

R. KOCH, E. REALO

TIME-DEPENDENT MÖSSBAUER SPECTRA OF ZnS—⁵⁷Co CRYSTAL

R. KOCH, E. REALO. ZnS—⁵⁷Co KRISTALLI AJASOLTUVUSEGA MÖSSBAUERI SPEKTRID

P. KOX, Э. РЕАЛО. ВРЕМЕННЫЕ МЕССБАУЭРОВСКИЕ СПЕКТРЫ КРИСТАЛЛА ZnS—⁵⁷Co

(Presented by K. K. Rebane)

Time-dependent Mössbauer spectra of a monocrystal ZnS—⁵⁷Co γ -source vs a $K_4[Fe(CN)_6] \cdot 3H_2O$ absorber for different preset time intervals of 12 ns in the range of 0 to 500 ns have been measured at 295 K. A time-dependent shift of the line position and other deviations from the calculated time-filtering spectra give evidence for a relaxation process with the lifetime of about 40 ns at ⁵⁷Fe²⁺ ions excited by the electron capture of ⁵⁷Co parent in a ZnS matrix.

Different aftereffects caused by the electron capture of ⁵⁷Co in solid matrices (e.g. localized lattice and electronic excitations and their relaxation processes) can be studied using the time-dependent (time-differential) ⁵⁷Fe Mössbauer spectroscopy. These aftereffects are observable if the lifetime of the corresponding excited state and that of the ⁵⁷Fe Mössbauer 14.4 keV level ($\tau=140$ ns) are of the same order. From the studies of time-dependent Mössbauer spectra (TDMS), a time-dependent Debye—Waller factor with the relaxation time $\tau_r \approx 10-100$ ns in ⁵⁷CoSO₄·7H₂O [1], a fast intramolecular charge transfer ($\tau_r \approx 10-20$ ns) in ⁵⁷Co₃(II)[Fe(III)(CN)₆]₂ [2] and a spin state relaxation with τ_r ranging from 20 to 400 ns in [⁵⁷Co(phen)₃](ClO₄)₂·2H₂O [3] have been found. We have shown the occurrence of a vibrational relaxation process ($\tau_r=70 \pm 30$ ns) at the ⁵⁷Fe²⁺ impurity in ZnS crystals at 295 K [4]. Earlier thorough studies of the conventional MS of ZnS—⁵⁷Co γ -sources by C. Garcin, P. Imbert et al. [5] have evidenced time-dependent effects (populations of electronic levels out of thermal equilibrium) at the ⁵⁷Fe²⁺ site at near 0 K temperatures.

This communication presents the results of our further measurements of TDMS with an increased time resolution.

For the preparation of ZnS—⁵⁷Co (~ 6 μ Ci) active ⁵⁷CoCl₂ in HCl solution was evaporated on a surface of a ZnS monocrystal under vacuum. The sample was heated at 900 °C for 24 hr in a vacuum sealed silica tube. An enriched (in ⁵⁷Fe) $K_4[Fe(CN)_6] \cdot 3H_2O$ absorber ($\beta = 8 \pm 0.5$) at 295 K was used.

A schematic diagram of the time-differential Mössbauer spectrometer is shown in Fig. 1. γ -sources were placed inside a side hole of a plastic scintillator coupled with a fast K14FS52 phototube to ensure 4π -counting for the 122 keV γ -ray detection [6]. The output pulses of a constant fraction discriminator served as the «start» pulses, corresponding to the formation of the 14.4 keV Mössbauer level, for a time-to-amplitude

