Thermoelectric effect in superconductive tunnel junctions

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The theory of hole superconductivity predicts the existence of a charge imbalance in the quasiparticle excitations in superconductors, which gives rise to a thermoelectric effect of universal sign across tunnel junctions when one or both electrodes are superconducting. Recently, temperature gradients of appreciable magnitude have been experimentally achieved in NIS tunnel junctions, opening up the possibility of testing this prediction. However, a thermoelectric effect across a tunnel junction could also arise from energy dependence of the transmission probability across the barrier, independent of the nature of the superconducting state of the electrodes. We explore the consequences of these two effects acting simultaneously and to what extent it is possible to differentiate between them experimentally. It is concluded that careful experiments should be able to single out the intrinsic effect arising from the properties of the superconducting state. These experiments would yield a measurable quantity that characterizes the superconducting state of a material, in addition to providing a stringent test of the theory of hole superconductivity. [S0163-1829(98)02437-0]

I. INTRODUCTION

The theory of hole superconductivity[1,2] predicts the existence of a charge imbalance in the quasiparticle excitations in the superconducting state: quasiparticles are positively charged on average. This gives rise to a thermoelectric effect in tunnel junctions when one or both electrodes are superconducting.[3] Measurement of this effect would provide information on a fundamental parameter of the superconductor, ν, that determines its degree of electron-hole asymmetry . The parameter ν is proportional to the slope of the superconducting gap function versus energy. The theory predicts the sign of ν to be universal (positive in our convention) and gives rough estimates for its magnitude, ranging from a few meV for high-T_c superconductors to a few μV or less for conventional superconductors.

It has recently been experimentally demonstrated that it is possible to establish large temperature gradients across *S*-*I*-*N* tunnel junctions by simply circulating an electric current across the junction and ensuring proper thermal insulation from the environment.[4–7] For the *electronic temperature*, a factor of 3 temperature drop has been achieved in Al-Cu tunnel junctions when appropiate thermal decoupling between electrons and lattice exists.[5] It has also been demonstrated that it is possible to cool the lattice itself of one of the electrodes by a small amount with respect to the other electrode, and it is speculated that a drop in the lattice temperature similar to what has been achieved in the electronic temperature will be attainable.[6] While these experiments have not yet been performed with high-T_c superconductors, it is likely that they will be done in the future.

These experimental developments open up the possibility of providing a stringent test of the theory of hole superconductivity. Establishing that the parameter ν is negative or zero for any superconductor would demonstrate that the theory does not apply to it. Moreover, because the theory is based on general principles applicable to all solids,[2] finding of a single example where ν is substantially different from the theoretical expectation would cast serious doubts on the applicability of the theory to *any* superconductor. More generally, measurement of the slope of the superconducting gap function is of intrinsic interest as a way to characterize a superconductor and could be important in other theoretical frameworks. Thus we believe it is an interesting task to perform ν spectroscopy on all known superconductors, by measurement of the thermoelectric effect or by other methods that may be developed in the future. Tabulation of ν, together with other fundamental parameters of the superconductor such as energy gap and critical fields, will provide useful information on each superconductor and may shed new light on relationships between materials parameters and superconductivity, that could suggest criteria helpful to the achievement of higher temperature superconducting materials.

However, a thermoelectric effect across a tunnel junction may also arise from energy dependence of the transmission probability across the barrier, independent of the nature of the states of the electrodes. This explanation was proposed to interpret the thermoelectric current that was observed in an early experiment by Smith, Tinkham, and Skocpol[8] when one side of a Pb-*I*-Al (I=insulator) tunnel junction was heated by laser irradiation. These authors found good agreement with a calculated effect using a one-band WKB approximation and no intrinsic electron-hole asymmetry in the electrodes themselves. As pointed out by these authors, energy dependence of the normal-state density of states in the electrodes would not be expected to lead to a thermoelectric effect, as it would be cancelled by a corresponding change in the group velocity of the carriers.[9] Thus, assuming that no temperature gradients exist in the electrodes themselves, only the intrinsic electron-hole asymmetry of the superconducting state discussed here and energy dependence of barrier transmission could be possible sources of an observed thermoelectric effect.

