EVIDENCE FOR FLUCTUATION SUPERCONDUCTIVITY IN BULK TYPE-II SUPERCONDUCTORS

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Electrical resistivity measurements on bulk specimens of very-short-coherence-distance $[(l\xi_0)^{1/2} \approx 50$ Å$]$ type-II superconducting alloys suggest the presence of fluctuation superconductivity at temperatures up to at least $2T_c$, where T_c approximates the bulk superconducting transition temperature. Apparent magnetic field quenching of fluctuation superconductivity is observed up to 50 kG both above and below T_c.

In the present Letter[1] we report evidence for fluctuation superconductivity in bulk[2] type-II superconductors at temperatures T and applied magnetic fields H well outside the $(H$-$T)$ realm usually associated with superconducitvity. Figure 1 shows curves of reduced electrical resistivity $\rho(t)/\rho_0$ vs $t \equiv T/T_c$ typical of those measured for many different specimens of magnetically quasireversible,[3] extreme type-II superconductors. Here T_c approximates (within $\approx 5\%$) the bulk superconducting transition temperature and is presently defined as the temperature at which the steep linear portion of the $\rho(t)$ curve extrapolates to $\rho = 0$ at a measuring current density $J = 3$ A/cm^2. The measured ρ_0 value approximates (within $\approx 1\%$) the normal-state residual resistivity ρ_n.[4] The long high-temperature tails of Fig. 1 suggest the persistance of some weak form of superconductivity up to temperatures of at least $2T_c$. For the $Ti_{92}Ru_8$ specimen of Fig. 1, the application of a magnetic field $H = 49$ kG at $(T_c = 3.3) < T \leq 4.2$°K (the present upper temperature limit for magnetic field application) increases $\rho(t)/\rho_0$ to about 1.0, consistent with the assumption of a superconductive mechanism for the resistive rounding.

The curves of Fig. 1 and similar data (to be published) on about 20 different specimens of $Ti_{84}Mo_{16}$, $Ti_{75}V_{25}$, $Ti_{92}Fe_8$, and $Ti_{92}Os_8$ show that the high-temperature diminution of the resistivity is an effect common to all the extreme type-II superconductors examined and is not critically dependent upon measuring current density $3.5 \leq J \leq 14$ A/cm^2 (Fig. 1), mechanical surface polishing, surface-to-volume ratio S/V (Fig. 1), or variables of the specimen preparation such as annealing, quenching, or cold working. This suggests that the apparent weak superconductivity is not associated with the surface[5] but is a bulk property of extreme type-II superconductors which is not markedly influenced by dislocation density, or by preparation-sensitive[3] trace amounts of secondary-phase inclusions or precipitates.

