Precision Measurement of Anisotropy in the Upper Critical Field of Superconducting Niobium*

D. E. FARRELL, B. S. CHANDRASEKHAR, AND S. HUANG†
Department of Physics and Condensed State Center, Case Western Reserve University, Cleveland, Ohio
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A sensitive vibrating-coil magnetometer has been employed to investigate anisotropy in the upper critical field of pure niobium from 1.2°K to the transition temperature. The results are analyzed using a four-term Kubic harmonic expansion. This is sufficient to represent the data to within experimental error above a reduced temperature of $t \simeq 0.5$, although as the temperature is reduced, small but systematic deviations occur, indicating the presence of higher harmonics. The temperature dependences of the first four harmonics are presented and discussed. Both the temperature dependence of the nth harmonic, and the reduction of that harmonic by impurity scattering, increase as n increases. Our observations are in qualitative accord with the detailed theory for upper-critical-field anisotropy due to Hohenberg and Werthamer. Where direct comparison is possible quantitative agreement is also obtained.

INTRODUCTION

ANISOTROPY of the upper critical field H_{c2} of a type-II superconductor was first observed experimentally[1] on a spherical single crystal of niobium. There has been some debate as to the physical origin of such anisotropy. The Ginzburg-Landau-Abrikosov-Gor'kov (GLAG) theory[2–5] of superconductivity and some of its further developments[6–9] assume a spherical Fermi surface. Other developments[10–13] have removed this restriction and it was suggested that Fermi-surface anisotropy may account for the observed anisotropy of H_{c2} in niobium. However, a detailed theory has been given by Hohenberg and Werthamer,[14] who show that, in the case of a cubic material such as niobium, any orientation dependence of H_{c2} arises from nonlocal corrections to the asymptotic expansion of the Gor'kov equations. No anisotropy can arise solely from lack of Fermi-surface sphericity. Following this work, the orientation dependence of H_{c2} for a single crystal of pure niobium was obtained by Reed *et al.*[15] and shown to be in broad agreement with the theory. In these measurements, H_{c2} was obtained exclusively from resistive data. In order to confirm and extend that work it appeared desirable to measure H_{c2} magnetically to high precision and we have done so using a sensitive vibrating-coil magnetometer.

EXPERIMENTAL DETAILS

A. Sample Preparation

The sample was in the form of a single-crystal disk (radius = 4 mm, thickness = 1 mm) cut from a large single-crystal ingot[16] of niobium. The axis of the disk was oriented along a ⟨110⟩ symmetry direction and applied magnetic fields were always in the plane of the disk. A thin rectangular parallelepiped was cut from the same ingot and its resistance measured at room temperature and at 4.2°K in a field of 10 kOe, from which was obtained the residual resistance ratio (RRR) of the material, viz., RRR = 100. No chemical analysis was performed on the sample but from the work of Finnemore *et al.*,[17] an RRR = 100 would imply a sample with an impurity content of the order of 0.1%. When measuring the resistance of the sample in increasing field we could detect no resistance up to $\sim 3H_{c2}$ (i.e., ~8 kOe), indicating a much-enhanced value of H_{c3}. This enhancement of H_{c3} in niobium has been investigated by DeSorbo,[18] who has shown it to be due to the oxidized surface layer which forms very rapidly in air; such a surface layer has undesirable consequences for any magnetization measurement, since it produces a much-enhanced "surface sheath" magnetization. Although H_{c2} itself is unaffected by any purely surface effects, the accuracy with which H_{c2} can be measured depends on the change of slope of the magnetization-field

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† National Science Foundation College Teachers Research Program participant. Permanent address: Cleveland State University, Cleveland, Ohio.
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curve at H_{c2} and this change of slope is reduced by an enhanced surface sheath magnetization; a vigorous etch of the resistance specimen in nitric acid reduced H_{c3} to its normal value ($\sim 1.6H_{c2}$) and the disk sample was given a similar treatment before making the magnetization measurements. A nonzero magnetization was always observed above H_{c2} due to the intrinsic surface sheath state, but its magnitude was much reduced from that observed if the disk was not etched before measurement. The transition temperature of the sample, obtained from the intercept of a plot of H_{c1} against temperature, was found to be $T_c = 9.21 \pm 0.02$°K. This may be compared with values found by others, viz., 9.25 ± 0.01°K by Finnemore *et al.*,[17] 9.26°K by Shen *et al.*,[19] and 9.19°K by Leupold and Boorse.[20] The result obtained by Finnemore *et al.* was for a very-high-purity sample (RRR$\sim$1500) and differences from their value are quite likely to be due to gaseous contamination; studies by DeSorbo[21] have shown that dissolved oxygen may depress T_c by as much as 0.5°K.

