Direct investigations of the superconducting surface sheath and nonlocal electrodynamics by polarized neutron reflections

K. E. Gray, G.-P. Felcher, R. T. Kampwirth, and R. Hilleke*
Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439
(Received 9 April 1990)

Using a very direct probe of surface magnetism, i.e., polarized neutron reflections, the penetration of a magnetic field into low-κ superconductors has been shown to be inadequately quantitatively described by the local Ginzburg-Landau (GL) theory. In addition, the existence of the surface sheath of superconductivity has been clearly and directly shown by using this probe on the diamagnetic surface sheath. In this case, numerical calculations based on the local GL theory are shown to provide a useful estimate of the size of the diamagnetism.

INTRODUCTION

In spite of the expulsion of magnetic induction, B, by the Meissner effect for an applied field, H, less than the thermodynamic critical field, H_c, for type-I superconductors (or the lower critical field, H_{c1}, for type-II superconductors), it is well known that finite magnetic fields always penetrate a superconductor to some extent. The most dramatic case is that of a type-II superconductor in an applied field between H_{c1} and H_{c2}, the flux-line entry field and upper critical field, respectively. In this case, a mixed state of quantized Abrikosov vortices[1] (flux lines) exists in a triangular lattice that has been studied by small-angle neutron scattering[2] and visualized directly by a decoration technique using small magnetic particles.[3] There are two situations that are strictly surface effects and cannot be conveniently studied by the preceding techniques. These are the Meissner state, in which the field penetrates only a small distance into the superconductor at its surface,[4] and the surface sheath,[5] in which superconductivity and diamagnetism exist only at the surfaces parallel to the applied field. The latter occurs between H_{c2} and the surface nucleation field,[5] H_{c3}. These effects could only be investigated somewhat indirectly until the development of the polarized neutron reflection technique,[6] in which the depth profile of magnetic induction $B(z)$, at the surface can be probed as a function of depth, z. For example, previous studies of the Meissner effect obtained $\int B(z)dz$ through measurements of the magnetization in colloids,[7] the rf penetration depth,[8] or tunneling,[9] and the surface sheath has been indirectly inferred from the measurements of resistance[10] or bulk magnetization.[11]

The paper reports direct confirmation of the surface sheath and further evidence on the importance of nonlocal effects[12] in the flux penetration below H_{c1} in low-κ superconductors using polarized neutron reflection studies of Pb and a dilute Bi in Pb alloy. Here, $\kappa \equiv \lambda_L/\xi$ is the Ginzburg-Landau parameter,[13] where ξ is the superconducting coherence length,[12] λ_L is the London magnetic-field penetration depth,[4] and $\kappa > 1/\sqrt{2} \approx 0.707$ defines a type-II superconductor. Note that Pb is a type-I superconductor[4] for which H_{c1} equals the thermodynamic critical field, H_c. Its value of κ, in the pure limit, is[14] ≈ 0.38, which is too small to exhibit surface superconductivity. As impurities are added to Pb, λ_L increases and ξ decreases,[4] so that κ increases toward the boundary with type-II superconductivity at $1/\sqrt{2} \approx 0.707$. The surface sheath first appears for $\kappa \approx 0.418$ and, for $\kappa < 1/\sqrt{2}$, extends from the bulk critical field to a value of $H_{c3} \approx 1.69$ H_{c2}, where $H_{c2} = \kappa\sqrt{2}\ H_c$. Calculations based on the full nonlinear Ginzburg-Landau equations[15] show a maximum diamagnetic response of the surface sheath for $\kappa \approx 1/\sqrt{2}$. Although these equations are based on local electrodynamics, we expect the conclusions to be qualitatively correct and therefore have used a dilute Bi impurity in Pb to fine-tune κ to be $\approx 1/\sqrt{2}$, and thus maximize the response. The 0.8% Bi impurity level used in the experiments is chosen[14] to be just below the crossover to type II, which thus also avoids the complications of the mixed state.[4]

