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Continuous melting and thermal-history-dependent freezing in the confined Na-K eutectic alloy

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^{23}Na NMR studies of the Na-K eutectic alloy embedded into porous glass with 7-nm pores showed that melting of Na_2K confined nanoparticles is a continuous process with smooth changes in the Knight shift of a narrow resonance line and nuclear spin relaxation between those in the crystalline and liquid states. The intermediate state, which occurs upon melting is stable and more favorable than the liquid state. The inverse freezing transformation can be sharp as at a first-order transition or continuous depending on the initial temperature of cooling. The results suggest revision of theoretical predictions for the melting and freezing transitions in confined geometry.

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Melting in bulk is a pure first-order transition that occurs when the chemical potentials of the solid and liquid states become equal. At a melting temperature the rigid crystalline lattice transforms to the fluid and physical parameters of the matter exhibit abrupt alterations. When the particle size decreases the melting temperature generally decreases due to the stronger impact of surface[1–3] and references therein). In addition, the formation of a liquid skin on the solid core before melting becomes more important since the liquid layer thickness and the particle size are comparable. When the liquid skin appears, its thickness rises upon further warming until the solid core melts sharply at a particular temperature.[4,5] The inverse process of freezing occurs via nucleation. In small particles there is a large thermal hysteresis between melting and freezing. For ultrafine clusters the computer simulation predicts a finite temperature range where the solid and liquid states coexist dynamically, clusters remaining solid or liquid below or above this range, respectively.[6,7]

Experimental studies of melting for small metallic particles were started long time ago and intensified more recently following the development of nanotechnology[7–10] and references therein). A general decrease in the melting temperature was observed when particles were not subjected to external disturbance[11,12] such as, for instance, mechanical strains, and could be considered free to some extent. The reduction in the melting temperature was found for ensembles of small particles, isolated as well as embedded into nanoporous matrices, and for single nanoparticles. For ensembles of nanoparticles, the diffused melting was usually observed, which is believed to be caused by particle size distribution,[2,13,14] however, the emergence of the liquid layer as a precursor was also suggested.[15] For individual particles, the formation of a liquid skin was proved by electron diffraction.[16] However, even when the emergence of a liquid skin on the particle surface led to some broadening of the melting transition, the well-defined solid and liquid states coexisted within a temperature range and the melting transition in the solid cores remained sharp. Ultrasmall supported and unsupported metallic clusters were studied predominantly by various calorimetric methods (see[1,7,8,17–20] and references therein). Smooth caloric curves were observed upon melting in some experiments, for instance for sodium clusters comprised of 139 atoms,[8] which agree with computer models, while sharp changes were found for larger sodium clusters.

Whether the continuous melting could happen in particles under nanoconfinement is still a totally open question while it is crucial for understanding the influence of size reduction on the melting process. Calorimetric methods being extremely useful for phase transition studies cannot answer this question as they provide only averaged information. Another challenging problem is whether the continuous melting, if confirmed, coexists with sharp or continuous freezing. Experimental methods, which are sensitive to microstructure, are required to investigate such matters. Among them, NMR has a lot of advantages for studying phase transitions in confined geometry.[14,15,21–24]

Here we present ^{23}Na NMR studies of the melting and freezing phase transition in the Na-K alloy of the eutectic composition embedded into silica porous glass. This alloy precipitates with formation of the cubic intermetallic compound Na_2K. The high symmetry of crystalline Na_2K facilitates the observation of resonance lines at freezing. We will show that the position of the ^{23}Na NMR line (Knight shift) exhibits continuous change upon warming through the solid to liquid transition until complete melting while it shows a steplike jump upon crystallization. The steplike freezing reproduces only after the alloy was previously completely melted. But the Knight shift changes gradually upon freezing when the alloy was first cooled down until complete crystallization, then warmed up to a temperature bellow the end of melting and cooled anew. In agreement with the behavior of the Knight shift, nuclear spin-lattice relaxation changes gradually upon melting, which evidences continuous acceleration in ionic mobility.

