# Spin-Lattice Relaxation Enhancement in Liquid Gallium Confined within Nanoporous Matrices

E. V. Charnaya,[1,2] T. Loeser,[3] D. Michel,[3] C. Tien,[1] D. Yaskov,[2] and Yu. A. Kumzerov[4]

[1]*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*

(Received 16 August 2001; published 15 February 2002)

Nuclear spin relaxation for liquid gallium embedded into nanoporous matrices was found to accelerate remarkably compared to the bulk melt. NMR measurements on two gallium isotopes showed that the dominant mechanism of relaxation was changed from magnetic to quadrupolar and the relation rate depended on the Larmor frequency. The correlation time of electric field gradient fluctuations was estimated using data for quadrupolar relaxation contribution and was found to increase drastically compared to bulk, which corresponded to slowing down mobility in confined liquid gallium.

DOI: 10.1103/PhysRevLett.88.097602 PACS numbers: 76.60.–k, 61.25.Mv, 61.43.Gt, 68.65.–k

Recently, a great deal of attention was focused on atomic mobility, relaxation, and flowing in liquids in confined geometry [1]. Various porous matrices filled with different kinds of liquids were studied intensively. It was shown that translational as well as rotational diffusion, nucleation kinetics, glass formation, and other processes in liquids embedded into nanoporous matrices are influenced strongly by confinement [2–10]. Since NMR is known to provide immediate information about dynamics in bulk liquid through nuclear spin relaxation measurements, the NMR methods were applied successfully to study mobility in liquids within pores [2,3,7,11–14]. Nevertheless, in spite of numerous studies of liquids within porous matrices, no studies were carried out to reveal peculiarities in spin relaxation and dynamics of confined metallic melts. Meanwhile, recent measurements on some low-melting-point metals as gallium, indium, and mercury inserted into porous glasses and artificial opals showed that confinement affects many of their properties, in particular, the melting and freezing processes, structure of solid phases, and the superconducting phase transition (see [15–19] and references therein). In the present Letter we report results of first studies of nuclear spin-lattice relaxation in liquid gallium confined within random and quasiregular pore networks of a porous glass and artificial opal. It will be shown that while spin relaxation in bulk liquid gallium is governed mainly by coupling with conduction electrons, the drastic enhancement of the relaxation rate for confined liquid gallium occurs due to a rise in the quadrupolar contribution which follows the strong increase in the spectral densities at the Larmor frequency of the electric field gradient fluctuations and might evidence the remarkable slowdown in atomic mobility.

Gallium has two isotopes, $^{69}$Ga and $^{71}$Ga, with slightly different abundance, with spin equal to $3/2$, and distinct gyromagnetic ratios $\gamma_n$ and quadrupole moments $Q$ ($Q = 0.168$ and 0.106 barn and $\gamma_n = 6.44 \times 10^{-7}$ and $8.18 \times 10^{-7}$ rad $\cdot$ T$^{-1}$ $\cdot$ s$^{-1}$ for $^{69}$Ga and $^{71}$Ga, respectively). This allows separating magnetic and electric spin interactions especially when NMR is measured in various external magnetic fields.

The melting point of bulk metallic gallium is 303 K; however, it can be supercooled very easy below room temperature, so spin-lattice relaxation for the bulk melt was measured in a wide temperature range including ambient conditions (see [20,21] and references therein). It was obtained that nuclear spin-lattice relaxation 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, the total relaxation is described by a single exponential (the extreme narrowing limit) with the field-independent relaxation times of about 710 $\mu$s for $^{69}$Ga and 530 $\mu$s for $^{71}$Ga [20] at room temperature.