In general, the electrodynamic response of superconductors to applied magnetic fields is contained in $K(q)$, which is the proportionality factor, in momentum space, q, between the vector potential, $A(q)$, and the induced supercurrents.[4] In the local limit ($\xi \ll \lambda_L$ or $\kappa \gg 1$), one finds $K(q) = 1/\lambda_L^2$, independent of q, and the Ginzburg-Landau (GL) theory correctly describes the flux penetration. The GL theory predicts exponential flux penetration below H_{c1}, i.e., $B(z) = B(0)\exp-(z/\lambda_L)$, and a surface sheath for $H_{c2} < H < H_{c3}$ with a flux profile, $B(z)$, which has been numerically evaluated.[15] The nonlocal limit ($\xi \gg \lambda_L$, or $\kappa \ll 1$) is outside the scope of the GL theory, but one can use the nearly equivalent Pippard[12] or BCS (Ref. 16) expressions for $K(q)$. Calculations of $B(z)$ below H_{c1} have been reported[17] in this limit and indicate a reversal in the direction (algebraic sign) of $B(z)$ deep inside the superconductor, although the magnitude of reversed flux is much smaller than the surface field, $B(0)$. No calculations of the surface sheath in the nonlocal limit are known to the authors, perhaps because the surface sheath cannot occur in the extreme nonlocal limit, including pure Pb, and before the present research, there have been no measurements to test such a calculation in the crossover region ($\xi \approx \lambda_L$) expected for our dilute Bi in Pb alloys. Thus, for the moment, our surface sheath results can only be compared to numerical calculations using the local, GL theory.[15]

POLARIZED NEUTRON REFLECTROMETRY

The principles of polarized neutron reflectometry are discussed in more detail elsewhere.[6] A collimated beam of neutrons strikes the surface to be analyzed at a small, grazing angle, θ, and is partially reflected by that surface, as well as any other interfaces which are below the surface and separate media with different neutron-scattering potentials. The propagation of neutrons inside the material is governed by a one-dimensional Schrödinger equation, in which the momentum normal to the surface changes, due to the local potential, from its vacuum value of $k_0 = (2\pi/\lambda)\sin\theta$ into

$$k(z)\pm = \{k_0^2 - 4\pi[b/V \pm cB(z)]\}^{1/2} , \quad (1)$$

for a given depth from the surface, z, where b/V is the nuclear scattering amplitude per unit volume and the sign depends on the relative orientation of the neutron spin to the applied field. The magnitudes of the spin-dependent reflectivities, $R^{\pm}$, depend on the variation of b/V and $B(z)$ with z, and are determined from the continuity of the wave function and its derivative at the surface. In other words, the reflectivities $R^{\pm}$ are transforms of the chemical and magnetic profiles, $b/V \pm cB(z)$.

The instrument used to collect the data, described in greater detail elsewhere,[6] is located at the Argonne Pulsed Neutron Source and measures the intensities of neutrons reflected from a sample surface at a fixed angle of incidence, θ. The neutron beam is "white," and the reflectivities at various neutron wavelengths are determined by the time of flight to the detector from the pulsed source. The neutron intensity at a given arrival time is recorded by a position-sensitive detector in the reflection plane. Typical data of Fig. 1 shows the transmitted beam and the polarization-dependent reflected beams, which have a width of several detector channels, each corresponding to an incremental reflection angle of 0.014 degrees. In order to use all the information of the reflected peaks, the side channels have been corrected for the slightly different scattering geometry. The resultant reflectivities should have an angular resolution equal to a single detector channel, but it is actually degraded by the finite sample size, vibrations, and especially imperfections in the detector.