B. Apparatus

The apparatus employs a modification of the conventional vibrating-coil technique and is described in detail elsewhere[22] but those features particularly relevant to this measurement will be briefly outlined here. The inner specimen chamber is shown schematically in Fig. 1. The disk specimen (1) is varnished onto a solid copper block (2). A pure lead reference sample (3) and a commercial germanium resistance thermometer (4) are set into the block with the same varnish (GE 7031). The surrounding copper heat leak can (5) is evacuated during the experiment and the whole assembly rests inside an outer brass can immersed in liquid helium (not shown). An electric heater (6) can raise the temperature of the copper block. The resistance thermometer is used over the whole temperature range, in conjunction with an electronic regulator[23] to maintain the temperature constant to ± 0.001°K. The zero-field superconducting transition of the lead sample was detected by applying an alternating field of 10^{-2} Oe amplitude at 700 Hz, and monitoring the signal from a coil wound directly onto the sample. The apparent T_c was then obtained from the manufacturer's calibration, viz., $T_c = 7.22$°K. This value differs slightly from the commonly accepted value of $T_c = 7.19$°K. The calibration of the thermometer showed a similar shift of 0.03°K at 4.2°K when compared with the vapor pressure of liquid He^4 using the T-58 helium vapor-pressure scale; moreover the *apparent* T_c of the lead sample varied by less than 0.005°K over a sequence of 10 separate runs, recycling to room temperature on each occasion. Because of the stability and reliability of the helium and lead fixed points, each measured temperature was corrected by subtracting the 0.03°K shift noted at both points. In view of these difficulties, however, the absolute temperature measurement is conservatively considered accurate to ± 0.02°K over the whole range, although it is most important to note that the relative temperature stability is considerably better, viz., ± 0.001°K. Below 4.2°K the thermometer was calibrated against the vapor pressure of liquid He^4. In this region the applied magnetic field (H_{c2}) values are large. The thermometer magnetoresistance was measured but it turned out that the apparent temperature shift resulting from the application of a field equal to $H_{c2}(T)$ was always less than 0.003°K. Hence, the magnetoresistance correction was neglected in our temperature measurements.

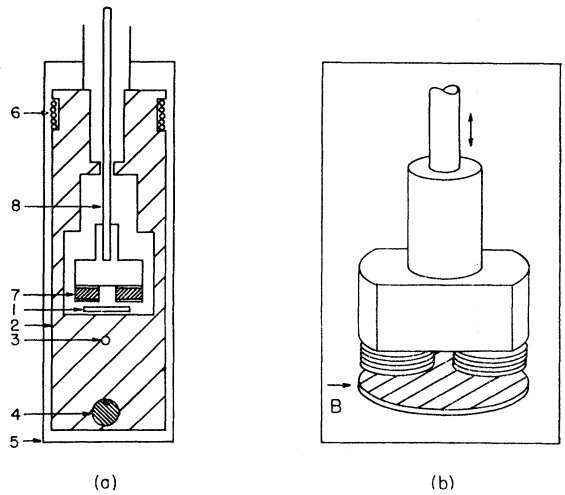

FIG. 1. (a) Specimen chamber of vibrating-coil magnetometer. (b) Expanded view of the vibrating-coil assembly.