The porous glass matrix was made from phase-separated soda borosilicate glass by acid leaching. The mean pore size, 7 nm, was found using mercury intrusion porosimetry. Pores with sizes from 6.6 to 7.5 nm corresponded to about 90% of the total pore volume. The pore fraction (the ratio of the pore volume to the sample volume) was near 23%.

Liquid alloy of the composition 67 at % K and 33 at % Na was embedded into the porous glass at room temperature under pressure up to 6 kbar. This composition corresponds to the eutectic point on the phase diagram of bulk sodium-potassium alloy with melting temperature 260.8 K where liquid and crystalline Na_2K and K are in equilibrium.[25] After the pressure was removed, some amount of the alloy flowed out of pores. The filling factor evaluated by weighing at ambient conditions was about 75%. The nanocomposite thus obtained remains stable when kept in the nitrogen atmosphere or in oil contrary to the case of pure Na metal when it is introduced at elevated temperature.[26] Two samples were cut from the filled porous glass. The results for both of them were quite similar, so the figures below are shown for one sample.

The liquid Na-K alloy forms a percolating structure within nanopores as the electric conductivity of the filled glass measured at room temperature was much higher than that of the empty porous glass. However, as a result of phase separation upon crystallization of the eutectic alloy, the size of solid Na_2K nanoparticles is less than pore size.

NMR measurements were carried out using a Bruker Avance400 spectrometer. The ^{23}Na line shape was recorded as a Fourier transform of free induction decay after a 90-degree pulse. The line position was referenced to a ^{23}Na signal from bulk alloy of the same composition at room temperature. The recovery of longitudinal magnetization was observed after a sequence of 180- and 90-degree pulses (the inversion recovery procedure).

Figure 1 shows variations of the Knight shift during two different cooling-warming cycles from room temperature down to 150 K and up to 380 K. The Knight shift varies weakly upon cooling when the confined alloy remains unfrozen. Near 210 K a signal from frozen Na_2K appears and the liquid and crystalline phases coexist within a narrow temperature range. The difference between the Knight shift in liquid and solid at freezing is more than 80 ppm which is much greater than the line width. Therefore the lines from solid and liquid are well separated as can be seen at 208 and 204 K in Fig. 2.

The behavior of the Knight shift upon warming is totally different. A smooth continuous increase from the Knight shift in the crystalline state is seen instead of a sharp change, which can be identified with the first-order phase transition from solid to liquid. The Knight shift eventually reaches the value corresponding to the melt at about 250 K. The NMR lines obtained upon cooling and upon warming coincided above 250 K. Such behavior (sharp freezing and continuous melting) was always reproducible during repetitive thermal cycles when the sample was warmed above 250 K and the alloy was completely melted. Not that the temperature of the melting completion is reduced compared to the eutectic temperature in bulk. The NMR spectra at several representative temperatures upon cooling and warming are shown in Fig. 2(a).

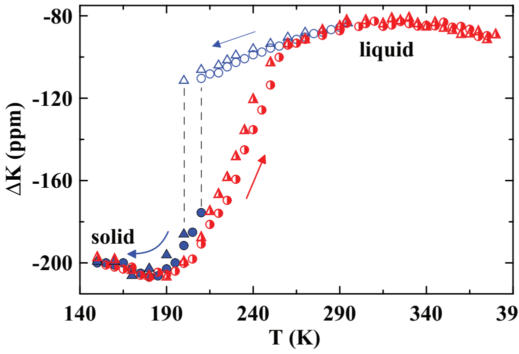

FIG. 1. (Color online) Variations with temperature of the ^{23}Na Knight shift in the confined Na-K alloy upon cooling from room temperature down to 150 K (open symbols, liquid; closed symbols, solid, blue) and consecutive warming up to 380 K (semiclosed symbols, red) during two thermal cycles marked with circles and triangles. Dashed lines indicate the coexistence of the melted and frozen alloy.

