PHYSICAL REVIEW B VOLUME 3, NUMBER 11 1 JUNE 1971

Hall Effect in Superconducting Niobium and Alloys

J. le G. Gilchrist and J-C. Vallier
Centre de Recherches sur les Très Basses Températures, Centre National de la Recherche Scientifique, Cedex 166, 38 - Grenoble-Gare, France
(Received 28 December 1970)

We have studied the Hall effect in niobium and some Nb-Ta alloys in the mixed state by calorimetric surface-resistance measurements. In certain conditions the tangent of the Hall angle is given by $(R_+^2 - R_-^2)/(2R_+R_-)$ where R_+, R_- are the surface resistances in right- and left-hand circularly polarized fields. The method of study is critically analyzed and its suitability for studying the mixed state is discussed. It is found that flux pinning causes the magnitude of the Hall angle to be overestimated, which is quite opposite to the influence of pinning on dc Hall-effect measurements. Interpreted like this, the data for moderately pure Nb are consistent with the Hall angle being independent of field in the mixed state. As increasing amounts of Ta are alloyed in, the mixed-state Hall angle becomes smaller compared with the normal state, and for $Nb_{96.8}Ta_{3.2}$ it is approximately zero in $0.5H_{c2}$. The small and negative Hall angles which have been reported for impure Nb and Nb-rich alloys therefore probably represent the true flux-flow behavior, at least qualitatively, and are not primarily due to pinning. A Ta-rich alloy has a relatively large positive Hall angle as also previously reported by Niessen *et al.*

I. INTRODUCTION

The Hall-effect results to be reported here (Sec. IV) were obtained by an unusual ac method, so we first discuss the method of measurement in general (Sec. II) and then the particular application to the mixed state (Sec. III) after reviewing the other results and methods. Throughout, u will denote the Hall tangent and $v=(1+u^2)^{1/2}$.

The Hall effect has been studied in mixed state Nb,[1–10] V,[11] Nb-Ta,[12–14] Nb-Mo,[15] Ti-Mo,[16] Pb-In,[5,17,18] and Pb-Bi.[18] The aim is to measure the Hall resistivity $u_f\rho_f$ associated with the flux-flow resistivity ρ_f in a flat specimen in a perpendicular field H_0. (Inside the specimen $B\approx\mu_0H_0$ and $H_z=\mu^{-1}B$.) It is usually convenient to compare u_f with the Hall tangent at H_{c2} and the same temperature u_{c2}. The first positive results were obtained using dc with six connections (the dc method). In $Nb_{50}Ta_{50}$ [13] (at.% always), $(E_\perp/E_\parallel)$ (H_0) rose to a maximum well in excess of u_{c2}, while in Nb,[1] $E_\perp/E_\parallel$ was less than $(H_0/H_{c2})u_{c2}$ and depended on the measuring current. Subsequent work has confirmed that $u_f>u_{c2}$ in Nb-Ta alloys with more than 35% Ta [13,14] as well as in Pb-In with more than 40% In,[5,17,18] in $Pb_{70}Bi_{30}$ [18] and in $Nb_{80}Mo_{20}$.[15] In other lead alloys u_f changes sign with respect to u_{c2} [17,18] but usually $u_f^2>u_{c2}^2$. The same appears to be true for Nb-Ta with 5–10% Ta [14] but not for $Nb_{75}Ta_{25}$ [14] or for $Ti_{84}Mo_{16}$.[16] None of these qualitative results appears to depend on temperature between 1.3 and 4.2 K. Niobium has been most often studied and Table I summarizes the situation. It seems that for resistance ratios higher than 100, $(H_0/H_{c2})u_{c2}\lesssim u_f\lesssim u_{c2}$, but whether u_f is nearer to $(H_0/H_{c2})u_{c2}$ or u_{c2} is uncertain since some very careful experiments point each way. We chose to study a series of dilute alloys which span the gap between pure Nb and dirty superconductors. In the latter category can be included the low-conductivity vanadium specimens.[11] In Nb of fairly low conductivity, the Hall angle appeared to change sign.[5] We will present evidence which suggests that this was substantially the true behavior of u_f and not a spurious pinning effect.

II. PRINCIPLE OF EXPERIMENT

The ac methods for measuring the Hall effect may be divided into three categories, depending on the relative magnitudes of the specimen thickness h and the skin depth δ of the alternating excitation. δ is defined as $(2\rho/\omega\mu)^{1/2}$ in what follows. If $h\ll\delta$, a uniform current distribution may be assumed. The limiting case is the dc method. The current must be introduced, and the potential differences determined, by means of contacts. When h and δ are similar in magnitude, the measuring current can conveniently be created by induction and the response detected by another induction coil. This is the helicon-resonance method and it depends on the interference of helicon waves penetrating from opposite surfaces of the specimen. The principal resonance occurs when $h/\delta\approx 2^{-1/2}\pi v^{1/2}$. Third, when $h\gg\delta$, so that the penetrating fields are attenuated before interfering with one another, the surface impedance may be measured. Our method is of this last category with the measuring current created by induction and the response measured by calorimetry.

A. Basic Principle

The specimen is a disc, 7 mm in diameter with a stalk 1 mm wide, punched out of a sheet of thickness 0.1–0.5 mm. As for a helicon-resonance experiment the disc is positioned with the flat surfaces perpendicular to H_0 and in a pair of crossed coils, each with axis perpendicular to H_0, but both coils are fed with ac. Figure 1 shows how the disc is subjected to a circularly polarized field. Its power absorption is determined by measuring the current in a heating coil that is necessary to maintain a constant temperature difference across a heat leak. The microwave analog of this arrangement has been used for a number of years.[19]

For isotropic conductors (having transverse resistivity ρ_T and Hall resistivity $\rho_H = u\rho_T$) we will use the notation in which a complex scalar $v = v_x + iv_y$ expresses a real vector perpendicular to $H_0\,(Oz)$, and the two circular polarizations at frequency $f = \omega/2\pi$ are $e^{\pm i\omega t}$. The surface impedance for a surface perpendicular to H_0 is then $R + iX = iE_\omega/H_\omega$, where E_ω and H_ω are the rotating field vectors at the surface. The Poynting vector $(E_x H_y - E_y H_x)$ equals $\mathrm{Re}(iE_\omega H_\omega^*)$ or RH_m^2, where $H_m = |H_\omega|$.

