



Determination of the Mössbauer parameters of rare-earth nitroprussides: Evidence for new light-induced magnetic excited state (LIMES) in nitroprussides

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ABSTRACT

Nitroprussides of the rare-earth elements and some mixed rare-earth-sodium nitroprussides are studied by Mössbauer spectroscopy at ambient and lower temperatures. The high precision Mössbauer measurements reveal fine changes in the electronic configurations of the nitroprusside anions. A small increase of the quadrupole splitting reveals charge polarization effects in the nitroprusside anion caused by the oblate or prolate shape of the rare-earth ion and the lanthanide contraction. Despite the very large magnetic moment of holmium a magnetic phase transition is not observed down to 300 mK. The population of the metastable states SI and SII are evidenced in europium and scandium nitroprussides, and most likely they can be populated in all rare-earth nitroprussides. No distinct correlation between the Mössbauer parameters and the decay temperatures T_c of the metastable states are found. In a very thin surface layer strong color change, which remains stable at room temperature, is detected. A quadrupole doublet with Mössbauer parameters typical for Fe(III), low spin $S = 1/2$ state is related to a new colored photoproduct. The photoproduct is called *light-induced magnetic excited state* (LIMES) and explained with a photochemical redox reaction, which changes the valence, spin, and magnetic state of 4f–3d bimetallic complexes.

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1. Introduction

Sodium nitroprusside $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$, (SNP), well-known from the college books of chemistry attracts special interest since the pioneering work of Hauser et al. has been published [1]. It is shown there that after irradiation of the SNP crystals with coherent light in the spectral range 350–580 nm at low temperatures two excited metastable states are coexisting with the ground state (GS). Both metastable states SI and SII have practically infinite lifetime below 200 and 150 K, respectively. The change of the crystal color (the so-called photochromatic effect) in such materials is a molecular effect and could be localized within the molecules or cluster of molecules, thus opening the possibilities for optical information storage with extremely high density [2]. The low critical temperature T_c at which the states decay, however, does not allow practical applications. Extremely high decay temperature of about 290 K was measured for SI excited state in irradiated *trans*- $[\text{Ru}(\text{NH}_3)_4 \cdot (\text{H}_2\text{O})\text{NO}]\text{Cl}_3 \cdot \text{H}_2\text{O}$ and *trans*-

$[\text{Ru}(\text{NH}_3)_4(\text{OH})\text{NO}]\text{Cl}_2$ ruthenium nitrosyl complex [3], which suggests that in the near future new materials working above room temperature might be found.

Population, depopulation and transition (SI into SII) dynamics as a function of the intensity, wavelength, polarization, and duration of the light exposure have been precisely studied for the SNP crystals only [4,5]. The high efficiency of the population and the easily obtainable large single crystals, however, made both sodium and guanidinium nitroprusside $(\text{CN}_3\text{H}_6)_2[\text{Fe}(\text{CN})_5\text{NO}]$, (GNP) [6] the most appropriate materials for systematic studies of the physical nature of the light-induced metastable states. The light-induced photochromatic effects have been extensively studied in a large number of pentacyanonitrosyl complexes containing various transition metal cations [7,8].

The detailed knowledge of the population conditions for SNP made it possible to determine exactly the Mössbauer parameters of the metastable states SI and SII. Assuming the Mössbauer isomer shift (IS) of GS at 77 K as a reference point: IS = 0.00 mm/s (or –0.191 mm/s relative to the α -Fe standard at room temperature), large changes were measured for SI and SII states, the values of IS being +0.178(3) and +0.194(3) mm/s, respectively. The value of the quadrupole splitting, ΔE_Q for the GS is +1.716(3) mm/s,

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while those measured for SI and SII are +2.755(3) and +2.862(3) mm/s, respectively [9].

There is a long-standing controversy regarding the structural changes between the excited states SI, SII, and GS in SNP. It was proposed by neutron-diffraction studies [10–12] that only a small change in the Fe–N bond length ($\approx 0.05 \text{ \AA}$) and in the C–Fe–N angle ($\approx 3.5^\circ$) are the rearrangements in the structure relevant to the excitation of SI and SII. The main molecular symmetry axis, N–C–Fe–N–O, remains unchanged. The X-ray diffraction (XRD) studies by Coppens and coworkers [13], however, gave totally different results and provided a physical explanation of the nature of the observed metastable states. In the SI state the $(\text{NO})^+$ -group is inverted, forming a new, so-called, isonitrosyl structure with bonding N–C–Fe–O–N. In the SII state a side-on molecular configuration for the $(\text{NO})^+$ -group and seven-coordinated iron atom was proposed. The XRD data are supported by density functional theory (DFT) calculations [14–18], IR and Raman studies of ^{15}N , ^{18}O and ^{54}Fe isotope-substituted nitroprussides [19,20], as well as nuclear inelastic scattering of a ^{57}Fe enriched GNP single crystal [21,22]. New neutron-diffraction studies confirmed that the metastable state SI indeed corresponds to isonitrosyl configuration of the $(\text{NO})^+$ -group [23], and a side-on bonded configuration of NO in the metastable SII state [24].

Investigations on a series of nitroprussides with different counter cations, and determination of the Mössbauer parameters like IS, ΔE_Q and the probability of recoilless absorption (the so called Lamb–Mössbauer factor f_{LM}) at room and liquid nitrogen temperatures, have shown that small changes in the values of these parameters could originate from a number of factors like the valence state of the counter ions and their number in the unit cell, the counter ion radius and its electronegativity, the number and the orientation of the NP-anions, the presence of crystallization water and its quantity, the space group in which the corresponding nitroprusside crystallizes, and many others. No distinct correlation between the Mössbauer parameters and the important decay temperature T_c of the metastable states was observed [7].

