}{2}$, $\frac{1}{3}$, $\frac{1}{6}$ respectively. The single non-Lorentzian line is broadened γ_{zz} is the characteristic relaxation parameter proportional to the relaxation time and to $\langle h_z(t)^2 \rangle_{av}$, $h_z(t)$ is the time dependent hyperfine field.

TABLE II

The line-width values (Γ) and the relaxation parameters (γ)

of $\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$, $\text{KFe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$, $\text{RbFe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ and $\text{TlFe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$.

The relaxation parameters (γ) were calculated by supposing isotropic relaxation process. χ^2 values show the quality of the fit.

Temperature K	Γ mm/s	χ^2	$\gamma/3$
$\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$			
300	1.97 ± 0.03	1.02	0.0304 ± 0.0005
$\text{KFe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$			
87	2.42 ± 0.03	1.00	0.0372 ± 0.0005
220	2.02 ± 0.03	1.00	0.0298 ± 0.0005
273	2.13 ± 0.04	1.03	0.0319 ± 0.0007
$\text{RbFe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$			
87	2.14 ± 0.02	1.00	0.0339 ± 0.0004
220	2.12 ± 0.02	1.00	0.0335 ± 0.0004
300	1.95 ± 0.02	1.10	0.0303 ± 0.0004
$\text{TlFe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$			
87	1.80 ± 0.06	1.09	0.026 ± 0.0002
220	1.75 ± 0.06	1.15	0.025 ± 0.0002

It can be seen that all but one of the alums both at liquid nitrogen and room temperature could be fitted by Lorentzian lines corresponding to the fact that isotropic

TABLE III

The line-width (Γ) and the relaxation parameters of $\text{CsFe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$. The results of the computers fit for isotropic and longitudinal relaxation are also summarized

Temp. K	Isotropic relaxation			Longitudinal relaxation		
	Γ mm/s	χ^2	$\gamma/3$	Γ mm/s	χ^2	γ_{zz}
87	2.96 ± 0.06	2.04	0.049	1.88 ± 0.08	1.50	1.68 ± 0.06
300	2.72 ± 0.06	2.02	0.045	1.77 ± 0.08	1.46	1.25 ± 0.06

relaxation of the iron electronic spins occur in these crystals. The line-width values are not strongly temperature dependent. This shows that the spin lattice relaxation is too slow to have any influence on the Mössbauer spectra. The line-width values differ only to a small extent in the different alums as a consequence of the value of the lattice parameters being almost the same. Therefore, the distances between the ferric ions in the lattices are almost the same.

It is surprising that the $\text{CsFe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ spectra cannot be fitted by a Lorentzian line although its structure is cubic, too. The spectra could be fitted rather by a line-shape which can be obtained by supposing longitudinal relaxation. To clear up this discrepancy two facts must be mentioned. The alums,

according the small difference in their structure, can be divided into α , β and γ subgroups [14]; the $\text{CsFe}(\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$ alum belongs to the β -group [15]. A study of the paramagnetic resonance spectrum of β -type alums showed that the splitting of the ^6S state of the ferric ion can be explained in terms of a spin Hamiltonian containing trigonal terms in addition to the cubic term [16]. The splitting parameter of the trigonal term in these cases is much larger than the value of the cubic term. Therefore the crystalline field energy level structure is different to the level structure of α -alums. The trigonal symmetry may involve the longitudinal relaxation process in the Cs alum.

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