PHYSICAL REVIEW B **70**, 052201 (2004)

Influence of confined geometry on nuclear spin relaxation and self-diffusion in liquid indium

E. V. Charnaya,[1,2] Cheng Tien,[1] Yu. A. Kumzerov,[3] and A. V. Fokin[3]

[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]*A.F.Ioffe Physico-Technical Institute RAS, St. Petersburg, 194021 Russia*

(Received 19 April 2004; published 23 August 2004)

The spin-lattice relaxation times for the ^{115}In isotope in liquid indium embedded into artificial opals and porous glass were found to be shortened remarkably compared to the bulk indium melt. The spin relaxation acceleration was ascribed mainly to the enhancement of the quadrupole contribution caused by the translational diffusion in liquid indium; the magnetic contribution was implied unchanged on the base of the Knight shift measurements and the Korringa relation. Calculations made for quadrupole relaxation showed that it dominated the spin relaxation process for indium in nanopores and that the correlation times of atomic motion increased by more than a factor of 6 depending on pore sizes. The increase in the correlation time evidenced drastic slowing down the atomic diffusion for confined melted indium.

DOI: 10.1103/PhysRevB.70.052201 PACS number(s): 61.25.Mv, 66.30.Pa, 68.65.−k, 76.60.−k

When liquids are embedded into nanoporous matrices their physical properties can be strongly affected by confinement conditions. In particular, the self-diffusion process within nanopores was shown to alter noticeably for many inorganic and organic liquids and their freezing and liquid-vapor phase transitions were shifted compared to bulk (see, for instance, Refs. 1–4 and references therein). The reduction of the freezing temperatures was also observed for some melted metals like mercury, gallium, and indium embedded into porous glasses and artificial opals (see Refs. 5–7 and references therein). However, atomic mobility in confined metallic melts was studied only for gallium[8] while this matter is of great importance for many physical and technological applications, especially in relation with the general problem of electronic device miniaturization.

In the present paper we will show that the self-diffusion in liquid indium embedded into nanoporous matrices is strongly slowed down compared to that in bulk melted indium. The slowdown of atomic mobility manifests itself as drastic acceleration of nuclear spin relaxation for confined liquid indium caused by enhancement of the quadrupole contribution to total relaxation.

Measurements of nuclear spin-lattice relaxation were carried out for the isotope ^{115}In in liquid metallic indium embedded into artificial opals and a porous glass. The opals under study consisted of close-packed silica spheres with diameters of about 240 and 210 nm. Hereinafter they will be referred to as Opal-1 and Opal-2. The porous glass had pores of about 7 nm in diameter. Liquid indium was introduced into the porous glass and between adjoined spheres in opals under high pressure. The pore filling factor was about 50%. Relaxation measurements were performed in magnetic field of 9.4 T (the NMR spectrometer operating frequency was about 88 MHz). The inversion recovery procedure was used to obtain the longitudinal magnetization versus time dependences. The Knight shift and NMR lineshape were also measured for ^{115}In as well as for ^{113}In. The ^{115}In line position in a 1 mol. water solution of indium sulphate was used as a reference. Similar measurements were performed also for bulk liquid indium.

The melting and freezing temperatures for confined indium in the samples under study were reduced compared to the bulk melting point (429.7 K) due to thermodynamic size effects in agreement with calorimetric studies of indium in porous glasses[5] and in discontinuous thin indium films.[9,10] According to our NMR data, the offset of melting indium in all porous matrices under study was between 422 and 425 K. However, liquid indium within pores can be supercooled to lower temperatures, thus, NMR measurements for confined indium were carried out within a range of 412 to 435 K. No regular temperature dependences of the longitudinal magnetization restoration rate or linewidth exceeding the experimental accuracy limits were observed. A weak decrease of the Knight shift with increasing temperature was seen, however it did not exceed that for bulk melted indium[11] and was actually within the experimental error because of strong NMR line broadening. The relevant NMR characteristics for bulk liquid indium were measured above 426 K; indium can be easily supercooled to this temperature.

The ^{115}In longitudinal magnetization restoration curves obtained at 415 K for the opal and porous glass samples are shown in Fig. 1. At that temperature the indium on the sample surface remains solid. Therefore, one can be sure that signals from the confined melts are not superimposed on those arisen from the melted surface indium. Figure 1 shows also the restoration curve for bulk indium obtained at 430 K.