Under normal-skin-effect conditions when δ is much larger than the mean free path l of any group of electrons contributing to the conductivity, we have $E_\omega = (1 - iu)\rho_T J_\omega$ to be used with Maxwell's equations $i\partial E_\omega/\partial z = -i\omega\mu_T H_\omega$ and $i\partial H_\omega/\partial z = J_\omega$. Here μ_T is the transverse differential permeability $(= B/H_z)$ since it is assumed that $H_m \ll H_0$. Then the alternating fields and current vary as e^{-ikz}, where

$$k^2 = -i\omega\mu_T(1 - iu)^{-1}\rho_T^{-1}, \qquad (2.1)$$

and we have $R = \omega\mu_T \mathrm{Re}(k^{-1})$. There will be two values of R, $R_\pm$, depending on the polarization sense with respect to H_0. To these should be added a third, R_z, for the edges of the specimen where the surface and the ac will be parallel to H_0. From Eq. (2.1) we deduce that

$$R_\pm = [\tfrac{1}{2}\omega\mu_T\rho_T(v \pm u)]^{1/2}, \qquad (2.2)$$

so that

$$(R_+^2 - R_-^2)/(2R_+R_-) = u. \qquad (2.3)$$

Let $P_{\pm\pm}$ denote the power absorbed by the specimen, where the first subscript defines the sense of the polarization and the second the sense of H_0. Then from the experiments we can deduce the ratio γ:

$$\gamma = \frac{(P_{++} + P_{--})^2 - (P_{+-} + P_{-+})^2}{2(P_{++} + P_{--})(P_{+-} + P_{-+})}.$$

TABLE I. Hall effect in mixed-state niobium.

Resistance ratio[a]	Crystals	Method	Temp. (K)	u_f/u_{c2}	Current dependent	ρ_H (in p Ω m)[b]	Ref.
1550	Single	dc	1.3–4.2	$< H_0/H_{c2}$	Yes	39.5	1
2500		Helicon	4.2	$\approx H_0/H_{c2}$	No	~80	2
4100		dc	4.2	$< H_0/H_{c2}$	No above 10^7 A m^{-2}	39.5	
6300	Poly	Helicon	4.2	≈ 1	No above 10^6 A m^{-2}	51.6[c]	4
11 000	Poly					52.0[c]	
27		dc	1.6–4.2	Changes sign	Not very	33.8[d]	5
6500	Poly	dc	4.2	$\approx H_0/H_{c2}$	Depinning by ac		6
6500	Poly	dc	4.2–7.8	≈ 1	No	34.6	7
7700	Poly						
160	Poly	e	2.0	$\approx H_0/H_{c2}$ [f]		37.1	8
620	Poly	e	2.0	≈ 1 [f]	No	36.3	
10 000	~4 mm^2	Helicon	g	$\approx H_0/H_{c2}$	No	41.5[h]	9
		dc	g	$\approx H_0/H_{c2}$	Yes	37.2[h]	
430		dc	1.5–4.2	$< H_0/H_{c2}$			10
990		dc	1.4–4.2	$\approx H_0/H_{c2}$			
			6.9–8.0	≈ 1			10

[a] Resistance ratio as given by the authors.
[b] Normal-state Hall resistivity in $\mu_0 H_0 = 0.40$ T.
[c] From resonance frequency and u, without reference to the residual resistance given, and ignoring finite-sample-width correction.
[d] From given resistivity (4.8 n Ω m).
[e] First results obtained by the method described in this paper, in rudimentary form.
[f] Interpreted in the light of Sec. III of this paper.
[g] $\mu_0 H_{c2}$ is shown as 0.247 T so the experiment must have been done at 4.74 K.
[h] As c, but resonance frequency in 0.40 T estimated by extrapolation.

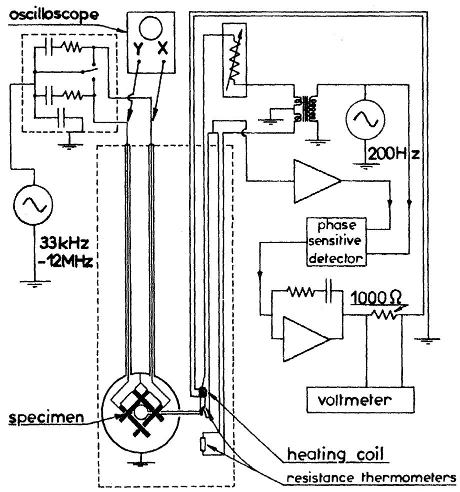

FIG. 1. Circuit diagram: A passive network gives two currents whose phase difference, $\frac{1}{2}\pi$, is controlled by an oscilloscope and which feed crossed Helmholtz coils so as to give a circularly polarized field. The specimen is thermally connected to a resistance thermometer maintained at approx 150 mdeg above the helium bath by a heating coil fed by a thermostat circuit and a 100 μWdeg^{-1} steel heat leak (not shown).

If the amplitudes H_m of the magnetic field of the two polarizations are $H_\pm$ and if the specimen is a disc of radius r and thickness h, then $P_{++} = 2\pi r^2 R_+ H_+^2 + 2\pi r h R_z H_+^2$, etc.,

$$\gamma = \frac{R_+^2 - R_-^2 + 2(R_+ - R_-) R_z h r^{-1}}{2R_+R_- + 2(R_+ + R_-) R_z h r^{-1} + 2R_z^2 h^2 r^{-2}}$$

$$\approx \frac{R_+^2 - R_-^2}{2R_+R_-}\left(1 - \frac{(R_+ - R_-)^2 R_z h r^{-1}}{2R_+R_-(R_+ + R_-)}\right), \qquad (2.4)$$

assuming $h^2 r^{-2} \ll 1$. Unless $R_z \gg (R_+R_-)^{1/2}$, γ may be equated to u in either of the following conditions: (a) $hr^{-1} \ll 1$ and $u \not\gg 1$; (b) $h^2 r^{-2} \ll 1$ and $u^2 h r^{-1} \ll 1$ but hr^{-1}, although small, is not necessarily negligible. If neither condition can be met, then several specimens of different thicknesses must be studied, but in what follows we will assume (a) or (b) is true and write γ to mean $(R_+^2 - R_-^2)/(2R_+R_-)$.

For two reasons we have found the method particularly well adapted for measuring u values between 10^{-2} and 1, and do not recommend it for larger values of the Hall angle. First, when $u > 1$ the helicon-resonance method is perfectly adequate. It is sufficient to determine the sharpness of the resonance and find $u = (4Q^2 - 1)^{1/2}$. But for small u the magnitude of the picked-up signal must be related to u either by extrapolation from higher fields where $u > 1$ or by use of a reference specimen of known properties. The method we have described enables u to be found by relative measurements only, at the field value in question even when $u \ll 1$. Second, to ensure that there is no interference effect it is sufficient to have $h \gg \delta$ when $u < 1$ ($h/\delta > 7.0$ for 1% accuracy[20] when $u \ll 1$), but when u is large the helicon wave penetrates much further and it is necessary to have $h \gg 2^{1/2} u^{3/2} \delta$. This will usually mean that hr^{-1} will be appreciable and $u^2 h r^{-1}$ even more appreciable, so that edge effects will be difficult to eliminate.

