# Magnetization of Small Lead Particles

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The magnetization of an ensemble of isolated lead grains of sizes ranging from 4 to 1000 nm is measured. A sharp disappearance of the Meissner effect with a lowering of the grain size is observed for the smaller grains. This is a direct observation by magnetization measurement of the occurrence of a critical particle size for superconductivity, which is consistent with Anderson's criterion.

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In 1957 Bardeen, Cooper, and Schrieffer introduced their mechanism for superconductivity [1], which gives an excellent description of low $T_c$ superconductivity in bulk samples. Very soon afterwards, the question of the size dependence of superconductivity arose, and in 1959 Anderson claimed [2] that for grains so small such that their level spacing $d$ is larger than the bulk gap $\Delta$, superconductivity would not exist, since such a grain will not have even one condensed level. Anderson's statement was particularly intriguing since it claims, on the other hand, that grains much smaller than the coherence length $\xi$ do have superconducting properties. The condition $d = \Delta$ is fulfilled at a grain of size $\xi^{(1/3)}\lambda_F^{(2/3)}$ which is much smaller than $\xi$. Here we used the relations $\xi = \hbar v_F/\Delta; d \approx E_F/N; N \approx (L/\lambda_F)^3$, where $E_F$, $v_F$, and $\lambda_F$ are the Fermi energy, velocity, and wavelength, respectively, $N$ is the number of electrons, and $L$ is the size of the grain. Motivated by this statement, Giaever and Zeller [3,4] measured the conductivity of small superconducting grains. They have indeed confirmed that grains much smaller than $\xi$ have a gap $\Delta$ in their single particle spectrum, but they could not confirm the loss of this property at smaller grains, in the regime where $d > \Delta$ (to be called the ultrasmall regime). The effect of fluctuations on thermodynamic superconducting properties of small grains [5] was studied experimentally by Buhrman and Halperin [6] who measured the diamagnetic transition of small aluminum grains, and by Worthington *et al.* [7] and Filler *et al.* [8] who measured the heat capacity of such grains. Recently Ralph, Black, and Tinkham (RBT) [9] have shown that a superconducting property persists when the size of the grain is reduced until the Anderson limit (where $d = \Delta$) but is lost in the ultrasmall regime. RBT have measured the tunneling spectrum of single aluminum grains in the range of 3–5 nm and have shown that for the larger grains, for which $d < \Delta$, there exists a gap of $2\Delta$ in the tunneling spectrum of grains with an odd number of particles. The smaller grains, with $d \approx \Delta$ did not show this property. This beautiful experiment initiated vast theoretical work, in which superconductivity of small grains was studied, and particularly the crossover between the regime where $d < \Delta$ and the ultrasmall regime (see [10] and references therein).

In this Letter we present magnetization measurements which reveal a sharp crossover between superconducting behavior to normal behavior as a function of the grain size. The crossover takes place at grain sizes which are consistent with the Anderson limit for lead. We measured the magnetization of an ensemble of $\approx 10^{12}$ Pb grains, ranging from 1000 nm down to 4 nm in size. The larger grains, down to 30 nm in size, showed a diamagnetic response with the well-known finite size correction [11]. However, at a smaller size, estimated to be roughly 6 nm, an abrupt change was found in the diamagnetic response, which, within the experimental accuracy, vanishes for the smaller grains. Thus, our results suggest that grains with $d < \Delta$ show the Meissner effect, and grains with $d > \Delta$ do not. In the case of RBT the loss of the superconducting property at the Anderson limit was a direct consequence of the criterion itself, i.e., as soon as $d > \Delta$ the superconducting gap cannot be distinguished from the gap due to the finite level spacing. For the Meissner effect measured here, the relation between the Anderson limit and the existence of the superconducting property is less immediate and, therefore, of a deep physical meaning, reflecting the connection between the superconducting correlations and the Meissner effect. It suggests that indeed, as long as there are even a few condensed levels, their correlations suffice to create the Meissner effect, but as soon as there is not even one condensed level, the Meissner effect disappears.

