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Slowdown of self-diffusion induced by partial freezing in confined liquid indium

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A remarkable slowdown of self-diffusion was found by NMR in liquid metallic indium confined within nanopores of an opal photonic crystal which becomes more pronounced within temperature ranges of diffused freezing and melting of indium. The additional decrease in atomic mobility in the confined melt upon partial indium freezing was shown to correlate with the portion of unfrozen liquid rather than immediately with temperature.

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One of the most intriguing problems facing the physics of low-dimensional systems concerns the influence of size effects and restricted geometry on such universal phenomena as diffusion at the atomic or molecular level. In particular, self-diffusion in liquids embedded into porous matrices has attracted a large amount of attention of experimenters and theoreticians over last years.[1–4] From the fundamental point of view this topic is of importance for a better understanding the role of pore sizes, interaction of liquids with the inner pore surface, and geometry and connectivity of the pore network in atomic or molecular mobility in confined liquids as well as for predicting dynamic properties of thin films and small drops. On the other hand, studies of dynamics in liquids within pores are of continuously increasing interest for various applications in technology, engineering, and chemistry, as well as in medicine and biology, since they improve our knowledge about, for instance, flow through rocks, concretes, and biological tissues, catalytic processes, and some aspects of the fabrication of nanostructures.

The key point of self-diffusion in liquids within porous matrices is the temperature variations of atomic or molecular mobility which are closely related to the nature of confinement-induced effects. The peculiarities of diffused crystallization and melting in confined liquids compared to bulk which were found lately[5] raise a general question whether mobility in liquids within nanoporous matrices is changed or not in the vicinity of those phase transitions. While the answer to this question could elucidate many aspects of the first-order phase transitions in restricted geometry, the influence of the crystallizing and melting processes on self-diffusion in liquids within pores is studied poorly and mostly for water and some organic materials (see Refs. 6–8 and references therein). It was shown that the temperature dependence of self-diffusion depends on whether the bulk-like liquid in pore centers or liquid near pore walls is examined; the mobility and freezing of those two parts of confined liquids differ remarkably (see Refs. 5–9 and references therein). For metallic melts embedded into nanoporous matrices the atomic mobility evolution upon melting and solidification was not in the least discussed. Meanwhile, the variations with temperature of self-diffusion in liquid metals within pores could be utterly different from that for the above-mentioned liquids since their behavior was found to be quite homogeneous and they do not reveal any division into "surface" and "core" parts (Refs. 10–14 and references therein). The more intricate problem is whether the temperature evolution of self-diffusion caused by confinement in particular liquids is driven by temperature itself or, under partial solidification, by other factors like the portion of the melt in pores. This problem remains open up to the present. The confinement conditions provide an opportunity to elucidate the matter since the temperature ranges where the crystalline and melted fractions coexist are shifted relative to each other upon warming and cooling and therefore the amount of the unfrozen liquid depends not only on temperature but also on the thermal history of the sample under study. In the present paper a drastic additional slowdown of self-diffusion in liquid metallic indium confined within nanopores of an opal photonic crystal through the melting and freezing phase transitions against the background of confinement-induced decrease in atomic mobility in completely melted indium will be shown, this additional slowdown correlating with the portion of unfrozen liquid.

Atomic diffusion was studied using ^{115}In nuclear spin-lattice relaxation in liquid metallic indium as a probe since both the self-diffusion and quadrupole contribution to the spin relaxation rate are directly related to the correlation time of atomic mobility.[15] The opal photonic crystal used as a porous matrix consisted of close-packed silica spheres with diameters of about 210 nm. (More details about opal photonic crystals are given in Ref. 16 and references therein.) Such an ideal structure should have octahedral and tetrahedral pores between adjacent spheres the radii of which are $r_1 = 0.414R$ and $r_2 = 0.224R$, respectively (R is the radius of constituent silica spheres). Mercury intrusion porosimetry for the porous matrix under study revealed a pore size distribution between 19 and 35 nm with distinct maxima at two radii of 30 nm and 20 nm. Liquid indium was introduced between adjoined spheres in the opal photonic crystal under high pressure. The pore filling factor evaluated by weighing the sample before measurements was 60%. Relaxation measurements were carried out by NMR in a magnetic field of 9.4 T using a NMR pulse spectrometer at the operating frequency ≅88.3 MHz. The inversion recovery procedure was used to obtain the longitudinal magnetization versus time dependences. The 90° pulse was 4 μs, repetition time 150 ms. Number of scans varied from 2048 to 10 240.

