Thermal motion in lead confined within a porous glass

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By neutron diffraction it was shown that Pb nanoparticles confined within a porous glass have an elongated form along the [111] direction which coincides with the pore axis. The mean-square displacements along and perpendicular to this direction are different. When approaching the melting point the mean-square displacement along the pore axis increases while the displacement in the perpendicular direction remains nearly constant as limited by the pore walls. The temperature dependence of the isotropic mean-square displacement greatly differs from that of the bulk. The softening of the atomic vibrations due to lattice expansion in confinement is negligible in contrast with the bulk.

The physical properties of condensed matter under the conditions of "confined geometry" are different from those of the bulk. Therefore the behavior of materials confined within nanometer scale pores is one of the "hot points" in modern solid-state physics for fundamental reasons as well as the promising possibilities for practical applications. The thermal motion of atoms is one of the fundamental properties of the solid state, however, little is known about the atomic vibrations when the size of the system becomes comparable with the correlation length of interatomic interactions.

Recent experiments have demonstrated that the thermal behavior in confinement greatly differs from that of the bulk. For example, the record value of dielectric permittivity observed for $NaNO_2$ embedded into an artificial opal matrix[1] has been explained by a giant increase of the thermal vibrations resulting in a formation of a "premelted state."[2] The unusual increase of the Debye-Waller factor in oxides MnO and CoO confined to a porous glass has been observed in our preliminary neutron-diffraction measurements.[3]

In this context the behavior of Pb in confinement is especially interesting. Because of the strong nonlinearity at high temperatures, large thermal lattice expansion, and low melting temperature, lead is a classic material for thermal motion studies. There is a series of investigations devoted to anharmonic effects in lead. Measurements by different techniques: Mössbauer,[4,5] single-crystal neutron,[6,7] and x-ray diffraction[8] have confirmed the existence of significant anharmonic contribution in the interatomic potential in the bulk Pb.

The neutron diffraction is a very powerful method for studies of thermal vibrations since it offers the direct measurement of the atomic displacements and gives insight into the structure of confined materials.

In the present work we report the neutron-diffraction studies of the structure and atomic motion in the nanoparticles of Pb embedded in a porous vycor-glass matrix. This silica matrix has a random interconnected network of elongated pores with a narrow distribution of the pore diameters.[9] In order to

observe the anharmonic effects at elevated temperature (the melting point for lead is 600.61 K), such matrix is preferable because of high thermoresistance. Moreover, the amorphous SiO_2 does not give any additional Bragg reflections in the diffraction pattern.

Lead was embedded in the glass matrix with the mean pore diameter approximately 70–75 Å by a special technique under pressure in the melted state and crystallized with decreasing temperature. The neutron-diffraction experiments have been performed with the diffractometer SLAD (Ref. 10) of the Studsvik Neutron Research Laboratory using a neutron wavelength of 1.118 Å at temperatures 25–583 K.

All diffraction patterns were analyzed with the FULLPROF program.[11] It should be noted that the atomic temperature factor $T_k(\mathbf{Q})$, describing the reduction of the Bragg intensity by thermal vibrations, was calculated in the approximation of the independent normal modes:

$$T_k(\mathbf{Q}) = \exp(-\tfrac{1}{2}\langle(\mathbf{Q}\cdot\mathbf{u}_k)^2\rangle), \tag{1}$$

where $\mathbf{Q}$ is a scattering vector and $\mathbf{u}_k$ is the displacement of k atom. It is customary to describe the displacements in terms of anisotropic temperature parameters β_{ij}, which are the refined variables and are related with the mean-square amplitudes by the unitary transformation.[12]

Form of the embedded nanoparticles. A typical neutron-diffraction pattern is shown in Fig. 1. The pattern of the pure matrix appeared to differ somewhat from the observed diffuse background. Therefore the latter was calculated as a set of experimental points with minimal Bragg contribution.