The method is liable to incur a few other errors of geometrical origin. There will be absorption by the stalk which serves to hold the specimen and connect it to the thermometer. The stalk may have reacted differently to thermal treatment than the disc itself and in any case will be in an elliptically polarized field. An error will arise if the surfaces are uneven on the scale of δ but this should be detectable if measurements are made at several frequencies. On the other hand, the thickness of the specimen need not be known with precision and may even be somewhat nonuniform. A certain amount of ellipticity of polarization can also be tolerated since if amplitude ϵH_m of the wrong circular polarization is always added to H_m of the right, the relative error in u will only be $-2v\epsilon^2$.

B. Mean-Free-Path Effect

In the normal-skin-effect limit, the surface impedance can be interpreted exclusively by means of μ, ρ, and u; but when l is not much less than δ, it becomes necessary to consider the various kinds of electron trajectories which contribute to the response and the scattering processes both in the volume and at the surface of the conductor. We do not wish to study the mixed state in these conditions since there are too many unknowns, so we estimate how strictly the condtion $l \ll \delta$ must be adhered to. For the free-electron relaxation-time model we look at the first terms in the expansions of $R + iX$ in powers of l/δ [21]:

$$R + iX = \tfrac{1}{2}\omega\mu\delta(1+i)(1+i\omega\tau)^{1/2}(1 + \tfrac{2}{15}\xi + \cdots)$$

for specular surface scattering and

$$R + iX = \tfrac{1}{2}\omega\mu\delta(1+i)(1+i\omega\tau)^{1/2}(1 + \tfrac{1}{8}\sqrt{3}\,\xi^{1/2} + \cdots)$$

for diffuse surface scattering, where

$$\xi = \tfrac{3}{2} i l^2 \delta^{-2}(1+i\omega\tau)^{-3}.$$

Replacing ω by[22] $(\omega - \omega_c)$ and $(\omega - \omega_c)\tau \approx -\omega_c\tau$ by $-u$ and evaluating $(R_+^2 - R_-^2)(2R_+R_-)^{-1}$, we find

$$\gamma/u = 1 - \tfrac{4}{5} v^{-3}(l/\delta)^2 + O(l/\delta)^3 \qquad (2.5)$$

$$= 1 - \tfrac{3}{4}(\tfrac{1}{2} + \tfrac{1}{2}v)^{1/2} v^{-1}(l/\delta) + O(l/\delta)^2 \qquad (2.6)$$

for specular and diffuse scattering, respectively. For other scattering we would expect to find Eq. (2.6), but with a smaller coefficient of l/δ.

If more than one type of closed orbit occurs, corrections to γ should still be proportional to δ^{-2} and δ^{-1} (ω and $\omega^{1/2}$, respectively). We calculated

γ by integration using the spatial Fourier transform of a two-band conductivity with various numerical characteristics and verified this. If the Hall coefficient is the sum of electron and hole contributions which nearly balance, γ/u can depend strongly on frequency. As $u \to \infty$, $\gamma/u \to 1$ still remains, a feature which the existence of open orbits would remove.

We conclude that, in general, $\gamma/u = 1 + O(l/\delta)$. Where l/δ is non-negligible, this can best be taken into account by measuring γ at several frequencies and extrapolating $\gamma(f^{1/2})$ to $f^{1/2} = 0$. Assuming that the mean free path in Nb can be defined and is given by $l\rho = 3.7 \times 10^{-16}$ Ωm^2,[23] the condition $l/\delta < 0.1$ means $f \times (10^{-3} \times \text{resistance ratio})^3 < 25$ kHz. It is worth noting that not only surface-resistance experiments but also helicon resonances for which this inequality is untrue will have been affected by the mean free path.[24]

C. Anisotropy

Usually the specimen consists of a crystal or crystals with dimensions larger than δ. Then current will be induced in each crystal nearly independently, so that the problem of the polycrystalline specimen reduces to one of a single crystal with arbitrary orientation and of averaging over all crystal orientations present. Suppose the representative crystal has a resistivity in the xy plane which approximates to a two-dimensional tensor with axes Ox, Oy. Abandoning the complex notation except to denote temporal variations, we have

$$(\rho_{xy}{}^2 + \rho_{xx}\rho_{yy})(\partial^2 E_x/\partial z^2) - i\omega\mu_T \rho_{yy} E_x + i\omega\mu_T \rho_{xy} E_y = 0 \, , \tag{2.7}$$

$$(\rho_{xy}{}^2 + \rho_{xx}\rho_{yy})(\partial^2 E_y/\partial z^2) - i\omega\mu_T \rho_{xx} E_y - i\omega\mu_T \rho_{xy} E_x = 0 \, .$$

Writing $u = 2\rho_{xy}(\rho_{xx} + \rho_{yy})^{-1}$ and $a = (\rho_{xx} - \rho_{yy})(2\rho_{xy})^{-1}$, the eigenvectors $E_{1,2}$ are $E_x + [a \pm (a^2 - 1)^{1/2}] E_y$ and their k values are given by

$$k^2 + 2i\omega\mu_T(\rho_{xx} + \rho_{yy})^{-1}[1 \mp u(a^2 - 1)^{1/2}]^{-1} = 0 \, . \tag{2.8}$$

The calculation was given by Galt *et al.*[19] If $a > 1$, we write $a = \cosh\theta$ so $E_{1,2}$ becomes $(E_x + e^{\pm\theta} E_y)$. This corresponds to linear polarization, and clearly $\gamma = 0$. If $a^2 < 1$, we write $a = \cos 2\theta$, and $E_{1,2}$ becomes $e^{\pm i\theta}[(E_x + E_y)\cos\theta \mp i(E_x - E_y)\sin\theta]$. The polarization is elliptical, with axial ratio $\tan\theta$. The surface resistances $R_{1,2}$ corresponding to the two modes are given by Eq. (2.2) in which ρ_T is replaced by $\frac{1}{2}(\rho_{xx} + \rho_{yy})$ and u by $u \sin 2\theta$. Splitting the applied rotating field into parts corresponding to the two modes, we find

$$R_\pm = \tfrac{1}{2} R_1 (1 \pm \sin 2\theta) + \tfrac{1}{2} R_2 (1 \mp \sin 2\theta) \, ,$$

so that

$$\gamma = u(1 - a^2)\{1 + \tfrac{1}{2}a^2[(1 + u^2(1 - a^2))^{1/2} - 1]\}^{-1} \, , \quad a^2 < 1$$

