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The Knight shift in liquid gallium confined within porous glasses and opals

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Abstract

⁷¹Ga nuclear magnetic resonance studies were carried out for liquid gallium embedded into porous glasses with different pore sizes and into artificial opals within the temperature range from about 320 K to complete confined gallium freezing. A general decrease in the Knight shift compared to the bulk melt depending on pore sizes was observed in contrast to theoretical predictions. Correlations between alterations in the Knight shift and pore sizes were established for particular pore geometry. It was also observed that confined geometry affects the temperature dependence of the Knight shift in liquid gallium.

1. Introduction

Recently, a great deal of attention was focused on surface and size effects induced by confined geometry. Properties of materials embedded into porous matrices with nanometre pore sizes were shown to differ remarkably from those in bulk. In particular, metals confined within porous glasses and artificial opals manifest pronounced alterations in their superconducting behaviour [1–3], atomic mobility in the melted state [4], melting and freezing processes (see [5] and references therein) and crystalline structure [6, 7]. Since metals embedded into nanoporous matrices form networks of small particles whose sizes depend on pore diameter, one could also expect noticeable changes in their electronic properties as predicted for isolated metallic particles and thin layers [8–11]. In addition to the surface induced and quantum size effects, electronic features of confined metals could be influenced by interaction with the inner surface of matrices and between particles in pores.

The effects induced by confinement allow the experimental verification by nuclear magnetic resonance (NMR) through studies of the Knight shift, which was proved to be a

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powerful probe of condensed-matter systems [12]. However, until now no special attempts were made to investigate the Knight shift for confined metals. Moreover, all NMR experimental studies of electronic properties for small isolated or supported metallic particles and thin layers were performed for metals in the solid state [8, 12–21] when size effects in the Knight shift produce some strong inhomogeneous NMR line broadening, which generally leads to a complex lineshape and to a deviation of the line centre of gravity relative to the intensity maximum. The strong resonance line broadening prevents clear observation of size dependence of the Knight shift. In contrast to the case of solid metals, one can expect that NMR lines for liquid nanoparticles should be narrowed due to atomic mobility. Then the Knight shift measured would correspond to the whole particle; this facilitates revealing its possible size dependence.

In the present paper we report the results of first systematic studies of the Knight shift in melted gallium confined within porous glasses with different pore sizes and within artificial opals. The measurements were carried out at temperatures where gallium in particular porous matrices was in the liquid or supercooled state from about 320 K to its complete freezing.

2. Experimental details

Most of the porous glass matrices used in the present work were prepared from phase-separated soda borosilicate glasses with pore structure produced by acid leaching. The pore size for the samples under study was determined using mercury intrusion porosimetry and electron microscopy. For four samples the average pore size was found to be equal to 3.5, 4, 5 and 8 nm. A sample of porous glass exhibited after acid leaching a well defined bimodal pore size distribution with diameters near 200 and 8 nm for coarse and fine pores, respectively. A sample of Vycor glass supplied by Corning Glass Company was also studied; the pore diameter was found to be near 6 nm. The pore size distribution was quite narrow for the glasses with 4 and 8 nm pores (with 90% of pores lying within 0.2 and 0.5 nm about the average size, respectively). For other samples these ranges were near 0.8 nm for fine pores and 40 nm for coarse pores. Opals consist of close-packed silica spheres with diameters near 100 and 250 nm forming a face-centred cubic lattice. Between touching silica spheres there is an interconnected network of voids. The detailed structure of artificial opals is described elsewhere [22]. The liquid gallium was introduced into the porous matrices under high pressure up to 10 kbar. The filling factor of the pore volume was 80–90%.