In this paper we explore the expected thermoelectric effect in *NIS* tunnel junctions when both the intrinsic effect predicted by the theory of hole superconductivity and energy dependence of the transmission probability exist. Is it possible to disentangle one effect from the other? Can such experiments be used to extract the value of the asymmetry parameter ν of the superconducting electrode? Can the theory of hole superconductivity be proven wrong by such experiments even in the presence of an unknown energy dependence of the transmission probability? We will see that the answer to these questions is affirmative. Furthermore, we examine the feasibility of measuring the effect under the experimental conditions of the experiment of Leivo, Pekola, and Averin,[5] and conclude that the experiment is quite feasible. Thus, both as a test of the theory of hole superconductivity and more generally as a way to measure an intrinsic property of a superconductor, the energy dependence of its gap function, we suggest that it is a worthwhile experiment to perform.

The paper is organized as follows. Section II reviews the effect predicted by the theory of hole superconductivity; Sec. III derives the effect expected due to the nature of the barrier, and in Sec. IV we obtain the expected current versus voltage in the presence of both effects. Section V presents numerical results in various cases, and Sec. VI considers the experimental feasibility. We conclude in Sec. VII with a discussion.

II. INTRINSIC THERMOELECTRIC EFFECT

In the theory of hole superconductivity the gap function varies linearly with band energy. We parametrize it as

$$\Delta_k = \Delta_m \left(-\frac{\epsilon_k}{D/2} + c \right) \equiv \Delta(\epsilon_k), \tag{1}$$

where ϵ_k is the hole kinetic energy measured from the center of the band and D is the bandwidth. A Hamiltonian that gives rise to this gap function is a tight-binding model with a correlated hopping interaction term,[1,2,10] and the parameters Δ_m and c are obtained from solution of the BCS equations for this model.[1] The nonzero gap slope

$$m = \frac{\Delta_m}{D/2} \tag{2}$$

is what distinguishes this case from the simplest s-wave superconductor with constant gap. More generally, a gap function described by the form Eq. (1), at least in the vicinity of the Fermi energy, could arise in other theoretical frameworks.

The quasiparticle energy is given by

$$E_k = \sqrt{(\epsilon_k - \mu)^2 + \Delta_k^2} = \sqrt{a^2(\epsilon_k - \mu - \nu)^2 + \Delta_0^2}, \tag{3}$$

with μ the chemical potential and

$$a = (1 + m^2)^{1/2}, \tag{4a}$$

$$\Delta_0 = \frac{\Delta(\mu)}{a}, \tag{4b}$$

$$\nu = \frac{m}{\sqrt{1+m^2}} \Delta_0 . \tag{4c}$$

Thus, the ''Fermi surface'' in the superconducting state, defined as the locus in k space of quasiparticle excitations of minimum energy, $\epsilon_k = \mu + \nu$, is different from the normal-state Fermi surface, $\epsilon_k = \mu$. The BCS coherence factors are given by the usual form

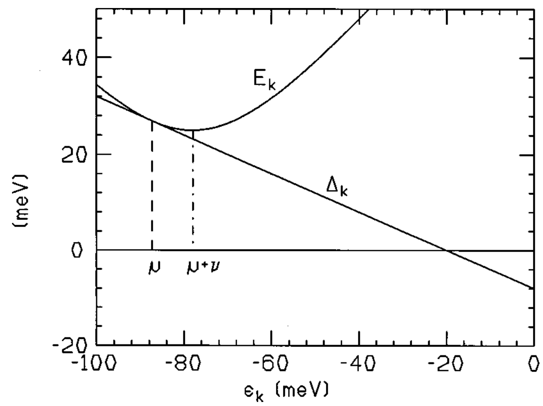

FIG. 1. Energy gap function Δ_k and quasiparticle energy E_k versus hole kinetic energy ϵ_k. The minimum in the quasiparticle energy is shifted from the chemical potential μ to $\mu + \nu$.