The freezing transition for gallium within nanopores is lowered compared to that in bulk [17,18] and confined gallium still remains liquid at room temperature. Thus, spin-lattice relaxation for liquid gallium embedded into a porous glass with the pore size of 8 nm and within an artificial opal consisted of close-packed silica spheres with a diameter of 250 nm was measured by us at ambient conditions. The sample preparation was described elsewhere [17]. The inversion recovery procedure was used for both gallium isotopes in magnetic fields of 7, 11, and 14 T in the case of the porous glass and in magnetic fields of 7 and 11 T in the case of the opal. The spin magnetization restoration curves obtained are shown in Figs. 1 and 2. They evice a drastic enhancement in the relaxation rate compared to bulk liquid gallium, data for bulk are depicted in Fig. 1(a) for comparison. The following main features can be noticed in Figs. 1 and 2 which contrast with those for bulk melted gallium: relaxation in the same field and in the same sample is noticeably faster for the $^{69}$Ga isotope with the greater quadrupole moment and the smaller gyromagnetic ratio; the relaxation rate

  

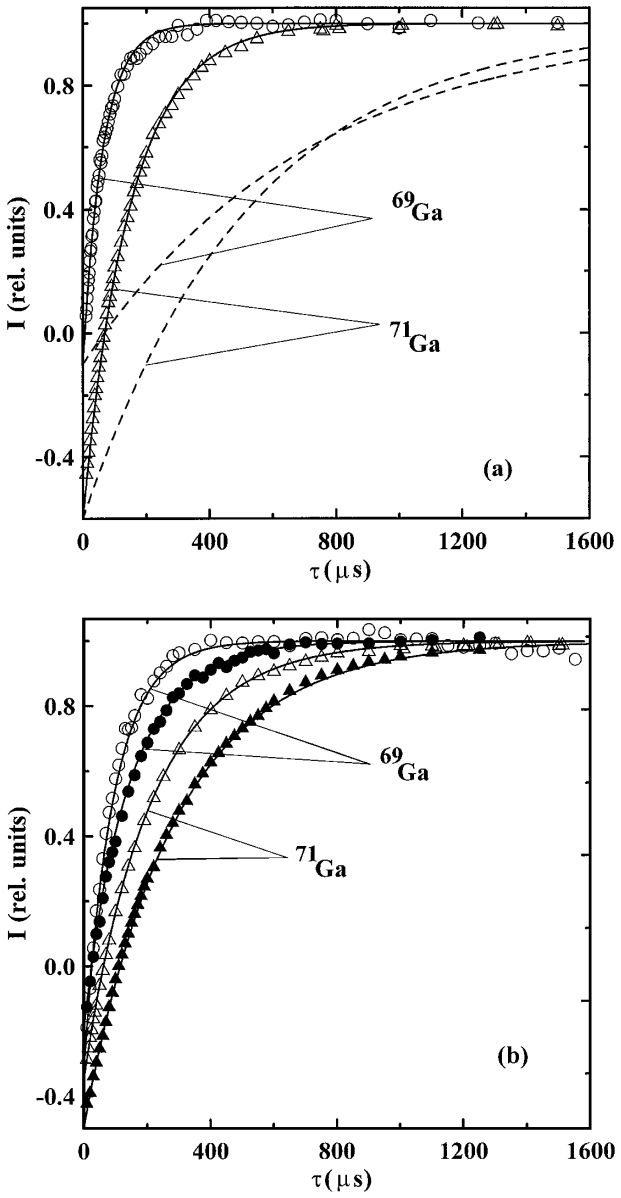


FIG. 1. Magnetization recovery curves ($I$ is the intensity of NMR signals; $\tau$ is the time between first and second pulses) for liquid gallium embedded into the porous glass. Circles and triangles mark experimental results for $^{69}$Ga and $^{71}$Ga, respectively. Solid lines are theoretical calculations using Eq. (1) as described in the text. (a) Measurements in magnetic field 7 T; dashed lines show restoration of magnetization in bulk liquid gallium. (b) Measurements in magnetic field 11 T (open symbols) and 14 T (closed symbols).

visibly depends on the magnetic field for gallium within the porous glass.