The refinement using the Thompson-Cox-Hastings approximation of the line shape with independent variation of the Gauss and Lorenz contributions[13] shows that the observed peak broadening is due to a size effect only without any contributions from inner stresses.

In Fig. 2 the full width at half maximum (FWHM) is shown versus the diffraction angle 2Θ. The reflections 111,
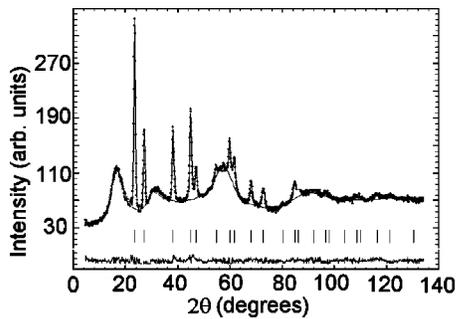
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FIG. 1. Observed, calculated, and difference neutron-diffraction patterns of Pb embedded in a porous glass at 300 K. Vertical lines mark the reflection positions.

222, 333, and 444 have systematically smaller FWHM than expected. It means that the volume average of a particle thickness along axis [111] is bigger than in perpendicular direction, i.e., nanoparticles have an elongated form along [111] axis.

The averaged diameters of nanoparticles along and perpendicular to the [111] axis were calculated for all temperatures (Fig. 3). The smaller diameter of nanoparticles, perpendicular to the [111] axis of 96(3) Å, is slightly larger than the estimated mean diameter of nanopore. This fact had been already marked practically for all compounds embedded in a porous glass (for example Ref. 14), and it was attributed to the irregular form of confined particles. It is worth to emphasize that in diffraction experiments we can measure the averaged sizes only.

From a refinement it follows which the peak broadening corresponding to the smaller diameter has a significant Lorentzian contribution, which means the diffuse boundary. While the peak broadening, corresponding to the larger size along the [111] axis, is described by a Gaussian term only, that means well-defined boundary. This can be understood assuming that the nanoparticles are elongated along the pore axis and the smaller diameter is defined by the pore walls.

Observed directional crystallization of confined lead is consistent with the equilibrium shape of the lead crystals. Indeed, it was shown by scanning electron microscopy that the nanometric size Pb crystals grew exactly along the [111] direction.[15]
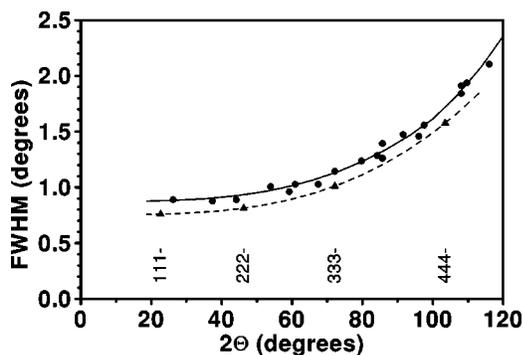

FIG. 2. Full width at half maximum. The reflections hhh type are shown by the triangles. The errors do not exceed the sizes of the symbols. The lines are guides for the eye.
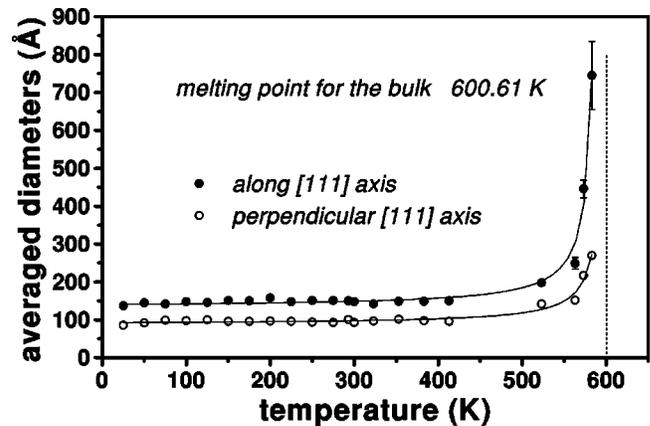

FIG. 3. Averaged diameters of nanoparticles along (solid circles) and perpendicular (open circles) to the [111] direction (the pore axis). The errors do not exceed the size of the symbols, if not shown. The solid lines are guides for the eye.