$$= 0 \, , \quad a^2 \geq 1 \, . \tag{2.9}$$

A specimen of many randomly oriented crystals will have $\langle a \rangle_{av} \approx 0$ but in general $\langle a^2 \rangle_{av} \neq 0$, so the difference between γ and v will be of the same order of magnitude as for a single crystal. For noncubic materials $a \sim H_0^{-1}$ in weak field, so that γ will, in general, seriously underestimate u. For cubic systems the anisotropy is limited to the magnetoresistance and $a \to 0$ as $H_0 \to 0$. For Nb with $\rho(H_0 = 0) = 1.94$ nΩm the transverse magnetoresistance in $\mu_0 H_0 = 1.0$ T varies in the range $4.10^{-3} < (\Delta\rho/\rho) < 10^{-2}$.[25] This is for fixed current direction (near [110]) and different field directions, and is markedly nontensorial, but we suppose the magnitude is approximately right. Now $\rho_H \approx 90$ pΩm, so that $u \simeq 0.05$, and $a^2 \simeq 5.10^{-3}$. Since $(\Delta\rho/\rho) \propto (H_0/\rho)^m$, with $m \approx 1.4$,[25] it is apparent that the anisotropy correction could be appreciable for any Nb specimen when $u > 0.2$.

III. MIXED STATE AND PINNING

If the surface-resistance method is to be applied to the mixed state and the measured quantity γ identified with u_f, three conditions will have to be satisfied: $\hbar\omega \ll \epsilon_0$, $\delta \gg l, \lambda$ and flux pinning must be negligible. The first merely states that the frequency should be negligible compared with the pair-breaking energy ϵ_0. The response has otherwise been shown to depend on frequency.[26] The second condition is to ensure that the alternating fields are virtually uniform over any volume element of dimensions l or the superconducting penetration depth, whichever is larger. This will ensure the absence of mean-free-path effects (see Sec. II) and of effects related to the behavior of vortices,[27] except via u_f.

The influence of pinning on each type of measurement must be examined closely. For the dc method, Fiory and Serin[7] point out that $(dE_y/dJ_x) \times (dE_x/dJ_x)^{-1}$ should differ from u_f only by a pinning error of second order in $J_c J^{-1}$ which can be made quite small.[28] For the helicon and surface-resistance methods we start from Eq. (2.1), which should apply to the mixed state if u_f is written for u and ρ_f for ρ_T. It applies, in particular, to the rotating part of the potential vector, A_ω ($A_{\omega z} \equiv 0$; $A_\omega = 0$ far inside the specimen). Equating A_ω to $-iBs$, where s is the displacement of the flux lines from their mean positions, $B\Phi_0\rho_f^{-1}$ to the flux-line viscosity η, and $H_z\Phi_0$ to their free energy per unit length $\mathfrak{F}$, Eq. (2.1) becomes

$$-\mathfrak{F}k^2 s - i\omega\eta(1 - iu_f)^{-1}s = 0 \, . \tag{3.1}$$

This is an equation of motion for the flux lines and the negative signs are to indicate the sense of the forces. We add a term to express the pinning force. If $J < J_c$ or the motion is of small amplitude, so that pinning constraints are not broken, we would expect the force to be of the form $-\beta s$, which means it is an elastic restoring force. The coefficient β will depend either on the elasticity of the flux-line lattice[29] which will undergo a jellylike motion between the points where it is pinned,[8] or on the strength and rigidity of the pinning interaction itself.[30] In general, it will be a function of H_0. This is a simplification which is no substitute for a proper theory of pinning[31] but shows as simply as possible how pinning is likely to affect the Hall-effect measurements. Equation (3.1) becomes

$$\mathfrak{F}k^2+\beta+i\omega\eta\,(1-iu_f)^{-1}=0\ . \qquad (3.2)$$

The pinning which modifies Eq. (3.1) to Eq. (3.2) is uniformly distributed throughout the volume of the specimen. There may also be some pinning located on the surfaces, so we allow for a surface pinning force of $-\mathfrak{F}\chi s_0$ per vortex (s_0 is the value of s at the surface, $z=0$). The surface condition then is $|(\chi+ik)s_0|\,H_z=H_m$. Equating the energy dissipated per unit area of surface to RH_m^2

$$\begin{aligned}R_+&=H_m^{-2}B\Phi_0^{-1}\int_0^\infty \mathrm{Re}[i\omega\eta\,(1-iu_f)^{-1}se^{i\omega t}(i\omega se^{i\omega t})^*]\,dz\\&=\omega^2\eta v_f^{-2}BH_z^{-2}\,\Phi_0^{-1}[i(k-k^*)\,(\chi+ik)\,(\chi-ik^*)]^{-1}\\&=\omega\mu_T\,\mathrm{Re}(k^{-1})\,kk^*\,[\,(\chi+ik)\,(\chi-ik^*)]^{-1}\\&=R_f v_f v_\beta^{-1}(v_\beta+u_\beta)^{1/2}[1+y+(2y)^{1/2}(1-u_\beta v_\beta^{-1})^{1/2}]^{-1}\ ,\end{aligned} \qquad (3.3)$$

where

$$R_f=(\tfrac12\,\omega\mu_T\rho_f)^{1/2}\ ,\quad u_\beta=u_f-v_f x\ ,\quad v_f=(1+u_f^2)^{1/2},\ \text{etc.},$$

$$x=v_f\,\beta\omega^{-1}\eta^{-1}\ ,\quad y=\chi^2(kk^*)^{-1}=v_f^2v_\beta^{-1}\,\mathfrak{F}\chi^2\omega^{-1}\eta^{-1}\ .$$

The x and y express the importance of volume and surface pinning at a given frequency. R_- is given by the same expression with $-u_f\ -v_f x$ in place of u_β.

When $u_f^2\ll 1$, we find

$$(R_+R_-)^{1/2}R_f^{-1}\approx\xi^{-1}(\xi-x)^{1/2}\times[1+y+(2y)^{1/2}(1+\xi^{-1}x)^{1/2}]^{-1}\ , \qquad (3.4)$$

$$\gamma/\mu_f\approx\xi^{-1}+2x\xi^{-2}+(2y)^{1/2}\,\xi^{-3/2}(R_+R_-)^{1/2}R_f^{-1}\ , \qquad (3.5)$$

where $\xi=(1+x^2)^{1/2}$. As x or y or both increases from 0 to ∞, $(R_+R_-)^{1/2}R_f^{-1}$ decreases monotonically to zero while γ/u_f first rises to a maximum, then falls. The highest value γ/u_f can attain is approximately 1.94, and occurs when $y=1$, $x\approx 0.6$. When both x and $y^{1/2}$ are small, but for any u_f,

$$(R_+R_-)^{1/2}R_f^{-1}\approx 1-\tfrac12 x-(2y)^{1/2}\ , \qquad (3.6)$$

$$\gamma/u_f\approx 1+2x+(2y)^{1/2}\ . \qquad (3.7)$$

These results warn us to ensure that $x, y\ll 1$ by comparing results at several frequencies and to suspect that the fractional error in the Hall angle may be as many as four times worse than the fractional error in R. Taking the form of a spurious enhancement, it contrasts with the pinning error to be expected in dc measurements.