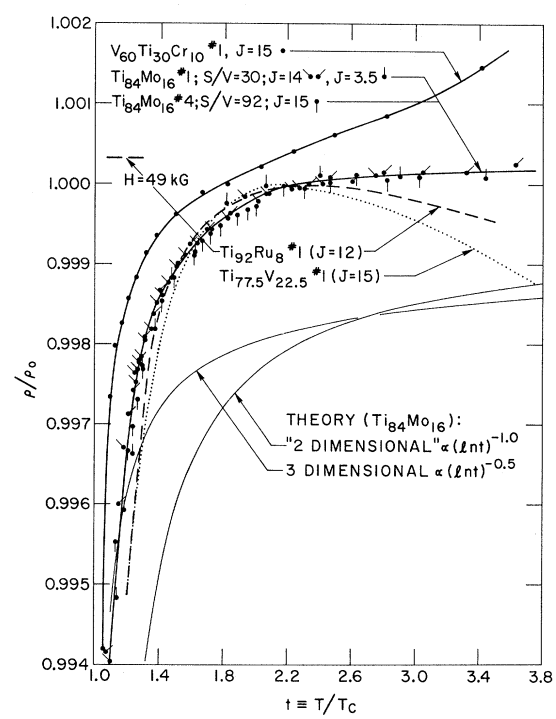

FIG. 1. Evidence for fluctuation superconductivity at high temperatures. The reduced electrical resistivity $\rho(t)/\rho_0$ in zero applied magnetic field (except where indicated) is plotted versus $t \equiv T/T_c$ for various bulk extreme type-II superconductors. The long high-temperature tails are attributed to fluctuation superconductivity. Here ρ_0 is a measured approximation to the normal-state resistivity, J is the measuring current density in A/cm^2, and S/V is the surface-to-volume ratio in cm^{-1}. For clarity data points are not shown for $Ti_{92}Ru_8$ No. 1 or $Ti_{77.5}V_{22.5}$ No. 1. Except for the flat-strip specimen $Ti_{84}Mo_{16}$ No. 4, the specimens here are hemispherically ended cylinders with length ≈ 21 mm, diam ≈ 1.5 mm. The two- and three-dimensional theoretical curves are explained just below Eq. (4) in the text. Measurements above 4.2°K were accomplished with an adjustable-heat-leak probe and a Cu-to-Au (0.07 at.% Fe) thermocouple thermometer as in Ref. 3. The T_c (°K), ρ_0 ($\mu\,\Omega$ cm), and $(l\xi_0)^{1/2}$ (Å) values are, respectively: $V_{60}Ti_{30}Cr_{10}$ No. 1, 5.7, 46, ≈ 59; $Ti_{84}Mo_{16}$ No. 1, 4.2, 100, 57; $Ti_{84}Mo_{16}$ No. 4, 4.1, 109, 55; $Ti_{77.5}V_{22.5}$ No. 1, 4.6, 147, 43; $Ti_{92}Ru_8$, 3.3, 142, ≈ 60.

Recent theories[6] of thermodynamic fluctuations in superconductors based on the Gor'kov[7] formulation of the Bardeen, Cooper, and Schrieffer (BCS)[8] theory or on the time-dependent Ginzburg-Landau equation[9] predict that for a three-dimensional[10] superconductor

$$\Delta\sigma_{f3}/\sigma_n = 0.037e^2/[\hbar\sigma_n(l\xi_0)^{1/2}(\ln t)^{1/2}] \quad (1a)$$

$$\approx 0.037e^3(\gamma T_c)^{1/2} \times(\hbar^3 k_B\gamma_0\sigma_n^3)^{-1/2}(\ln t)^{-1/2}, \quad (1b)$$

where $\Delta\sigma_f \equiv (\sigma-\sigma_n)$ is the extra conductivity in zero H due to fluctuations ("paraconductivity"[11]), σ_n (esu) is the normal-state conductivity,[12] l is the electron mean free path, ξ_0 is the BCS[8] coherence distance, $(l\xi_0)^{1/2}$ is proportional to the Ginzburg-Landau coherence distance[13] $\xi_G(T<T_c) \approx 0.85(l\xi_0)^{1/2}/(1-t)^{1/2}$, γ is the electronic specific-heat coefficient, and $\gamma_0 = 1.78$ is Euler's constant. Equation (1b) follows from the relationship[3]

$$(l\xi_0)^{1/2} \approx [\hbar\gamma_0 k_B\sigma_n/(e^2\gamma T_c)]^{1/2}. \quad (2)$$

For the two-dimensional case of a film of thickness d, theory[6] predicts

$$\Delta\sigma_{f2}/\sigma_n = e^2/(16\hbar d\sigma_n \ln t), \quad (3)$$

as at least approximately observed by Glover[14] and others in thin films for $1.001 \lesssim t \lesssim 2$. For the case $\Delta\sigma_f/\sigma_n \ll 1$ of present concern,

$$\Delta\sigma_f(t)/\sigma_n = -\Delta\rho_f(t)/\rho_n \equiv [\rho_n-\rho(t)]/\rho_n = 1-\rho(t)/\rho_n. \quad (4)$$

Figure 1 shows the theoretical three-demensional $\rho(t)/\rho_n$ as given by Eqs. (1b) and (4), utilizing the measured values of $\rho_0 = 100\ \mu\Omega\ \mathrm{cm} \approx \rho_n$ ($\gamma = 7500\ \mathrm{erg\ cm^{-3}\,°K^{-2}}$),[15] and $T_c = 4.2$°K for $Ti_{84}Mo_{16}$ No. 1. For comparison, the effect of replacing $(\ln t)^{-1/2}$ in Eq. (1b) with $(\ln t)^{-1}$ as in the two-dimensional Eq. (3) is also shown by the curve marked "two-dimensional." At $t \gtrsim 1.2$ the experimental $\rho(t)/\rho_0$ curve for $Ti_{84}Mo_{16}$ No. 1 is higher than the theoretical curve. However, this difference does not necessarily indicate experimental inconsistency with Eq. (1) since (a) the comparison relies on the approximate Eq. (2), and (b) the experimental values of $\rho(t)/\rho_0$ are probably upper limits to $\rho(t)/\rho_n$ since it is likely that $\rho_0 < \rho_n$.[16]

