Physica C 468 (2008) 944–947

Contents lists available at ScienceDirect

Physica C

journal homepage: www.elsevier.com/locate/physc

Effect of screening current induced pair breaking on magnetization of superconducting lead nanoparticles

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ARTICLE INFO

Article history:
Received 24 March 2008
Accepted 9 April 2008
Available online 15 April 2008

PACS:
74.40.+k
74.20.De

Keywords:
Nanoparticle
Screening current
Magnetization

ABSTRACT

Magnetization measurements on lead nanoparticles in the size range 35–45 nm are presented. It is shown that the critical fields in these nanoparticles are enhanced significantly above their bulk values with temperature dependence also distinct from that of bulk. The observed "type II" like shape of the magnetization curves is explained on the basis of the Ginzburg–Landau phenomenology by invoking the pair breaking effect of the London screening currents, which makes the effective penetration depth an increasing function of the field. The temperature dependence of critical field is found to be consistent with our explanation.

1. Introduction

Studying various phenomena in nano-scale materials and in particular superconducting particles [1–4] and nano-wires [5,6] of dimensions much smaller or comparable to the superconducting penetration depth λ and coherence length ξ is of current interest. According to the Anderson criterion [7], Cooper pairing is possible as long as the separation of the electronic levels δ ($\approx 1/N(0)V$ where $N(0)$ is the density of states at the Fermi surface and V is the volume of the particle) at the Fermi surface in the normal state is smaller than the superconducting energy gap Δ. In lead and other elemental superconductors, the critical particle size r_c below which this criterion breaks down is approximately an order of magnitude smaller than the coherence length ξ. It is indeed experimentally confirmed that the critical temperature T_c of nanoparticles of lead (Pb) remains unaffected down to about 5–10 nm of size, while $\xi \approx 83$ nm [8]. Further, experiments suggest that the condensation energy given by the integral

$$-\mu_0 \int_0^{H_c} M(H)\mathrm{d}H \tag{1}$$

remains independent of particle size provided it is above the critical size r_c [1]. In the above expression H_c is the critical field at which diamagnetism eventually vanishes, $M(H)$ is the field dependent magnetization. It is well known that the magnitude of the zero field slope of M–H curve decreases with decreasing particle size. It is therefore easy to imagine that H_c should increase with decreasing particle size in order that the above integral is particle size independent. But the integral gives no details about the shape of the $M(H)$ curves.

It is commonly observed that $M(H)$ curves in both nanoparticles and nano-wires are "type II" like [5,6], in the sense that the diamagnetism increases at low fields and then decreases gradually after attaining a maxima. According to Michotte et al. [6], the lead nano-wire transforms into type II superconductor due to a sharp reduction in the electronic mean free path. We argue that the observed magnetic behavior is of an origin basically different from the samples turning to type II. Even in micro-sized superconductors, vortex formation above a first critical field is expected to be highly energy intensive and is accompanied by sharp discontinuities in magnetization [9,10]. It is therefore difficult to envisage that the nano-sized superconductors exhibit type II behavior.

Other possible reasons for the type II like magnetic behavior in nanoparticles is order parameter fluctuations. Effectiveness of the order parameter fluctuations depends on the ratio of thermal energy kT to the condensation energy $VH_{c0}^2/2\mu_0$ where H_{c0} is the thermodynamic critical field. This ratio is usually negligible for particles of size comparable to the London penetration depth λ or ξ (such as in our experiments) for most elemental superconductors, and

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doi:10.1016/j.physc.2008.04.006

therefore order parameter fluctuations are unlikely to be responsible for any magnetic effects, except at temperatures very close to the T_c.

In this paper, we present magnetization measurements on lead nanoparticles, reproducing the type II like behavior observed by others. Further, temperature dependence of the critical field H_c exhibits interesting deviations from the bulk behavior. We present an understanding based on the Ginzburg–Landau theory for both these observations.

