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Thermoelectric flux in superconducting rings

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Definitive measurements by Van Harlingen *et al.* in 1980 show that the flux induced by a temperature difference across the two junctions of a Pb-In ring exceeds theoretical expectation by a factor, $\sim 10^5$. The theory fails owing to (mis)use of a Boltzmann transport equation to describe the thermal diffusion of quasiparticle excitations, a treatment which violates electron conservation. An electron-conserving transport theory is developed and explains the data. [S0163-1829(97)15717-4]

I. INTRODUCTION

It has been known for sixty years that thermoelectric effects—Seebeck, Peltier, and Thomson—are absent in superconductors.[1,2] Nevertheless it was noticed that the ''normal electrons'' of a two-fluid model could be driven out of equilibrium by a temperature gradient, and so cause an observable phenomenon.[3] During 1974 Garland and Van Harlingen[4] and, independently, Gal'perin *et al.*[5] proposed that imposing a temperature difference across the junctions of a superconducting, bimetallic ring should create an unquantized magnetic flux through the ring. The anticipated size of the effect is near the sensitivity limit of SQUID technology.

The origin of a thermoelectric flux can be easily understood by considering a Pb-In ring as shown in Fig. 1. The critical temperature, $T_c = 7.2$ K, of Pb is sufficiently high that one can neglect any quasiparticle excitations (in the Pb) when the ring is kept slightly below the T_c of In, 3.4 K. However, an imposed temperature gradient in the In will generate a bulk thermal diffusion (electric) current density,

$$\vec{j}_d = \alpha_s \nabla T. \tag{1}$$

Calculation of the transport coefficient, α_s, is the focus of the present study. Now the Meissner effect in the interior of In requires that the total current density be zero. Accordingly there must be a compensating supercurrent, $\vec{j}_s$, so that

$$\vec{j}_s + \vec{j}_d = 0. \tag{2}$$

Naturally, this equation does not apply within a London penetration depth of the surface, where the current generating the thermoelectric flux is found. In the London two-fluid model the supercurrent is[6]

$$\vec{j}_s = -\frac{n_s e^2}{mc}\vec{A}, \tag{3}$$

where n_s is the density of the superconducting electrons. On combining Eqs. (1)–(3) the vector potential along an interior path (where there is no magnetic field or current) is

$$\vec{A} = \frac{mc\,\alpha_s}{n_s e^2}\nabla T. \tag{4}$$

The thermoelectric flux Φ is of course the line integral of $\vec{A}$. However, since α_s in Pb is negligible,

$$\Phi(T) = \frac{mc}{e^2}\int_{T_0}^{T}\frac{\alpha_s}{n_s}dT', \tag{5}$$

the path having been taken counterclockwise from T_0 to T through the In side of Fig. 1.

Numerical evaluation of Eq. (5) will be given below. The conventional theory predicts that the flux, Φ, expected from a $\Delta T \sim 10$ mK near T_c is $\sim 10^{-3}\Phi_0$, where $\Phi_0 = hc/2e$, the flux quantum. Such a small value indicates that isolation of the superconducting ring from stray fields is of paramount importance.[7]

Van Harlingen and Garland[8] achieved the required sensitivity and isolation by adopting the toroidal geometry shown in Fig. 2. The axis of symmetry coincides with the axis of a Pb cylinder, which is capped at the ends by In plates and surrounded by a 0.25 mm thick In cylinder, 7 mm in diameter and 4 cm long. The thermoelectric flux ''circulates'' through the annular cavity between the Pb and In cylinders. A Nb coil of six to ten turns was threaded through the hole along the axis of the Pb post and wrapped tightly (at equally spaced azimuthal angles) around the exterior of the In cylin-

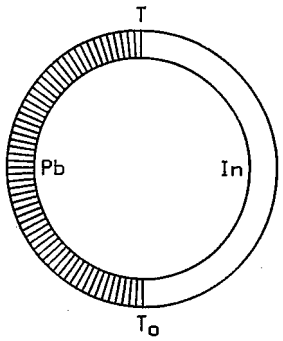

FIG. 1. A small temperature difference applied to the junctions of a Pb-In ring, kept below T_c of In, drives the In quasiparticles out of equilibrium. On account of the Meissner effect, the bulk current density must be zero, so a supercurrent (proportional to $\vec{A}$) cancels the diffusion current. An unquantized flux through the ring (equal to the line integral of $\vec{A}$) is generated by a current in the London penetration depth of the ring's inner surface.

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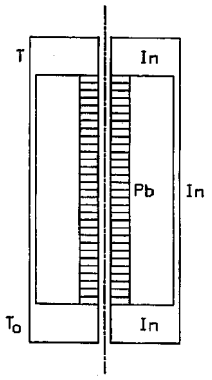

FIG. 2. The Pb-In ''rings'' employed by Van Harlingen *et al.* have toroidal geometry. The thermoelectric flux circulates through the annular space between the Pb rod and the In cylinder, and arises from currents in the London penetration depth on the outer surface of the Pb rod and the inner surface of the In cylinder.

der. The coil was then coupled to a SQUID galvanometer. The toroidal design proved to be free from temperature dependent stray fields, even when 10^4 flux quanta were deliberately frozen in the primary circuit of the flux transformer.

Typical data for $\Phi(T)$ are shown in Fig. 3. T_0 was fixed at T_c-7 mK, and T was raised in 50 μK steps to T_c-1 mK. The observed thermoelectric flux of ~ 200 quanta exceeded theoretical predictions by more than 10^5. Data from seven toroidal samples were published by Van Harlingen *et al.*[9] It is convenient to display $d\Phi/dT$ by a log-log plot, as in Fig. 4. The theoretical curve based on conventional treatments[5,10] is also shown. The discrepancy between theory and experiment is a factor ranging from 10^5 to 10^6.