The remarkable enhancement of spin-lattice relaxation for confined indium compared to relaxation in bulk is seen in Fig. 1. For the opals the relaxation rate increased by more than a factor of 4. The relaxation acceleration is even more pronounced for indium within the porous glass. It is well known that spin relaxation in liquid nontransition metals for nuclei with spin $I > \frac{1}{2}$ occurs mainly due to two independent contributions—the interaction of the nuclear magnetic moment with conduction electrons and the interaction of the nuclear quadrupole moment with electric field gradients produced by atomic motion in melts.[11,12] The relative effectiveness of the contributions differs for different metals and depends, in particular, on the value of nuclear quadrupole

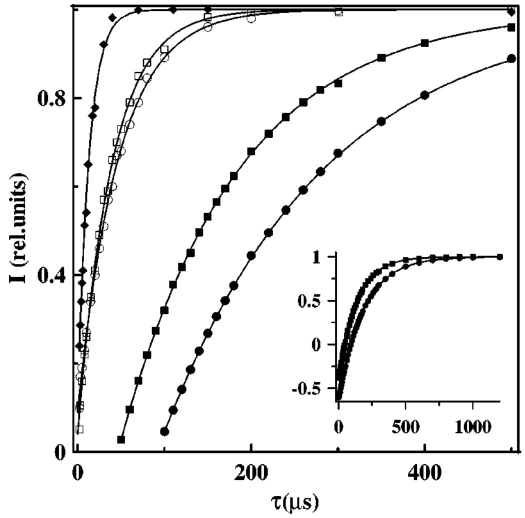

FIG. 1. ^{115}In longitudinal magnetization recovery curves (I is the integral intensity of NMR signals; τ is the time between first and second pulses) for melted indium embedded into the porous glass (closed diamonds), Opal-1 (open circles), and Opal-2 (open squares), for bulk liquid indium (closed circles), and for melted indium on the surface of Opal-1 (closed squares). The inset shows full recovery curves for bulk and surface liquid indium. Solid lines are single exponentials with T_1 listed in Table.

moments and on the correlation time of atomic motion.[11,13,14] The ^{115}In isotope having a large quadrupole moment, the quadrupole contribution to relaxation in the bulk indium melt is expected to be significant.[12] Thus, the drastic acceleration of spin-lattice relaxation in confined liquid indium can arise because of increasing either the magnetic or the quadrupole contribution.

The most convenient way to separate the two contributions which was used for bulk rubidium, antimony, and gallium melts (see Ref. 12 and references therein) and for confined liquid gallium[8] is to measure the spin relaxation rate for two isotopes with different magnetic and quadrupole moments. However, while indium has two naturally occurring isotopes, ^{115}In and ^{113}In, they have the same spin $I=\frac{9}{2}$ and almost identical nuclear gyromagnetic ratios γ_n, 5.8845 $\times 10^7$ rad$\cdot T^{-1}\cdot$s^{-1} and 5.8972$\times 10^7$ rad$\cdot T^{-1}\cdot$s^{-1}, and quadrupole moments Q, 0.799 barn and 0.81 barn, for ^{115}In and ^{113}In,[15] respectively. It prevents the separation of magnetic and quadrupole relaxation from a comparison of the two isotopes. In addition, the natural abundance of the ^{113}In isotope is very low and relaxation measurements for it need too much time. Nevertheless, one can estimate the possible alteration of the magnetic contribution for the opals and porous glass compared to bulk using the Korringa relation between the spin-lattice relaxation time caused by the interaction with conduction electrons T_{1m} and the Knight shift K_s of the NMR line: $T_{1m}TK_s^2=\text{const}/(\gamma_n K)$, where T is the temperature and K is the correction factor which accounts for the effects of electron correlation and exchange.

Our measurements of NMR line positions for bulk and confined liquid indium showed that the Knight shift in the opals coincided with that in bulk within the experimental accuracy limits (Fig. 2). The Knight shift in the porous glass was slightly decreased compared to bulk by about 100 ppm, that is, by about 1% of the Knight shift in the bulk indium melt (Fig. 2). The fact that the Knight shift remained almost unchanged indicates clearly that the magnetic contribution to nuclear spin relaxation for confined liquid indium remained unchanged also. Thus, we should ascribe the relaxation acceleration to the enhancement of the quadrupole contribution.