2. Experiment

Pb nanopartcles of different sizes have been synthesized using Polyol method. In a typical synthesis of 40–42 nm (sample code Pb-1) particles, a mixture of 500 mg lead acetate and 20 ml of glycol was held at 160° for 4 h while refluxing. Ethylene glycol served both as a solvent and a reducing agent when heated to 160°. To prepare particles less than 40 nm size, (sample code Pb-2) ethylene glycol along with ascorbic acid and oleic acid were used as solvents. The mixture has been heated at 160° for 4 h while refluxing. While, both ethylene glycol and ascorbic acid served as reducing agents, oleic acid plays the role of a capping ligand. These solutions were allowed to cool to room temperature and the centrifuged particles were washed using absolute ethanol followed by vacuum drying. Same method has been followed to prepare 42–45 nm size (sample code Pb-3) lead nanoparticles except that no oleic acid has been added in this case. Phase purity and the structure of the samples were analyzed using Cu Kα radiation by employing a Philips Diffractometer (model PW 1071) fitted with graphite crystal monochromater. The average crystallite size was determined from the extra broadening of the X-ray diffraction peaks (Fig. 1) of the sample using Scherer's formula applied to the strongest peak.

Magnetization measurements are carried out using Quantum Design MPMS5 SQUID magnetometer. Temperature dependent magnetization measurement in an applied field of 50 Oe yielded T_c = 7.2 K (Fig. 2) similar to that of bulk lead [8]. In Fig. 3, we present the field dependent magnetization curves at different temperatures, which exhibit a hysteresis (see the inset of Fig. 3), albeit small. The origin of the hysteresis in such small particles is not well understood but may be due to the sharp corners in the particles and/or weak coupling between the various particles in the conglomerates taken. As the focus of the paper is on the shape of the

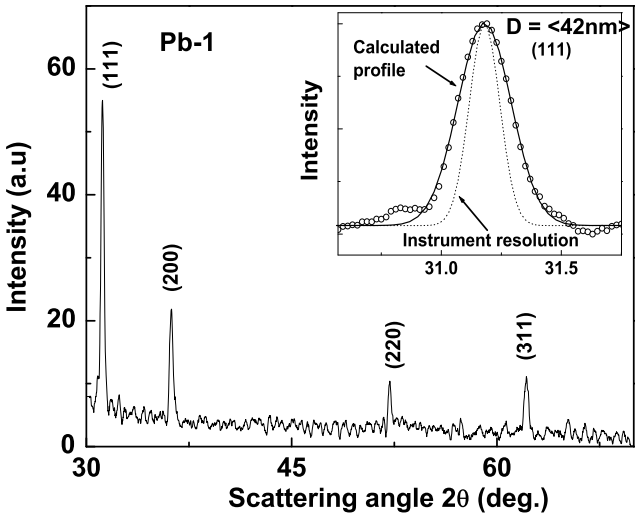

Fig. 1. X-ray diffraction of the sample Pb-1. Inset blows up the strongest peak. The continuous and dotted lines are the Gaussian fits to the peak and the instrument resolution, respectively.

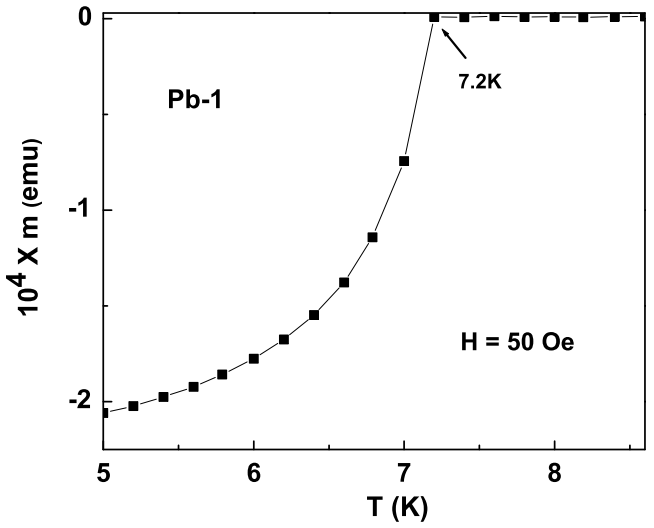

Fig. 2. ZFC Magnetization of Pb-1 particles showing the superconducting transition.