An important feature of the data of Fig. 1 is that the observed temperature limits T_w for the persistence of superconductivity for each binary alloy $A_{100-xa}B_{xa}$ of average percentage alloy concentration xa is always considerably larger than the temperature T_m, where T_m is defined as the maximum $T_c(x)$ in the system $A_{100-x}B_x$; e.g., $Ti_{84}Mo_{16}$ No. 1: $T_c = 4.2$°K, $T_m = 4.2$°K,[17] $T_w = 10$°K. [We take T_w to be the temperature of the peak[4] in $\rho(t)/\rho_0$ or, if there is no peak, as the temperature where $\rho(t)/\rho_0$ departs from near linearity with decreasing t.] The inequality $T_w > T_m$ tends to rule out explanations of the weak high-temperature superconductivity based only on macroscopic or statistical[18] spatial variation of x over domains of dimension $\gtrsim\xi_G$. However, such x variation might still influence the $\rho(t)/\rho_0$ curves especially at low $t \approx 1$ and in specimens for which dT_c/dx near xa is large.

Figure 2 shows evidence for fluctuation superconductivity in high magnetic fields below T_c but well above both the upper critical field H_{c2} and the sheath critical field H_s. Considering the upper portion of Fig. 2 for $H \perp J$, as H is increased from zero a J-dependent voltage $V \propto \rho$ is first observed in the mixed state (associated with flux flow), and then in the sheath region between H_{c2} and H_s.[19] Above H_s the voltage $V(H=H_s) \equiv V_s \propto \rho_s$ is balanced out with a six-dial microvolt potentiometer, and an $\approx 10^2$ increase in amplification al-

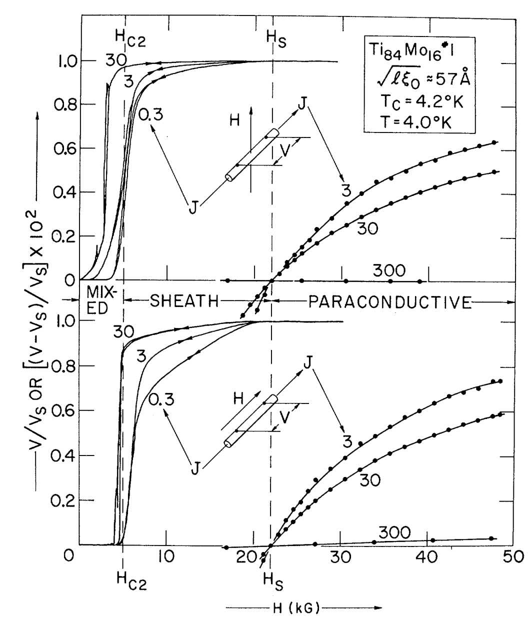

FIG. 2. Evidence for fluctuation superconductivity in high magnetic fields. The reduced resistive voltage $V(H)/V_s$ (left-hand side) or the reduced resistive difference voltage $[V(H)-V_s]/V_s \equiv P$ (right-hand side) for $Ti_{84}Mo_{16}$ No. 1 is plotted versus applied magnetic field H for various measuring current densities J (A/cm²). Here $V_s \equiv V(H=H_s)$ where H_s is the sheath critical field. The P vs H characteristics are attributed to the magnetic-field quenching of fluctuation superconductivity. [$P(H \parallel J$, $J = 300$ A/cm²) was measured at $T = 4.2$°K rather than $T = 4.0$°K.]