To control the melting and solidification processes and to get information about the relative amount of unfrozen indium, the integral intensity of the NMR signal from liquid

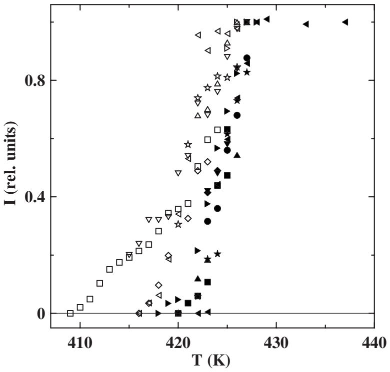

FIG. 1. Temperature variations of the integral intensity I of the ^{115}In NMR signal from confined liquid indium upon warming (solid symbols) and cooling (open symbols). Different symbols correspond to different thermocycles.

indium was measured upon warming and cooling. The intensity of NMR signal I as a function of temperature relative to the intensity of the NMR signal obtained at temperatures where total confined indium was melted is shown in Fig. 1 for different warming-cooling cycles. Both melting and freezing for confined indium in the sample under study were diffused and the melting and freezing temperatures were pronouncely 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[10] and in discontinuous thin indium films.[17,18] The freezing process could occur in a different way depending on the highest temperature achieved upon warming, thus providing the opportunity for relaxation measurements at the same temperature for various full amounts of unfrozen indium. The melting process was complete until 428 K.

The ^{115}In longitudinal magnetization restoration curves obtained at 427 and 419 K are shown in Fig. 2. They correspond to totally melted indium and to partly frozen indium ($I=0.03$), respectively. Figure 2 shows also the restoration curve for bulk indium obtained at 430 K. One can see a remarkable enhancement of spin-lattice relaxation for totally melted confined indium compared to relaxation in bulk, reported also in Ref. 14. Even stronger enhancement of the spin restoration rate occurs at the lower temperature and reduced relative intensity corresponding to coexistence of liquid and frozen indium within pores.

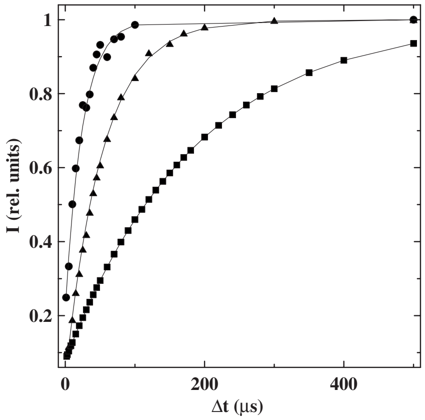

FIG. 2. ^{115}In nuclear magnetization restoration curves for confined liquid indium obtained at 427 K (triangles) and 419 K (circles) and for bulk melted indium (squares) obtained at 430 K.

The nuclear spin-lattice relaxation acceleration for confined liquid indium is closely related to the slowdown of indium self-diffusion within nanopores. It is well known that spin relaxation in liquid nontransition metals for nuclei with spin $I>1/2$ occurs mainly due to two competing 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.[19,20] The relative effectiveness of the contributions depends, in particular, on the value of nuclear quadrupole moments and on the correlation time of atomic motion.[19,21,22] The ^{115}In isotope having a large quadrupole moment [$Q=0.799$ barn (Ref. 23)], the quadrupole contribution to relaxation in the bulk indium melt is significant.[20] Thus, the drastic acceleration of spin-lattice relaxation in confined liquid indium can arise because of increasing either the magnetic or the quadrupole contribution.

One can estimate the possible alteration of the magnetic contribution for the sample under study compared to bulk using the Korringa relation[15] 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: $T_{1m}TK_s^2=\mathrm{const}/(\gamma_n K)$, where T is the temperature, γ_n is the nuclear gyromagnetic ratio, 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 opal photonic crystal coincided with that in bulk [K_s in bulk liquid indium at 430 K referred to the ^{115}In signal in 1 mol water solution of indium sulfate at 295 K was equal to (7950 ± 3) ppm] within the experimental accuracy limits in agreement with Ref. 14 and its temperature variations also did not exceed the experimental accuracy of about ±10 ppm. This fact indicates clearly that the magnetic contribution to nuclear spin relaxation for confined liquid indium remained unchanged also. Thus, we should ascribe the relaxation acceleration observed to the enhancement of the quadrupole contribution.

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.[15] 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.[19] Within the framework of this 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.[21] As we will show below, the extreme narrowing approximation remains still valid for liquid indium within the opal photonic crystal under study in the whole temperature range of melting and freezing, 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 with the spin-lattice relaxation rate T_{1q}^{-1} due to the quadrupole interaction given by[21]

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

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 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 is described by a single exponential with the spin-lattice relaxation rate T_1^{-1} given by $T_1^{-1}=T_{1m}^{-1}+C\tau_c$. Implying T_{1m} not to be influenced by confined geometry, we must suggest that the acceleration of relaxation is caused by enhancement of the quadrupole term $C\tau_c$.

