Prediction of unexpected behavior of the mean inner potential of superconductors

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Off-axis electron holography can measure the mean inner electric potential of materials. The theory of hole superconductivity predicts that when a material is cooled into the superconducting state it expels electrons from its interior to the surface, giving rise to a mean inner potential that increases with sample thickness. Instead, in a normal metal and in a conventional BCS superconductor the mean inner potential is expected to be independent of sample thickness and temperature. Thus, this experiment can provide a definitive test of the validity of the theory of hole superconductivity.

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Off-axis electron holography measures the interference of a reference electron wavefront propagating in vacuum with one propagating through a material. Conceptually it is simply Young's double slit interference experiment with electron waves where one of the 'slits' contains the material to be studied. The wave passing through the material undergoes a phase shift that depends on the electrostatic and magnetostatic fields in the material. Thus, the interference pattern provides direct information on the electric and magnetic fields and potentials in the sample. The lateral spatial resolution of the technique is a few nm, and sample thicknesses up to 500nm can be studied with electron beam energies of order hundreds of keV's, yielding electric potential resolution better than 0.1V. These characteristics make it ideal for the problem of interest here.

The theory of hole superconductivity predicts that electrons are expelled from the interior of the sample to a surface layer of thickness given by the London penetration depth when a material goes superconducting, thus giving rise to an electrostatic field in the interior. This charge expulsion is a key component of the theory and intimately related to many other aspects of the theory, in particular it is at the heart of the explanation of the Meissner effect within this theory, the prediction that macroscopic spin currents exist in the ground state of superconductors, and the prediction that superconductivity is kinetic energy driven. Instead, within conventional BCS theory no such charge expulsion nor spin currents exist in superconductors, no explanation of the Meissner effect exists, and superconductivity is potential energy driven. In this paper we point out that the technique of off-axis electron holography should be able to definitely confirm or rule out the charge expulsion predicted by the theory of hole superconductivity, thus strongly supporting or ruling out the theory.

Figure 1 shows the conceptually very simple experimental setup. The superconducting slab of thickness $d$ is predicted to have excess negative charge in the regions within a distance $\lambda_L$, the London penetration depth, of the surfaces and excess positive charge in the deep interior. The maximum electric field in the interior, denoted by $E_m$, is predicted to be given by the lower critical field $H_{c1}$ (e.g. $H_{c1} = 200G$ corresponds to $E_m = 60,000V/cm$). The electric field goes to zero as one approaches the boundaries of the sample.

The phase change of the electron wave passing through a sample slab relative to the wave propagating in vacuum is given by

$$\phi(x) = C_E \int V(x, z) dz$$

with

$$C_E = \frac{2\pi|\epsilon|}{\lambda E} \frac{E + m_e c^2}{E + 2m_e c^2}$$

with $E$ the electron kinetic energy in vacuum, $\lambda = hc/\sqrt{E^2 + 2Em_e c^2}$ its wavelength and $m_e$ and $e$ its mass and charge respectively. $z$ is the propagation direction perpendicular to the slab and $x$ is the horizontal direction. In a normal metal the electrostatic potential $V(x, z)$

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**FIG. 1**: Schematic depiction of off-axis electron holography experiment. The object wave traversing the superconducting sample will advance its phase due to the presence of an additional positive potential in the superconductor.
for samples of various thicknesses $d$ of the sample. The electric field points in the $+z$ direction. 

is expected to be approximately constant and Eq. (1) is simply, assuming uniform thickness $d$

$$\phi = C_E \bar{V}_0 d$$

with $\bar{V}_0$ termed the “mean inner potential” \cite{9,11} which is a characteristic of the material, typically between 5 and 30 Volts (positive). Thus, for the superconductor in the normal state the phase shift Eq. (3) is directly proportional to the thickness of the sample $d$. The expected linear dependence of the phase shift on sample thickness in electron holography experiments with non-superconductors has been verified experimentally for a variety of materials \cite{10}.

According to the theory of hole superconductivity the charge density in the interior of superconductors satisfies the differential equation \cite{12}

$$\rho(\vec{r}) = \rho_0 + \lambda_L^2 \nabla^2 \rho(\vec{r})$$

with $\rho_0$ a positive constant denoting a positive charge density deep in the interior of the superconductor. Eq. (4) and the condition of overall charge neutrality predict that there is excess negative charge within a London penetration depth of the surfaces of the sample. The resulting electrostatic field $\vec{E}(\vec{r})$ satisfies the equation

$$\vec{E}(\vec{r}) = \vec{E}_0(\vec{r}) + \lambda_L^2 \nabla \bar{E}(\vec{r})$$

with $\vec{E}_0(\vec{r})$ the electrostatic field resulting from a uniform charge density $\rho_0$ throughout the superconductor. Deep in the interior $\vec{E}(\vec{r}) = \vec{E}_0(\vec{r})$. The value of $\rho_0$ is determined by the condition that the electric field approaches a maximum value $E_m$ near the surface of a sample of dimensions much larger than $\lambda_L$, with $\lambda_L$

$$E_m = -\frac{\hbar c}{4e\lambda_L}$$

i.e. essentially the lower magnetic critical field $H_d$ \cite{13}.

