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NIOBIUM BY SMALL-ANGLE NEUTRON DIFFRACTION

D. K. Christen, S. Spooner, P. Thorel, and H. R. Kerchner

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DETERMINATION OF LOW-FIELD CRITICAL PARAMETERS OF SUPERCONDUCTING NIOBIUM
BY SMALL-ANGLE NEUTRON DIFFRACTION*

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ABSTRACT

The perfect double-crystal small-angle diffraction technique enables measurement of scattering angles to within 0.3 arc sec. accuracy. At a wavelength of 2.55 Å, this provides a resolution of $3 \times 10^{-6} \text{ Å}^{-1}$ in the scattering vector. This technique has been used to study the anisotropic behavior of the critical parameters B_0 and H_{c1} , characteristic of the first-order magnetic phase transition which occurs in low- κ type-II superconductors. Magnetic fields were applied parallel to several crystal axes in the $(1\bar{1}0)$ and (100) planes of a large single-crystal sphere of pure niobium, resulting in well-defined flux-line lattices (FLL). Measurement of the FLL cell area in the intermediate mixed state field region gives the equilibrium flux density B_0 , which results from an attractive interaction between fluxoids. In addition, field variation of the scattered neutron intensity allows measurement of the transition field between the mixed state and intermediate mixed state. This transition field is related to the lower critical field H_{c1} and enables its determination to a precision 0.2%. Data at $T = 4.3 \text{ K}$ display a small anisotropic effect of about 2% in B_0 and 1% in H_{c1} . Although orientation effects of this magnitude are difficult to resolve by bulk measurements, the neutron data are in accord with magnetization data. Observations

regarding the temperature dependence of these parameters also will be presented, and comparisons made with current theoretical models.

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DETERMINATION OF LOW-FIELD CRITICAL PARAMETERS OF SUPERCONDUCTING VANADIUM
BY SMALL-ANGLE NEUTRON DIFFRACTION

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INTRODUCTION

It has been recognized that for certain specialized problems in small-angle neutron scattering the double-perfect-crystal technique is useful because of its extremely high angular resolution. Specifically, it is well suited for those physical systems which possess translational invariance in one dimension, such as a fibrous or filamentary material. Such a system is the two-dimensional flux-line lattice (FLL) which results when a sufficiently large magnetic field is applied to a type-II superconductor. Previous studies have demonstrated the quantitative precision of the double-crystal small-angle neutron-scattering (DCSANS) arrangement in exploring the equilibrium FLL properties in the pure, low- κ , type-II material, niobium.⁽¹⁾ Briefly, in (1) the following important points were shown.

- (a) DCSANS can be used to determine the FLL symmetry. This is true even in the case of a highly mosaic FLL, because the symmetry can be ascertained precisely from the scattering angle of three successive lowest-order Bragg reflections, without need of finding the centroid of (broad) sample rocking curves.
- (b) For a sample of well-defined non-zero demagnetizing factor n , an attractive interaction between fluxoids is manifested by an interval in the applied magnetic field H_a , known as the intermediate mixed

state (IMS) for which the FLL cell area A_{co} is constant. This basic cell yields the equilibrium attractive flux density $B_0 = \phi_0/A_{co}$.

- (c) DCSANS detects a microscopically sharp transition between the IMS and mixed state (MS), from which one can accurately determine the lower critical field H_{c1} of the material.

It has been known for quite some time that there exist correlations between superconducting properties and the orientation of the anisotropic material with respect to the applied magnetic fields.⁽²⁾

In pure niobium, the observed anisotropy in H_{c2} and κ_2 is relatively large,⁽³⁾ while, until recently, almost no experimental information has been available concerning the orientation dependence of H_{c1} and B_0 .⁽⁴⁾ Mainly, this has been due to sample-preparation problems: poor geometry and purity, and inhomogeneities which produce flux pinning, especially near H_{c1} .

