Spin-lattice relaxation of Nd^{3+} and Tb^{3+} in phosphate and sodium borate silica glasses

B.M. Epel, S.B. Orlinskii, R.M. Rakhmatullin and and Yu.K. Rosenzweig
Kazan State University, Kremlevskaya str. 18, Kazan 420008, Russia
E-mail: boris.epel@ksu.ru

Abstract

The experimental study of the electron spin-lattice relaxation (SLR) of Nd^{3+} and Tb^{3+} ions in phosphate and sodium borate silica glasses was performed. Measurements were made with electron spin echo technique. Temperature dependences of spin-lattice relaxation of the rare earth ions reveal the contribution of different relaxation mechanisms. A stepped like change of the SLR rate observed for Tb^{3+} and Nd^{3+} ions was explained by cross relaxation.

1   Introduction

The study of the spin-lattice relaxation (SLR) of impurity ions in glasses is of importance as it allows one to obtain information about their spatial distribution and vibrational states in amorphous solids. The spectral density of vibrational states in inorganic glasses at low energies deviates from the Debye spectrum of crystalline solids. This is commonly supposed to be caused by contributions of two-level systems and localized vibrational excitations. Recently, a cross relaxation model was developed [1] that explained the observed SLR features of Yb^{3+} ions in the phosphate glass. It was supposed that the phase transition of tunneling two-level systems (TLS) in the orientational pseudospin glass occurs at low temperatures. The goal of this study was to find out if the similar features in SLR can be detected with another impurity ions and on another glass structure.

2   Experimental

The SLR of Tb^{3+} and Nd^{3+} ions in oxide glasses was studied. Compositions of glasses are given in the Table 1. Samples were synthesized in Vavilov Science Center in St. Petersburg.

Measurements of SLR times T1 were made on an electron-spin echo (ESE) spectrometer with a working frequency of 9.4 GHz and a time resolution of 10^{-7} s, in the temperature range of 1.6 - 7 K. The SLR time was measured with a technique in which two pulses forming the echo signal followed by a long microwave pulse saturating the spin system. The pulse sequence was long saturating pulse (1 ms) - t - $2\pi/3$ - τ - $2\pi/3$, where τ was kept constant, while t was varied. Experiments showed that the recovery profile of the ESE amplitude after the saturating pulse was non-exponential so that relaxation times were measured from the exponential tail. To avoid the sample heating some measurements were done in the liquid helium medium.

Table 1. Compositions of studied glasses

Short notation	Concentration, mol%	x Re_2O_3, mol%	
		Tb_2O_3	Nd_2O_3
PL	$75P_2O_5$+(25-x)La_2O_3+x Re_2O_3	1	1
		0.3	0.3
		0.1	0.1
			0.03
SNBL	$59SiO_2$+20Na_2O+20B_2O_3+x Re_2O_3+ (1-x)La_2O_3	1	
		0.3	
		0.1	
		0.03	

2.1 Nd^{3+} in the PL glass

Fig.1 shows the typical decay profile of SLR time of Nd^{3+} in the semi - logarithmic scale. The echo detected EPR (EDEPR) spectrum of Nd^{3+} in

the PL glass presented in fig.2. The strong modulation due to anisotropic hyperfine interaction of Nd^{3+} ions with close ^{31}P nuclei observed in the EDEPR spectrum. To avoid distortions, caused by the modulation, measurements were done at the increased time delay τ. The temperature dependences of SLR rates T_1^{-1} of Nd^{3+} ions are presented in fig.3. SLR measurements were done at three magnetic field points 0.325 T, 0.434 T, 0.56 T. Because there is no any significant dependence of SLR times

of Nd^{3+} were found for the samples on magnetic field for all concentrations, we present here the data measured at 0.56 T. At temperatures 3.5 - 5 K the dependence of $T_1^{-1} \sim T^9$ was observed. The dependence of SLR on the concentration of Nd^{3+} ions was found. We fitted temperature and concentration dependences of SLR rates of Nd^{3+} ions by the formula

$$T_1^{-1} = DT^n + CT^9, \tag{1}$$

where the first term is the power dependence typical for glasses, and the second term is the Raman process. Parameters of D, n for different ion concentrations summarized in the table 2.

Table 2. Fitting parameters for temperature dependences of SLR rates of Nd^{3+} ions in the PL glass.