We find, differently again, that this type of pinning force should cause little error in the helicon-resonance measurements. This can be seen in the Fourier series which expresses the response across the specimen thickness.[32] The dispersion relation (3.2) shows that for each real k value, the complex frequency is modified but that the ratio of the imaginary to the real part is unaffected by the term β. The frequency of the basic resonance will therefore be shifted (upwards), but the sharpness (Q) and the amplitude of the signal at maximum will only be affected to the extent of the interference from the higher Fourier terms, whose frequencies will be less affected. Surface pinning will, however, reduce the amplitude of the response.

Niessen *et al.*[33] have shown that rolled sheets usually exhibit anisotropic pinning. They studied the resulting transverse voltages and calculated the influence on dc Hall-effect measurements. The corresponding calculations for the surface-resistance method yield a similar result, in that there is no enhancement of the apparent Hall angle related specifically to the anisotropy. For volume pinning we would replace the force $-\beta s$ by $(-\beta(1+\alpha)s_x,\ -\beta(1-\alpha)s_y)$. Following the same lines as for anisotropic resistivity in Sec. II, we find the polarization is elliptical, with axial ratio r equal to $(1+\alpha^2x^2)^{1/2}+\alpha x$ when $u_f^2\ll 1$. The surface resistances $R_{1,2}$ of the two modes are given by Eq. (3.3) with $\frac12(r+r^{-1})u_f$ in place of u_f in the definition of u_β, but the two modes take proportions $\frac12\pm(r+r^{-1})^{-1}$ of the incident power, so that γ/u_f is the same as for isotropic pinning with $\alpha=0$. When the surface pinning is anisotropic, the analogous calculation gives the following results:

$$(R_+R_-)^{1/2}R_f^{-1}\approx[1+(2y)^{1/2}+(1+\alpha^2)y]\times[1+(2y)^{1/2}+(1-\alpha^2)y]^{-2}\ , \qquad (3.8)$$

$$\gamma/u_f\approx 1+[\,(2y)^{1/2}-2y\alpha^2]\times[1+(2y)^{1/2}+(1+\alpha^2)y]^{-1}\ . \qquad (3.9)$$

Here we have put $u_f^2\ll 1$, $x=0$ and the surface pinning force $(-\mathfrak{F}\chi(1+\alpha)s_{x0},\ -\mathfrak{F}\chi(1-\alpha)s_{y0})$. The γ/u_f is less than for isotropic pinning but remains greater than 1.0 unless $(2y)^{1/2}\alpha^2>1$, which also implies $y>0.5$, and $(R_+R_-)^{1/2}R_f^{-1}<0.75$. This means that the pinning would be readily noticeable in the surface resistance.

We have found that unless the volume pinning is very strong or the surface pinning both strong and anisotropic, $\gamma/u_f\geqslant 1$. We would expect the same qualitative result to be true if the pinning is randomly, not uniformly, distributed, or if it is concentrated at grain boundaries. It is worth noting, in fact, that Eq. (3.4) with $y=0$ gives a rather accurate description of the variation of surface resistance with frequency in at least one type of superconducting material[34] in which we believe the pinning is randomly dispersed throughout the volume. But it must be emphasized that we have assumed that the pinning force is nondissipative. Otherwise the results could be quite different, as the following example shows.

We assume that the motion of flux lines is subject to a retarding force corresponding to a surface critical current density,[35] J_s ($\mathrm{A\,m^{-1}}$). The force being directed opposite to the flux-line velocity, may be written $-iJ_s\Phi_0 s_0|s_0|^{-1}$. The boundary condition becomes $|(J_s+k|s_0|H_z)|=H_m$. Using Eq. (3.1) and assuming $u_f^2 \ll 1$,

$$R_+ = H_m^{-2} B\Phi_0^{-1}\{\omega J_s\Phi_0|s_0| + \int_0^\infty \mathrm{Re}[i\omega\eta(1-iu_f)^{-1}s(i\omega s)^*]\,dz\}$$

$$\approx R_f\{1-z^2+u_f[\tfrac{1}{2}+\tfrac{1}{2}z^2-z(2-z^2)^{1/2}]\},$$

where

$$z=J_s H_m^{-1}<1,$$

so that

$$(R_+R_-)^{1/2}R_f^{-1}\approx(1-z^2),$$

$$\gamma/u_f\approx(1-z^2)^{-1}[1+z^2-2z(2-z^2)^{1/2}].$$

The correction to γ/u_f is of first order in z, and negative while the correction to R is only of second order. It is therefore important to verify that this type of pinning force does not occur in the experiments, by checking that the response is independent of H_m. Providing $s_0 \ll \xi$, we can also argue that pinning constraints should not be irreversibly broken because pinning forces can not meaningfully extend over a distance of much less than the coherence length ξ.

IV. EXPERIMENTS AND RESULTS

The experiments were all done with the helium bath at 1.98 K and the specimen slightly above 2.13 K. The heat generated in the exciting coils around the specimen was removed from the calorimeter harmlessly by helium channels terminating near their ground connection. Trouble from fluctuations was reduced by using a superconducting solenoid in the short-circuited mode to provide H_0, by using stable ($\pm 1.10^{-4}$) voltage supplies for the high-frequency oscillator to maintain H_m constant, and by reading the results on a digital voltmeter (see Fig. 1) of 10s integrating period. The power absorption of the specimen was then determined to ± 3 nW. The random error in an individual estimate of u appears to have been $\pm 0.001 \pm 2\%$, except for $H_0 < 0.3\,H_{c2}$, where data are more erratic.

Specimen properties are listed in Table II. Rods of the constituent metals were zone melted together to make the alloys which were then laminated. Specimens were punched out and annealed at 50–100 deg below their melting points, the pressure being $1\text{–}2\times10^{-9}$ Torr at the end of 50 h. The Nb 2100 had a similar anneal and then, like the alloys, was found to consist of about 20 grains (2 $\mathrm{mm^2}$ each). The Nb 700 and Nb 500 were annealed for 3 and 14 h, respectively (end vacuum 5×10^{-9} Torr). Specimens were not polished, except the Nb 500 for a final run in order to reaffirm that such treat-

TABLE II. Alloys specimens are designated by atomic composition, niobium by approximate resistance ratio. Transverse and Hall resistivities (ρ_T and ρ_H) are in $\mu_0 H_0 = 0.4$ T. Both are for the normal state, ρ_T being measured at 4.2 K, and ρ_H obtained from ρ_T and γ; the latter is extrapolated, where necessary, from $H_0 > H_{c2}$. $\gamma = (R_+^2 - R_-^2)/(2R_+R_-)$.