$$u_k^2 = \frac{1}{2}\left(1 + \frac{\epsilon_k - \mu}{E_k} \right), \tag{5a}$$

$$v_k^2 = \frac{1}{2}\left(1 - \frac{\epsilon_k - \mu}{E_k} \right). \tag{5b}$$

Figure 1 shows a schematic plot of the gap function and quasiparticle energy versus hole kinetic energy. Note that quasiparticle excitation energies are larger for $\epsilon_k - \mu < 0$ than for $\epsilon_k - \mu > 0$, which implies (within our convention) that quasiparticles are positively charged on average.

The quasiparticle current from the normal metal to the superconductor in a NIS tunnel junction for quasiparticles of energy E_k is proportional to[3]

$$J_{NS} = \left(1 + \frac{\nu}{E_k} \right) [f_n(E_k - \mathrm{eV}) - f_s(E_k)] + \left(1 - \frac{\nu}{E_k} \right) [f_s(E_k) - f_n(E_k + \mathrm{eV})] \tag{6}$$

for processes involving quasiparticles of energy E_k. Here, V is the voltage of the normal metal relative to the superconductor and f_n and f_s denote the Fermi distribution functions for the normal metal and the superconductor at temperatures T_n and T_s, respectively. In the derivation of Eq. (6) (Ref. 3), it is assumed that the transmission probability across the barrier is independent of energy.

Equation (6) predicts the existence of both an asymmetry in I-V characteristics in the absence of temperature gradient,[11] and of a thermoelectric effect in the presence of a temperature gradient. The theory of hole superconductivity predicts ν to be positive for all superconductors, of order meV for high-T_c materials and μeV for conventional superconductors. Thus, in the absence of other effects, a *positive* current should flow from the hotter to the colder electrode, and a thermoelectric voltage should exist under open circuit conditions with the hotter electrode positive with respect to the colder one.[3] The temperature dependence of the parameter ν is shown in Fig. 2. It scales proportionally to Δ_0^2 so

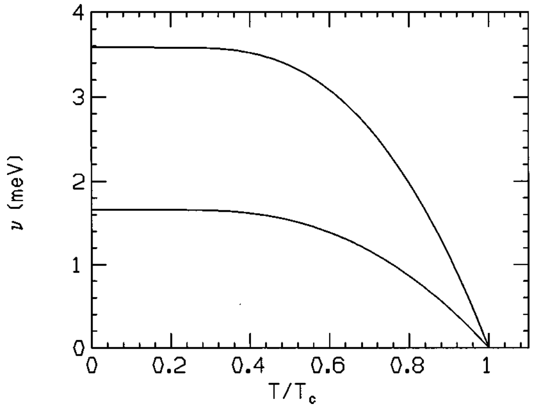

FIG. 2. Temperature dependence of the parameter ν in the model of hole superconductivity for two sets of Hamiltonian parameters that give rise to $T_c = 93$ K.

that it goes to zero linearly as $T \to T_c$. The carrier concentration dependence of ν in the theory of hole superconductivity follows approximately that of the critical temperature.[3]

For small temperature gradient the asymmetry parameter ν directly gives the thermopower of the junction, through the relation

$$V_0 = \frac{\nu}{e}\frac{T_s - T_n}{T_n}, \tag{7}$$

with V_0 the open circuit thermoelectric voltage. This is valid for $|T_s - T_n| \ll T_s$. Without restriction to small temperature gradients, we obtain at low temperatures ($T_s, T_n \ll T_c$) the approximate relation

$$V_0 = \frac{\nu}{e}\frac{kT_n}{\Delta_0}\left[e^{(\beta_n - \beta_s)\Delta_0} - 1\right]. \tag{8}$$

Thus, the thermoelectric voltage can be orders of magnitude larger than ν/e when the normal metal is much colder than the superconductor. In the recent experiments,[4–6] it was shown that cooling of the normal electrode with respect to the superconducting electrode is achieved when an *NIS* tunnel junction is biased with voltage smaller than the superconducting energy gap.