Concentration, mol%	D	n	C
1	70.8±6.8	3.26±0.08	
0.3	29.5±1.6	2.32±0.15	0.0024±0.0001
0.1	6.9±1.4	2.33±0.28	
0.03	3.3±0.4	1.9±0.15	

2.2 Tb^{3+} in phosphate and sodium borate silica glasses.

The low field part of the EDEPR spectrum of Tb^{3+} ions in studied glasses is shown in fig.4 [2]. The shape of the low field EDEPR spectrum of Tb^{3+} ions was explained by the phase relaxation influence.SLR times were measured at two maxima of the spectrum at magnetic field points of 12 mT and 42 mT. Within an experimental error SLR rates were independent on the magnetic fields. Temperature dependences of SLR rates of Tb^{3+} ions in SNBL glass are
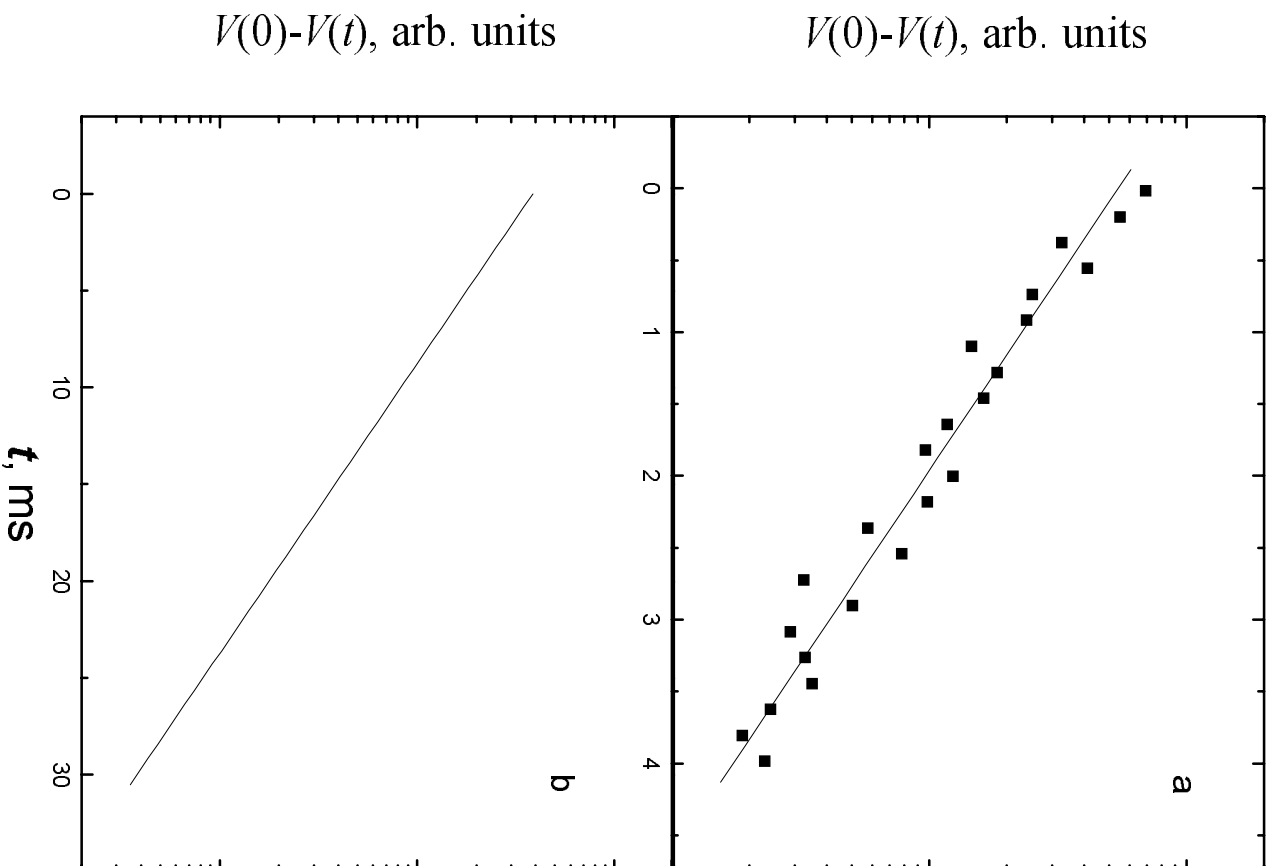
Figure 1: The recovery profile of the ESE amplitude after the saturating pulse. a - $T = 4K$; b - $T = 1.6K$. Nd^{3+} in PL, $x = 0.3mol\%$. $V(0) - V(t) = V(0)exp(-t/T1)$, where $V(t)$, $V(0)$ are echo amplitudes at time t, zero; T_1 is the spin - lattice relaxation time.

