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LOW-DIMENSIONAL SYSTEMS

Nuclear Magnetic Resonance Investigation of Metallic Sodium Nanoparticles in Porous Glass

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Abstract—Sodium nanoparticles embedded in porous glass have been studied by NMR. The measurements have been carried out on pulse spectrometers in magnetic fields of 9.4 and 17.6 T in a wide temperature range. Changes in the magnitude and temperature dependence of the ^{23}Na Knight shift with respect to those in bulk sodium have been discovered. An additional component of the NMR line shifted to high frequencies has been observed in the temperature range from 240 to 100 K. Investigation of the specific heat has revealed a considerable decrease in the melting and crystallization temperatures of sodium under nanoconfinement, which were not accompanied by abrupt changes in the Knight shift.

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1. INTRODUCTION

Many physical properties of metals are changed considerably under nanostructuring owing to size effects of both quantum-mechanical and classical nature. The quantum size effects caused primarily by discreteness of the electron levels lead, in particular, to a difference in the low-temperature electronic susceptibility of metallic clusters with even and odd number of conduction-band electrons [1]. The classical size effects revealed to date include shifts of the melting and crystallization temperatures, structure features of small metallic particles, slowing down of atomic diffusion in liquid nanoparticles and thin films, and changes in the electronic susceptibility and the Knight shift of NMR line in solid and liquid metallic particles [2–5].

Metallic nanostructures can be fabricated by embedding metals into nanoporous matrices, such as porous glasses and opals. A network of metallic particles with the size determined by the geometry of pores is formed in the matrix. The nanoconfinement allows studying various size effects, which can, however, differ from the size effects in isolated metallic particles, owing to interactions between the particles and a possible influence of the matrix.

In this work, we present the results of the NMR study of small metallic sodium particles embedded in porous glass.

2. SAMPLES AND EXPERIMENT

The porous glass was made from phase-separated sodium-boron silicate glass by leaching. The average pore size found by mercury porosimetry was 3.5 nm. On the other hand, according to nitrogen porosimetry, the pore diameter was 4.5 nm. Sodium was embedded into pores in a melted state at a temperature of 400 K under high pressure. The 3 × 3 × 8 mm samples for measurements were cut from the filled glass. Since sodium can interact with both oxygen present in air and atmospheric water vapor, the samples were stored in oil between the measurements and packed into an oil-soaked Teflon tape during the measurements. Nevertheless, the sample surface appeared to be coated by sodium-oxide patina.

The NMR measurements were carried out on Bruker Avance 750 and Avance 400 pulse spectrometers in magnetic fields of 17.6 and 9.4 T, respectively. The NMR line of ^{23}Na was recorded as a Fourier transform of a free induction decay signal after a 90-degree pulse. The position of the resonance lines was determined with respect to the resonance fre-

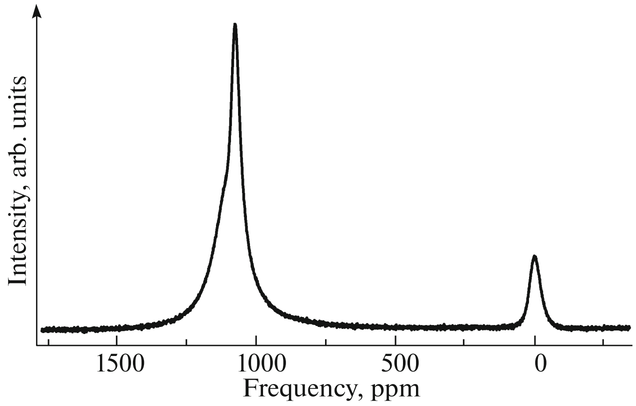

Fig. 1. The ^{32}Na NMR spectrum of sodium nanoparticles in porous glass at a temperature of 190 K in a magnetic field of 17.6 T.

quency of ^{23}Na in a NaCl single crystal, similar to the NMR studies of bulk sodium [6, 7]. The measurements on the Avance 400 and Avance 750 spectrometers were performed in the temperature ranges from 80 to 330 K and from 100 to 385 K, respectively. The temperature varied at a rate of no higher than 2 K/min. The sample was kept for at least 10 min before each measurement. The measurements were carried out at both heating and cooling of the samples.