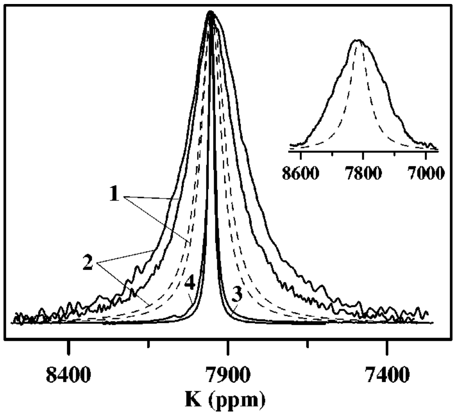

FIG. 2. ^{115}In NMR lines for melted indium embedded into Opal-2 (1) and Opal-1 (2), for bulk liquid indium (3), and for melted indium on the surface of Opal-1 (4). The inset shows ^{115}In NMR lines for melted indium within the porous glass. Solid lines show experimental NMR lines and dashed lines show NMR lines calculated on the basis of the equality $T_2=T_1$. For bulk and surface liquid indium the experimental NMR lines coincided with the calculated ones.

The general consideration of quadrupole relaxation in liquids has shown that when the spin I of nuclei is larger than 1, the restoration of longitudinal as well as transverse magnetization is described by a sum of exponentials.[16] However, for bulk liquid indium as well as for other bulk metallic melts, the extreme narrowing approximation corresponding to the case of fast atomic motion is normally valid.[11] Within the framework of the extreme narrowing approximation the spectral densities of the electric field gradient correlation function at the nuclear site reduce to the spectral density at zero frequency $J_{00}(0)$, all exponents become equal to each other, and the relaxation process can be described by a single exponential.[13] As we will show below, the extreme narrowing approximation remains still valid for liquid indium within the opal and porous glass samples under study, thus simplifying the treatment of the quadrupole relaxation for confined indium.

In the fast atomic motion limit, quadrupole relaxation is described by a conventional relaxation equation $dM_z/dt=(M_z^o-M_z)/T_{1q}$, where M_z^o is the equilibrium magnetization and the spin-lattice relaxation rate T_{1q}^{-1} due to quadrupole interaction is given by[13]

$$T_{1q}^{-1}=\frac{3}{2}\left(\frac{eQ}{\hbar}\right)^2\frac{2I+3}{I^2(2I-1)}J_{00}(0), \tag{1}$$

where e is the electron charge. The relationship (1) can be rewritten as $T_{1q}^{-1}=C\tau_c$, where τ_c, is the correlation time of

TABLE I. ^{115}In spin-lattice relaxation rate T_1^{-1} (measured at 415 K for confined indium and at 430 K for bulk and surface indium), rate of quadrupole relaxation T_{1q}^{-1}, correlation time of atomic motion τ_c, and linewidth at half-height δ for the samples under study, bulk indium and indium on the surface of Opal-1. T_{1q}^{-1} and τ_c are calculated starting from two values of T_{1q}^{-1} in bulk liquid indium, 3200 s^{-1} (upper lines) and 1900 s^{-1} (lower lines), as discussed in the text.

	Bulk In	In in Opal-1	In in Opal-2	In in porous glass	In on surface
T_1^{-1} (s^{-1})	5320 ± 50	$21\,300 \pm 800$	$25\,700 \pm 1200$	$77\,000 \pm 15\,000$	7340 ± 90
T_{1q}^{-1} (s^{-1})	3200	19 200	23 600	75 000	5220
	1900	17 900	22 300	73 000	3920
τ_c (μs 10^{-6})	12	71	87	280	19.3
		113	140	460	24.5
δ (ppm)	19.4	166	235	510	26.5

atomic motion, and C is a constant proportional to the squared product of the nuclear quadrupole moment and static electric field gradient at the nuclear site. Thus, the total longitudinal magnetization restoration process should be described by a single exponential with the spin-lattice relaxation time T_1 given by

$$T_1 = (T_{1m}^{-1} + C\tau_c)^{-1}. \tag{2}$$

Implying T_{1m} not to be influenced by confined geometry in agreement with the Korringa relation, we must suggest that the acceleration of magnetization restoration is caused by enhancement of the $C\tau_c$ term.