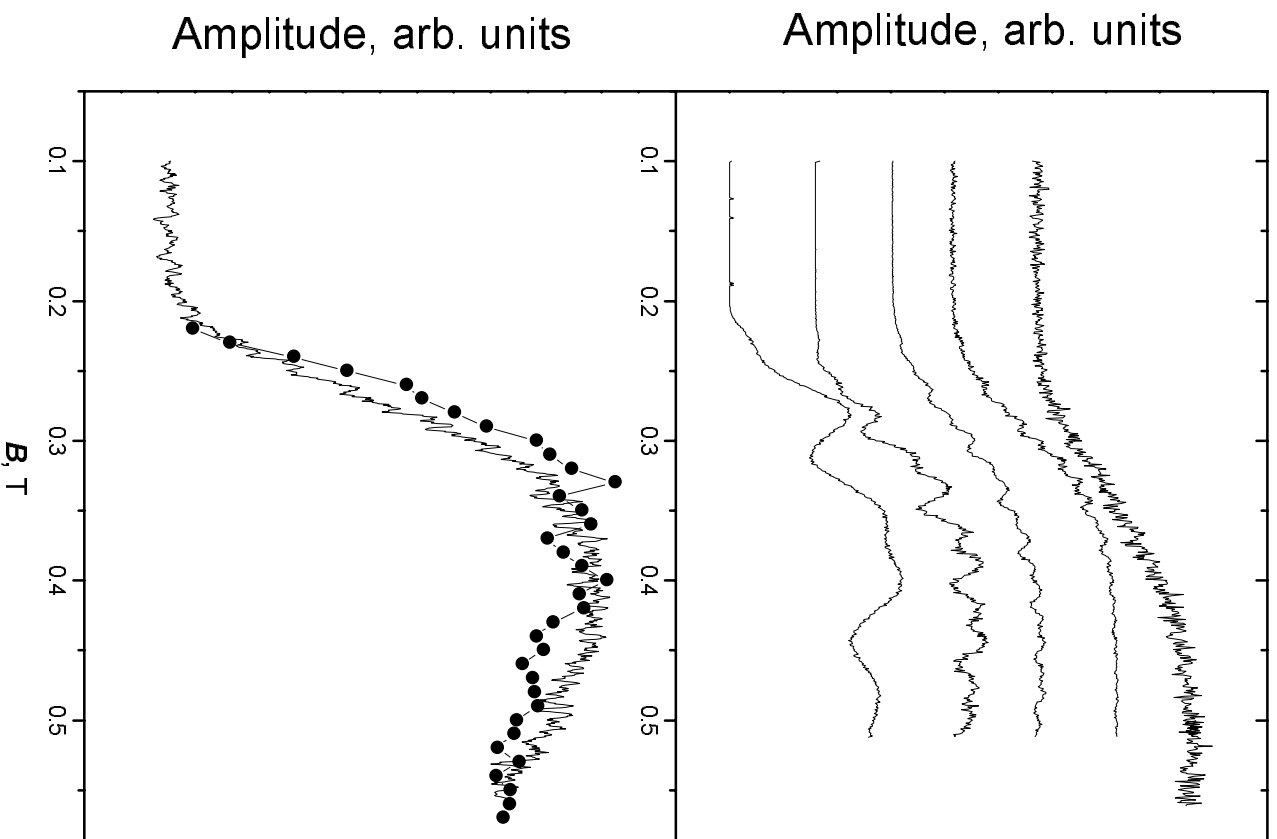Figure 2: EDEPR spectra of Nd³⁺ ions in the PL glass. a - EDEPR spectra at time delays between pulses (from top) 5.14, 4.14, 3.19, 2.14, 0.9 mks. Oscillations are due to modulation effects. b - The solid line is the EDEPR spectrum at $2\tau = 8.5$ mks, connected points are the reconstructed spectrum $V(0)$. The concentration $x = 0.03$ mol %, $T = 1.6$ K.
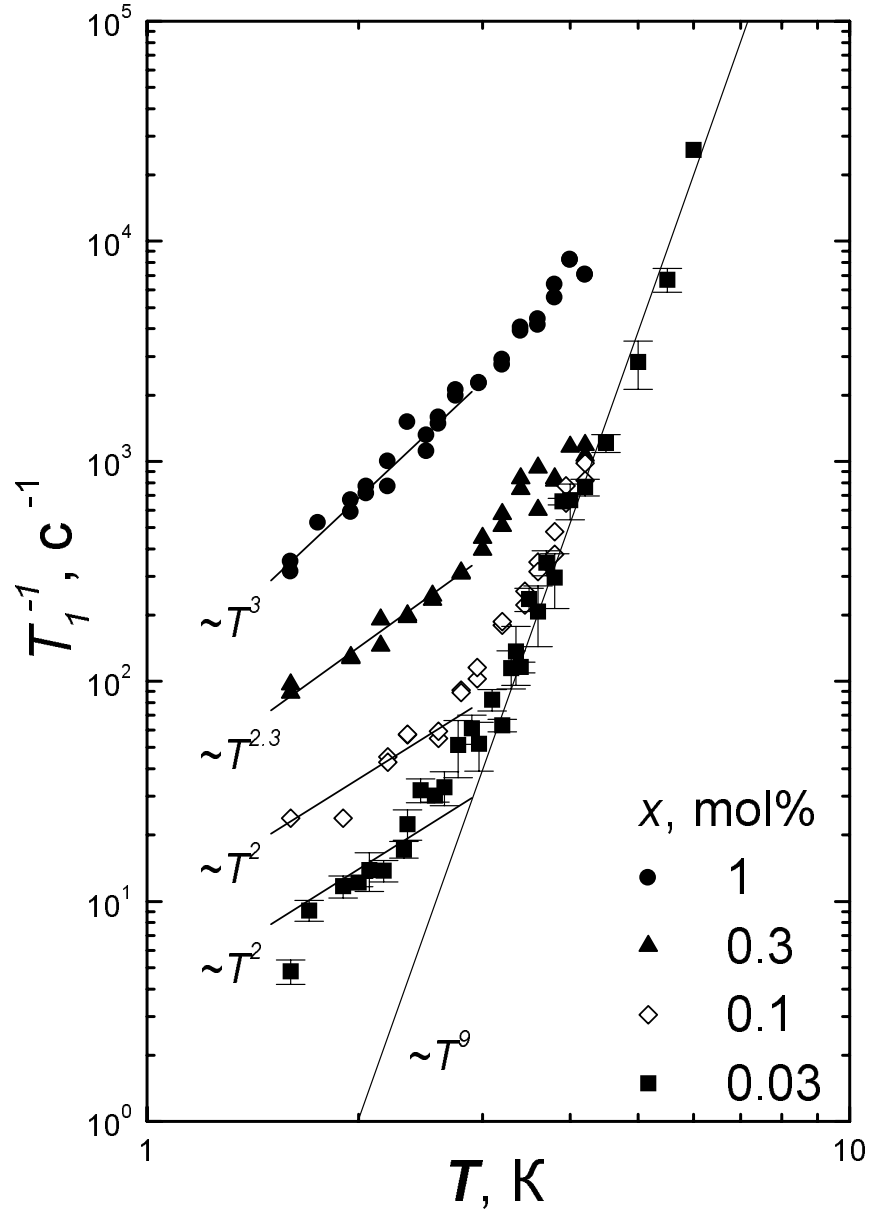
