dielectric solids,¹⁶ should also be important in metals. Such scattering of the phonons mediating superconductivity should limit pair lifetimes as does an applied magnetic field. Thompson¹⁷ has suggested that in the absence of significant pair breaking, higher order diagrams than the first order ones considered by AL will become important. We would suggest that phonon mean free path effects may be important pair-lifetime limiting mechanisms.

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NONLOCAL CHARACTERISTICS OF THE BULK UPPER CRITICAL FIELD OF NIOBIUM

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Measurements of the anisotropic critical field H_{c2} of Nb at temperatures down to 0.06 K show that its temperature dependence contains a logarithmic factor as predicted by Gor'kov on the basis of a nonlocal theory for an isotropic type-II superconductor. The critical field extrapolated to zero temperature, when averaged over all crystallographic directions and normalized to the slope of the critical field for $T \approx T_c$, has an enhancement close to that predicted by the Hohenberg-Werthamer calculation for the nonlocal effects of Fermi-surface anisotropy, as evaluated by Mattheiss for a band model of niobium.

Considerable interest has been focused upon the temperature dependence of the upper critical field H_{c2} of pure Nb, since this metal is an elemental example of a pure type-II superconductor, yet the bulk critical field is known¹ to deviate substantially from the rigorous solution obtained by Helfand and Werthamer² for the linearized Ginzburg-Landau-Abrikosov-Gor'kov (GLAG) theory. Observations by Tilley, van Gurp, and Berghout and by Reed et al.⁴ showed that H_{c2} is anisotropic and, therefore, must reflect "real metal" effects. Reed et al.⁴ found that the temperature dependence of the anisotropy near the critical temperature T_c was qualitatively in agreement with the calculation of Hohenberg and Werthamer⁵ (hereafter, HW), which

attributed such effects to Fermi-surface anisotropy as included in a first-order nonlocal correction to the GLAG theory. However, no quantitative test of the theory was possible, nor was the temperature dependence of H_{c2} at low temperatures predicted. More recently it has been suggested by Sung and Wong⁶ that two-band effects, such as are indicated at low temperatures by specific-heat⁷ and thermal-conductivity⁸ measurements, might influence $H_{c2}(T)$ if interband coupling parameters are properly chosen; however, again, no quantitative test of this theory has been made.

We report in this Letter that H_{c2} values for the applied field parallel to the [001], [110], and [111] directions and for temperatures as low as

T = 0.06 K have the low-temperature limiting dependence

$$H_{c2}(t)/H_{c2}(0) = 1 + \eta t^2 \ln(t), \tag{1}$$

where $t = T/T_c$ and η is a constant whose value depends upon crystallographic direction. The presence of the logarithmic factor, which contrasts with the simple quadratic temperature dependence observed for "dirty" Nb-Zr alloys,9 has been predicted by Gor'kov on the basis of the nonlocal model for an isotropic type-II superconductor.¹⁰ Although the presence of this factor thus rests upon general theoretical grounds, neither the HW calculation nor the two-band model⁶ has yet been shown to predict the limiting form of Eq. (1). We also report that the reduced critical field $h(t) = H_{c2}(t)/(dH_{c2}/dt)_{t=1}$ when averaged over all crystallographic directions has the zero-temperature extrapolated value $\langle h(0) \rangle = 0.96$ ± 0.03 . This value is in good agreement with Mattheiss's evaluation¹¹ of the HW enhancement factor for a band model of niobium which generally agrees with de Haas-van Alphen effect measurements. The anisotropic Fermi surface was found to elevate $\langle h(0) \rangle$ from 0.73 for the pure isotropic model to 0.99 for niobium. Thus, the HW nonlocal effects explain the observed $\langle h(0) \rangle$ without recourse to adjustable parameters, unlike the two-band theory.⁶

Critical-field measurements were performed on a cylindrical single crystal of Nb whose axis is parallel to $[1\overline{1}0]$. The sample, which had been annealed in high vacuum, had a resistance ratio $\Gamma = \rho_{300 \text{ K}} / \rho_{4.2 \text{ K}} = 750$. A magnetic field was applied perpendicular to the sample axis by a superconducting or copper coil pair in a near Helmholtz configuration.¹² The transition at H_{c2} was detected by application of a small ac magnetic field parallel to the sample axis while monitoring with a lock-in detector the resulting voltage from a pickup coil encircling the sample. Thermal-conductivity measurements for 1.5 < T< 4.2 K demonstrated that the magnetic transition thus measured coincided with a bulk transition and consequently defined H_{c2} . Refrigeration of the sample at very low temperatures was provided with a ³He cryostat or a ³He-⁴He dilution refrigerator slightly modified from the design of Wheatley, Vilches, and Abel.¹³