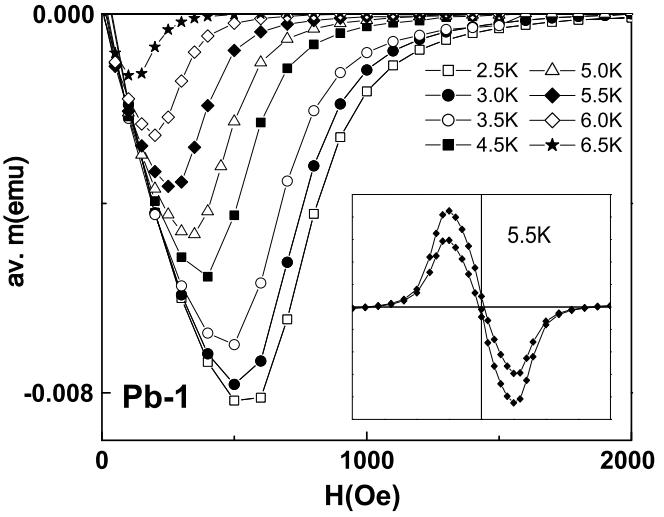

Fig. 3. Reversible part of magnetic moment m vs. H data of Pb-1 at different temperatures. Inset shows hysteresis loop.

equilibrium magnetization curves and the highest field H_c upto which the diamagnetism persists, we have drawn the reversible part of the magnetization in Fig. 3, obtained by averaging the increasing and decreasing field branches of the magnetization curves thereby eliminating the irreversible part.

We note the following important features of the magnetization data generally observed in all the three samples studied. First, the nature of the M–H curve significantly deviates from the typical type I behavior, i.e., after attaining a maximum, the diamagnetism gradually decreases towards zero. The field H_c upto which superconductivity persists is significantly larger compared to the critical field in the bulk. The zero temperature critical field in lead is known to be about 800 Oe [8] while the H_c in the samples studied are about three to four times larger. The critical field H_c^{ext} is extracted from the M–H curves by drawing a tangent at the field where the slope dM/dH is maximum as shown in the inset of Fig. 4. The intersection of the tangent on the field axis gives H_c^{ext}, which is a lower limit on the actual critical field H_c. The reversible part of M–H curves at different temperatures obey a simple scaling as depicted in Fig. 5. We therefore rule out the role of thermal

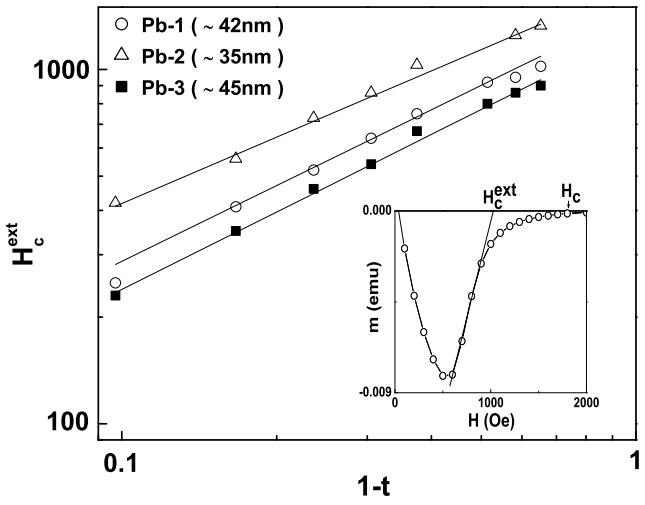

Fig. 4. Log–log plot of H_c^{ext} and $(1-t)$ for the samples Pb-1, Pb-2 and Pb-3. The inset shows the criterion (discussed in the text) used to extract H_c^{ext}.

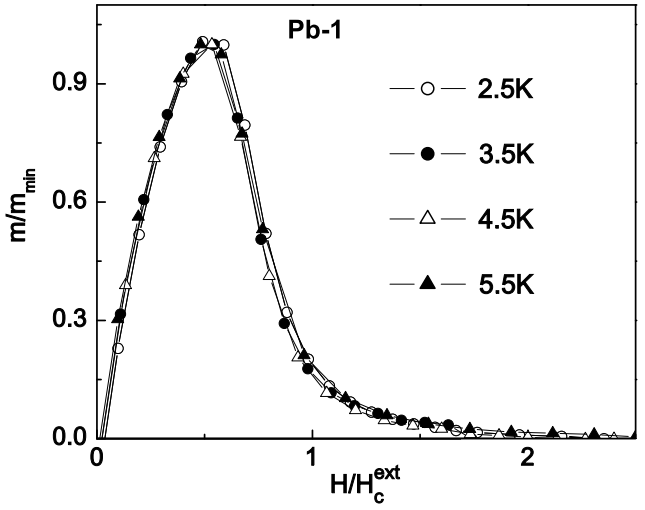

Fig. 5. Data in Fig. 3 re-plotted in scaled form, i.e., $m/m_{\min}$ vs. H/H_c^{ext}.

fluctuations of the order parameter as an explanation for the observed behavior.

