values of n, m^*, and v_F appropriate to aluminum,[8] we find an equivalent bulk mfp of 250 Å and $D = 23.6$ cm^2 sec^{-1}. The remarkably good agreement with the measured value (5%) is almost certainly fortuitous, as neither τ_γ nor the film thickness are known to this accuracy.

The quasiparticle recombination process involves the emission of phonons of energy $\geq 2\Delta_{Al}$. Rothwarf and Taylor[9] have pointed out that these phonons have a high probability of creating new quasiparticle pairs before either leaving the film or being annihilated in other processes, thus leading to an apparent enchancement of τ_γ. We have extended their calculations to include diffusion effects. We find that the phonons do not contribute directly to the diffusion process because of their low velocity and short lifetime against pair creation. However, the recombination time which enters into the diffusion length δ is also enhanced, so that the appropriate value of τ_γ is in fact the measured value, without further correction for phonon effects.

We would like to thank Dr. P. J. Price, Dr. A. G. Redfield, and Professor S. H. Koenig for helpful discussions.

*Physics Department, Columbia University, New York, N. Y.

[1]I. Giaever and K. Megerle, Phys. Rev. 122, 1101 (1961).

[2]J. R. Schrieffer and D. M. Ginsberg, Phys. Rev. Letters 8, 207 (1962); A. Rothwarf and M. Cohen, Phys. Rev. 130, 1401 (1963).

[3]J. L. Levine and S. Y. Hsieh, Phys. Rev. Letters 20, 994 (1968).

[4]B. I. Miller and A. H. Dayem, Phys. Rev. Letters 18, 1000 (1967).

[5]J. Bardeen, G. Rickayzen, and L. Tewordt, Phys. Rev. 113, 982 (1959).

[6]L. S. Palatinik, M. Ya. Fuks, B. T. Boyko, and P. A. Panchekha, Fiz. Metal. i Metalloved. 21, 848 (1966) [translation: Phys. Metals Metallog. (U.S.S.R.) 21, 4 (1968)].

[7]K. Fuchs, Proc. Cambridge Phil. Soc. 34, 100 (1938); A. M. Toxen, M. J. Burns, and D. J. Quinn, Phys. Rev. 138, A1145 (1965).

[8]J. Bardeen and J. R. Schrieffer, in Progress in Low Temperature Physics, edited by C. J. Gorter (North-Holland Publishing Company, Amsterdam, The Netherlands, 1961), Vol. III, p. 170.

[9]A. Rothwarf and B. N. Taylor, Phys. Rev. Letters 19, 27 (1967).

SUPERCONDUCTIVITY OF SMALL TIN PARTICLES MEASURED BY TUNNELING

I. Giaever and H. R. Zeller
General Electric Research and Development Center, Schenectady, New York
(Received 9 May 1968)

We have used tunneling to study the superconductivity of small Sn particles imbedded in an oxide film. In contradiction to existing theories, no lower size limit for superconductivity has been found down to a particle radius $r = 25$ Å. The junction characteristic shows a large peak in resistance at zero bias even for normal particles. This resistance maximum can be explained in terms of a capacitor model of the particle.

We have studied the superconductivity of small tin particles imbedded in an oxide film. Superconductivity of small particles has been investigated previously by magnetic-susceptibility[1] and Knight-shift measurements.[2] In our experiment we have studied the current flow through small particles of tin in the temperature range of 1.6-300°K and magnetic fields from 0 to 35 kOe. Contact was made with the particles by tunneling through an oxide layer; thus we do not expect the electronic properties to be severely distorted.

It was recently predicted by Markowitz[3] that, in conflict with existing experimental evidence, isolated small particles with radius below about 100 Å cannot be superconducting, and that particles with radius in the range between 100 and 500 Å should show significant deviations from the bulk superconductive properties. The reason is that the coherency of the electrons in the superconducting state implies large charge fluctuations. Since a superconductor cannot have both maximum correlation energy and uniform charge density (i.e., minimum Coulomb repulsion energy), it optimizes the two. For small particles the Coulomb repulsion energy should become comparable with, or larger than, the gap energy, thus leading to occupied singlet states in the superconducting ground state or even to destruction of superconductivity. Earlier, Anderson[4] had estimated that when the energy-level spacing in a small particle is of the same order as the energy gap, the particle would not become superconducting. We have been able