The basic component of the magnetometer consists of the "figure-of-eight" coil assembly (7) formed from two 700-turn disk coils wired in opposition with the plane of the coil assembly parallel to the field and the specimen disk. The coil assembly is vibrated up and down with an amplitude of ~ 0.03 cm at 26 Hz by a stainless-steel tube (8) driven from the top of the cryostat. The resulting signal from the coils is phase-sensitively detected in the normal way. The system as described above is rather different from previous vibrating coil arrangements described in the literature. In addition to simplicity, it has certain merits for this particular type of experiment: For the crystal orientation that was chosen, the variation of H_{c2} has two mutually orthogonal lines of reflection symmetry. By suitably mounting the crystal a rotation of the field by $\frac{1}{4}\pi$ in each direction completely maps out H_{c2} as a function of direction in that crystal plane, the sensitivity of the

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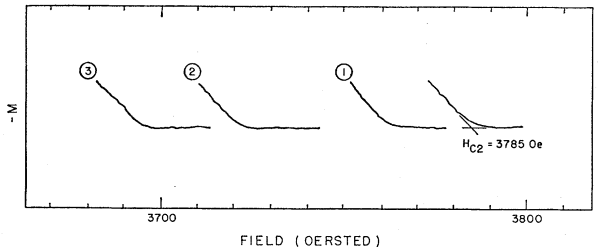

FIG. 2. Magnetic moment (in arbitrary units) of a single-crystal niobium disk at $T=2.5$°K and near H_{c2}. Axis of the disk is oriented along the [110] direction with the applied field in the plane of the disk and for the trace at the right along the [$\bar{1}$11] direction. Traces 1, 2, and 3 were obtained with the field, respectively, 10°, 20°, and 30° away from this direction.

detection system varying by less than a factor of 2 between any two field directions. Hence, we can measure H_{c2} at all orientations in that plane and over a very wide range of reduced temperature without either interfering with the sample mounting or suffering any large variations in sensitivity. In addition, the double-coil arrangement as described above minimizes many of the sources of error of the single-coil technique, viz., background signal due to field inhomogeneity, external pickup, and spurious vibration modes. No absolute sensitivity calibration was made but for the disk sample below H_{c1}, a field change of 10^{-2} Oe produced a change of magnetization above the noise level. Moreover, of more interest in the present context, the value of H_{c2} can be measured to a relative accuracy of better than ± 1 Oe from the sharp change in slope of the magnetization field curve. Magnetic fields are produced with a 12-in. electromagnet and are uniform to 1 part in 10^5 over the sample.

Figure 2 displays a typical recorder tracing of the magnetization near H_{c2} in increasing field for various inclinations of the field to the [$\bar{1}$11] axis. The upper critical field is defined to be the intercept shown in Fig. 2. The complete magnetization curve of the sample proved to be quite hysteretic, but the change in slope of the magnetization curve on reducing the field always took place at a field H_{c2}* which was only very slightly lower than H_{c2} as defined above. In fact, it was found that $(H_{c2}/H_{c2}^*)\simeq 1.005$, the ratio being practically independent of both temperature and field orientation. Since the primary concern is with critical-field anisotropy, it would thus appear to be immaterial which of the two fields is chosen to represent the upper critical field. However, H_{c2} was so chosen, since the change of slope is much larger in increasing field and hence H_{c2} is more precisely defined than H_{c2}*; the absolute accuracy of the measurement is limited by the calibration accuracy of our magnet which was checked to be good to 1% by using a portable Hall-effect probe to compare the field with that of a nuclear-magnetic-resonance (NMR)-calibrated magnet. This is the precision with which the first harmonic can be extracted from the data. However, the precision of the higher harmonics depends upon the accuracy with which the small changes in H_{c2} can be measured on rotating the magnetic field. As stated previously the sensitivity of the magnetometer allows us to find the change in slope of the magnetization curve to ± 1 Oe or better. The remaining uncertainty, particularly at higher temperatures, arises from uncertainties in the temperature itself. At $t=0.2$ a temperature uncertainty of 0.001°K produces a negligible change in H_{c2} but at $t=0.8$ it implies an uncertainty of $\sim\pm 1$ Oe. At lower temperatures the major additional uncertainty arises from the accuracy of the field setting, viz., ± 0.1°K. At $t=0.16$ this gives an error of $\sim\pm 1$ Oe. In summary, at any temperature, one can consider the angular variation of H_{c2} to be known to ± 2 Oe. This is about 1% of the total angular variation of H_{c2} at $t=0.16$; in practice, repeated measurements at any given temperature are reproducible to within ± 2 Oe.