Although the reflectivity is measured as a function of λ, the physically important quantity is k_0. Evaluating k_0 requires an accurate knowledge of the incidence angle, θ, which is measured directly from the difference in position of the transmitted and reflected peaks in Fig. 1 and the sample-to-detector distance. The result is consistent with the value of θ obtained by comparing the measured spin-independent reflectivity of a Pb film with that calculated using tabulated values[18] of the nuclear scattering amplitude, b (i.e., $b/V = 3.1\times10^{-4}$ nm^{-2} for bulk Pb).

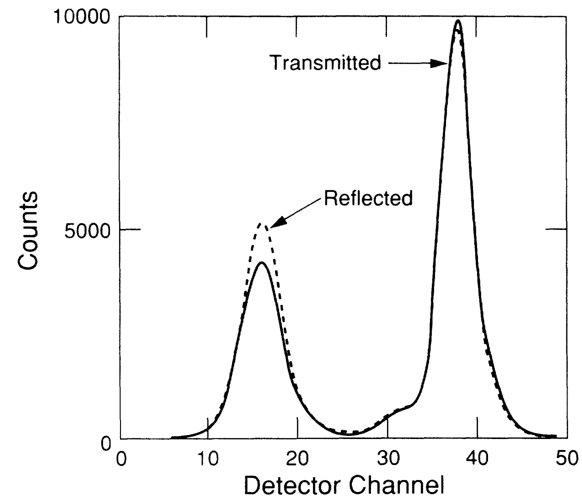

FIG. 1. Typical data collected from the position-sensitive detector showing the transmitted beam (at right) and the reflected beam (at left) for both polarizations of incident neutrons.

EXPERIMENTAL

The samples used for this research consisted of 2-μm-thick films, of either pure Pb or a dilute (0.8%) Bi in Pb alloy, vapor deposited from an electron-beam heated hearth onto a polished, polycrystalline Ti substrate with lateral dimensions of 1.5×5 cm^2. The substrate must have a neutron reflectivity which is less than the superconducting overlayers so that the reflectivity at the film/substrate interface does not overshadow the magnetic response of the film. The low neutron reflectivity of Pb rules out most substrate materials. Preliminary studies on highly polished Si single-crystal substrates yielded poor results because of considerable surface roughness (of order 7 nm) found on the deposited Pb films. Considerably smoother film surfaces were obtained, as verified by neutron reflectivity, with Ti substrates (Ti has a negative scattering amplitude, b, and thus never totally reflects the neutrons). The samples were mounted on a Cu finger which was cooled by liquid ^{4}He at 4.2 K in a cryostat containing a superconducting magnet which provided a magnetic field up to a few kOe parallel to the film surface. The sample temperature could be varied with a heater from a minimum of about 5.5 K to above the superconducting transition temperature, T_c, of about 7.2 K.

RESULTS

In principle, the effect of the chemical profile can be evaluated *a priori* since the values of b/V are known for Pb and Ti. However, the inevitable presence of oxides on each surface complicates the analysis and it is necessary to first fit the spin-independent reflectivity with an appropriate chemical profile. The data used for these fits were taken at room temperature for the pure Pb film and at about 6 K for the Pb(Bi) film, but in a field of 507 Oe so that the magnetic contribution to Eq. (1) is almost completely suppressed. As a result, the spin-averaged reflectivity should be representative of the spin-independent function. Unfortunately, the inverse transform, from reflectivity as a function of neutron momentum into chemical and/or magnetic profile as a function of z, is not easily done, and the lack of knowledge of the phase of the reflected beam raises the mathematical question of uniqueness of the solution. Therefore, one must guess the appropriate chemical and/or magnetic profile, calculate the expected reflectivities and compare with experiment. Such a comparison is shown in Fig. 2, for the Pb(Bi) film data together with calculations, both with and without oxide layers, for the film and substrate. Since the reflectivity becomes inversely proportional to k_0^4 for large momentum transfer, the comparison of the chemical profile is best visualized over the full range of momentum by multiplying the reflectivities by k_0^4. Good agreement is found for a thickness of 6 nm of titanium oxide, and a similar oxygen profile also gives the best fit for pure Pb films, showing that chemical profiles of these two samples, grown on the same batch of Ti substrates, are not too different. Although this oxygen profile is not unique in fitting these data, the difference between this and other plausible profiles (or for that matter, pure Ti) scarcely affects the spin dependence of the reflectivity due to the magnetic profile.

