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^{111}Cd time differential perturbed angular correlation studies of high specific activity ^{111}In in frozen aqueous solutions

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Abstract

^{111}Cd – time differential perturbed $\gamma\gamma$-angular correlation measurements have been made using the high specific activity of ^{111}In in the frozen eutectic HNO_3 and NaOH aqueous solutions at temperatures below the corresponding T_{eut}. The experimental attenuation coefficients were measured using the *slow* and *fast* (*shock*) means of freezing of the samples. In the case of *fast* freezing in both HNO_3 and NaOH solutions the formation of homogeneous phases with similar local structures as in the liquid state occurs. The observed dynamic character of the perturbation of the angular correlation is explained by mobility of the oriented and ionic defects in the ice structure.

1 Introduction

The technique of time-differential perturbed angular correlation of γ-rays (TDPAC) is a sensitive tool for hyperfine-interaction studies in condensed-matter systems with applications in chemistry, biology, nuclear medicine, and environmental research [1, 2, 3]. A key advantage of TDPAC is its applicability to extremely low concentrations (down to 10^{-15} M) [4]. The method enables determination of dynamic characteristics of molecules and their complexes in aqueous solutions, such as relaxation constants λ_c and rotational correlation times τ_c. Therefore, investigating the chemical form and physical state of high-specific-activity radionuclide probes in ultramicroconcentrations in aqueous media is of considerable interest.

^{111}In is a relevant radionuclide for nuclear medicine due to a convenient half-life ($T_{1/2} = 2.8$ d) and emission of γ-ray photons suitable for detection by Single-Photon Emission Tomography (SPECT) imaging. At the same time ^{111}In (EC)$\rightarrow^{111}$ Cd is one of the most popular probes used for TDPAC measurements. The excited state ($7/2^+$, 420 keV) of ^{111}Cd populated via the EC decay of ^{111}In de-excites by the $\gamma\gamma$-cascade of 171–245 keV to the ground state ($1/2^+$) through the isomeric intermediate state ($5/2^+$, 245 keV, $T_{1/2} = 84.5$ ns, $Q = +0.83$ b). The angular correlation of this cascade has a large anisotropy ($A_{2\max} = -18.0\%$). The short-lived isomer $^{111\text{m}}$Cd (IT, $T_{1/2} = 48.6$ min)$\rightarrow^{111}$ Cd has the same half-life of the intermediate state of spin $I = 5/2$ and the anisotropy of the angular correlation of the $\gamma\gamma$-cascade 151–245 keV is $A_{2\max} = +16\%$ (see Fig. 1).