The foregoing serious shortcoming of elementary transport theory in the superconducting state has defied explana-

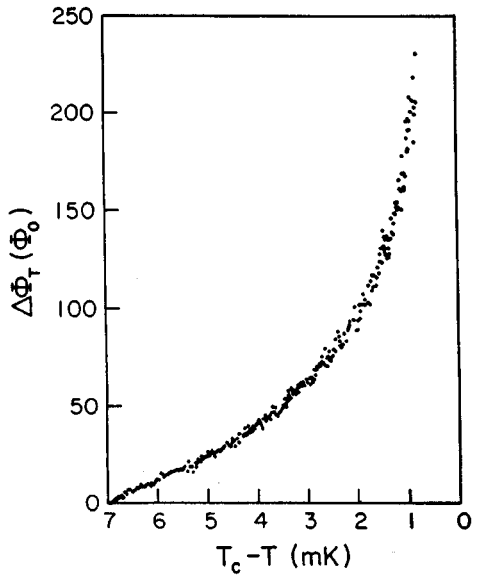

FIG. 3. Thermoelectric flux (in flux quanta units) measured by Van Harlingen *et al.* in a toroidal Pb-In sample below the T_c of In. The temperature of one junction was fixed at T_c-7 mK. The temperature of the other junction was increased in 50 μK steps toward T_c.

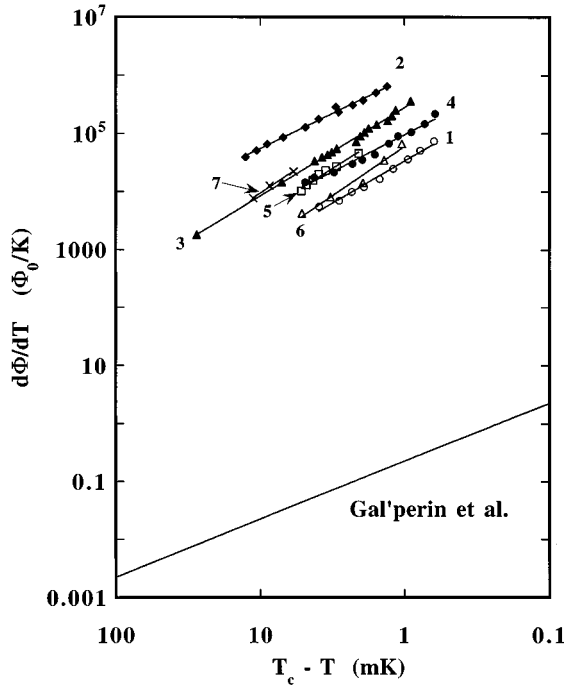

FIG. 4. Thermoelectric flux, $d\Phi/dT$, measured by Van Harlingen *et al.* on seven Pb-In toroidal samples. The theoretical prediction of Gal'perin *et al.*, based on solution of a quasiparticle transport equation (due to Bardeen *et al.*) is also shown.

tion for eighteen years. To forestall any concern regarding the In cylinders, which were of five 9s purity and typically had residual resistivity ratios of $\sim 10^4$, Van Harlingen *et al.* studied an eighth toroidal specimen having an In post (instead of a Pb post).[8,9] The thermoelectric flux was then zero, the expected behavior for an all In circuit devoid of inhomogeneities.

II. REVIEW OF THE CONVENTIONAL THEORY

It is necessary to recapitulate some statistical aspects of the Bardeen-Cooper-Schrieffer (BCS) theory.[11] Any equilibrium, or nonequilibrium ensemble is a collection of BCS Fock-space wave functions:

$$\Psi=\prod \left\{ \begin{array}{l} (v_k-u_k c^{\dagger}_{\vec{k}\uparrow} c^{\dagger}_{-\vec{k}\downarrow}) \\ c^{\dagger}_{-\vec{k}\downarrow} \\ c^{\dagger}_{\vec{k}\uparrow} \\ (u_k+v_k c^{\dagger}_{\vec{k}\uparrow} c^{\dagger}_{-\vec{k}\downarrow}) \end{array} \right\} \Psi_{\text{vacuum}}. \tag{6}$$

We refer to the set of four choices for a given $\vec{k}$ as a ''quartet.'' Each of the four operators is chosen with a statistical probability: f_{1k}, f_{2k}, f_{3k}, or f_{4k} (from bottom to top). Of course,

$$f_{1k}+f_{2k}+f_{3k}+f_{4k}=1. \tag{7}$$

$u_k(T)$ and $v_k(T)$ depend on temperature, and are given by

$$u_k^2=\frac{1}{2}\left(1+\frac{\epsilon_k}{E_k}\right), \tag{8}$$

$$v_k^2=\frac{1}{2}\left(1-\frac{\epsilon_k}{E_k}\right)$$

where $\epsilon_k=(\hbar^2k^2/2m)-\epsilon_F$ is the one-electron energy measured with respect to the Fermi level, ϵ_F, and

$$E_k=[\Delta(T)^2+\epsilon_k^2]^{1/2}. \tag{9}$$

In equilibrium the probabilities, f_{jk}, are given by

$$f_{1k}=(1-f_k)^2,$$
$$f_{2k}=f_{3k}=f_k(1-f_k), \tag{10}$$
$$f_{4k}=f_k^2,$$

where

$$f_k=(e^{\beta E_k}+1)^{-1}, \tag{11}$$

and $\beta=1/k_BT$. f_k is the equilibrium probability that a Bogoliubov-Valatin (BV) excitation for spin-up (or spin-down) occurs,[12,13] i.e., the quartet is excited from level 1 to 2 (or 3). f_k^2 is the equilibrium probability that both BV excitations occur. We will denote non-equilibrium BV excitation probabilities by $\tilde{f}_k$. (In general we would need a spin index; but for the problem at hand $\tilde{f}_k$ for spin up and down are the same.)