Figure 3: Temperature dependences of spin - lattice relaxation rates of Nd^{3+} ions in the PL glass. Concentrations of Nd^{3+} are denoted by x. Straight lines correspond to the dependence $T_1^{-1} \sim T^n$.
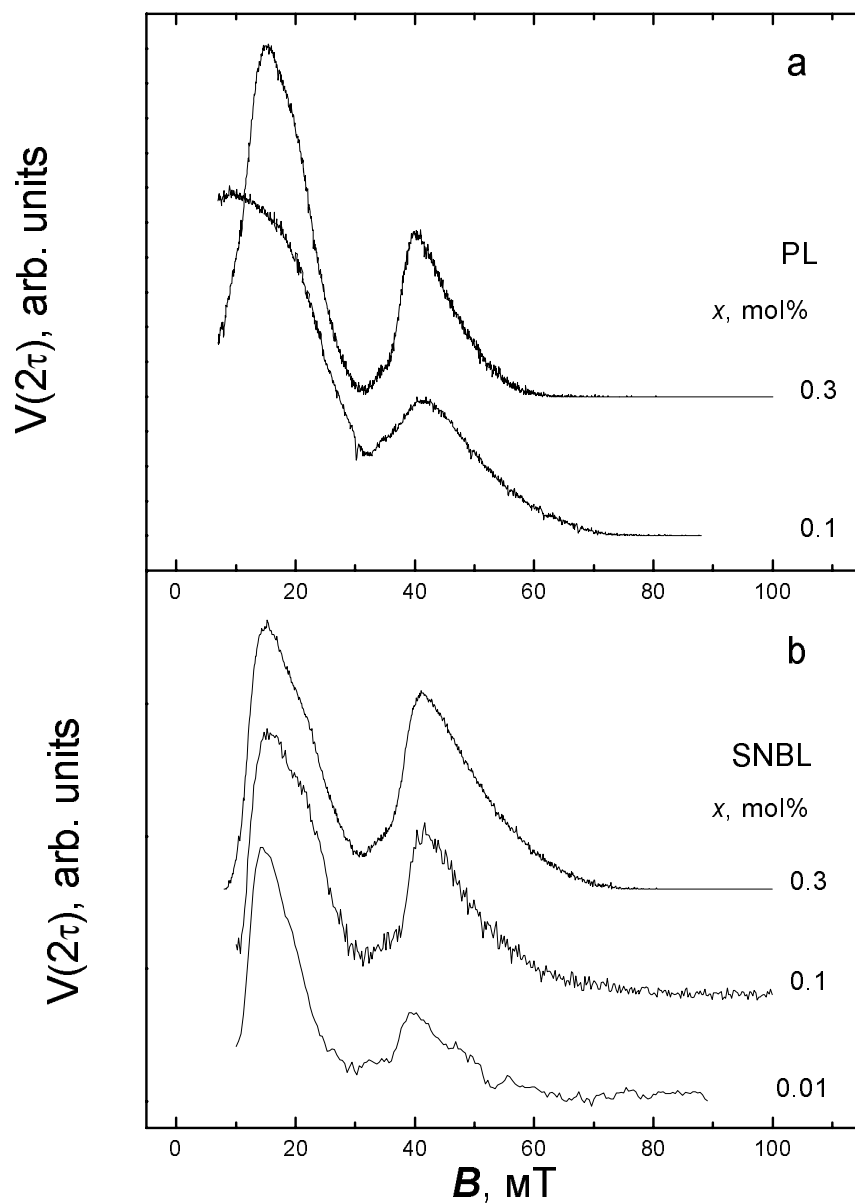
Figure 4: EDEPR spectra of Tb^{3+} ions in glasses. a - PL + xTb_2O_3, b - SNBL + xTb_2O_3. Spectra was recorded at temperature $T = 1.6K$, at the microwave magnetic field b parralel to the extenal magnetic field B, $2\tau = 0.62$ mks, the working frequency 9.35 GHz.

