

Relaxation processes in the time-dependent differential Mössbauer spectra of ZnS-⁵⁷Co

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The time-dependent line shift and other deviations from the theoretical spectra of the time filtration, which were observed in the time-dependent differential Mössbauer spectra, indicate that the relaxation processes with a lifetime of about 40 nsec occur in the ⁵⁷Fe²⁺ ions after the nuclear decay of ⁵⁷Co in a ZnS single crystal.

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The time-dependent differential Mössbauer spectroscopy offers a means to investigate the various post-effects of the electron capture of ⁵⁷Co by the daughter iron atoms in rigid matrices. The relaxation of local vibrational and electronic excitations and other processes, whose relaxation times τ_r are comparable to the lifetime of the Mössbauer level 14.4 keV ($\tau = 140$ nsec), occur in the time-dependent differential Mössbauer spectra (TDMS) as modifications of the pattern of so-called time filtration. The TDMS study yields the time dependence of the Debye-Waller factor in ⁵⁷CoSO₄·7H₂O with $\tau_r = 36$ nsec,^[1,2] fast intramolecular charge exchange ($\tau_r = 10$ –20 nsec),^[3] relaxation of the nonuniformity of local environment with $\tau_r = 30$ nsec^[4] in ⁵⁷Co[Fe(CN)₆]₂, and relaxation of the spin states with τ_r in the range 20–400 nsec in [⁵⁷Co(phen)₃] (ClO₄)₂·2H₂O.^[5]

We identified the time functions of the line shift (position) and the Debye-Waller factor in TDMS of the dopant ⁵⁷Fe²⁺ impurity in the ZnS single crystals at 295 K.^[1]

The ZnS-⁵⁷Co source (~6 μ Ci) was prepared by vacuum evaporation of the ⁵⁷CoCl₂ solution in HCl sputtered on the surface of a ZnS single crystal and by subsequent annealing at 900°C for 24 hours in a sealed, evacuated quartz tube. A ⁵⁷Fe-enriched absorber K₄Fe(CN)₆·3H₂O with a thickness $\beta = 8 \pm 0.5$ at 295 K was used.

The Mössbauer spectrometer with a delayed coincidence system provided simultaneous recording of 4 TDMS at different fixed time intervals with a 12 to 14-nsec width after formation of the 14.4-keV level, i.e., after recording of the 122-keV γ ray. The resolution of the delayed coincidence systems was 5.6 nsec. All the TDMS in the interval 0–500 nsec were measured at 295 ± 2 K. To compare and control the equipment, we recorded the TDMS for a ⁵⁷Co single line source in metallic palladium.

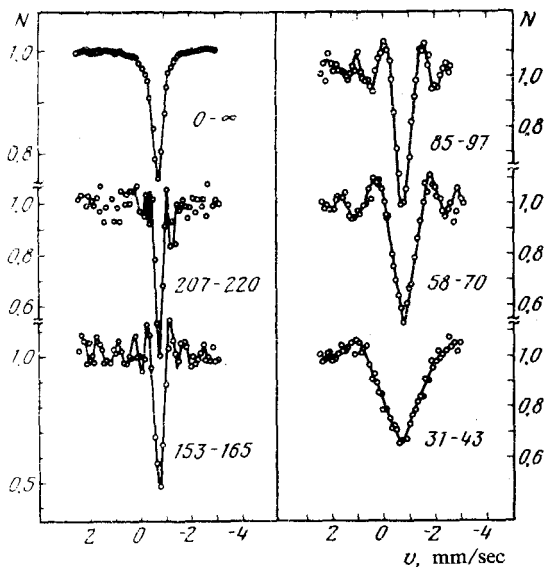


FIG. 1. Usual Mössbauer spectrum ($0-\infty$) and TDMS of the source $\text{ZnS-}^{57}\text{Co}$ for different delay intervals (in nsec) at 295 K.

Figure 1 shows a normal (time integrated) spectrum and 5 TDMS of the $\text{ZnS-}^{57}\text{Co}$ single crystal at 295 K for different time intervals. The normal spectrum represents a single absorption line with the isomeric shift $S = 0.73 \pm 0.03$ mm/sec and width $\Gamma_{\text{exp}} = 0.43 \pm 0.03$ mm/sec that parametrically corresponds to the $^{57}\text{Fe}^{2+}$ impurity ions at the cation sites of the matrix. The special features of the time filtration (variation of the line width with delay and oscillations at the "wings" of the line) are clearly defined in all the TDMS; moreover, a noticeable asymmetry of oscillations was observed for $\text{ZnS-}^{57}\text{Co}$.

