ANALYSIS OF ASYMMETRY OF THE MOSSBAUER BANDS OF Fe_xZn_{1-x}(4-AMINO-1,2,4-TRIAZOLE)_3(NO_3)_2 COMPLEXES WITH THE SPIN TRANSITION $^{1}A_1 \neq ^{5}T_2$.

PROOF OF ANISOTROPY OF IRON ATOM VIBRATIONS

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This paper analyzes the nature of asymmetry of quadrupole doublets in the Mössbauer spectra of the high-spin (HS) and low-spin (LS) forms of Fe_xZn_{1-x}(ATr)_3(NO_3)_2 complexes possessing a polynuclear chain structure. It is assumed that the quantization axis z is directed along the polymer chain. The asymmetric character of bands in the spectra is explained by the anisotropy of iron atom vibrations along the z axis or perpendicular to it, i.e., by Goldanskii–Karyagin’s effect. The quadrupole splitting is theoretically analyzed and compared with experiment; the electric field gradient on the iron nuclei is negative for the HS form and positive for the LS form. The standard deviations of iron atoms are $\langle \chi^2 \rangle = 2.78 \times 10^{-18}$ cm$^2$, $\langle \chi^2 \rangle = 0.72 \times 10^{-18}$ cm$^2$ for the HS form and $\langle \chi^2 \rangle = 1.63 \times 10^{-18}$ cm$^2$, $\langle \chi^2 \rangle = 0.72 \times 10^{-18}$ cm$^2$ for the LS form at 295 K; $\langle \chi^2 \rangle = \langle \chi^2 \rangle = 0.26 \times 10^{-18}$ cm$^2$ for the LS form at 78 K.

In our previous works we showed that during partial replacement of iron in Fe(4-aminol,2,4-triazole)_3(NO_3)_2 by zinc, the iron atoms undergo a transition from the LS state at 295 K ($^1A_1$) to the HS state ($^5T_2$) [1, 2]. The electronic structure and symmetry of the local environment of iron atoms remaining in the LS state were found to be affected by zinc atoms.

A remarkable feature of quadrupole doublets of both (HS and LS) forms is their asymmetry. The aim of this work is to investigate the nature of asymmetry. Before discussing our data, we note that asymmetric quadrupole doublets were observed earlier for some Fe(II) complexes possessing spin transitions [3-8]. However, the nature of asymmetry was not considered in these papers. A brief discussion is offered only for [Fe_xZn_{1-x}(2-Pic)_3]:Cl_2:CsH_2OH [3]. Without giving any arguments, the authors of [3] related the asymmetry to the sample texture, disregarding an alternative effect of the anisotropy of iron atom vibrations (Goldanskii–Karyagin’s effect) [9, 10].

As a matter of fact, there are only two explanations for the integral asymmetry of quadrupole doublets with equal band widths — the texture effect and Goldanskii–Karyagin’s effect. In any case, investigation of the nature of asymmetry is important as it gives valuable information about the structure of the compounds.

When analyzing the asymmetry of the bands of Fe_xZn_{1-x}(ATr)_3(NO_3)_2, we employed rather simple techniques. Let us consider the first one. We used it for a single crystal sample for which the intensity ratio of spectral bands depends on the angle $\theta$ between the quantization axis and the gamma-quantum beam according to the formula [9, 10]

$$\frac{I_{\pm 3/2 \pm 0}}{I_{\pm 1/2 \pm 0}} = \frac{1 + \cos^2 \theta}{\sqrt{3} - \cos^2 \theta}.$$  

(1)

The ratio varies from 3:1 for $\theta = 0$ to 3:5 for $\theta = \pi/2$.

As we can see, a change in the orientation of the single crystal relative to the gamma-quantum beam may significantly affect the relative intensity of the quadrupole doublet.

A textured sample has predominant orientations of separate crystallites relative to the gamma-quantum direction. As for the single crystal, one can change the band intensity ratio in the spectrum by turning the sample. By comparing the spectra of the plane-parallel sample (absorber) conventionally oriented with those of the sample turned, e.g., by 45°, we can draw a conclusion about the nature of asymmetry. The relative intensities of bands are expected to change considerably if the asymmetry is induced by texture but remain unchanged in the case of Goldanskii–Karyagin's effect. It should be noted that the absorber should be reasonably thin; otherwise, the intensity ratio will be additionally influenced by a change in the effective thickness of the absorber due to variation of its orientation.