In an infinite slab of thickness $d$ with normal in the $z$ direction and centered at $z = 0$ the electric field points in the $\pm z$ direction and is given by

$$E(z) = \frac{2E_m z}{d} \left(1 - \frac{d}{2z} \sinh \left(\frac{z}{\lambda_L}\right)\right).$$

Figure 2 shows the electric field as function of $z$ for samples of increasing thickness for fixed $\lambda_L$. Note that even for $d/\lambda_L = 50$ the maximum electric field is only about 0.8 of its limiting value $E_m$.

The electric potential in the slab arising from charge expulsion is given by

$$V_{cc}(z) = \frac{E_m d}{4} \left(1 - \frac{4z^2}{d^2}\right) + \frac{E_m \lambda_L}{\sinh \left(\frac{d}{2\lambda_L}\right)} \left[cosh \left(\frac{z}{\lambda_L}\right) - cosh \left(\frac{d}{2\lambda_L}\right)\right]$$

and its contribution the mean inner potential, defined by

$$\bar{V}_{cc} = \frac{2}{d} \int_0^{d/2} V_{cc}(z) dz$$

is given by

$$\bar{V}_{cc} = \frac{E_m d}{6} + 2 E_m \left(\frac{\lambda_L^2}{d^2}\right) - E_m \lambda_L \frac{cosh \left(\frac{d}{2\lambda_L}\right)}{\sinh \left(\frac{d}{2\lambda_L}\right)}$$

This potential should be added to the ordinary mean inner potential $\bar{V}_0$ arising from the local electronic charge distribution in the unit cell \cite{8}, which is independent of sample thickness. For a slab of thickness $d$ the phase shift is then

$$\phi = C_E (\bar{V}_0 + \bar{V}_{cc})d$$

and in particular if $d$ is much larger than the London penetration depth the first term in Eq. (10) dominates and the phase shift is

$$\phi = C_E (\bar{V}_0 + \frac{E_m d^2}{6})$$

that is, it has a linear and a quadratic contribution in the slab thickness $d$, in contrast to the purely linear behavior expected in a normal metal.

Let us consider for definiteness a Pb sample. The London penetration depth at low temperatures is $\lambda_L = 39 \text{nm}$. There is approximately one excess electron every $10^6$ atoms near the surface, and $E_m = 0.0241 \text{V/nm}$ \cite{8}.

Figure 3 shows the electric potential arising from charge expulsion as function of $z$ from the center to the top (or bottom) of the slab for samples of varying thicknesses. The potential goes to zero at the surface of the sample and is maximum at the center. The difference between the solid and corresponding dashed lines in Fig. 3 illustrates the effect of the finite $\lambda_L$. 

FIG. 2: Electric field resulting from charge expulsion from the center of the sample ($z = 0$) to the upper edge ($z = d/2$) for samples of various thicknesses $d$, far from the lateral edges of the sample. The electric field points in the $+z$ direction.
the upper edge ($z$ for Fig. 3: Electric potential resulting from charge expulsion for $z$ ranging from the center of the sample ($z = 0$) to the upper edge ($z = d/2$) for samples of thicknesses $d = 100, 200, 300, 400, 500 nm$, far from the lateral edges of the sample, for $\lambda_L = 39 nm$ (solid lines) and $\lambda_L = 0$ (dashed lines). The electric potential goes to zero at the upper edge of the sample ($z = d/2$). The magnitude of the electric potential corresponds to the case of $Pb$ (see text).

Figure 4 shows the contribution to the mean inner potential arising from charge expulsion Eq. (10) as a function of sample thickness assuming the value of $E_m$ for $Pb$ and various values for the London penetration depth. In the limit of small $\lambda_L$ the dependence on $d$ is linear as given by the first term in Eq. (10). As $\lambda_L$ increases, the behavior becomes nonlinear and the magnitude decreases.

Such inner potentials should give rise to easily detectable phase shifts in an electron holography experiment. For example, in an experiment with $300keV$ electrons the constant $C_E$ is $0.0065(nm)^{-1}V^{-1}$ and the contribution to the mean inner potential arising from charge expulsion for a $500nm$ thick $Pb$ sample is predicted to be $1.22V$ (Fig. 4), giving rise to an additional phase shift of $3.5$ radians. The non-linear dependence of the phase shift $\phi$ on the sample thickness should provide direct evidence for the physics discussed here, and should be fittable with the formulas given here with a value of $\lambda_L$ that agrees with the value of the London penetration depth obtained independently from magnetic measurements.

