

KINETICS OF THE FAST CHARGE AND SPIN RELAXATION OF COORDINATION
COMPOUNDS STUDIED BY THE MÖSSBAUER EMISSION SPECTROSCOPY

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Abstract -The method of Mössbauer Emission Spectroscopy (MES) allows to study the kinetics of various chemical conversions of Mössbauer emitters if the time of such conversions τ_r is comparable to the life-time of Mössbauer level $\tau_M \approx 10^{-7}$ sec. MES kinetical data on the fast transformation of Turnbull blue (TB) into the Prussian blue (PB) at 400-12 K are presented. The existence of low-temperature plateau of the rate of this transformation testifies its electron-nuclear tunneling nature.

MES data on the HS \rightarrow LS spin relaxation of hexacoordinate iron (II)-nitrogen donor complexes are described and compared with the Mössbauer absorption spectroscopy (MAS) data on the corresponding spin crossover HS \rightleftharpoons LS transitions.

Mössbauer Emission Spectroscopy (MES) deals with the emitters of resonance γ -rays i.e. it reflects the structural and dynamic properties of the atoms whose nuclei find themselves in the excited Mössbauer state.

The possibilities of the study of relaxational changes of these properties are determined by the comparison between the life-time of Mössbauer level τ_M and characteristic relaxation time τ_r .

At $\tau_r \ll \tau_M$ the relaxation proceeds mostly before the nuclear transition and therefore the time-integral ME spectra (TIMES) represent mainly the properties of the emitters which already have suffered the relaxation.

Nevertheless the use of delayed coincidences circuits with the resolution time $\tau_{cc} < \tau_M$ - i.e. the studies of time differential ME spectra (TDMES) - opens additional possibilities of the studies of fast relaxation processes.

At $\tau_r \gg \tau_M$ the relaxation involves mainly the atoms with already deexcited nuclei in their ground states, and the MES is therefore deprived here of any additional informativity.

Thus, the most favourable condition for the applications of the MES in its simplest TIMES variant corresponds to $\tau_r \sim \tau_M$.

Usual values of τ_M lie within $10^{-5} - 10^{-10}$ sec, the most developed case of $^{57}\text{Fe}(14,4 \text{ keV})$ corresponds to $\tau_M \approx 1.4 \cdot 10^{-7}$ sec, and the emission of resonance

γ -ray is preceded here by the K-capture in ^{57}Co with the formation of the short-lived ($\tau_0 \approx 12.5 \text{ nsec}$) 136.3 keV excited state of ^{57}Fe and subsequent emission of ca. 122 keV non-Mössbauer γ -ray. Thus the use of delayed $\gamma(122) \gamma(14.4)$ coincidences with the variable time of delay (TDMES) opens here the possibility of the studies of relaxation with charac-

teristic times between $\tau_r \sim \tau_{cc} \sim 10^{-9}$ sec and $\tau_r \gg \tau_m$.

Well-known are various chemical consequences of nuclear transformations, e.g. the "shake-off" of the electron shells due to the prompt change of nuclear charge and subsequent Auger-transitions, Coulomb explosions of multiply ionized molecules, spot-heating, autoradiolysis etc. (1,2). We shall not discuss here such processes (which are moreover usually completed before the population of 14,4 resonance ^{57}Fe level) and will restrict ourselves just by the chemical relaxation.

That means that we will treat the systems where the pre-Mössbauer nuclear conversion does not lead by itself to the change of ligand environment or charge state of daughter Mössbauer atoms (^{57}Fe), which primarily are stabilized in the same environment and valence state as the parent (^{57}Co) radioactive atoms.

However some particular chemical (valence and spin) states being stable for the parent atom can well be unstable for the daughter atom (with the excited Mössbauer nucleus) and then the system will tend towards the stable chemical state i.e. it will undergo chemical relaxation.

