Type-I superconductivity in carbon-coated Sn nano-spheres

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\section{Introduction}

The interest in type-I superconductors has recently revived, investigating samples of size smaller than the superconducting coherence length, $\xi$, or the penetration depth, $\lambda$. In such samples, significant deviations from bulk superconducting properties have been predicted and observed. Specifically, a significant enhancement of the critical field, $H_c$, was observed in nano-size type-I superconductors [4–7]. A pitfall in such a study may arise from agglomeration and/or oxidation of the nano-particles. These may be prevented by protecting the particles with various materials. For example, carbon coating is commonly used to protect tin nanoparticles [13,15,16].

In this paper we show that the coating process may cause doping of the superconducting material and thus may affect drastically its superconducting properties. We report on magnetization measurements in carbon-coated tin nano-spheres fabricated by a sonochemical technique [15]. The magnetic behavior of two samples were compared: Spheres of diameter $\sim$120 nm (which is in between $\lambda_0 = 34$ nm and $\xi_0 = 230$ nm of bulk tin), and larger spheres of diameter $\sim$1400 nm, both coated with sub-nanometer layers of carbon. Our magnetization measurements show clearly a type-I superconducting behavior of both samples with well-defined ‘superheating’ and ‘supercooling’ fields, and an intermediate state manifested by a gradual increase of the magnetization to zero as the superheating field is approached. However, unexpectedly, no significant change was found in the critical field of the small spheres as compared to the large ones. We attribute this result to the doping of the tin spheres with carbon atoms during the coating process. The doping reduces the effective coherence length to below the sphere size, thus eliminating the size effect. To get insight into the intermediate state in tin spheres we performed simulations based on the time dependent Ginzburg-Landau (GL) equations. The simulations show that the structure of the intermediate state depends on the sphere size which, in turn, affects the shape of the magnetization curve.

\section{Experimental}

Granules of 99.998\% pure $\beta$ tin (Sn) metals were melted and over-layered by silicone oil in a quartz test tube that was gently heated up. The mixture was irradiated for 5 min with 20 kHz ultrasonic energy, forming a grey suspension of particles in the Si-oil. After precipitation, the particles were separated using a centrifuge, washed several times with n-hexane and dried in vacuum, and then two sizes, ‘small’ and ‘large’, of Sn spheres were chosen for the magnetic measurements described in the next section. In the following, we refer to the samples with the small and large spheres as ‘sample S’ and ‘sample L’, respectively. The size distribution of the two samples, measured by Dynamic Light Scattering (DLS) technique show a distribution maximum for spheres with di-
Fig. 1. Magnetization versus temperature measured in the small (S) and large (L) tin spheres. The solid line is a fit to $M \propto (1 - T/T_c)^{1/2}$, see text. The upper and lower insets show TEM images of the small and large spheres, respectively. The scale bars in the images are 50 and 200 nm, respectively.

ameter $\sim 120$ nm and $\sim 1400$ nm and a full width at half maximum of $\sim 20$ nm and $\sim 200$ nm for samples S and L, respectively.

Energy-dispersive X-ray spectroscopy (EDS) shows the existence of only one element – Sn – confirming the purity of the sample. X-ray diffraction (XRD) of the small and large particles show multiple peaks, all matching with the database of $\beta$ tin. No peaks of any other elements were observed, suggesting the presence of a pure metallic tin. CHNSO analysis and Rutherford Backscattering Spectroscopy (RBS) indicates that the amount of carbon atoms varies between 0.27 to 0.41 weights percent in different samples. Transmission Electron Microscope (TEM) images show that the large and small Sn particles are spherical, see insets to Fig. 1. The magnetic measurements described in the next sections were performed using a Superconducting Quantum Interference Device (SQUID - Quantum Design MPMS-5XL) magnetometer.

3. Results

Fig. 1 shows the temperature dependence of the magnetization, measured in samples S (diamonds) and L (circles) with an external field of 30 Oe. The magnetization in sample L approaches zero with a diverging slope, indicating a well-defined transition temperature $T_c = 3.6$ K, consistent with the zero-field transition temperature for bulk tin reported in the literature [4]. Sample S exhibits a gradual approach of $M(T)$ to zero with an inflection point around 3.4 K, suggesting a distribution of transition temperatures in this sample.

Magnetization curves were measured at several temperatures between 1.9 and 3.5 K. Typical data at $T = 1.9$ K are shown in Fig. 2. Both samples exhibit characteristics of type-I superconductors, namely magnetic hysteresis with superheating and supercooling fields [17]. The supercooling fields, $H_{sh}^c$ for sample L and $H_{sh}^c$ for sample S, are well defined. The superheating field, $H_{sh}^h$, in the large sample is also well-defined, however, sample S exhibits a long magnetization 'tail', suggesting a distribution of superheating fields. For this sample we define $H_{sh}^h$ for the majority of the spheres by a linear extrapolation of the magnetization at the maximum slope (see the dotted line in the figure). The measured temperature dependencies of the characteristic fields, $H_{sh}^h$, $H_{sh}^c$, $H_{sc}^c$, and $H_{sc}^h$, are plotted in Fig. 3. As expected, all these fields decrease to zero as $T_c$ is approached. Notably, at all temperatures the supercritical fields for sample S are bounded by those of sample L, i.e., $H_{sh}^h > H_{sh}^h$ and $H_{sc}^c < H_{sc}^c$.