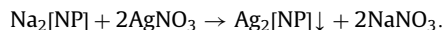
In continuation of the studies on the photochromatic effects in various nitroprussides, aiming to get more insight in this phenomenon with potential practical applications, a series of nitroprussides with rare-earth (RE) cations was selected. The RE elements have been chosen as counter ions due to the following advantageous properties: (1) the valence (oxidation state) of the RE cations is always +3; (2) the stoichiometry of the corresponding nitroprussides is always $\text{RE}_2[\text{NP}]_3 \cdot x\text{H}_2\text{O}$; (3) there are reasons to suppose that the number of the RE cations and the nitroprusside anions is the same in the unit cell of all RE nitroprussides; (4) the radius of the RE cations monotonously decreases from 103 pm (La) to 86 pm (Lu), the so-called lanthanide contraction. On the other hand, the radius of scandium is 75 pm and the one of yttrium is 90 pm; (5) the electronegativity of the RE ions vary slightly, being 1.0 for Eu, 1.2 for Sc and 1.1 for the others and (6) the way of filling the 4f shell (according to the Hund's rules), the change of the quantum numbers and their magnetic moments are well-known [25]. We report here a systematic study of the Mössbauer parameters of these compounds performed at ambient temperature. Population experiments were carried out on polycrystalline samples and confirmed the accessibility of light-induced metastable states in the nitroprussides containing RE elements, too. Moreover, a change in the color of these nitroprussides, which remains stable at room temperature, was observed. Evidence for a new light-induced magnetic excited state (LIMES), observed for the first time in nitroprussides is provided. Such photo-induced changes in valence, spin, and magnetization at low temperatures have been discovered for Prussian blue analogs [26]. Accordingly, in the current paper the possibility of coexistent

light-induced metastable states, such as SI and SII, and the new LIMES in the RE nitroprussides are discussed.

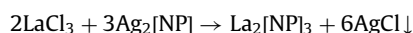
2. Experimental section

2.1. Samples

The chemical preparation of the RE nitroprusside solutions was carried out in two exchange reaction steps. In the first step on the basis of commercial SNP and silver nitrate (all the reagents used were of AR grade), silver nitroprusside was precipitated from aqueous solutions by the following reaction:



In the second exchange reaction treatment of the washed silver nitroprusside precipitates with the corresponding RE chlorides, for example LaCl_3 in water,



yielded an aqueous solution of the required RE nitroprusside after stirring of the reaction mixture in dark for 20 h. The obtained precipitate of silver chloride was filtrated and the required RE nitroprusside was isolated after evaporation of the solvent. Attempts for single crystal growth from aqueous solutions by slow evaporation of the solvent were unsuccessful, and only polycrystalline powder samples, with unknown quantity of crystallization water, were obtained. The water would slightly influence on the Coulomb interactions between the counterion and the neighboring cyanide ions but do not influence strongly the population of the metastable states because they were observed with large population in waterless single crystal as for example GNP [6]. Synthesis with Pm was not performed, since this element has only radioactive nuclides.

2.2. Mössbauer study

The Mössbauer absorbers were prepared by pressing a powdered mixture of the investigated nitroprusside and polyvinyl alcohol (PVA). The spectra were obtained using a standard spectrometer working in a constant acceleration mode. A NaI(Tl) scintillation detector with a very thin (0.1 mm) scintillator or proportional counter filled with 90/10 mixture of argon/methane were used to detect the Mössbauer γ -quanta (14.4 keV). The measurements were performed in transmission geometry at room temperature, 77 and 4.2 K. The measurements at 300 mK were carried out with a HeliOX cryostat from Oxford Instruments. The cryostat works with a ^3He closed-cycle refrigerator and allows measurement between 300 mK and 4.2 K. The measurements at 4.2 K in an external magnetic field $\mathbf{B} = 7 \text{ T}$ (wave vector of the γ -quanta $\mathbf{k} \parallel \mathbf{B}$) were carried out with a SpectroMag 4000 cryostat equipped with a superconducting magnet from Oxford Instruments.

We emphasise several methodological characteristics of the room temperature Mössbauer measurements. Since the results from [7] show that the expected differences in the Mössbauer parameters are very small, we used a new $^{57}\text{Co}[\text{Rh}]$ source with activity of 45 mCi, which allowed acquisition of a spectrum with very high statistics (more than 10^7 pulses per channel, with 500 channels used) only for one day. The spectrometer was calibrated in the beginning and at the end of each measurement, and the average values of the calibration constants were used for calculation of the Mössbauer parameters of the studied RE nitroprusside. A single crystal b-cut of SNP, with parameters $\Delta E_Q = 1.7048 \text{ mm/s}$ and $\text{IS} = -0.257 \text{ mm/s}$ relative to $\alpha\text{-Fe}$ at room temperature (after [27]), was used for calibration. The

experimental uncertainty at these conditions was estimated to be ± 0.002 mm/s.

2.3. Population conditions

The efficiency of the generation of excited states depends on the angle between the main axis N–C–Fe–N–O of the nitroprusside anion and the plane of polarization of the incident light. For polycrystalline samples or unpolarized light this angle is not defined and takes all possible values between 0° and 180° . Usually, 10–15% of the nitroprusside anions can be transferred into the SI and SII. For the population experiments with RE nitroprussides a very simple and cheap self-made irradiation cell of 12 light-emitting diodes (LEDs) described in [6] was used. Each of the diodes mounted on the irradiation cell emits unpolarized light in the blue spectral region centered at 470 nm, in the green spectral region centered at 505 nm, and in the red spectral region centered at 625 nm with an intensity of 5, 16 and 5 cd, respectively. The irradiation cell works under conditions of the continuous-flow cryostat at all temperatures down to 4.2 K.

3. Results and discussion

3.1. Mössbauer parameters

It has already been reported in our previous study [7] that the value of one of the main Mössbauer parameters, the IS, is slightly dependent on the type of the counter cation in the composition of the nitroprussides. The measured values for the IS and other parameters of the studied RE nitroprussides are summarized in Fig. 1. As can be seen, the ISs are very close to the value $-0.004(2)$ mm/s relative to the standard SNP at room temperature. Maximum deviation, but not substantially different, from this value is observed in yttrium nitroprusside (Y_2NP_3), $IS = +0.003(2)$ mm/s.