Two groups of chemical relaxation processes were found up to now to proceed with life-times comparable to τ_m and to be manifested therefore in the MES :

1. Change of the charge state of the daughter atom (^{57}Fe) as compared to the parent atom (^{57}Co) caused by the interionic oxidation-reduction transfer of electrons, with the conservation of spin state as either the high-spin (HS) or the low-spin (LS) state (3-8).
2. Change of the spin state of the daughter atom (^{57}Fe) as compared to the parent atom (^{57}Co) with the conservation of its charge state (9-17).

INTERIONIC ELECTRON TRANSFER

As is well known from the numerous Mössbauer absorption spectroscopy (MAS) data (see e.g. Ref.7) the interactions between HS ferric and LS ferrocyanide states as well as between HS ferrous and LS ferricyanide states lead to the formation of ferriferrocyanide, Prussian blue (PB) $\text{Fe}^{3+}/[\text{Fe(II)(CN)}_6]^{4-}$ rather than of ferroferricyanide, Turnbull blue (TB) $\text{Fe}^{2+}/[\text{Fe(III)(CN)}_6]^{3-}$ i.e. the electron is promptly transferred from HS reducer (Fe^{2+}) to the LS oxidizer $[\text{Fe(III)(CN)}_6]^{3-}$.

The search for the short-lived TB by the methods of MES was based on the use of cobalt ferricyanide complexes $^{57}\text{Co}^{2+}/[\text{Fe(III)(CN)}_6]^{3-}$ as sources in TIMES ($t=0-60$ nsec) experiments.

Preliminary experiments with labeled cobalticyanide sources $\text{M}^{n+}/[^{57}\text{Co(III)(CN)}_6]^{3-}$ where $\text{M}^{n+} = \text{Ni}^{2+}, \text{Co}^{2+}, \text{Cu}^{2+}, \text{Fe}^{3+}$ and with the $^{57}\text{Co}^{2+}/[\text{Fe(II)(CN)}_6]^{4-}$ source have indicated the formation of daughter ^{57}Fe atoms in the same states as were parent ^{57}Co atoms (5,6) and - in such a way - they have demonstrated the elimination of chemical aftereffects of K-capture in ^{57}Co in ME spectra.

Cobaltferricyanide $^{57}\text{Co}^{2+}/[\text{Fe(III)(CN)}_6]^{3-}$ was used as a source and yellow blood salt $\text{K}_4\text{Fe(II)(CN)}_6 \cdot 3\text{H}_2\text{O}$ - as an absorber in first main experiments (3,4). The results obtained at 77 K - for both TIMES and TDMES ($t = 0-60$ nsec) variants - are presented in Fig.1.

The treatment of the MES data was based on the determination of the contribution of broad Fe^{2+} doublet which could be expected for the unstable TB, however was not observed in absorption spectra.

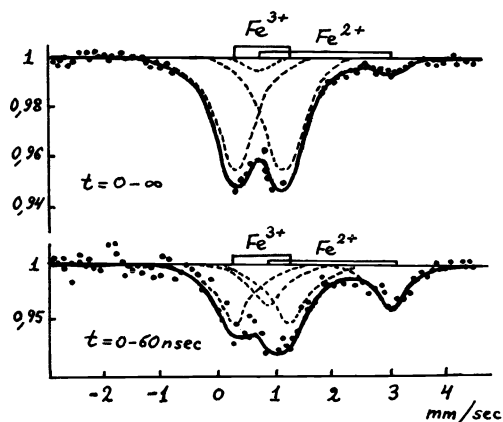


Fig. 1. Mössbauer emission spectra of cobaltoferricyanides $^{57}\text{Co}^{2+}/[\text{Fe(III)(CN)}_6]^{3-}$ at 77 K. Above: TIMES, below: TDMES ($t=0-60\text{nsec}$). Narrow Fe^{3+} doublet and broad Fe^{2+} doublet are indicated (Ref. 3).

