3 it is not possible to have a constant density over a decade in energy. We believe, however, that the dependence of ΔE on ρ_p is strongly affected by the dimensionality and it is possible that a more linear dependence can be obtained in two and three dimensions.[10]

Finally, we would like to mention that the present model is quite appropriate to describe the one-dimensional superionic conductor hollandite.[6,7,11] This material consists of chains with sites that are only about 77% occupied by potassium ions. The parameters for this material are $\alpha \simeq 0.3$ and $J_0 \simeq 0.2$ eV. A calculation performed for a system with $N=12$ and $N_s=16$ predicts a specific heat anomaly at about 40°K. This high value is due to the rather low density that reflects in a large ΔE. We have estimated the corresponding intensity to be about 20% of the Debye specific heat at his temperature. Also we predict that the position of this anomaly strongly depends on the potassium concentration.

It is a pleasure to thank Dr. H. U. Beyeler for interesting discussions and Professor R. Orbach for a critical reading of the manuscript.

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Direct Observation of the Equilibrium Misalignment between Fluxoids and an Applied Magnetic Field Due to Anisotropy Effects in a Type-II Superconductor

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The anisotropic interaction between the crystal lattice and the flux-line lattice results in a misalignment between the applied magnetic field and the fluxoids in a type-II superconductor. Small-angle neutron diffraction has been used to provide the first direct observations of this phenomenon. It is shown that the misalignment angle in the intermediate mixed state is related to the relative anisotropy in the lower critical field H_{c1}, and this relationship is tested for a spherical sample of pure niobium.

The macroscopic properties of a single-crystal type-II superconductor in the mixed state are influenced by the crystal lattice (CL) direction along which the applied field is directed. These effects are due to the anisotropies of the superconducting electronic system.

Because of both experimental and theoretical difficulties, little information has been acquired in the past regarding anisotropy in the low-field critical parameters H_{c1} and B_0.[1] (B_0 is the minimum flux density due to an attractive fluxoid interaction in type-II/1 materials.) Recently, however, theoretical models have been proposed to describe the fluxoid system at low flux density,[2,3] and we have reported reliable measurements of the anisotropy in B_0 and H_{c1} for pure niobium[4] in which we employed double-perfect-crystal small-angle neutron diffraction and magnetization techniques. We describe here neutron-diffraction studies that show in a direct way that the flux-line lattice (FLL) in equilibrium may be nonparallel to the applied magnetic field when the field is aligned along low-symmetry crystal directions.

For applied fields which lie in the intermediate mixed-state (IMS) range of a finite, type-II/1 superconductor, this misalignment effect is related to the anisotropy in H_{c1}. In the following, this relationship is tested by independent experimental determinations of the misalignment angle and H_{c1} anisotropy.

For a finite sample, the Gibbs potential (relative to the sample in the normal state) is given by

$$G=(F_s-F_N)V_s+(8\pi)^{-1}\int(\vec{b}-\vec{H}_a)^2dV,$$

where the integral should be taken over all space. The quantities F_s and F_N are the Helmholtz free energies, excluding the field energy, per unit volume of the sample in the superconducting and normal state, respectively, and V_s is the volume of the sample. The field-energy volume integral involves the total microscopic field $\vec{b}$ and the applied field H_a which would exist if no sample were present (or if it were in the normal state). It is assumed in the following that at low field the free energy can be expressed as[5]

$$(F_s-F_N)V_s+(8\pi)^{-1}\int_{V_s}\vec{b}^2dV =\textstyle\sum_i l_i[I+\frac{1}{2}\sum_j\epsilon(\vec{r}_{ij})]-V_sH_c^2/8\pi. \tag{1}$$

Here, I and $\epsilon(\vec{r}_{ij})$ are, respectively, the self-energy and interaction energy per unit length of fluxoids whose axes are separated by $\vec{r}_{ij}$. In general, the interaction energy $\epsilon(\vec{r}_{ij})$ may contain core effects, but is sufficiently short ranged that the important neighbors of a given fluxoid i have its same length l_i (in a material of finite dimensions). The last term on the right-hand side is the zero-field condensation energy in terms of the thermodynamic critical field H_c.

Although theory can provide the detailed dependences of I and ϵ on the material parameters in the isotropic limit, at present there exists no complete anisotropic theory at low field, and so these details will not be invoked here. On the other hand, we will simply generalize that, for an anisotropic material, these quantities are well-defined functions of the fluxoid axes direction with respect to the CL, and therefore possess the symmetry of the CL. The equilibrium fluxoid state then results from minimization of the free energy.