The quadrupole contribution to spin relaxation for the ^{115}In isotope in bulk liquid indium was found experimentally and theoretically in Refs. 24–26. 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. 26) and 1900 s^{-1} (Ref. 24) near the melting point, while from experiment $C\tau_c < 1900\ \text{s}^{-1}$ (Refs. 19 and 24). The total spin-lattice relaxation rate T_1^{-1} measured by us for bulk liquid indium just near the melting point at 430 K is 5320 s^{-1} ($T_1=188\ \mu\text{s}$) (Fig. 2), in very good agreement with Refs. 14 and 19. 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} is 2120 s^{-1}, while, for a $C\tau_c$ value of 1900 s^{-1}, $T_{1m}^{-1}=3420\ \text{s}^{-1}$. We will use these two values of T_{1m}^{-1} in our further calculations of the quadrupole contribution to spin relaxation in confined indium. According to the Korringa relation and since the temperature dependence of the Knight shift is weak, the magnetic contribution to the spin relaxation rate should follow the linear temperature dependence, thus decreasing by a factor of 0.95 at a minimal temperature of 410 K in our measurements. While such small alterations are actually within accuracy of our measurements, we took them into consideration in our calculations of temperature changes of the quadrupole relaxation rate for confined liquid indium.

The quadrupole relaxation rate can be enhanced because of the increase in the constant C or due to the increase in the correlation time τ_c. The low-frequency spectral density, which determines the value of C, depends on structure of melts.[21] It is known that the structure of liquids confined within pores with sizes greater than 4 nm does not change compared to bulk;[1,5] this agrees with x-ray patterns for melted indium within the sample under study obtained by us. Therefore, we can assume that alterations in relaxation arise mainly due to the increase in the correlation time of 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 the average interatomic distance.[19,20] For d and D taken from Refs. 27–29, respectively, we have $\tau_c \sim 12\times10^{-12}$ s, in agreement with Ref. 20.

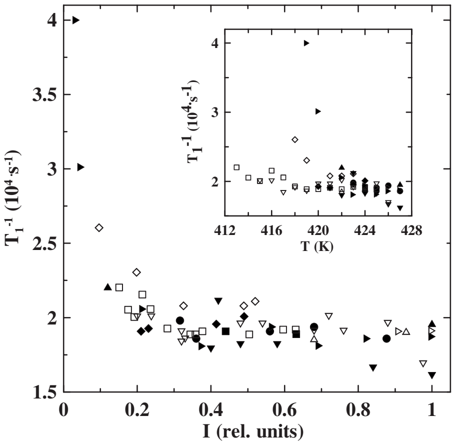

FIG. 3. The ^{115}In spin-lattice relaxation rate T_1^{-1} versus the integral intensity of the NMR signal upon warming (solid symbols) and cooling (open symbols). Different symbols correspond to different thermocycles. The inset shows the temperature dependences of T_1^{-1}.

The average value of τ_c for confined liquid indium calculated from our measurements at $I=1$ when the total indium was in the melted state was 6.1×10^{-11} s and 9.5×10^{-11} s for T_{1m}^{-1} in bulk indium equal to 2120 s^{-1} and 3420 s^{-1}, respectively. It follows from these estimates that the correlation time increased more than by a factor of 5 for indium in the opal photonic crystal under study. As a result, quadrupole relaxation became dominant for liquid indium within the pores.

Measurements of T_1 at various temperatures and various relative intensities of the NMR signal revealed clear correlations between the relaxation time and the relative intensity of the NMR signal—that is, the portion of unfrozen confined indium (Fig. 3). In contrast, no evident correlations were found between the relaxation time and temperature as is shown in the inset in Fig. 3. Thus, the additional acceleration of nuclear spin-lattice relaxation in confined liquid indium is driven by the amount of unfrozen indium within pores rather than by temperature itself. And as follows from the above analysis this acceleration occurs mainly due to the enhancement of the quadrupole contribution. It should be noted that our NMR measurements cannot provide information on whether indium confined in a particular pore crystallizes gradually or abruptly through the diffusive freezing phase transition, but the correlations mentioned above testify rather for the gradual solidification within a particular pore.