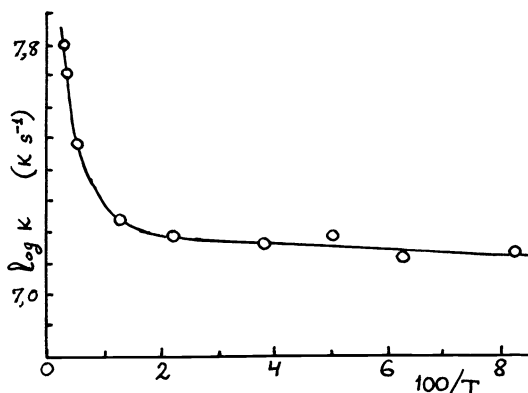


Fig. 2. Temperature dependence of the rate constants of TB \rightarrow PB transition (data of Ref. 3, 4, and 8 - summarized and analyzed in Ref. 22).

Besides the change of the shape of spectra caused by the simple "steady-state" admixture of TB to PB one could also expect in the MES experiments the manifestations of the so-called time-filtering effects (18,19) as well as various distortions (e.g. the broadening) of lines caused by relaxation processes proceeding within $\tau_r \lesssim \tau_m$ (20, 21).

Nevertheless we have used for the crude estimate of the rate of electron transfer the simplified representation of the observed emission spectra by two undistorted components - narrow Fe^{3+} (PB) and broad Fe^{2+} (TB) symmetric quadrupole doublets (supposing that $f'_{\text{PB}} = f'_{\text{TB}}$).

Under such assumption the fraction of TB in TDME spectra obtained with the gate of delayed $\gamma\gamma$ -coincidences from $t = 0$ to $t = \tau$ should be equal to:

$$P_\tau = P_0 \lambda [1 - e^{-(\lambda+K)\tau}] / (\lambda+K)(1 - e^{-\lambda\tau}) \quad (1)$$

where $\lambda = \tau_m^{-1}$, K is the rate constant of chemical transition (TB \rightarrow PB), P_0 - the initial population of TB state.

With increasing τ the value of P_τ should decrease approaching at $\tau \rightarrow \infty$ the value of $P_\infty = P_0 \lambda / (\lambda + K)$ characteristic for TIMES measurements.

Results of such calculations of K values between 77 and 400 K are illustrated by the left part of the curve in Fig. 2 taken from Ref. 22. Right part of this curve represents the data obtained at 77-12 K by TIMES method in our joint work with Helsinki group (8) (with the $\text{Na } ^{57}\text{Co}^{2+}/[\text{Fe(III)(CN)}_6]$ source). As can be seen from Fig. 2 the temperature dependence of the rate of electron transfer from Fe^{2+} to $[\text{Fe(III)(CN)}_6]$ is gradually changing from the Arrhenius-type dependence above ca. 200 K (activation energy E reaches

here the value of $E \sim 0.025$ eV) down to the low-temperature plateau $\lesssim 50$ K. Such temperature dependence of the rate of electron transfer is typical for the electron-nuclear tunneling which has attracted recently very wide attention (see e.g. Ref. 23,24) and is usually treated in terms of the theory of radiationless electron transitions.

The probability of a radiationless electron transition W_{if} is determined by the overlap of electron (Ψ_e) and nuclear vibrational (Ψ_v) wave functions in the initial (i) and final (f) states described - respectively - by the matrix element of the electron transition $L_e^2 = |\langle \Psi_{e_i} | \hat{L} | \Psi_{e_f} \rangle|^2$ and by the Franck-Condon factor $F_v = |\langle \Psi_{v_i} | \Psi_{v_f} \rangle|^2$:

$$W_{if} = (2\pi/\hbar) L_e^2 F_v \rho_f \quad (2)$$

where \hat{L} is a transition operator such as the non-adiabaticity operator and $\rho_f = (\hbar\omega)^{-1}$ is the density of vibrational levels in the final state (it is assumed that the dissipation of the heat of exothermic transitions in solids in the form of phonons proceeds very fast and by no means can be treated as a rate-determining step).

The scheme of electron-nuclear tunneling is shown in Fig. 3.