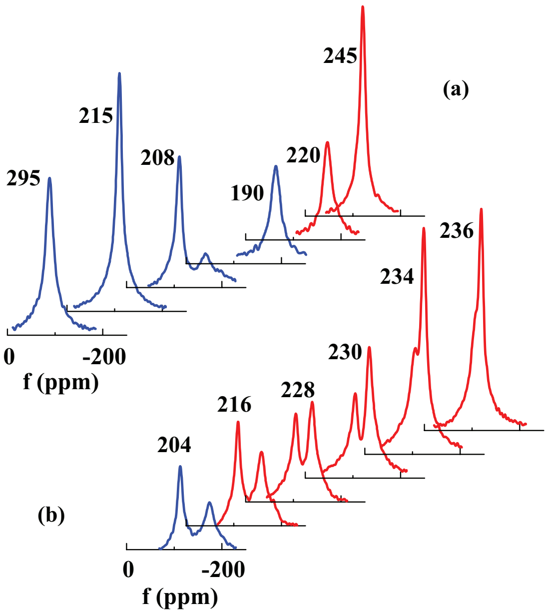

FIG. 2. (Color online) Two sets of ^{23}Na NMR spectra for different thermal cycles. (a): at 295, 215, 208, and 190 K (blue) upon cooling from room temperature down to 150 K and at 220 and 245 K upon subsequent warming (red). (b): at 204 K (blue) after cooling from room temperature and at several temperatures upon warming from 204 K up to room temperature (red).Temperatures in K are indicated in the panel.

Then we changed the thermal cycling conditions and started warming before the whole amount of the confined liquid alloy was frozen (that is at a temperature where the NMR signals from liquid and crystalline states coexist). Figures 2(b) and 3 correspond to the lowest temperature of 204 K. Two lines from liquid and solid can be seen upon warming within a rather large temperature range which behavior is quite unexpected. The line which is attributed to sodium in the melt [the left one in Fig. 2(b)] decreases gradually in intensity and vanishes completely until 240 K. Another line which emerged as a result of partial freezing and was associated with the signal from crystalline Na_2K increases continuously in intensity and transforms into the signal from melted alloy upon further warming (Fig. 3). Such behavior is also fully reproducible.

When the sample is cooled down in order that the confined melt freezes completely, warmed up to a temperature below 250 K, and then cooled down again, the freezing phase transition differs drastically from that illustrated by Fig. 1. The Knight shift changes continuously upon second cooling

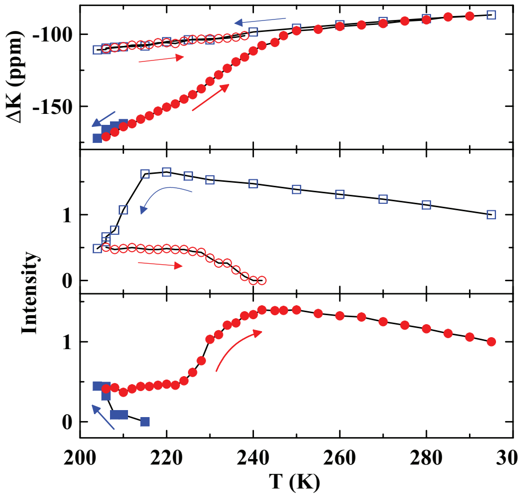

FIG. 3. (Color online) Variations with temperature of the ^{23}Na Knight shift and intensity of lines upon cooling from room temperature down to 204 K (squares, blue) and subsequent warming up to the initial temperature (circles, red). Open symbols correspond to the NMR line associated to liquid, closed symbols to the second component of NMR spectra, associated at low temperature with solid. The integral intensities of the NMR lines are normalized to their values at room temperature. Solid lines are guides for the eye.

(Fig. 4). Finally, the NMR line joins the line associated with the crystalline state. The gradual decrease in the Knight shift is in striking contrast to a jump associated to the first-order transition from the liquid to solid state. Smooth variations in the Knight shift repeat upon subsequent warming and cooling (Fig. 4).