RESULTS AND DISCUSSION

Figure 3 shows the observed values of $H_{c2}(t)$ at $t=0.163$, as a function of the angle which the applied field makes with the [001] direction. As the temperature is increased the basic character of the anisotropy remains unchanged, but its magnitude divided by the "average" upper critical field (to be defined precisely below) rapidly decreases. This is just the behavior predicted[14] and first observed by Reed *et al.*[15]

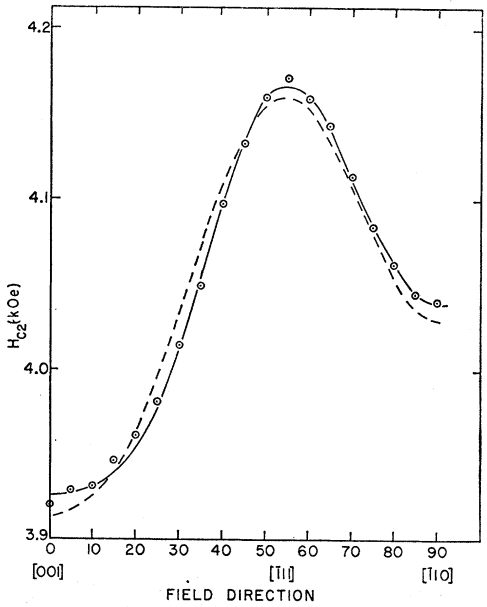

FIG. 3. Angular variation of $H_{c2}(t)$ at $t=0.163$, as a function of the angle indicated on the abscissa between the applied field and the [001] direction. Axis of the disk is oriented along the [110] direction. ⊙, Observed value for H_{c2}. – – –, Calculated H_{c2} value using three Kubic harmonics. ——, Calculated H_{c2} value using four Kubic harmonics.

The rapid decrease of anisotropy with increasing temperature contrasts markedly with the expected[14] temperature-*independent* anisotropy in noncubic materials. The difference arises because in the cubic lattice anisotropy can only appear as a result of the essentially temperature-dependent nonlocal corrections to the GLAG[2–5] theory. Unfortunately the theoretical expression[14] containing the angular variation of these corrections has not been evaluated to date. In order, therefore, to analyze the data in more detail, the approach suggested in Ref. 15 is used and the observed values of H_{c2} are fitted to a series expansion in Kubic harmonics, viz.,

$$H_{c2}(\alpha, \beta, \gamma, t) = \sum_{i=1}^{n} K_i(t) H_i(\alpha, \beta, \gamma). \qquad (1)$$

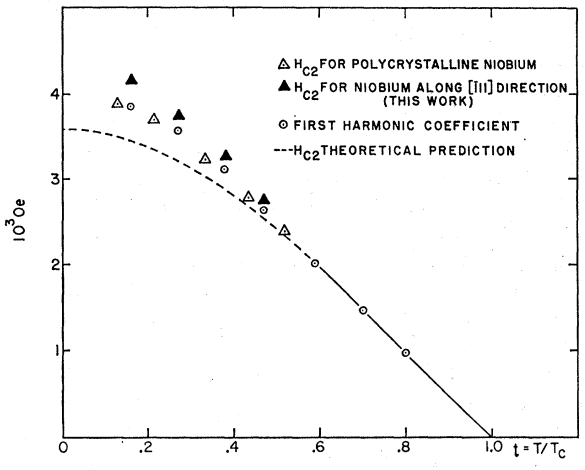

FIG. 4. ⊙, Observed value for $K_1(t)$, the first harmonic coefficient, plotted as a function of reduced temperature. △, $H_{c2}(t)$ for pure polycrystalline niobium (Ref. 17). – – –, Theoretical prediction (Ref. 9) for $H|_2(t)$ for a pure polycrystalline sample with a spherical Fermi surface. ▲, $H_{c2}(t)$ observed in this work for the applied field along the [$\bar{1}$11] direction.

In this expression, $H_{c2}(\alpha, \beta, \gamma, t)$ is the observed upper critical field at reduced temperature t when the field is applied in the direction specified by the direction cosines α, β, γ with respect to the crystal axes. $H_i(\alpha, \beta, \gamma)$ are the Kubic harmonics and the $K_i(t)$ are temperature-dependent coefficients which are extracted at each temperature by performing a least-mean-squares fit of the observed values of H_{c2} using Eq. (1). H_1 is just equal to unity, so that $K_1(t)$ represents the "average field" alluded to above, angular variation of H_{c2} deriving from the higher terms.