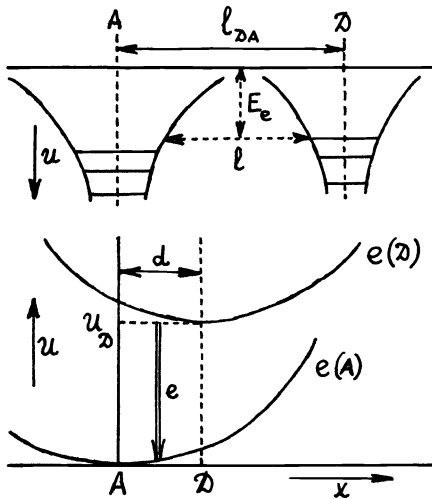


Fig. 3. Scheme of the electron-nuclear tunneling for electron transfer from the donor (D) to the acceptor (A).

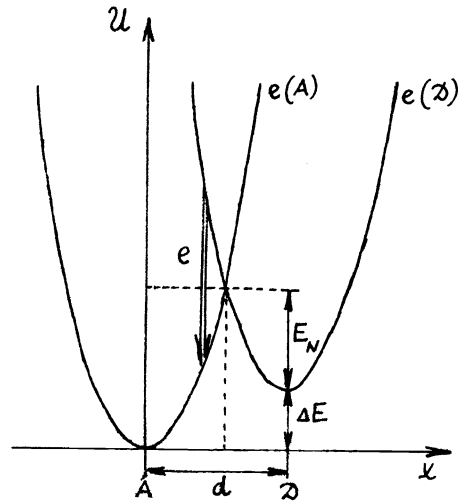


Fig. 4. Scheme of the tunneling displacement of the nuclei. Transition heat is indicated as E , activation energy - as E_N .

The electron penetration through the potential barrier of the width l and the height E_e is accompanied here by much smaller (d) barrierless displacement of nuclei. However with the increasing d , when the nuclear displacement strongly exceeds the amplitude of the nuclear vibrations (for the n -th vibrational level of the harmonic oscillator, $\Delta_n = \sqrt{2n+1} (\hbar/M\omega)^{1/2}$ where M is the nuclear mass and ω - the characteristic vibrational frequency), the potential barrier appears for the nuclear transfer too (see Fig. 4), and that can result in the process of molecular chemical tunneling (24). The wave functions $\Psi_e(x)$ are proportional to $\exp(-x/\alpha)$ (for $x > \alpha$) where

$\alpha = \hbar / \sqrt{2mE_e}$ and for $l \gg \alpha$ the matrix element L_e^2 takes a form of the Gamov-type tunneling factor: $L_e^2 \approx \exp[-\beta l \sqrt{2mE_e} / \hbar]$ where $\beta \sim 1$ (and depends on the shape of barrier), m is the electron mass.

This expression for L_e^2 is valid for the low-temperature plateau while above the so-called "tunneling temperature" (25)

$$T_{t_e} = (\hbar / k_B \pi \sqrt{2} l) \sqrt{E_e / m} \approx 6000 \sqrt{E_e (\text{eV})} / l (\text{\AA})$$

the Arrhenius-type temperature dependence is valid:

$$L_e^2 \approx \exp(-E_e / K_B T)$$

The wave functions $\Psi_V(x)$ are proportional to $\exp[-(x/\Delta)^2]$ (for $x > \Delta$), and therefore the Franck-Condon factor at $d > \Delta$ can be approximately expressed as $F_V \approx \exp[-(\alpha d / \Delta)^2]$, where α is of the order of one. Since the statistically averaged vibrational amplitude increases with the temperature - and for the harmonic oscillator $\langle \Delta^2 \rangle$ is at $kT \gg \hbar\omega$ proportional to T , the high-temperature behaviour of the Franck-Condon factors is of Arrhenius type for both barrierless (Fig. 3) and overbarrier (Fig. 4) nuclear displacement.

With the decreasing temperature when Δ approaches the amplitude of zero-vibrations Δ_0 , the Franck-Condon factor reaches a certain minimum constant value (as the L_e^2 does) and that results in the appearance of the low-temperature plateau of the total rate (W_{if}) of the radiationless electron transition.