NMR measurements were run using a pulse Bruker MSL500 NMR spectrometer. The temperature dependences of ^{71}Ga NMR signals corresponding to liquid gallium were studied. The operating frequency was 152.5 MHz. First, the samples under study were warmed up to temperatures well above the bulk gallium melting point (303 K) to be assured that the total amount of gallium in the pores was melted [6, 7]. Then, the samples were cooled down to temperatures where confined gallium was frozen and warmed up again to room temperature. Similar thermal cycles were repeated several times. The rate of warming and cooling was very slow to prevent temperature overshoots, which did not exceed 0.2 K in our measurements. Prior to each measurement, the samples were kept at a fixed temperature for about 5 min. The accuracy of temperature control was better than 0.2 K. To detect the NMR line, a single pulse sequence with phase cycling or a solid echo sequence was applied with pulse duration of 2.6 μs . The repetition time was 0.2 s. The Knight shift was measured as the position of the ^{71}Ga NMR line peak relative to the NMR signal from a crushed GaAs single crystal which was placed together with the samples under study. It is known that the temperature dependence of the chemical shift in the GaAs crystal is very weak within the relevant temperature range [23]. At room temperature, the ^{71}Ga chemical shift in GaAs was measured relative to 1 M $\text{Ga}(\text{NO}_3)_3$

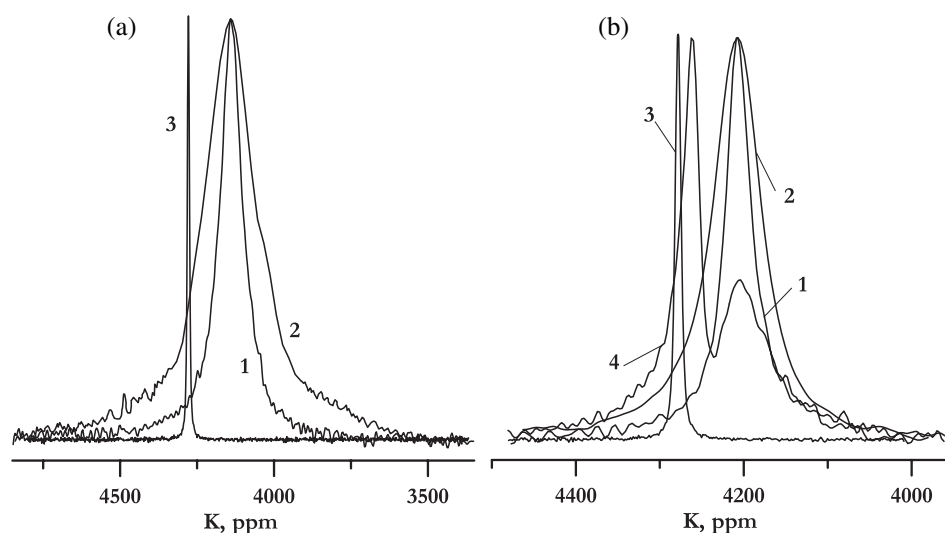


Figure 1. NMR lineshape for liquid gallium at room temperature. (a) For ^{71}Ga (1) and ^{69}Ga (2) in porous glass with 4 nm pores and for both isotopes in bulk gallium (3). (b) For ^{71}Ga (1) and ^{69}Ga (2) in the opal with silica sphere diameter of 100 nm, for both isotopes in bulk gallium (3), and for ^{71}Ga in porous glass with bimodal pore size distribution (4).

and was found to be 244 ppm, in good agreement with [24]. In addition, for every target temperature, the integral intensity of the ^{71}Ga NMR signal was evaluated. The intensity of the NMR signal was also measured relative to the NMR signal from GaAs. The signal from solid confined gallium was not detected. To compare the Knight shift for confined liquid gallium with that in the bulk, we performed measurements for gallium dispersed within voids of a glass filter with dimensions of 16 μm . Gallium so prepared could be supercooled easily down to 180 K.

3. Results and discussion

Except for the porous glass with the bimodal pore size distribution, the ^{71}Ga NMR signal corresponding to liquid gallium in all other samples under study was a single line. Some examples are presented in figure 1. While NMR lines for confined melted gallium are broadened compared to the bulk (see figure 1), they are quite symmetric and could be fairly well fitted with the Lorentzian function as in bulk liquids. In the sample with bimodal pore size distribution, the NMR signal consisted of two partly superimposed lines (figure 1(b)). Taking into account the peculiarities of pore geometry in this sample and simple NMR spectra for other samples, one can suggest that the two lines correspond to two pore species, coarse and fine.