For measurements taken in the superconducting state, there was a significant difference in the reflectivities for the two spin directions. This is shown in the data of Fig. 3 for the Pb(Bi) film taken at 6 K in a field of 323 Oe, which is below H_{c1}. The angle of incidence, θ, was 0.319 ± 0.015 degrees, with the spread being due to a

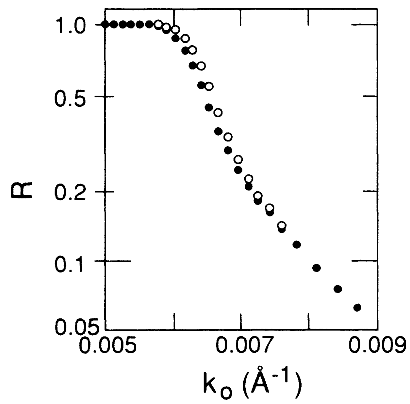

FIG. 3. Differences in the spin-dependent reflectivity for the Pb(Bi) film taken at 6 K in a field of 323 Oe, which is below H_{c1}.

combination of the divergence of the incoming beam and to the lack of flatness of the sample surface. To amplify the differences in spin, the polarization, $P\equiv(R^+-R^-)/(R^++R^-)$, for this data is shown in Fig. 4, together with data for a field of 507 Oe. The integral of P over momentum, which is plotted against magnetic field for both the Pb an Pb(Bi) samples in Fig. 5, is strikingly similar to the expected magnetization curves for these materials[4] [recalling the anticipated surface sheath for Pb(Bi), but not pure Pb, above the bulk critical field]. In fact, P is proportional to the magnetization if the field profile does not change, as is expected below the bulk critical field, but not in the surface sheath regime. However, the residual polarization above ≈ 500 Oe for Pb(Bi) is interpreted as direct evidence for the surface sheath since it involves a surface sensitive probe. Its disappearance at a field of about 1.5 times the bulk critical field is consistent with a κ value of about 0.6.

Although the data of Fig. 5 could be interpreted as belonging to a marginally type-II material with $\kappa\approx 1$, there

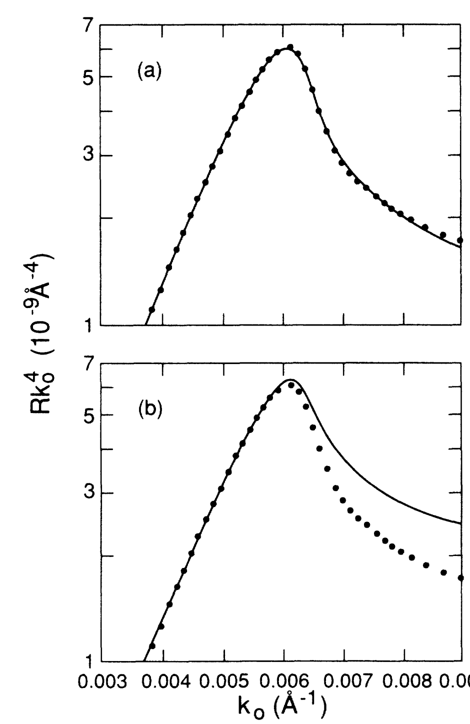

FIG. 2. Demonstration of the improved fit of the unpolarized reflection data by including a 6 nm surface oxide layer (a) compared to no layer (b).