4. Discussion

As mentioned above, the $M(T)$ data of Fig. 1 indicate a well-defined transition temperature, $T_c$, for sample L. Indeed, the $M(T)$ data of sample L can be well fitted to $M \propto (1 - T/T_c)^{1/2}$ [17] with $T_c = 3.6$ K, as shown by the solid curve in Fig. 1. The data of sample S, however, cannot be fitted to the above expression, suggesting a distribution of transition temperatures. The origin of this distribution cannot be associated with size distribution of the spheres, since the particle size does not affect $T_c$ (see, e.g., [4]). On the other hand, it is well known that $T_c$ may be affected by doping (see, e.g., [18]). It is thus plausible to attribute the distribution of $T_c$ in sample S to a distribution in the degree of carbon doping in the tin spheres. We note that although sample L went through the same carbon coating process, the carbon doping in this sample is less effective as the ratio of the surface area to the volume of the spheres in this sample is much smaller.

The effect of carbon doping is also manifested in the $M(H)$ data of Figs. 2 and 3. These data show that at all temperatures $H_{sh}^c < H_{sh}^l$ and $H_{sh}^h > H_{sh}^c$. The first observation ($H_{sh}^c < H_{sh}^l$) is puzzling as it seems to contradict previous observations in type-I superconductors, demonstrating clearly an increase in $H_{sh}$ as the particle size is reduced [7–12,14,16]. The solution to this puzzle lies in the large increase in the Ginzburg–Landau parameter, $\kappa = \lambda/\xi$, in the small sample, caused by the carbon doping. The increase of $\kappa$ in the small spheres results from a concurrent decrease in $\xi$ and increase in $\lambda$ because of carbon doping, as follows from the equa-

![Fig. 2](image2.png)  
![Fig. 3](image3.png)
tions for $\xi$ and $\lambda$ in the dirty limit [17]:

$$\xi(T) = 0.85(\xi_0 l)^{1/2}(1 - t)^{-1/2},$$

(1)

$$\lambda(T) = 0.62\xi_0 l (\xi_0 l)^{1/2}(1 - t)^{-1/2},$$

(2)

Where $t = T/T_c$ and $l$ is the mean free path of the electrons. Evidently, the ratio $\kappa = \lambda/\xi$ is inversely proportional to $l$, thus as $l$ decreases because of doping, $\kappa$ increases.

The value of $\kappa$ in both samples can be derived from the measured values of the super-critical fields. For spherical particles [19]:

$$H_{sh} = \frac{2}{3}2^{-1/4}k^{-1/2}H_c$$

(3)

$$H_{sc} = 1.69\sqrt{2}\kappa H_c.$$  

(4)

Thus, the value of $\kappa$ can be deduced from the ratio

$$H_{sh}/H_{sc} = 0.235/k^{3/2}.$$  

(5)

The calculated values of $\kappa$ are shown in Fig. 4 as a function of temperature for both samples. The solid curves through the data points in the Figure are calculated based on the empirical approximation [17]:

$$\kappa = \kappa(0)/(1 + t^2).$$

(6)

The fit yields $\kappa(0) = 0.37$ and 0.24 for samples S and L, respectively. Evidently, the values of $\kappa(0)$ for the large spheres are similar to that reported in the literature for bulk tin [3]. However, the deduced values of $\kappa$ for sample S are significantly larger.

The differences in the values of $H_{sh}$ and $H_{dc}$ between the samples (Figs. 2 and 3) can be explained as resulting from the large value of $\kappa$ in each sample. The increase in the value of $\kappa$ in sample S causes a decrease in $H_{sh}$ (Eq. (3)) and an increase in $H_{dc}$ (Eq. (4)) as compared to the corresponding values in sample L.

Knowledge of the values of $\kappa$ allows calculation of the critical field, $H_c$, from either $H_{sh}$ or $H_{sc}$, using Eqs. (3) or (4), respectively. In Fig 5 we show $H_c$ vs. temperature for sample L as deduced from $H_{sh}$ (open circles) and $H_{dc}$ (triangles), and for sample S as deduced from $H_{sh}$ (open squares) and $H_{dc}$ (crosses). The supercooling and superheating fields yield the same $H_c$ values for a given sample; these values are quite similar and close to that reported for clean bulk tin (~300 Oe) [4], implying no effect of the size on $H_c$. In the following we argue that the size effect expected in sample S is eliminated by a significant reduction of the coherence length to a value smaller than the size of the sample.

The effective coherence length, $\xi_{eff}$, is related to the coherence length at zero temperature, $\xi_0$, and the electron mean free path, $l$, [20]

$$\xi_{eff} = \xi_0 l / (\xi_0 + l).$$

(7)

The value of $l$ can be found from the value of $\kappa$ at $T_c$ using the dirty limit formula [17]

$$\kappa(T_c) = \frac{0.72\lambda_1(0)}{l}.$$  

(8)

Inserting $\lambda_1(0) = 34 nm$ and the experimental value of $\kappa(T_c) = 0.19$ for sample S (Fig. 4), yields $l = 129 nm$. With $\xi_0 \approx 230 nm$, Eq. (7) yields $\xi_{eff} = 83 nm$. As the doping reduces the value of $\xi_{eff}$ below the size of the sample (~120 nm), no size-effect is expected.