For the simplest case of resonance nuclear tunneling ($\Delta E = 0$ in Fig. 4) the Franck-Condon factor takes a Gamov-type form (see e.g. Ref. 26) and the "tunneling temperature" T_t which describes the gradual transition from the Arrhenius ($T > T_t$) to tunneling ($T < T_t$) regions for nuclear displacement would be equal to $T_{t_N} = (\hbar / k_B \pi \sqrt{2} d) \sqrt{E_A / M} \approx 20 \sqrt{E_A (\text{eV})} / d (\text{\AA})$

for iron nuclei.

The structure of ferriferrocyanide crystals is well-known and corresponds to the distance of electron interionic tunneling $l \sim 5 \text{\AA}$. The typical energy of the charge transfer from metal to ligand in first-row transition metal complexes is $E_e \sim 4 \text{ eV}$ (15). Therefore the Gamov-type tunneling factor for the parabolic barrier ($\beta = \pi \sqrt{2} / 2$) is ca. $2.5 \cdot 10^{-4}$. Meanwhile the total deceleration factor for the TB \rightarrow PB conversion at the low-temperature plateau, where the rate constant $K \sim 10^7 \text{ sec}^{-1}$, is ca. 10^{-7} . That means that the contribution of the nuclear displacement (Franck-Condon factor) to such deceleration is here practically the same as of the electron tunneling:

$$F_V \sim \exp[-(\alpha d / \Delta)^2] \sim 4 \cdot 10^{-4}$$

The estimate value of $(\alpha d / \Delta_0) \sim 2.8$ can be combined with the data on the probability of Mössbauer effect for PB at low temperatures:

$$f' = \exp[-(\Delta_0^2 / \lambda^2)] \approx 0.6 \text{ where } \lambda = 0.14 \text{\AA}$$

Thus $\Delta_0 \approx 0.1 \text{\AA}$, and $\alpha d \approx 0.3 \text{\AA}$. This reasonable latter estimate together with $E_A \approx 0.025 \text{ eV}$ would correspond in the case of resonance nuclear displacement to $T_t \sim (10\alpha) \text{ K}$ and thus favours the conclusion that just the

nuclear displacement rather than the electron transfer is the process which determines the appearance of the plateau in the temperature dependence of the rate of TB \rightarrow PB conversion only below ca. 50 K and not at higher temperatures (thermally activated electron tunneling).

In general the combination of the experimental data on the plateau rate of chemical conversion ($\alpha_{\text{HS}} \sim \alpha_{\text{M}}$), on f' - value at $T \rightarrow 0$ and on the temperature of the beginning of plateau can lead to sufficiently reliable estimates of both α and d .

RELAXATION OF SPIN STATES

Mössbauer emission spectroscopy (MES) was successfully applied by Gütlich, et al. in its both - TIMES ((9-14, 16), see also Ref. 17) and TDMES (15) - variants to the studies of relaxation of spin states of iron (HS \rightarrow LS) for numerous hexacoordinate iron (II) - nitrogen donor complexes.

Cobaltous complexes ($^{57}\text{CoN}_6$) used as the sources in the MES experiments find themselves usually in the stable HS state $^4T_1(O_h)$ while the data of Mössbauer absorption spectroscopy (MAS) and magnetic measurements indicate the existence of three various classes of corresponding ferrous complexes (Fig. 5) characterized by the different strength of ligand field.