lows an x-y recorder display of a small difference voltage $[V(H)-V_s]$ {replotted for clarity in Fig. 2 as $[V(H)-V_s]/V_s=[\rho(H)-\rho_s]/\rho_s\equiv P$} which we attribute to the magnetic-field quenching of superconductive fluctuations in the paraconductive region ("magnetoparaconductance"[11]). Somewhat similar behavior is observed in the mixed, sheath, and paraconductive regions for $H\parallel J$ as shown in the lower portion of Fig. 2, except that flux-flow voltage is not observed in the mixed state, and the sheath effect is enhanced. The nearly flat $P(J=300\ \mathrm{A/cm^2})$ curves of Fig. 2 indicate high-J quenching[20] of the weak superconductivity and show that the ordinary normal-state magnetoresistance is relatively small in accord with a rough estimate[21] based on Kohler's rule. Log-log plots of dP/dH vs $(H-H_{c2})$ for the curves of Fig. 2 and similar curves for $Ti_{84}Mo_{16}$ No. 1 at $0.85\leq t\leq 0.98$, $2.5\leq(h\equiv H/H_{c2})\leq 21$, $P\ll 1$, $H\parallel J=30\ \mathrm{A/cm^2}$, yield superimposed straight lines which suggest

$$\Delta\sigma_{f3}(H)/\sigma_n=-\Delta\rho_{f3}/\rho_n=K(H-H_{c2})^{-n}, \qquad (5)$$

where K is independent of t and h, and with scatter in the data such that $0.6<n<1.0$.[22] Within the experimental uncertainty of $\approx$10% at $T=4.0°\mathrm{K}$ (Fig. 2) there is no change in n in the present high-h region for $J=3\ \mathrm{A/cm^2}$, $J=30\ \mathrm{A/cm^3}$, or for $H\parallel J$, $H\perp J$.[22]

For various extreme type-II superconducting alloys with $T_c<4.1°\mathrm{K}$ we have obtained isothermal magnetoparaconductive data[1] at $T_c<T\leq 4.2°\mathrm{K}$ and at $0<H\leq 50$ kG which are qualitatively similar to those of Fig. 2 at $T<T_c$ and $H_s<H<50$ kG. The isofield line determined by the 49-kG points for $Ti_{92}Ru_8$ is shown in Fig. 1. Magnetic field saturation of the paraconductance is not observed even at $t=1.3$ and $H=50$ kG.

Further paraconductive measurements on type-II superconductors are in progress to determine ρ_n accurately in high magnetic fields above 4.2°K so as to test the quantitative validity of Eq. (1). The present observations suggest the possibility of experimental investigation of superconductivity in domains of temperature and magnetic field well beyond those heretofore investigated, through the observation of paraconductivity in bulk short-coherence-distance superconductors with $T_c \gtrsim 15°\mathrm{K}$.

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[1]Preliminary accounts of this work have appeared: R. R. Hake, Bull. Am. Phys. Soc. 14, 731 (1969); Proceedings of the Naval Ship Research and Development Center Energy Conversion Colloquium, April, 1969 (to be published).

[2]Recently J. I. Gittleman, R. W. Cohen, and J. J. Hanak, Phys. Letters 29A, 56 (1969), have independently reported apparent zero H bulklike fluctuation effects in 1900- to 3200-Å "granular" In and Al films with $(l\xi_0)^{1/2}\approx 90$ Å, although D. G. Naugle and R. E. Glover, Phys. Letters 28A, 110 (1968) observe apparent two-dimensional fluctuation behavior in a 2200-Å "amorphous" Bi film with similar $(l\xi_0)^{1/2}$. More recently J. P. Gollub, M. R. Beasley, R. S. Newbower, and M. Tinkham, Phys. Rev. Letters 22, 1288 (1969), report apparent fluctuation-induced excess diamagnetism in pure bulk In at $1.0<t\lesssim 1.1$.

[3]R. R. Hake, Phys. Rev. 158, 356 (1967).

[4]The negative slopes of $\rho(t\geq 2.2)/\rho_0$ for the $Ti_{92}Ru_8$ and $Ti_{77.5}V_{22.5}$ specimens of Fig. 1 are characteristic of Group-IV rich bcc transition-metal alloys in the range $4.2<T<300°\mathrm{K}$; see e.g., R. R. Hake, D. H. Leslie, and T. G. Berlincourt, J. Phys. Chem. Solids 20, 177 (1961); T. S. Luhman, R. Taggart, and D. H. Polonis, Scripta Met. 2, 169 (1968). For such alloys ρ_0 is taken as the value of ρ at the peak in $\rho(t)$. For alloys which do not display such a peak, ρ_0 is taken as $\rho(T=10°\mathrm{K})$.