The fact that relaxation is faster for the isotope with the larger quadrupole moment shows that the quadrupolar contribution dominates longitudinal relaxation in confined geometry contrary to the bulk case. This is also valid for transverse spin relaxation as it follows from the line shapes measured for gallium in porous matrices. Line shapes for the porous glass are presented in Fig. 3 together with data for bulk gallium. Figure 3 shows that while NMR lines for both gallium isotopes are narrow and coincide for bulk, they are noticeably broadened for confined gallium and NMR linewidths are larger for $^{69}$Ga than for $^{71}$Ga. Moreover, the NMR linewidth against the parts per million frequency scale increases with decreasing magnetic field, which corresponds to the quadrupolar nature of line broadening as in viscous liquids [22]. Similar results were obtained for the opal sample.

The remarkable enhancement of the quadrupolar relaxation rate as well as its dependence on the magnetic field shows 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. In fact, the longitudinal quadrupolar relaxation in liquids for the spin $3/2$ is given by the following general relationship [23]:

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

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, $\omega_0$ is the Larmor frequency, and $J_{-ii}(\omega)$ are the spectral densities of the electric field gradient correlation function at the nuclear site. In the extreme narrowing case the exponents in (1)

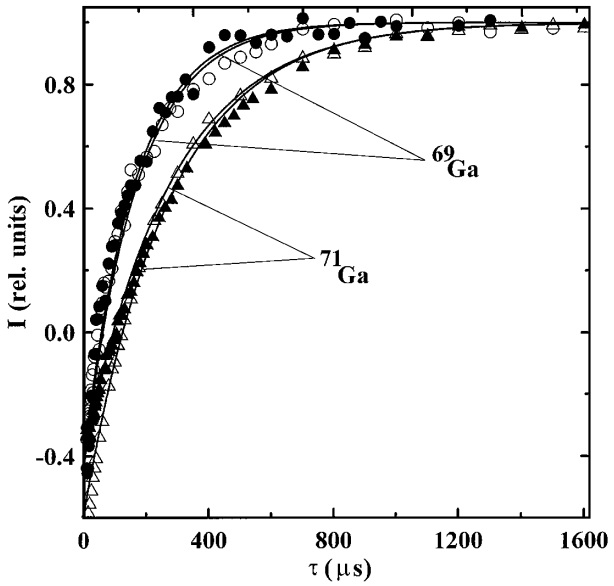


FIG. 2. Magnetization recovery curves ($I$ is the intensity of NMR signals; $\tau$ is the time between first and second pulses) for liquid gallium embedded into the opal. Circles and triangles mark experimental results for $^{69}$Ga and $^{71}$Ga, respectively, obtained in magnetic field 7 T (open symbols) and 11 T (closed symbols). Solid lines are theoretical calculations using Eq. (1) as described in the text.

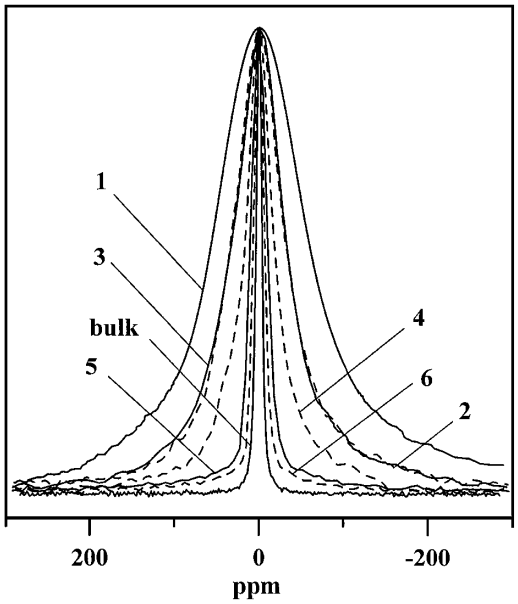


FIG. 3. NMR lines for $^{69}$Ga (solid lines) and $^{71}$Ga (dashed lines) in the porous glass measured in the field 7 T (1, 2), 11 T (3, 4), and 14 T (5, 6). NMR lines in bulk liquid gallium are coincided for both isotopes.

are reduced to $-C\tau_c t$ [24], where $C$ is a constant, which is proportional to $Q^2$, and $\tau_c$ is the correlation time. 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 $\tau_c$ is of the order of $10^{-12}$ s in agreement with the diffusion rate in liquid metals [24].