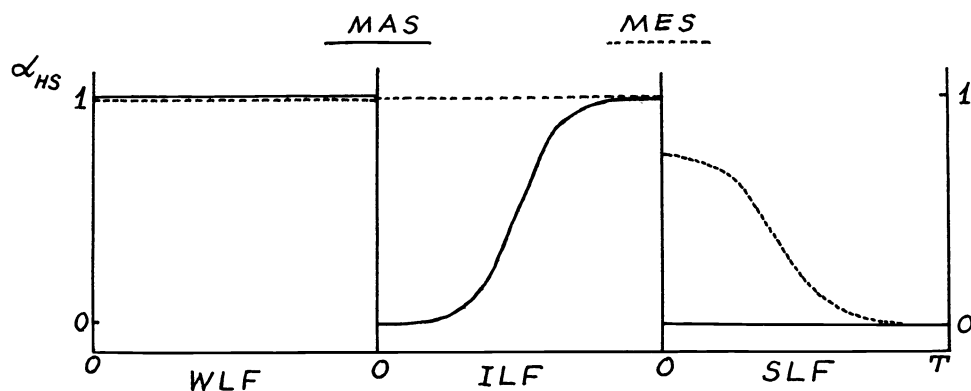
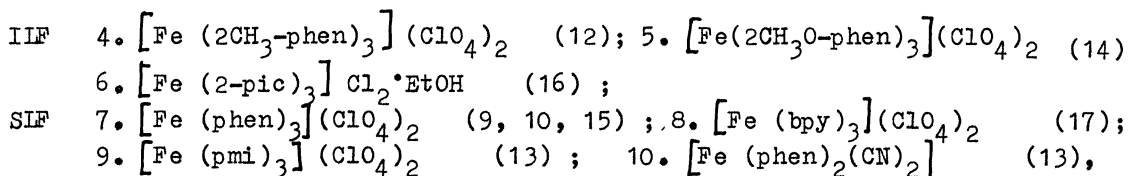


Fig. 5. Schematic presentation of the temperature dependence of HS fraction (α_{HS}) for the hexacoordinate iron (II) nitrogen - donor complexes with the weak (WLF), intermediate (ILF) and strong (SLF) ligands field. MAS - solid lines, MES - dotted lines.

1. Weak ligand field (WLF) - HS state of iron in the whole temperature interval (4-300 K) ;
2. Intermediate ligand field (ILF) - domination of LS state at lower and HS state at higher temperatures, with more or less abrupt temperature - dependent cooperative crossover spin transition ;
3. Strong ligand field (SLF) - LS state of iron in the whole temperature interval (4 - 300.K).

The list of the MES - studied ferrous complexes follows :

- WLF 1. $[\text{Fe}(\text{2Cl-phen})_3](\text{ClO}_4)_2$ (14)
 ILF 2. $[\text{Fe}(\text{phen})_2(\text{NCS})_2]$ (11) ; 3. $[\text{Fe}(\text{bpy})_2(\text{NCS})_2]$ (11) ;



where (phen) stands for 1, 10 - phenantroline, (bpy) for 2,2 - bipyridyl; (pmi) - for 2-pyridinal-N-methylimine; (2-pic) - for 2-picolyamine (2-aminomethylpyridine).

Mössbauer spectroscopy opens the possibility to distinguish between various spin states of Fe(II) since the spectra of LS state (1A_1) and of each of two HS substates (5A_1 , 5E) formed from the splitting of the $^5T_{2g}(O_h)$ HS state by the trigonal distortion have somewhat different quadrupole splittings and isomer shifts.

WLF class is represented by the sole example of the complex 1. The stable spin state of iron (II) seen here from the MAS data appears throughout to be the HS state - equally to the ferrous state seen from the MES data. The increase of the probability of the appearance of HS state for daughter ^{57}Fe atoms as compared to stable iron can be expected a priori as a manifestation of the retained "memory" of ^{57}Co state and - in particular - due to the marked reduction of ligand field potential originated from various consequences of ^{57}Co decay.

Indeed, as can be seen from Fig. 5 the α_{HS} values for the MES spectra of the IIF and SLF complexes are sufficiently higher than for the corresponding MAS spectra, and the virtual possibility of the observation of the HS \rightarrow LS relaxation in the emission spectra is obvious. However the careful investigations of the shapes of emission spectra performed in Ref. 11, 12, 14 and 16 for five IIF complexes numbered above as 2 - 6 have led to the conclusion that ferrous LS state makes no contribution to those spectra (observed deviations of Fe(II) HS fraction from $\alpha_{\text{HS}} = 1$ - mostly at higher temperatures, illustrated by Fig. 6, should apparently be attributed to the ferric HS species rather than to the formation of Fe(II) LS state).