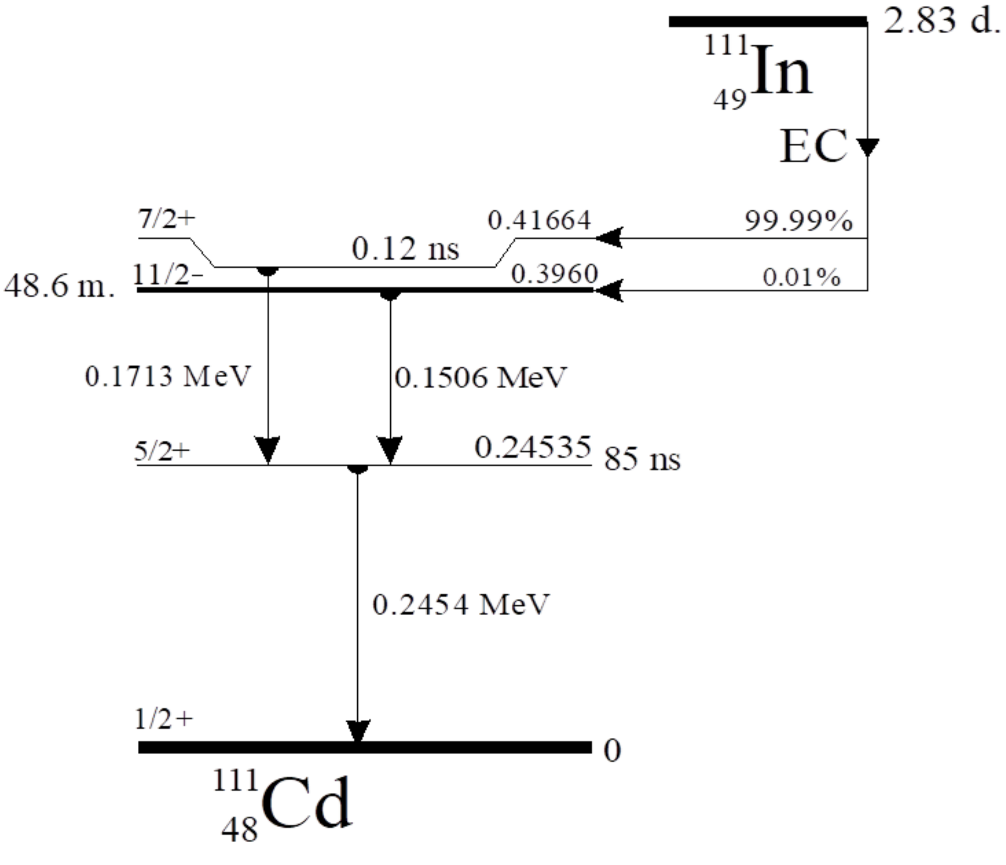

Figure 1: Decay scheme of ^{111}In.

Our previous TDPAC measurements of ^{111}In in frozen (up to $T = -100\ ^\circ$C) aqueous solutions of the Cl^-, NO_3^- (pH = 2) revealed the dynamic character of the perturbed angular correlation [5]. The dynamic character of the perturbation of the angular correlation might be attributed to: (*i*) the ice freezing from the solution and, consequently, an increase of the acid concentration may occur and the indium might be located in the liquid phase of the concentrated acid; (*ii*) the formation of an apparent liquid phase in the ice structure might be due to after-effects of the $^{111}\mathrm{In}\,(\mathrm{EC}) \rightarrow ^{111}\mathrm{Cd}$ electron capture decay; and (*iii*) the effects due to the ice structure and the hydrogen coupling. The feasibility of (*ii*) had been examined by means of the TDPAC technique with the source of $^{111\mathrm{m}}\mathrm{Cd}$ [6]. The results of [7] allow concluding that $^{111}\mathrm{In}$ after-effects do not significantly influence the measured hyperfine parameters of the daughter $^{111}\mathrm{Cd}$ nuclei in the frozen aqueous solutions studied here.

The motivation of the present work was (*i*) to reveal the factors responsible for the dynamic character of the perturbation of the angular correlation in the ($^{111}\mathrm{In} \rightarrow ^{111}\mathrm{Cd}$)-frozen eutectic aqueous solutions even across the eutectic temperature and (*ii*) to investigate the influence of the freezing rate of the sample solutions on the hyperfine parameters of the $^{111}\mathrm{Cd}$ daughter nuclei.

2 Experimental Methods

2.1 Production, Concentration and Ultra-Purification of ^{111}In

$^{111}\mathrm{In}$ was produced via the reaction $^{109}\mathrm{Ag}(\alpha, 2n)^{111}\mathrm{In}$ by irradiation of a metallic silver target with α-particles with $E_\alpha = 30$ MeV at the U-200 cyclotron at JINR. A radiochemical separation method to isolate $^{111}\mathrm{In}$ from a bombarded Ag target consisted of a multi-step purification technique described in detail in [8]. This allowed the production of high specific activity of $^{111}\mathrm{In}$ preparation with a ratio of $^{111}\mathrm{In}$ to other (chemically similar) metal atoms less than 1:10 [9]. The $^{111}\mathrm{In}$ isolation from the irradiated silver target as well as radionuclidic purity at all the stages of the cleaning was analyzed by means of a semiconductor Ge detector with SAMAR software.

