Fluctuation Diamagnetism in a "Zero-Dimensional" Superconductor*

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The diamagnetic transition of ensembles of single-crystal aluminum particles with radii less than the superconducting coherence length \(\xi\) has been measured over a wide range of temperature, field, and average radius. The particles are sufficiently small that the Ginzburg critical region is experimentally accessible. Fluctuation effects are observed inside and outside this critical region. The data agree with recent exact theoretical calculations based on the Ginzburg-Landau functional.

The effect of thermodynamic fluctuations on a zero-dimensional superconductor, i.e., one with all of its dimensions less than the superconducting coherence length, has been the object of recent theoretical interest\(^1,2\) because the Ginzburg critical region, within which the mean field theory cannot be expected to be valid, was expected\(^3\) to become accessible to experiment in sufficiently small particles. This case permits a detailed investigation for the first time of the true critical region in a superconductor to determine whether the analytical form of the Ginzburg-Landau (GL) free energy breaks down completely, or whether this free energy can be used as an energy functional in a canonical average over all accessible values of the order parameter. Fortunately, there also exists an exact fluctuation theory\(^4,5\) based on the GL functional which is expected to be valid both outside and inside this critical region. Since spatial variations of the order parameter are energetically too costly to be thermally activated, only spatially uniform fluctuations need be considered, and the quartic term in the free-energy functional can be included exactly in fluctuation calculations. In systems of higher dimensionality this quartic term is either approximated or neglected. Thus most fluctuation calculations tend to fail as the critical region is approached. The feature of the zero-dimensional superconductor that greatly facilitates measurements is the suppression of the magnitude of the mean-field diamagnetism below \(T_c\) as particle size decreases. Hence, fluctuation effects, though small in absolute magnitude, can be readily observed at and below \(T_c\) as well as above.

We report here the results of an extensive set of measurements that we have made both inside and outside the critical region on the superconducting diamagnetic transition of ensembles of small electrically isolated nearly perfect single-crystal Al particles. The average radius of these mostly spherical particles varied from over 4000 Å to less than 125 Å and readily satisfied the zero-dimensional criterion. The measurements were carried out in magnetic fields varying from less than 0.01 Oe to more than 1500 Oe and over a temperature range extending from less than 0.5\(T_c\) to more than 3\(T_c\). This large variation in experimental parameters allowed clear identification of the various features of the transitions and permitted close comparisons to be made with theoretical calculations.

Shmidt\(^1\) and others\(^2,5,6\) have calculated the susceptibility of zero-dimensional particles in the temperature region around \(T_c\) by assuming the validity of the GL free-energy functional and evaluating the integral

\[\langle |\psi|^2\rangle = \int \psi^2 \exp(-F_{GL}/k_B T) d^3 r,\]

where

\[F_{GL} = \int (\alpha |\psi|^2 + \frac{\lambda}{2} |\psi|^4 + \hbar^2 |\nabla \psi|^2 / 2m) d^3 r\]
and $\psi$ is the GL order parameter. Exact evaluation of the complete integral in zero dimensions yields an expression for the susceptibility $\chi$ which, assuming the electron mean free path is limited by surface scattering, can be written as

$$\chi = R^2 \chi' \epsilon_0 \epsilon f(\epsilon/\epsilon_c)$$  \hspace{1cm} (1a)$$
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or

$$\chi = \frac{g}{20 \pi \lambda L^2(0) \xi_0} \epsilon_0 \epsilon f(\epsilon/\epsilon_c).$$  \hspace{1cm} (1b)$$

Here $\lambda L(0)$ is the London penetration depth, $\xi_0$ the BCS coherence length, $\epsilon = \ln(T/T_c) = \Delta T/T_c$, $R$ the particle radius, and $\epsilon$ a factor of order 1, the exact value of which depends on the relative amounts of diffuse and specular surface scattering. If $f(x) = 1/\sqrt{x} \text{erfc}x - 1$, where erfc is the complimentary error function. The essential parameter $\epsilon_c$ is given by

$$\epsilon_c^2 = 6k_b T_c/R^3 \frac{\partial H_{\text{eff}}}{\partial T} |_{\epsilon_c}^2,$$