In view of the results obtained in (1), it was decided to investigate the anisotropy in H_{c1} and B_0 of pure niobium by means of DCSANS. In addition, well-controlled bulk measurements were conducted using the same sample, to facilitate comparison, and to provide supplementary information in the ranges inaccessible by neutron diffraction.⁽⁴⁾ The results of these investigations are presented in the present paper. Information regarding FLL-CL correlations also was obtained and is described in the accompanying paper.

EXPERIMENT

The experiments were performed using the double-perfect silicon-crystal diffractometer located earlier at the Oak Ridge Research Reactor,

and more recently at the High Flux Isotope Reactor at Oak Ridge National Laboratory. The present experimental arrangement is shown schematically in Fig. 1. It should be noted that the flux-line filaments are vertical, and the neutron beam horizontal. The angular separation between the direct-beam peak and a (10) FLL Bragg peak for the IMS is illustrated. In this example, the scattering vector is of magnitude $3.58 \times 10^{-3} \text{ \AA}^{-1}$ and can be determined to a precision $3 \times 10^{-6} \text{ \AA}^{-1}$. In practice, the angle $4\theta_{hk}$ is found by relative measurement of the (hk) and $(\bar{h}\bar{k})$ FLL peaks. In this way, for the above conditions, the FLL basic-cell area A_c can be determined to 0.1% precision.

A remark concerning the width of the 2θ peaks may be in order. The theoretical Darwin width of the direct-beam peak for the $\langle 111 \rangle$ silicon reflections is about 2.5 arc sec. In fact, with no sample present, this peak FWHM is measured to be 3.4". This discrepancy can be explained, for example, by as little as a 4° cut angle of one of the Si crystal surfaces with respect to the reflecting planes. When the niobium sample is present, the direct-beam peak width goes to 5", with the additional broadening in quantitative agreement with neutron-refraction effects of the spherical sample.

The fluxoid Bragg peak is always somewhat broader than the direct peak. However, no simple conclusions can be derived from this regarding the FLL coherence range, or interplanar spacing distribution. The reason for this is that some broadening is expected, even for "ideal" Bragg conditions in the FLL, due to the angular breadth and the resulting small defocusing of the incident beam with respect to the analyzer crystal. Estimates of the size of this effect are in reasonable accord with the observed FLL peak widths.

Two samples of pure niobium were used for the neutron-diffraction studies, Nb-ND1 and Nb-ND3. Both samples were spark-machined from the same niobium stock to near spherical geometry, and given identical annealing treatments at 2200°C in a pressure of 2×10^{-10} torr for 50 hrs. Prior to the UHV anneal, however, Nb-ND1 was machine lapped to a near-perfect sphere (13 mm diameter and of maximum eccentricity 0.035), and acid etched to remove approximately 50 microns of surface layer damaged by the lapping process. Both spheres were surface oxidized at 400°C for 5 minutes, a familiar procedure used to reduce the surface barrier to the entrance and exit of magnetic flux.⁽⁵⁾ Only Nb-ND1 was used for the bulk magnetization measurements, and from these data a value $\kappa = 0.774 \pm .003$ was obtained. For the technique used in determining the anisotropy of H_{c1} , the geometrical perfection of the specimen is an important and necessary requirement. This point will be discussed in more detail later.

For the neutron-diffraction measurements, sample Nb-ND1 was mounted on a goniometer insert which provided *in situ* orientation of the sample in the external field by rotation about a well-defined, horizontal CL axis. Of course, the entire system could be rotated about a vertical axis parallel to the field. Temperature stability was facilitated by an electronic temperature controller capable of $\pm .002$ K stability at $T = 4.30$ K.