A measurement of the magnetic response of small superconducting grains required the possibility to produce a large ensemble of small grains, with good size control, which are isolated one from the other. We achieved this by using a method developed in our laboratory in 1990 [12]. The lead particles are deposited into the pores of polycarbonate nuclepore (NP) membranes, and due to the confinement in the pores the particles do not agglomerate. The deposition of lead particles into NP membranes was performed by countercurrent diffusion of a Pb salt and a reducing agent from opposite sides of the membranes (see the experimental setup in Fig. 1 of

  

Ref. [12]). These hydrophilic polyvinyl pyrrolidone coated polycarbonate membranes have straight-through pores distributed randomly on the surface and penetrating the surface at an angle of incidence smaller than 34°. The NP membranes were equilibrated in triple distilled water for an hour; the membranes were mounted into the cell.

Upon completion of the mounting process, the two stirred chambers were filled with lead salt on the dull side of the membrane and with the reducing agent on the shining side. The reducing agent was a 0.2 M aqueous $NaBH_4$ solution. The lead salt solution was 80 $cm^3$ of 0.03 M $PbNO_3$ + 20 $cm^3$ of 1 M $HNO_3$. These two solutions were introduced simultaneously into the two chambers of the diffusion cell. The deposition time varied with the pore size of the membranes and the desired lead loading into the pores. This time varied from a few minutes for a full loading of a 1000 nm membrane to a few hours for a 10 nm NP. Upon completion of the deposition process, both chambers were emptied and filled with absolute alcohol for 1 min. The NP membranes were then dried on blotting paper. Note that the lead salt was introduced in an acidic solution to prevent the formation of hydroxide species which may lead to the formation of lead oxide. To reveal the morphology of the lead particles in the pores of the NP membranes TEM (transmission electron microscope) imaging was carried out. NP membranes were embedded in epoxy resin and sectioned into thin (50–70 nm) slices. Slices were cut parallel to the NP membrane surface, thus approximately perpendicular to the pores in the membranes. Figure 1 shows such slices through the membranes for few NP diameters. In Fig. 2 we show a slice which is almost parallel to the pores of the NP. The TEM micrographs show good control of the diameter of the embedded particles. However, the particle length can vary. This is the case at high loading, as is shown in Fig. 2. The samples of 10 nm and below are in the low loading regime and therefore are roughly spherical, with good size control in all three dimensions. The lead weight content per unit surface of a membrane was determined by inductively coupled plasma emission spectroscopy (ICP) after digestion of lead into a 65% $HNO_3$ solution. X-ray diffraction characterization of the lead loaded NP membranes showed the presence of metallic lead.

Magnetization measurements were performed with a $MPMS_2$ field screened magnetometer. All magnetization curves presented are corrected for the diamagnetic contribution of the polymeric membranes. For the larger grains, of sizes 30–1000 nm, we obtain the known magnetization curves of small superconducting particles [11,13]. In Fig. 3 we present magnetization ($M$) vs magnetic field ($H$) curves at 5 K for a few pore sizes in the above range. The critical temperature was measured to be size independent (7.2 ± 0.05 K) down to a grain size of 10 nm (see Fig. 4), in agreement with previous experiments (see, e.g., Refs. [14,15]). The magnetization measurements presented in Fig. 3 were performed with $H$ parallel to the membrane surface. The data were normalized according to Eq. (1), assuming that the difference between the free energy density $g_n - g_s$ is independent of the size of the particles;