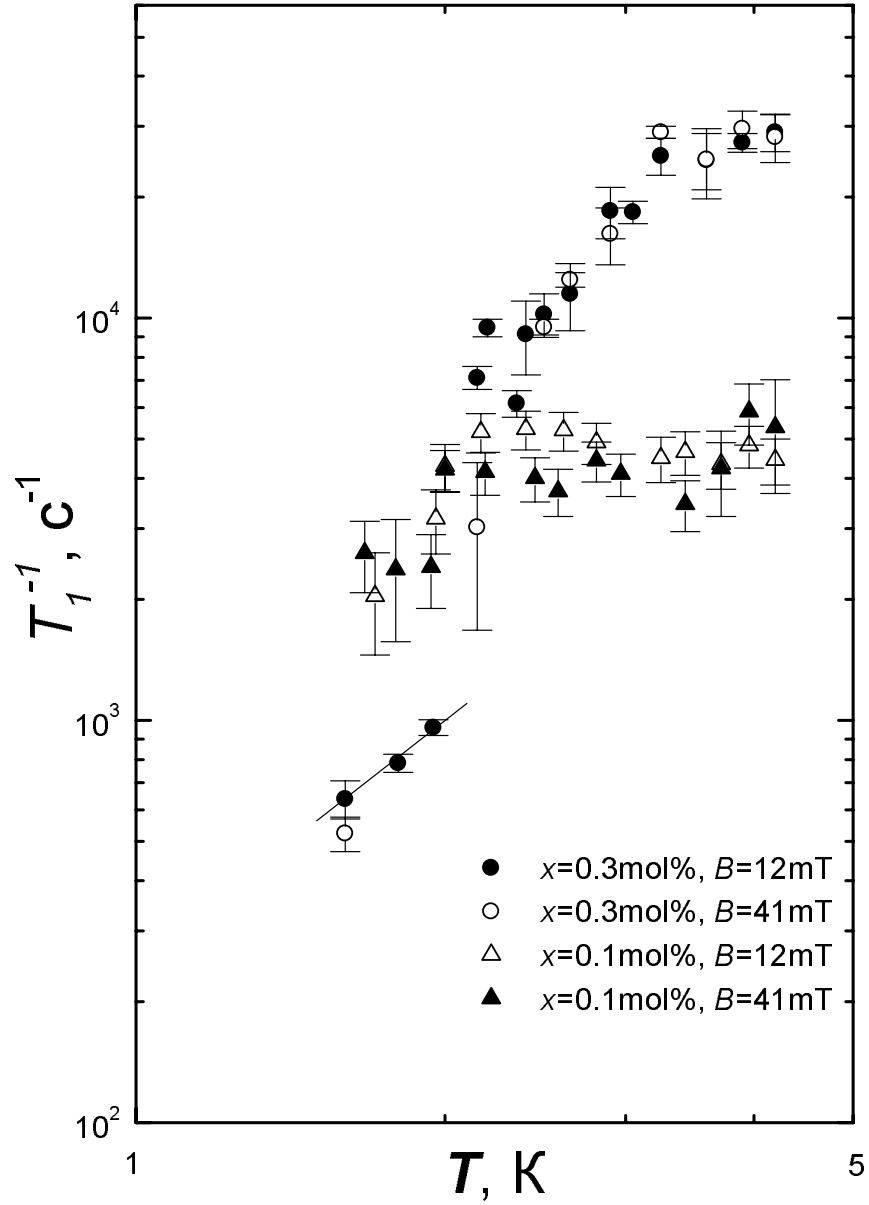Figure 5: Temperature dependences of spin - lattice relaxation rates of Tb^{3+} ions in the SNBL glass at different concentrations x and at different magnetic fields B. $\nu = 9.35$ GHz. The straight line is the dependence $T_1^{-1} = 250\ T^2$.

