

Atomic mobility in liquid gallium under nanoconfinementE. V. Charnaya,^{1,2} Cheng Tien,¹ W. Wang,¹ M. K. Lee,¹ D. Michel,³ D. Yaskov,² S. Y. Sun,¹ and Yu. A. Kumzerov⁴¹*Department of Physics, National Cheng Kung University, Tainan, 70101 Taiwan*²*Institute of Physics, St.Petersburg State University, St.Petersburg, Petrodvorets, 198504 Russia*³*Faculty of Physics and Geosciences, University of Leipzig, Leipzig, D-04103 Germany*⁴*A.F. Ioffe Physico-Technical Institute RAS, St. Petersburg, 194021 Russia*

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Results of NMR studies of nuclear spin-lattice relaxation in liquid metallic gallium confined within random pore networks of two different porous glasses with 16 and 2 nm pore sizes are presented. The measurements were run in the temperature range from 330 K to confined gallium freezing. Relaxation for both gallium isotopes ⁷¹Ga and ⁶⁹Ga was found to accelerate remarkably compared to the bulk melt, the dominant mechanism of relaxation changing from magnetic to quadrupolar. The correlation time of electric field gradient fluctuations caused by atomic motion was estimated at various temperatures using data for quadrupolar relaxation contribution and was found to increase drastically compared to bulk, which corresponded to a pronounced slowdown of atomic mobility in confined liquid gallium. The influence of confinement was more effective for smaller pore sizes. The temperature dependence of the correlation time for confined gallium was found to be noticeably stronger than in bulk, an additional slowdown of atomic mobility being observed at low temperatures.

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I. INTRODUCTION

Recent studies of atomic mobility, relaxation, and flowing in liquids embedded into various porous matrices have evidenced remarkable alterations compared to bulk (see Refs. 1–8, and references therein). It was shown that translational as well as rotational diffusion, nucleation kinetics, glass formation, crystallization, and other processes are influenced strongly by confinement. Alterations induced by confinement depend on whether liquids wet the inner surface of matrices, on pore sizes and tortuosity of the pore network, on length of molecular chains for polymers, and on other factors. Since NMR is known to provide immediate information about dynamics in bulk liquids through nuclear spin relaxation measurements, the NMR methods were applied successfully to study mobility in liquids within pores.^{3,4,6,9–12} Nevertheless, in spite of numerous studies of liquids within porous matrices, very little is known about peculiarities in spin relaxation and dynamics of confined metallic melts.^{13–15} Measurements of spin-lattice relaxation for liquid gallium and indium embedded into porous glass with 8 nm pore size and into artificial opals revealed drastic enhancement in quadrupole relaxation caused by slowdown of atomic mobility under confinement.^{13,14} The results obtained in Ref. 15 showed that slowdown of self-diffusion becomes noticeable already for small gallium droplets of 5 microns in size. Studies of spin relaxation for confined gallium^{13,15} were carried out at room temperature only, which proved to be possible due to strong shifts of the gallium freezing phase transition within nanopores.^{16,17} Measurements of spin relaxation for confined indium were also performed at a fixed temperature just below the melting point of bulk indium.¹⁴ Thus, no information is obtained until now concerning temperature dependences of spin relaxation and atomic mobility in confined liquid metals and the measurements at fixed temperatures were limited to the abovementioned porous matrices. Meanwhile, this matter

is of great interest for applied physics and nanotechnology as well as for fundamental physics of nanostructured materials. Nanoporous matrices filled with metals serve as model systems for further understanding features of nanostructured metals and small metallic particles which are used in microelectronics, catalysis, and others.

In the present paper we report results of NMR studies of nuclear spin-lattice relaxation in liquid metallic gallium confined within random pore networks of two different porous glasses with 16 and 2 nm pore sizes. The measurements were run in a temperature range from 330 K down to confined gallium freezing. Studies of spin relaxation in bulk liquid and supercooled gallium were also carried out for better comparison with the results for the confined melts. Using data obtained, the correlation time of electric field gradient fluctuations on nuclear site was calculated at various temperatures, which allowed us, in particular, to obtain information about temperature dependence of the atomic mobility slowdown in confined melted gallium.