If the series expansion is terminated at $n=3$ one obtains the broken line in Fig. 3 for the best fit to the data at that temperature. Most of the discrepancies in this fit are eliminated by including the fourth harmonic ($n=4$), which yields the full line as shown. In fact, above a reduced $t\sim0.5$, the four-harmonic fit does reproduce the data to the experimental accuracy (±2 Oe). Below that temperature small systematic deviations arise which increase as the temperature is lowered, but it has not been possible to extract reliable values of $K_5(t)$ in this region. However, since Fig. 3 exhibits the *largest* deviations which were encountered in fitting the data it is quite clear that terms with $n\geq5$ are making only very small contributions to the observed anisotropy, at least in the temperature range covered. The coefficients obtained from fitting the observed $H_{c2}(\alpha, \beta, \gamma, t)$ to expression (1) are discussed below in turn.

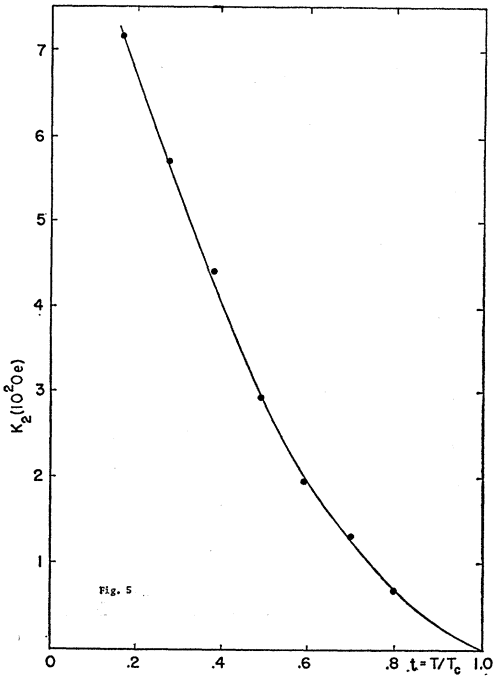

FIG. 5. Observed values for $K_2(t)$, the second-harmonic coefficient, plotted as a function of reduced temperature.

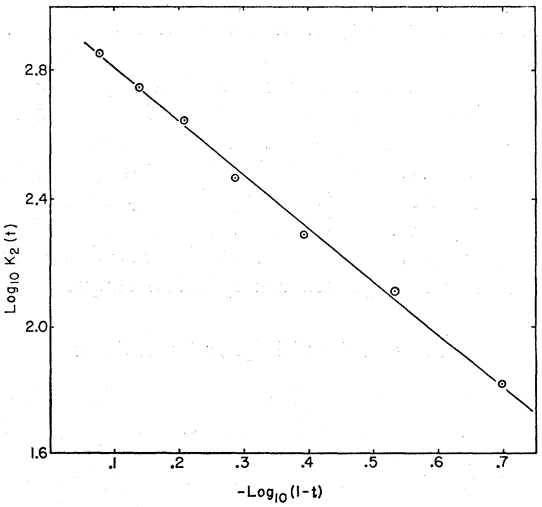

FIG. 6. Logarithmic plot of the observed values of K_2 as a function of reduced temperature.

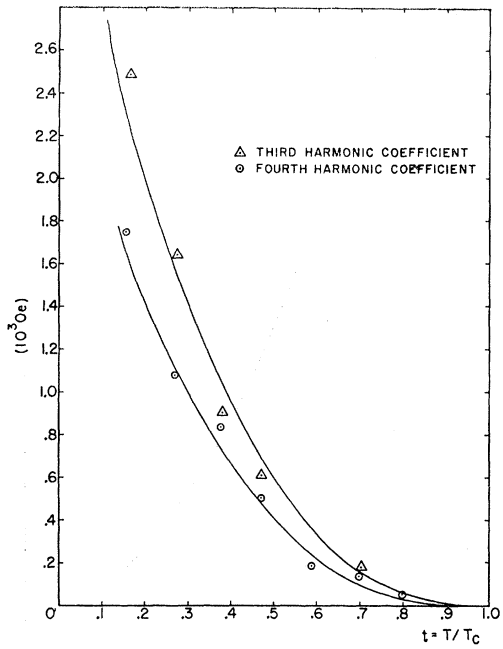

FIG. 7. The third- and fourth-harmonic coefficients plotted as a function of reduced temperature. Full lines are simple power function fits as described in the text.

