We predict that superconducting particles will show an apparent increase in thickness at low temperatures when measured by electron holography. This will result not from a real thickness increase, rather from an increase in the mean inner potential sensed by the electron wave traveling through the particle, originating in expansion of the electronic wavefunction and resulting negative charge expulsion from the interior to the surface of the superconductor, giving rise to an increase in the phase shift of the electron wavefront going through the sample relative to the wavefront going through vacuum. The temperature dependence of the observed phase shifts will yield valuable new information on the physics of the superconducting state of metals.

I. INTRODUCTION

Electron holography is a sensitive tool to measure the thickness of small particles, as demonstrated experimentally already several decades ago. Initially, experiments yielded a resolution of only tens of nanometers, corresponding to phase difference of $2\pi$ between neighboring contour lines. However it was soon shown that the resolution could be improved by large factors using phase difference amplification techniques, and phase shift differences of $2\pi/100$ could be detected. Interference micrographs such as shown in Figs. 1 and 2 depict contours of constant phase shift, and for a spherical sample the contours are circles as shown in those figures. The phase difference between neighboring contours in Figs. 1 and 2 is $\pi$ (two-times phase difference amplification).

A given circle of radius $r$ in the contour map corresponds to a given phase shift $\Delta \varphi$. Imagine the thickness of the sample were to increase as the temperature is lowered. The phase shift for that value of $r$ will increase, so the radius of the circle that will give to the original phase shift $\Delta \varphi$ has to increase. In other words, the contours of given phase shift will move outward as shown in Figs. 1 and 2 by the dashed lines. In this paper we predict that this will be observed for any superconducting particle cooled sufficiently below its critical temperature. The contour shift will appear to indicate that the
sphere becomes a prolate ellipsoid of revolution with the longer axis along the beam direction. In reality, no change in the physical dimensions of the sample will have occurred. The behavior shown in Figs. 1 and 2 will signal that a change in the mean inner potential sensed by the electron beam will have occurred, originating in electronic charge redistribution inside the superconductor: namely, that negative charge has moved from the interior of the superconductor to the surface. The predicted charge distribution, electric field and electric potential inside the superconductor is shown schematically in Figure 3. For a spherical particle no electric field outside the particle is generated through this charge redistribution due to the spherical symmetry and the fact that the particle remains charge neutral.

In an electron holography experiment, the phase shift of the electron wave going through the particle at a distance \( r_0 \) from the center of the sphere, relative to a reference wave going through vacuum is given by\[1\]

\[
\varphi(r) = C_T \int_{-z_0(r_0)}^{z_0(r_0)} (V_0 + V_{ce}(r(z, r_0)))
\]

where

\[
C_T = \frac{2\pi e}{\lambda T} \frac{T + E_0}{T^2 + 2TE_0}
\]

with \( T \) the kinetic energy of the electron, \( E_0 \) the electron rest energy and \( \lambda = \hbar c/\sqrt{T^2 + 2TE_0} \) the electron wavelength. The points where the electron wave enters and exits the spherical particle for a phase contour of radius \( r_0 \) are \( \pm z_0(r_0) \), with

\[
z_0(r_0) = \sqrt{R^2 - r_0^2}
\]

with \( R \) the radius of the particle. \( V_0 \) is the ordinary mean inner potential of the solid which is expected to be constant inside the material. The additional potential \( V_{ce} \) resulting from the charge redistribution shown in Fig. 3 is not constant but depends on the radial distance \( r \) to the center of the sphere:

\[
r(z, r_0) = \sqrt{r_0^2 + z^2}.
\]

The total potential energy of the electron wave inside the material

\[
eV(z) = e(V_0 + V_{ce}(r(z, r_0)))
\]
depends on the position along the electron trajectory, as shown in Fig. 4 for several values of $r_0$. This additional potential well increases the phase shift of the high energy electron wave going through the material, giving rise to the contour shifts shown in Figs. 1 and 2. For the examples of Figs. 1 and 2 we used $T = 300\, keV$, $R = 500\, nm$.