For the case of a spherical specimen, Eq. (1) leads to the following result for the Gibbs free energy in the IMS:

$$G(H_a)-G(0)=V_s\left[\frac{3}{2}H_a^2+\frac{\vec{B}\cdot\vec{H}_{c1}}{4\pi}-\frac{3}{2}\frac{BH_a}{4\pi}\cos\Delta\psi+\frac{B^2}{16\pi}\right]+\Delta U. \tag{2}$$

Here, we have provided that the FLL and the applied field may be misaligned by the angle $\Delta\psi$. For a type-II/1 superconductor, where the fluxoid interaction energy is attractive and possesses its minimum value for the set of interfluxoid spacings $\{\vec{r}_i^{\,0}\}$, the lower critical field H_{c1} is defined by

$$\hat{B}_0\cdot\vec{H}_{c1}=(4\pi/\varphi_0)[I+\tfrac{1}{2}\textstyle\sum_i\epsilon(\vec{r}_i^{\,0})]. \tag{3}$$

This definition follows from the fact that, for an infinite specimen, the Meissner-state energy is equal to that of the fluxoid state at the applied field H_{c1}. This attractive interaction is responsible for a first-order phase transition at H_{c1}, and the phenomenon of an IMS field regime for a sample of nonzero demagnetizing factor.[6] The quantity ΔU is a small positive energy due to the existence of the domains and this small correction has been neglected in the result which follows. The bulk average flux density in the sample is $B=(\varphi_0/A_c)\sum_i l_iA_c/V_s$, where φ_0/A_c is the average flux density per unit cell of the FLL (B_0 in the IMS), given by the flux quantum φ_0 and the area A_c of the FLL basic cell.

For a given CL orientation in the applied field the equilibrium misalignment angle $\Delta\psi$ is that which minimizes G:

$$\sin\Delta\psi=-\tfrac{2}{3}[\partial(\hat{B}_0\cdot\vec{H}_{c1})/\partial\Delta\psi]H_a^{-1}.$$

Since the parameters of Eq. (3) are functions of the FLL-CL orientation, one has that $\partial(\hat{B}_0\cdot\vec{H}_{c1})/\partial\Delta\psi\simeq d(\hat{B}_0\cdot\vec{H}_{c1})/d\alpha$, where α is an angle which describes the applied-field direction with respect to the CL in a reflection plane of the CL. That is, a virtual rotation of the FLL through $\delta\Delta\psi$ within the sample is equivalent to a rotation of the sample through $\delta\alpha$ in the fixed field, to within a factor $1+d\Delta\psi/d\alpha\simeq1$. Moreover, $d(\hat{B}_0\cdot\vec{H}_{c1})/d\alpha=dH_{c1}/d\alpha$ to the same order of approximation in the small quantities $\Delta\psi$ and its angular derivative. Then

$$\Delta\psi=-\tfrac{2}{3}[dH_{c1}/d\alpha]H_a^{-1}; \tag{4}$$

it is seen that $\Delta\psi$ is related to the anisotropy in H_{c1} and is inversely proportional to the applied field in the IMS.

The sample used for these studies was a high-purity niobium single-crystal sphere, approximately 13.6 mm diam, with measured deviations

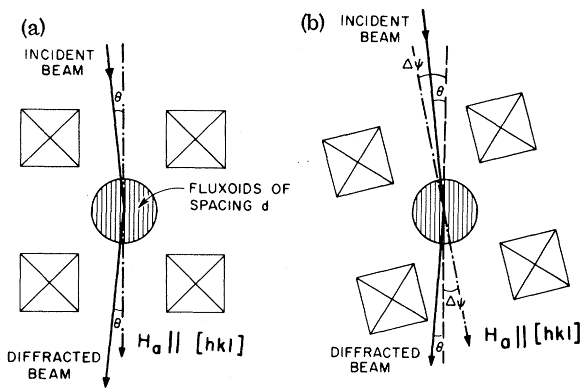

FIG. 1. A schematic top view of the small-angle scattering geometry used to measure the misalignment angle. (a) The special case when $[hkl]$ is a high-symmetry CL axis. Here the fluxoids are parallel to $\vec{H}_a$ and the Bragg angle $\theta = \lambda/2d$. (b) $[hkl]$ is a low-symmetry direction, and the misalignment angle $\Delta\psi$ lies in the horizontal plane (plane of the figure), which is taken to be a CL reflection plane. The neutron wavelength is λ. Here the fluxoids are nonparallel to $\vec{H}_a$. The entire magnet-sample assembly must be rotated by $\Delta\psi$ in order to preserve the Bragg angle θ.

in the diameter of only $\pm 7\ \mu$m. The sample was surface oxidized at 400°C for 5 min to minimize surface pinning, and the Ginzburg-Landau parameter was determined from bulk magnetization measurements to be $\kappa = 0.774 \pm 0.003$.[4]

The small-angle neutron-scattering technique used to measure the anisotropy in H_{c1} is described elsewhere,[4] while the geometrical arrangement for the determination of the misalignment angle is described schematically in Fig. 1. With the use of this technique, the relative shift in the so-called rocking-curve intensities can yield $\Delta\psi$ to $\pm 0.02°$ at $T = 4.30$ K (the temperature at which all data were obtained).