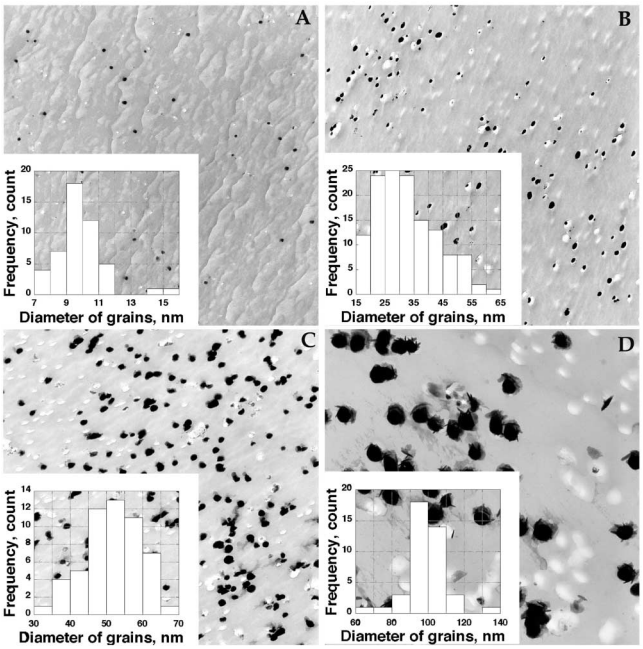


FIG. 1. TEM micrographs, slices parallel to the membrane for (a) 10 nm NP membrane loaded with lead, (b) 30 nm NP membrane, (c) 50 nm NP membrane, and (d) 100 nm NP membrane. The size distribution of the particles is also presented.

$$g_n - g_s = -\int_0^h M dH_e = A, \tag{1}$$

where $H_e$ is the external field and $A$ is the area under the magnetization curve [13]. Since the slope of the magnetization curve is smaller for a small specimen than for a bulk one of the same shape, the magnetization continues to higher fields to have the same area; i.e., the critical field, $h$, as determined from the intercept of the tangent to the rising branch of magnetization and the horizontal field independent branch, shifts to higher fields for smaller particles. We observe this shift, as well as a shift of the magnetization minimum to higher field values upon the decrease in the diameter of the particles. Plotting $h/H_c$ as a function of $1/R$, where $R$ is the radius of the pores in the NP membrane and $H_c$ is the critical field for the bulk lead ($H_c = 415$ Oe at 5 K), we obtain (see the inset of Fig. 3) the relationship [11,13]

$$\frac{h}{H_c} = 1 + \frac{b}{R} \tag{2}$$

with $b = 7.62 \times 10^{-6}$ cm (for the data in Ref. [13] a similar relation was found, with $b = 11 \times 10^{-6}$ cm [11]).

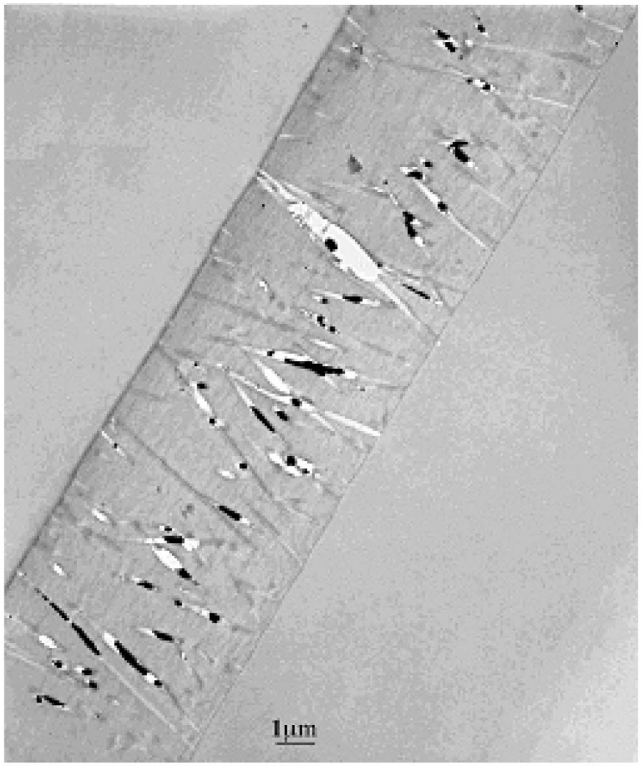


FIG. 2. TEM micrograph for 50 nm NP membrane, slice perpendicular to the membrane.