2.2 Preparation of samples

Samples for the TDPAC measurements were prepared by dissolving $^{111}\mathrm{In}$ in HNO_3 (pH = 3) with a specific activity up to ≈ 5 Ci/l. The solution aliquot ($\approx 30\ \mu$Ci) was evaporated to dryness on the Teflon mount and then $\approx 50\ \mu$l H_2O was added and again evaporated to dryness at the same temperature ($T \approx 80\ ^\circ$C). $^{111}\mathrm{In}$ was removed from the mount by the adequate volume of the eutectic solution of HNO_3 (32.7 w.%, $T_{\mathrm{eut}} = -43\ ^\circ$C) or NaOH (19.1 w.%, $T_{\mathrm{eut}} = -28.2\ ^\circ$C), as well as the aqueous solutions of KOH (34.1 w.%, $T_{\mathrm{eut}} = -78\ ^\circ$C) and $HClO_4$ (40.7 w.%, $T_{\mathrm{eut}} = -60\ ^\circ$C) with estimated values of pH and the reagent concentrations, and then transferred to the Eppendorf tube.

2.3 Freezing of sources

***slow* freezing:** the ampoule with the solution under study was placed into the cryostat at the rate of freezing ≈ 5 °C /min before reaching the final temperature for TDPAC measurements.

***Fast* freezing:** the volume (150 μl) of the solution under study had been frozen by injection of small portions (15 μl) into liquid nitrogen. After the liquid nitrogen evaporated, these portions were collected and placed into the cryostat at the rate of heating ≈ 5 °C /min before reaching the final temperature for TDPAC measurements.

2.4 TDPAC spectroscopy

TDPAC measurements have been made using a 4-detector spectrometer with NaI(Tl) scintillators (40 × 40 mm) arranged in the plane with intervals of 90°. Coincidence counts $W(\theta, t)$ within a resolution time of 2.5 ns were accumulated between $\theta = 90^\circ$ and 180° [9].

Experiments at low temperature were performed using a cryostat. The sample temperature was kept constant (±0.5 K) by preheating the nitrogen vapor.

The least-squares fitting was used for electric–field gradient (EFG) parameter determination from the angular correlation perturbation models:

$$A_2G_2(t) = a_0 + a_1 \exp(-\lambda_2 t) \quad \text{(dynamic)}, \tag{1}$$

$$A_2G_2(t) = a_0 + a_1 \cos(\omega_0 t) \exp(-\Lambda t) \quad \text{(static)}, \tag{2}$$

where $G_2(t)$ is the perturbation function extracted from the time spectra; λ_2 is the relaxation parameter; ω_0 is the quadrupole frequency; and Λ characterizes the width of the quadrupole-frequency distribution about ω_0 due to local disorder around the radionuclide probes.

3 Results and discussion

The partial phase diagrams for the H_2O–NaOH and the H_2O–HNO_3 systems are shown in Fig. 2 and Fig. 3, respectively. At the *slow* freezing below the eutectic points the eutectic concentrations of HNO_3 and NaOH solutions decompose into two solid phases: (*i*) in NaOH the first phase is ice (H_2O) and the second phase is crystallohydrate of $NaOH \cdot 7H_2O$; (*ii*) in HNO_3 the first phase is ice (H_2O) and the second phase is crystallohydrate of $HNO_3 \cdot 3H_2O$.

The results of the temperature-dependent TDPAC studies for the *slow* and *fast* frozen samples of the eutectic NaOH and HNO_3 solutions are shown in Fig. 4 and Fig. 5. The experimental points have been fitted with a least-squares method, the result of which is represented by the full lines in Fig. 4 and Fig. 5. Computed values from the fitting are presented in Table 1.