Thus the HS \rightarrow LS relaxation of iron (II) - nitrogen IIF complexes seems to proceed much slower than the de-excitation of Mössbauer level ($\tau_r \gg \tau_m$). Same conclusion can be made from the careful analysis of the MAS data for the abovementioned IIF complexes (27-32).

General problems of the application of the MAS to the studies of spin crossover were discussed in Ref. 33 and 34, comprehensive survey of this phenomenon was published recently by Gütlich (35).

Main attention in the MAS studies was always paid to the equilibrium of spin crossover rather than to the rate of HS \rightarrow LS transitions whereas the shape of absorption spectra can give certain information concerning this rate.

Indeed the existence of two different states of Mössbauer atoms (HS and LS in the studied compounds) with the possible thermal relaxation (interconversion) between these states can lead to the appearance of two main types of resulting absorption spectra:

1. Superposition spectrum - formed by the simple overlap of two individual

spectra (inherent to HS and LS states in our case) represented in accordance with the statistical weights of contributing states. This is the case of slow relaxation: $\tau_r \gg \tau_m$

2. Hopping (delocalization) spectrum - single spectrum with the HFS parameters intermediate between those of two represented individual states. This is the case of fast interconversion: $\tau_r \lesssim \tau_m$, which leads to the delocalization of electrons between the configurations inherent to each of two contributing states.

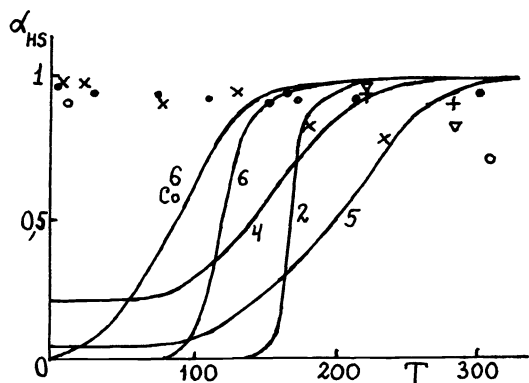


Fig. 6. Spin crossover transitions (HS \rightarrow LS) in the IIF ferrous complexes. Lines - MAS data, points - MES data. Numbers 2.(+), 3.(∇), 4.(\bullet), 5.(x), 6.(o) correspond to the list of complexes given in the text of paper. Curve 6(Co) - for

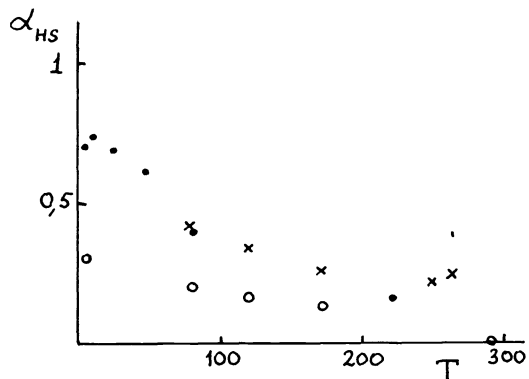
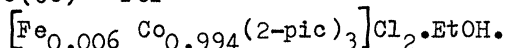


Fig. 7. Fraction of the HS state (α_{HS}) in the time-integrated emission spectra of SLF ferrous complexes: 7.(\bullet), 9(o), 10(x).

Among the various hexacoordinate iron (II) complexes studied by the MAS only the $[\text{Fe}(\text{III})\text{S}_6]$ - type ferric tris-dithiocarbamates (36, 37) possess the hopping-type spectra while all composite spectra of abovementioned IIF $[\text{Fe}(\text{II})\text{N}_6]$ complexes were found to be of superposition type (27 - 32). Thus the MAS data clearly demonstrate that within the whole investigated range of temperatures (or - according to Ref. 28 - at least below ca. 240 K) the HS \rightarrow LS spin crossover processes for hexacoordinate iron (II) - nitrogen donor complexes proceed much slower than the de-excitation of 14.4 keV Mössbauer level of ^{57}Fe .