3. EXPERIMENTAL RESULTS

The NMR spectra measured at various temperatures contained the lines corresponding to metallic sodium which had a resonance frequency shift similar to the Knight shift in bulk sodium (the room-temperature Knight shift in bulk sodium is 1120 ppm [8]) and sodium cations (a shift of the order of 20 ppm with respect to the line position for sodium chloride). Figure 1 exemplifies the spectrum of ^{23}Na in the sample under investigation at 190 K. The presence of sodium cations can be associated with oxide on the sample surface and with the interaction of sodium with the matrix, as was observed in the cases of sodium-filled silica gels and zeolites [9, 10]. The intensity ratio of the lines of metallic sodium and sodium cations slightly varied among the samples but the positions of the lines were identical in all samples. In this work, we present the results of studying the NMR lines of metallic sodium.

At temperatures above 240 K, the resonance line had a Lorentzian shape. The second component with a 60-ppm greater Knight shift appeared in the spectrum upon cooling below 240 K. The additional component of the NMR line strongly broadened with a further decrease in temperature and became completely buried behind the base line below 100 K so that again only one main line remained in the spectrum. The ^{23}Na NMR lines measured at several temperatures in the field of 17.6 T are shown in Fig. 2. In the temperature range from 100 to 240 K, the NMR line of metallic nanoparticles can be fitted with a high accuracy to a sum of two Lorentzian components. The deconvolutions of the resonance lines are exemplified in Fig. 2.

Figure 3 shows the temperature dependence of the Knight shift for both components of the line in comparison with the relevant dependences for bulk solid and liquid sodium found from the data of [7, 8, 11]. The Knight shift of the main component of the NMR line was found directly from measurements above 240 K and below 100 K. In the intermediate temperature range, where the line was split, the Knight shift was found by fitting the line to two components. The values of the Knight shift found at heating and cooling coincided within the experimental error. Note a difference in the Knight shifts of the main component of the NMR line measured in different magnetic fields above 250 K.

4. DISCUSSION

Crystalline sodium has a body-centered cubic lattice in a wide temperature range including room temperature. Bulk sodium melts at 371 K. With decreasing temperature, sodium undergoes a martensitic transition, which is of partial character, at about 32 K. Owing to cubic symmetry, the NMR lines of sodium can be observed for nanoparticles in porous matrices in both melted and solid phases, since the lines are not broadened by anisotropy of the Knight shift. Until recently, the NMR studies of all metals except sodium under nanoconfinement were carried out only for melts, in which the NMR lines are narrowed by fast atomic motion.

Studies performed in this work showed considerable changes in the NMR characteristics of sodium nanoparticles in porous glass, as compared to bulk sodium. As is seen in Fig. 3, the Knight shift of both components of the NMR line of sodium nanoparticles in pores decreases with increasing temperature, in contrast to bulk sodium in solid and liquid phases. The Knight shift in nanoparticles near 80 K is close to the Knight shift in bulk solid sodium. However, the difference between the Knight shifts increases with temperature and exceeds 260 ppm at the maximum temperature of measurements.