To simplify consideration of the general case we can assume [22] that the correlation function is represented by $\exp(-t/\tau_c)$; thus, the exponents in (1) are reduced to $-C\tau_c t/(1 + k^2\omega_0^2\tau_c^2)$, where $k = 1, 2$. The quadrupolar relaxation rate can be enhanced because of the increase in $C$ or, compared to the extreme narrowing case, due to the increase in the correlation time. The static correlation of the electric field gradient fluctuations, which determines the value of $C$, depends on the structure of melts [24]. It is known that the structure of liquids confined within pores with sizes greater than 4 nm does not change compared to bulk [1,10]; this agrees to x-ray patterns for melted gallium in pores [18,25]. Thus, it is unlikely that $C$ could increase enough to explain the alteration in the character of relaxation from magnetic to quadrupolar. Moreover, the increase in $C$ does not explain the strong dependence of the relaxation rate on the Larmor frequency observed in the porous glass sample under study. Therefore, we can assume that alterations in relaxation for liquid confined gallium arise mainly due to slowing down the correlation time.

The results obtained for spin-lattice relaxation make it possible to estimate the alterations in the correlation time when implied that total spin-lattice relaxation for confined gallium includes the magnetic contribution described by $\exp(-t/T_{1m})$ [20,21]. The time $T_{1m}$ of magnetic relaxation caused by coupling with conduction electrons is related to the Knight shift by the Korringa relation: $T_{1m}TK_s^2 = \text{const}/(\gamma_n K)$, where $T$ is the temperature, $K_s$ is the Knight shift, and $K$ is the correction factor. Since the Knight shift in liquid gallium is influenced by confinement but very slightly [26], the time $T_{1m}$ for confined gallium can be assumed for estimates to keep its bulk value. The magnetic and quadrupolar contributions to spin-lattice relaxation in bulk liquid gallium were separated [20,21] for both gallium isotopes using their gyromagnetic ratios and quadrupole moments. The rate of quadrupolar relaxation was also calculated theoretically [21]. The $T_{1Q}$ values obtained for $^{69}$Ga range between 2900 and 4500 $\mu$s. With some accepted numerical values for $T_{1Q}$ and $\tau_c$ in bulk, one can estimate the constant $C$ for both isotopes. The constant $C$ evaluated, the correlation time in confined gallium can be found from fitting the experimental magnetization recovery curves presented in Figs. 1 and 2. The fitting shown in Figs. 1 and 2 was obtained when $T_{1Q} = 3900$ $\mu$s was accepted for the $^{69}$Ga quadrupole relaxation time and $\tau_c$ in bulk was assumed to be equal to $8 \times 10^{-12}$ s. Under these conditions, the correlation times for liquid gallium within the porous glass and the opal were found to increase up to $8 \times 10^{-10}$ s and $2 \times 10^{-10}$ s, respectively. Note that the conclusion concerning the pronounced elongation of the correlation time remains true for any reasonable estimates for the relaxation and correlation times in bulk liquid gallium. As can be seen in Figs. 1 and 2 the agreement between the experimental results and the model for six curves for the porous glass and four curves for the opal seems to be excellent, while only one free fitting parameter was used for each sample. The shorter correlation time for the opal agrees with the absence of the noticeable magnetic field dependence of the relaxation rate for this sample.