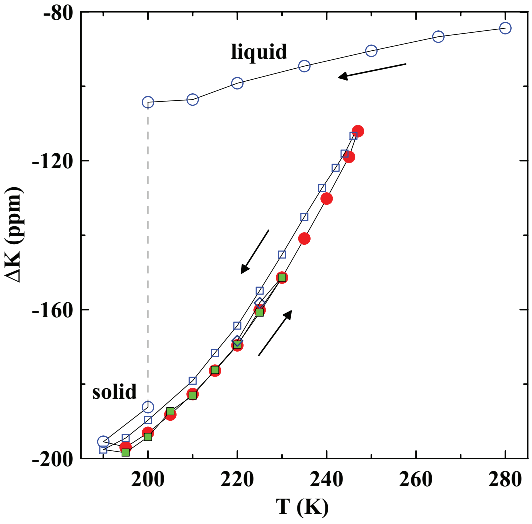

FIG. 4. (Color online) Variations with temperature of the ^{23}Na Knight shift upon cooling (open symbols) and warming (closed symbols). Circles, cooling from room temperature down to 190 K (blue) and warming up to 245 K (red); squares, cooling to 190 K (blue) and warming to 230 K (green); diamonds (blue), cooling to 220 K. Solid curves are guides for the eye. The dashed straight line shows the coexistence of liquid and solid upon first cooling.

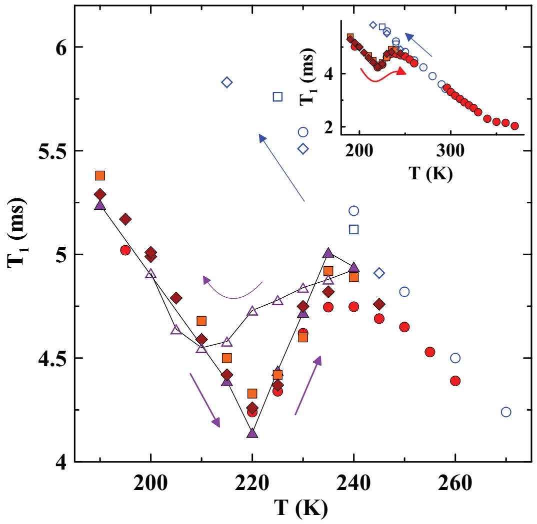

FIG. 5. (Color online) Temperature dependencies of the spin-lattice relaxation time for several cooling and warming cycles shown with different symbols. Open (blue) symbols, cooling; closed (various reddish colors) symbols, warming. Triangles correspond to warming from 190 K to 245 K and consecutive cooling to 200 K. Circles on the panel and inset show data obtained upon cooling from room temperature down to 190 K and subsequent warming up to 380 K. Other symbols correspond to cooling from room temperature to 190 K and warming again to room temperature. The solid line is a guide for the eye. The inset shows results in the extended temperature range.

The temperature dependencies of the NMR spectra, Knight shift, and intensity are in accordance with variations of spin-lattice relaxation. As is well known, spin-lattice relaxation of quadrupole nuclei in bulk metals[27,28] goes along two main paths: due to magnetic interaction of the nuclear dipole moments with conduction electrons and due to electric interaction of the nuclear quadrupole moments with dynamic gradients of electric fields resulted from ionic movement. Quadrupole relaxation is very sensitive to alterations in mobility under nanoconfinement and becomes more effective for metals embedded into nanopores.[22,24] ^{23}Na nuclei have spin 3/2 and thus possess the quadrupole moment. Therefore, one can expect that longitudinal spin relaxation for sodium nuclei should change upon melting and freezing in the confined alloy.