Structural data on various nitroprussides show that the counter ions are bound to the equatorial cyanide groups. The main component of the electric field gradient (EFG), V_{zz} , is perpendicular to the equatorial plane of the nitroprusside anion and collinear with the main symmetry axis, N–C–Fe–N–O. The EFG is axially symmetric, so that $V_{xx} = V_{yy}$, which would imply a zero asymmetry parameter η . The slightly distorted NP-octahedron with nearly $4m$ symmetry, however, results in a small, but non-negligible value of $\eta = 0.02$ [22].

The Coulomb interactions between counter ions and the neighboring cyanide ions are more pronounced when the radius of the counter ion is smaller. This results in an increase of the radial components of the EFG and a small decrease in the asymmetry of the central iron ion geometry. Therefore this diminishes the difference between the radial, V_{xx} and V_{yy} , and axial, V_{zz} , components of the EFG resulting in a smaller value of the quadrupole splitting, ΔE_Q . In the case of frozen-solution measurements (with low concentration of SNP), where the individual nitroprusside anions are supposed to be relatively free, the value of ΔE_Q is found to be $+1.950(2)$ mm/s [7]. In the solid state (for example SNP) the measurements give the ΔE_Q equal to $+1.704(2)$ mm/s. The Mössbauer spectrum of a powder sample of SNP, recorded at room temperature, is shown in Fig. 2a. As a comparison, the Mössbauer spectra of mixed samarium–SNP ($SmNa[NP]_2 \cdot 7H_2O$) with $\Delta E_Q = +1.804(2)$ mm/s and samarium nitroprusside (Sm_2NP_3) with $\Delta E_Q = +1.832(2)$ mm/s, are presented in Fig. 2b and c, respectively. The differences in the ΔE_Q are not large, but larger than the experimental uncertainty and are in accordance with the expected tendency, i.e. increase of the ΔE_Q

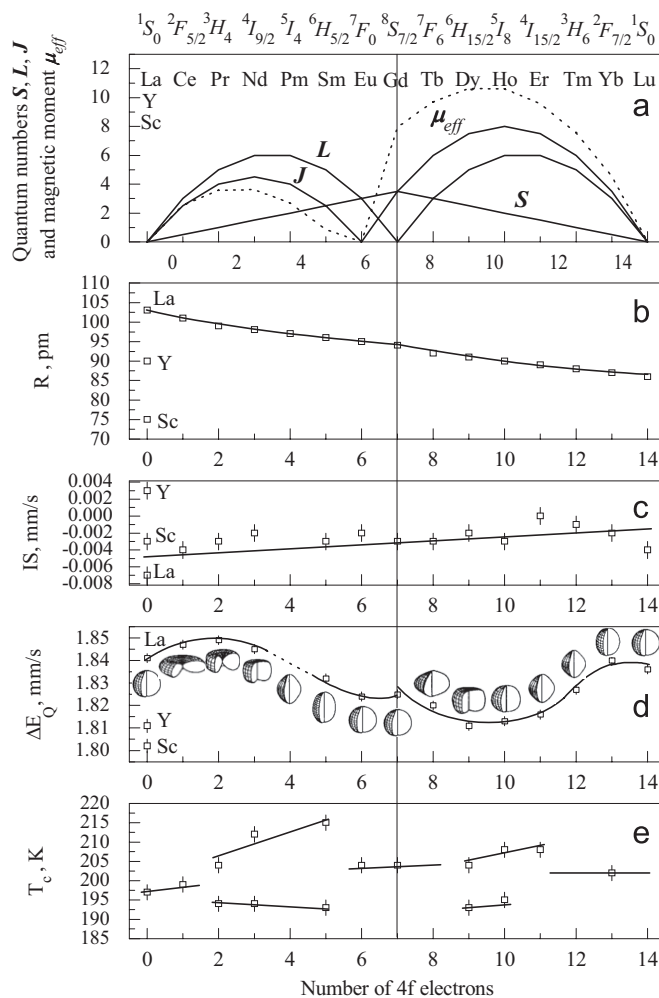


Fig. 1. Summarized data for: (a) quantum numbers of the RE³⁺ cations: S—total spin angular momentum, L—total orbital angular momentum, J—total angular momentum and μ_{eff} —magnetic moment, the spectral term $^{2S+1}L_J$ associated with the ground state; (b) atomic radius, R, of the RE³⁺ cations; (c) isomer shift (IS), relative to the standard SNP at room temperature; (d) quadrupole splitting, ΔE_Q and the electronic charge distribution of the corresponding RE³⁺ cations are also shown after [28]; (e) critical temperature, T_c , at which the metastable state SI decays, after [32].

value with the increase of the counter ion radius. In general, the values of ΔE_Q for the RE nitroprussides are higher compared to the values of the SNP falling in the range from +1.81 to +1.85 mm/s.

On the other hand, another tendency in the change of the ΔE_Q values of the studied RE nitroprussides is observed, which cannot be explained only with the values of the cation radius. The measured values of ΔE_Q are given in Fig. 1d as a function of the electronic configuration of the corresponding lanthanide ion from La to Lu according to the Hund's rule for occupation of the atomic orbitals. Moreover, geometrical representation of the electronic charge distribution of the corresponding RE cations is also given in Fig. 1d after [28]. The observed changes in the ΔE_Q values could be described as an undulating line having maximum values for Ce, Pr and Nd, and minimum for Dy and Ho. A possible explanation of this alteration could be the anisotropy of the electron density distribution of the lanthanide cations. La³⁺ ($4f^0$, no electrons in the 4f shell), Gd³⁺ ($4f^7$, half-filled 4f shell) and Lu³⁺ ($4f^{14}$, completely filled 4f shell) cations are spherically symmetric. From a quantum mechanical point of view, the asymmetry of the electron charge distribution for Ce, Pr, Nd are well-pronounced and the ions have an oblate shape, while Pm, Sm and Eu have a prolate shape.