[5]V. L. Ginzburg, Phys. Letters 13, 101 (1964); W. Silvert, Physics 2, 153 (1966); F. R. Gamble and E. J. Shimshick, Phys. Letters 28A, 25 (1968). Enhanced fluctuation superconductivity at the specimen surface might also influence the high temperature $\rho(t)/\rho_0$.

[6]L. G. Aslamasov and A. I. Larkin, Fiz. Tverd. Tela 10, 1104 (1968) [translation: Soviet Phys.—Solid State 10, 875 (1968)]; A. Schmid, Z. Physik 215, 210 (1968); H. Schmidt, Z. Physik 216, 336 (1968); E. Abrahams and J. W. F. Woo, Phys. Letters 27A, 117 (1968); K. Maki, Progr. Theoret. Phys. (Kyoto) 40, 193 (1968); J. P. Hurault, Phys. Rev. 179, 494 (1969); K. D. Usadel, to be published. Equation (1a), suggested by Usadel, replaces the usual $\tau\equiv t-1$ with $\ln t$ as suggested by Abrahams and Woo, agrees with Hurault at low t where $\ln t\approx\tau$, and is smaller than expressions given by Aslamazov and Larkin and by Schmidt by a factor of $\approx\pi^{1/2}$. The latter difference is due to the omission of π^{-1} in Schmidt's Eq. (3).

[7]L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. 36, 1918 (1959) [translation: Soviet Phys.—JETP 9, 1364 (1959)], and Zh. Eksperim. i Teor. Fiz. 37, 1407 (1959) [translation: Soviet Phys.—JETP 10, 998 (1960)].

[8]J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

[9]A. Schmid, Physik Kondensierten Materie 5, 302 (1966); E. Abrahams and T. Tsuneto, Phys. Rev. 152,

416 (1966).

[10]Here "N dimensional" means N dimensions greater than $\xi_G(T>T_c)\approx 0.85(l\xi_0)^{0.5}/(t-1)^{0.5}$.

[11]The terms "paraconductivity" and "magnetoparaconductivity" were suggested, respectively, by R. A. Ferrell, Batsheva Lecture Notes, 1968 (unpublished), and S. J. Williamson.

[12]In experimentally convenient units of $\sigma_n(\mathrm{ohm}^{-1}\,\mathrm{cm}^{-1})$ and $\gamma(\mathrm{erg\,cm^{-3}\,{}^\circ K^{-2}})$, Eqs. (1a) and (1b) become $\Delta\sigma_{f3}/\sigma_n = 8.9\times10^{-6}/[\sigma_n(l\xi_0)^{1/2}(\ln t)^{1/2}]\approx 8.9(\gamma T_c)^{1/2}/[\sigma_n^{3/2}(\ln t)^{1/2}]$; and Eq. (2) becomes $(\xi_0 l)^{1/2}=10^{-6}(\sigma_n/\gamma T_c)^{1/2}$.

[13]See e.g., P. G. de Gennes, Superconductivity of Metals and Alloys (W. A. Benjamin, Inc., New York, 1966), p. 225.

[14]R. E. Glover, Phys. Letters 25A, 542 (1967), obtains agreement with the more usual form of Eq. (3), with $\ln t$ replaced by $\tau=t-1$, but the two forms differ by <5% at $t\le 1.1$ and <16% at $t\le 1.4$.

[15]L. J. Barnes and R. R. Hake, Phys. Rev. 153, 435 (1967); see also Ref. 3.

[16]This conjecture can eventually be checked by the application of large H above 4.2°K.

[17]A. K. Sinha, J. Phys. Chem. Solids 29, 749 (1968).

[18]A. Calverly and A. C. Rose-Innes, Proc. Roy. Soc. (London), Ser. A 255, 267 (1960); R. R. Hake, Phys. Rev. 123, 1986 (1961); J. F. Cochran, Ann. Phys. (N.Y.) 19, 186 (1962); B. B. Goodman, J. Phys. Radium 23, 704 (1962).

[19]Here H_{c2} is defined as the field at which the steep linear portion of $V(J=3\ \mathrm{A/cm^2},\ J\parallel H)/V_s$ extrapolates to zero; and H_s is defined to be about 5% higher than the field at which $[V(H)-V_s]$ at $(J=3\ \mathrm{A/cm^2},\ J\parallel H)$ bends sharply towards the H axis (this sharp bend is "off scale" in Fig. 2).