It can be seen that the spectra obtained under *slow* freezing conditions retain a predominantly dynamic character even below the eutectic temperature, while the *fast* freezing procedure leads to deviations that point toward the formation of locally homogeneous phases. This difference suggests that the kinetics of solidification plays

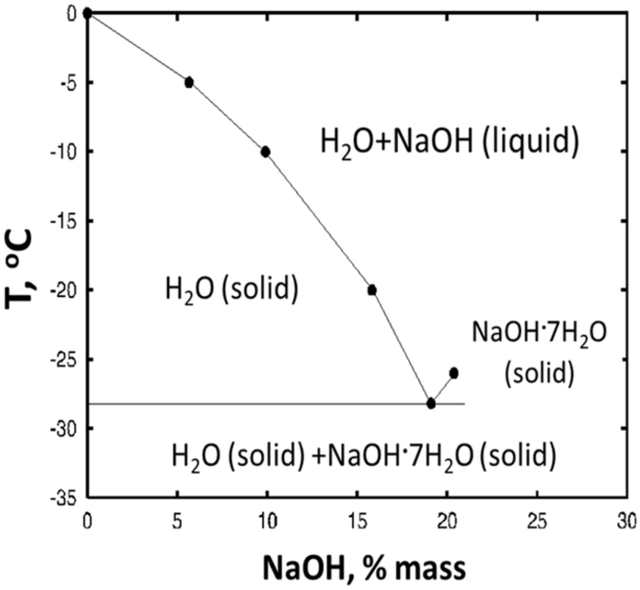

Figure 2: The partial phase diagram for the H_2O–NaOH system.

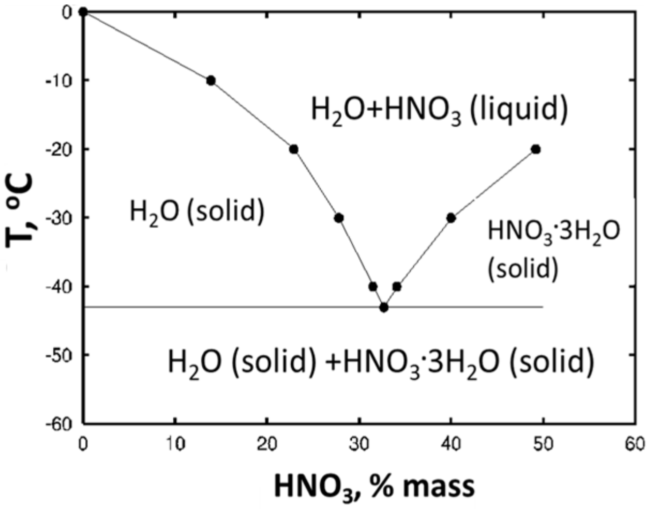

Figure 3: Partial phase diagram for the H_2O–HNO_3 system.

a decisive role in defect mobility and in the stabilization of structural configurations around the probe nuclei. In particular, NaOH solutions show indications of reduced defect mobility compared to HNO_3, which may explain the stronger tendency toward a static character of the hyperfine interaction. Such behavior highlights the importance of freezing conditions in determining the microscopic environment of the probe atoms and, consequently, the measured hyperfine parameters.

As seen from the spectra in Fig. 4 and Fig. 5 and Table 1, in the case of *slow* freezing the dynamic character of the time spectra for both considered eutectic solutions at the temperature below T_{eut} is roughly maintained. However, in the case of *fast* freezing the patterns are different. It is possible that in both HNO_3 and NaOH solutions the formation of homogeneous phases with similar local structures as in the liquid state occurs.

It is known that ice is characterized by high mobility of the oriented and ionic

Table 1: Parameters from TDPAC fits for HNO_3 and NaOH: dynamic vs. static hyperfine interaction (HFI).

Sample	Condition	T (°C)	Dynamic HFI			Static HFI		
			a_0	a_1	λ_2 (10^9 s^{-1})	a_0	a_1	ω_0 (10^6 s^{-1}), Λ (10^6 s^{-1})
HNO_3	*Fast*	−52	0.0(2)	−0.144(2)	0.011(1)			
	Slow	−52	0.0(2)	−0.16(1)	0.043(2)			
NaOH	*Fast*	−36				−0.018(2)	−0.18(2)	33(53), 147(33)
	Slow	−36	0.0(1)	−0.136(2)	0.010(1)			

defects in its structure. It is possible that these processes of the diffusion of the defects are responsible for the dynamic character of the perturbation of the angular correlation. In the case of NaOH the differences between static and dynamic character lie in the fact that, contrary to the case of HNO_3, there is smaller mobility of defects in the frozen state. Moreover, this conclusion is supported by the absence of peculiarities in the dynamic character of the time spectra (HNO_3) across the eutectic temperature (230 K).