II. EXPERIMENTAL

Nuclear spin-lattice relaxation and the Knight shift for both isotopes ⁶⁹Ga and ⁷¹Ga in melted gallium were measured at room temperature in four magnetic fields (7, 9, 11, and 17 T) using Bruker MSL300, Avance400, MSL500, and Avance750 NMR pulse spectrometers. At elevated and reduced temperatures, the measurements were carried out using an Avance400 spectrometer. The inversion recovery procedure was applied to observe the restoration of longitudinal nuclear magnetization. To detect NMR line, a single pulse sequence with phase cycling was applied. The repetition time was 0.2 s. The Knight shift was measured as the position of the ⁷¹Ga or ⁶⁹Ga NMR line peak relative to the NMR signal from a crushed GaAs single crystal which was placed to-

gether with the samples under study. In addition, the integral intensity of the NMR signal corresponding to liquid gallium versus temperature was evaluated to control gallium solidification and to get information about temperatures where confined gallium remains in melted state. The rate of warming and cooling was very slow to prevent temperature overshoots, which did not exceed 0.5 K in our measurements. Prior to each measurement, the samples were kept at a fixed temperature for about 5 min.

The two gallium isotopes have slightly different abundance, spin equal to 3/2, and distinct gyromagnetic ratios γ_n and quadrupole moments Q ($Q=0.171$ and 0.107 barn and $\gamma_n=6.44 \times 10^7$ and $8.18 \times 10^7 \text{ rad T}^{-1} \text{ s}^{-1}$ for ^{69}Ga and ^{71}Ga , respectively). This allows separating magnetic and electric spin interactions especially when NMR measurements are carried out in various external magnetic fields.

Porous glasses used in the present work were prepared from phase-separated soda borosilicate glasses with pore structure produced by acid leaching. The pore size, 16 and 2 nm, for the samples under study was determined using mercury intrusion porosimetry. The liquid gallium was embedded into the porous matrices under high pressure up to 10 kbar. The filling factor of the pore volume was about 70%.

III. EXPERIMENTAL RESULTS

Earlier NMR, acoustic, and x-ray diffraction studies of gallium embedded into nanoporous matrices revealed noticeable decrease in temperatures of its freezing transition compared to bulk.^{16–18} In addition, freezing and melting of confined gallium is affected by formation of different crystalline modifications within pores.^{19–22} NMR can provide information about the freezing process through measurements of temperature dependence of the integral intensity of liquid metal NMR signal, which is proportional to the total amount of the metal in the melted state. Since the melting and freezing phase transitions for gallium within glasses with 2 and 16 nm pores were not previously studied, we measured temperature dependence of the ^{71}Ga signal integral intensity corresponding to liquid gallium to find temperature intervals where gallium remains still liquid. First, the samples under study were warmed up to 330 K well above the bulk gallium melting point (303 K) to be assured that the total amount of gallium in the pores was melted. Then, the samples were cooled down to 155 K, the lowest temperature achievable in our experiments, and warmed up again. Under such conditions, the temperature dependences of the integral intensity were quite reproducible. The results for thermocycles described above are shown in Fig. 1. Gallium within the porous glass with 16 nm pore size remained melted until about 265 K where the abrupt complete freezing occurred. Solidification of gallium within a glass with 2 nm pore size was diffused. It started at about 185 K and was still incomplete till 155 K. Melting was smeared in both samples under study.

The results on gallium freezing showed that at room temperature the confined gallium can occur in melted state. The longitudinal magnetization recovery curves obtained at room temperature for gallium within the porous glasses are depicted in Figs. 2 and 3 along with the results for bulk liquid

