# Specific heat of disordered Xe films at low temperatures

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We report measurements of the specific heat $C$ (0.08 K $< T <$ 7 K) of Xe films condensed at low temperatures ($\approx 6$ K). Low-$T$ x-ray diffraction indicates that the films are crystalline but strongly disordered, with very small crystallites. The specific heat is very large compared to bulk Xe, and the excess specific heat can be attributed to surface modes and to tunneling states.

Disordered solids exhibit a large variety of low-temperature behavior. Often these features can be traced back to atomic degrees of freedom not available in perfect crystals. One of the major manifestations of atomic dynamics at low temperatures are the tunneling states in amorphous solids.[1] These states have been found in insulating and metallic glasses, and also in crystalline materials. In the latter case, the extra degrees of freedom result, for instance, from the possibility of atomic or molecular rotations, such as in $KBr_{1-x}(CN)_x$.[2] The tunneling states are observed, e.g., by their roughly linear contribution to the specific heat and via their strong interaction with thermal or acoustic phonons.[1]

Rare-gas solids are among the simplest solids (except the lighter ones where quantum effects become important). Therefore, it appears interesting to look into the possibility of atomic tunneling states in disordered rare-gas solids. Also, atomic dynamics is often studied numerically using model systems with a Lennard-Jones (LJ) potential, and rare gases can—to a certain extent—be regarded as realizations of such model systems. In addition, generation of amorphous solids by rapid solidification is often simulated using LJ potentials.[3]

In the present paper, we report on specific-heat measurements on disordered Xe films condensed at low temperatures ($\approx 6$ K). In order to determine the structure, similarly prepared films were investigated with a low-temperature x-ray diffractometer. The main results of our study are as follows: Well below 1 K, we observe a specific-heat contribution varying linearly with $T$, with a large coefficient ($\approx 0.5$ mJ/mol K$^2$), hinting at the possibility of tunneling states. In addition, we find a very large enhancement of the vibrational specific heat (compared to bulk Xe) up to the highest measuring temperature (7 K). Our x-ray measurements indicate that the films are crystalline with a very small grain size. Hence, our results constitute an example of a simple crystalline system with a large number of atomic degrees of freedom.

The specific-heat experiments were carried out between 0.1 and 7 K in a dilution refrigerator and He$^3$ cryostat. Xe (99.996%) was condensed with rates between 0.1 and 5 nm/s onto a single-crystal quartz substrate. Background pressure was $< 10^{-7}$ mbar. The substrate was in weak thermal contact with the cold part of the cryostat. Thus,

its temperature could be kept constant during evaporation and could be as low as $\approx 6$ K. The heat capacity was measured with the $ac$ method.[4] Prior to each run, the heat capacity of the empty substrate (with heater and thermometer) was measured. The advantage of a quartz substrate is that it could be used to directly determine the mass and, thus, the specific heat of the sample without any ambiguity due to, e.g., sublimation during annealing. Typically, the film mass was 0.5 mg, from which a thickness of $\approx 1$ $\mu$m can be inferred. The films could be annealed up to $\approx 50$ K before any sublimation occurred. Annealing time $t_a$ was typically several ($\approx 4$) hours. A systematic check showed negligible time effects for $t_a > 1$ h.

The x-ray diffractometer (Cu $K\alpha$ radiation) was operated using a flow cryostat with the minimum temperature of $\approx 5$ K. Film preparation was done in the same way as discussed above. All films exhibited a structure compatible with fcc structure. The inset of Fig. 1 shows, as an example, the (111) reflection (always measured at 5 K) of Xe films with three different treatments. For films deposited at $T_d = 6$ K only the Xe (111) reflection was found, indicating a preferential film growth (close-packed planes parallel to the substrate). This texture remained after annealing up to 50 K. A film condensed at 50 K showed all reflections allowed by the fcc structure factor. Although the single Bragg reflection observed for the films with $T_d = 6$ K could also be interpreted as the (002) reflection of an $hcp$ structure, the systematic shift of the diffraction maximum towards lower angles and a strong narrowing with decreasing disorder renders this possibility unlikely. Intermediate annealing stages (not shown) confirm this behavior. In particular, no indication of coexistence of the two possible phases (fcc and hcp) was seen.