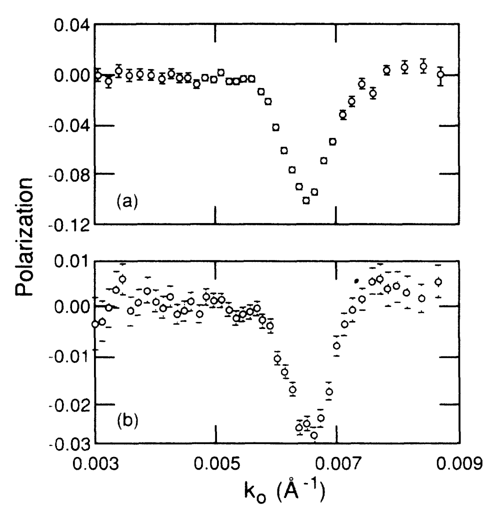

FIG. 4. To amplify the differences in spin, the polarization, $P\equiv(R^+-R^-)/(R^++R^-)$, for the data of Fig. 3 is shown (a) together with the data (b) for a field of 507 Oe.

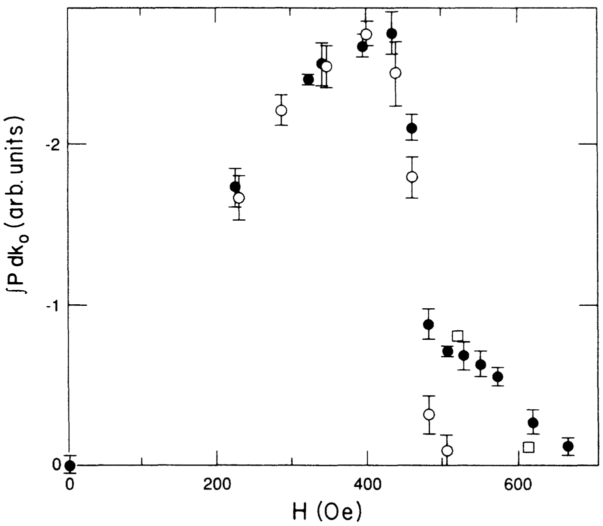

FIG. 5. The integral of the polarization, P, over momentum is plotted against magnetic field for both the Pb (open circles) and Pb(Bi) (solid circles) samples for $T = 5.5$ K. They are strikingly similar to the expected magnetization curves for these materials. Estimated values for the surface sheath, based on the local GL theory calculations (Ref. 15), are also shown (open squares).

is considerable evidence against such an interpretation. For example, the condensation energy for Pb and a 0.8% alloy of Pb with Bi should be very similar, and in fact T_c does not change significantly. Therefore, if the Pb(Bi) sample is type-II, its H_{c1} should have dropped below H_c for pure Pb, and Fig. 5 shows that it has not. Interpreting the Pb(Bi) data in Fig. 5 to represent the magnetization of a type-II superconductor implies a 15% increase in the condensation energy with respect to Pb. Also the magnetic signature of a type-II superconductor in the mixed state would still include a similar surface penetration as in the Meissner state below H_{c1}, rather than the precipitous drop above 500 Oe shown in Fig. 5. Finally, there should be oscillations in the reflectivities due to scattering from the *bulk* periodic flux lattice[2] of a type-II superconductor in the mixed state: These are not found. For these reasons, we conclude that the magnetic signature is a direct confirmation, *by a surface sensitive probe,* for the existence of a superconducting surface sheath.

To analyze the magnetic profiles in detail, both the front and back surfaces of the superconducting films must be considered. The interface of Pb with oxidized Ti presents a discontinuity of the refractive index very similar to that of the vacuum-Pb interface. Hence the reflectances of the two interfaces are very similar. The composite reflectivity for the Pb film also contains, in principle, terms due to the interference of the reflectances of the front and back faces. However, in view of the relatively large thickness of the film, these terms are rapidly fluctuating with k_0, and even with a beam divergence as small as 0.015 degrees, when averaged they are negligible. As a result, the measured polarization is approximately the sum of the polarizations from the magnetic discontinuities at the front and back interfaces, and their individual shapes cannot be distinguished. In the following analysis, the field penetration for $H < H_{c1}$ is assumed identical for both interfaces, while for $H_{c2} < H < H_{c3}$, the surface sheath is assumed to be at the front surface only.