The same model as was used for treating longitudinal relaxation can be applied to transverse relaxation. The rate of transverse relaxation in the samples under study can be estimated from the width of NMR lines. Note, however, that the experimental line shapes might also be influenced by the inhomogeneity of the Knight shift due to pore size distribution [26]. The relationship for the time decay of transverse magnetization $M_\perp$ due to quadrupolar spin relaxation in liquids can also be found in [23] and simplified in the same manner as (1). The magnetic contribution to transverse relaxation is easy to estimate from linewidths measured for bulk liquid gallium. An example of the transverse magnetization decay calculated for liquid gallium confined within the porous glass at fields of 7 and 14 T is presented in Fig. 4. The parameters used were the same as those for the longitudinal time calculations. The agreement between the model and estimates from line shapes in comparison with results for bulk gallium seems excellent for $^{69}$Ga and somewhat worse for $^{71}$Ga. The distinction arises, probably, because of stronger relative influence of magnetic broadening mainly due to the Knight shift

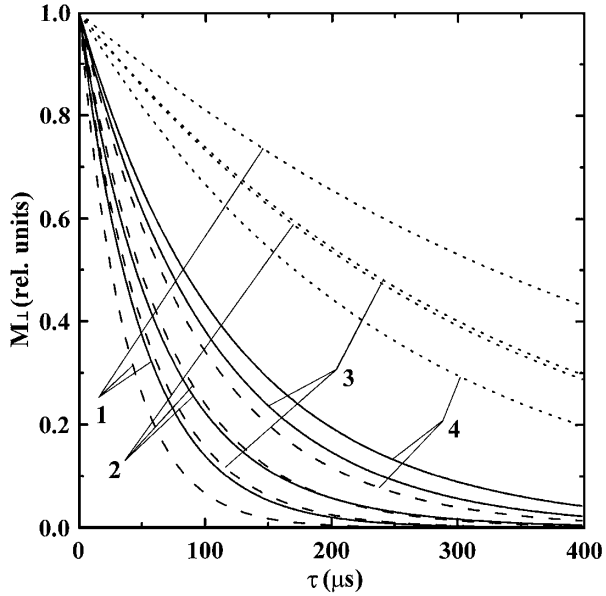


FIG. 4. Transverse magnetization decay versus time $\tau$ for $^{69}$Ga (1, 2) and $^{71}$Ga (3, 4) in the porous glass and in bulk at the field 7 T (1, 3) and 14 T (2, 4). Solid lines are single exponential curves calculated from experimental linewidths. Dashed lines are theoretical calculations as described in the text. Dotted lines are single exponential curves calculated from experimental linewidths for bulk gallium.

inhomogeneity for the isotope with the smaller quadrupole moment. Similar results were obtained for the field of 11 T and for gallium embedded into the opal.

The values of $\tau_c$ in confined liquid gallium are more than 1 order of magnitude greater than in bulk. The drastic increase in the correlation time reflects remarkable changes in atomic dynamics for confined liquid gallium. Note that some trend in slowing down the mobility in liquid gallium thin films was reported in [27].

The fact that the same model with the only change in the correlation time gives an explanation for spin relaxation in the porous glass and in the opal which have different geometry of pores shows that the tendency observed to enhance relaxation under the confinement conditions is not influenced noticeably by the particular pore configuration. The alterations in the spin relaxation times for gallium within the porous glass are more pronounced than for gallium embedded into the opal, probably revealing a general trend to slow down mobility in confined liquid gallium with decreasing the pore size.

In conclusion, studies of nuclear spin relaxation for two gallium isotopes $^{69}$Ga and $^{71}$Ga in liquid gallium confined within nanoporous matrices 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. It was also observed that the rate of quadrupolar relaxation for confined liquid gallium depended on the magnetic field, which showed that the extreme narrowing approximation was no longer valid. The results obtained are consistent with the assumption about a strong increase in the correlation time of the electric field gradient fluctuations which reflects a remarkable slowing down atomic dynamics for liquid gallium in nanopores.