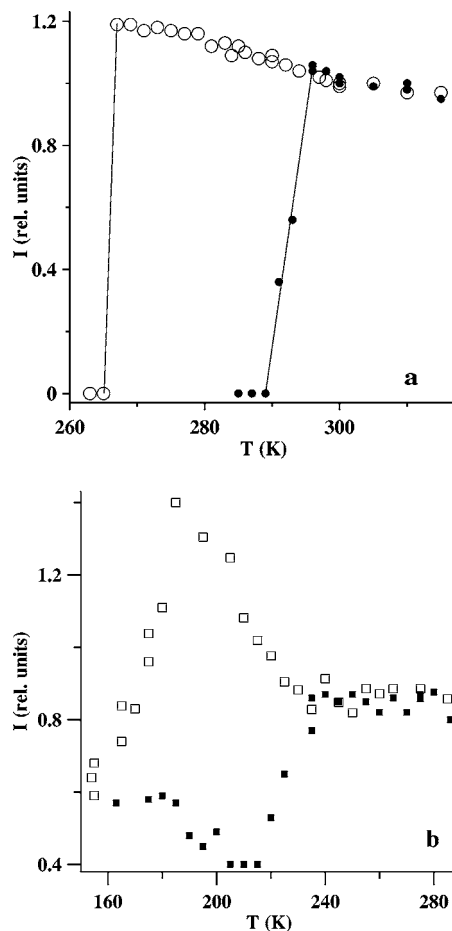


FIG. 1. Temperature dependences of the NMR signal integral intensity I determined by total amount of liquid gallium in porous glasses with 16 (a) and 2 nm (b) pores. Open symbols—cooling, closed symbols—warming. Solid lines are guides for the eye.

gallium. The measurements at ambient conditions for bulk gallium were possible while the melting point of bulk metallic gallium is 303 K since it can be supercooled very easily below room temperature.²³ Note that for spin relaxation in confined liquid gallium, the extreme narrowing limit is no longer valid because of strong slowdown of atomic mobility as will be discussed in Sec. IV. Consequently, the magnetization recovery is not described by a single exponential and cannot be characterized by a spin-lattice relaxation time.²⁴ For gallium within the porous glass with 16 nm pore size, the results were obtained using the four spectrometers, while, because of worse signal-to-noise ratio for the porous glass with 2 nm pore size, measurements at 7 T for both isotope and for ^{69}Ga at 11 T failed.

When changing temperature, pronounced alterations in the relaxation rate for gallium within nanoporous matrices were observed, especially upon decreasing temperature. Some examples are shown in Fig. 4. The data obtained at different temperatures will be used in Sec. IV for calculating temperature-induced variations in the correlation time of electric field gradient fluctuations caused by atomic motion.

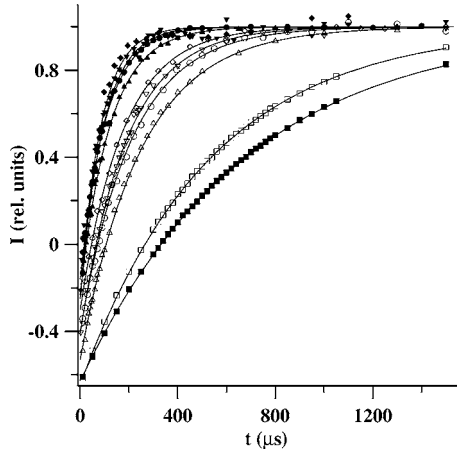


FIG. 2. NMR signal integral intensity I versus time after a 180° pulse for the porous glass with 16 nm pores and in bulk (squares). Closed and open symbols correspond to ^{69}Ga and ^{71}Ga , respectively. Diamonds, inverted triangles, circles, and triangles correspond to measurements at magnetic field of 7, 9, 11, and 17 T, respectively. Solid lines are theoretical calculations as described in the text.

IV. DISCUSSION

Studies of nuclear spin-lattice relaxation for the bulk melted gallium (see Refs. 23 and 25, and references therein) have shown that it occurs via coupling of nuclear magnetic moments with conduction electrons and of nuclear quadrupole moments with dynamic gradients of electric fields produced by atomic motion, the main contribution to relaxation is magnetic. Since atomic mobility in bulk liquid gallium is fast enough, total relaxation is described by a single exponential (the extreme narrowing limit) with the field-independent relaxation times. The relaxation time T_1^{71} for ^{71}Ga is shorter than T_1^{69} for ^{69}Ga since magnetic interaction with conduction electrons dominates relaxation. In our mea-