In Fig. 3 it is seen that approaching the melting point the particle size rapidly increases showing the softening and spreading ("percolation") of lead throughout the interconnected network of pores.

We observed the diffraction reflections at the maximal used temperature of 583 K. It means that significant amount of confined lead at this temperature is solid. It is interesting to note that for droplets of lead embedded in SiO at the same temperature and of similar size the full fusion was observed.[16] Apparently, the melting temperature depends on both the particle size[17] and on the matrix. Therefore we attribute the observed discrepancy to the difference in the "restricted geometry" for the droplets immersed into SiO and nanoparticles confined to irregular pores of SiO_2 matrix.

Thermal motion of atoms. It is well known that for the precise evaluation of the integrated peak intensities the contribution from the thermal diffuse scattering (TDS) under the Bragg reflection is important. However, in our case it is practically impossible to extract TDS from the diffraction pattern because of the nonlinear background from the glass matrix. Nevertheless, since only a small amount of lead is embedded in the pores and a signal is rather low, the TDS contribution is of the order of the statistical error and can be neglected up to the temperatures about 400 K. At the higher temperatures TDS was taken into account by the proper correction of the background.

Because the nanoparticles have an elongated form along the [111] axis it is natural to search for the corresponding anisotropy of the mean-square displacement taking into consideration the off-diagonal terms $\beta_{12}=\beta_{13}=\beta_{23}$ in addition to the diagonal terms $\beta_{11}=\beta_{22}=\beta_{33}$. The condition of equality of the off-diagonal terms corresponds to the rhombic symmetry with the axis of anisotropy along [111] direction.[12] Indeed the refinement shows that the off-diagonal terms differ from zero at high temperatures (Fig. 4).

The mean-square displacements along and perpendicular the [111] direction calculated from the anisotropic Debye-Waller factors are shown in [Fig. 5(a)]. It is seen that the atomic vibrations perpendicular to the pore axis weakly change at high temperatures in contrast with the vibrations
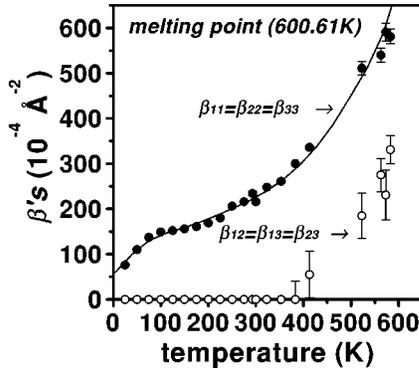
FIG. 4. Anisotropic temperature parameters vs temperature for confined Pb. The solid and open circles correspond to the diagonal and off-diagonal terms, respectively. The errors do not exceed the size of the symbols, if not shown. Lines are guides for the eye.

along the pore axis. This could be readily explained that the pore walls limit the atomic motion, while atoms vibrate more freely along the pore axis. Note that because of the low statistics, it is possible to distinguish between the atomic motions along and perpendicular to the pore axis only at high temperatures when the displacements are maximal.

The observed experimental results are consistent with the prediction in Ref. 16 that thermal vibrations of the atoms located at interface are limited by the material having the higher melting temperature, in our case SiO_2.

Anharmonic terms in atomic motion. In Fig. 5(b) the isotropic mean-square displacements in confinement and in the bulk[6–8] measured by the diffraction method are shown. An anomaly of the mean-square displacements in confined Pb is clearly seen around the Debye temperature of 105 K. The similar anomaly is also seen in the temperature dependence of the lattice parameter (Fig. 6).