In the bulk, critical field derived from the Ginzurg–Landau theory is given by the expression $H_{c0} = \varphi_0/2\pi\lambda\xi$, which gives the temperature dependence $H_{c0}(t) \sim (1-t)$ where $t = T/T_c$. In Fig. 4 we plot the temperature dependence of H_c^{ext}. In contrast to the temperature dependence of the bulk critical field, $H_c^{ext}(t)$ obeys the relation

$$H_c^{ext}(t) \approx H_c^{ext}(0)(1-t)^{\alpha} \tag{2}$$

where the exponent $\alpha \approx 0.6$–0.7, significantly less than 1 as expected in the case of bulk superconductors. We now present a possible explanation for the observed M–H curves and the temperature dependence of the critical field in the nanoparticle regime.

3. Discussion

In bulk type I superconductors, magnitude of induced London screening currents in Meissner state is governed by the London equation $\mathbf{J_s} = \mathbf{A}/\lambda^2$, where $\mathbf{J_s}$ is the supercurrent density and $\mathbf{A}$ is the vector potential. The screening current increases linearly with the increasing applied field resulting in a linear relation between magnetization M and applied field H. For particles of size comparable to λ, Meissner screening currents pervade all over the volume of the particle and therefore diminish the overall phase space of zero momentum pairs $(k\uparrow, -k\downarrow)$ resulting in suppression of the Ginzburg–Landau order parameter ψ. We therefore argue that the pair breaking effect results in an increase in the penetration depth and thus weaker magnetic screening at higher magnetic fields. Therefore, λ must be replaced by an effective penetration depth λ_{eff} renormalized by the field dependent order parameter as given by

$$\lambda_{\text{eff}}^2 = \frac{\lambda^2}{\langle|\psi|^2\rangle} \tag{3}$$

such that $\langle|\psi|^2\rangle$ tends to unity at zero applied field and decreases at higher magnetic field. The triangle brackets indicate averaging over the volume of the superconducting particle. We believe that this effect becomes very prominent in samples whose length scales are smaller than or comparable to λ.

Now we apply the Ginzburg–Landau theory to small particles by idealizing them to be spherical in shape with radius R, in order to determine the field dependence of $\langle|\psi|^2\rangle$ and thereby understand the peculiar magnetic behavior and the temperature dependence of the critical field observed experimentally. In a simply connected system, such as a sphere, with an appropriate choice of gauge for the vector potential $\mathbf{A}$, the order parameter ψ is real. Further, for a particle size small compared to the coherence length ξ, we can neglect the spatial derivatives of the order parameter ψ and consider it to be a constant over the volume of the sphere [11]. The first GL equation then becomes

$$\left(\frac{2\pi\xi}{\varphi_0}\right)^2 \mathbf{A}^2\psi - \psi + |\psi|^2\psi = 0 \tag{4}$$

which gives

$$|\psi|^2 = 1 - \left(\frac{2\pi\xi}{\varphi_0}\right)^2 \mathbf{A}^2 = 1 - \left(\frac{1}{H_{c0}\lambda}\right)^2 \mathbf{A}^2 \tag{5}$$

with critical field in the bulk $H_{c0} = \varphi_0/2\pi\lambda\xi$. In the above equation, we must emphasize that λ is the zero field penetration depth and is merely a constant for a given temperature. Eq. (5) describes the pair breaking effect of the magnetic field, which eventually results in a decrease in the magnetic screening (increase in penetration depth) which is accounted by Eq. (3). To understand the magnetization of a superconducting nanoparticle at non-zero field, we consider the solution of the London equation $\nabla^2\mathbf{A} = (1/\lambda_{\text{eff}}^2)\mathbf{A}$ for a spherical particle given by $\mathbf{A} = \hat{\varphi}A_\varphi$ where [12]

$$A_\varphi = \left(\frac{3H}{2\beta^2 r^2}\right)\frac{R}{\sinh\beta R}[\sinh\beta r - \beta r\cosh\beta r]\sin\theta \tag{6}$$