In Fig. 2 are experimental data of FLL misalignments for applied-field directions in a $(1\bar{1}0)$ CL symmetry plane. It is seen that the direction of $\Delta\psi$ is such that the fluxoids are always deviated toward the nearest $\langle 111\rangle$ CL direction. In addition, a systematic dependence of $\Delta\psi$ on the history of the FLL was observed, with the largest disparity occurring for histories of opposite rotation of the sample in the fixed applied field. This effect is most likely due to small remnant bulk or surface flux pinning, which tends to "drag" the fluxoids with the sample when it is in rotational motion. Consequently, the FLL is left with a "memory" of the rotational history after the sample is stopped. This small effect was compensated by averaging the $\Delta\psi$ values for equivalent orientations symmetric

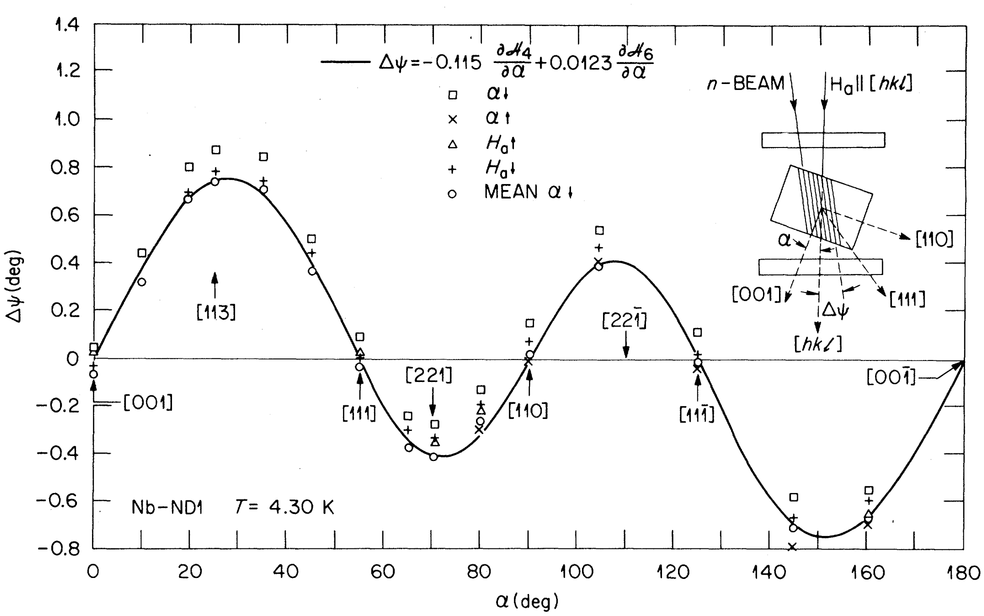

FIG. 2. The misalignment angle $\Delta\psi$ at a constant applied-field magnitude 1175 Oe in the IMS, for various field directions in a $(1\bar{1}0)$ CL plane. The field direction α is measured relative to [001] CL axis, and the sense of the angles is shown in the inset. The solid curve shows the best fit of these data with a series expansion in the angular derivatives of orthonormal Kubic harmonic functions.

about high-symmetry directions. These mean values were then least-squares fitted by an expansion in the angular derivatives of orthonormal Kubic harmonic functions, $\mathcal{K}_l$.[7]

This type of fit was made in view of the relation Eq. (4), and the fact that H_{c1} is directly expressed in terms of Kubic harmonics according to[4]

$$H_{c1} = 1429.5 + 2.931\mathcal{K}_4 - 0.285\mathcal{K}_6.$$

The above result was derived from fits to independent experimental H_{c1} data for field directions in both the $(1\bar{1}0)$ and (100) planes. From Eq. (4) and the H_{c1} measurements, one obtains

$$\Delta\psi H_a = -112.0\, d\mathcal{K}_4/d\alpha + 10.9\, d\mathcal{K}_6/d\alpha \qquad (5)$$

in units of degrees oersted. For the case of Fig. 2, where $H_a = 1175$ Oe in the IMS, the predicted misalignment angle is $\Delta\psi(\deg) = -0.095\, d\mathcal{K}_4/d\alpha + 0.009\, d\mathcal{K}_6/d\alpha$. This relation is to be compared with the expansion coefficients found by fitting the $\Delta\psi$ data of Fig. 2. This comparison reveals that the $\Delta\psi$ predicted by Eq. (4) are approximately 18% smaller than the actual measured values, although the functional dependence of the anisotropy agrees to within 3%. This is not unreasonable since the $\Delta\psi$ measurements are a sensitive indication of the relative anisotropy of H_{c1}, which is itself only 1% of H_{c1} (i.e., we observe an 18% inconsistency in the magnitude of a 1% effect).