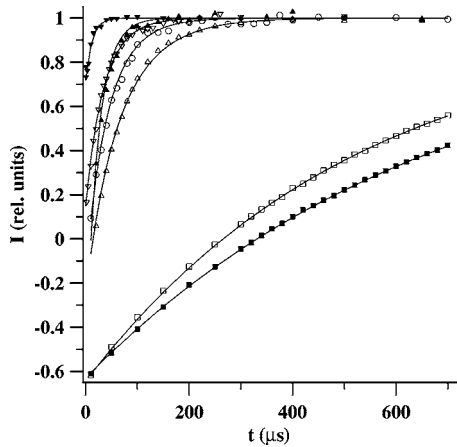


FIG. 3. NMR signal integral intensity I versus time after a 180° pulse for the porous glass with 2 nm pores and in bulk (squares). Closed and open symbols correspond to ^{69}Ga and ^{71}Ga , respectively. Inverted triangles, circles, and triangles correspond to measurements at magnetic field of 9, 11, and 17 T, respectively. Solid lines are theoretical calculations as described in the text.

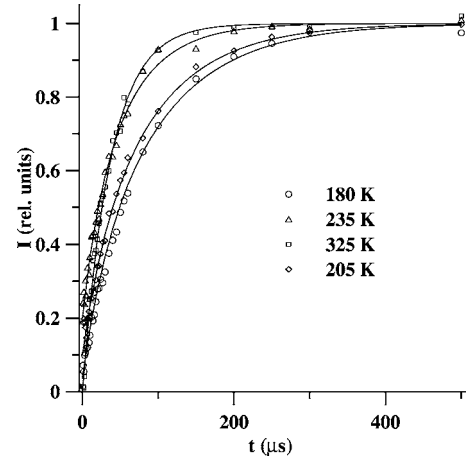


FIG. 4. ^{71}Ga NMR signal integral intensity I versus time after a 180° pulse for the porous glass with 2 nm pores at different temperatures. Solid lines are theoretical calculations as described in the text.

surements $T_1^{69} = 678 \mu\text{s}$ and $T_1^{71} = 534 \mu\text{s}$ at room temperature in perfect agreement with Refs. 23 and 25.

Figures 2 and 3 show drastic enhancement in the relaxation rate for both gallium isotopes in confined melts compared to bulk liquid gallium. In contrast to relaxation in bulk melted gallium,^{23,25} relaxation for confined gallium in the same field and in the same sample is noticeably faster for the ^{69}Ga isotope with greater quadrupole moment and smaller gyromagnetic ratio. Moreover, the relaxation rate visibly depends on magnetic field for gallium within the porous glasses. The fact that relaxation is faster for the isotope with larger quadrupole moment shows that the quadrupolar contribution dominates longitudinal relaxation in confined geometry contrary to the bulk case. At reduced and elevated temperatures, spin relaxation under confinement remained much faster than for bulk and quadrupolar contribution dominated the total relaxation process as at room temperature.

The remarkable enhancement of the quadrupolar relaxation rate under nanoconfinement as well as its dependence on the magnetic field show that the spectral densities of the electric field gradient correlation function which determine quadrupolar spin relaxation in confined gallium are strikingly increased and the extreme narrowing approximation is no longer valid. Generally, the longitudinal quadrupolar relaxation in liquids for the spin 3/2 is given by the following relationship:²⁶

$$\frac{M(t)}{M_0} = 1 - b \left\{ \frac{4}{5} \exp \left[-2 \left(\frac{eQ}{\hbar} \right)^2 J_{-22}(2\omega_0)t \right] + \frac{1}{5} \exp \left[2 \left(\frac{eQ}{\hbar} \right)^2 J_{-11}(\omega_0)t \right] \right\}, \quad (1)$$

where $M(t)$ and M_0 are time-dependent and equilibrium magnetizations, respectively, $1-b$ is the starting relative magnetization, e is the electron charge, ω_0 is the Larmor frequency, $J_{-ii}(\omega)$ are the spectral densities of the electric field gradient correlation function at the nuclear site.

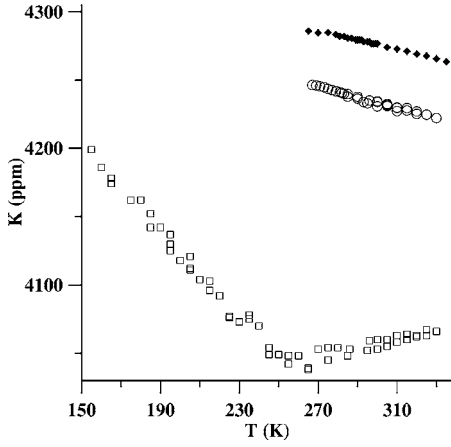


FIG. 5. Temperature dependences of the liquid gallium Knight shift K relative to GaAs for the porous glasses with 2 nm pores (squares) and 16 nm pores (circles) and for bulk (diamonds).