However, for smaller grains, of sizes 10 nm and below, we find a very different behavior of $M$ vs $H$. We use a membrane with 10 nm pores and control the size of the lead grains inside these pores by varying the deposition time. The content of lead per unit area of the membranes

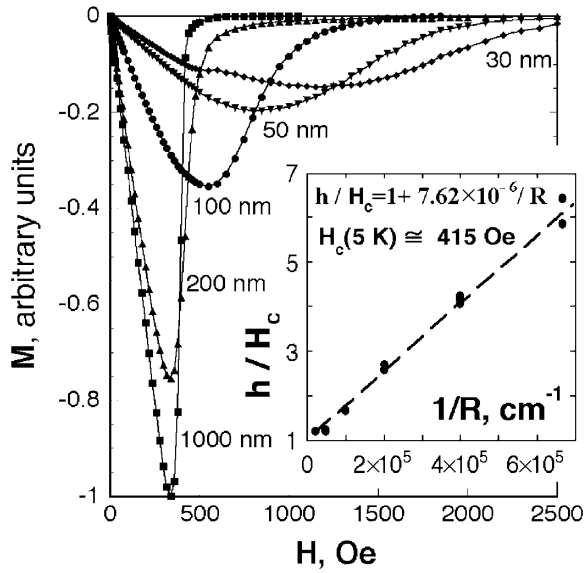


FIG. 3. Normalized magnetization vs $H$ at 5 K according to Eq. (1) for different pore size NP membranes loaded with lead. Inset: normalized critical fields $h/H_c$ vs $1/R$ (see text).

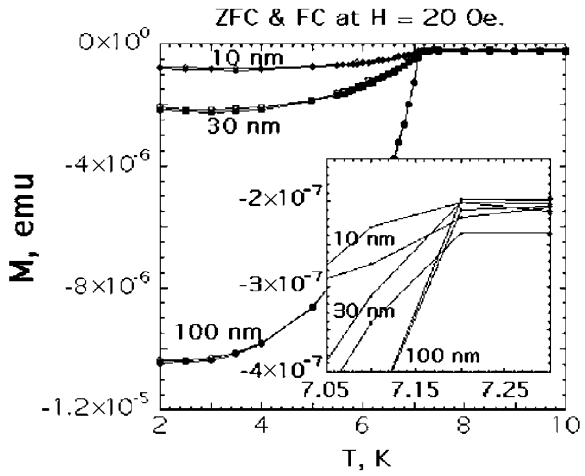


FIG. 4. Field cooled (FC) and zero field cooled (ZFC) magnetization vs temperature of lead grains of sizes 100, 30, and 10 nm. The critical temperature is unchanged within the experimental accuracy. Note that the magnetization is not normalized per weight. Inset: blowup of the transition region.

was determined by the ICP technique. We find that below 5 $\mu$g/cm$^2$ loading no Meissner effect is observed; see Fig. 5. The transition, as a function of size, between the regime where the Meissner effect is observed and the regime where it is not observed is sharp, as can be seen in the inset of Fig. 5, where the integral values under the

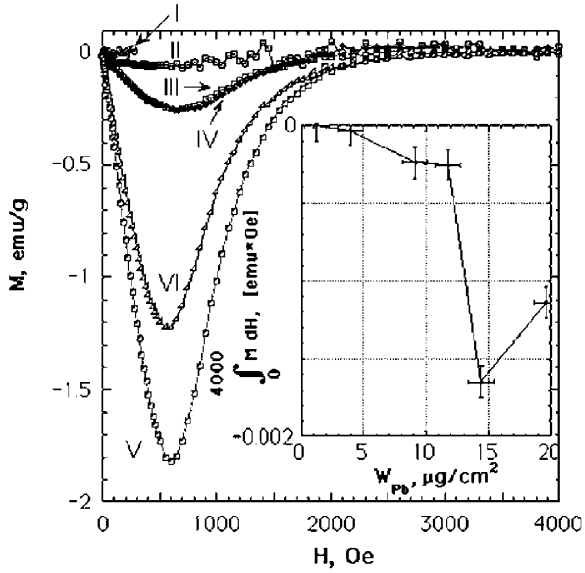


FIG. 5. $M$ per gram vs $H$ at 5 K for different loads of lead into 10 nm NP membranes. Inset: the integral under the magnetization curves in the field limits 0–4000 Oe, as a function of lead loading into pores. Graphs correspond to lead loads and deposition times as follows: (I) 1.2 $\mu$g/cm$^2$, 0.5 h; (II) 3.9 $\mu$g/cm$^2$, 1 h; (III) 9.1 $\mu$g/cm$^2$, 2 h; (IV) 11.7 $\mu$g/cm$^2$, 2.5 h; (V) 14.6 $\mu$g/cm$^2$, 3 h; (VI) 19.6 $\mu$g/cm$^2$, 4 h.