For the case of $H < H_{c1}$, the polarization of the Pb(Bi) film at 323 Oe is compared with calculations for an exponential decay of magnetic field in Figs. 6(b) and 6(c). Although the gross features can be duplicated with an exponential decay length, λ_L, of about 25 nm, the agreement is not as good as warranted by the quality of the experimental data. These results can only be explained by a magnetization profile that is changing more rapidly than an exponential function. We have been unable to invert our polarization data to find $B(z)$, but an example of a profile which fits the data [see Fig. 6(a)] extremely well is

$$B(z) = B(0)\exp\{(z/\lambda_1)[1+0.6\cos(z/\lambda_2)]\} , \qquad (2)$$

where $\lambda_1 = 38$ nm and $\lambda_2 = 100$ nm. Other analytical forms can be constructed which fit the data equally well, however these all have essentially identical magnetic profiles as Eq. (2) in regions near to the surface, although they may differ significantly deep inside the material. This is a manifestation of the fact that the measured reflectivities are most sensitive to the gradient, $dB(z)/dz$. In the absence of a theoretical description of the nonlocal behavior of these low-κ superconductors, the meaning of λ_1 obtained from such a fit is obscure, but it cannot be

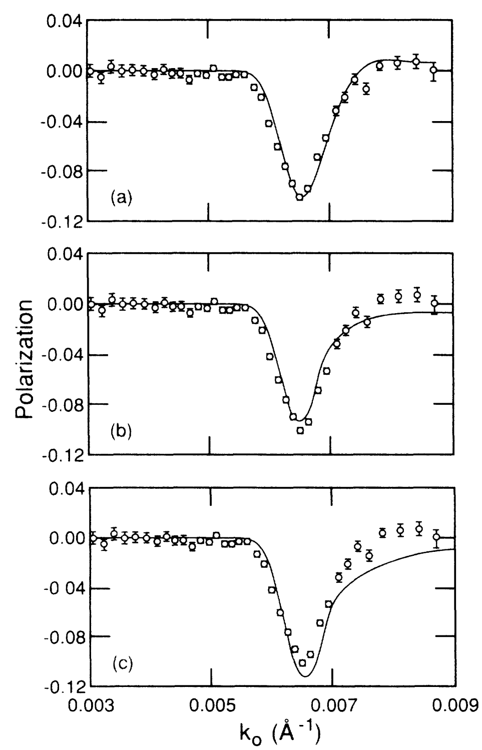

FIG. 6. Demonstration of the improved fit of the polarization data for the Pb(Bi) film in a field of 323 Oe at 5.5 K, through the use of Eq. (2) for the field profile (a) compared to the exponential decay of the local GL theory using $\lambda_L = 30$ nm (b) and $\lambda_L = 20$ nm (c).

directly equated to λ_L. The profile of Eq. (2) does not have a reversal in the direction (algebraic sign) of $B(z)$ deep inside the superconductor, as the calculations of $B(z)$ have found[17] in this nonlocal limit below H_{c1}. It is likely that one must go beyond the scope of the GL theory, and use the nearly equivalent Pippard[12] or BCS (Ref. 16) expressions for $K(q)$ to calculate $B(z)$ and hence the spin-dependence polarization for comparison with the data of Fig. 6.

It would be interesting to compare these results with those of pure Pb: unfortunately, all our samples (five in total) have a smeared-out reflectivity due to the "springing" of the Ti substrate after the thick Pb film was deposited, which prevented a detailed analysis. For reasons we do not understand, such "springing" did not occur for Pb(Bi).