The temperature coefficient of the Knight shift in bulk sodium under various pressure was analyzed theoretically in [12]. The Knight shift for metals with filled closed inner electron shells is known to be largely caused by the interaction of nuclei with conduction-band electrons and can be written as

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

where χ_s is the electronic susceptibility, Ω is the volume per atom, and $\langle|\psi_F(0)|^2\rangle$ is the square modulus of

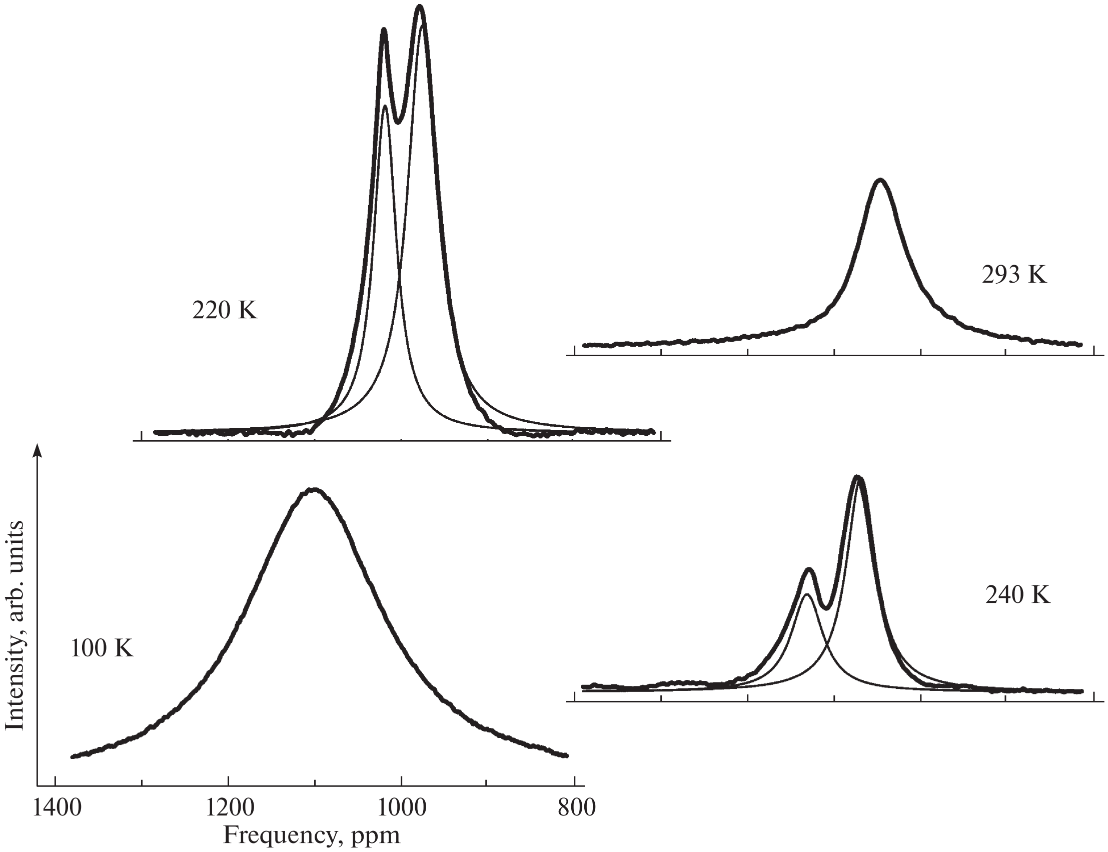

Fig. 2. Resonance lines of ^{23}Na nuclei measured on the Avance 750 spectrometer at various temperatures. Thin solid curves are deconvolutions of the lines into two components.

the wave function of *s* electrons on the Fermi surface at the position of the nucleus. The contributions from the polarization of the electron shell and the orbital hyperfine interaction are small. The variation of the Knight shift with temperature is largely associated with thermal expansion. The electronic susceptibility increases with volume, whereas the electron density at the nucleus decreases. In bulk sodium, the effect of the electronic susceptibility prevails, which explains an increase in the Knight shift with temperature. However, the role of the hyperfine field at the nucleus increases at a higher pressure and the Knight shift starts to decrease with increasing volume. Presumably, the main role in the temperature dependence of the Knight shift of sodium in porous glass is played by the electron density at the nucleus, similar to bulk sodium at high pressure, which leads to a change in the sign of the temperature coefficient. Note that the temperature dependence of the Knight shift for sodium nanoparticles in the pores of the opal matrix with a much larger diameter nearly coincided below 300 K with the temperature dependence of the Knight shift in the bulk [4]. This manifests the effect of the nanoparticle size on the temperature coefficient of the Knight shift.