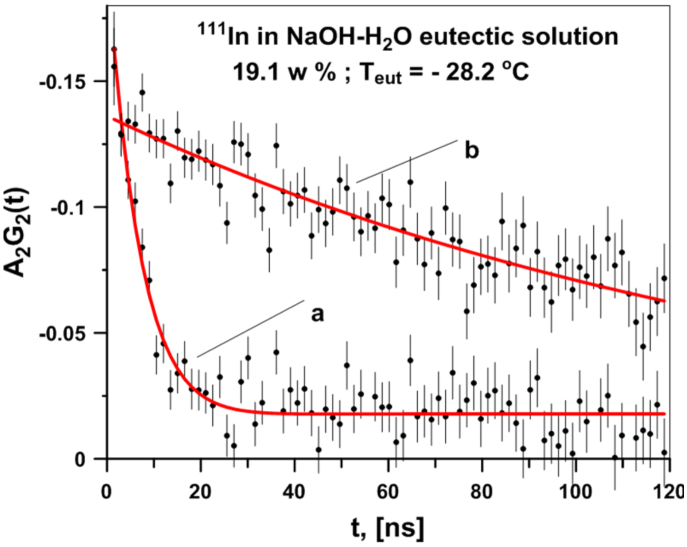

Figure 4: TDPAC spectra of the 171–245 $\gamma\gamma$-cascade in ^{111}Cd, measured at $T = -36$ °C: (a) *fast* and (b) *slow* freezing.

The hypothesis that at *fast* freezing homogeneous phases are formed with a local structure similar to the liquid state is supported by ^{111}In-TDPAC results obtained for the liquid solutions of $HClO_4$ and KOH, which are similar to the HNO_3 and NaOH solutions. The temperature dependencies of the relaxation parameter $\lambda_2(T)$ for $HClO_4$ and KOH solutions are shown in Fig. 6.

These observations indicate that the microscopic freezing mechanism strongly influences the hyperfine interaction parameters measured by TDPAC. The distinction between static and dynamic regimes reflects differences in defect concentration and mobility, which in turn depend on the solidification pathway. Furthermore, the similarity of results obtained for chemically different systems suggests that the phenomena observed here are of general character and not restricted to a particular solute. This underlines the role of structural disorder and defect dynamics as key factors governing the hyperfine fields in frozen aqueous systems.

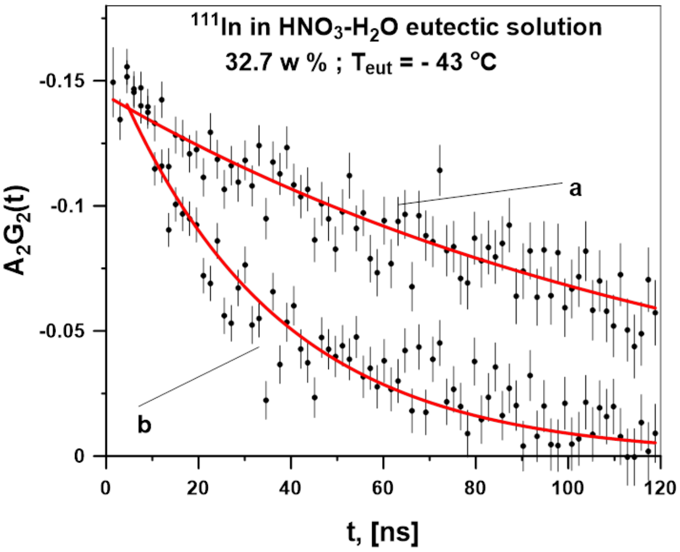

Figure 5: TDPAC spectra of the 171–245 $\gamma\gamma$-cascade in ^{111}Cd, measured at $T = -52\ ^\circ$C: (a) *fast* and (b) *slow* freezing.