For the case of $H_{c2} < H < H_{c3}$, no calculations of the surface sheath in the nonlocal limit are known to the authors, thus for the moment, the polarization of the Pb(Bi) film at 507 Oe can only be compared to numerical calculations[15] using the local, GL theory. The results, indicated in Fig. 5, are estimated using the initial slopes and minimum field values found in Fig. 5 of Ref. 15 without accounting for the detailed profiles. Although the overall magnitude is reasonable, the experimental data do not drop as quickly with field. Although this could be due to sample inhomogeneities, i.e., the polarization decreases to zero over a finite field range, even for the pure Pb, it is perhaps more reasonable to conclude that such a quantitative comparison is beyond the limits of usefulness of the local, GL theory.[15]

CONCLUSIONS

Using a very direct probe of surface magnetism, i.e., polarized neutron reflection, the penetration of a magnetic field into low-κ superconductors has been shown to be inadequately quantitatively described by the local Ginzburg-Landau theory. In addition, the existence of the surface sheath of superconductivity has been clearly and directly shown by using this proble on the diamagnetic surface sheath. In this case, numerical calculations[15] based on the local, GL theory are shown to provide a useful estimate of the size of the diamagnetism.

ACKNOWLEDGMENTS

This work was supported by the U. S. Department of Energy, Division of Basic Energy Sciences–Materials Sciences under Contract No. W-31-109-ENG-38.

---

*Present address: The Citadel, Charleston, SC 29409.

[1] A. A. Abrikosov, Zh. Eksp. Teor. Fiz. **32**, 1442 (1957) [Sov. Phys.—JETP **5**, 1174 (1957)].

[2] D. Cribier, B. Jacrot, L. M. Rao, and B. Farnoux, Phys. Lett. **9**, 106 (1964).

[3] U. Essmann and H. Träuble, Phys. Lett. **24A**, 526 (1967).

[4] M. Tinkham, *Introduction to Superconductivity* (McGraw-Hill, New York, 1975).

[5] D. Saint-James and P. G. de Gennes, Phys. Lett. 7, 306 (1963).

[6] G.-P. Felcher, R. O. Hilleke, R. K. Crawford, J. Haumann, R. Kleb, and G. Ostrowski, Rev. Sci. Instrum. **58**, 609 (1987).

[7] D. Schoenberg, Proc. R. Soc. (London) A **175**, 49 (1940).

[8] A. B. Pippard, Proc. R. Soc. (London) A **191**, 399 (1947); **203**, 98 (1950).

[9] R. F. Broom, J. Appl. Phys. **47**, 5432 (1976).

[10] W. F. Druyvesteyn, D. J. van Ooijen, and T. J. Berben, Rev. Mod. Phys. **36**, 58 (1964); W. C. H. Joiner and R. D. Blaugher, Rev. Mod. Phys. **36**, 67 (1964).

[11] W. J. Tomasch and A. S. Joseph, Phys. Rev. Lett. **12**, 148 (1964).

[12] A. B. Pippard, Proc. R. Soc. (London) A **216**, 547 (1953).

[13] V. L. Ginzburg and L. D. Landau, Zh. Eksp. Teor. Fiz. **20**, 1064 (1950).

[14] M. Strongin, A. Paskin, D. G. Schweitzer, O. F. Kammerer, and P. P. Craig, Phys. Rev. Lett. **12**, 442 (1964).

[15] R. Felici and K. E. Gray, Phys. Rev. B **29**, 6129 (1984).

[16] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. **108**, 1175 (1957).

[17] R. Sommerhalder and H. Thomas, Helv. Phys. Acta **34**, 29 (1961); **34**, 265 (1961); J. Halbritter, Z. Phys. **243**, 201 (1971).

[18] *International Tables for X-ray Crystallography,* edited by J. Ibers and W. Hamilton (Kynoch, Birmingham, 1976), Vol. IV, p. 270.