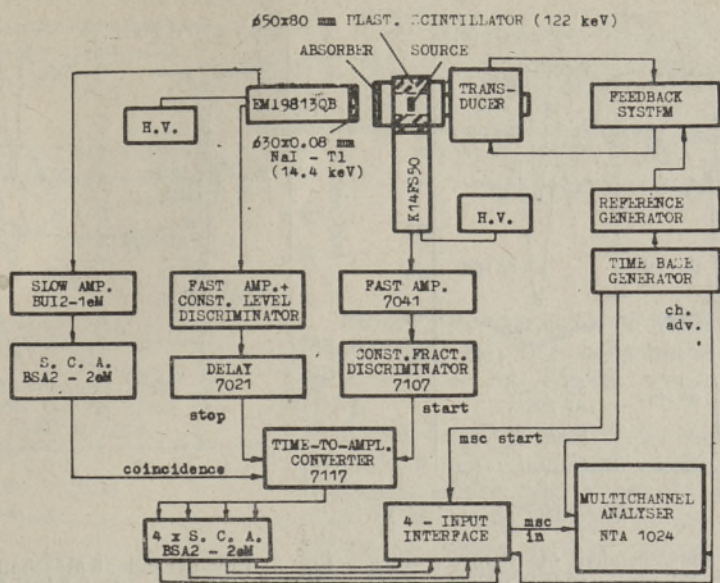


Fig. 1. Schematic diagram of the time-differential Mössbauer spectrometer.

converter (TAC) «Schlumberger 7117». A thin (0.08 mm) NaI—Tl scintillator and a fast EMI19813B photomultiplier assembly was used as a «stop» detector for 14.4 keV γ -quanta transmitted through a single-line absorber moving in constant acceleration mode. Four TDMS for different predetermined delay time intervals were recorded simultaneously to reduce the total counting time, temperature and electronic drifts. Four single channel analyzers were coupled to the TAC output for the time window selection. A zero «dead» time 4-input interface, similar to [7], as well as the address scaler of the NTA-1024 multichannel analyzer and the servo system for Doppler modulation were controlled by an external quartz-stabilized time-base generator. The long term drifts of the time window were measured to be less than 2 ns, while the velocity drifts were less than 0.03 mm/s. The time resolution of the delayed coincidence system was 5.6 ns.

TDMS for 12–14 ns time intervals in the range from 0 to 500 ns were measured at 295 ± 2 K. For comparison and checking, the measurements of TDMS for a single-line ^{57}Co in Pd metal source were carried out. In metal matrices aftereffects are assumed to decay within $< 10^{-11}$ s and the time-dependent changes in their spectra are caused by the time-filtering effects (changes in the linewidth and oscillations) only.

Figs. 2 and 3 represent some TDMS of a ^{57}Co in Pd source and a ZnS— ^{57}Co monocrystal, respectively. A conventional MS of ZnS— ^{57}Co was a single line with $\delta_{\text{PFC}} = (0.73 \pm 0.03)$ mm/s and $\Gamma_{\text{exp}} = (0.43 \pm 0.03)$ mm/s, corresponding to $^{57}\text{Fe}^{2+}$ ions substituting host Zn^{2+} ions. No other charge state of iron was found in MS. Time-filtering features were clearly seen for both series of TDMS.

The time-dependent central line parameters (the linewidth Γ , the effect magnitude ε and the lineshift δ) derived from TDMS (Fig. 4), were compared with the theoretical estimates calculated for the single-line time-filtering model of Hamermesh and Harris [8]. The transmission spectrum at the time $T = t/\tau$ after the formation of the Mössbauer level is given by

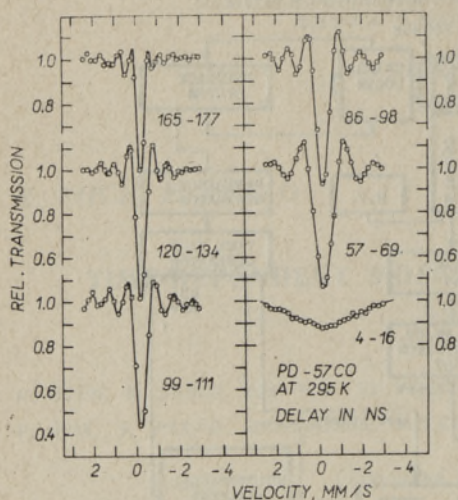


Fig. 2. Time-dependent Mössbauer spectra of ^{57}Co in Pd source vs $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ absorber at 295 K.