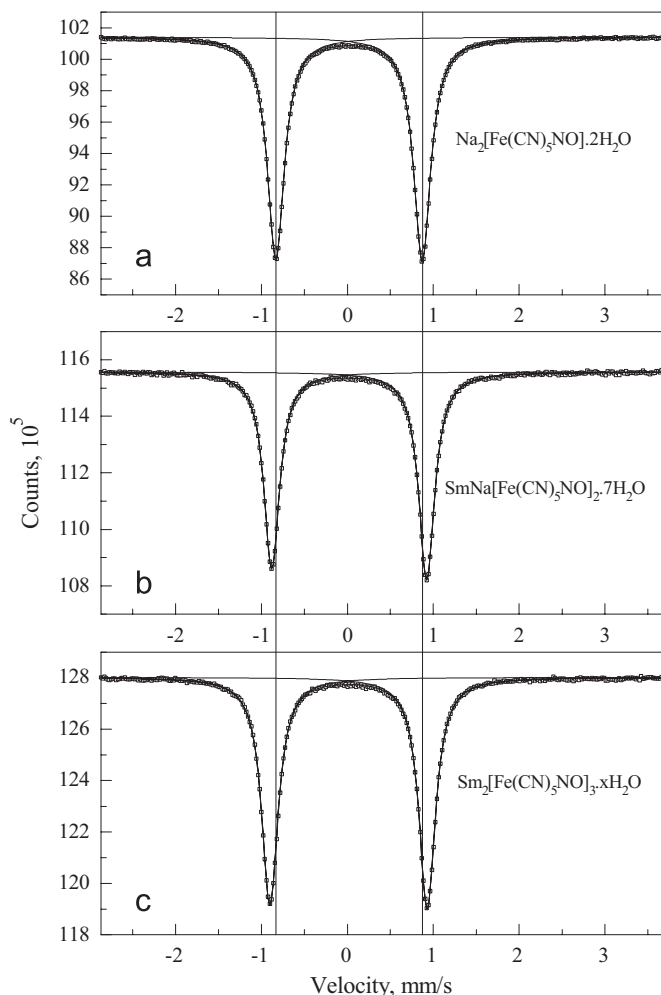


Fig. 2. Mössbauer spectra of: (a) sodium nitroprusside; (b) mixed samarium–sodium nitroprusside; (c) samarium nitroprusside, all recorded at room temperatures on powder samples. The vertical lines mark the position of lines in the Mössbauer spectrum of the standard. Velocity scale is related to the standard, SNP at room temperature.

Passing from Gd^{3+} to Lu^{3+} again an asymmetrization of the electron charge distribution is present; Tb, Dy and Ho possess an oblate shape, while Er, Tm and Yb ions exhibit a prolate shape (see Fig. 1d). The observed small differences in the ΔE_Q values of the different RE nitroprussides could be explained with the slight polarization effects of the electron density of the nitroprusside anions caused by the asymmetry of the charge distribution of the counter RE cations. Unfortunately, these small differences (± 0.1 mm/s) in the ΔE_Q values can hardly be confirmed by the means of computational chemistry.

The experimental line widths of the observed Mössbauer lines are within the range 0.226–0.240 mm/s, which is very close to the smallest measurable values for absorbers with non-zero thickness. Using the same spectrometer, and radioactive source, and single crystalline GNP we measured a value of 0.213(2) mm/s for the experimental line width extrapolated to zero absorber thickness [29]. The reported here small values of the experimental line widths suggest the presence of only one crystallographic site of the Mössbauer atom in the RE nitroprussides with relatively good crystalline quality.

The ratio of the left hand and right hand line intensities of the quadrupole doublets in most cases differ from 1 only by few hundredths. Taking into account that the measurements are performed on powder samples pressed in PVA most likely the

detected asymmetry results from a slight texture within the absorber rather than from vibrational anisotropy and Goldanskii-Karyagin effect [30].

Measurements of the recoilless absorption probability were not performed for this series of nitroprussides. Previous study [7], including Ce_2NP_3 , suggested that practically all nitroprussides with inorganic lattice cation show Lamb–Mössbauer factor of about 0.3–0.4 at room temperature reaching the values of 0.5–0.6 at 77 K.

The Mössbauer parameters obtained at low temperatures (77 and 4.2 K) revealed the same tendencies as the ones observed at room temperatures, i.e. an average increase of the IS by 0.07 mm/s at 77 K, which is due to the well-known second order Doppler effect [30].

In the RE nitroprussides with large magnetic moment of the RE cations a possible magnetic phase transition at low temperatures is expected. Due to the high magnetic moments (in the order of $10.6\mu_B$) the transition is most likely to be observed in the case of Ho^{3+} and Dy^{3+} . On the other hand, the distance between the RE cations in the corresponding RE nitroprussides is about 5.6 Å (through space) and about 8 Å (along the sequence RE–C–N–Fe(II)–C–N–RE). In the latter case the RE cations are separated by diamagnetic cyanide bridges and a Fe(II) center, which is known to be in a low spin ($S = 0$) diamagnetic state. In the case of such large distances between the paramagnetic centers the possible magnetic ordering could not be observed even at