$H_{\text{eff}}$ being the thermodynamic bulk critical field. $\epsilon_c$ determines the temperature scale which divides the susceptibility behavior into three different regimes. For $\epsilon < -\epsilon_c$, $\chi$ is expected to approach rapidly the form

$$\chi = 1.33gR^2 \epsilon/20 \pi \lambda L^2(0) \xi_0$$

which is just the mean-field result in the temperature region not too far below $T_c$. For $\epsilon > \epsilon_c$, $\chi$ more slowly approaches the value

$$\chi = -3g(1.33)(0.74^2) \xi_0 k_b T/5q_0^2 \epsilon,$$  \hspace{1cm} (2)

where use has been made of the GL relation

$$T_c \frac{\partial H}{\partial T} |_{T_c} = 0.96 q_0/\sqrt{2} \pi \xi_0 \lambda L(0).$$

This temperature region can be considered the mean-field fluctuation regime since the fluctuation amplitude of $\psi$ is small and the quartic term can be neglected. For $-\epsilon_c < \epsilon < \epsilon_c$ defines the critical region. Here $\chi$ varies only slowly with temperature. At $\epsilon = 0$,

$$\chi = 1.33gR^2(12k_b T_c)^{1/2}/33,9k_1(0)q_0,$$  \hspace{1cm} (3)

The susceptibility is independent of $R$ for $\epsilon >> \epsilon_c$, varies as $R^{1/2}$ for $\epsilon = 0$, and varies as $R^{3}$ for $\epsilon << -\epsilon_c$. Thus although the absolute magnitude of $\chi$ at $T_c$ is expected to decrease with decreasing $R$, the predicted effect of decreasing size is to increase $\chi(T_c)$ relative to $\chi(0)$.

The Al particles were produced by evaporating 99.9999% Al in an inert-gas atmosphere. The pressure and atomic mass of the gas and the evaporation rate determined the average particle size of each sample. In order to achieve electrical isolation of the particles from one another and thereby eliminate excess diamagnetism caused by supercurrents flowing between the particles, a small amount of oxygen was admitted slowly into the evaporation chamber during the production process. Only enough oxygen to form a few atomic layers of oxide on the surface of each particle was required.

The particles were examined with an electron microscope and were found to be mostly spherical single crystals with few defects. Electron diffraction studies revealed only the diffraction pattern typical of Al, indicating that only a thin layer of oxide covers each particle even though they are exposed to air after their production. The particle distributions $g(R)$ were obtained from electron micrographs for each sample. From these distributions the effective average radii for the three temperature regimes were determined:

$$R_{\epsilon_1} = (\langle R^3 \rangle / \langle R^2 \rangle)^{1/3}, \quad \epsilon = -\epsilon_c;$$

$$R_{\epsilon_2} = (\langle R^3 \rangle / \langle R^2 \rangle)^{1/3}, \quad \epsilon = 0;$$

$$R_{\epsilon_3} = (\langle R^3 \rangle)^{1/3}, \quad \epsilon > \epsilon_c.$$  

The powder samples, each of which consisted of about 0.05 g of material packed to a density of approximately $\frac{1}{4}$ the bulk density, were cooled with a $^3$He cryostat. The sample magnetization was measured as a function of temperature in a variety of magnetic fields with a calibrated superconducting point-contact quantum magnetometer system. Experimental details will be given elsewhere.

Considering first the mean-field region well below $T_c$, the reduced susceptibility $\chi(T)/\chi(0)$ was found here to be the same for all those samples which had $R_{\epsilon_1}^{1/2} > \lambda_L(0)\xi_0^{1/2}$. The temperature dependence of $\chi(T)/\chi(0)$ was approximately as predicted by Bardeen’s mean-field calculation—the main difference being that the measured susceptibility varied as $T^0$ for temperature further below $T_c$ than expected. Since all of the samples studied satisfied the relation $R_{\epsilon_1}^{1/2} < \lambda_L(0)\xi_0^{1/2}$, sufficiently near to $T_c$, plotting $\chi$ versus $T^4$ and extrapolating linearly to 0 gave the transition temperature $T_c(R_{\epsilon_1})$ for each sample. $T_c$ was found to vary smoothly but not very rapidly with particle size—being 1.156 K for $R_{\epsilon_1} = 4000$ Å and 1.228 K for $R_{\epsilon_1} = 255$ Å. Similar low values of $T_c$ for Al particles have been reported by
Saxena, Crow, and Strongin.\textsuperscript{14}