The theory of BV quasiparticle transport was developed by Bardeen, Rickayzen, and Tewordt (BRT) and applied to the thermal conductivity of a superconductor.[14] BRT found the expected result for the group velocity of a BV excitation:

$$\dot{\vec{r}}=\frac{1}{\hbar}\nabla_k E_k=\frac{\epsilon_k}{E_k}\frac{\hbar\vec{k}}{m}. \tag{12}$$

It should be noticed that $\dot{\vec{r}}_k$ changes sign when ϵ_k becomes negative. When Δ varies with position as, for example, in the case of a temperature gradient, a BV quasiparticle will experience an acceleration. $\dot{\vec{k}}$ can be obtained from the condition $dE_k/dt=0$. Accordingly, with $\Delta=\Delta[T(\vec{r})]$,

$$\frac{dE_k}{dt}=(\nabla_{\vec{r}}E_k)\cdot\dot{\vec{r}}+(\nabla_{\vec{k}}E_k)\cdot\dot{\vec{k}}=0. \tag{13}$$

On using Eq. (12), one can solve for $\dot{\vec{k}}$:

$$\hbar\dot{\vec{k}}=-\nabla_{\vec{r}}E_k. \tag{14}$$

Since the dominant scattering mechanism (caused by impurities) is elastic, the collision term of the Boltzmann equation will be

$$\left(\frac{\partial\tilde{f}_k}{\partial t}\right)_{\text{coll.}}=-\frac{\tilde{f}_k-f_k}{\tau_s}, \tag{15}$$

where τ_s is the relaxation time in the superconducting state. The solution of the transport equation is then

$$\tilde{f}_k=f_k-\tau_s(\dot{\vec{r}}\cdot\nabla_{\vec{r}}f_k+\dot{\vec{k}}\cdot\nabla_{\vec{k}}f_k). \tag{16}$$

Observe that the equilibrium distribution, f_k, appears in the $\dot{\vec{r}}$ and $\dot{\vec{k}}$ terms because both terms are already proportional to ∇T (which is sufficient for linear response).

One can easily verify that a cancellation occurs for two of the terms which arise in Eq. (16). The $\nabla_{\vec{r}}f_k$ yields a ∇T term from the explicit dependence on $T(\vec{r})$ in Eq. (11), since $\beta=1/k_BT$. However, a second ∇T terms arises from the implicit dependence of E on T through $\Delta(T)$. This latter term is cancelled by the $\dot{\vec{k}}$ term of Eq. (16) when Eq. (12) is utilized. The steady-state solution for the quasiparticle distribution function is therefore

$$\tilde{f}_k=f_k-\tau_s\left(\frac{\beta\hbar\epsilon_k}{mT}\right)f_k(1-f_k)\vec{k}\cdot\nabla T. \tag{17}$$

Equation (12) has been used to eliminate $\dot{\vec{r}}$; and the factor $f_k(1-f_k)$, arises from the derivative of Eq. (11). The relaxation time τ_s is related to the relaxation time τ_n for impurity scattering in the normal state. For quasiparticle transitions from $\vec{k}$ to $\vec{k}'$,

$$\frac{1}{\tau_s}=\left|\frac{E_k}{\epsilon_k}\right|(u_ku_{k'}-v_kv_{k'})^2\frac{1}{\tau_n}. \tag{18}$$

The absolute-value factor is the ratio of the BCS to normal density of states. The term involving the u's and v's, from Eq. (8), is the BCS coherence factor for transitions which do not flip an electron spin.[11] For elastic scattering $u_k=u_{k'}$ and $v_k=v_{k'}$, so from Eq. (8) the coherence factor is $(\epsilon_k/E_k)^2$. The steady-state distribution, Eq. (17), can now be written in a final form which depends on the normal-state relaxation time, τ_n,

$$\tilde{f}_k=f_k-\frac{\hbar\tau_nE_k\epsilon_k}{mk_BT^2|\epsilon_k|}f_k(1-f_k)\vec{k}\cdot\nabla T. \tag{19}$$

This solution was used by BRT to evaluate the energy flux in order to find the thermal conductivity in the superconducting state.[14] Here we employ Eq. (19) to calculate the electric current and, thereby, deduce the thermal diffusion current, $\vec{j}_d$, obtained by Gal'perin *et al.*[5,10] (which leads to the small $d\Phi/dT$ shown in Fig. 4).

The current is merely the sum of Eq. (19) multiplied by, $-2e\hbar\vec{k}/m$; the factor of 2 arises from the two spin states.

$$\vec{j}_d=-\frac{2e\hbar}{m}\sum_{\vec{k}}(\tilde{f}_k-f_k)\vec{k}. \tag{20}$$

The sum can be converted to an integral; and we adopt the traditional approximation that the density of states, $N(0)$ per spin, is constant in the interval $[-\hbar\omega_D,\hbar\omega_D]$. Accordingly,

$$\vec{j}_d=\frac{4e\tau_nN(0)}{3mk_BT^2}\nabla T\int_{-\hbar\omega_D}^{\hbar\omega_D}(\epsilon+\epsilon_F)f(1-f)\frac{E\epsilon}{|\epsilon|}d\epsilon. \tag{21}$$

We have omitted the $\vec{k}$ subscripts since ϵ, E, and f depend only on the magnitude of $\vec{k}$. $\vec{j}_d$ is parallel to ∇T; so the factor, 1/3, arises from the average of $\cos^2\theta$ over solid angle (where θ is the angle between $\vec{k}$ and ∇T). $\hbar^2k^2/2m$ has been replaced by $(\epsilon+\epsilon_F)$; and f is given by Eq. (11). The factor

in the integrand to the right of $(\epsilon+\epsilon_F)$ is odd, so the ϵ_F term contributes nil. The integral can now be converted from ϵ to E on using (for $\epsilon \geqslant 0$):

$$d\epsilon = \frac{d\epsilon}{dE} dE = \frac{E}{|\epsilon|} dE. \tag{22}$$

On account of the symmetry of the integral,

$$\vec{j}_d = \frac{8e\tau_n N(0)}{3mk_B T^2} \nabla T \int_{\Delta}^{\hbar\omega_D} E^2 f(1-f) dE. \tag{23}$$

Since $f(1-f)$ is negligible beyond the upper limit, one can replace $\hbar\omega_D$ by ∞. Furthermore,

$$N(0) = \frac{3n}{4\epsilon_F}, \tag{24}$$

where n is the electron density. With $x=\beta E$, it follows that the transport coefficient α_s of Eq. (1) is

$$\alpha_s = \frac{ne\pi^2 k_B^2 T\tau_n}{3m\epsilon_F} G(\Delta), \tag{25}$$

where

$$G(\Delta) = \frac{3}{2\pi^2} \int_{\beta\Delta}^{\infty} \left[\frac{x}{\cosh(\frac{1}{2}x)} \right]^2 dx. \tag{26}$$

Near T_c, $\beta\Delta \ll 1$; so $G \simeq 1-[(\beta\Delta)^3/2\pi^2] \approx 1$. For electron conduction, the thermal diffusion current is parallel to ∇T and positive.