In the extreme narrowing case the exponents in Eq. (1) are reduced to $-C\tau_c t$,²⁶ where C is a constant, which is proportional to Q^2 , and τ_c is the correlation time of low-frequency electric field gradient fluctuations produced by atomic motion. The constant C includes ion contribution corrected for the antishielding factor. The product $C\tau_c$ has the meaning of the inverse time T_{1Q}^{-1} of quadrupolar relaxation. The correlation time τ_c in bulk should be of the order of 10^{-11} – 10^{-12} s in agreement with the self-diffusion rate in liquid metals.²⁷ To simplify consideration of the general case we can assume²⁴ that the correlation function of atomic mobility is represented by $\exp(-t/\tau_c)$. Thus the exponents in Eq. (1) are reduced to $-C\tau_c t / (1 + k^2 \omega_0^2 \tau_c^2)$, where $k=1, 2$.

The relaxation time T_{1m} corresponding to magnetic contribution to the total relaxation process in confined gallium caused by coupling with conduction electrons is related to the Knight shift by the Korringa relation²⁸ $T_{1m} T K_s^2 = \text{const} / (\gamma_n K)$, where T is the temperature, K_s is the Knight shift, K is the correction factor that accounts for the effects of electron correlation and exchange. Our measurements have shown that the Knight shift in liquid gallium is influenced by confinement but very slightly (Fig. 5). Similar results were obtained in Ref. 16 for gallium within other porous matrices. Thus, the time T_{1m} for confined gallium can be assumed for estimates to keep its bulk value, and total relaxation can be described by the following relationship:

$$\frac{M(t)}{M_0} = 1 - b \left[\frac{4}{5} \exp\left(-\frac{C\tau_c t}{1 + 4\omega_0^2 \tau_c^2}\right) + \frac{1}{5} \exp\left(-\frac{C\tau_c t}{1 + \omega_0^2 \tau_c^2}\right) \right] \exp\left(-\frac{t}{T_{1m}}\right). \quad (2)$$

The magnetic and quadrupolar contributions to spin-lattice

relaxation in bulk liquid gallium can be separated^{23,25} for both gallium isotopes using their gyromagnetic ratios and quadrupole moments according to $T_{1Q}^{71} = (Q_{69}^2 / Q_{71}^2) T_{1Q}^{69}$ and $T_{1m}^{71} = (\gamma_{n69}^2 / \gamma_{n71}^2) T_{1m}^{69}$. At room temperature from our measurements $T_{1m}^{69} = 585 \mu\text{s}$, $T_{1m}^{71} = 944 \mu\text{s}$, $T_{1Q}^{71} = 6130 \mu\text{s}$, and $T_{1Q}^{69} = 2400 \mu\text{s}$ in agreement with previous theoretical calculations and experimental data.^{23,25,29}

Using relationship (2) and the found bulk values of T_{1m} we can fit the full set of recovery curves for confined gallium within porous glasses under study at room temperature using only two fitting parameters, C_{69} and τ_c , for each sample, taking into account that $C_{71} = (Q_{71}^2 / Q_{69}^2) C_{69}$.²⁶ The best fit for the porous glass with 16 nm pore size was obtained when C_{69} and τ_c were assumed to be $3 \times 10^{13} \text{ s}^{-2}$ and $3.7 \times 10^{-10} \text{ s}$, respectively. The fitting is shown in Fig. 2 together with the experimental results. The value of C_{69} actually coincides with the relevant value $3.2 \times 10^{13} \text{ s}^{-2}$ found in Ref. 13 upon treating results for spin relaxation in liquid gallium confined within a synthetic opal and porous glass with 8 nm pores. It also agrees well with theoretical calculations of the quadrupolar relaxation rate^{25,29} in bulk liquid gallium. The spectral density at low frequencies, which determines the value of C for both isotopes, depends on structure of melts.^{27,29} It is known that the structure of liquids confined within pores with sizes greater than 4 nm does not change compared to bulk;^{1,2,5} this agrees with x-ray patterns for melted gallium in pores larger than 4 nm in diameter.^{19,20} Thus, it seems well founded that C keeps the same value from bulk liquid gallium to pore size of about 8 nm at least. Assuming $C_{69} = 3 \times 10^{13} \text{ s}^{-2}$ in bulk melt, one can estimate the correlation time in bulk liquid gallium from our measurements at room temperature $\tau_c \cong 1.4 \times 10^{-11} \text{ s}$. The result obtained shows that the correlation time for liquid gallium in the porous glass is considerably increased compared to bulk. It should be emphasized that this conclusion does not depend on the assumed particular value of C_{69} .