The NMR line peaks for all samples under study were shifted to low frequencies as can be seen from examples depicted in figure 1 while both reduction and enhancement of the Knight shift was reported in some NMR studies of melting in confined liquid gallium [25, 26]. The Knight shift reduction relative to that in the bulk melt depends on the pore geometry and temperature. Examples of alterations in the Knight shift evaluated from experimental NMR line peak positions for confined gallium upon cooling and warming are shown in figures 2–4 together with the temperature dependence of the shift in bulk liquid gallium. Differences in the Knight shift between bulk and confined liquid gallium at room temperature are listed in

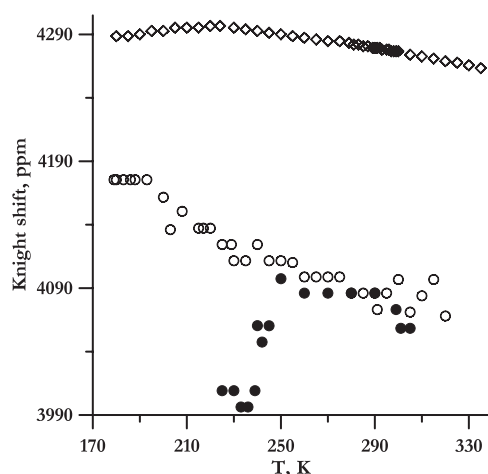


Figure 2. Temperature dependence of the Knight shift for liquid gallium in the porous glass with pore size of 3.5 nm (circles) and for bulk liquid gallium (diamonds). Open circles—cooling; closed circles—warming.

Table 1. Difference ΔK between the Knight shift in bulk and confined liquid gallium at room temperature and coefficient of linear regression dK/dT calculated for the temperature range 220–310 K.

Sample	Bulk	Porous glasses						Vycor glass	Opals	
Pore size (nm)		3.5	4	5	8	200	200	6	100 ^a	250 ^a
						(8 nm)	(200 nm)			
ΔK (ppm)	0	192	137	74	54	74	17	143	71	14
dK/dT (ppm K ⁻¹)	-0.29	-0.58	-0.77	0 ^b	-0.32	-0.76	-0.66 ^b	-0.22	-0.46	-0.31

^a Size of silica spheres.

^b Coefficients calculated for the temperature range 260–320 K.

table 1. For the sample of porous glass with the bimodal pore size distribution, two values related to two pore sizes, 200 and 8 nm, are included in table 1. For the opal samples, the size of silica spheres is noted in table 1 instead of the pore size. The Knight shift for bulk liquid gallium at room temperature relative to the GaAs line position was 4278 ppm. One can see from table 1 that the Knight shift in confined liquid gallium decreases generally with decreasing pore size. The values of changes did not exceed 200 ppm (about 4.5% of the shift for bulk), that is considerably less than the experimental shifts or broadening of resonance lines observed until now for small solid metallic particles [16, 20, 21, 27–30].

Theories predict for small isolated particles at low temperatures alterations in the Knight shift due to the quantum size effects arising from increasing the conduction electron level separation [8, 9]. However, at higher temperatures and for partly connected particles within pores, the Knight shift could be affected chiefly by surface induced spatial variations in the density of electrons on the Fermi level which influence the total electron spin susceptibility because of the increase of surface to volume ratio (see [10, 11] and references therein). The surface induced effects in the spin susceptibility depend on the electron structure of the metals under study. For transition metals the tight-binding approximation [11] predicts changes in the density of d electrons near the surface which should lead to pronounced local shifts of NMR lines compared to the bulk. The experimental results obtained for platinum and rhodium solid