The time-dependent parameters of the central line (the width Γ_{exp} , the effect ϵ , and the line shift S as a function of the average delay time t), which were determined from the experimental TDMS (Fig. 2), were compared with the corresponding theoretical spectra, that were calculated by a computer on the basis of a model for the time filtration of a single Hammermesh-Harris line.⁽⁷⁾ The expressions for them were integrated over a fixed 14-nsec-wide time interval for the absorber $\beta = 8$. Figure 2 shows the calculated functions $\epsilon(t)$ and $\Gamma(t)$ as solid lines.

A good coincidence of the calculated and experimental TDMS was obtained for the ^{57}Co source in Pd, which is compatible with the fact that the post-effects in the metallic matrices are attenuated during the time $\tau_r < 10^{-11}$ sec, and the time-dependent variation of the TDMS are constrained only by the effects of the time-dependent filtration.

The following systematic deviations from the theoretical model were observed for the TDMS of the $\text{ZnS-}^{57}\text{Co}$ crystal:

1) The time-dependent shift of the line position (center of mass of the central line) $S(t)$. The shift decreases as $T \rightarrow 0$ according to the empirical dependence:

$$S(t) = [-0,74 + 0,14 \exp(-t/\tau_r)] \text{ mm/sec},$$

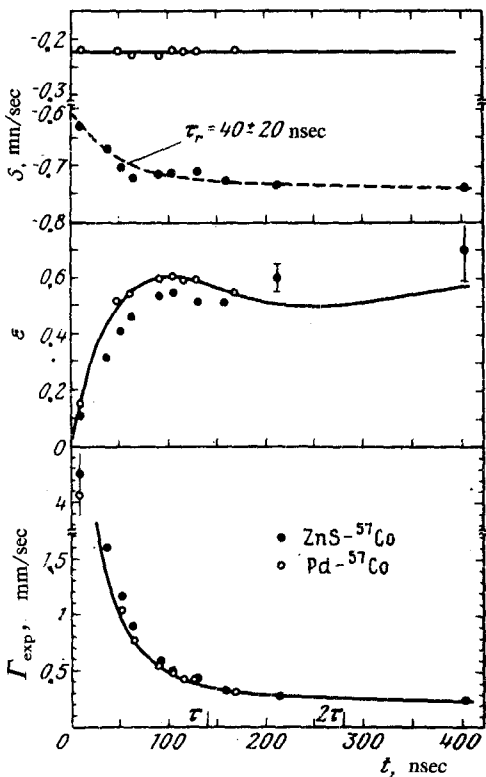


FIG. 2. Dependence of TDMS central line parameters of ZnS-⁵⁷Co and Pd-⁵⁷Co on the average delay time t . The continuous lines represent the $S(t)$, $\epsilon(t)$, and $\Gamma(t)$ dependences calculated according to Ref. 7.

where t is in nsec and $\tau_r = 40-20$ nsec.

2) The effect $\epsilon(t)$ is smaller for delay times 0-1.2 τ and approximately 20% larger for 1.5-3 τ .

3) The line broadening above the theoretical width for delays from 0 to τ .

The above peculiarities indicate that the time filtration is superimposed by a relaxation process on the ⁵⁷Fe²⁺ ions with the lifetime $\tau_r = 40-20$ nsec comparable with τ , which is excited by the decay of the ⁵⁷Co parent ion in the ZnS matrix.

The observed effects in TDMS can be qualitatively explained in terms of the following relaxation processes:

1) Local heating due to rearrangement of the electron shells or electronic-vibrational transitions in the excited ⁵⁷Fe²⁺ ion, which is characterized by the rms amplitudes and oscillation rates that are higher than those at thermal equilibrium, causes deviations of the dependences $S(t)$ and $\epsilon(t)$ via the time-dependent, second-order Doppler shift and the Debye-Waller factor, respectively. A rough estimate shows that the local effective temperature should exceed 500 K at $t = 5$ nsec. The same mechanism explains the additional line broadening in the initial stages of relaxation.

2) Attenuation of the excited electronic state of the Fe²⁺ ion causes time-dependent variation of the Coulomb interaction and, consequently, of the isomeric line shift

(see Ref. 8) and of the $\epsilon(t)$ and $\Gamma_{\text{exp}}(t)$ dependences.

Further experiments at different temperatures and calculations of the relaxation models should explain the role of the indicated mechanisms.

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¹The special features of conventional Mössbauer spectra of ZnS-⁵⁷Co at temperatures near 0 K, which Imbert *et al.*¹⁶ explain as a manifestation of thermally unbalanced level populations of Fe²⁺, were not observed at high temperatures.

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