III. SUPERCURRENT AND THE THERMOELECTRIC FLUX

The induced thermoelectric flux, Φ (or its derivative $d\Phi/dT$), depends on both α_s and n_s according to Eqs. (3)–(5). The density n_s of superconducting electrons can be defined by BCS theory. The Ginzburg-Landau diamagnetic current is[15]

$$\vec{j}_s = -\frac{2e^2}{mc} |\Psi|^2 \vec{A}, \tag{27}$$

which has the form of Eq. (3), so $n_s = 2|\Psi|^2$. Ψ is the Ginzburg-Landau order parameter and is proportional to the BCS gap parameter, Δ, provided T is near T_c:[15]

$$\Psi(T) = \left[\frac{7\zeta(3)n}{8(\pi k_B T_c)^2} \right]^{1/2} \Delta(T). \tag{28}$$

ζ is the Riemann zeta function; $\zeta(3)=1.202$. The temperature dependence of $\Delta(T)$ close to T_c is[15]

$$\Delta(T) = \pi k_B T_c \left[\frac{8}{7\zeta(3)} \left(1 - \frac{T}{T_c} \right) \right]^{1/2}. \tag{29}$$

From Eqs. (28) and (29) it follows that

$$n_s = 2n \left(1 - \frac{T}{T_c} \right). \tag{30}$$

All of the parameters needed for the flux Φ, Eq. (5), are now at hand. From Eqs. (25) and (30), and on taking $G=1$,

$$\frac{d\Phi}{dT} = \frac{\pi k_B^2 T_c \tau_n}{6\hbar\epsilon_F [1-(T/T_c)]} \Phi_0 \tag{31}$$

(Φ_0 is the flux quantum.) The room temperature resistivity of In is 8.75 $\mu\Omega$ cm, so the low temperature relaxation time, on assuming a residual resistivity ratio $\sim 8\times 10^3$, is

$$\tau_n \sim 2.8\times 10^{-11} \text{ s}. \tag{32}$$

Accordingly, with $\epsilon_F = 8.6$ eV and $T_c = 3.4$ K, the flux derivative (when T is just below T_c) is

$$\frac{d\Phi}{dT} = 6.5\times 10^{-5} [1-(T/T_c)]^{-1} \Phi_0 K^{-1}. \tag{33}$$

This theoretical prediction, equivalent to that of Gal'perin *et al.*[5,10] is shown in Fig. 4. Not only is the magnitude of Eq. (33) smaller than the data by 5 to 6 orders of magnitude, but the temperature dependence, $[1-(T/T_c)]^{-1}$, differs from that observed, which approximates a power law, ~ -1.5.

We are forced to conclude that the BRT transport theory is fundamentally incorrect. It is surprising that an error so flagrant could survive uncorrected for many years. The mistake must be a very deep one. What is perhaps most perplexing is that the unique solution, Eq. (19), of the quasiparticle transport equation can imply a reasonable energy flux and at the same time yield so faulty a diffusion current. Apparently a compensating error occurs in BRT's thermal conductivity study.

IV. ELECTRON-CONSERVING TRANSPORT THEORY

There is no novelty in emphasizing that transport equations must respect the conservation laws. Ordinarily such concerns arise in a treatment of collision terms by the relaxation-time approximation. Particles must be conserved locally whether they be neutral or ionized atoms,[16] electrons,[17] or spin-polarized ^{3}He.[18] This difficulty does not appear in the present problem since BV quasiparticles which scatter elastically do indeed leave the local electron density unchanged.

Nevertheless, there is a very serious problem with BV quasiparticles. For example, the BV creation operator which takes the quartet, $\vec{k}$, from level 1 to level 2 in Eq. (6) is

$$\eta_{\vec{k}\uparrow}^{\dagger} = u_k c_{\vec{k}\uparrow}^{\dagger} - v_k c_{-\vec{k}\downarrow}. \tag{34}$$

Excitation of such a quasiparticle involves both electron creation and annihilation. The relative amplitudes depend on position (when there is a temperature gradient) since, from Eqs. (8) and (9), these amplitudes depend on $\Delta[T(\vec{r})]$. Consequently, when a BV wave packet travels with the velocity given by Eq. (12), the total number of electrons associated with the Fock-space wave function, Eq. (6), changes continuously. Similarly, the amplitudes in Eq. (34) depend on $\vec{k}$ since E_k, Eq. (9), depends on $\epsilon(\vec{k})$. Accordingly, electron conservation is also violated when a BV wave packet experiences the acceleration given in Eq. (14).

The flow terms of the Boltzmann equation are based on strict conservation of invariable objects. In a superconductor only electrons qualify as appropriate particles for a transport equation. The fact that BCS theory employs a grand canonical ensemble is not relevant to this particular issue. Each (many-electron) system of the ensemble obeys strict local conservation of electrons. An ensemble average of systems, each of which obeys local electron conservation, will also exhibit local conservation. There is no infinite set of ''umbilical cords'' which connect an electron reservoir to every volume element, $d^3r d^4k$, in phase space in order to enforce conservation rules. Once a grand ensemble is established, all umbilical cords are severed, and each system of the ensemble evolves ''on its own.''