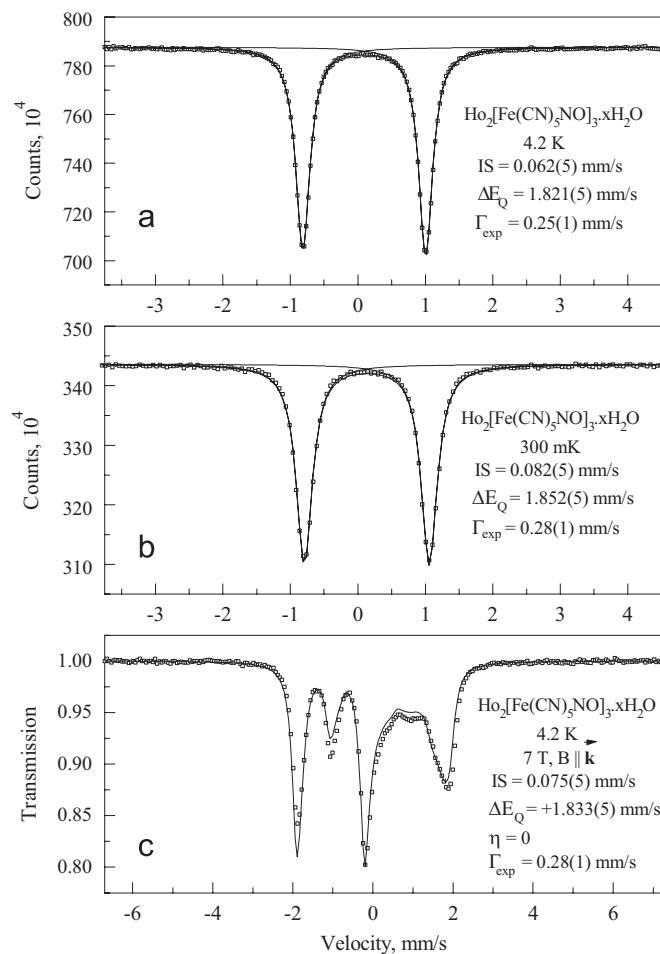


Fig. 3. Mössbauer spectra of holmium nitroprusside recorded at (a) 4.2 K; (b) 300 mK and (c) 4.2 K and external magnetic field, B, with intensity of 7 T applied parallel to the wave vector of the γ -quanta \mathbf{k} . Velocity scale is related to the standard, SNP at room temperature.

extremely low temperatures. In Fig. 3a the Mössbauer spectrum of Ho_2NP_3 , recorded at liquid helium temperature is presented. At this temperature the studied RE nitroprusside is in paramagnetic state and the Mössbauer spectrum is a quadrupole doublet. The Mössbauer spectrum recorded at the lowest possible temperature (300 mK) is shown in Fig. 3b. Even in this case no magnetic ordering is detected. The same result was obtained when an external magnetic field of 7 T was applied (at 4.2 K), Fig. 3c. The spectrum shows magnetic splitting; however, the value of the effective magnetic field is equal to the intensity of the external magnetic field. Due to the high intensity of the applied magnetic field the left hand line of the doublet overlaps with the right hand one of the triplet. The position of the triplet (in the left at lower energies) and the doublet (in the right at higher energies) unambiguously shows that the gradient has a positive sign, which has been confirmed in other nitroprussides [6,9,29,31] and most likely applies for all nitroprusside compounds. The asymmetry parameter is again close to but not exactly zero, which is typical for nitroprusside anions due to the octahedral surrounding of the iron atom and the very small deformation of the nitrosyl group.

3.2. Photo-induced changes

Like in all investigated nitroprussides so far the population of the two new states, stable at temperatures below 150 and 200 K, has been observed also in the RE nitroprussides. In some of them accessible as large single-crystals the population conditions have been studied in detail, which however, is not the case of the RE nitroprussides. In the opposite, the available experimental data are incomplete, rather contradictory, and mainly based on private communications [32]. Fig. 1e summarizes the available experimental data. A new, especially interesting, and disputable result is the double exothermal effect detected by the differential scanning calorimetry (DSC) scan during the depopulation of the SI state at about 200 K. After irradiation of powder samples with an Ar^+ laser (457.9 nm) at 80–90 K the temperature is controllably increased up to 300 K measuring the enthalpy difference between the irradiated and non-irradiated, reference sample. Since the decay of the metastable states is an exothermal process, one observes peaks at the corresponding decay temperatures T_c [33]. In some of the RE nitroprussides a double exothermal peak corresponding to the decay of the SI is detected, Fig. 1e. In case of SmNP, for example, the notable difference between the decay temperatures 193 and 215 K results in well-separated exothermal peaks. Among the proposed explanations of this effect are the coexistence of two crystal structures of the RE nitroprussides due to the different amount of crystalline water, the presence of crystalline and amorphous components, influence of the surface layers, impurities, etc. [32].

The first photoswitching experiments on RE nitroprussides (La and Gd) are described in [22], and most likely the new metastable states can be produced in all RE nitroprussides. Europium nitroprusside is a new, especially important example, which we discuss below. Fig. 4a shows the Mössbauer spectra of EuNP obtained at 77 K, while Fig. 4b shows the Mössbauer spectrum of the sample both irradiated with blue light emitted from LEDs and measured at 77 K. As in all other nitroprussides the metastable states SI and SII are populated up to 10–15%, which is typical for powder samples. The color change occurs only in a thin surface layer of a few micrometers and such micro quantity cannot be detected by transmission Mössbauer spectroscopy. Therefore presence of a subspectrum, which can be assigned to the changed surface layer, is not observed. In order to increase the quantity of the light-induced and color-changed phase, the irradiation of

about 1 g of EuNP was carried out for a long time (about four weeks) accompanied by everyday mixing of the material. Fig. 4c shows the resulting Mössbauer spectrum measured at 77 K and a photograph of the color-changed phase. Similar experiments have also been performed on iron nitroprusside [34,35]. In the case of EuNP, however, one observes the formation of a photoproduct with a rather complicated Mössbauer spectrum consisting of one singlet and one or two doublets, Fig. 4c. These results have to be considered with caution because the irradiation has been performed at room temperature and the observed changes are most likely induced by photochemical reactions. A considerable decrease of the sample weight after the irradiation has also been detected, which confirms the chemical changes of the composition. Most likely the entire NO^+ and CN^- groups are released yielding Prussian blue analogs $[\text{Fe}^{\text{II}}(\text{CN})_6]$ with singlet line Mössbauer spectrum, and even if NP would be destroyed, Fe^{2+} ions were present as lattice cations with a Mössbauer doublet exhibiting large values for the IS and ΔE_Q .