where $\hat{\varphi}$ is the azimuthal unit vector in the spherical polar coordinate system, r and θ are the radial coordinate and polar angle, respectively. H is the applied field and $\beta = 1/\lambda_{\text{eff}}$. Upon applying the limit $\beta R < \pi$ and $\beta r < \pi$ on Eq. (6) and averaging over the volume of the sphere gives

$$\langle\mathbf{A}^2\rangle \approx 0.1(HR/2)^2[1 - \beta^2R^2/3]. \tag{7}$$

We note that the above inequalities are valid as $R \sim 20$ nm while $\pi\lambda \sim 100$ nm. Combining the above equation with Eq. (5), we obtain

$$\langle|\psi|^2\rangle = 1 - (0.1) \times \left(\frac{HR}{2H_{c0}\lambda}\right)^2\left[1 - \frac{\beta^2R^2}{3}\right]. \tag{8}$$

Critical field H_c is defined as the field H where $\langle|\psi|^2\rangle = 0$ [11] and we obtain,

$$H_c = \sqrt{10} \times H_{c0}\lambda/R \tag{9}$$

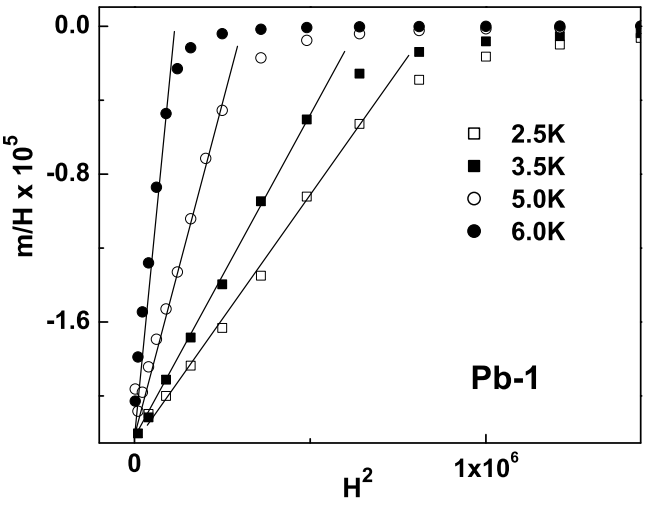

Fig. 6. Data in Fig. 3 re-plotted in the form m/H vs. H^2.

clearly suggesting that the critical field increases with reducing particle size. Further $H_{c0} \sim (1-t)$ and $\lambda \sim (1-t)^{-1/2}$ therefore $H_c \sim (1-t)^{1/2}$ where the exponent 0.5 is close to the observed exponent 0.6–0.7.

To understand the field dependence of the magnetization, let us consider λ_{eff}^2 to the lowest significant order in R/λ by combining Eqs. (3) and (8) to obtain

$$\lambda_{\text{eff}}^2 = \lambda^2 \left[1 + 0.1\left(\frac{HR}{2H_{c0}\lambda}\right)^2\right]. \tag{10}$$

We now calculate the magnetization of a sphere of radius R following London [10] in the small particle limit, i.e., $R/\lambda_{\text{eff}} < \pi$ to obtain

$$M \approx -\frac{3}{8}\left(\frac{R}{\lambda}\right)^2 \left[1 - 0.1\left(\frac{HR}{2H_{c0}\lambda}\right)^2\right] H. \tag{11}$$

Following above equation, we re-plot the M–H data in Fig. 6 in the form M/H vs. H^2, which exhibits linear behavior in the entire field range between zero and H_c, where the superconductor exhibits its diamagnetism. In bulk materials, m/H is expected to be a constant. The analysis presented in Fig. 6 clearly indicates the London screening current induced pair breaking and the whole field range falls under a single regime of field dependent penetration depth as discussed above, and the type II like description is perhaps not necessary in the case of nano-scale superconductors.

In conclusion, we presented magnetization measurements on lead nanoparticles in the size range 35–45 nm with critical temperature same as that in the bulk. It is shown that the critical fields in these nanoparticles are enhanced significantly above their bulk values. Further the critical fields are higher for smaller particles. Moreover, they exhibit magnetic behavior reminiscent of type II superconductors. The results are interpreted by invoking the pair breaking effect of the London screening currents which pervade all over the volume of the particles. This makes the penetration depth increase with field. Further, the enhancement in the critical field H_c and its temperature dependence in the nanoparticles are shown to be consistent with the Ginzburg–Landau theory.

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