As a verification of the applied-field dependence predicted by Eq. (4), the misalignment angle was measured for fields aligned along the [113] CL axis, a direction near to that of maximum misalignment. These results are shown in Fig. 3 and are compared with the relation $\Delta\psi H_a$ = 863 deg Oe, which is obtained from $\Delta\psi$ fit of Fig. 2. The expected result lies between the experimental data for different field histories. Again, the hysteretic effect is probably due to weak pinning and the fact that the equilibrium FLL tends to rotate within the sample when the field is swept, because of the field dependence of the equilibrium misalignment angle. This latter fact is verified by the experimental data in the mixed state, where both the misalignment angle and the hysteresis decrease as the field increases.

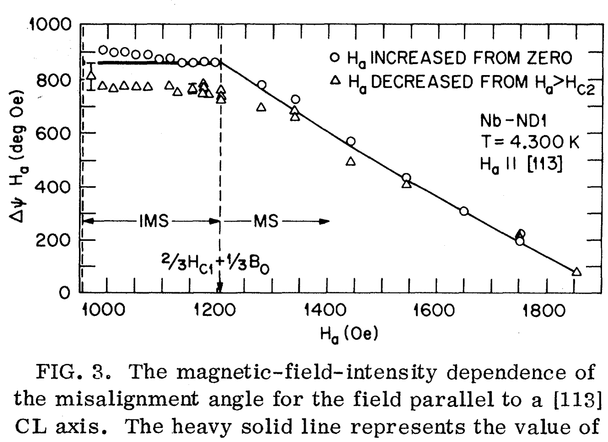

FIG. 3. The magnetic-field-intensity dependence of the misalignment angle for the field parallel to a [113] CL axis. The heavy solid line represents the value of $\Delta\psi H_a$ in the IMS. The curve in the mixed state is drawn by hand.

The various anisotropies in the fluxoid system result in an orientation-dependent free energy, Eq. (2). This implies that a sample should experience a torque when placed in a uniform field aligned off a high-symmetry CL axis.[8,9] This torque is given by $\Gamma = -dG/d\alpha$, where α is the orientation angle in the direction of the maximum rate of change in G. From Eqs. (2) and (4) the torque density in the IMS is given by

$$\Gamma/V_s = \tfrac{3}{2} B H_a \Delta\psi/4\pi. \qquad (6)$$

Again, in deriving these expressions, we have neglected any orientation-dependent contribution of the FLL-domain surface energy, or its effect on the fluxoid-field energy external to the sample.

From experimentally measured parameters, the torque can be calculated according to Eq. (6) and compared with experiment. Although there have been no direct torque measurements performed on the present sample, we have compared Eq. (6) to the recent experimental results of Schneider, Schelten, and Heiden,[8] who measured the torque for field directions in the (110) plane, transverse to the axis of a cylindrical niobium specimen. Taking care to account for the difference in demagnetizing geometry, we find low-field agreement with Ref. 8 to within 5% for the relative functional dependence of the torque. In absolute magnitude, the Ref. 8 data for the maximum torque are 45% lower than those given by Eq. (6).

It has been shown above that simple quantitative relationships can be found among some low-field macroscopic anisotropies of the superconducting niobium system. These relationships are verified qualitatively by comparison of data obtained from quite different experimental techniques, among which are the first direct observations of the equilibrium fluxoid–applied-field misalignment. These types of measurements should help provide a definitive test for recent microscopic theories relating the fluxoid-CL anisotropies.[10]

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In Eq. (9) J^2 should be replaced by J^r. In the first line after Eq. (9) "$\sin^{1/2}\theta S_1(\theta)e^{-im\varphi}$ and $\sin^{1/2}\theta S_2(\theta)e^{-im\varphi}$" should be replaced by "$\sin^{-1/2}\theta \times S_1(\theta)e^{-im\varphi}$ and $\sin^{-1/2}\theta S_2(\theta)e^{-im\varphi}$."

CO ON Cu(100)—EXPLANATION OF THE THREE-PEAK STRUCTURE IN THE X-RAY–PHOTO-EMISSION-SPECTROSCOPY CORE SPECTRUM. O. Gunnarson and K. Schönhammer [Phys. Rev. Lett. 41, 1608 (1978)].

A phrase was omitted from the last sentence before the acknowledgments. The sentence should read, "We have also shown that the analytically solvable filled-band model is very useful for qualitative estimates of the shape of the spectrum, where it gives a simple relation to the substrate density of states, and for the interpretation of the results of more complicated calculations."