Obviously, since the potential distribution in the nano-structured objects and in the bulk drastically differ, this causes the large difference in the atomic motion in confine-
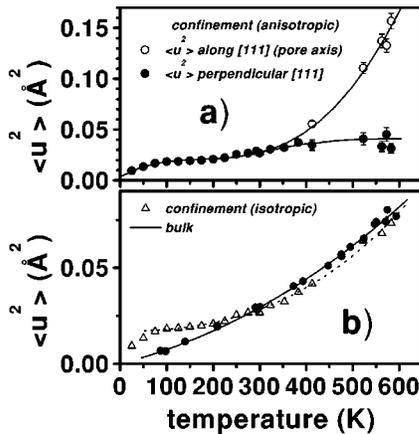

FIG. 5. (a) Anisotropic mean-square displacement vs temperature for confined Pb along (open circles) and perpendicular (solid circles) to the [111] direction. (b) Isotropic mean-square displacement vs temperature for confined (triangles) and the bulk Pb (circles). The errors do not exceed the size of the symbols, if not shown.
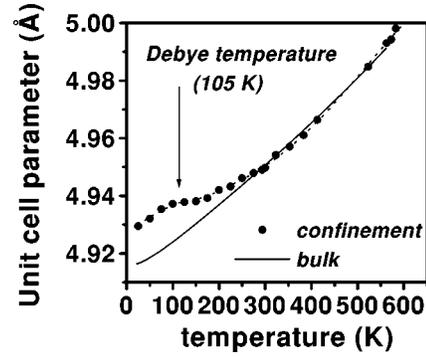

FIG. 6. Unit-cell parameters of confined (circles) and the bulk Pb (solid line) versus temperature. The latter curve was calculated from the temperature dependence of the thermoexpansion coefficient (Ref. 19).

ment and in the bulk. Therefore neither the model of one-particle potential used in Ref. 7 for the description of the mean-square displacement in the bulk lead, nor the numerical calculations based on the Lennard-Jones potential[18] can be applied in the case of the confined lead.

Therefore to describe the mean-square displacement we used a power-series expansion of $\langle u^2 \rangle$. Following Ref. 4 the mean-square displacement for cubic crystals may be written as follows:

$$\langle u^2 \rangle_{bulk} = \frac{3\hbar^2}{mk_B\Theta_D}T + \alpha_2 T^2 + \alpha_3 T^3, \tag{2}$$

where α_2 and α_3 are isotropic, anharmonic contributions due to the cubic and quartic terms in the interatomic potential, m is the atomic mass, k_B is the Boltzmann constant, and Θ_D is the Debye temperature.

Setting the Debye temperature to 105 K, the best fit of the experimental data reported for the bulk[7] gives the coefficients α_2 and α_3 of $1.1(3) \times 10^{-7}$ ($Å^2/K^2$) and $2.0(3) \times 10^{-11}$ ($Å^2/K^3$), respectively. In Fig. 5(b) the corresponding curve is shown by the solid line.

The similar fitting for confinement at temperatures above 70 K gives the coefficients α_2 and α_3 of 0.79×10^{-7} ($Å^2/K^2$) and 16×10^{-11} ($Å^2/K^3$), respectively. In this case a constant of $0.017(1)$ $Å^2$ appears and cannot be neglecting. Surprisingly, the linear term turns out to be close to zero. In Fig. 5(b) the corresponding curve is shown by the dashed line.

The linear term in Eq. (2) corresponds to the well-known effect of a reduction in the frequencies of the normal modes due to the thermal expansion. To outline this effect the mean-square displacement in quasiharmonic approximation can be written as follows:[12]

$$\langle u^2 \rangle = \langle u^2 \rangle_0 \{1 + T[2\gamma_G\chi - \alpha(T)]\}, \tag{3}$$

where $\langle u^2 \rangle_0$ is the isotropic mean-square displacement, χ is the volume coefficient of expansion, γ_G is the Grüneisen constant, and $\alpha(T)$ is the intrinsic anharmonic term.