The quadrupole and magnetic contributions to spin relaxation of the ^{115}In isotope for bulk liquid indium were separated in Refs. 17 and 18 based upon temperature dependences of the relaxation rate. The quadrupole contribution for ^{115}In was also estimated theoretically.[17,19] Theoretical models taking into account electric field gradients produced by conduction electrons predict for the quadrupole relaxation rate $C\tau_c$ in bulk a value of about 3200 s^{-1} (Ref. 19) and 1900 s^{-1} (Ref. 17) near the melting point, while from experiment $C\tau_c < 1900$ s^{-1}.[11,17] In our further estimates for the quadrupole relaxation rate in confined liquid indium we will use both the above values of $C\tau_c$ in bulk. The total spin-lattice relaxation rate T_1^{-1} measured by us for bulk liquid indium just near the melting point is 5320 s^{-1} ($T_1 = 188$ μs) (Fig. 1 and Table I), in the very good agreement with earlier data.[11] Thus, if we assume for $C\tau_c$ in bulk the value 3200 s^{-1}, the relaxation rate due to the magnetic contribution $T_{1m}^{-1} = 2120$s^{-1}, while for a $C\tau_c$ value of 1900 s^{-1} $T_{1m}^{-1} = 3420$ s^{-1}. This allows calculating the quadrupole relaxation rates for the opals and porous glass. All the $C\tau_c$ values obtained are listed in Table I. It follows from the estimates for $C\tau_c$ that the quadrupole relaxation rate increased more than by a factor of 6 in both opal samples and by a factor of 20 in the porous glass, this conclusion keeps valid independently of assumptions made for quadrupole relaxation in bulk indium. Moreover, quadrupole relaxation is seen from Table I to become dominant for liquid indium within the porous matrices.

The quadrupole relaxation rate can be enhanced because of the increase in the C constant or due to increase in the correlation time τ_c. The spectral density at zero frequency, which determines the value of C, depends on structure of melts.[13] It is known that the structure of liquids confined within pores with sizes greater than 4 nm does not change compared to bulk;[1,4] this agrees with x-ray patterns for melted indium within the samples under study obtained by us. Thus, it is unlikely that C could increase enough to induce the observed acceleration of the relaxation rate for confined indium. Therefore, we can assume that alterations in relaxation arise mainly due to the increase in the correlation time of the atomic movements. The correlation time in bulk can be estimated from the known value for the self-diffusion coefficient D just above the melting point $\tau_c = d^2/6D$, where d is average interatomic distance.[11,12] For d and D taken from Refs. 20 and [21] and [22], respectively, we have $\tau_c \sim 12 \times 10^{-12}$ s in agreement with Ref. 17 The values of τ_c for confined liquid indium calculated under the assumption of constant C are listed in Table I. It is easy to see that the product $\omega_o \tau_c$ (ω_o is the Larmor frequency) remains much less than unity, which validates the extreme narrowing approximation assumed.

The increase of the correlation times of atomic motion for liquid indium in the opals and porous glass estimated from the spin relaxation measurements evidences a drastic slowing down of the translational diffusion in confined indium melt. Since alterations in spin relaxation are more noticeable for the porous glass with the finest pores among the samples under study, and then for Opal-2, which consists of smaller silica spheres compared to Opal-1 and therefore has smaller pores, we can presume the general trend to exist for the slowdown of atomic motion in liquid indium with decreasing pore sizes. The remarkable slowdown of the self-diffusion was also observed in liquid gallium within nanoporous matrices,[8] in thin gallium films[23] and for isolated gallium particles.[24]

The increase in the correlation time for indium within pores should also influence the quadrupole contribution to transverse spin relaxation. Within the framework of the extreme narrowing approximation, the longitudinal and transverse relaxation times are equal to each other, thus T_2 for liquid indium should be given by the relationship (2).[16] On the other hand, the acceleration of transverse spin relaxation in liquids leads to the NMR line broadening. As is seen from Fig. 2 and Table I, the experimental resonance lines for confined melts are much broader than in bulk. It agrees with shortening the spin-lattice relaxation time for indium within the porous matrices. However, the NMR lines for confined indium calculated using the equality $T_2 = T_1$ are narrower than the experimental ones (see Fig. 2), which evidences the influence of some additional mechanism of broadening. Similar excess NMR line broadening was observed for liquid gallium in confined geometry.[8] Note that some strong NMR line broadening similar to that found for ^{115}In was also seen for the ^{113}In isotope.

We also observed the ^{115}In spin-lattice relaxation acceleration and line broadening for a thin film of melted indium on the surface of Opal-1 (Figs. 1 and 2). The film thickness was not quite homogeneous, but its average value can be estimated as 5 microns. Following the above used outlines, we calculated changes in the correlation time for this film (see Table I). The results allow us to suggest that the slowdown of the atomic diffusion in liquid metallic indium is noticeable even for dimensions of 5 microns.

