COMMENTS AND ADDENDA

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Comment on "Thermodynamic Properties of Small Superconducting Grains"

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The effect of order-parameter fluctuations on the thermodynamics of a "zero-dimensional" superconducting particle (diameter $L \ll \xi(T)$, where $\xi(T)$ is the temperature-dependent coherence length) was recently studied in Refs. 1 and 2. In both of the above-mentioned papers, the partition function Q was calculated in the generalized Landau-Ginzburg (GLG) formulation, in which one has,[3] for the zero-dimensional case,

$$Q = \int e^{-\beta F(\psi)} d^2\psi , \qquad (1)$$

where $\beta = 1/k_B T_c$ and $F(\psi)$ is the Ginzburg-Landau (GL) free energy,

$$F(\psi) = a\,|\psi|^2 + \tfrac{1}{2}b\,|\psi|^4 + \tfrac{1}{3}c\,|\psi|^6 + \cdots . \qquad (2)$$

In Ref. 1, the results of the GLG calculation with coefficients given, as usual, by

$$a = \bar{a}\epsilon , \quad b = \text{const.} , \quad c = 0 \quad [\epsilon \equiv (T - T_c)/T_c] \qquad (3)$$

were compared with the results of a static approximation based on microscopic theory. For the latter treatment the effects of the discreteness of the electronic levels, due to the finite grain size, were also approximately taken into account, using an equal-level-spacing model. The results obtained in this way below T_c and outside of the critical region are different from that of the GLG theory, even for grain sizes such that the level splitting at the Fermi energy δ_F is much smaller than $k_B T_c$ (see Fig. 6 of Ref. 1). It is claimed that "away from T_c, the GLG result fails to adequately describe the quasiparticle contribution while the equal-level result approaches the bulk behavior as expected." This conclusion contradicts the result of a detailed discussion in Ref. 2 on the range of validity of the GLG theory.

In this paper we wish to point out a minor inconsistency in the derivation of the specific heat $C(T)$ in Ref. 1 and, more importantly, to show that the results obtained with the GL and GLG theories with coefficients given by Eq. (3) should not have been expected to agree with the microscopic calculation. In fact, a more careful GL-type expansion is sufficient to achieve such an agreement.

It is well known that under the usual assumptions of Eq. (3) the GL theory gives the correct specific-heat jump at T_c. However, to obtain $C(T)$ in any finite temperature range below T_c, one has to take into account $O(\epsilon^2)$ terms in $a(T)$, $O(\epsilon)$ terms in $b(T)$, and the magnitude of c at T_c. From the microscopic theory of Ref. 1, one finds

$$a = \alpha T^2 \ln(T/T_c), \quad \tfrac{1}{2}b = \alpha T^2 \tfrac{7}{16}\zeta(3), \quad \tfrac{1}{3}c = -\alpha T^2 \tfrac{31}{128}\zeta(5) , \qquad (4)$$

where α is a constant. One then obtains

$$\left(\frac{dC(T)}{dT}\right)_{T=T_c^-} = 2.63\,\frac{\Delta C}{T_c} , \qquad (5)$$

where ΔC is the specific-heat jump at T_c. This result is in agreement with the microscopic theory.[4] However, under the assumptions of Ref. 1 [Eq. (3) above], one gets

$$\left(\frac{dC(T)}{dT}\right)_{T=T_c^-} = \frac{\Delta C}{T_c} . \qquad (6)$$

When fluctuations are taken into account, the GL jump is spread[2] over a reduced-temperature region

$$\epsilon_c^2 = k_B T_c / (\overline{a}^2/2b) L^3 \quad (\text{we assume } \epsilon_c \ll 1), \tag{7}$$

i.e., for $|\epsilon| \gg \epsilon_c$ the GL result is recovered. For $\epsilon \ll -\epsilon_c$, this result is given by Eq. (5) or Eq. (6), depending on the assumptions made on the coefficients a, b, and c. The result obtained in Ref. 1 for $\epsilon < -\epsilon_c$ [Eq. (2.13) therein] is

$$C(T) = \Delta C \mid 1 + 4\epsilon + (\epsilon/\epsilon_c \sqrt{\pi})\, e^{-\epsilon^2/\epsilon_c^2} \mid \tag{8}$$

giving a slope larger by a factor of 4 than in the appropriate Eq. (6) or Eq. (11b) of Ref. 2. This is due to the approximation $T/T_c = 1$ made in Ref. 1. This approximation is good enough to give the specific-heat jump but not the specific-heat slope near T_c. The correct expression for $C(T)$ in the model of Eq. (3) was given in Ref. 2.

To summarize, in Ref. 1 it was found that the GLG expression, which led to the above Eq. (8), did not agree with their microscopic calculation, which also included the discreteness effect. However, for $\epsilon_c \ll 1$ this discrepancy is simply due to inconsistent approximations made in the GLG treatment of the microscopic theory and not to any small-size quasiparticle effects. For $\epsilon_c \lesssim 1$ the discreteness effect might have a significant impact on the thermodynamic properties, and the methods of Ref. 1 may be adequate to compute them. However, to appreciate the significance of this effect more closely, the results should be compared with the appropriate GLG treatment.

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Effect of Chemisorbed Water on the Magnetic Quenching of Orthopositronium in Silicon Dioxide Powders*

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Positron-annihilation angular-correlation measurements have been made on compressed pellets of powdered SiO_2. The results show an anomolously strong magnetic quenching of orthopositronium which disappears with the removal of chemisorbed water.

The formation in finely divided silicon dioxide powders of substantial amounts of positronium[1] with lifetimes approaching that of free positronium[2] have been previously reported. We report here the effect of the presence of surface water on the magnetic quenching of positronium in these powders.

The angular-correlation-measurement apparatus has been previously described.[3] The detector slits subtended an angle of 0.6 mrad. The total number of coincidence counts per point recorded at the maximum ranged from a low of 6000 for $H = 0$ kG up to more than 10 000 for $H = 12$ kG.

The sample was placed in a stainless-steel container and inserted between the poles of an electromagnet which provided a magnetic field perpendicular to the plane of the detectors. Special care was taken to ensure that no positrons could annihilate in the walls of the sample chamber regardless of the magnetic field. Contributions from the empty sample chamber were found to be nil. Two nearly identical samples were prepared by compressing silicon dioxide powder[4] with a mean particle diameter of 50 Å into cylindrical pellets $\frac{1}{2}$ in. in diameter and 0.07 in. thick. These pellets were produced with a pressure of approximately 4 tons/in.^{2} and the resultant density of both pellets was 0.6 g/cm^3.

The experimental arrangement is shown in Fig. 1. Not shown in the figure are adjacent lead slits