Since the linear term is absent, the Grüneisen constant should be also negligibly small. It means that the softening

of the vibration due to the thermal expansion is very small in confined nanoparticles in contrast with the bulk, where this effect was demonstrated.[7]

Because the long-wavelength vibrations are strongly reduced or absent in the nanostructured particles, obviously the observed difference in the temperature behavior for the bulk and confinement reflects the fundamental difference in their vibration spectra.

Conclusion. By using neutron diffraction it was shown that Pb nanoparticles confined to a porous glass have an elongated form along the [111] direction, which coincides with the pore axis. As a result, the mean-square displacements along and perpendicular to the [111] direction are different. When approaching the melting point the mean-square displacement along the pore axis increases while the mean-square displacement in the perpendicular direction remains limited by the pore walls.

The temperature dependence of the isotropic mean-square displacement radically differs from that in the bulk by the presence of the large anomaly around the Debye temperature and the negligible small softening of atomic vibration due to the lattice expansion.

[1] S.V. Pan'kova, V.V. Poborchii, and V.G. Solov'ev, J. Phys.: Condens. Matter **8**, L203 (1996).

[2] A.V. Fokin, Yu.A. Kumzerov, N.M. Okuneva, A.A. Naberezhnov, S.B. Vakhrushev, I.V. Golosovsky, and A.I. Kurbakov, Phys. Rev. Lett. **89**, 175503 (2002).

[3] I. Golosovsky, D. Toebbens, and M. Tovar, BENSC Experimental Reports 2002, Hahn-Meitner Institüt, Berlin (2003).

[4] J.T. Day, J.G. Mullen, and R.C. Shukla, Phys. Rev. B **52**, 168 (1995).

[5] C.K. Shepard, J.G. Mullen, and G. Schupp, Phys. Rev. B **61**, 8622 (2000).

[6] J. Lisher, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **32**, 506 (1976).

[7] M. Merisalo, M. Lehmann, and F. Larsen, Acta Crystallogr., Sect. A: Found. Crystallogr. **40**, 127 (1984).

[8] S.L. Schuster and J.W. Weymouth, Phys. Rev. B **3**, 4143 (1971).

[9] P. Levitz, G. Ehret, S.K. Sinha, and J.M. Drake, J. Chem. Phys. **95**, 6151 (1991).

[10] A. Wannberg, A. Mellergard, P. Zetterstrom, R. Delaplane, M. Gronros, L. Karlsson, and R. McGreevy, J. Neutron Res. **8**, 133 (1999).

[11] J. Rodriguez-Carvajal, computer code FULLPROF (LLB, Saclay, 2003).

[12] B.T. Willis and A.W. Pryor, *Thermal Vibration in Crystallography* (Cambridge University Press, Cambridge, 1974).

[13] P. Thompson, D. Cox, and B. Hastings, J. Appl. Crystallogr. **20**, 79 (1987).

[14] I.V. Golosovsky, I. Mirebeau, G. Andre, D.A. Kurdyukov, Y.A. Kumzerov, and S.B. Vakhrushev, Phys. Rev. Lett. **86**, 5783 (2001).

[15] C. Rottman, M. Wortis, J.C. Heyraud, and J.J. Metois, Phys. Rev. Lett. **52**, 1009 (1984).

[16] R. Kofman, P. Cheyssac, A. Aouaj, Y. Lereah, G. Deutscher, T. Ben-David, J.M. Penisson, and A. Bourret, Surf. Sci. **303**, 231 (1994).

[17] Ph. Buffat and J.-P. Borel, Phys. Rev. A **13**, 2287 (1976).

[18] G.A. Heiser, R.C. Shukla, and E.R. Cowley, Phys. Rev. B **33**, 2158 (1986).

[19] Y.S. Touloukian, R.K. Kirby, R.E. Taylor, and P.D. Desai, *The Thermo-physical Properties of Matter* (IFI/Plenum, New York, 1975), Vol. 12.