For the normal and superconducting electrodes at the same temperature, Eq. (6) predicts a larger tunneling current when positive current flows from the normal metal to the superconductor, i.e., when the superconductor is negatively biased. This is seen most clearly in the appearance of different size peaks in dI/dV for bias voltages close to the superconducting gap.[11] Note that this effect is opposite in sign to the thermoelectric current generated when the normal metal is colder than the superconductor, which is the situation that prevails when current flows. Nevertheless, the nature of the effects is such that one does not compensate the other, and, in particular, the tunneling asymmetry persists even in the presence of a temperature gradient.

III. BARRIER EFFECTS

As discussed above, when the gap as function of band energy has a finite slope, such as predicted in the theory of hole superconductivity, a tunneling asymmetry as well as a thermoelectric effect arises from the intrinsic nature of the superconducting state. However as we discuss in this section, such effects can also arise from the nature of the tunneling barrier.

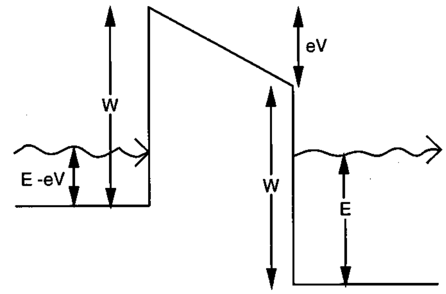

FIG. 3. Diagram of barrier across which tunneling occurs. Both electrodes are assumed to have the same work function *W*.

For tunneling between nonidentical electrodes the tunneling current will in general not be an even function of the voltage across the barrier.[12] Because of the different work functions of the two electrodes, an electric field across the barriers exists when the Fermi levels of the two electrodes coincide; this causes the transmission coefficients in both directions to be different. This effect is not dependent on whether the electrodes are in the normal or superconducting state. Here we will assume that any such asymmetry that persists in the normal state can be substracted out, and will treat electrodes with equal work functions for simplicity.

A second source of asymmetry, as well as of a thermoelectric effect, arises from energy dependence of the transmission probability across the junction.[8,12] The tunneling probability between two metals with work function W across a gap of width d is given within the WKB approximation by

$$T = Ce^{-2\int_0^d dx \sqrt{\frac{2m}{\hbar^2}[V(x)-(E-\mathrm{eV})]}}, \tag{9a}$$

$$V(x) = W - \frac{V}{d}x, \tag{9b}$$

where V is the applied voltage, E is the electron energy, and we have assumed $W - \mathrm{eV} > E$. Figure 3 shows a diagram of the barrier assumed. Integration yields

$$T(E,V) = Ce^{-4/3\sqrt{2m/\hbar^2}d/V\{[W-(E-\mathrm{eV})]^{3/2}-(W-E)^{3/2}\}} \tag{10}$$

and assuming $W \gg E, V$ we expand and obtain

$$T(E,V) = T_0\left[1 + \sqrt{\frac{2m}{\hbar^2}}\frac{d}{W^{1/2}}(E - \mathrm{eV}/2)\right] \tag{11}$$

which for the free-electron mass yields

$$T(E,V) = T_0\left[1 + 0.51 d(\mathrm{A}) W(\mathrm{eV})^{1/2}\frac{E-\mathrm{eV}/2}{W}\right]. \tag{12}$$

Note that this expression satisfies

$$T(E,V) = T(E - \mathrm{eV}, -V), \tag{13}$$

yielding a symmetric transmission probability, as assumed. Thus we will take the transition probability of an electron to be of the form (we omit the argument V on the left side for brevity)

$$T(E)=T_0[1+c(E-\mathrm{eV}/2)] \tag{14}$$

and the parameter c is given by

$$c=0.51\frac{d(\mathrm{A})}{W(\mathrm{eV})^{1/2}}. \tag{15}$$

For a typical barrier with $d=20$ A and $W=4$ eV this yields

$$c=5.1\ \mathrm{eV}^{-1}. \tag{16}$$

In our numerical examples we will consider c's ranging from 0 to 10 eV^{-1}.