### III. ELECTRIC POTENTIAL DUE TO CHARGE EXPULSION

The theory of hole superconductivity predicts that the charge distribution in any superconductor at sufficiently low temperatures is macroscopically inhomogeneous, with more negative charge near the surface and more positive charge in the interior, resembling a ‘giant atom’, as shown schematically in Figure 3. The charge inhomogeneity is very small: the excess negative charge resides within a London penetration depth (typically several hundreds Angstrom) of the surface and is only of order 1 extra electron per 1 million atoms.

There is no direct experimental evidence of this physics so far, nor, we argue, is it ruled out by any existing experiment. Electron holography experiments on superconductors performed in the past have not tested this scenario. Electron holography experiments on superconductors performed in the past have not tested this hypothesis, and electron holography experiments on superconductors performed in the past have not tested this hypothesis, and electron holography experiments on superconductors performed in the past have not tested this hypothesis. A compelling reason in favor of this scenario is that it provides a dynamical explanation of the Meissner effect, not provided by the conventional BCS theory: in essence, magnetic field lines are dragged outward by outward electron flow.

The charge density distribution in the interior of a spherical superconductor of radius $R$ is predicted to be

$$
\rho(r) = \rho_0\left[1 - \frac{R^3}{3\lambda_L^3} \frac{1 - \sinh(r/\lambda_L)}{r} \right]
$$

Equation (6a)

$$
f(x) = xcosh(x) - \sinh(x)
$$

Equation (6b)

$$
\rho_0 = \frac{3E_m}{4\pi R}
$$

Equation (6c)

The charge density in the interior is the same as the one given by

$$
\rho(r) = \rho_0\left[1 - \frac{R^3}{3\lambda_L^3} \frac{1 - \sinh(r/\lambda_L)}{r} \right]
$$

Equation (6a)

$$
f(x) = xcosh(x) - \sinh(x)
$$

Equation (6b)

$$
\rho_0 = \frac{3E_m}{4\pi R}
$$

Equation (6c)

The expression for potential given in the previous section are the limiting values achieved at

$\rho_0$ is the uniform positive charge density deep in the interior of the superconductor. The resulting electric field in the interior of the sphere is

$$
\vec{E}(r) = E_m R \left[1 - \frac{R^3}{3\lambda_L^3} \frac{f(r/\lambda_L)}{f(R/\lambda_L)} \right]
$$

Equation (7)

or, for $R >> \lambda_L$

$$
\vec{E}(r) = E_m \frac{R}{3\lambda_L^3} \left[1 - e^{-(R-r)/\lambda_L} \right]
$$

Equation (8)

giving the behavior shown qualitatively in Fig. 3. $E_m$ is the maximum value attained by the electric field near the surface in samples of radius much larger than $\lambda_L$, and is given by

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

Equation (9)

which is essentially the lower magnetic critical field $H_{c1}$ of a type II superconductor. The resulting electric potential is

$$
V_{ce}(r) = \frac{E_m}{2R} \left[R^2 - r^2\right]
$$

Equation (10)

$$
+ \frac{E_m R^2}{f(R/\lambda_L)} \left[1 - \frac{1}{r} \sinh\left(\frac{r}{\lambda_L}\right) - \frac{1}{R} \sinh\left(\frac{R}{\lambda_L}\right)\right].
$$

The potential is always positive in the interior of the sample, of parabolic form except near the surface where it approaches zero with vanishing slope. This positive potential enters in the expression for the phase shift Eq. (1) giving always an increase in the phase shift relative to the situation where the charge is uniform in the interior of the particle. The situation is similar to the case of a planar slab of material discussed in Ref. 13.

### IV. NON-HOMOGENEOUS SAMPLES

For a perfectly homogeneous sample the theory predicts the situation shown in Fig. 3. One may wonder whether the expected effect would be washed out in non-homogeneous samples, because of random positive and negative phase shifts cancelling out.

In fact, that is not what happens. Consider a sample that has random regions of superconducting material embedded in normal material, with the superconducting regions of spherical shape for simplicity, as shown in Fig. 5. As the high energy electron enters a superconducting region within the sample it will always speed up first, decreasing its wavelength and hence increasing its phase shift relative to the situation where the entire sample is normal, and it will slow down to its original speed when exiting the superconducting region. These increased phase shifts add up, all with the same sign, as the electron travels through a non-homogeneous sample with superconducting inclusions.