The reason of such leisureliness of HS \rightarrow LS transitions (tightly connected to their mechanism) still remains unexplained.

It seems plausible that these transitions in solids require the rearrangement of the crystalline lattice and thus are connected to the necessity of surmounting of high activation barriers.

Indeed the rate constants for the spin interconversion of iron (II) complexes in CH_2Cl_2 - CH_3OH solutions at 0 - 25°C were found to be considerably higher: $K \sim (1-2) \cdot 10^7 \text{sec}^{-1} > \tau_m^{-1}$, and the activation energy for solutions-

- close to zero (38).

Some additional light on the problem of mechanism of spin crossover processes might be shed by the MES studies of HS \rightarrow LS conversions in the SLF iron(II) - nitrogen complexes (9,10,13,15,17). Absorption spectra of such complexes (numbered above as 7 -10) throughout the whole range of temperatures demonstrate the existence of only LS ferrous states.

However the HS states are clearly represented in the emission spectra of the SLF complexes (Fig. 7), their contribution being determined here exclusively by the rate of spin relaxation (rather than by the HS \rightarrow LS equilibrium) and decreasing therefore gradually with the rising temperature.

Most detailed study of the kinetics of spin relaxation was performed by Gütlich et al. for the tris-phenantroline iron (II) perchlorate (9,10,15) - using both TIMES and TDMES variants of Mössbauer emission spectroscopy. Temperature dependence of the rate constant of the HS \rightarrow LS transition for this complex (Ref. 15) is of the same type as for the abovedescribed case of interionic electron transfer (TB \rightarrow PB). Here again one can observe the gradual passage from the high-temperature Arrhenius region ($E \approx 0.015$ eV) to the low-temperature plateau of the spin relaxation rate. Similar conclusion can be made for other SLF complexes, represented at the Fig. 7.

Two mechanisms of spin relaxation processes which could lead to such temperature dependence of their rate were discussed in Ref. 15.

One of suggested explanations was based on the treatment of the rate of strongly forbidden slow ($\Delta S = 2$) transition: $^5T_2 \rightarrow ^1A_1$ (vertical relaxation at the Tanabe-Sugano diagram). However the laser excitation and picosecond spectroscopy of $[\text{Fe}(\text{phen})_3](\text{ClO}_4)_2$ in ethanol-methanol (4:1) glass at 10-80 K (Ref. 39) demonstrated the formation of excited states with much shorter life-times than in the MES experiments (4-6 ns in contrast to 100 - 400 ns). That brings some doubts to the identification of the HS state observed by the MES as an excited crystal field state. Another explanation suggested in Ref. 15 was based on the autoradiolytic formation of $[\text{Fe}(\text{II})(\text{phen})_2(\text{phen}^+)]$ with the increased Fe^{2+} - ligand distance and weakened ligand field and subsequent passing of an electron from the $[\text{Co}(\text{phen})_3]^{2+}$ host to a positively charged ligand (horizontal relaxation at the Tanabe-Sugano diagram). However the laser flash excitation of $[\text{Fe}(\text{III})(\text{phen})_3](\text{ClO}_4)_3$ (Ref. 40) lead again to the observation of much more unstable products than the MES data (life-times of the metal-to-ligand CT state are ca. 10 ps at room temperature and ca. 20 ps in a sulfuric acid glass, with almost no temperature dependence down to ca. 10 K). Thus the treatment of the HS \rightarrow LS relaxation as of the electron-nuclear tunneling turns to be questionable too. It would be of certain interest to examine closely the possibility of the application of Sorai-Seki cooperative domain model ((41, 42), see also Ref. 43) to the kinetics of spin relaxation in solids. According to this model the spin transition proceeds in a cooperative manner through a coupling between the spin state and the lattice vibrational modes. Thus the application of Mössbauer spectroscopy and - in particular - of the MES to the studies of charge and spin relaxation in coordination compounds opens new horizons for the development of modern solid-state chemical kinetics based on the ideas of cooperative phenomena, of radiationless electron transitions, of quantum mechanical tunneling of chemical species.

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