As is seen in Fig. 3, the Knight shift of the main component of the NMR line is lower for nanoparticles than for bulk sodium nearly in the entire temperature range. A similar decrease in the Knight shift with respect to bulk metal was observed for liquid mercury, gallium, indium, and tin embedded in nanoporous matrices [13]. This effect cannot be explained by the direct influence of the Laplace pressure in the nanoparticles, since changes in the Knight shift under the applied hydrostatic pressure had different signs in the studied metals.

The Knight shift in bulk sodium changes abruptly upon melting and crystallization. A jump of the Knight shift was also observed upon melting and crystallization of sodium nanoparticles in the pores of the opal matrix [4]. Since the melting temperature of sodium in the opal matrix decreased with respect to the melting point of bulk sodium owing to the size effect, the jump of the Knight shift was observed at lower temperatures. A sharp change in the Knight shift at the melting point was also observed in other metals [8]. However, the Knight shift for sodium nanoparticles in porous glass does not exhibit anomalies associated with melting up to 385 K. It can be assumed that either melting is shifted to the region above 385 K or

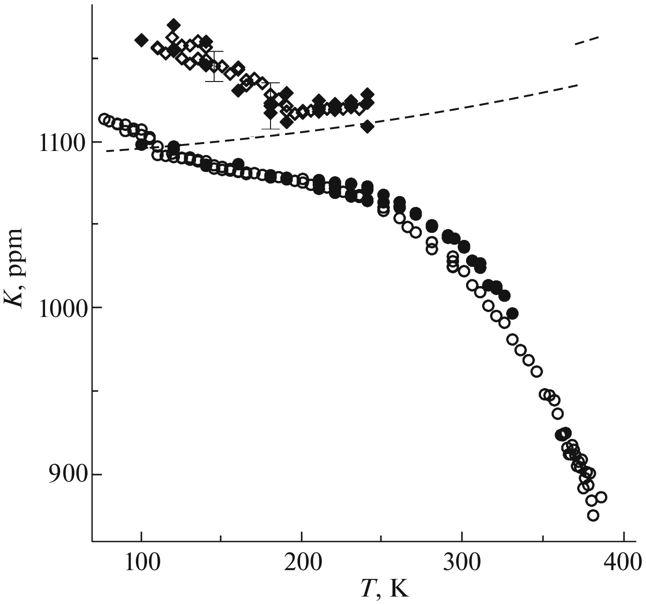

Fig. 3. Knight shifts of the (circles) main and (diamonds) additional components of the ^{23}Na NMR line at various temperatures measured on the (open symbols) Avance 400 and (closed symbols) Avance 750 spectrometers. The dashed line shows the temperature dependence of the Knight shift of bulk solid and liquid sodium found in literature.