Turning to the mean-field fluctuation region well above $T_c$, we found the amplitude of the susceptibility to vary only slightly from sample to sample. This variation, $<15\%$, is readily accounted for by experimental error and the small changes in $T_c$ with particle size. In Fig. 1 the data above $T_c$ for several samples are plotted versus $[T - T_c((R^* / R)^{3/2})]^{-1}$. The data here have been normalized to their mean value of $\chi$ for $T \gg T_c$ by factors of $1 \pm 0.07$. $\chi$ has also arbitrarily been taken to be 0 at $T = 3.5$ K. Over significant temperature ranges the samples exhibit a Curie-Weiss-type susceptibility, $\chi = C / (T - T_c)$. Upon correcting for the variation of transition temperature with particle size to a normalized $T_c = 1.175$ K, the data gave an average value for $C$ of $(-3.6 \pm 0.8) \times 10^{-7}$ K. There is no experimental consensus for the value of $\xi_0$ for Al, values differing by a factor of 3 being found in the literature.\textsuperscript{15,16} If the value for $\xi_0$ obtained by Maloney, de la Cruz, and Cardona\textsuperscript{15} from thin-film measurements is used, Eq. (2) gives a value of $2.5 \times 10^{-7}$ K for $C$, while our own mean-field susceptibility and critical-field measurements below $T_c$ give a value for $g\xi_0$ which in Eq. (2) yields the result $C = (-2.9 \pm 0.9) \times 10^{-7}$ K.

For $T > 1.5 T_c$ a departure from the predicted mean-field fluctuation behavior, $\chi = C / (T - T_c)$, is observed with the fluctuation diamagnetism being quenched more rapidly with increasing $T$ than expected. This is not surprising since a calculation based on the simple GL theory can only be expected to be valid fairly near to $T_c$. A more complete theory is needed to give an adequate description of the high-temperature effects.

FIG. 1. Susceptibility of six aluminum-powder samples above $T_c$ as a function of $[T - T_c((R^* / R)^{3/2})]^{-1}$.\textsuperscript{10}

Within the critical region the susceptibility data were compared with the fluctuation theory by computing the predicted susceptibility within the critical region using the formula

$$\chi = \chi^* \int R^2 g(R) \epsilon_R f(\epsilon / \epsilon_c) dR / \int R^2 g(R) dR.$$  

By determining $\chi^*$ and $\epsilon_c$ from the low- ($\epsilon \ll \epsilon_c$) and high-temperature ($\epsilon \gg \epsilon_c$) measurements and then computing the integral using the measured particle distribution, an excellent description of $\chi$ within the critical region is obtained. This is illustrated in Fig. 2 which summarizes all of the low-field behavior of the susceptibility of the powders near $T_c$. Sample 1 has a small critical width, $1.5 \times 10^{-5}$, and follows a $1 / \Delta T$ dependence very close to $T_c$. Sample 7 has the same value of $\chi$ well above $T_c$, but it drops below that of sample 1 as the transition temperature is approached. Below $T_c$ the susceptibility is small enough that the change to mean-field behavior, $\chi \propto T - T_c$, can be seen. The critical width of sample 8 ($\epsilon_c = 0.055$) is so large that it covers almost the entire temperature range shown. Only well above $T_c$ does this susceptibility approach that of the other samples.

Equation (1) is only valid for zero or low magnetic fields, but it can readily be extended to higher fields by replacing $\epsilon$ by $\epsilon + H^2 / H_c^2$, where $H_c(R) = (20 \xi_0 / g R)^{1/2} H_c(0)$ is the second-order critical field of a particle of radius $R$. At $T = T_c$ this results in the high-field susceptibility being given by

$$\chi = (1.33) 3 k_B T_c / \pi (1.73)^2 (R^*)^2 H^2.$$
The only material parameter is $T_c$. Figure 3 verifies that $\chi$ does vary as $H^{-2}$ in the high-field limit, at least for those samples that had $H_c$ small enough to make this limit accessible. Normalizing to $T_c = 1.175$ K, the average high-field value of $\chi$ at $T = T_c (R^2)^{1/3}$ was found to be $\chi = (-6.6 \pm 1.3) \times 10^{-17} / (R^2) H^2$ cm$^3$ Oe$^2$. The predicted value is $\chi = -6.9 \times 10^{-17} / (R^2) H^2$ cm$^3$ Oe$^2$. The variation in the onset of the high-field behavior with temperature has also been found to be in accord with the fluctuation-theory predictions.

We conclude that the pronounced effects of fluctuations on the superconducting transition of zero-dimensional particles, in particular the size, temperature, and field dependence of the measured susceptibility near $T_c$, are all in quantitative accord with the theoretical predictions. The results indicate that the use of the GL free-energy functional in a thermal average over all possible values of the order parameter gives an excellent description of the zero-dimensional superconductor both inside and outside the critical region.

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