The best fit for the porous glass with 2 nm pore size was obtained when $C_{69} = 1.9 \times 10^{14} \text{ s}^{-2}$ and $\tau_c = 7 \times 10^{-10} \text{ s}$. The fitting curves are depicted in Fig. 3. In contrast to the sample with 16 nm pores, the quadrupolar relaxation rate in the porous glass with 2 nm pore size appeared to be enhanced due to increase in both C and the correlation time. The alterations in C indicate some changes in structure or chemical bonds for confined gallium melt which influence electric field gradients at gallium nuclei in such fine pores.

The values of the correlation time τ_c found in the present paper and in Ref. 13 are listed in Table I. One can see from Table I that, when C remains unchanged, there is a monotonic increase in the correlation time with decreasing pore size. And for the finest pores the correlation time is about the same as for the 8 nm porous glass. Note that monotonic alterations with decreasing pore size were also seen for the

TABLE I. Correlation times of electric field gradient fluctuations at room temperatures. Asterisks mark data from Ref. 13.

sample	Porous glass 2 nm	Porous glass 8 nm*	Porous glass 16 nm	Opal*	Bulk
$\tau_c (10^{-11} \text{ s})$	70	80	37	20	1.4

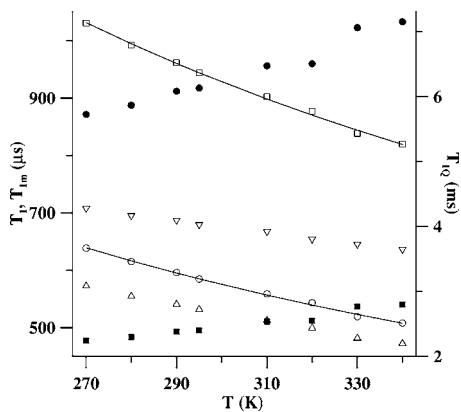


FIG. 6. Temperature dependences of relaxation times for the gallium isotopes in bulk melt. Open and closed symbols relate to left and right axes, respectively. Triangles and inverted triangles are T_1^{71} and T_1^{69} . Open and closed circles are T_{1m}^{71} and T_{1m}^{69} . Open and closed squares are T_{1m}^{69} and T_{1m}^{71} . Solid lines represent $1/T$ dependences.

Knight shift in confined liquid gallium.¹⁶ The increase in the correlation time for liquid gallium embedded into nanoporous matrices evidences drastic slowing down of the atomic diffusion at room temperature under confinement, the self-diffusion coefficient being inversely proportional to τ_c .²⁴ Some trend in slowing down the mobility in liquid gallium thin films was also reported in Ref. 30 according to quasi-elastic neutron scattering study where it was found that the self-diffusion coefficient was too low to be resolved, at least less than 10^{-5} cm²/s compared to 3×10^{-5} cm²/s in bulk.

Assuming that the values of C do not vary with temperature, one can use relationship (2) for evaluating temperature dependences of the correlation time in confined liquid gallium from relaxation measurements at different temperatures. To obtain the values of T_{1m}^{69} and T_{1m}^{71} in bulk at elevated and reduced temperatures which are necessary for such calculations, we measured temperature dependences of spin-lattice relaxation for ^{69}Ga and ^{71}Ga in bulk melt in the range from 340 to 270 K until bulk gallium was frozen. The results are shown in Fig. 6. Using the data obtained and relationships between the relaxation times for the gallium isotopes T_{1m}^{69} and T_{1m}^{71} were then calculated at various temperatures. The temperature dependences of the magnetic contribution were found to satisfy perfectly the Korringa relation, in agreement with previous studies.^{23,25} This justifies the use of the $1/T$ law to evaluate the magnetic relaxation times T_{1m}^{69} and T_{1m}^{71} below the bulk gallium freezing point. The measurements performed also allowed calculating the dependence of the correlation time on temperature for bulk gallium using the times of quadrupolar relaxation.