In order to understand clearly the technique employed here, it is helpful to observe what one measures with DCSANS for a given sample orientation at fixed temperature. In Fig. 2, we illustrate an idealized flux density-applied field relationship, given by the solid curve, for a spherical specimen, compared to the actual average flux density/basic cell of the FLL, as measured by DCSANS. Due to the demagnetizing factor $n = 1/3$

for a sphere, the effective internal magnetic field H equals the lower critical field H_{c1} for an applied field $H_a = 2/3 H_{c1}$. Thus, fluxoids nucleate to form FLL of constant cell area in the IMS-field region

$$2/3 H_{c1} \leq H_a \leq 2/3 H_{c1} + 1/3 B_0, \text{ as described in (1).}$$

The microscopic transition to constant cell-size which occurs at the applied field $H_p = 2/3 H_{c1} + 1/3 B_0$ is very sharp, and can be detected easily by DCSANS using the following technique. For a given low-order reflection, the diffractometer analyzer crystal is set up to diffract at the $2\theta_0$ angle corresponding to the IMS-FLL. The scattered neutron intensity is then recorded as the applied field H_a is stepped from the MS to the IMS, or vice versa. As an example, decreasing field scans are shown for two different temperatures in Fig. 3. The position of peak intensities is the applied-field boundary H_p between the MS and IMS, and typically it may be determined to a precision ± 1 Oe. In the IMS, the field dependence of scattered intensity is due to the volume-filling-fraction effect described in (1).

Since B_0 is determined independently by the FLL cell-size measurement in the IMS, one may use the value of $H_p = 2/3 H_{c1} + 1/3 B_0$ to calculate $H_{c1} = 3/2 (H_p - 1/3 B_0)$. It is for this procedure that perfection in the sample geometry is important. For near-spherical spheroidal geometry, the demagnetizing factor is given by $n = 1/3 (1 - \epsilon^2)$, where ϵ is the eccentricity (zero for a sphere). Then, using the technique described above, the possible error in H_p due to geometry alone is, $\Delta H_p = \pm 1/3 \epsilon^2 (H_{c1} - B_0)$, where H_{c1} is the true lower critical field of the material. Thus, the error in the derived H_{c1} value would be, $\Delta H_{c1} = \pm 1/2 \epsilon^2 (H_{c1} - B_0)$. For example, at $T = 4.30$ K, where $H_{c1} = 1429$ Oe and $B_0 = 748$ G

(see Fig. 4), the maximum eccentricity $\epsilon = 0.035$ of Nb-ND1 yields a possible geometrical error in the H_{c1} determination of ± 0.4 Oe. Although this is a small effect, it should be noted that ϵ for Nb-ND1 is at least a factor of three less than can usually be obtained for samples this size by spark-machining alone. In the latter case, the geometrical error in H_{c1} can easily become comparable to the size of the anisotropy!

RESULTS

In Fig. 4, we present the results of anisotropy measurements of H_{c1} and B_0 at $T = 4.300$ K. These data were obtained for applied fields in the $(1\bar{1}0)$ and (100) niobium-crystal planes. The angle α is always measured from the $[001]$ axis. Here, the solid curves result from least-squares fits of the data to a series expansion in the ortho-normal Kubic Harmonic functions H_ℓ . These functions are defined in terms of the direction cosines α , β , and γ of the applied field with respect to three orthogonal cube faces. The three lowest-order Kubic Harmonics are⁽⁶⁾

$$H_0 = 1,$$

$$H_4 = \frac{5\sqrt{21}}{4} \left(\alpha^4 + \beta^4 + \gamma^4 - \frac{3}{5} \right),$$

$$H_6 = \frac{231\sqrt{26}}{16} \left[\alpha^2\beta^2\gamma^2 + \frac{1}{22} \left(\alpha^4 + \beta^4 + \gamma^4 - \frac{3}{5} \right) - \frac{1}{105} \right].$$

In this case, only the data for fields in the $(1\bar{1}0)$ CL plane were fit, allowing comparison of the (100) CL plane data with a curve obtained from expansion coefficients found independently. Agreement in this sense confirms self-consistency of the measurements. It is seen that the magnitude of the anisotropy is about 1% for H_{c1} and 2% for B_0 , much smaller than the

effect observed for the upper critical field H_{c2} .⁽³⁾ This is in qualitative agreement with theoretical estimates.⁽⁶⁾ Unfortunately, no quantitative theory yet exists describing these low-field orientation effects in low- κ type-II materials.