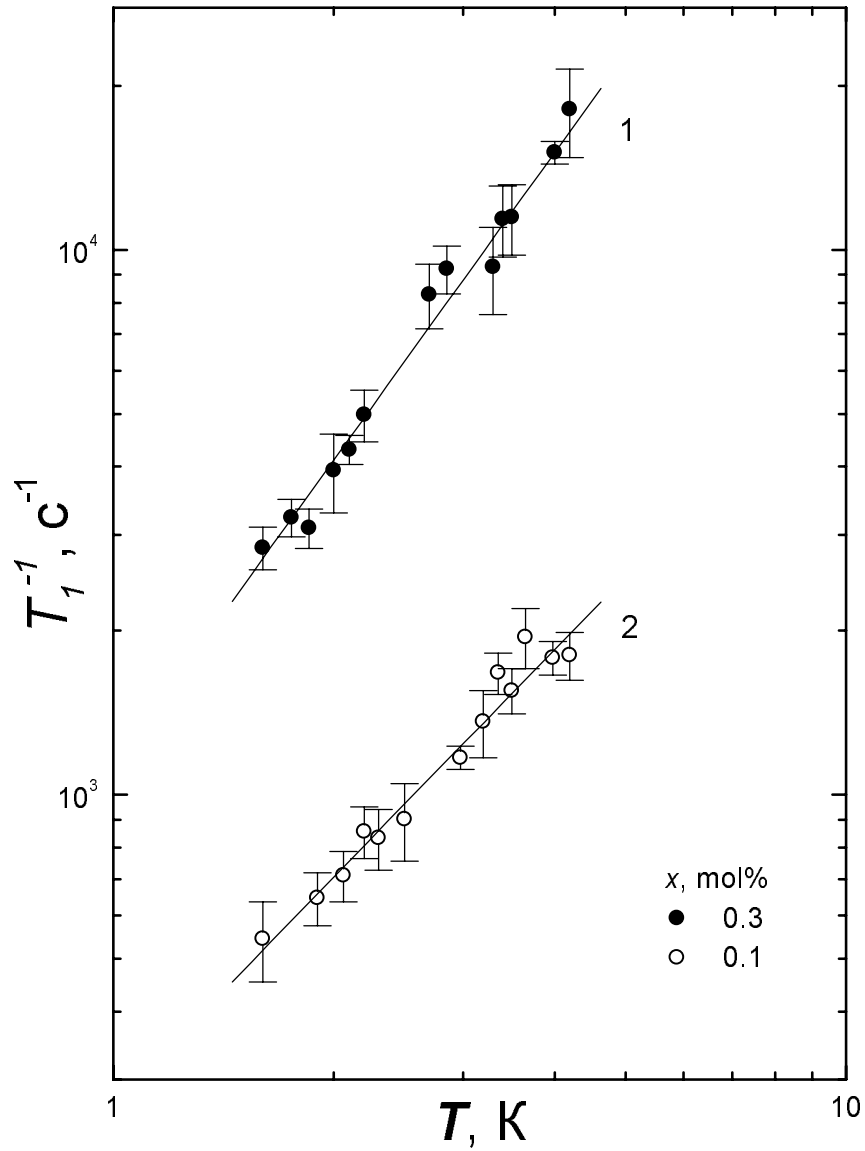Figure 6: Temperature dependences of spin - lattice relaxation rates of Tb^{3+} ions in the PL glass. $\nu = 9.35$ GHz. 1 - the dependence $T_1^{-1} = 1122\ T^{1.87}$, 2 - the dependence $T_1^{-1} = 269\ T^{1.38}$.