In conclusion, NMR studies of spin-lattice relaxation for the ^{115}In isotope in liquid metallic indium confined within two different opal matrices and within a porous glass revealed the remarkable enhancement of the relaxation rate compared to bulk liquid indium. The relaxation acceleration was more pronounced for the samples with smaller pores. The magnetic and quadrupole contributions to the total spin relaxation process in confined geometry were separated using the Korringa relation between the time of magnetic relaxation due to interaction with conduction electrons and the Knight shift, data for bulk liquid indium, and the fact that the Knight shift was not practically influenced by confinement. The quadrupole contribution was shown to increase drastically for the indium melt in nanopores and to dominate spin relaxation. The quadrupole relaxation enhancement was ascribed to the increase of the correlation times of atomic motion in liquid indium and consequently to the decrease of the self-diffusion coefficient. The NMR line broadening for both indium isotopes in confined melts was mainly related to shortening the T_2 time which is also caused by the increase of quadrupole relaxation.

The present work was supported by the National Science Council of Taiwan under Grant No. 92-2811-M-006-014.

---

[1] *Dynamics in Small Confining Systems V*, edited by J.M. Drake J. Klafter P.E. Levitz R.M. Overney, and M. Urbakh (MRS, Warrendale, PA, 2001).

[2] P. Levitz, J.P. Korb, and D. Petit, Eur. Phys. J. E **12**, 29 (2003).

[3] M. Weber, A. Klemm, and R. Kimmich, Phys. Rev. Lett. **86**, 4302 (2001).

[4] H.K. Christenson, J. Phys.: Condens. Matter **13**, R95 (2001).

[5] K.M. Unruh, T.E. Huber, and C.A. Huber, Phys. Rev. B **48**, 9021 (1993).

[6] E.V. Charnaya, D. Michel, C. Tien, Yu.A. Kumzerov, and D. Yaskov, J. Phys.: Condens. Matter **15**, 5469 (2003).

[7] B.F. Borisov, E.V. Charnaya, P.G. Plotnikov, W.-D. Hoffmann, D. Michel, Yu.A. Kumzerov, C. Tien, and C.-S. Wur, Phys. Rev. B **58**, 5329 (1998).

[8] E.V. Charnaya, T. Loeser, D. Michel, C. Tien, D. Yaskov, and Yu.A. Kumzerov, Phys. Rev. Lett. **88**, 097602 (2002).

[9] M. Zhang, M.Yu. Efremov, F. Schiettekatte, E.A. Olson, A.T. Kwan, S.L. Lai, T. Wisleder, J.E. Greene, and L.H. Allen, Phys. Rev. B **62**, 10 548 (2000).

[10] M.Yu. Efremov, F. Schiettekatte, M. Zhang, E.A. Olson, A.T. Kwan, R.S. Berry, and L.H. Allen, Phys. Rev. Lett. **85**, 3560 (2000).

[11] J.M. Titman, Phys. Rep. **33**, 1 (1977).

[12] F.A. Rossini and W.D. Knight, Phys. Rev. **178**, 641 (1969).

[13] J. Bosse, D. Quitmann, and C. Wetzel, Phys. Rev. A **28**, 2459 (1983).

[14] W.W. Warren, Phys. Rev. A **10**, 657 (1974).

[15] *CRC Handbook of Chemistry and Physics* (CRC, Boca Raton, FL, 1998).

[16] A. Abragam, *Principles of Nuclear Magnetism* (Clarendon, Oxford, 1989).

[17] F.A. Rossini, E. Geissler, E.M. Dickson, and W.D. Knight, Adv. Phys. **16**, 287 (1967).

[18] W.W. Warren and W.G. Clark, Bull. Am. Phys. Soc. **11**, 916 (1966).

[19] C.A. Sholl, Proc. Phys. Soc. London **91**, 130 (1967).

[20] T. Iida and R.I.L. Guthrie, *The Physical Properties of Liquid Metals* (Clarendon, Oxford, 1993).

[21] G. Mathiak, A. Griesche, K.H. Kraatz, and G. Frohberg, J. Non-Cryst. Solids **205–207**, 412 (1996).

[22] R.E. Eckert and H.G. Drickamer, J. Chem. Phys. **20**, 13 (1952).

[23] H. Konrad, J. Weissmüller, R. Birringer, C. Karmonik, and H. Gleiter, Phys. Rev. B **58**, 2142 (1998).

[24] C. Tien, E.V. Charnaya, P. Sedykh, and Yu.A. Kumzerov, Phys. Solid State **45**, 2352 (2003).