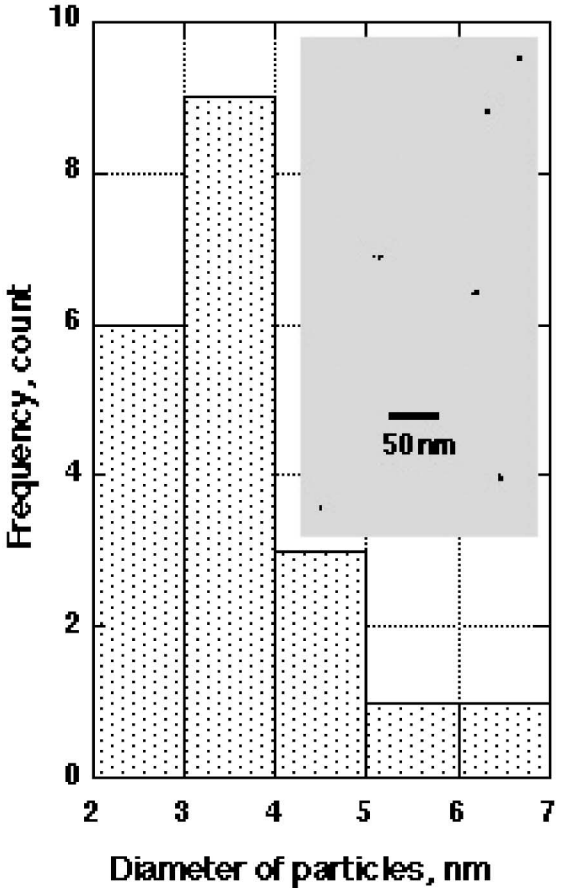


FIG. 6. Size distribution for lead particles in a 10 nm pore membrane with a loading of 1.2 $\mu g/cm^2$. Inset: a contrast enhanced TEM micrograph of these particles in a $\approx 50$ nm slice parallel to the membrane surface.

magnetization curves as a function of the lead loadings are drawn. The size distribution of the lead particles was measured from TEM micrographs for the 1.2 $\mu g/cm^2$ (see Fig. 6) and for the 19.6 $\mu g/cm^2$ loadings leading to average sizes of 4 nm and 10 nm, respectively. The critical size $D$ was estimated by interpolation using the approximation $D \approx (\text{mass}/\text{cm}^2)^{(1/3)}$ to be roughly 6 nm. This estimate is consistent with the condition $d = \Delta$ for lead particles, which gives an approximate size of 5 nm. This is the central result of this Letter.

Two scenarios are possible for the sharp loss of magnetization across the Anderson size. One is that $T_c$ does not change across the transition; i.e., grains large enough to have finite magnetization would have a transition at 7.2 K. The other scenario is that the transition temperature is also lowered abruptly across the Anderson size. Both scenarios are consistent with a sharp loss of superconducting properties across the Anderson size. Here we have shown that $T_c$ does not change down to grains of size 10 nm. Also, the grains of intermediate sizes in Fig. 5, of 11.7 and 9.1 $\mu g/cm^2$ loadings, have a $T_c$ larger than the measured temperature of 5 K. Still, the second scenario cannot be ruled out, and a temperature dependent measurement at sizes smaller than 10 nm would be of interest.

Another observation for these grain sizes is that the critical field, $h$, does not obey Eq. (2) but is considerably smaller. We do not have a clear understanding of the physics responsible for this observation. We mention, in this regard, that recent experimental [16] and numerical [17] works have found that at grain sizes of this order, lead grains change their crystalline structure due to the large portion of surface atoms. Such a change could affect the superconducting properties of the grain. We stress that the lowering of the critical field and the loss of the Meissner effect occur at different grain sizes and are therefore clearly two different phenomena.

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