The foregoing mandate requires the introduction of new distributions, $\tilde{g}_{k\uparrow}$ and $\tilde{g}_{-k\downarrow}$, to describe electrons excited out of level 1 of each quartet. From Eq. (6),

$$\tilde{g}_{k\uparrow}=(\tilde{f}_{k1}v_k^2+\tilde{f}_{2k}+\tilde{f}_{4k}u_k^2)-v_k^2, \tag{35}$$

and similarly,

$$\tilde{g}_{-k\downarrow}=(\tilde{f}_{k1}v_k^2+\tilde{f}_{3k}+\tilde{f}_{4k}u_k^2)-v_k^2, \tag{36}$$

since the number of, say, $\vec{k}\uparrow$ electrons excited is the $\vec{k}\uparrow$ total in the quartet minus the number there would be if $f_{k1}=1$ and $f_{k2}=f_{k3}=f_{k4}=0$. $\{u_k^2\}$ and $\{v_k^2\}$ in Eqs. (35) and (36) are the equilibrium values given by Eqs. (8) and (9) at the local temperature, i.e., for $\Delta=\Delta[T(\vec{r})]$. Now, it is of particular interest to examine the equilibrium values, $g_{k\uparrow}$ and $g_{-k\downarrow}$, of Eqs. (35) and (36). One merely replaces $\tilde{f}_{jk}$ by f_{jk} from Eq. (10) to find that

$$g_{k\uparrow}=g_{-k\downarrow}=f_k(1-2v_k^2). \tag{37}$$

Then, from Eq. (8), the equilibrium g's are

$$g_{k\uparrow}=g_{-k\downarrow}=\frac{\epsilon_k}{E_k}f_k. \tag{38}$$

f_k is of course just the equilibrium probability of a BV excitation, Eq. (11). These equilibrium g's will be used in the flow terms of the (new) transport equation for the same reason invoked in writing Eq. (16)—the flow terms are automatically linear in ∇T. The correct (steady state) Boltzmann equation for spin-up electrons is, therefore,

$$\left(\frac{d\tilde{g}_{k\uparrow}}{dt}\right)=\left(\frac{\partial\tilde{g}_{k\uparrow}}{\partial t}\right)_{\text{coll.}}-\dot{\vec{r}}\cdot\nabla_{\vec{r}}g_{k\uparrow}-\dot{\vec{k}}\cdot\nabla_{\vec{k}}g_{k\uparrow}=0. \tag{39}$$

The main issue remaining is the collision term for $\tilde{g}_{k\uparrow}$. We will show that

$$\left(\frac{\partial\tilde{g}_{k\uparrow}}{\partial t}\right)_{\text{coll.}}=-\frac{\tilde{g}_{k\uparrow}-g_{k\uparrow}}{\tau_s}, \tag{40}$$

where τ_s is the relaxation time, Eq. (18), derived by BRT for the quasiparticle distribution, $\tilde{f}_{k\uparrow}$. It is true, as already pointed out, that elastic scattering (by impurities) of BV quasiparticles conserves electrons, but that alone is not sufficient since the relations, Eqs. (35) and (36), between the $\tilde{g}$'s and $\tilde{f}$'s are complicated. It is necessary to employ in Eqs. (35) and (36) the nonequilibrium analogs of Eq. (10):

$$\begin{aligned}\tilde{f}_{k4}&=\tilde{f}_{k\uparrow}\tilde{f}_{-k\downarrow},\\ \tilde{f}_{k3}&=(1-\tilde{f}_{k\uparrow})\tilde{f}_{-k\downarrow},\\ \tilde{f}_{k2}&=\tilde{f}_{k\uparrow}(1-\tilde{f}_{-k\downarrow}),\\ \tilde{f}_{k1}&=(1-\tilde{f}_{k\uparrow})(1-\tilde{f}_{-k\downarrow}).\end{aligned} \tag{41}$$

One finds readily

$$\begin{aligned}\tilde{g}_{k\uparrow}&=u_k^2\tilde{f}_{k\uparrow}-v_k^2\tilde{f}_{-k\downarrow},\\ \tilde{g}_{-k\downarrow}&=u_k^2\tilde{f}_{-k\downarrow}-v_k^2\tilde{f}_{k\uparrow}.\end{aligned} \tag{42}$$

The inverted relations are the ones needed:

$$\begin{aligned}\tilde{f}_{k\uparrow}&=\frac{u_k^2\tilde{g}_{k\uparrow}+v_k^2\tilde{g}_{-k\downarrow}}{u_k^2-v_k^2},\\ \tilde{f}_{-k\downarrow}&=\frac{v_k^2\tilde{g}_{k\uparrow}+u_k^2\tilde{g}_{-k\downarrow}}{u_k^2-v_k^2}.\end{aligned} \tag{43}$$

The important observation is that the flow terms of Eq. (39) create deviations from equilibrium which are odd in $\vec{k}$, that is,

$$\delta\tilde{g}_{k\uparrow}=-\delta\tilde{g}_{-k\downarrow}. \tag{44}$$

This relation follows from the fact that $\dot{\vec{r}}$, Eq. (12), is odd in $\vec{k}$ and also that $\nabla_{\vec{k}}$ in Eq. (39) is operating on a function, Eq. (38), which is even in $\vec{k}$. Therefore, when small variations of Eq. (43) are considered, and Eq. (44) is employed,

$$\delta\tilde{f}_{k\uparrow}=\delta\tilde{g}_{k\uparrow},\quad \delta\tilde{f}_{-k\downarrow}=\delta\tilde{g}_{-k\downarrow}. \tag{45}$$

It follows immediately that the collision terms, Eqs. (15) and (40), have the same relaxation time, τ_s, i.e., Eq. (18). It should be appreciated that Eqs. (44) and (45) do not hold in general, but apply only to deviations (from equilibrium) that arise from a temperature gradient. This caveat is similar to one noted first by Peierls:[19] A relaxation time approximation can be used for impurity scattering in (the normal state of) metals only when the nonequilibrium distortion of the distribution involves spherical harmonics having but one value of l, typically $l=1$. (Ultrasonic attenuation requires a different relaxation time, τ_2, i.e., for $l=2$.)