The lattice constant for the disordered films ($a \approx 6.11$ Å for $T_a = 6$ K) is actually *smaller* than for bulk Xe ($a_b = 6.131$ Å). This is in marked contrast to the macroscopic density deficit of $\sim 35\%$ found, e.g., by optical measurements[5] or adsorption of He and H$_2$ (Ref. 6) for Xe films condensed below 10 K. Obviously, our results suggest a rather open structure of these films with many voids and internal surfaces. Our observation $a < a_b$ is in accord with a recent calculation of the properties of rare-gas sur-
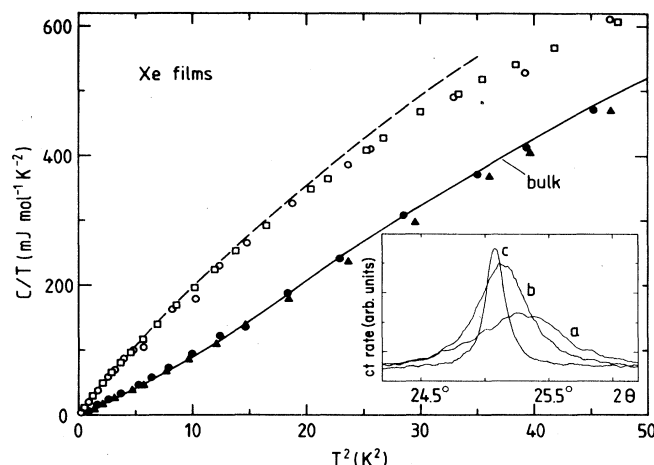
FIG. 1. Specific heat of Xe films plotted as $C/T$ vs $T^2$. Open symbols: films deposited at $T_d = 6$ K; closed circles: one of these films annealed at $T_a = 55$ K; closed triangles: film deposited at 50 K. Solid line indicates specific heat of bulk Xe, $C_b$ (Ref. 8), dashed line indicates a fit $C = C_b + aT^2$. Inset shows x-ray diffraction pattern of Xe films near the fcc (111) reflection. (a) film deposited at $T_d = 6$ K; (b) after annealing at $T_a = 50$ K; (c) film deposited at $T_d = 50$ K.
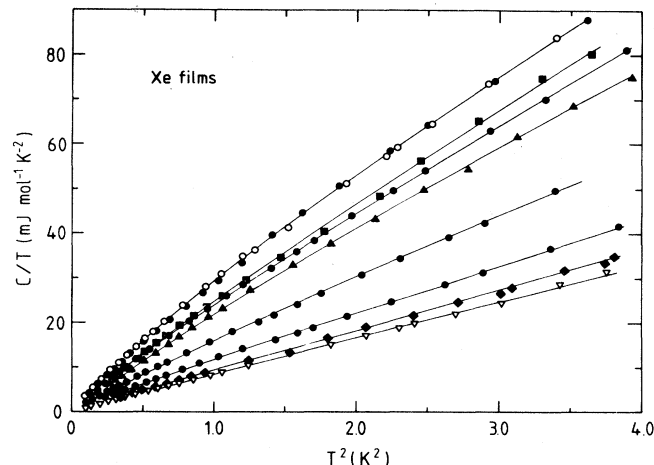


FIG. 2. Specific heat of Xe films plotted at $C/T$ vs $T^2$ in the temperature range 0.3–2 K, after heat treatment at various temperatures. From top to bottom: film evaporated at 6 K (open circles) and annealed at 10 K (closed circles) (top line), 12, 15, 20, 25, 35, and 55 K, and film evaporated at 50 K.

faces[7] using the Barker potential (which is more realistic than the LJ potential). These calculations show that at low temperatures (corresponding to our temperature range) the mean distance between surface layers of Kr is considerably smaller than in the bulk.

We now turn to the specific-heat ($C$) results. Figure 1 shows $C/T$ vs $T^2$ between ~0.3 K and 7 K. Open symbols denote results for two different films condensed at $T_d = 6$ K, one of which was subsequently annealed at $T_a = 55$ K (solid circles). Finally, solid triangles indicate data for a film condensed at 50 K. The main features of these results are as follows: For films deposited or annealed at high temperatures (~50 K), $C$ is close to the bulk specific heat $C_b$ (cf. solid line[8]). There is a large enhancement of $C$ over $C_b$ for films condensed at low temperature. Below ~4 K, the additional specific heat $\Delta C = C - C_b$ can be adequately represented by $\Delta C \sim T^2$, cf. dashed line in Fig. 1. This temperature dependence suggests a contribution by surface modes. Upon subsequent annealing at intermediate temperatures, the specific heat evolves smoothly all the way from the largest values for a deposition temperature $T_d = 6$ K, to the bulk data, as shown in Fig. 2. We also mention that no appreciable difference was found in $C$ for films condensed or annealed at the same temperature.