In order to characterize the photoproduct, which is formed after irradiation of the sample at low temperatures, and which in our view differs from the photochemical product, obtained after the room temperature irradiation, nearly the same set of measurements were carried out with scandium nitroprusside, $\text{Sc}_2[\text{Fe}(\text{CN})_5\text{NO}]_3 \cdot x\text{H}_2\text{O}$ (ScNP). The ScNP was selected due to (1) the high Fe concentration (22.7 wt%) in water-free scandium nitroprusside, for comparison in EuNP the value is 17.6 wt%; (2) the mass absorption coefficient of ScNP is $19.5 \text{ cm}^2/\text{g}$, which is more than two times lower than in EuNP ($43.7 \text{ cm}^2/\text{g}$). In order to increase the surface-to-volume ratio and thus to enhance the contribution of the photoproduct generated predominantly at the surface in the total Mössbauer spectrum the sample surface thickness was made very small 3–5 mg/cm^2 . Fig. 4 shows room temperature Mössbauer spectra of ScNP before irradiation (d) and at 77 K measured after irradiation (e). The inset shows a photograph of the light illuminated area and the γ -beam transmitted (measured) area, obtained at room temperature after the experiment. Fig. 4f shows the Mössbauer spectrum of the same sample measured at room temperature and only from the sample area characterized with the strongest color change. The inset in this figure shows shielded areas by Pb foils and the measured area of the sample. The Mössbauer spectra measured at 77 K, Fig. 4e, confirm the population of the metastable states SI and SII up to 8.6(5)% with parameters: $\text{IS} = 0.06(1) \text{ mm/s}$, $\Delta E_Q = 2.82(1) \text{ mm/s}$ and $\Gamma_{\text{exp}} = 0.29(1) \text{ mm/s}$. More important is the second weak quadrupole doublet (partial area 5.2(5)%) with Mössbauer parameters: $\text{IS} = 0.12(1) \text{ mm/s}$, $\Delta E_Q = 1.08(1) \text{ mm/s}$ and $\Gamma_{\text{exp}} = 0.28(1) \text{ mm/s}$, which most likely originates from a photoproduct generated predominantly at the surface layer. The insets of Fig. 4e, f show that the measured area is not the one with the highest population due to the geometrical constrains in the illumination cell. Mirror images (black dots) of the LEDs can be identified. During the room temperature measurement, Fig. 4f, we have shielded part of the illuminated area so that the γ -beam crosses only the highly populated area. Of course at room temperature the metastable states SI and SII do not any longer exist and all molecules are in the GS. However, the quadrupole doublet of the new photoproduct with partial population of 15.6(5)% and Mössbauer parameters at room temperature, $\text{IS} = -0.02(1) \text{ mm/s}$, $\Delta E_Q = 0.76(1) \text{ mm/s}$ and $\Gamma_{\text{exp}} = 0.48(1) \text{ mm/s}$, remains. It seems that in the RE nitroprussides, besides the common SI and SII states, a third state called photoproduct is produced by irradiation at 77 K and it remains stable at room temperature. This light-grey to black colored state could not be related to the blue colored Prussian blue analogs and its Mössbauer parameters are typical for a Fe(III) low spin $S = 1/2$ complex.