The solution of the electron-conserving transport equation can now be written. Eqs. (38)–(40) provide, after dropping the spin index (since no spin dependence arises),

$$\tilde{g}_k=g_k-\tau_s\left[\dot{\vec{r}}\cdot\nabla_{\vec{r}}\left(\frac{\epsilon_k}{E_k}f_k\right)+\dot{\vec{k}}\cdot\nabla_{\vec{k}}\left(\frac{\epsilon_k}{E_k}f_k\right)\right]. \tag{46}$$

The flow terms differ from Eq. (16) only by the extra factor of ϵ_k/E_k. After carrying out the differentiations, one obtains a revised version of Eq. (17):

$$\tilde{g}_k=g_k-\frac{\hbar\tau_s}{m}\left[\frac{\beta\epsilon_k^2}{TE_k}f_k(1-f_k)-\frac{f_k\Delta}{E_k^2}\left(\frac{d\Delta}{dT}\right)\right]\vec{k}\cdot\nabla T. \tag{47}$$

The second term in brackets appears because the $\dot{\vec{k}}$ term of Eq. (46) is no longer completely cancelled by one of the $\dot{\vec{r}}$ terms. The thermal diffusion current $\vec{j}_d$ and, therefore, the transport coefficient α_s is found by following the analysis between Eqs. (20) and (22),

$$\alpha_s=\frac{4eN(0)}{3mk_BT^2}\int_{-\hbar\omega_D}^{\hbar\omega_D}\tau_s(\epsilon+\epsilon_F)\times\left[f(1-f)\frac{\epsilon^2}{E}-\frac{k_BT^2f\Delta}{E^2}\left(\frac{d\Delta}{dT}\right)\right]d\epsilon. \quad (48)$$

We have not yet converted τ_s to τ_n, using Eq. (18), because an expanded discussion of τ_s, given below, is required.

At this point it is possible to appreciate why the new α_s will be orders of magnitude larger than the former value. Recall that the integrand factor multiplying $(\epsilon+\epsilon_F)$ in Eq. (21) was odd in ϵ on the $(-\hbar\omega_D,\hbar\omega_D)$ interval, so the ϵ_F term dropped out. Now, the corresponding factor in Eq. (48) is even in ϵ, so the ϵ_F term survives, and the ϵ term is nil. The comparative ratio of the two is $\sim 10^5$ K:3 K, i.e., the Fermi temperature of In to T_c. Furthermore since f, Eq. (11), is even, the second term (in brackets) of Eq. (48) is also even; and it is also positive because $d\Delta/dT$, from Eq. (29), is negative. It turns out that in the final analysis this second term contributes about four times more than the first. Therefore the needed 10^5-fold boost in the (theoretical) thermoelectric flux is already at hand.

It can be seen from Eq. (18) and the $(\epsilon/E)^2$ coherence factor that τ_s diverges as $1/|\epsilon|$ near $\epsilon=0$. This behavior doesn't cause a problem for the first term (in brackets) of Eq. (48); but it does for the second, which will generate a logarithmic divergence of the integral. Consequently we must explore possible mechanisms which prevent the scattering time, τ_s, from being infinite at $\epsilon=0$. (It seems ironic that the problem here is to prevent the hoped-for 10^5-fold enhancement of the predicted thermoelectric flux from being too large.) Inelastic scattering can limit τ_s at $\epsilon=0$, but such events are relatively rare at 3 K (and those which occur do not retard much momentum). Similarly, an anisotropic energy gap will shorten τ_s, but an heuristic model with unknown parameters would have to be invented. However, there is an unambiguous scattering process that puts an adequate ceiling on τ_s.

V. SPIN-FLIP SCATTERING OF QUASIPARTICLES

The divergence of the elastic scattering time at $\epsilon=0$ arises from the BCS coherence factor $(\epsilon/E)^2$ which reduces the scattering rate to zero for $\epsilon=0$. However, if the spin of the quasiparticle is flipped, the coherence factor for an elastic transition from a state ϵ to another state having the same ϵ is unity. The divergence would then not occur. Another type of transition, involving a spin flip to a final state having, $\epsilon'=-\epsilon$, is also elastic because E_k, Eq. (9), depends on ϵ^2. However, this process violates electron conservation, as can be seen easily by considering the two quartets, c.f. Eq. (6), for $\vec{k}$ and $\vec{k}'$. One such transition is from ($\vec{k}$, level 2; $\vec{k}'$, level 1) to ($\vec{k}$, level 1; $\vec{k}'$, level 3). The change in the total electron number would be

$$\Delta N=2[v(\epsilon)]^2-2[v(-\epsilon)]^2=-2\frac{\epsilon}{E}. \quad (49)$$

Accordingly, we shall neglect these events and focus on the allowed, electron-conserving ones.

The spin-flip scattering we consider here is caused by the Fermi hyperfine coupling to the nuclear spins. Such processes have been studied previously,[20] and we follow that treatment. If the nuclear spin is $I=1/2$, the Fermi coupling is

$$\mathcal{H}=\frac{8\pi}{3}\beta_e\beta_n\vec{\sigma}_e\cdot\vec{\sigma}_n\delta(\vec{r}). \quad (50)$$

$\delta(\vec{r})$ is the Dirac delta function, β_e is the Bohr magneton, and β_n is the nuclear moment. The σ's are the usual Pauli matrices, and $\vec{\sigma}_e\cdot\vec{\sigma}_n$ can be expressed in terms of the raising and lowering operators:

$$\vec{\sigma}_e\cdot\vec{\sigma}_n=2(\sigma_n^+\sigma_e^-+\sigma_n^-\sigma_e^+)+\sigma_n^z\sigma_e^z. \quad (51)$$