shown in fig.5. It can be seen that the SLR rate T_1^{-1} has the temperature independent part at a low concentration.

Temperature dependences of SLR rates of Tb^{3+} ions in the PL glass presented in fig.6 were fitted with the formula:

$$T_1^{-1} = DT^n. \tag{2}$$

Parameters of D, n for Tb^{3+} ions in the PL glass are summarized in Table 3.

Table 3. Fitting parameters of the temperature dependences of Tb^{3+} ions in the PL glass.

Concentration, mol%	D	n
0.3	1122 ± 108	1.87 ± 0.08
0.1	269 ± 19	1.38 ± 0.055

3   Discussion

Electron SLR models of paramagnetic centers in glasses were considered in several works. Orbach with coworkers [3], [4] developed the theory of SLR taking into account a localization of vibrations in amorphous media. They used the concept of localized phonons and fractons and obtained temperature dependences of SLR rates for Raman and direct processes. In case of localized fractons authors [4] deduced for the Raman like process

$$\begin{aligned} (T_1^{ave})^{-1} &\propto T^{4.63} \text{ for Kramers ions} \\ (T_1^{ave})^{-1} &\propto T^{2.63} \text{ for non Kramers ions} \end{aligned} \tag{3}$$

In case of localized phonons the temperature dependences of SLR have the same function as in crystalline solids for the Raman process

$$\begin{aligned} (T_1^{ave})^{-1} &\propto T^9 \text{ for Kramers ions} \\ (T_1^{ave})^{-1} &\propto T^7 \text{ for non Kramers ions} \end{aligned} \tag{4}$$