The tunneling current between two normal electrodes n_1 and n_2 (from n_1 to n_2), with n_1 at voltage V relative to $n2$, is proportional to

$$J_{n_1n_2}(E_k,V)=\left[1-c\left(E_k-\frac{\mathrm{eV}}{2}\right)\right][f_{n_1}(E_k-\mathrm{eV})-f_{n_2}(E_k)], \tag{17}$$

where E_k is the quasiparticle energy at electrode n_2. For the two electrodes at the same temperature it gives rise to symmetric tunneling characteristics, as expected, since

$$J_{n_1n_2}(E_k,V)=J_{n_2n_1}(E_k-\mathrm{eV},-V) \tag{18}$$

for temperatures $T_{n_1}=T_{n_2}$. There is however a thermoelectric effect due to the energy-dependent transmission. For zero voltage Eq. (17) is

$$J_{n_1n_2}(E_k,0)=[1-cE_k][f_{n_1}(E_k)-f_{n_2}(E_k)] \tag{19}$$

and the current involving quasiparticles of energy $-E_k$ is

$$J_{n_1n_2}(-E_k,0)=[1+cE_k][f_{n_2}(E_k)-f_{n_1}(E_k)], \tag{20}$$

so that when $c\neq 0$ there is a zero voltage thermoelectric current when $T_{n_1}\neq T_{n_2}$ proportional to

$$\begin{aligned}J_0(|E_k|)&=J_{n_1n_2}(E_k,0)+J_{n_1n_2}(-E_k,0)\\&=2cE_k[f_{n_1}(E_k)-f_{n_2}(E_k)]\end{aligned} \tag{21}$$

from quasiparticles of energy $|E_k|$. For tunneling between a normal and a superconducting electrode the current is proportional to

$$\begin{aligned}J_{NS}=&\left[1-c\left(E_k-\frac{\mathrm{eV}}{2}\right)\right][f_n(E_k-\mathrm{eV})-f_s(E_k)]\\&+\left[1+c\left(E_k+\frac{\mathrm{eV}}{2}\right)\right][f_s(E_k)-f_n(E_k+\mathrm{eV})],\end{aligned} \tag{22}$$

where now $E_k>0$ and N is at voltage V relative to S. Equation (22) reduces to the sum of Eq. (17) for E_k and $-E_k$ when both electrodes are normal. The current Eq. (22) is no longer symmetric in the voltage, and will be larger when the superconductor is positively biased if $c>0$ when the electrodes are at the same temperature.

In the above WKB analysis it was assumed that the tunneling probability for an electron increases with energy, which gives rise to positive c in Eq. (22). This will always be the case for tunneling across vacuum, but not necessarily so for tunneling across an insulator. If the Fermi level is in the bandgap of the insulator close to the top of the valence band, in fact the opposite may be true. Modeling the insulator with a valence and a conduction band (two-band model) it is shown in Ref. 13 that the tunneling probability for an electron of energy E is proportional to

$$T(E)=Ce^{-2\int dx\sqrt{\frac{2m}{\hbar^2}\frac{(E_c-E)(E-E_v)}{E_g}}}, \tag{23}$$

with $E_g=E_c-E_v$ the energy gap. Thus, for E close to E_v the transmission will *decrease* as E increases. This will give rise to a transmission coefficient of the form Eq. (14), but now the parameter c can also be negative.