The first term flips an electron spin from up to down and the nuclear spin from down to up. The transition rate from $\vec{k}\uparrow$, level 2 of quartet $\vec{k}$, to all possible spin-down possible final states having the same ϵ is

$$R_\epsilon=\frac{2\pi}{\hbar}\left(\frac{N}{2}\right)\left(\frac{16\pi\beta_e\beta_n}{3}\right)^2|\Psi(0)|^4N(0)\times[f_1(\epsilon')+f_4(\epsilon')]\frac{E}{|\epsilon|}. \quad (52)$$

$N/2$ is the down-spin density of nuclear spins, and $|\Psi(0)|$ is the magnitude of the conduction-electron wave function at the nucleus. $N(0)$ is the density of states (per spin), Eq. (24), which is also

$$N(0)=(mk_F)/(2\pi^2\hbar^2), \quad (53)$$

and the last factor, $E/|\epsilon|$, is its BCS enhancement. Finally, the factor in square brackets appears because the quartet, $\vec{k}'$, before the transition must be either in level 1 or 4. (After the transition, quartet, $\vec{k}$, will be in level 1 or 4, respectively.) Since $\epsilon'=\epsilon$, Eqs. (10) and (11) determine this factor

$$f_1+f_4=\frac{\cosh(\beta E)}{2\cosh^2(\frac{1}{2}\beta E)}. \quad (54)$$

The generalization of Eq. (52) for arbitrary nuclear spin I is obtained by the following substitutions:[20]

$$\frac{N}{2}\to\frac{N}{2I+1},\quad \beta_n\to\frac{\beta_n}{2I}. \quad (55)$$

One must also include the multiplicity of transitions, $\{m_I\to m_I+1\}$ between the $2I+1$ nuclear magnetic states by the multiplication factor

$$G=\sum_{m=-I}^{m=I}(I+m-1)(I-m)=\frac{2}{3}I(I+1)(2I+1). \quad (56)$$

The final expression for the scattering rate involving a spin flip is, from Eqs. (52)–(56),

$$R_\epsilon=\frac{64\pi N m k_F \beta_e^2 \beta_n^2 |\Psi(0)|^4 (I+1) E\cosh(\beta E)}{27\hbar^3 I|\epsilon|\cosh^2(\frac{1}{2}\beta E)}. \quad (57)$$

The complexity of the foregoing transition rate can be eliminated by the measured nuclear spin relaxation rate for In in the normal state. In the notation employed here, the nuclear-spin relaxation time T_{1n} is[20]

$$T_{1n}=\frac{9\pi\hbar^5 I^2}{64 m^2 k_F^2 \beta_e^2 \beta_n^2 k_B T|\Psi(0)|^4}, \quad (58)$$

equivalent to a result first derived by Korringa.[21] The product of Eqs. (57) and (58) provides considerable cancellation

$$R_\epsilon=\frac{2N\epsilon_F I(I+1)E\cosh(\beta E)}{9nk_B|\epsilon|\cosh^2(\frac{1}{2}\beta E)T_{1n}T}. \quad (59)$$

Now, the last factor in the denominator has been measured in a nuclear magnetic resonance study of In[22]

$$\frac{1}{T_{1n}T}=12.7(sK)^{-1}. \quad (60)$$

Since $I=9/2$, $\epsilon_F=8.6$ eV, and $n/N=3$, the spin-flip transition rate is

$$R_\epsilon=\frac{2.3E\cosh(\beta E)}{|\epsilon|\cosh^2\left(\frac{1}{2}\beta E\right)}\times 10^6 \ \ \mathrm{s}^{-1}. \quad (61)$$

VI. THERMAL DIFFUSION CURRENT AND THE INDUCED FLUX

The thermal diffusion coefficient α_s, defined by Eq. (25) and expressed in closed form by Eq. (48), requires insertion of the ϵ-dependent relaxation time τ_s to allow completion of the indicated integration. The total scattering rate is

$$\frac{1}{\tau_s}=\frac{|\epsilon|}{E\tau_n}+\frac{2.3\times 10^6 E\cosh(\beta E)}{|\epsilon|\cosh^2(\frac{1}{2}\beta E)}. \quad (62)$$

The first term is the transition rate, Eq. (18), caused by impurity scattering; and the second term is the spin-flip scattering rate, Eq. (61), caused by hyperfine interactions with In nuclear spins. The integral in Eq. (48) is now well defined and can be evaluated after conversion to an integration in dE, as done previously in Eqs. (22) and (23). Accordingly, for a normal state relaxation time τ_n (taken constant) and ω_D set (without compromise) to ∞,

$$\alpha_s=\frac{8e\epsilon_F\tau_n N(0)}{3mk_B T^2}\times\int_\Delta^\infty\left[f(1-f)E-k_B T^2\Delta\left(\frac{d\Delta}{dT}\right)\frac{f}{E^2-\Delta^2+A}\right]dE, \quad (63)$$

where

$$A=2.3\times 10^6\tau_n\frac{E^2\cosh(\beta E)}{\cosh^2(\frac{1}{2}\beta E)}. \quad (64)$$

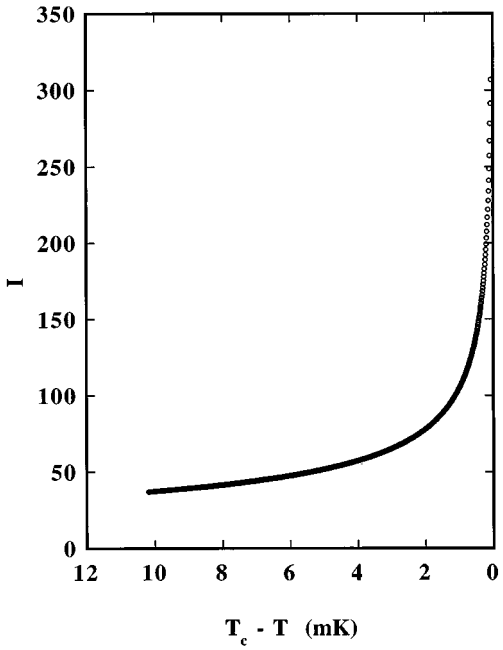

FIG. 5. Temperature variation of the dimensionless factor $I(T)$, Eq. (66), near T_c of In. The thermoelectric flux, $d\Phi/dT$, is proportional to $I(T)/[1-(T/T_c)]$.