Neither of the predicted temperature dependences observed in our experiments. Another theory of SLR in glasses was proposed independently by Askew [5] and Stutzman [6]. They supposed that TLS are in strong interaction with the phonon system and therefore a nearby spin can relax through it. Supposing that energies of TLS considerably larger that the energies of the spin system

and that the density of the energy distribution of TLS follows to $P(E) \sim E^{\lambda}$ in some energy range $Emin \leq E \leq Emax$, they give the expression for the average SLR time

$$(T_1^{ave})^{-1} \propto T^{2+\lambda} \int\limits_{x_{\min}}^{x_{\max}} \frac{x^{1+\lambda}}{\sinh(x)} dx. \tag{5}$$

Some of the temperature dependences of SLR can be fitted with this formula, and we suppose that this indicates interaction with TLS. But the concentration dependence as well as temperature dependence $T_1^{-1} \sim T^9$ should be explained by the other or additional mechanism. The presence of temperature independent regions in SLR strongly indicates cross relaxation processes in our experiments. To explain the concentration dependence in our experiments we used the model that was applied to interpret results of the study of SLR of Yb^{3+} in the PL glass [1]. This cross relaxation model [1] takes into account the fast relaxing center (FC) which is the local paramagnetic center that tunnels between states of different wells of the many-well potential. The case of the states localized in separate wells which refers to the small value of a tunneling matrix element as compared with the natural width $1/\tau_0$ of the level or with the splitting between single-well states ΔU_{ij} within a random (defect) field was considered in [7]. The FC arises in this case [7] when the external magnetic field is applied. Namely, when the average Zeeman splitting $\beta B_0 (g_1 + g_2)/2$ is equal (with an accuracy of $1/\tau_0$) to the corresponding value of ΔU_{ij}, where g_1, g_2 are g-factors of spin states in potential wells "1" and "2" with a tunneling transition between them. In this case the states with a different spin projection being in different wells are in resonance. TLS efficiently interact with each other through the acoustic phonon field. As the temperature decreases a percolate phase transition can occur which results in the tunneling pseudospin systems in the orientational glass phase. Calculations showed that the transition temperature T_g is of the order of some Kelvin. The distribution function $g(\Delta U)$ has a minimum in the orientational pseudospin glass phase. This is related with the appearance of the near order in the pseudospin system. As a result the number of FC sharply diminishes, this leads to the sharp decrease of the SLR rate. Earlier the sharp decrease of the SLR rate of Yb^{3+} in PL was reported at $T_g \approx 2$ K. A stepped like change of the SLR rate is observed for the Tb^{3+} ion in PL. For some concentration of Nd^{3+} ions in PL the small stepped like change in SLR also was observed. The position of the transition temperature T_g is independent on the type of ion. Similar dependences were observed for the SNBL glass, where $T_g \approx 2.5$ K. Such a small difference of Tg between two glasses is consistent with theory [8].

3.1   Conclusions

Temperature dependences of SLR rates for Nd^{3+} and Tb^{3+} ions in phosphate and sodium borate silica glasses were investigated. A stepped like change of the SLR rate observed for the Tb^{3+} and Nd^{3+} ions in some concentrations. This experimental result was explained by cross relaxation theory developed in [1]. While some of the features of SLR of rare earth ions in studied glasses can be explain by separate theories, they are failed to explain all SLR features from the unified approach. This indicates the contribution of different mechanisms to the SLR of paramagnetic centers in glasses and the necessity to develop a new theory of SLR.

References

[1] Vikhnin V.S., Gromov I.A., Orlinskii S.B., Rakhmatullin R.M., Rozentsvaig Y.K. Phys. Solid State, V 37, p.818 - 824. (1995).

[2] Gromov I.A., Orlinskii S.B., Rakhmatullin R.M. Applied Mag. Res., N3, p.1147-1158. (1992).

[3] Alexander S., Entin-Wohlman Ora and Orbach R. Phys. Rev. B., V 32, N 10, p.6447- 6455. (1985).

[4] Alexander S., Entin-Wohlman Ora and Orbach R. Phys. Rev. B., V 33, N 6, p.3935- 3955. (1986).

[5] Askew T.R., Stapleton H.J. and Brower K.L. Phys.Rev. B., V 33, N 7, p.4455-4463. (1986)

[6] Stutzman M., Biegelsen D.K., and Stuke J., Bull. Am. Phys Soc., V 28, p. 532. (1983).

[7] Vikhnin V.S. Sov.Phys.Solid State, V 20, 771. (1978).

[8] Parshin D.A. Phys. Solid State, V 36, p. 991-1024. (1994).