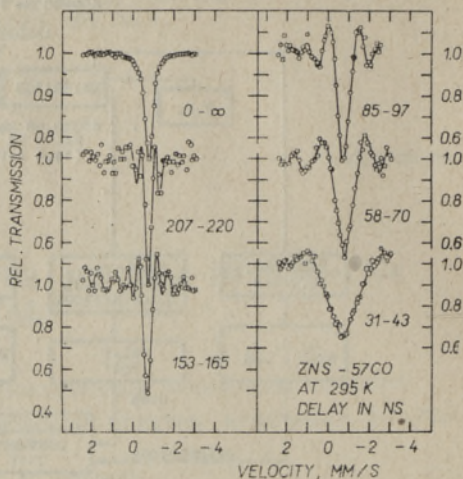


Fig. 3. Time-dependent Mössbauer spectra of $\text{ZnS}-^{57}\text{Co}$ monocystal vs $\text{K}_4[\text{Fe}(\text{CN})_6] \cdot 3\text{H}_2\text{O}$ absorber at 295 K. The TDMS are corrected for random coincidences.

$$I(\Delta\omega, T) = e^{-T} \left| \sum_{n=0}^{\infty} (2i\Delta\omega\beta^{1/2}T^{1/2}/\beta\Gamma_0)^n J_n(\beta^{1/2}T^{1/2}) \right|^2$$

for $2\Delta\omega\beta^{1/2}T^{1/2}/\beta\Gamma_0 < 1$ and

$$I(\Delta\omega, T) = e^{-T} \left| -\exp[i(\Delta\omega T/\Gamma_0 + \Gamma_0\beta/4\Delta\omega)] + \sum_{n=1}^{\infty} (i\beta\Gamma_0/2\Delta\omega\beta^{1/2}T^{1/2})^n J_n(\beta^{1/2}T^{1/2}) \right|^2$$

for $2\Delta\omega\beta^{1/2}T^{1/2}/\beta\Gamma_0 > 1$. $\Delta\omega$ — the frequency difference between the emission and absorption lines. $\Gamma_0 = 0.0973$ mm/s is the natural linewidth of the 14.4 keV level, J_n — integer Bessel functions. These expressions were integrated over the predetermined time window ΔT for the absorber thickness $\beta = 8.0$. The calculated dependences of $\epsilon(T)$ and $\Gamma(T)$ were plotted in Fig. 4 (solid lines). A reasonable agreement between theoretical calculations and experiment was found for the Pd— ^{57}Co source, while systematic deviations for the TDMS parameters of the ZnS— ^{57}Co crystal were present:

1) a time-dependent shift of the mean line position (the centre of gravity of the central line) $\delta(T)$, $|\delta|$ decreases as $T \rightarrow 0$. An empirical expression $\delta(t) = [-0.74 + 0.14\exp(-t/40)]$ mm/s fits the data best (t in ns);

2) the effect magnitude $\epsilon(T)$ was about 10 to 30% smaller for the delay time range from 0 to 1.2τ and about 20% higher for $1.5\tau - 3\tau$;

3) an additional broadening over the theoretical linewidth was observed for the delay time from 0 to τ .

These features, in accordance with the former results [4], provide an evidence that «time-filtering» is superimposed by some time-dependent solid state effect, i.e. local electronic or/and vibrational relaxation with the lifetime ($\tau_r \approx 40$ ns) comparable to τ at the $^{57}\text{Fe}^{2+}$ site excited by the decay of the ^{57}Co parent in the ZnS matrix.