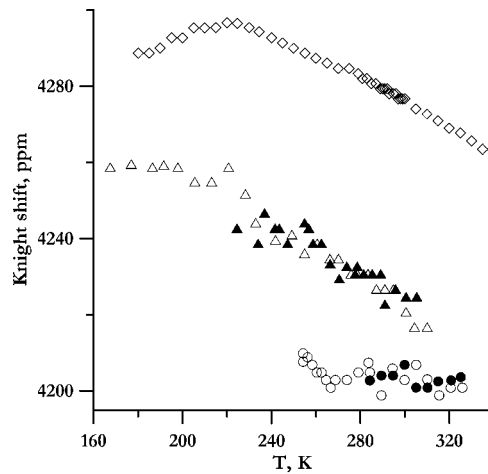


Figure 3. Temperature dependence of the Knight shift for liquid gallium in the porous glasses with pore size of 5 nm (circles) and of 8 nm (triangles) and for bulk liquid gallium (diamonds). Open symbols—cooling; closed symbols—warming.

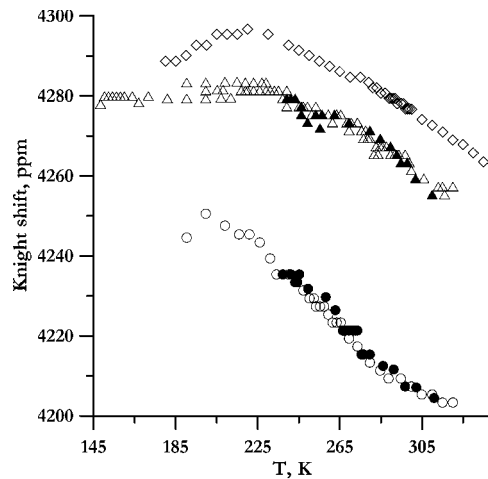


Figure 4. Temperature dependence of the Knight shift for liquid gallium in the opals with silica sphere diameters of 100 nm (circles) and of 250 nm (triangles) and for bulk liquid gallium (diamonds). Open symbols—cooling; closed symbols—warming.

particles agree to a certain extent with this model [14, 15, 19]. The Knight shift in metals like gallium originates mainly from the Fermi contact interaction of the spin polarized conduction electrons with nuclei [31]:

$$K_s = \frac{8}{3}\pi\chi_s\Omega\langle|\Psi_F(0)|^2\rangle, \quad (1)$$

where χ_s is the electron spin susceptibility per unit volume, Ω is the atomic volume and $\langle|\Psi_F(0)|^2\rangle$ is the probability density at the nucleus of s -like electrons on the Fermi surface. The contributions from the orbital hyperfine interaction and core polarization for non-transition metals are small. According to theoretical calculations carried out using the local density functional formalism the spin susceptibility for simple metals with closed inner electron

subshells should show damped Friedel oscillations near the metal surface; the integral surface magnetic susceptibility increases compared to bulk [10]. This model was applied to treat the strong broadening of NMR lines due to broad distribution in the Knight shift for small solid particles of such metals as Pb, Cu or Ag [16, 19–21, 27] while the line centres for silver and copper were reported not to shift within experimental accuracy. According to (1) one should expect that the enhancement predicted of the integral surface electron susceptibility could lead to a total increase in the Knight shift for liquid nanoparticles of non-transition metals. However, the observed shift of ^{71}Ga NMR lines for confined liquid gallium to low frequencies contradicts these theoretical predictions. It should also be noted that the experimental Knight shift reduction remains noticeable even for pores of about 200 nm in diameter, that is for sizes which are much greater than the depth of Friedel oscillations [11].

A possible explanation of this discrepancy consists in the influence on the Knight shift in liquid gallium of the core polarization effects. While the main contribution occurs due to contact hyperfine interaction with conduction electrons [31, 32], the surface induced alterations in core polarization effects might be more noticeable and thus control the size dependence of the Knight shift. Another possible explanation of the stark contrast between the experimental results and theory could stem from the influence on the confined gallium electron properties of the chemical interaction with the matrix inner surface. Note that the free surface of gallium is normally covered by an oxide layer [33]. However, x-ray powder diffraction patterns for porous matrices filled with liquid gallium did not reveal any presence of the gallium oxide; its formation could be prevented by confinement. Hence, the Knight shift reduction cannot be related to the oxide on the gallium surface. Nevertheless, some kind of incipient oxidization may exist near the surface and initiate the Knight shift reduction. It should be noted that the Knight shift reduction was also observed in [34] for liquid mercury confined within porous glass.