Figure 3 shows $C/T$ vs $T^2$ between 0.1 and 0.6 K for two different films. At these low temperatures, the curvature of the data due to the $T^2$ contribution is hardly visible. Surprisingly, a finite intersection with the ordinate, i.e., a specific-heat contribution linear in $T$, with a coefficient of 0.5 mJ/mol K$^2$, is clearly observed for the disordered film deposited at 6 K and annealed at 12 K. This is 7 times larger than observed for vitreous silica (for 1 mol SiO$_2$). The much less disordered film ($T_d = 50$ K) comes close to the (extrapolated) $C_b$; in particular, no

linear contribution to $C$ is seen. The linear specific heat of the disordered films which vanishes gradually upon annealing, must arise from excitations with a constant density of states, and, in the spirit of the above-mentioned tunneling model developed for glasses, it is tempting to attribute them to atomic tunneling modes.

We will now discuss in more detail the two extra contributions to $C$ in the disordered films: (i) surface contribution varying roughly as $T^2$ below 4 K, and (ii) the tunneling contribution proportional to $T$.

(i) Harmonic vibrations with a linear dispersion relation (for experiments on surface modes, see Ref. 9) lead to a density of states $\sim \omega^{d-1}$ and $C \sim T^d$ in the continuum approximation; hence, for surface modes (dimension $d = 2$) $C_s \sim T^2$. However, a more realistic treatment must
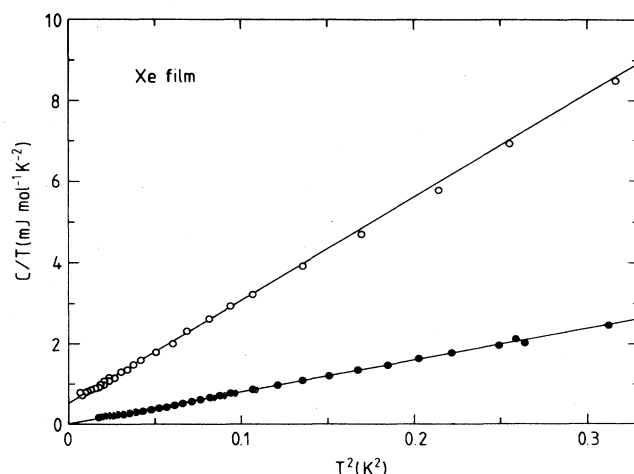


FIG. 3. Low-temperature specific heat plotted as $C/T$ vs $T^2$. Open circles: Xe film with $T_d = 6$ K and $T_a = 12$ K; closed circles: film with $T_d = 50$ K. Solid lines are intended as guides to the eye only.

of course incorporate the discreteness of the surface. Allan and de Wette[10] calculated $C_s$ for fcc solids where the atoms interact through an LJ potential by means of a numerical simulation. From this work, we can obtain $C_s$ for the Xe (100) surface using the commonly accepted values $\epsilon = 3.156 \times 10^{-21}$ J and $\sigma = 3.95 \times 10^{-10}$ m for the LJ parameters.[11] This is compared to the measured excess specific heat $\Delta C$ in Fig. 4 (the linear contribution is negligible in this plot). Very good agreement in the $T$ dependence of $\Delta C$ and $C_s$ is found. The only free parameter in this plot is the absolute magnitude of $C_s$. This is directly related to the ratio of the number of surface atoms to the total number of atoms $N_s/N$ which depends on the size of the crystallites. The magnitude of $C_s$ needed to match the data in Fig. 4 corresponds to $N_s/N = 0.17$.