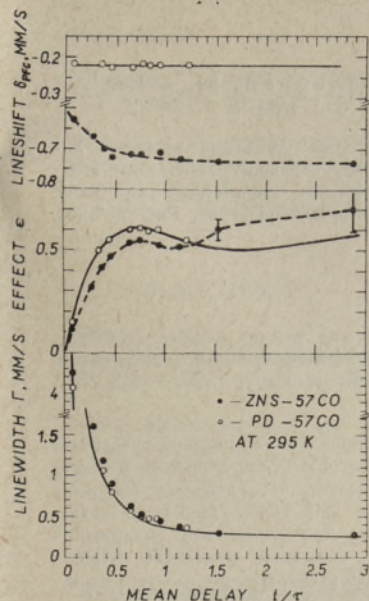


Fig. 4. Time-dependences of central line parameters for ^{57}Co in Pd and ZnS— ^{57}Co γ -sources. The dashed line for $\delta(T)$ is an empirical dependence $\delta(t) = [-0.74 + 0.14 \exp(-t/40)]$ mm/s (t in ns) to fit the data. The solid lines for $\epsilon(T)$ and $\Gamma(T)$ are the corresponding theoretical dependences calculated for $\beta=8$, according to [8].

Several mechanisms of the aftereffects responsible for the occurrence of solid state effects in TDMS were proposed [3, 9].

Local heating caused by the re-arrangement of the electron shells (or the electronic-vibrational transitions of excited $^{57}\text{Fe}^{2+}$ ions) leading to the increased values of mean square amplitudes and velocities of vibration, can qualitatively explain the observed relaxational phenomena in the TDMS of ZnS— ^{57}Co . The increased mean effective temperature and its relaxation would be responsible for the deviations in the $\delta(T)$ and $\epsilon(T)$ dependences via the time-dependent thermal shift and the Debye-Waller factor. A rough estimate shows that the mean effective temperature should be more than 500 K for $T=0$. The line broadening found for the earlier stages of the nuclear decay, which becomes negligible for $t > \tau$, seems to confirm this relaxation mechanism [10]. Unfortunately, a full theoretical analysis of the TDMS in the presence of a heated localized mode as well as other possible mechanisms, including charge deficiencies on the S^{2-} ligands or the internal pressure from the difference of the ionic radii of $^{57}\text{Fe}^{2+}$ and $^{57}\text{Co}^{2+}$, is not performed. On the basis of our experiments theoretical treatments (see [5]) considering electronic relaxation (isomeric interaction) only do not seem to be applicable at present, since a single line is found in the conventional and TDMS of ZnS— ^{57}Co .

REFERENCES

- Hoy, G. R., Wintersteiner, P. P., Phys. Rev. Lett., 28, № 14, 877—879 (1972).
- Alekseev, V. P., Goldanskii, V. I., Prusakov, V. E., Nefedev, A. V., Stukan, R. S., JETP Lett., 16, 43—46 (1972).
- Grimm, R., Gütlich, P., Kankeleit, E., Link, R., J. Chem. Phys., 67, № 12, 5491—5500 (1977).
- Realo, E., Koch, R., In: Magnetic Resonance and Related Phenomena, Ed. by E. Kundla, E. Lippmaa, T. Saluvere, Tallinn, 1979, p. 248.
- Garcin, C., Imbert, P., Jehanno, G., Solid State Commun., 21, № 6, 545—549 (1977); Imbert, P., Garcin, C., Jehanno, G., Gerard, A., Proc. Int. Conf. Mössbauer Spectroscopy, Bucharest, 1977, II, p. 123.
- Kobayashi, T., Shimizu, S., Phys. Lett., 54A, № 4, 311—312 (1975).
- Kaindl, G., Maier, M. R., Schaller, H., Wagner, F., Nucl. Instrum. Meth., 66, № 2, 277—282 (1968).
- Lynch, F. J., Holland, R. E., Hamermesh, M., Phys. Rev., 120, № 2, 513—520 (1960); Harris, S. M., Phys. Rev., 124, № 4, 1178—1185 (1961).
- Kankeleit, E., Z. Phys., A275, № 2, 119—121 (1975).
- Dash, J. G., Nussbaum, R. H., Phys. Rev. Lett., 16, № 13, 567—570 (1966).