	Thickness (mm)	ρ_T (nΩm)	T_c (K)	κ	$l\xi_0^{-1}$	$\mu_0 H_{c2}$ (T)	u_{c2}	ρ_H (pΩm)
$Nb_2\,Ta_{98}$	0.50	10.5				0.093	0.0010	
$Nb_{96.8}\,Ta_{3.2}$	0.49	7.58	8.94	1.26	1.26	0.480	0.0047	29.6
$Nb_{98.4}\,Ta_{1.6}$	0.48	2.99	9.14	0.97	3.18	0.400	0.0109	32.6
$Nb_{99.2}\,Ta_{0.8}$	0.37	1.72	9.18	0.89	5.5	0.382	0.0182	32.5
$Nb_{99.6}\,Ta_{0.4}$	0.45		9.22	0.845		0.375	0.027	
$Nb_{99.6}\,Ta_{0.4}$	0.15							
Nb 500	0.15		9.28	0.80		0.365	0.115	
Nb 700	0.15			0.79		0.365	(0.17)	
Nb 2100	0.14			0.78		0.361	0.516	

ment made no appreciable difference.[8]

Comparing the ρ_H values in Tables I and II, we first notice that all the helicon-resonance data are anomalously high. The other results in Table I lie within $\pm 10\%$ of 36.6 pΩm, which corresponds to a Hall coefficient of 91.5×10^{-12} $A^{-1}\sec^{-1}m^3$. The Nb data obtained by surface resistance[8] are close to this value but the Nb-rich alloys of the present series appear to have lower Hall coefficients.

The shape of our specimens does not facilitate dc resistance measurements, and data obtained from wires and foils made from other parts of the sample proved to be unreliable, so we estimated the resistivities of the three Nb specimens from the Hall angles in 0.4 T and by assuming $\rho_H = 36.6$ pΩm. This gave $\rho_T = 290$, 200, 67 pΩm, approximately 500, 700, and 2100 times smaller than 140 nΩm, and by these ratios the specimens are denoted.

Various amplitude data of the measuring excitation are given in Table III. In a field $H_0 = 0.5\ H_{c2}$, J_0 and s_0 would be about $\sqrt{2}$ times higher than the values given. Since for each material $\xi \approx 40$ nm, it is clear that $s_0\xi^{-1} \ll 1$ always, a supposition on which the analysis of Sec. III was based. The figures shown for Nb 700 relate to a search for amplitude dependence in the mixed state. Neither the normalized surface resistance nor γ showed any significant dependence on amplitude (10 pairs of γ values).

Results for one alloy are shown in Fig. 2. In addition to γ are shown curves representing the surface resistance at the highest and lowest frequencies. The 760-kHz curve is slightly lower than the 7.85-MHz curve when $H_0 \approx 0.95H_{c2}$ and considerably lower when $H_0 < 0.2H_{c2}$. According to the analysis in Sec. III these differences could be attributed to pinning. If so there should be a small enhancement

TABLE III. Amplitude of measuring excitation in $H_0 \approx H_{c2}$. From power absorption (P), surface resistance (R), and skin depth (δ) are estimated the amplitudes of the rotating field (H_m), current density (J_0), and flux-line displacement (s_0) at the surface of the specimen.

	P (μW)	R ($\mu\Omega$)	H_m ($A\ m^{-1}$)	δ (μm)	J_0 ($MA\ m^{-2}$)	s_0 (nm)
$Nb_{98.4}\ Ta_{1.6}$						
1.4 MHz	15	130	38	23	2.3	2.0
8 MHz	12	310	22	10	3.1	0.5
Nb 2100						
60 kHz	10	4	180	17	15	7.5
2.2 MHz	11	24	76	2.8	38	0.5
Nb 700						
1.03 MHz	31	28	120	7	24	2.0
	2.5		34		7	0.6

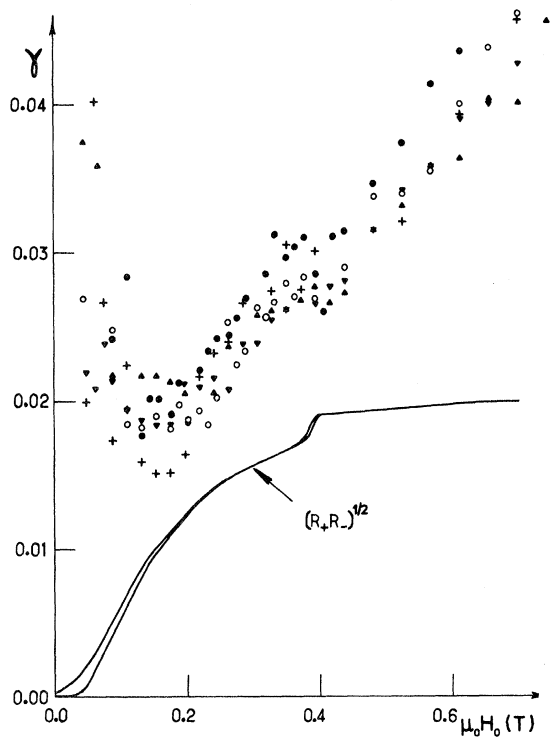

FIG. 2. Hall angle (γ) of $Nb_{99.6}Ta_{0.4}$ (at.%) as a function of applied field (μ_0H_0 in T): ●, ○, ▲, ▼, thicker specimen at 760 kHz, and 1.49, 3.96, and 7.85 MHz; +, thinner specimen at 1.03 MHz. The thicker specimen was also studied at three other intermediate frequencies and the thinner specimen at one other frequency. The latter did not reproduce the anomalously low points between $0.2H_{c2}$ and $0.5H_{c2}$. Surface-resistance curves are for the thicker specimen at 7.85 MHz (upper curve) and 760 kHz (lower curve) drawn to different scales so as to coincide above H_{c2}.

of γ when $H_0 = 0.95H_{c2}$; and when $H_0 = 0.15H_{c2}$, γ might be anomalously increased by a factor of up to 1.94. It is therefore highly probable that the data of Fig. 2 reflect the influence of pinning in the neighborhood of these two fields and that really the Hall angle u_f varies monotonically between about $0.5u_{c2}$ and u_{c2} in fields from 0 to H_{c2}.

