Magnetization of small lead particles

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Abstract

The magnetization of an ensemble of isolated lead grains of sizes ranging from below 6 nm to 1000 nm is measured. A sharp disappearance of Meissner effect with 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.

In 1957 Bardeen, Cooper and Schrieffer (BCS) 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 $\xi^{(1/3)} \lambda_F^{(2/3)} \ll \xi$ where $\lambda_F$ is the Fermi wave length). Motivated by this statement, Giaver 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). Only recently Ralph Black and Tinkham (RBT) [5] 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 [6] and references therein). However, on the experimental side the work of RBT remained the single work which investigated the crossover across the Anderson limit.

In this paper we present measurements of the magnetization of an ensemble of $10^{12}$ Pb grains, ranging in size from 1000 nm down to grains smaller than 6 nm. The larger grains, down to 30 nm in size, showed diamagnetic response with the well known finite size correction [7]. However, at a smaller size, estimated to be roughly 5 nm, an abrupt change was found in the diamagnetic response, which, within the experimental accuracy, vanishes for the smaller grains. The above size is in agreement with the Anderson limit for lead. 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 can not 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 [8]. The lead particles are deposited into the pores of polycarbonate nuclepore membranes (NP), and due to the confinement in the pores the particles do not agglomerate. The deposition of lead particles into NP membranes was performed by counter-current diffusion of a Pb-salt and a reducing agent from opposite sides of the membranes (see experimental setup in Fig.1). These hydrophilic polyvinyl pyrrolidone (PVP) coated polycarbonate membranes have straight-through pores distributed randomly on the surface and penetrating the surface at an angle of incidence $\pm 34^\circ$. The NP membranes were equilibrated in triple distilled water for an hour; the membranes were mounted into a cell shown in Fig.1.

Upon completion of the mounting process, the two stirred chambers were filled with lead salt on the dull side of the membrane and with reducing agent on the shining side. The reducing agent was 0.2M aqueous NaBH$_4$ solution. The lead salt solution was 80cc of 0.03M PbNO$_3$ + 20cc of 1M HNO$_3$. These two solutions were introduced simultaneously to 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 one minute. 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 (50−70nm) slices. Slices were cut parallel to the NP membrane surface, thus approximately perpendicular to the pores in the membranes. Fig. 2 shows such slices through the membranes for few NP diameters. In Fig. 3 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, especially at high loading, varies as shown in Fig. 3. 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. XRD 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 [7,9]. In Fig. 4 we present Magnetization ($M$) vs. magnetic field ($H$) curves at 5K for few pore sizes in the above range. These measurements 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;

$$g_n - g_s = -\int_0^h M dH = A$$  \hspace{1cm} (1)

where $H_e$ is the external field and $A$ is the area under the magnetization curve [9]. 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 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 5K), we obtain (see insert of Fig 4) the relationship [7,9]

$$\frac{h}{H_c} = 1 + \frac{b}{R}$$  \hspace{1cm} (2)

with $b = 7.62 \cdot 10^{-6}$ cm (for the data in Ref. [9] a similar relation was found, with $b = 11 \cdot 10^{-6}$ cm [7]).

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 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 function of size, between the regime where Meissner effect is observed and the regime where it is not observed is sharp, as can be seen in the insert of Fig. 5, where the integral values under the magnetization curves as function of the lead loadings are drawn. We estimate the size of the grains for which the transition occurs to be below 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 paper.

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 would like to mention, in this regard, that recent experimental [10] and numerical [11] 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 would like to 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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FIGURES

FIG. 1. Diffusion Cell. 1: PMMA transparent body. 2 and 4: pressure clamp. 3: magnetic stirrer. 5 and 6: shaft assembly for the stirrers. 7: NP membrane.

FIG. 2. TEM micrographs, slices parallel to the membrane for (A) 10 nm membrane loaded with lead (B) 30 nm NP membrane (C) 50 nm NP membrane (D) 100 nm NP membrane.

FIG. 3. TEM micrograph for 50 nm NP membrane, slice perpendicular to the membrane.

FIG. 4. Normalized magnetization vs. $H$ at $5K$ according to Eq. 1 for different pore size NP membranes loaded with lead. Insert: normalized critical fields, $h/H_c$ vs. $1/R$ (see text).

FIG. 5. $M$ vs. $H$ at $5K$ for different loads of lead into 10 nm NP membranes. Insert: the integral under the magnetization curves in the field limits $0 - 4000$ Oe, as 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 hours (ii) $3.9 \mu g/cm^2$, 1.0 hours (iii) $9.1 \mu g/cm^2$, 2.0 hours (iv) $11.7 \mu g/cm^2$, 2.5 hours (v) $14.6 \mu g/cm^2$, 3.0 hours (vi) $19.6 \mu g/cm^2$, 4.0 hours
Fig. 1

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Fig. 2

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Fig. 4

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$h/H_c = 1 + \frac{7.62 \times 10^{-6}}{R}$

$H_c (5 K) \cong 415 \text{ Oe}$
Fig. 5

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