The reason that all the phase shifts are of the same sign is that the superconducting regions of the sample expel electrons. As a consequence, the electric field inside the superconducting region points towards the nearest boundary surface to a normal region and acts to accelerate the electron entering through that surface. If instead a superconducting region would have higher positive charge near its boundary and higher negative charge in the interior, the beam electron traveling through that region would indeed slow down and acquire a negative phase shift. However such a situation never happens within the theory discussed here.

### V. TEMPERATURE AND MATERIAL DEPENDENCE

The expressions for electric field and potential given in the previous section are the limiting values achieved at
Ref. [13] we estimated that at temperature zero exponentially fast as the temperature is lowered. In conducting energy gap, the density of quasiparticles goes to zero, due to the existence of a superconductor. Due to the existence of a superconductor there will also be non-superconducting electrons, i.e., excited quasiparticles, that will tend to screen the electric field produced by the charge redistribution resulting from expansion of the electronic wavefunction in the superconducting state [10], giving rise to a gradual increase in the mean inner potential as the material is cooled below $T_c$. The observation of the phase shifts behaviors as a function of temperature in high resolution electron holography experiments should play a key role in providing experimental input for further development of the theory.

This theory is expected to applied to all superconductors, both the class termed “conventional” and the classes termed “unconventional”. The properties of the particular superconducting material enter the predicted phase shifts through the values of $\lambda_L$ and $E_m$ (which is the same as $H_{c1}$). Smaller values of $\lambda_L$ make the predicted effects larger, but they are usually associated with smaller values of $T_c$, putting larger demands on the experimental setup. For the contours calculated in Figure 2, we assumed only two-times phase amplification and the parameters associated with the high temperature superconductor YBCO, namely $\lambda_L \sim 150 nm$ and $H_{c1} \sim 70 G$. With a critical temperature of $T_c = 90 K$, these effects should be observable at temperatures of order $10 K$ and possibly substantially higher. All these conditions are well within the reach of current experimental facilities.

**VI. DISCUSSION**

Electron holography provides a unique tool for the measurement of electrostatic potentials in the interior of materials, and thus is ideally suited for examination of the physics discussed here. The spherical samples discussed in this paper should make the interpretation of the observed results particularly simple because of the absence of electric fields outside the sample, but the predicted effect should also be seen for more general shapes. For non-spherical shapes, electric fields outside the sample are also predicted to be generated as a consequence of charge expulsion [15], with electric field lines going from regions of low surface curvature to regions of high surface curvature. In a subsequent step it will be interesting to use electron holography to study such samples and detect electric potential variations both inside and outside the sample to confront with the theoretical predictions.

Admittedly, the examples of phase shifts shown in Figs. 1 and 2 are for sample thicknesses somewhat larger than typically used in electron holography experiments (a few hundred nm). As the sample thickness increases one has to worry about effects such as (i) inelastic scattering processes that would increase the temperature of the sample, and (ii) generation of secondary electrons and re-

![Diagram](image-url)
sulting positive charging of the sample. On (i) we note that it can be minimized by reducing the intensity of the electron beam. On (ii) we point out that any such charging effect would presumably occur both above and below \( T_c \), so that one can still hope to discern the effect discussed here specifically due to superconductivity. We also point out that the examples shown in Figs. 1 and 2, with particle radii 500 nm, assumed only two-times phase amplification. With phase shift sensitivity of e.g. \( 2\pi/100 \) one would detect an effect for the superconducting material parameters assumed in Figs. 1 and 2 for particle radii as small as approximately 130 nm and 250 nm respectively.

With the high spatial resolution currently attainable in electron holography experiments it should be possible to measure the magnitude of the shift of a contour line as function of the radius of the contour line very accurately, and contrast it with the predictions resulting from our theory, Eqs. (1), (4), (5) and (10). It should also be of great interest to obtain spatial maps of phase shifts, potentials and charge densities for non-homogeneous samples, and in particular to study the temperature dependence of these quantities in the neighborhood of grain boundaries [16].

Another prediction of this theory that may be amenable to test by electron holography is that electrons will “spill out” from the surface of the sample as the temperature is lowered below \( T_c \) [7]. This may have an observable effect on Fresnel fringes arising from diffraction from the edge of a superconducting sample and will be explored in future work.