Figure 1 gives the observed H_{c2} at low temperatures for the three principal crystallographic axes The relative precision of the data is better than 0.2% although the accuracy of the ordinate is only 1% because of the finite magnetic-transition width and field-calibration uncertainties. As is shown in the figure, the anisotropy continues to increase down to the lowest temperature.

The data are accurately described by a $t^2 \ln(t)$ temperature dependence over a range of more than two decades in $t^2 \ln(t)$. Within the same range of temperature, the data are inconsistent with a simple t^2 dependence. Gor'kov¹⁰ has predicted that within the framework of the nonlocal isotropic model a logarithmic factor would be expected, since the linearized gap equation

$$\Delta^*(\vec{\mathbf{r}}) = \int K(\vec{\mathbf{r}}, \vec{\mathbf{r}}') \Delta^*(\vec{\mathbf{r}}) d\vec{\mathbf{r}}'$$
(2)

has a logarithmic singularity for $T \rightarrow 0$, and thereby influences the critical field. The basis for the singularity can be seen in the form of the kernel

$$K(\mathbf{\vec{r}},\mathbf{\vec{r}}') \sim |\mathbf{\vec{r}} - \mathbf{\vec{r}}'|^{-2} \sum_{n=0}^{n \max} \exp\left[\frac{-2\pi T |2n+1||\mathbf{\vec{r}} - \mathbf{\vec{r}}'|}{v_{\mathrm{F}}}\right] \\ \times \exp\left[-2ie \int_{\mathbf{\vec{r}}'}^{\mathbf{\vec{r}}} \mathbf{\vec{A}}(\mathbf{\vec{s}}) \cdot d\mathbf{\vec{s}}\right], \qquad (3)$$

where the notation of Hu and Korenman¹⁴ is employed and multiplicative constants are omitted. The summation is limited by $n_{\max} \approx \omega_D/4\pi T$, since the minimum range of the kernel is restricted by the Heisenberg uncertainty condition as a result of limiting the phonon interaction component of the BCS Hamiltonian to include only those plane-wave electronic states that lie within an energy ω_D of the Fermi energy. This finite range provides a nonlocal character to the theory. Thus, for $T \rightarrow 0$, summation over *n* is approximated by $[\sinh(2\pi T|r-r'|/v_F)]^{-1}$ which produces a logarithmic singularity in Eq. (2) and consequently a logarithmic factor in $H_{c2}(t)$.¹⁰



FIG. 1. Observed $H_{C2}(T)$ for the three principal crystallographic directions in Nb, versus $t^2 \ln(t)$, where $t = T/T_{c^*}$

Since the logarithmic factor in $H_{c2}(t)$ arises from general considerations, it might be expected to apply also to the anisotropic superconductor, although such has not yet been predicted from the HW theory. From Fig. 1 we find that $\eta = 1.30$ for [001], 1.39 for [110], and 1.69 for [111], in contrast to $\eta = 0.65$ as predicted by the isotropic model.¹⁰

Although Eq. (1) implies that the free energy of an ideal superconductor at H_{c2} would be nonanalytic for $T \rightarrow 0$, as has been discussed by Brandt,¹⁵ Maki and Tsuzuki¹⁶ pointed out that for a real metal with finite electron-collision time, the argument of the logarithm would be limited to $1/\tau T_c$ as $t \to 0$, thus eliminating a divergence in the parameter κ_2 and insuring that H_{c2} approaches its zero-temperature value quadratically in T. Estimates from ultrasonic studies¹⁷ give $1/\tau \approx 0.6$ K, so that the observed H_{c2} trend should fall slightly under the straight lines of Fig. 1 for temperatures below $T \approx 0.3$ K. The precision of our data is inadequate to reveal unambiguously such a deviation although a slightly better fit would be obtained if the argument of the logarithm in Eq. (1) were $t + 1/\tau T_c$. Agreement between the data and Eq. (1), which predicts that H_{c2} approaches its zero-temperature extrapolation with zero slope, would seem to discourage speculation¹⁸ that critical-field measurements of Nb might show that the transition assumes third- or higher-order characteristics as t approaches zero.