The dependence of the correlation time on the relative intensity of NMR signal is shown in Fig. 4 when $T_{1m}^{-1}=3420\ \text{s}^{-1}$ was assumed for bulk. A similar curve can be plotted for another estimate of T_{1m}^{-1}. One can see that the correlation time increases by 3 times upon decreasing the relative amount of melted indium from 1 to 0.03. Note that the product $\omega_0\tau_c$ (ω_0 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 confined liquid indium evidences drastic slowing down the translational diffusion in confined indium melt since the cor-

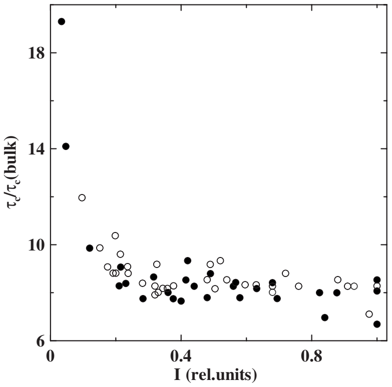

FIG. 4. The correlation time of atomic mobility τ_c in confined liquid indium relative to that in bulk versus the integral intensity of the ^{115}In NMR signal through the melting and freezing phase transitions. Here T_{1m}^{-1} was assumed to be 3420 s^{-1} at 430 K. Solid symbols correspond to warming, open symbols to cooling.

relation time is proportional to the self-diffusion coefficient.[15] The slowdown of self-diffusion becomes more pronounced at partial freezing. Note that the remarkable slowdown of self-diffusion was also observed near room temperature in liquid gallium within nanoporous matrices,[11] in thin gallium films,[30] and in isolated gallium particles[31] and at reduced temperatures in liquid gallium embedded into porous glasses.[12]

The increase in the correlation time for indium within pores upon decreasing the amount of the unfrozen melt 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.[15] On the other hand, the acceleration of transverse spin relaxation in liquids leads to the NMR line broadening. Actually, the lines for indium within pores are much broader than in bulk and the linewidth increases with decreasing the amount of unfrozen indium from 190 ppm at $I=1$ down to 240 ppm at $I=0.03$ while the linewidth in bulk is about 19 ppm. However, the NMR lines for confined indium calculated using the equality $T_2=T_1$ are narrower than the experimental ones, which evidences the influence of some additional mechanism of broadening. Similar excess NMR line broadening was observed for liquid gallium and indium within nanopores in Refs. 11 and 14.

In conclusion, NMR studies of the spin-lattice relaxation for the ^{115}In isotope in liquid metallic indium confined within pores of an opal photonic crystal revealed the remarkable enhancement of the relaxation rate under the conditions of partial indium freezing compared to bulk liquid indium against the background of spin relaxation acceleration in the indium melt within nanopores. The additional relaxation acceleration depended on the portion of unfrozen indium while no clear correlations were found between temperature and enhancement of relaxation. The magnetic and quadrupole contributions to total spin relaxation in confined geometry were separated and the quadrupole contribution was shown to be responsible for the relaxation enhancement. Quadrupole relaxation being directly related with the correlation time of atomic motion in liquid indium and consequently with the self-diffusion coefficient, the results obtained manifest the drastic slowdown of self-diffusion in confined indium within the temperature range of the freezing and melting phase transitions in addition to the general slowdown of confined indium self-diffusion compared to bulk. The decrease of the self-diffusion coefficient under partial indium crystallization follows the portion of unfrozen indium within pores rather than temperature.

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[1] *Dynamics in Small Confining Systems V*, edited by J. M. Drake *et al.* (Materials Research Society, Warrendale, PA, 2001).

[2] J. Karger and D. M. Ruthven, *Diffusion in Zeolites and Other Microporous Solids* (Wiley, New York, 1992).

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

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

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

[6] K. Overloop and L. Van Gerven, J. Magn. Reson., Ser. A **101**, 179 (1993).

[7] J. Banys *et al.*, J. Phys.: Condens. Matter **17**, 2843 (2005).

[8] E.-M. Choi *et al.*, Phys. Rev. Lett. **95**, 085701 (2005).

[9] D. Wallacher *et al.*, Phys. Rev. B **69**, 134207 (2004).

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

[11] E. V. Charnaya *et al.*, Phys. Rev. Lett. **88**, 097602 (2002).

[12] E. V. Charnaya *et al.*, Phys. Rev. B **72**, 035406 (2005).

[13] Cheng Tien *et al.*, Phys. Rev. B **74**, 024116 (2006).

[14] E. V. Charnaya *et al.*, Phys. Rev. B **70**, 052201 (2004).

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

[16] C. Lopez, Adv. Mater. (Weinheim, Ger.) **15**, 1679 (2003).

[17] M. Zhang *et al.*, Phys. Rev. B **62**, 10548 (2000).

[18] M. Yu. Efremov *et al.*, Phys. Rev. Lett. **85**, 3560 (2000).

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

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

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

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

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

[24] F. A. Rossini *et al.*, Adv. Phys. **16**, 287 (1967).

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

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

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

[28] G. Mathiak *et al.*, J. Non-Cryst. Solids **205-207**, 412 (1996).

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

[30] H. Konrad *et al.*, Phys. Rev. B **58**, 2142 (1998).

[31] C. Tien *et al.*, Phys. Solid State **45**, 2352 (2003).