[20]Heating at the current contacts may occur at $J=300\ \mathrm{A/cm^2}$ but since ρ is constant to within ≈8% for $10<T<300$°K such heating should, according to Kohler's rule, have little effect on the ordinary normal-state magnetoresistance.

[21]A merely suggestive application of Kohler's rule to previous data on pure polycrystalline Ti by R. R. Hake, T. G. Berlincourt, and D. H. Leslie, Phys. Rev. 127, 170 (1962), yields an ordinary normal-state magnetoresistance of $\Delta\rho(H=50\ \mathrm{kG})/\rho(H=0)\approx10^{-6}$ for a hypothetical "pure" Ti with $\rho_n=10^{-4}\ \Omega$ cm as for $Ti_{84}Mo_{16}$.

[22]A comparison of our data with recent theories of high-H paraconductivity by K. Maki, Progr. Theoret. Phys. (Kyoto) 39, 897 (1968), and to be published; L. W. Gruenberg, Bull. Am. Phys. Soc. 14, 420 (1969), and to be published; K. D. Usadel, to be published; and H. J. Mikeska and H. Schmidt, to be published.

NEW EFFECT IN THE ELECTRON-PHONON RESISTIVITY OF DILUTE METAL ALLOYS

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The electron-phonon contribution to the resistivity of a dilute metal alloy at low temperatures is drastically different from that of the ideally pure host metal if the conduction-electron cross section for impurity scattering varies with energy on a scale comparable with or less than the Debye energy of the host metal. Experimentally the effect should be of particular importance for magnetic or nearly magnetic transitional impurities in appropriate nontransitional hosts.

Consider an ideally pure metal A in which is dissolved a small concentration c of a dissimilar metal B. Denote by $\rho_{\mathrm{ep}}{}^0(T)$ the electron-phonon (el-ph) resistivity of the pure metal A at temperature T and by $\tau_0(\epsilon_{\vec{k}})=\tau_0(\epsilon_{\vec{k}};c,T)$ the conduction-electron relaxation time for elastic scattering from the B impurities in the dilute binary alloy. The conduction-electron energy associated with the momentum state $\hbar\vec{k}$ is $\epsilon_{\vec{k}}$. In this Letter we point out that the resistivity which results from el-ph scattering in the alloy, $\rho_{\mathrm{ep}}(T,c)$, is appreciably different from $\rho_{\mathrm{ep}}{}^0(T)$, i.e.,

$$[\rho_{\mathrm{ep}}(T,c)-\rho_{\mathrm{ep}}{}^0(T)]/\rho_{\mathrm{ep}}{}^0(T)>1,$$

if, in the region of the Fermi energy ϵ_{F}, $\tau_0(\epsilon_{\vec{k}})$ varies with $\epsilon_{\vec{k}}$ on a scale comparable with or less than the Debye energy $\hbar\omega_{\mathrm{D}}$ of the host metal. In the latter situation the difference $\rho_{\mathrm{ep}}(T,c)-\rho_{\mathrm{ep}}{}^0(T)$ is a direct consequence of the inelasticity of the el-ph scattering event. For spherical energy bands coupled to an isotropic acoustic-phonon field we obtain the simple result

$$\rho_{\mathrm{ep}}(T,c)=\rho_{\mathrm{ep}}{}^0(T)[1+a^2] \qquad (1)$$

for temperatures sufficiently low that $\rho_0\gg\rho_{\mathrm{ep}}{}^0(T)$, that is, $T\ll T_0(c)$, where $\rho_{\mathrm{ep}}{}^0(T_0)\equiv\rho_0$. Here ρ_0 denotes the impurity resistivity $m/ne^2\tau_0(\epsilon_{\mathrm{F}})$, and

$$a=\hbar\omega_{\mathrm{F}}[\partial\ln\tau_0(\epsilon_k)/\partial\epsilon_k]_{\epsilon_k=\epsilon_{\mathrm{F}}}, \qquad (2)$$

where $\omega_{\mathrm{F}}=sk_{\mathrm{F}}$, s denotes the isotropic sound velocity, k_{F} the Fermi wave vector, and m, n, and e the electronic mass, number density, and charge, respectively. The quantities a and ρ_0