The present work was supported by the National Science Council of Taiwan under Grant No. 89-2112-M-006-039, by the Deutsche Forschungsgemeinschaft (DFG), and by RFBI.

[1] *Dynamics in Small Confining Systems,* edited by J. M. Drake, G. S. Grest, J. Klafter, and R. Kopelman (MRS, Warrendale, PA, 1999).
[2] S. Granick, Science **253**, 1374 (1991).
[3] S. Stapf, R. Kimmich, and R.-O. Seitter, Phys. Rev. Lett. **75**, 2855 (1995).
[4] S. H. Anastasiadis, K. Karatasos, G. Vlachos, E. Manias, and E. P. Giannelis, Phys. Rev. Lett. **84**, 915 (2000).
[5] J. Schuller, R. Richtert, and E. W. Fischer, Phys. Rev. B **52**, 15 232 (1995).
[6] C. Steck, Yu. B. Mel'nichenko, and R. Richter, Phys. Rev. B **53**, 5341 (1996).
[7] J.-P. Korb, M. Whaley-Hodges, T. Gobron, and R. G. Bryant, Phys. Rev. E **60**, 3097 (1999).
[8] P. Levitz, Europhys. Lett. **39**, 593 (1997).
[9] B. J. Loughnane and J. T. Fourkas, J. Phys. Chem. B **102**, 10 288 (1998).
[10] H. K. Christenson, J. Phys. Condens. Matter **13**, R95 (2001).
[11] J.-P. Korb, M. Whaley-Hodges, and R. G. Bryant, Phys. Rev. E **56**, 1934 (1997).
[12] J.-P. Korb, L. Malier, F. Cros, Shu Xu, and J. Jonas, Phys. Rev. Lett. **77**, 2312 (1996).
[13] R. Kimmich and H. W. Weber, Phys. Rev. B **47**, 11 788 (1993).
[14] M. Weber, A. Klemm, and R. Kimmich, Phys. Rev. Lett. **86**, 4302 (2001).
[15] K. M. Unruh, T. E. Huber, and C. A. Huber, Phys. Rev. B **48**, 9021 (1993).
[16] C. Tien, C. S. Wur, K. J. Lin, E. V. Charnaya, and Yu. A. Kumzerov, Phys. Rev. B **61**, 14 833 (2000).
[17] B. F. Borisov, E. V. Charnaya, T. Loeser, D. Michel, C. Tien, C. S. Wur, and Yu. A. Kumzerov, J. Phys. Condens. Matter **11**, 10 259 (1999).
[18] E. V. Charnaya, C. Tien, K. J. Lin, and Yu. A. Kumzerov, Phys. Rev. B **58**, 11 089 (1998).
[19] E. V. Charnaya, C. Tien, K. J. Lin, C.-S. Wur, and Yu. A. Kumzerov, Phys. Rev. B **58**, 467 (1998).
[20] A. L. Kerlin and W. G. Clark, Phys. Rev. B **12**, 3533 (1975).
[21] J. M. Titman, Phys. Rep. **33**, 1 (1977).
[22] A. Abragam, *Principles of Nuclear Magnetism* (Clarendon Press, Oxford, 1989).
[23] P. S. Hubbard, J. Chem. Phys. **53**, 985 (1970).
[24] J. Bosse, D. Quitmann, and C. Wetzel, Phys. Rev. A **28**, 2459 (1983).
[25] E. V. Charnaya, C. Tien, K. J. Lin, and Yu. A. Kumzerov, J. Phys. Condens. Matter **10**, 7273 (1998).
[26] D. Michel, B. F. Borisov, E. V. Charnaya, W.-D. Hoffmann, P. G. Plotnikov, and Yu. A. Kumzerov, Nanostruct. Mater. **12**, 515 (1999).
[27] H. Konrad, C. Karmonik, J. Weissmüller, H. Gleiter, R. Birringer, and R. Hempelmann, Physica (Amsterdam) **234B–236B**, 173 (1997).