A. First Coefficient

Figure 4 shows the observed $K_1(t)$ values plotted against t. One sees that $K_1(t) \propto (1-t)$ for $t \lesssim 1$. On the same figure are plotted data given by Ref. 17 for H_{c2} in pure polycrystalline niobium. The agreement is very good, indicating that $K_1(t)$ does indeed represent the value of $H_{c2}(t)$ appropriate to a polycrystalline sample. For comparison the present data for $H_{c2}(t)$ with the field along the [111] direction are plotted on the same figure, revealing the substantial trend away from $K_1(t)$ as the temperature is reduced. The broken curve in the figure is the theoretical prediction[9] for $H_{c2}(t)$ for a pure polycrystalline sample with a *spherical* Fermi surface, normalized to the present data in the region where $K_1(t) \sim (1-t)$. The deviation from this prediction is in the correct sense to be explained by Fermi-surface anisotropy[14] and indeed is rather small considering that it may be doubted that the Fermi surface of niobium even approaches a spherical shape.

B. Second and Higher Coefficients

Figure 5 shows $K_2(t)$ as calculated from the experimental data plotted against t. Some simple functional relationship is indicated, and Fig. 6 shows $\log_{10}K_2(t)$ plotted against $-\log_{10}(1-t)$. From this plot one concludes that $K_2(t) \propto (1-t)^x$ over the whole temperature range, where $x=1.7\pm0.1$. For $t \sim 1$, the theory predicts[14] a value of $x=2$, which is quite close to the experimental result over the whole temperature range. The resistive data of Ref. 15 did suggest a value of $x=2$, but no quantitative estimate of error was given. The higher terms of the expansion are progressively smaller and are correspondingly more difficult to extract from the data with precision. This remark is made more precise by observing that at $t=0.163$ the contributions of the first four terms are in the ratios 1000:61:19:13; at $t=0.7$ the ratios have declined to 1000:29:5:3. The observed values of $K_3(t)$ and $K_4(t)$ are shown in Fig. 7 together with simple power functions $(1-t)^x$ to which they were fitted. A number of points can be made.

(a) The predicted temperature dependence[14] of $K_3(t)/K_1(t)$ should go as $(1-t)^2$ for $t \sim 1$, i.e., $x=3$ for $K_3(t)$ near $t=1$. This is quite close to the value obtained here ($\chi=2.6\pm0.2$) over the whole temperature range and again is in reasonable agreement with the resistive work.[15]

(b) There are no predictions or independent data available with which to compare the temperature dependence of $K_4(t)$ but the present data give $K_4(t) \sim (1-t)^x$, $x=2.7\pm0.4$.

(c) The samples used in previous work on niobium[15,17] were very pure (RRR$\simeq$1500) whereas that employed here has an RRR=100 and it is expected that increased scattering will reduce the absolute magnitudes of the anisotropy[14]; indeed only very small anisotropies have been observed for alloys.[15] In view of this it is interesting to compare the numerical values of the anisotropy coefficients obtained here with those obtained in previous work.[15,17] If one denotes by R_i the ratio of K_i(RRR$\sim$1500) to K_i(RRR=100) then one finds at $t=0.2$

$$R_1=1,\ R_2=0.82,\ R_3=0.65.$$

This shows the interesting regularity that impurity scattering not only reduces the *over-all* anisotropy but effects a more drastic reduction on the higher harmonics.

CONCLUSIONS

We have presented our experimental data for the temperature dependences of the first four coefficients of the Kubic harmonic expansion of the upper critical field in pure niobium. It is observed that both the temperature dependence of the nth harmonic and its reduction by impurity scattering increases with n. It is clear then that in order to extract full information on the nonlocality of the superconducting interaction in niobium, it is desirable to extend this work by examining a higher purity crystal at a lower temperature. However, it has been shown that the observations reported here are in qualitative agreement and, where direct comparison is possible, also in quite close quantitative agreement with the detailed theory of Hohenberg and Werthamer.[14]