Figure 5 shows dependencies of the ^{23}Na spin-lattice relaxation time on temperature in the sample under study upon thermal cycling. All measurements were carried out when only a single NMR line was seen which corresponded to pure liquid, solid, or intermediate state. Note that ^{23}Na longitudinal relaxation was single exponential for liquid alloy and very close to single exponential for the crystalline and intermediate states. One can see that the spin-lattice relaxation time changes in the steplike manner when the sample was cooled down from room temperature down to 190 K. Upon freezing, relaxation becomes faster in solid. The relaxation acceleration as a result of freezing cannot be related to alterations in the Knight shift as when the Knight shift decreases, magnetic relaxation slows down according to the Korringa relation.[29] Thus, the effect of ionic mobility dominates the changes in nuclear spin relaxation at the transition due to the quadrupole contribution. When the sample was warmed up from 190 K to room temperature or higher, the relaxation time increases continuously. Relaxation is slower when ionic mobility accelerates and the relevant correlation time differs strongly from the inverse Larmor frequency. Therefore, the continuous change in spin-lattice relaxation evidences the continuous change in ionic mobility through the transition from solid into liquid. During a partial thermal cycle, which corresponded to variations in the Knight shift upon warming to 245 K and cooling to 190 K shown in Fig. 4, longitudinal relaxation also changed gradually.

The NMR responses, which are shown in Figs. 1–5 correspond to a big ensemble of nanoparticles embedded into the glass matrix. They are averaged over particles with a size distribution. However, the pore size distribution cannot imitate the observed gradual transformation of the NMR spectrum between the liquid and solid states. The particle size distribution could lead to the broadening of the temperature range where the NMR lines associated with solid and liquid coexist but not to smooth alteration in the Knight shift of a narrow NMR line and in the relaxation rate. Note once more that the whole set of NMR measurements was repeated for the second nanocomposite sample and the results obtained were quite similar.

On the other side, we have repeated the same study with the alloy confined to opals (photonic crystals). The opals have much larger pores and the melting and freezing phase transitions for confined alloy were expected to be more similar to the transitions in bulk. In agreement with such expectations both the melting and freezing transitions were found to be steplike as in bulk while they were shifted to lower temperatures.

The Knight shift is caused by conduction electrons and is proportional to electron susceptibility.[29] In bulk metals the steplike changes in the Knight shift upon melting or freezing agree with alterations in electron density as a result of the first-order phase transition. Therefore, the smooth gradual alteration in the Knight shift observed here should be treated as an evidence of continuous structural transformation in the confined alloy upon melting and also upon freezing at particular conditions. Other evidence is given by continuous alteration in spin-lattice relaxation reflecting smooth changes in ionic mobility.

Our experiments suggest that melting occurs through formation of an intermediate state. This state shows no noticeable time evolution at a fixed temperature and is more favorable at melting than the liquid state (Fig. 3). Freezing, which started from this state, is continuous. Such experimental results contradict the simplest model of melting in small particles based on the Gibbs-Thompson equation which leads to the melting temperature reduction, only. They apparently do not agree to the liquid skin model as there is no coexistence of the NMR lines from solid core and liquid skin. The continuous changes in the Knight shift of NMR lines through the melting transition and freezing from the intermediate state could be consistent with the computer models, which predict the dynamic coexistence of liquid and solid states for small clusters within a finite temperature range if the NMR spectrum is implied to be merged into a single line with mean parameters due to fast exchange. However, for such a dynamic coexistence model there is no direct way to interpret the gradual changes in spin-lattice relaxation within the temperature range where the intermediate state emerges. There are other experimental results, which require additional theoretical elucidation, such as transformation of liquid into the intermediate state upon warming, which are shown in Figs. 2(b) and 3. The full set of experimental data is in best accordance with the suggestion of smooth softening of the Na_2K structure from the crystalline lattice to liquid while such a model was not discussed until now.

In conclusion, the gradual transformation in the ^{23}Na NMR line and spin-lattice relaxation from solid to liquid upon warming evidences continuous melting of confined Na_2K nanoparticles. The melting is irreversible and the freezing is sharp, steplike when cooling is started from completely melted alloy. However, the melting is reversible and the freezing is smooth when cooling starts from the intermediate state.

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