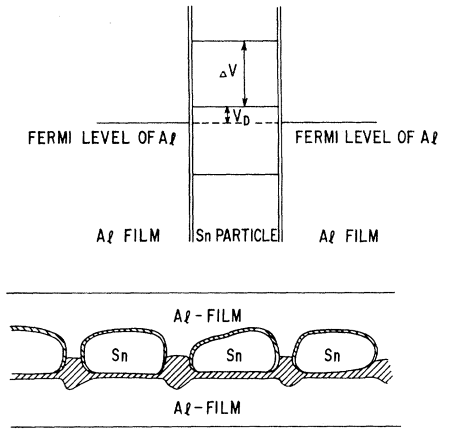

FIG. 1. Model and level scheme of Sn particles in a tunnel junction. V_D is the energy in eV of the last filled state at $T=0$ of the Sn particle, with respect to the Fermi energy of Al. $\Delta V=e/C$ is the voltage change of the particle caused by addition of one electron. In equilibrium $-e/2C \geq V_D \geq e/2C$ holds.

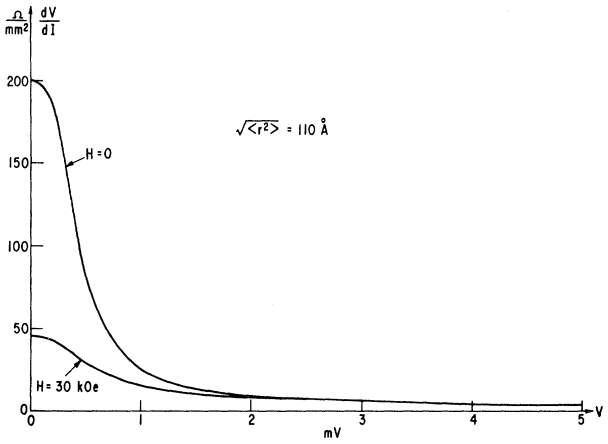

FIG. 2. Dynamical resistance-versus-voltage characteristics for normal and superconducting particles at $T=1.6$°K. For particles with $r=110$ Å, H_c is 13 kOe so that all particles are normal at $H=30$ kOe.

to show that Sn particles down to 25-Å radius are still superconducting. This is at least in the range considered by Anderson and is well below that estimated by Markowitz.

The samples have been prepared by evaporating Sn onto a slightly oxidized aluminum film. The Sn agglomerates into small islands with an average size that depends mainly upon the amount of Sn evaporated. The sample is then further oxidized until a rather thick aluminum-oxide layer grows between the Sn particles; and at the same time a thin tin oxide is formed on the particles. Finally, an aluminum layer is evaporated for the top electrode (Fig. 1). Because the space between the particles is essentially filled with a thick aluminum oxide, the tunnel current between the two aluminum layers flows mainly through the particles. Electron-micrograph pictures enable us to determine the distribution of particle size fairly accurately.

The normal-superconducting transition of the particles manifests itself in a change in the resistance-versus-voltage characteristic (Fig. 2). The critical field, H_c, can be determined from the magnetic-field dependence of the resistance change, and from the temperature dependence we get the critical temperature, T_c.

The critical field at 1.6°K has been measured for particles ranging in radius from 50 to 1000 Å as determined from electron micrographs, and it can be described approximately by the relation

$$H_c = (1550 \text{ kOe Å})/r.$$

A similar relationship, $H_c \sim 1/r$, has been found previously for thin superconducting filaments.[5] The maximum field attainable in our experiments is 35 kOe. While we are unable to determine the critical field of particles with $r \lesssim 50$ Å, the resistance of our samples is appreciably affected even when the maximum size of the particle radius is 25 Å. Thus we conclude that Sn particles are superconducting at least down to a radius of 25 Å. The present size limitation is due to the experimental equipment, and we have no evidence that this is a lower limit for superconductivity. It should be noted that the transition temperature increases with decreasing particle size, reaching ~4.2°K for particles with a radius of about 70 Å. While we can think of several esoteric reasons for this, we have no way of ruling out a simple strain effect.