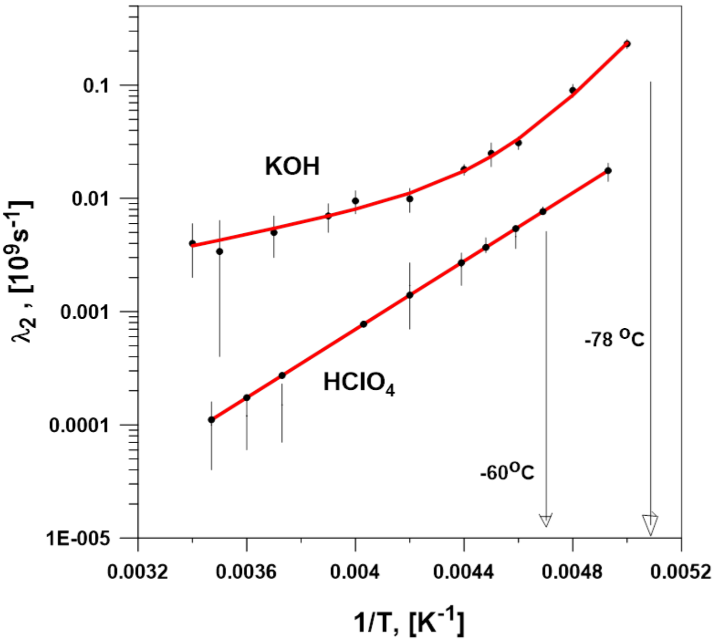

Figure 6: The relaxation parameter $\lambda_2(T)$ for the aqueous solutions of KOH (34.1 w.%, $T_{\rm eut} = -78\ ^\circ$C) and HClO$_4$ (40.7 w.%, $T_{\rm eut} = -60\ ^\circ$C).

4 Conclusion

^{111}Cd frozen eutectic HNO$_3$ and NaOH aqueous solutions using both *fast* and *slow* freezing were measured at temperatures below the corresponding $T_{\rm eut}$ via TDPAC. The obtained TDPAC spectra of both solutions suggest that at *slow* freezing the dynamic character is observed. On the contrary, at *fast* freezing different patterns are observed, which may indicate that homogeneous phases with similar local structures as in the liquid state occur. In the case of NaOH solution the difference in static and dynamic character lies in smaller mobility of defects in the frozen state.

The insights gained from studying these hyperfine interactions in model frozen systems are directly relevant to the broader applications of TDPAC mentioned in the introduction. In chemistry, understanding the formation of homogeneous phases and defect mobility under different freezing conditions is crucial for cryochemical synthesis and the study of reaction mechanisms at low temperatures. In biology, these findings can inform the development of cryopreservation techniques for biomolecules and cells, where the local molecular environment and dynamics upon freezing are critical for maintaining viability. For nuclear medicine, specifically in the use of ^{111}In-based radiopharmaceuticals, this research helps clarify the stability and chemical state of the radionuclide probe in biological environments that may experience localized freezing or low temperatures, ensuring accurate diagnostic imaging. Finally, in environmental research, understanding the behavior and speciation of metal ions (like Cd, a potential environmental contaminant) in frozen aqueous matrices is essential for modeling their transport and reactivity in cold regions, such as ice sheets and permafrost.

In the case of liquid solutions of KOH we observed a non-monotonic change in the relaxation parameters of the angular correlation anisotropies with decreasing solution temperature. This was due to two different factors of dynamic perturbation of the angular correlation. In the case of $HClO_4$ we observed a uniform change in the relaxation of the angular correlation as a result of the dynamics of one defect, presumably due to the reorientation of the proton bond.

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