Finally, we note that the shape of the magnetization curves of Fig. 2 are different from that reported in the literature for large, mm-size spheres [21]. Specifically, an approximate linear increase of the magnetization to zero was reported for large Pb spheres whereas Fig. 2 exhibits a much more gradual increase. We attribute this difference to different intermediate structures. To gain insight into the intermediate state in our samples we exploited the time-dependent Ginzburg–Landau (TDGL) scheme [22–26] to numerically calculate the local order parameter and induction in spheres of different radius $R > \xi_{eff}$, and GL parameter, $\kappa$. We start with the dimensionless GL Hamiltonian [20]

$$G[A, \psi] = \iint \iint \int d^3r \left[ - (1 - T)|\psi|^2 + \frac{1}{2}|\psi|^4 + \left( \frac{\partial}{\partial t} - iA_0 \right) \psi \right]^2 \tau(r) + \kappa^2(\partial \times A - H)^2;$$

(9)

where $\psi$ is the order parameter, $A$ the vector potential in units of $\sqrt{2}\lambda_1 H_c$, $H$ the applied magnetic field in units of $\sqrt{2} H_c$, $r$ the length coordinate scaled by the effective coherence length, $\tau(r)$ is a step function incorporating the boundary condition at the sphere surface [27]; $\tau(r) = 1$ for $r < R$ and zero at $r > R$. We solve numerically the time-dependent GL equations in a gauge with zero scalar potential [22–27]

$$\frac{\partial \psi}{\partial t} = \frac{\delta G}{\delta \psi} - \frac{1}{2} \frac{\delta G}{\delta A_v},$$

(10)
using a rectangular Cartesian grid, embedding the sphere in a cube of size $L > R$. The magnetic field is applied in the $z$-direction, defining $H = H_z$ as the boundary conditions on the cube sides.

A link-variables approach method \[28\] was applied to solve numerically the set of Eq. (10) up to a stationary state for a given external magnetic field. The stationary state solution provides the local magnetic field inside the sphere $H(r)$ and the magnetic induction $B = \int H(r) d^3r / d^3r$. The magnetization $M(H)$, in units of $\sqrt{\frac{a}{4\pi}}$, is calculated from $M = (B - H)/4\pi$.

The numerical simulations provide the structure of the intermediate state for the spheres. Fig. 6a shows the calculated density of the superconducting phase $n_b = |\psi|^2$ in the YZ plane inside the sphere of $R = 6\xi$, $\kappa = 0.22$, for $H = 0.09$ and $T = 0.5T_c$. Apparently, only one superconducting domain, surrounded by a normal phase, is observed. The normal phase continuously invades the sphere as the field increases. Evidently, in our experiment the radius of both S and L spheres ($\sim 60$ and $\sim 700$ nm, respectively) is less than $6\xi$. Thus, one may expect that the intermediate state in both of these samples consists of only one superconducting domain.

A more complex intermediate state is obtained in the simulations for large spheres. This is demonstrated in Fig. 6b that shows the density of the superconducting phase inside a sphere of $R = 15\xi$, $\kappa = 0.18$, $H = 0.07$ and $T = 0.5T_c$. Several superconducting domains are now observed, separated by normal domains. Interestingly, images in the XY plane (not shown here) reveal that the intermediate state of the large sphere includes clusters of vortices surrounded by the superconducting phase \[27\]. A more detailed description of the intermediate state in type-I spheres and its dependence on size, temperature and field, will be published elsewhere \[29\].

The calculated $M(H)$ for the spheres of Fig. 6a and b are shown in Fig. 6c and d, respectively. A pronounced difference between the two magnetization curves is observed in the initial drop of $M$ vs. $H$ after the minimum in $M$. The sharp drop of $M$ in the large sample is associated with an abrupt change in the topology of the superconducting phase, from a simply connected single domain at $H = 0.05$ to a multiply connected domain at $H = 0.07$. The absence of such a sharp drop in the experimental data for samples S and L is consistent with the above expectation that the intermediate state in these samples consists of only one simply connected superconducting domain surrounded by a normal region.

5. Summary and conclusions

Magnetic measurements in carbon-coated tin spheres with size smaller than the coherence length, $\xi_0$, of clean tin, show type-I superconductivity with a critical field, $H_c$, similar to that of bulk tin. The absence of the expected increase in $H_c$ is attributed to carbon doping which significantly decreases the effective coherence length below the size of these spheres. Simulations based on the TDGL equations explains the measured gradual drop in the magnetization curves as resulting from an intermediate state consisting of only one superconducting domain surrounded by a normal domain. This normal domain invades the sphere gradually as the external field increases. The simulations also predict a rich multi-domain structure in larger Sn spheres, a prediction that has yet to be experimentally confirmed.

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