In contrast to tunneling into bulk samples, the dynamical resistance-versus-voltage characteristic shows a large peak at zero bias even when the particles are normal. Figure 3 shows the temperature dependence of the resistance-versus-voltage characteristic for a sample with an average particle radius of 70 Å. A sufficiently high magnetic field has been applied so that the particles are in the normal state. The height of the peak increases and the width decreases with decreasing temperature, and the zero-bias resistance can exceed the resistance at 100 mV bias by two orders of magnitude. The qualitative behavior is similar to that of a Cr-I-Ag junction discussed by Rowell and Shen,[6] and we think that

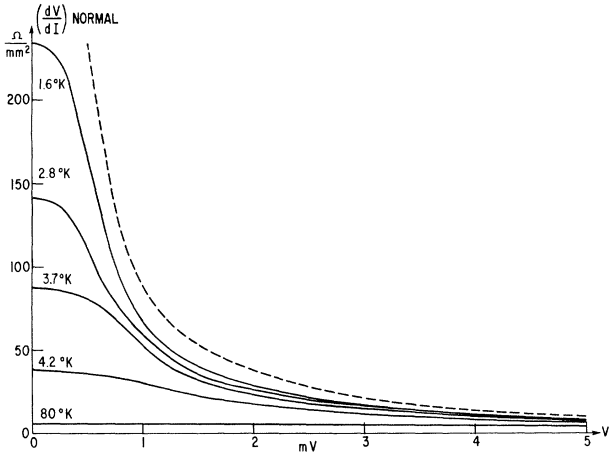

FIG. 3. Dynamical resistance-versus-voltage characteristic for normal particles of an average radius of 70 Å at different temperatures. The dashed curve is calculated from Eq. (2) for $T=0$. $f(C)$ in Eq. (2) has been computed from the electron micrographs assuming a 15-Å-thick oxide with $\epsilon=10$ and disklike particles. The particles are kept normal by a large magnetic field. That most of the particles are indeed in the normal state even at the lowest temperature can be verified by examing the change in the resistance as a function of the applied field.

at least some of the reported anomalies in tunneling experiments are caused by inclusion of small metal particles in the insulating barrier.[7,8]

The qualitative behavior of the junction can be discussed in terms of the following model (Fig. 1). The Sn particle is considered as the inner sphere of a spherical capacitor with capacitance C. Since charge is quantized, to put only one electron onto the Sn particle charges it by a voltage

$$\Delta V = e/C.$$

For a spherical particle with radius $r=50$ Å surrounded by a 15-Å-thick oxide layer with a dielectric constant $\epsilon=10$, the voltage is $\Delta V \sim 7$ mV. This model gives an upper limit for C. Under the above conditions, but with disklike particles, $\Delta V = 12$ mV results.

The electron has three different possibilities to go from one side of the junction to the other:

(1) Direct tunneling through the oxide between Sn particles. This process is unaffected by the Sn becoming superconducting and can be made small because of the relative thickness of the oxide layers, so that it normally results in a small, constant, background conductivity.

(2) Tunneling onto the particle and localizing the electron there. This process needs an activation energy E and is, therefore, forbidden for $kT, eV \ll E$. However, it is the important mechanism for the current flow at $eV>E$, or $kT>E$, and is sufficient to explain our results.

(3) Direct tunneling through the metal particle without localizing the electron on the particle. This process may contribute to the zero-bias conductivity at low temperatures, but is not needed to explain the present experimental results.

It is important to distinguish between the voltage and the energy required to put an electron onto the Sn particle; the energy of a charged capacitor, of course, is proportional to the square of the voltage. We shall assume an ideal configuration with an equal capacitance between the Sn particle and each of the two Al films. In equilibrium there would normally be a small voltage difference V_D between the Fermi level of the films and the last filled level in the Sn particle. For macroscopic particles V_D is zero. Because of the charge quantization V_D is not normally zero for small particles, and in equilibrium we expect

$$-e/2C < V_D < e/2C.$$

We shall assume V_D to be uniformly distributed in this interval. Considering process (2) alone, the minimum activation energy required to localize an additional electron onto an Sn particle in the normal state is the difference between the energies of the initial and final states, i.e.,

$$E = \tfrac{1}{2}[e/C + V_D]^2 C - \tfrac{1}{2} V_D{}^2 C. \qquad (1)$$

The minimum voltage to add (V_A) or subtract (V_S) an electron from the particle is therefore

$$V_A = [e/C + 2V_D],$$

$$V_S = [e/C - 2V_D].$$

We shall assume that the tunneling probability of an electron onto or out of a particle is constant, i.e., independent of voltage. To obtain the conductivity we must also average over the distribution of particle capacitances; this distribution is obtainable from the electron micrographs, assuming $C \sim r^2$. In general, the dynamical conductivity can be written

$$\sigma \sim \int_0^\infty dC\, C f(C) \int_{-e/2C}^{e/2C} dV_D\, C[\theta(V-(e/C-2V_D)) + \theta(V-(e/C+2V_D))], \qquad (2)$$

where θ is a unit step function and $f(C)$ the distribution of particle capacitances. The conductance through a particle is proportional to the area of the particle which in turn is proportional to the capacitance. The other C factor in the second integral stems from our choice of a uniformly distributed V_D.