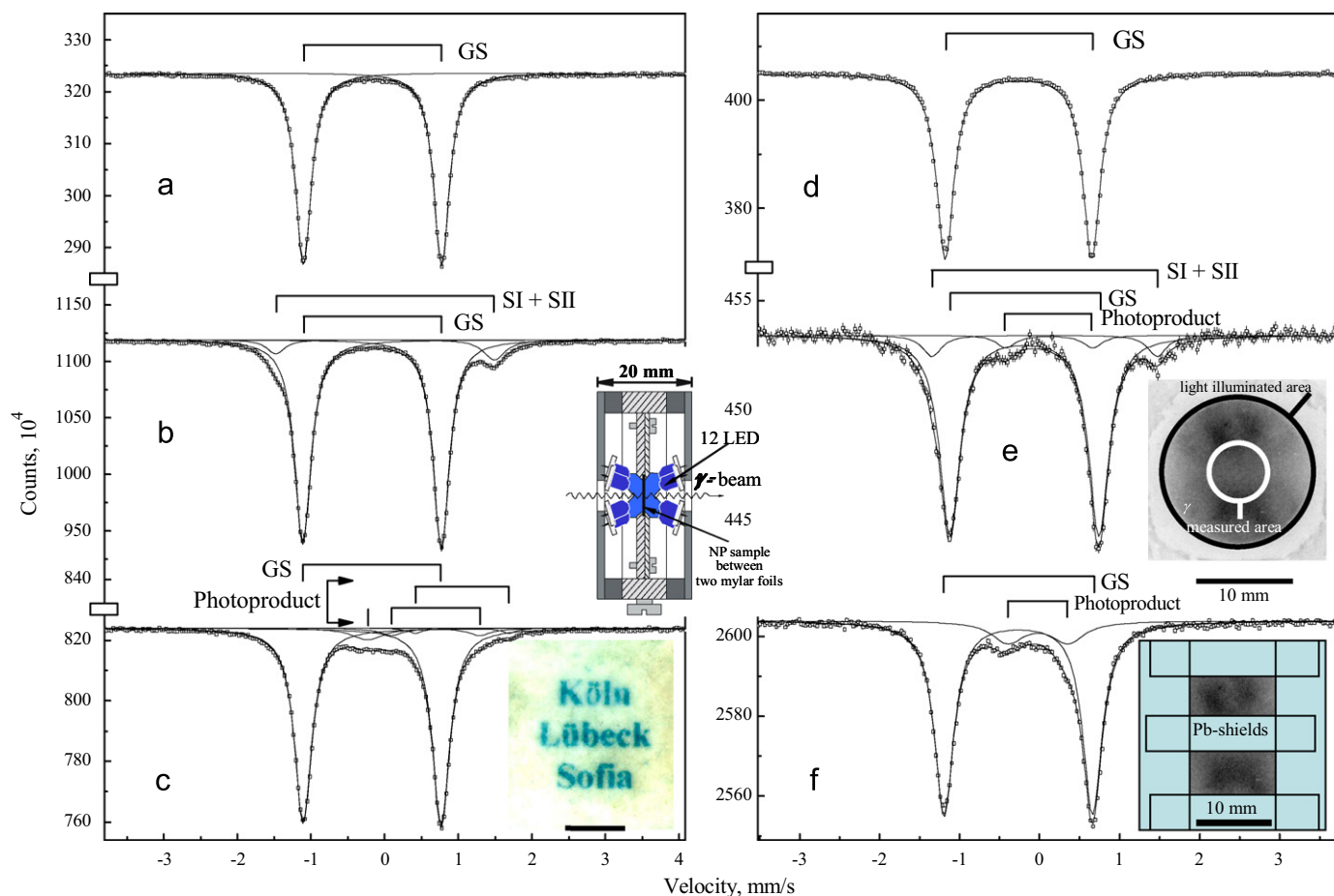


Fig. 4. Mössbauer spectra of europium nitroprusside (a) before irradiation, measured at 77 K; (b) irradiated with blue light (about 470 nm) from LEDs at 77 K and measured at 77 K. The inset shows the scheme of the irradiation cell; (c) irradiated at room temperature and measured at 77 K. The inset shows a thin europium film irradiated through a template at room temperature with blue light. Prussian blue colored inscription Köln, Lübeck, Sofia is formed due to a light-induced photochemical reaction. Mössbauer spectra of scandium nitroprusside (d) non-irradiated and measured at room temperature; (e) irradiated and measured at 77 K. The inset shows the light illuminated area and γ -beam transmitted (measured) area, the picture is taken at room temperature after the irradiation and measurement were performed; (f) Mössbauer spectrum of the same sample obtained at room temperature and only from the area with maximum change of the color. The inset shows the areas shielded by Pb-foils and the measured area. Velocity scale is related to the standard, α -Fe at room temperature.

A possible explanation for the appearance of the photoproduct state is based on an internal photochemical redox reaction. Such reaction has firstly observed in the Prussian blue analog $K_{0.2}Co_{1.4}[Fe(CN)_6] \cdot 6.9H_2O$ by Sato et al. and was named charge transfer-induced spin transition (CTIST) [26]. The irradiation with red light at low temperatures converts the iron and the cobalt atoms from low spin, diamagnetic state Fe(II, $S = 0$)–C–N–Co(III, $S = 0$) to a new excited magnetic state with an induced spin change Fe(III, $S = 1/2$)–C–N–Co(II, $S = 3/2$) by an electron transfer from Fe to Co via the cyano bridge. The photoproduct in $K_{0.5}Co_{1.25}[Fe(CN)_6] \cdot 3.6H_2O$ was characterized by Mössbauer spectroscopy [36]. Before irradiation the hexacyanoferrate shows a single absorption line (excepted IS = 0.00 mm/s), indicating the presence of only Fe(II, $S = 0$). Under illumination at 25 K in the Mössbauer spectrum a quadrupole doublet with IS = –0.06 mm/s, $\Delta E_Q = 0.93$ mm/s of Fe(III, $S = 1/2$) appeared. In the new 4f–3d cyano-bridged hetero-bimetallic compounds such as $\{RE(HP)_2(H_2O)_3(\mu-N-C)_3Fe(CN)_3\}_n$, RE = Ce, Nd, HP = 4-hydroxypyridine, the presence of a photo-induced magnetization was revealed [37]. The photo-induced magneto-optic effects in complicated RE compounds containing nitroprusside anion have also been studied by Mössbauer spectroscopy. When a solid sample was irradiated by a Xe lamp (wavelength 450 nm), *nota bene* at room temperature for 2 h no evident change occurs in both

its color and Mössbauer spectrum. Only photochemical reactions with formation of Prussian blue analogs are detected [38].

In order to explain the nature of the photoproduct in the RE nitroprussides we follow the mechanism proposed by Sato et al. [26]. At low temperatures, via the cyano bridges, from Fe(II) one electron could be transferred to the empty 3d orbital of Sc, or to the 4d orbital of Y, or to the 4f orbital, if there are still (normally there are) vacant electronic states in lanthanides, and-if 4f orbitals are completely occupied (Lu^{3+} , $4f^{14}$)–to the empty 5d orbitals in lutetium. In all cases light-induced molecular magnetism is accompanied by changes in the valence and the spin state of the 4f–3d hetero-bimetallic complex. The absorption bands in the electronic spectra of the lanthanides are divided into three types: $f \rightarrow f$, $4f \rightarrow 5d$ and ligand $\rightarrow f$ metal transitions (electron-transfer bands). The latter usually represent intense, broad bands which lie in the violet and the ultraviolet region [39]. The charge transfer means that in the LIMES, there is one more 4f electron than in the GS. New chains of the type Fe(III, $S = 1/2$)–C–N– RE^{2+} are formed and coexist with the GS Fe(II, $S = 0$)–C–N– RE^{3+} . Exactly the same structural changes and formation of a photoproduct with similar Mössbauer parameters is observed if scandium nitroprusside is irradiated with light in the green spectral region centered at 505 nm, Fig. 5a. No change occurs in both surface color and Mössbauer spectrum when