The apparent increase in thickness referred to in the title of this paper is of course not a real change in thickness but a virtual one, a pictorial way of describing the increase in the mean inner potential predicted to take place in superconductors at low temperatures. Alternatively, one may describe the predicted effect as an apparent increase of the atomic number of the ions in the material, \( Z \). It is interesting to note that the theory predicts the largest tendency for superconductivity for materials where conduction occurs through negatively charged ions [17], hence the effective ionic charge \( Z \) sensed by the conduction electrons in the normal state is smallest, and the excess negative charge in the conducting substructures is largest. As the sample becomes superconducting it attempts to counter these effects.

It is also interesting to note that the mean inner potential is related to the diamagnetic susceptibility of a material [18]: materials with higher mean inner potential have higher diamagnetic susceptibility [18, 20]. As a system goes superconducting its diamagnetic susceptibility of course increases dramatically, and thus it could be argued that it is not surprising that its mean inner potential should increase, as predicted here. However, conventional BCS theory of superconductivity does not predict such an effect. The relation between diamagnetic susceptibility and mean inner potential follows from the fact that both can be shown to be proportional to the mean square atomic radius of the electronic wavefunction [4, 21]. Within our theory, superconductivity is associated with expansion of the electronic wavefunction [14, 22], and thus it is natural that it is associated with an increase in the mean inner potential. This is not the case in BCS theory.

Or, put another way: as discussed in ref. [4], the mean inner potential “has two important interpretations - first, as a measure of diamagnetic susceptibility, and secondly, as a measure of the ‘size’ of an atom”. Within our theory, a superconductor is a ‘giant atom’ because of its magnetic and electric properties that include charge redistribution [7], and the connection remarked by Spence [4] qualitatively holds. In the conventional theory of superconductivity superconductors have also been described as ‘giant atoms’ by London [23] and others [24, 25] but only with respect to their magnetic properties, hence no implication for the mean inner potential results from it and the connection between mean inner potential and diamagnetic susceptibility does not exist. The fact that within our theory the connection between diamagnetic susceptibility and mean inner potential does exist strongly suggests that small positive phase shifts will onset immediately below \( T_c \), as the diamagnetic susceptibility starts to increase due to wavefunction expansion [22]. However only far below \( T_c \) should the larger phase shifts resulting from macroscopic charge redistribution discussed here appear.

Note that when the temperature of a material is lowered, its dimensions usually decrease rather than increase. A key contrary example is the behavior of superfluid \( ^4\text{He} \), which expands as the temperature is lowered below the \( \lambda \) transition. We have proposed elsewhere [26, 27] that the negative thermal expansion of \( ^4\text{He} \) in its superfluid state is intimately related to the physics discussed here for superconductors, and results from the fact that both the transitions to the superfluid \( ^4\text{He} \) state and to the superconducting state of metals are driven by lowering of kinetic energy [22, 28], or equivalently quantum pressure [29]. Still another example of this physics is the anomalously small thermal expansion observed in metallic ferromagnets [30], which can also be understood if metallic ferromagnetism is driven by lowering of kinetic energy [31].

As we have discussed for homogeneous as well as non-homogeneous samples, the predicted phase shifts for electrons traveling through superconducting regions are always positive. In other words, the beam electron’s kinetic energy increases. This fact reflects the fundamental electron-hole asymmetry on which the theory of superconductivity discussed here is based [22]: if positive rather than negative charge would sometimes be expelled from the interior of superconducting regions towards the surface, the phase shifts for beam electrons traveling through those regions would be negative. That will never happen according to our theory. It is interesting that the kinetic energy decrease of the superconducting electrons predicted by our theory [28] that is associated with the
negative charge expulsion is mirrored by the kinetic energy increase of the beam electrons traveling through the sample predicted to take place in electron holography experiments.

The physics underlying the properties of the superconducting state discussed here is expansion of the electronic wave function and associated expansion of the negative charge cloud as phase coherence is established through the superconducting regions of the sample, originating in increased outward quantum pressure. It is very remarkable that the outward motion of the constant phase contours imaged by electron holography will provide a vivid picture of this expansion physics driven by quantum pressure, since it mimics the behavior that would result if the radius of the sample was increasing, even though the physical radius of the sample is actually not increasing. It will be, in the words of A. Tonomura, a new demonstration of “the quantum world unveiled by electron waves”[33].

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