In the normal state above H_{c2} there is a slight tendency for γ to be lower as the frequency is higher. This is partly explained by the value of the mean free path; $l/\delta \approx 0.04$ at 7.85 MHz. There is no distinct frequency variation of γ in the mixed state from which to draw more conclusions about pinning so we have preferred to reduce the random error of the points by taking the mean value over all the experimental determinations (see Fig. 4, below). This is also true for the other alloys but not for Nb.

In Sec. II we showed that systematic deviations from $\gamma/u = 1$ increase with the conductivity. This is exemplified by our most conductive specimen,

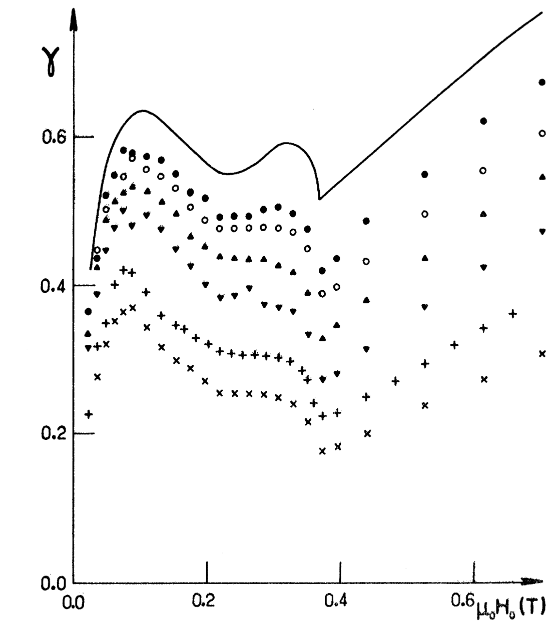

FIG. 3. Hall angle (γ) of Nb 2100: ●, ○, ▲, ▼, +, ×, at 60, 100, 223, 500 kHz, and 1.03 and 2.22 MHz. The curve was obtained by plotting the points for each field against $f^{1/2}$ and extrapolating the smoothest curve through them to $f^{1/2}=0$.

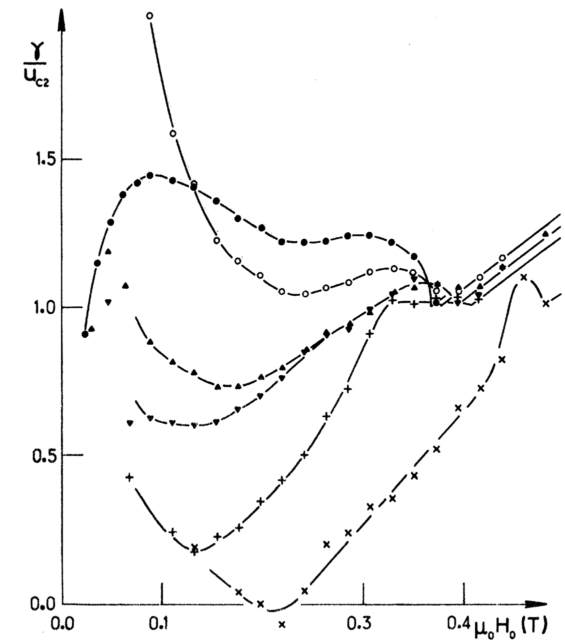

FIG. 4. Hall angle (γ) normalized with respect to $\gamma(H_{c2})$; ●, Nb 2100, mean of two series of data, at 60 and 100 kHz; ○, Nb 500, mean of three experiments (740 kHz–2.1 MHz); ▲, $Nb_{99.6}Ta_{0.4}$, mean of seven expt (760 kHz–7.8 MHz); ▼, $Nb_{99.2}Ta_{0.8}$, mean of four expt (780 kHz–8.0 MHz); +, $Nb_{98.4}Ta_{1.6}$, mean of three expt (1.4–5.0 MHz); ×, $Nb_{96.8}Ta_{3.2}$, mean of four expt (965 kHz–4.5 MHz).

see Fig. 3. For each H_0 value we extrapolated to zero frequency as indicated in Sec. II, in order to eliminate the effect of the mean free path. The u_{c2} value given in Table II was obtained by this procedure (also u_{c2} of Nb 700 and Nb 500, where the effect was smaller but non-negligible, and the ρ_H of the specimen of resistance ratio 620 in Table I). The γ varies less strongly with frequency in the mixed state than in the normal state, but this could be for various reasons. The normal-state data do not extrapolate linearly back to the origin. This has frequently been noticed before, but in the present data it is more marked than usual. This is because, in addition to the genuinely nonlinear behavior of $u(H_0)$, there is the influence of the anisotropy of the magnetoresistivity on the measurements (see Sec. II) which increases with field and means that γ underestimates u. That being so, the resistance ratio 2100 is also doubtlessly an underestimate. The value obtained by extrapolation to zero field is approximately 2600.

Figures 4 and 5 summarize the mixed-state results for the whole series of the specimens. Nb 700 would have appeared very close to Nb 500 on Fig. 4. The results for Nb 500 and Nb 700 can best be understood by supposing that, as for the $Nb_{99.6}Ta_{0.4}$, peak-effect pinning is responsible for the small maximum near $0.9H_{c2}$ and that below $0.2H_{c2}$, stronger pinning causes the large values of γ. Then the observed behavior of γ is consistent with $u_f \simeq u_{c2}$ in all fields below H_{c2}. The compositions of the alloys are different from those of Niessen *et al.*[14] but the results are a consistent extrapolation of theirs since the Ta-rich alloy has $u_f > u_{c2}$ and the Nb-rich alloys have a Hall angle which is smaller than u_{c2} and changes more and more rapidly below H_{c2} as Ta is added until with 3.2% Ta it drops to zero at $0.5H_{c2}$. Niessen *et al.* believed that the results for Ta-rich alloys displayed the true behavior of u_f but that the Nb-rich

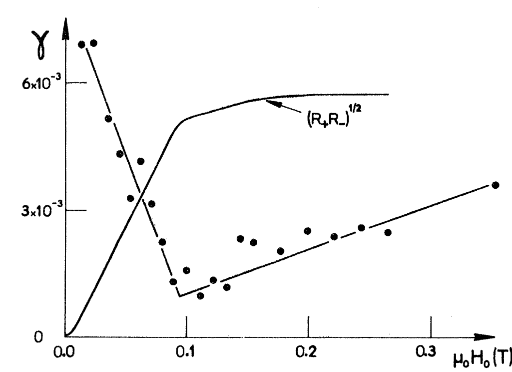

FIG. 5. Hall angle (γ) of Nb_2Ta_{98}: mean of four experiments (950 kHz–2.1 MHz). Surface-resistance curve on arbitrary scale.