It is easy to adapt this model to account for the effect of the superconducting transition of the Sn particles. The main effects are to increase the activation energy by half the superconducting energy gap in the particle and to change the density of states. Calculations of the dynamical resistance-versus-voltage characteristic using Eq. (2) gives good agreement with the experiment. In Fig. 3 the dashed curve is calculated for $T=0$ and with $f(C)$ computed from the electron micrograph assuming disklike particles with a 15-Å-thick oxide layer on both sides and a dielectric constant of 10.

We wish to thank E. F. Koch for carrying out the electron microscopy.

[1]D. Shoenberg, Proc. Roy. Soc. (London), Ser. A 175, 49 (1940).
[2]F. Wright, Phys. Rev. 163, 420 (1967).
[3]D. Markowitz, Physics 3, 199 (1967).
[4]P. W. Anderson, J. Phys. Chem. Solids 11, 26 (1959).
[5]J. H. P. Watson, Phys. Rev. 148, 223 (1966).
[6]L. Y. L. Shen and J. M. Rowell, Phys. Rev. 165, 566 (1968).
[7]F. Mezei, Phys. Letters 25A, 534 (1967).
[8]A. F. G. Wyatt and D. J. Lythall, Phys. Letters 25A, 541 (1967).

CRITICAL PROPERTIES OF THE XY MODEL*

D. D. Betts and M. H. Lee
Theoretical Physics Institute, University of Alberta, Edmonton, Alberta, Canada
(Received 9 May 1968)

The XY model of a quantum lattice fluid or a ferromagnet is studied by the method of exact high-temperature series expansion. Nine terms are obtained in the free-energy series and seven in the series for the square of the fluctuation in the long-range order. Analysis of these series yields the critical values $kT_C/J=4.84\pm0.06$, $\gamma=1.00\pm0.07$, and $\alpha=-0.20\pm0.20$ for the fcc lattice.

The XY model of interacting spin-$\frac{1}{2}$ particles is characterized by the interaction Hamiltonian,

$$\mathcal{H}_0=-J\sum_{\langle ij\rangle}(a_i^{\dagger}a_j+a_ia_j^{\dagger})$$
$$\equiv-J\sum_{\langle ij\rangle}(\sigma_{ix}\sigma_{jx}+\sigma_{iy}\sigma_{jy}), \quad (1)$$

where the sum is over nearest-neighbor pairs of sites on a lattice and the σ's are Pauli matrices. Like the Ising and Heisenberg models,[1] the XY model is a special case of the anisotropic Heisenberg model.

Matsubara and Matsuda[2] introduced in 1956 a lattice model for liquid helium which reduces to the XY model for a hard-core molecular-interaction potential. In that case $J=\hbar^2d/4mqa^2$, where d is the dimensionality of the lattice, m is the molecular mass, q the coordination number, and a the nearest-neighbor distance on the lattice. Matsubara and Matsuda were able to show that, even in the molecular-field approximation, the XY model is more successful than the ideal Bose gas in several respects in predicting properties of the λ transition.

The XY model may also be realized in certain magnetic insulators in which $g_{\perp}\gg g_{\parallel}$ because of a strong crystalline field splitting the $s_z=\pm\frac{1}{2}$ Kramers doublet below the other magnetic substates of an ion such as Gd. In particular, $Gd_2(SO_4)_3\cdot 8H_2O$ seems to be such a substance.[3]

The physical significance of the anisotropic Heisenberg model, both as a lattice gas and as a ferromagnet, has been discussed recently by Fisher[4] and Whitlock and Zilsel[5] without, however, their making very extensive calculations. On the other hand, Yang and Yang[6] have obtained a number of exact results concerning the energy of the anisotropic Heisenberg model. Exact high-temperature series expansion techniques have been applied over a range of anisotropy including the case of the XY model by Obokata, Ono, and Oguchi[7] and by Pirnie,[8] but their series have not been extended sufficiently far to obtain reliable information about the critical region.

A high-temperature expansion of the zero-field partition function, Z, can be obtained starting from the expression

$$Z=\mathrm{tr}\{1-\beta\mathcal{H}_0+\beta^2\mathcal{H}_0^2/2!-\cdots\}. \quad (2)$$