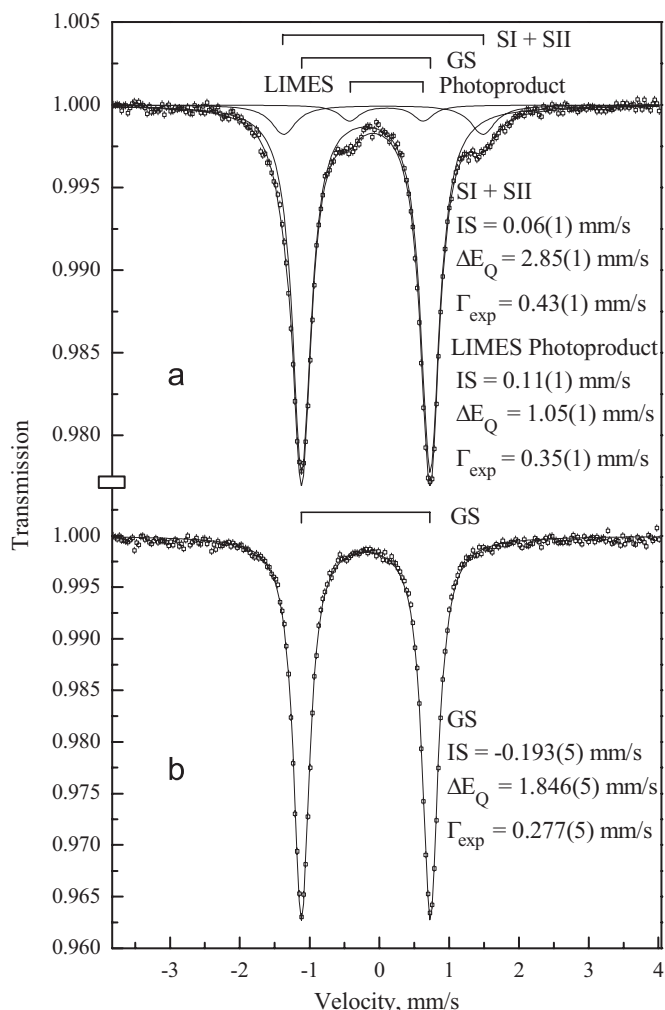


Fig. 5. Mössbauer spectra of scandium nitroprusside (a) irradiated at 77K with light in the green spectral region centered at 505 nm and measured at 77 K. The quadrupole doublets of the metastable states SI+SII and the new LIMES photoproduct are identified together with the GS; (b) no change occurs in both surface color and Mössbauer spectrum when the sample is irradiated at 77K with light in the red spectral region centered at 625 nm and measured at 77 K. Velocity scale is related to the standard, α -Fe at room temperature.

the sample is irradiated with light in the red spectral region centered at 625 nm, Fig. 5b.

4. Conclusions

All rare-earth (RE) based (without promethium, which does not have a stable isotope) and mixed RE–sodium based nitroprussides were synthesized and studied by Mössbauer spectroscopy at ambient and lower temperatures. The high sensitivity of the Mössbauer measurements verified some fine changes in the electronic configuration of the nitroprusside anion. The isomer shifts of the RE nitroprussides show very close values to that of the standard SNP. The values of the quadrupole splitting are very close to each other and fall in the range from +1.81 to +1.85 mm/s. The small differences are assigned to the polarization effects in the NP ions caused by the oblate or prolate shape of the RE ions and the lanthanide contraction. Despite of the large magnetic moments of some of the RE ions a phase transition to a magnetically ordered state was not observed down to 300 mK. The population of the metastable states SI and SII was evidenced in europium and

scandium nitroprussides, and most likely these photo-induced changes are typical for all RE nitroprussides.

The formation of a thin surface layer with a strong color change stable at room temperature was demonstrated in some RE nitroprussides. New quadrupole doublet with Mössbauer parameters at room temperature: $IS = -0.02$ mm/s and $\Delta E_Q = 0.76$ mm/s typical for the Fe(III) low spin, $S = 1/2$ complex was assigned to the colored photoproduct. The observed photoproduct is formed by an internal photochemical redox reaction proposed by Sato and firstly observed in Prussian blue analogs. One electron is transferred from the Fe(II, $S = 0$) nitrosyl complex, via the cyano bridges, to the RE counter ion. The iron center, thus, is transferred to the Fe(III, $S = 1/2$) state. For the first time such a light-induced magnetic excited state (LIMES), which is characterized by charge transfer and change in the valence and spin state of a $4f-3d$ bimetallic nitrosyl complex, was observed.

Due to the small penetration depth of the light in powder samples, the new LIMES as well as the metastable states SI and SII are formed in a thin surface layer of the sample. After longer illumination two different species of NP ions coexist within this surface layer: NP anions in the ground state Fe(II, $S = 0$) and in the LIMES with an Fe(III, $S = 1/2$) center. The isonitrosyl structure with inverted $(NO)^+$ -group (SI) and side-on bounded $(NO)^+$ -group (SII) can be populated in both types of NP anions. Probably the decay temperatures T_c of SI and SII in these species are slightly different, which manifests in the double exothermal effect observed in the DSC measurements.

Due to the fact that all changes, related to the creation of LIMES and metastable states SI and SII, occur only in a very thin surface layer for future investigations the method of integral conversion electron Mössbauer spectroscopy will be advantageous. Europium nitroprusside could be studied simultaneously with ^{151}Eu and ^{57}Fe Mössbauer isotopes. We have shown that at all temperatures down to 0.3 K in the RE nitroprussides the RE ions are in +3 valence state. The LIMES leads to a valence change from Eu^{3+} to Eu^{2+} resulting in a change of the isomer shift of Eu by about 10 mm/s [30], which is easily detectable and would be a direct evidence for the mechanism proposed by Sato. The change of the valence state in LIMES from Eu^{3+} to Eu^{2+} is light-induced effect not intermediate valence state. The effect was observed in RE nitroprussides as Sc and Gd [22] for which intermediate valence state is not typical.

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