The spin-flip relaxation was omitted in the first term of the integrand, but its non-negligible role in the second term is evident. $f(\beta E)$ is given by Eq. (11).

The first term of the integral can be done exactly. However, the second must be carried out numerically. Equation (29) is used to calculate $\Delta(d\Delta/dT)$. With $x=\beta E$, Eq. (63) becomes

$$\alpha_s=\frac{8ek_B\epsilon_F\tau_n N(0)}{3m}I, \quad (65)$$

where

$$I(T)=\beta\Delta f(\beta\Delta)+\ln(1+e^{-\beta\Delta})+\frac{4\pi^2 T}{7\zeta(3)T_c}I_0 \quad (66)$$

and

$$I_0(T)=\int_{\beta\Delta}^\infty\left[x^2-\beta^2\Delta^2+2.3\times 10^6\tau_n\frac{x^2\cosh x}{\cosh^2(\frac{1}{2}x)}\right]^{-1}f(x)dx. \quad (67)$$

The variation of Δ with temperature is taken from Eq. (29). $I(T)$, which is dimensionless, is shown in Fig. 5 for temperatures within 10 mK of T_c.

The flux derivative, $d\Phi/dT$, is now found from Eqs. (5), (24), (30), (32), and (65). With $\Phi_0=\hbar c/2e$,

$$\frac{d\Phi}{dT}=\frac{1.2I(T)}{1-(T/T_c)}\Phi_0 K^{-1}. \quad (68)$$

(The coefficient, 1.2, is just $k_B\tau_n/\pi\hbar$.) This final result is shown with the data of Van Harlingen *et al.*[9] in Fig. 6. Not only is the theoretical magnitude correct but so is the power-law slope, i.e., ~ -1.5. No unknown or adjustable parameters were involved in the foregoing derivation.

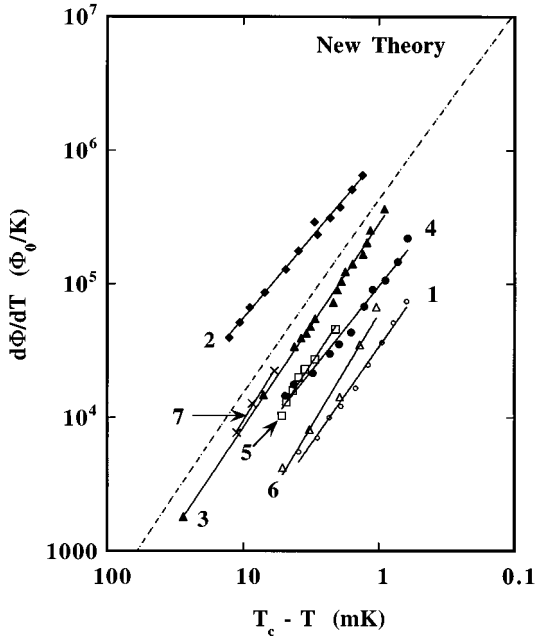

FIG. 6. Comparison of the thermoelectric flux, $d\Phi/dT$, measured by Van Harlingen *et al.*, with the theoretical variation obtained by solving the electron-conserving transport equation, Eq. (39). There are no unknown or adjustable parameters in the theory.

VII. DISCUSSION

A question which arises on inspection of Fig. 6 is why the data exhibit a large spread in values. The variations are in fact more dramatic than they appear since the thermoelectric flux observed in samples 2 and 7 has an algebraic sign opposite to that of the other five. Van Harlingen *et al.* plotted $|d\Phi/dT|$.[9] They also measured the thermoelectric power, S, of each In sample in the normal state, and found that S is proportional to $d\Phi/dT$, including the sign reversal. Since a reasonable explanation of such a variation is possible (and is given below), the disparate data of Fig. 6 are indeed expected.

In has a tetragonally distorted fcc lattice.[23] The c/a ratio is 1.078, so transport coefficients will be anisotropic. Caplin *et al.* measured the absolute $S(T)$ of single crystalline In parallel to both the a and c axes.[24] Near 10 K, S is positive parallel to the a axis, but is negative parallel to the c axis. Therefore one expects that measurements on polycrystalline In should vary substantially and depend on the orientational texture of the sample. The 0.25 mm thick In cylinders shown in Fig. 2 were constructed from freshly rolled In pellets. The rolling process creates an orientational texture, presumably with the c axis dominant in the rolling direction. Therefore one should expect that the observed magnitude and sign of S and $d\Phi/dT$ in the toroidal samples will depend on the orientation of ∇T with respect to the rolling direction, an unrecorded datum.

The theoretical message of this work is that one is not allowed to use a Boltzmann transport equation to study the time evolution of BV quasiparticles in an inhomogeneous environment. What is surprising is that failure to conserve electrons locally in each volume, $d^3k d^3r$, of phase space can lead to theoretical errors as large as factors of 10^5–10^6. In retrospect, were such a severe pathology not forthcoming and, instead, if only minor discrepancies were evident, the strict imperative to conserve electrons might have escaped notice for many more years. The Garland–Van Harlingen experiment is a most significant event.

It seems likely that past confidence placed in the Boltzmann equation for BV quasiparticles is primarily due to the apparent success[25] of BRT's analysis of thermal transport.[14] Obviously, this problem needs to be revisited. One cannot combine the solution, Eq. (46), of the electron-conserving transport equation with BRT's assumed energy flux, $\Sigma f_k E_k \dot{\vec{r}}$, and find a satisfactory thermal current. Naturally, we believe that the energy flux needs to be reformulated.[26] A truly basic problem in the theory of superconductivity awaits solution.

ACKNOWLEDGMENTS

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[26] For example, it seems evident (to us) that the energy carried by an electron in, say, level 2 or level 3 of a quartet is ϵ, not E; its wave function is a pure plane wave and it does not interact with other quartets.