The expression Eq. (10) for the inner potential arising from charge expulsion applies for electron beam paths far away from the lateral edges of the sample. Approaching a lateral edge, the internal electric field direction changes and points towards the lateral surface when the distance to the lateral surface becomes smaller than $d/2$ (roughly speaking the internal electric field arising from charge expulsion points towards the closest surface[12]). From that point on the contribution to the inner potential from this physics starts to decrease rapidly and even more so as the distance to the lateral edge becomes smaller than the London penetration depth. Thus, a mapping of the phase shift as a function of $x$ and $d$ should yield detailed information to check the theoretical predictions. Other sample geometries may also be useful, for example the wedge geometry used in Ref. [10]. The electric potential and the mean internal potential arising from charge expulsion for samples of arbitrary shape can be calculated by numerical solution of the differential equations describing the electrodynamics of the superconducting state within this theory[12].

Next we need to examine at what temperatures will these effects be observable. We can think of the superconductor at finite temperature as a mixture of superfluid and normal fluid. According to the theory of hole superconductivity superfluid is expelled to the surface, however this effect will be countered to some extent by a backflow of normal fluid to attempt to preserve charge neutrality. We can estimate the effect of temperature using a simple two-fluid description. In a BCS superconductor the normal fluid density at finite temperature is given by[13]

$$n_n(T) = 2n_s \int_\Delta^\infty dE \frac{-\partial f}{\partial E} \frac{E}{\sqrt{E^2 - \Delta^2}}$$

where $n_s$ is the superfluid density at zero temperature, $\Delta$ is the superconducting energy gap and $f(E)$ the Fermi function. This expression applies also approximately to the model of hole superconductivity[14]. At low temperatures we can approximate Eq. (12) by

$$n_n(T) = (2\pi \beta \Delta)^{1/2} e^{-\beta \Delta}$$

with $\beta = 1/k_B T$. Assuming the normal particles carry a full electron charge, the normal fluid will not be sufficient
to screen the positive charge $\rho_0$ in the interior resulting from the superfluid expulsion when the condition

$$|e| n_n(T) < \rho_0$$

(14)

is satisfied. According to the theory$^8$

$$\rho_0 = 2\rho - \frac{\lambda_L}{d}$$

(15)

with $\rho_-$ the density of negative charge near the surface, given by$^8$

$$\rho_- = \frac{r_q}{2\lambda_L} e n_s$$

(16)

with $r_q = h/(2mc) = 0.00193\,\text{Å}$. Therefore the condition Eq. (14) is

$$n_n(T) < \frac{r_q}{d} n_s$$

(17)

or, using Eq. (13)

$$(\beta \Delta)^{1/2} e^{-\beta \Delta} < \frac{r_q}{\sqrt{2\pi d}}.$$

(18)

Using $2\Delta/k_B T_c = 3.53$ with $T_c$ the critical temperature, and $d = 500\,\text{nm}$ yields

$$T < 0.10 T_c$$

(19)

as a necessary condition for the internal electric field not to be screened by the normal quasiparticles. For $Pb$ with $T_c = 7.193\,\text{K}$ this would require cooling the sample to about $0.7\,\text{K}$. For smaller values of $d$, Eq. (18) suggests that the required temperature is higher, however there are additional corrections and one finds that the required temperature is within 5% of Eq. (19) in the entire range $50\,\text{nm} < d < 500\,\text{nm}$.

In reality we believe that the condition Eq. (19) is much too stringent, because it was obtained assuming that the normal quasiparticles carry a full electron charge. In a BCS superconductor in fact quasiparticles are exactly charge neutral on average. Within the theory of hole superconductivity quasiparticles carry a positive charge on average, but it is much smaller than one electron charge$^{13}$. Thus we argue that the condition Eq. (19) can certainly be expected to be sufficient for the effects predicted here to be seen, and in fact the effects may show up already at substantially higher temperature.

As discussed earlier, a dependence of the mean inner potential on the thickness of the sample and the position $x$ of the beam with respect to the edge of the sample should not be seen in the normal state. Such effects should be seen in superconductors at sufficiently low temperatures according to our theory. For given sample thickness and position $x$ a substantial increase in phase shift will be seen when the temperature is lowered sufficiently below $T_c$ and the internal electric field resulting from charge expulsion becomes unscreened. In addition, the increase in phase shift can be reversed by application of a magnetic field in the $z$ direction larger than the critical field, that would render the system normal and undo the charge expulsion. None of these effects should be seen in a normal metal nor in a conventional BCS superconductor: in those systems the phase shift will be independent of sample thickness and position $x$, independent of temperature, and would not change under application of a magnetic field in the $z$ direction (it would with a magnetic field in the in-plane direction).

In summary: the theory of hole superconductivity predicts that superconductors expel electrons from the interior to the surface, and that as a consequence a macroscopic electric field and resulting electric potential exist in the interior of superconductors at sufficiently low temperatures. The conventional theory of superconductivity does not predict this behavior. Off-axis electron holography can test this prediction and render unambiguous experimental evidence for or against it. The experiment can be performed with any superconductor, since the theory is predicted to apply to all superconductors. Clear experimental evidence for any superconductor that electrons are not expelled from the interior to the surface in the superconducting state would falsify the theory of hole superconductivity. On the other hand, the opposite experimental result would falsify BCS theory only for that particular material, since BCS theory is not expected to apply to all superconducting materials$^{16}$.

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