One can see from table 1 and figures 2–4 that there is a general tendency for the Knight shift to decrease with decreasing size of pores, while the dependence of the Knight shift on the pore size is not quite regular. Nevertheless, if we select the porous matrices with similar pore geometry, namely, the porous glasses produced by the same technology or the opals, the size dependence for the selected samples becomes monotonic. The Knight shift at room temperature versus inverse pore diameter is shown in figure 5 for the glasses with 3.5, 4, 5 and 8 nm pores. The size dependence in figure 5 can be rather well fitted by the empirical relation

$$K = K_b\{1 - \alpha \exp(-d/d_0)\}, \quad (2)$$

where K and K_b are the Knight shift in confined and bulk liquid gallium, respectively, d is the pore diameter and α and d_0 are the fitting parameters. The fitting curve is also shown in figure 5. The fitting parameters for these porous glasses are $\alpha = 0.14$ and $d_0 = 2.6$ nm. For other porous matrices the empirical relation (2) with the above fitting parameters is no longer valid; this might evidence the pronounced role of pore geometry in the dependence of the Knight shift on pore sizes.

One can see from figures 2–4 that the temperature dependence of the Knight shift varies for various porous matrices and generally differs from that in bulk liquid gallium. Upon cooling, the Knight shift dependence on temperature is rather smooth and can be approximated by a straight line in its high-temperature range. The calculated coefficients of linear regression are also listed in table 1. At lower temperatures the slope of the curves for confined gallium generally decreases. Some weakening of the temperature dependence of the Knight shift is also observed for bulk supercooled gallium in agreement with early studies [31, 32]. According to theoretical predictions, the contact interaction with conduction electrons is temperature independent while other contributions to the Knight shift such as core polarization or orbital

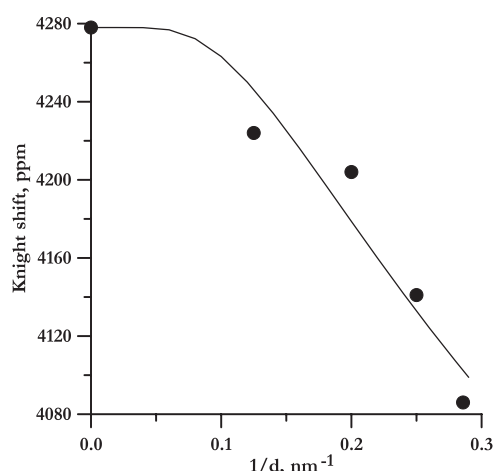


Figure 5. Dependence of the Knight shift in porous glasses on the inverse pore diameter at room temperature. The solid curve is an exponential approximation as explained in the text.

hyperfine interaction may have some weak temperature dependence [14, 35]. Thus, the noticeable changes in the temperature dependence of the Knight shift in confined liquid gallium compared to bulk (see table 1) could arise due to surface induced alterations in core polarization or orbital hyperfine effects. The temperature dependence of the Knight shift may also be affected by surface oxidization discussed above.

In addition to data regarding size induced alterations in the liquid gallium Knight shift, the present studies yielded some information about the melting and crystallization processes within pores. Actually, the parts of the curves in figures 2–4 obtained upon cooling as well as those of the relevant curves for other samples under study correspond to the continuous process of the gallium freezing in pores. This can be seen from an example presented in figure 6 where the integral intensity of the NMR signal from liquid confined gallium in the porous glass with 3.5 nm pores is shown versus temperature. It is worth noting that formation of solid gallium particles inside pores does not visibly affect the temperature dependence of the Knight shift for the rest of the melt. Meanwhile, if freezing started for gallium within the biggest pores as observed for isolated metallic particles because of thermodynamic size effects (see [36, 37] and references therein), one should expect a further reduction of the Knight shift in agreement with the general tendency of decreasing the shift with decreasing pore size. Thus, the smearing of the gallium freezing process within pores is not caused directly by the distribution of freezing temperatures due to confined particle size variation. This conclusion agrees with results obtained for gallium in porous glasses and opals by x-ray diffraction [6, 7].