The calculated correlation times at different temperatures relative to their values at room temperature for liquid gallium in the porous glasses under study and for bulk melt are shown in Fig. 7. While for bulk liquid gallium the temperature dependence of τ_c is rather weak, it becomes much stronger under confinement. Above and within the temperature range of freezing, the correlation time increases by more than a factor of 3 for both porous matrices. This shows that the slowdown of atomic mobility with decreasing temperature is

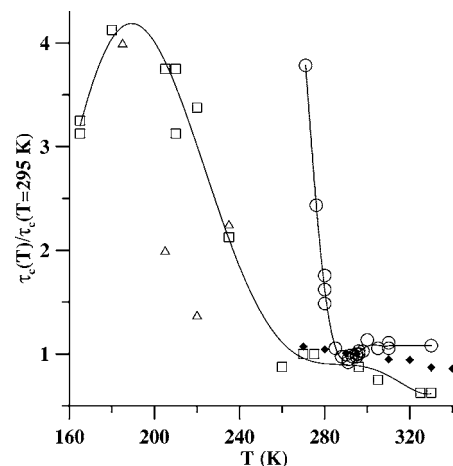


FIG. 7. Correlation times versus temperature relative to their magnitudes at room temperature for bulk gallium melt (solid diamonds), porous glass with 16 nm pores (circles), and porous glass with 2 nm pores (squares: cooling, triangles: warming). Solid lines are guides for the eye clarifying temperature dependences of the correlation time for the porous glass with 16 nm pores and for the porous glass with 2 nm pores upon cooling.

much more pronounced for gallium within nanoporous matrices compared to bulk. However, the temperature dependence of the correlation time in bulk liquid gallium was found in Refs. 23 and 25 in agreement with our results (Fig. 6) to be noticeably weaker than it should be expected from the temperature dependence of the self-diffusion coefficient. Therefore, the increase in the correlation time for confined gallium at low temperature might reflect but partly the temperature dependence of slowing down the self-diffusion within nanopores. It should be also noted that for gallium within pores of 2 nm in size the correlation times obtained upon warming could differ from those obtained upon cooling (see Fig. 7). In addition, magnetization restoration curves and, therefore, correlation times calculated could be slightly different for different measurements. This evidences some instability in liquid gallium within very fine pores which was not observed by us for larger pores.

The increase in the correlation time in confined geometry also leads to shortening the transverse spin relaxation time as was found in Refs. 13 and 14. It appears, in particular, in the broadening of NMR lines. However, the experimental line shapes might be also influenced by inhomogeneity of the Knight shift^{13,15} and therefore are less suitable for evaluating the correlation time of electric field gradient fluctuations on nuclear sites. The detailed analysis of line broadening for the samples under study will be presented elsewhere.

In conclusion, studies of nuclear spin-lattice relaxation for two gallium isotopes ^{69}Ga and ^{71}Ga in liquid gallium confined within porous glasses with 16 and 2 nm pore sizes revealed drastic enhancement in the quadrupolar relaxation rate led to the change in the dominant mechanism of relaxation compared to bulk melt from magnetic to quadrupolar. Analysis of the longitudinal magnetization restoration in different magnetic fields allowed calculating the correlation times of electric field gradient fluctuations on nuclear sites caused by atomic motion and the constants which determine

quadrupole coupling in liquid gallium. The remarkable increase in the correlation time found for both porous matrices under study reflected a strong slowing down atomic dynamics for liquid gallium in nanopores. A pronounced increase in the magnitude of quadrupole coupling was found for gallium within the porous glass with 2 nm pores in contrast to the case of coarser pores. NMR measurements at reduced and elevated temperatures revealed an additional strong slow-

down of atomic mobility under confinement above gallium freezing within pores.

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