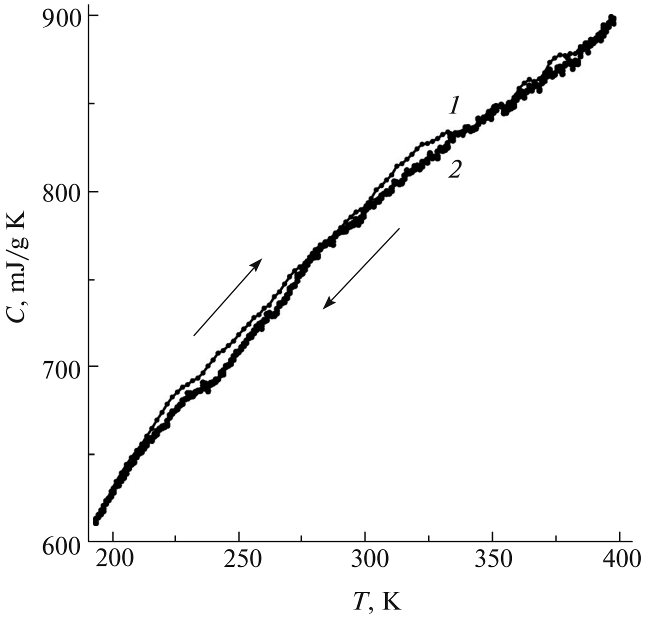

Fig. 4. Temperature variation of the specific heat *C* of the nanocomposite with sodium at (*1*) heating and (*2*) cooling.

melting and crystallization of sodium in the porous glass-based nanocomposite under study is not accompanied by considerable changes in the Knight shift. To clarify this matter, we studied additionally the specific heat of the sodium-filled porous glass samples. The measurements were carried out in zero magnetic field on a Quantum Design PPMS-9 setup for studying physical properties. The temperature dependences of the specific heat measured at heating and cooling are shown in Fig. 4. The specific heat exhibits a broad maximum near 320 K at heating and a broad minimum near 240 K at cooling. These anomalies are presumably associated with melting and crystallization of sodium nanoparticles. Smearing out of the anomalies can be caused by a scatter of the nanoparticle size in the pores and by broadening of the phase transitions owing to the size effects. The difference between the temperatures of the maximum and minimum of the specific heat reflects a melting-crystallization hysteresis that appears under nanoconfinement [14].

The data on the specific heat agree with a size-induced decrease in the melting temperature of isolated sodium particles observed by ESR and calorimetry [15–17]. As was shown in [15], melting of an isolated sodium particle containing 139 atoms is shifted to 267 K. Much lower shifts were observed for 2.4-nm sodium particles produced by irradiating the NaN_3 salt [16]. As mentioned above, a decrease in the melting temperature was observed for sodium particles in the pores of the opal matrix [4]. Thus, the results of specific heat measurements and the analysis of published data allow making a conclusion that the Knight shift in a particular case of sodium nanoparticles in the porous glass with a pore size of 3.5 nm does not exhibit considerable change under melting and crystallization. It should be mentioned, however, that the temperature dependence of the Knight shift diverges considerably from the linear one in the temperature range from 240 to 320 K (Fig. 3).

A difference in the positions of the lines measured in different magnetic fields in the temperature range of 250–330 K can be attributed to the dynamic quadrupole shift [18]. Under the condition that the product $\omega_0\tau_c$ is close to unity (ω_0 is the Larmor frequency and τ_c is the correlation time of the atomic motion) the position of the NMR line of quadrupole nuclei depends on the precession frequency, i.e., on the magnetic field. The influence of the dynamic quadrupole shift was also observed for gallium nuclei in a Ga–In alloy [19].

The emergence of the additional component of the NMR line of metallic sodium in the temperature range of 100–240 K possibly indicates the formation of another crystalline structure of sodium. This effect requires further investigation.

5. CONCLUSIONS

Thus, the NMR investigation of sodium particles embedded in a porous glass with a pore size of 3.5 nm has revealed considerable changes with respect to bulk sodium. The Knight shift of the ^{23}Na NMR line decreases with increasing temperature, whereas the Knight shift in bulk sodium exhibits a positive temperature coefficient. The Knight shifts in the nanoparticles and bulk sodium coincide within the experimental error at about 80 K. At higher temperatures, the Knight shift under nanoconfinement is much lower than in the bulk. Melting of sodium nanoparticles occurs near 320 K. The Knight shift does not change abruptly at melting and crystallization, but varies with temperature in the region of these phase transitions. An additional component presumably associated with polymorphism of sodium under nanoconfinement emerges in the spectrum below 240 K.

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