Upon warming above the offset of melting, the Knight shift coincides with that measured upon cooling (figures 2–4). However, within temperature ranges of incomplete melting, the Knight shift in the samples of porous glasses with 3.5 (figure 2) and 4 nm pores and of Vycor glass is noticeably smaller. Similar behaviour was seen for mercury in porous glass [34]. For porous matrices filled with metals one could expect the rise of mechanical stresses during melting of confined materials. On the other hand, it is known that the contribution to the Knight shift of the contact interaction with conduction electrons reduces with increasing pressure [38] and the Knight shift changes in some expanded liquid metals [39]. Thus, one can speculate that the observed additional reduction of the Knight shift for the three samples arises due to local internal mechanical stresses occurring in the composites upon warming. In that case, NMR could be used to detect mechanical stresses in some metallocomposite materials.

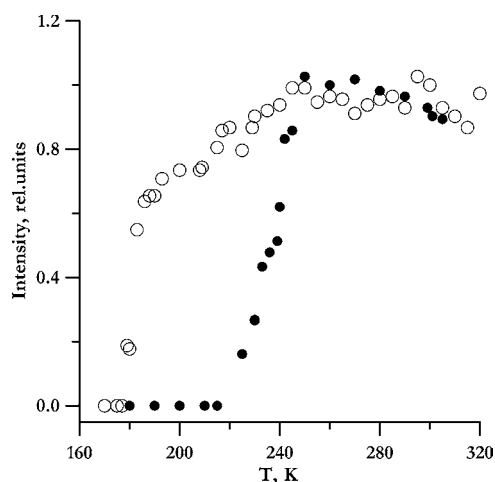


Figure 6. Temperature dependence of the integral intensity of NMR line for liquid gallium within the porous glass with pore size of 3.5 nm. Open symbols—cooling; closed symbols—warming.

While NMR lines in confined melted gallium are rather narrow, they are noticeably broadened compared to that in the bulk melt (figure 1). This broadening was shown in [4] to be driven by slowing down the atomic mobility in confined liquid gallium and is mainly quadrupolar in nature. The quadrupole nature of NMR line broadening agrees with figure 1 where NMR lines for the second gallium isotope, ^{69}Ga , are also shown for some samples (two isotopes, ^{71}Ga and ^{69}Ga , have different gyromagnetic ratios and quadrupole moments, $\gamma = 10.2 \text{ MHz T}^{-1}$ and $Q = 0.17 \times 10^{-24} \text{ cm}^2$ for ^{69}Ga compared to $\gamma = 13.0 \text{ MHz T}^{-1}$ and $Q = 0.11 \times 10^{-24} \text{ cm}^2$ for ^{71}Ga). Note, however, that the alterations measured in the gallium NMR line positions were the same for both gallium isotopes (figure 1) and thus are not related to changes in quadrupole interactions.

It should be also noted that, while the pore network within porous glasses is random and that within opals is quasi-regular [22], this distinction in pore geometry does not affect the main trends observed in the present paper.

In conclusion, ^{71}Ga NMR studies of liquid gallium nanoparticles embedded into porous matrices have revealed the Knight shift reduction compared to the bulk melt in contrast to predictions of the local density functional formalism for the free surface of spin polarized electron gas. The Knight shift difference between confined and bulk melted gallium depended on the pore size and temperature; the general trend of decreasing shift with decreasing particle size was observed. The partial freezing of confined gallium did not noticeably affect the Knight shift for the remaining liquid fraction, that clarifies some aspects of freezing in confined geometry. An additional decrease in the Knight shift upon warming was found for some porous matrices and was treated as the result of mechanical stresses rising upon incomplete melting.

Acknowledgments

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