From cubic harmonic fits to the anisotropy of H_{c2} observed for H in the (110) plane, the average of H_{c2} for all crystallographic directions can be established. The results for $\langle h(t) \rangle$ are shown in Fig. 2. The zero-temperature intercept $\langle h(0) \rangle = 0.96 \pm 0.03$ is considerably higher than previous determinations, which may be a result of our employing only data very near T_c to determine $(dH_{c2}/dt)_{t=1}$. For $H_{c2} > 400$ Oe, we observed a positive curvature in H_{c2} which-if not recognized-could lead to erroneously high values for the slope. The observed $\langle h(0) \rangle$ is in good agreement with the value 0.99 calculated by Mattheiss from the HW theory and thus corroborates his estimate that H_{c2} can be enhanced by some 30% with respect to the isotropic model as a result of band-structure effects. Similar measurements which we have performed¹⁹ on a sample of V (Γ = 140) gave an intercept of $\langle h(0) \rangle$ $= 0.93 \pm 0.03$. The general agreement with the Nb results would be expected if the Fermi surfaces were similar, as suggested by magnetoresis-



FIG. 2. Representative experimental values for H_{c2} when averaged over all crystallographic directions and normalized to the slope at $t \simeq 1$. Considerable enhancement over the Helfand-Werthamer theory (Ref. 2) for a clean, isotropic superconductor is evident. For comparison, the behavior predicted by the dirty-limit theory, as well as a linear extrapolation of the slope, are also shown.

tance studies.²⁰ Since the ratio of critical temperature to Debye temperature for Nb is 2.6 times that for V, the agreement between $\langle h(0) \rangle$ values for the two metals would imply that strong-coupling effects do not appreciably affect $\langle h(t) \rangle$.²¹ The success of the HW model without adjustable parameters indicates that two-band effects are also not appreciable for h(t), even though a theory with adjustable parameters for such effects is capable of qualitatively describing h(t) for a particular crystallographic direction.⁶

Although Mattheiss's band model yields good results for $\langle h(0) \rangle$, the prediction¹¹ for $(dH_{c2}/dt)_{t=1}$, when strong-coupling corrections are made, is 40% below our experimental result of 4.42 ± 0.08 kOe for Nb. This discrepancy would correspond to a 20% error in the calculated average Fermi velocity. However, adjustment of the *d*-band width to improve agreement with the specific-heat density of states would also reduce the discrepancy for the slope, while affecting $\langle h(0) \rangle$ very little. In view of the present accuracy of band calculations for Nb, the discrepancy in predicting the slope is not considered to be serious.

One aspect of the nonlocal theory still to be verified experimentally is the effect upon $\langle h(0) \rangle$ of a decrease in τ through alloying. Experiments by Ohtsuka and Kimura²² on polycrystalline Nb-Ta alloys show that h(0) does not rapidly decrease with increase in Ta concentration, unlike what might intuitively be expected. This remains an open question which further experiments on single-crystal specimens should resolve.

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PRESSURE DEPENDENCE OF THE ELECTRICAL RESISTIVITY OF EuO*

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The room-temperature electrical resistivity of EuO is reported as a function of pressure up to 10 kbar. For the higher resistivity samples the pressure coefficient corresponds very closely to the observed shift of the optical absorption edge with pressure. Both the temperature and pressure dependence of the electrical resistivity are explained in terms of a model in which electrons are distributed between a temperature- and pressure-sensitive conduction band and a localized stationary trap level.

The optical, electrical, and magnetic properties of the Eu chalcogenides, EuO, EuS, and EuSe, have been extensively investigated in recent years, both experimentally and theoretically.¹ These ferromagnetic semiconductors exhibit many interesting phenomena, among which is a large temperature dependence of the optical absorption edge characterized by a sizable red shift with decreasing temperature below the ordering temperature, T_c . Electrically conducting

materials also show a large temperature dependence of their electrical resistivity and a giant negative magnetoresistance in the vicinity of T_c .

Two models have been proposed to explain the temperature and magnetic field dependence of the electrical resistivity in lightly doped material.²⁻⁴ In both of these models electrical conductivity at high temperature takes place through a thermally activated hopping process, and the large temperature and magnetic field dependence