Hall angles were seriously depressed by pinning and guided motion. We have seen (Sec. III) that in our experiment weak pinning whether in the volume or at the surface and whether isotropic or not, would make us overestimate u_f; the γ/u_f would only be depressed below 1.0 by pinning strong enough to have a very marked effect on the surface resistance, which is not what we observe except when $H_0 < 0.2H_{c2}$. We therefore believe that if u_f is different from γ as represented in Fig. 4, it can only be lower. This would mean that Niessen's results for Nb-rich alloys and van Beelen's[5] for impure Nb most likely describe the true behavior of u_f.

V. CONCLUSIONS

The main result of the experiment has been to confirm the qualitative differences in the behavior of the mixed-state Hall effect in (a) pure niobium, (b) impure Nb or Nb-rich alloys, and (c) Ta-rich alloys. For moderately pure Nb the data can so be unstood as to be consistent with $u_f \approx u_{c2}$[4,7] for $0 < H_0 \leq H_{c2}$ but not with $u_f \approx (H_0/H_{c2})u_{c2}$.[6,9] As the mean free path is reduced by stages by the addition of Ta solute, u_f/u_{c2} takes successively lower values until it starts becoming negative.[5,14] We have also confirmed that $u_f/u_{c2} > 1$ for a Ta-rich alloy.[14] Owing to the new measurement method that we used, the evidence for the surprisingly opposite behaviors of Nb-rich and Ta-rich alloys is considerably strengthened, and it must be concluded that any adequate theory would have to be refined enough to distinguish between these two alloys.

ACKNOWLEDGMENT

This paper forms part of a thesis submitted by one of us (J-C. V.) to the University of Grenoble for a doctorate ès-Sciences d'Etat. We are grateful to M. Ferrari who prepared the specimens.

---

[1] W. A. Reed, E. Fawcett, and Y. B. Kim, Phys. Rev. Letters 14, 790 (1965).

[2] W. F. Druyvesteyn, G. J. Van Gurp, and C. A. A. J. Greebe, Phys. Letters 22, 248 (1966).

[3] B. W. Maxfield and E. F. Johnson, Phys. Rev. Letters 16, 652 (1966).

[4] B. W. Maxfield, Solid State Commun. 5, 585 (1967); see also Phys. Rev. Letters 19, 569 (1967).

[5] H. Van Beelen, J. P. Van Braam Houckgeest, H. M. Thomas, C. Stolk, and R. de Bruyn Ouboter, Physica 36, 241 (1967).

[6] A. T. Fiory and B. Serin, Phys. Letters 25A, 557 (1967).

[7] A. T. Fiory and B. Serin, Phys. Rev. Letters 21, 359 (1968).

[8] J. le G. Gilchrist and P. Monceau, Phil. Mag. 18, 237 (1968).

[9] B. Slettenmark, H. U. Astrom, and P. Weissglas, Solid State Commun. 7, 1337 (1969).

[10] K. Noto and Y. Muto, in *Proceedings of the Twelfth International Conference on Low Temperature Physics*, Kyoto, Japan, 1970 (Academic Press of Japan, Tokyo, to be published).

[11] N. Usui, T. Ogasawara, and K. Yasukochi, Phys. Letters 27A, 139 (1968); N. Usui, T. Ogasawara, K. Yasukochi, and S. Tomoda, J. Phys. Soc. Japan 27, 574 (1969).

[12] A. K. Niessen and F. A. Staas, Phys. Letters 15, 26 (1965).

[13] F. A. Staas, A. K. Niessen, and W. F. Druyvesteyn, Phys. Letters 17, 231 (1965).

[14] A. K. Niessen, F. A. Staas, and C. H. Weijsenfeld, Phys. Letters 25A, 33 (1967).

[15] Y. Muto, K. Noto, M. Hongo, and K. Mori, Phys. Letters 30A, 480 (1969).

[16] R. R. Hake, Phys. Rev. 168, 442 (1968).

[17] C. H. Weijsenfeld, Phys. Letters 28A, 362 (1968); in *Proceedings of the Eleventh International Conference on Low Temperature Physics*, edited by J. F. Allen, D. M. Finlayson, and D. M. McCall (University of St. Andrews Printing Dept., St. Andrews, Scotland, 1969).

[18] C. H. Weijsenfeld, Physica 45, 241 (1969).

[19] J. K. Galt, W. A. Yager, F. R. Merritt, B. B. Cetlin, and A. D. Brailsford, Phys. Rev. 114, 1396 (1959).

[20] J. le G. Gilchrist, J. Phys. (Paris) 29, 990 (1968).

[21] R. B. Dingle, Physica 19, 311 (1953).

[22] R. G. Chambers, Phil. Mag. 1, 459 (1956).

[23] B. B. Goodman and G. Kuhn, J. Phys. (Paris) 29, 240 (1968).

[24] W. J. A. Goossens and D. Polder, Phys. Rev. 187, 943 (1969).

[25] G. Perriot, J. Phys. (Paris) 28, 472 (1967).

[26] C. Caroli and K. Maki, Phys. Rev. 164, 591 (1967); H. Takayama and H. Ebisawa, in Ref. 10.

[27] A. A. Abrikosov, M. P. Khemoklidze, and I. M. Khalatnikov, Zh. Eksperim. i Teor. Fiz. 48, 765(L) (1965) [Sov. Phys. JETP 21, 506 (1965)].

[28] J. Baixeras and S. J. Williamson deliberately studied the effect of strong pinning in cold-rolled $Nb_{99}Zr_1$ [Solid State Commun. 5, 599 (1967)].

[29] J. Matricon, Phys. Letters 9, 289 (1964).

[30] J. I. Gittleman and B. Rosenblum, Phys. Rev. Letters 16, 734 (1966), where $\beta \simeq 2\pi J_c (B\Phi_0)^{1/2}$.

[31] R. Labusch, Cryst. Lattice Defects 1, 1 (1969).

[32] R. G. Chambers and B. K. Jones, Proc. Roy. Soc. (London) A270, 417 (1962).

[33] A. K. Niessen and C. H. Weijsenfeld, J. Appl. Phys. 40, 384 (1969).

[34] B. Salce, thesis (University of Grenoble, 1970) (unpublished). The material is PbIn with dispersions of insulating powders.

[35] The analogous problem with volume critical current density, $J_c(\mathrm{A\,m^{-2}})$ is more complex. In the quasistatic limit, $H_\omega(z) = H_\omega(0)\,(1 - 3^{-1/2} J_c H_m^{-1} z)^{(1+\sqrt{2}\,i)}$, $R_\pm = 6^{-1/2}\omega\mu_0 J_c^{-1} H_m$ [C. P. Bean, J. Appl. Phys. 41, 2482 (1970)].