Assuming, in a very simple model, a random packing of crystallites of roughly uniform spherical shape and size, a packing fraction of $\sim 64\%$ is obtained[12] which is in good agreement with the above-mentioned measurements of the macroscopic density.[5,6] Taking 15 nm as a typical diameter for the most disordered films, as inferred from the x-ray diffraction measurements (Fig. 1), we obtain $N_s/N = 0.16$. In view of the various assumptions made in this simple model, the agreement is surprisingly good. Above 6 K, the measured data deviate systematically from the calculated $C_s$. This could be due to the neglect of anharmonic effects or of dynamical displacements at the surface in the calculation.[10] However, since these deviations occur at the limit of our measuring range, we do not attach too much significance to them. Also, in this simple interpretation of our data entirely in terms of additional surface modes, we have ignored possible changes in the Debye behavior of the disordered films, i.e., of the "interior" of the grains.

In view of the inhomogeneous structure of the disordered films, an interpretation of the enhanced specific heat in terms of a phonon-fracton crossover[13] might be intriguing. However, such a crossover would lead to a positive curvature in $C/T$ vs $T^2$ at low $T$, followed by an inflection point at roughly the crossover temperature, in clear disagreement to what is observed (cf. Fig. 1).

(ii) We now turn to the linear specific-heat contribution which is resolved only well below 1 K (Fig. 3). There are two different possibilities which might lead to atomic tunneling dynamics at these low temperatures. The first of these starts from the idea that double-well potentials can arise for atoms at grain boundaries. The distribution of grain-boundary angles in disordered Xe could provide a natural explanation for the distribution of tunneling barriers and distances necessary to account for the roughly constant energy density of states. Upon annealing, as the grain boundaries and voids gradually disappear and the macroscopic density of the films approaches the bulk density, the tunneling density of states is expected to decrease, as observed.

The second possible origin of atomic tunneling states is related to the fcc-hcp competition in the heavy rare-gas
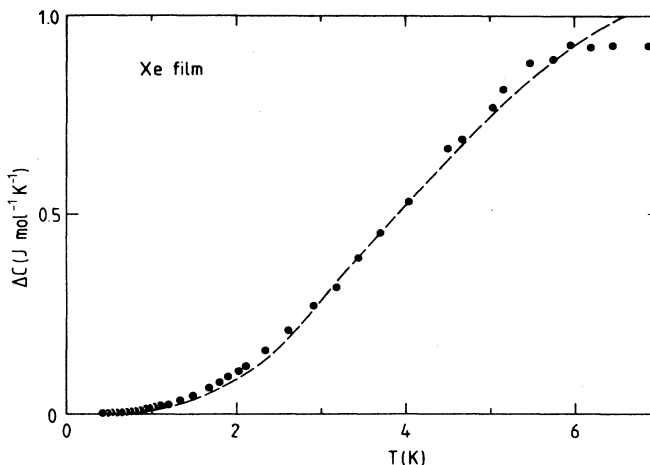


FIG. 4. Excess specific heat $\Delta C = C - C_b$ vs $T$ for a Xe film with $T_d = 6$ K. Dashed line indicates surface contribution $C_s$ calculated after Ref. 10.

solids. It is well known that the relative free-energy difference between both phases of Xe is only a fraction of a percent.[14] In fact, calculations for all reasonable two-body potentials show that the hcp phase should be slightly more stable than the fcc phase, contrary to what is observed. Hence, the stacking fault energy in the (111) direction (i.e., the preferred growth direction in our disordered films) is very small.[14] In addition, there is probably a high dislocation density[14] in our films. Together, these features suggest that small groups of atoms may be able to undergo a dynamical collective rearrangement fcc-hcp and vice versa. This picture is somewhat similar to the dynamical $\beta$-$\omega$ transformation in, e.g., Zr-Nb alloys. Indeed, in these materials evidence for tunneling states was found.[15]

At present, a definite conclusion which of the above interpretations is correct, cannot be drawn. We slightly favor the second alternative because in nanocrystalline Pd alloys[16] where the first possibility for tunneling states should also come to bear, no indication of an enhancement of the linear specific heat (by $\sim 0.5$ mJ/mol K$^2$) over the electronic contribution was observed. In any case, the existence of low-energy excitations which are attributed to atomic tunneling states in disordered rare-gas crystals is well established by the present work. Recent ultrasonic measurements[17] have also shown evidence for tunneling states.

In conclusion, our specific-heat results reveal that disordered rare-gas films exhibit a surprisingly rich variety of atomic dynamics at low temperatures. We hope that this work will stimulate molecular-dynamics calculations for double-well potentials in LJ solids. Our results are also of relevance in view of the widespread use of rare-gas solids for matrix isolation in cluster research.

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