The reproducibility of the data in Fig. 4 is slightly worse than that expected from the precision of the diffraction measurements alone, since the latter should yield precision of approximately ± 1 G in B_0 and ± 2 Oe in H_{c1} . (Of course, any geometrical errors, discussed previously, are systematic and will not result in irreproducibility.) There is, however, another experimental parameter of considerable importance; this is the temperature stability of the sample. For example, assuming a simple quadratic dependence of H_{c1} on the reduced temperature $t = T/T_c$, $H_{c1}(t) = H_{c1}(0)(1 - t^2)$, it is possible to explain an additional ± 1 -Oe error in H_{c1} due to a 5-mK temperature drift at $T = 4.300$ K. This difficulty is more pronounced at higher temperatures, where there is greater sensitivity of $H_{c1}(T)$, smaller anisotropy, and more difficulty in maintaining stable temperature control for the longer counting times required.

It was mentioned previously that there presently exist no theories which predict quantitatively the anisotropy in B_0 and H_{c1} . There are, however, theoretical descriptions in the isotropic limit of the temperature dependence of these quantities. It is worthwhile to compare the experimental data obtained for applied fields parallel to the [111] CL axis, with two different theories. In Fig. 5, we present the temperature dependence of H_{c1} , normalized to the thermodynamic critical field H_c which has been found by bulk measurements, obtained from DCSANS for both samples, compared to the theory of Pesch and Kramer,⁽⁸⁾ and of Mancini,

Umezawa, et al.⁽⁹⁾ These two theoretical approaches are quite different. The work of Pesch and Kramer involves numerical solutions of Eilenberger's form of the Gorkov equations. On the other hand, Mancini et al. have employed quantum field theory to develop a boson formalism which yields different superconducting macroscopic equations. It can be seen that neither theory describes the experimental data extremely well.

It should be noted that there exists about a 2% discrepancy between the H_{c1}/H_c data of Nb-ND1 and those of Nb-ND3. At present, it has not been ascertained whether this is due to differences in sample purity, or to the geometrical imperfections in Nb-ND3.

In Fig. 6 are the temperature-dependent B_0 data, normalized to B_0 at $T = 0$ K, compared with the theoretical computations of the boson formalism. In this case, the experimental results are described quite well.

Although we have not emphasized this point, the above experimental results obtained by DCSANS are in excellent agreement with the complementary bulk magnetometer measurements,⁽⁴⁾ which we believe are the most precise ever made on pure niobium. In the field and temperature range of their applicability, the DCSANS measurements provide superior precision over all bulk techniques, of which we are aware, which measure the same quantities. These are the first definitive measurements of anisotropy in H_{c1} and B_0 , and should provide the information needed for critical tests of the newly emerging refinements on theories of the attractive-fluxoid interaction.

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FIGURE CAPTIONS

- Fig. 1. Schematic representation of the double-silicon-crystal, small-angle diffractometer, and typical diffraction peaks of the direct beam and a (10) fluxoid reflection.
- Fig. 2. The idealized flux density B vs applied field H_a for a niobium sphere at $T = 5.06$ K, compared to the experimental average flux density/FLL basic cell obtained from DCSANS.
- Fig. 3. Typical applied-field scans at two different temperatures, used for determination of the field boundary between the mixed and intermediate mixed states.
- Fig. 4. Experimental data at $T = 4.300$ K for the anisotropy of H_{c1} and B_0 for applied fields in the $(1\bar{1}0)$ and (100) niobium crystal planes. Solid curves are derived from Ku Harmonic fits to the $(1\bar{1}0)$ data.
- Fig. 5. Experimental data for the temperature dependence of H_{c1}/H_c compared to the theory of Pesch and Kramer, and to that of Mancini, Umezawa et al.
- Fig. 6. Experimental results for the temperature dependence of $B_0(T)/B_0(0)$ compared to the theory of Mancini, Umezawa, et al.

Fig. 1

Fig. 2

Fig. 3

NIOBIUM - ND1

T = 4.300

ORNL-DWG 77-16472

Fig. 4

Fig. 5

Fig. 6