For the case where c is positive, which we expect to be more likely, the thermoelectric current will be opposite to the temperature gradient (negative thermopower), i.e., opposite to what the intrinsic asymmetry in the model of hole superconductivity predicts. Similarly the tunneling asymmetry will be such that larger current flows for positively biased superconductor, opposite to what is predicted by the model of hole superconductivity. However for negative c as could be obtained from the two-band model, the effects due to the barrier and due to intrinsic asymmetry are of the same sign. We will consider both signs of c in the numerical studies.

IV. TUNNELING CURRENT

We follow Tinkham's[14] analysis of tunneling through a barrier distinguishing between electron and holelike branches of the quasiparticle spectrum. The tunneling current from normal to superconducting electrode involving quasiparticles of energy E_k is given by

$$\begin{aligned}J_{NS}=&u_k^2|T_{k,q<q_F}|^2[f_n(E_k-\mathrm{eV})-f_s(E_k)]\\&+v_k^2|T_{k,q>q_F}|^2[f_s(E_k)-f_n(E_k+\mathrm{eV})],\end{aligned} \tag{24}$$

where q is the momentum of an electron in the normal metal, k the quasiparticle momentum in the superconductor, and $T_{k,q}$ the transition amplitude in the tunneling Hamiltonian.[14] The transmission probabilities are taken to be

$$|T_{k,q<q_F}|^2=T_0[1-c(E_k-\mathrm{eV}/2)], \tag{25a}$$

$$|T_{k,q>q_F}|^2=T_0[1+c(E_k+\mathrm{eV}/2)]. \tag{25b}$$

On summing over the quasiparticle momenta k that give rise to the same quasiparticle energy E_k, we use Eq. (5) and the relation

$$\epsilon_k-\mu=\nu\pm\frac{1}{a}\sqrt{E_k^2-\Delta_0^2}, \tag{26}$$

so that

$$\sum_k u_k^2=1+\frac{\nu}{E_k}, \tag{27a}$$

$$\sum_k v_k^2 = 1 - \frac{\nu}{E_k}, \tag{27b}$$

and the current in the presence of both intrinsic asymmetry and energy-dependent transmission probability is, for quasiparticles of energy E_k, proportional to

$$J_{NS}(E_k,V) = \left(1+\frac{\nu}{E_k}\right)[1-c(E_k-\mathrm{eV}/2)][f_n(E_k-\mathrm{eV}) - f_s(E_k)] + \left(1-\frac{\nu}{E_k}\right)[1+c(E_k+\mathrm{eV}/2)] \times[f_s(E_k)-f_n(E_k+\mathrm{eV})], \tag{28a}$$

so that the total current from normal to superconducting electrode is

$$I_{NS}(V) = \frac{1}{eRa}\int_{\Delta_0}^{\infty} dE \frac{E}{\sqrt{E^2-\Delta_0^2}} J_{NS}(E,V), \tag{28b}$$

with R the junction resistance in the normal state, and a given by Eq. (4a).

For a small temperature gradient, the zero-current thermoelectric voltage is now given by

$$V_0 = \frac{(\nu - c\Delta_0^2)}{e}\,\frac{T_s-T_n}{T_n}, \tag{29}$$

and at low temperatures $(T_s, T_n \ll T_c)$ by

$$V_0 = \frac{(\nu - c\Delta_0^2)}{e}\,\frac{kT_n}{\Delta_0}[e^{(\beta_n-\beta_s)\Delta_0}-1]. \tag{30}$$

More generally, the magnitude of the effects due to intrinsic asymmetry and energy-dependent transmission will be comparable if

$$c \sim \frac{\nu}{\Delta_0^2}, \tag{31}$$

otherwise one of the two effects will dominate. Note that this implies that the relative importance of barrier effect and intrinsic asymmetry will be similar for high- and low-T_c materials for similar barriers, since ν is expected to scale approximately as Δ_0^2.

V. NUMERICAL RESULTS

We consider as an example a superconductor with $T_c = 100$ K and zero-temperature gap $\Delta_0 = 16$ meV. This could be a representative case for high-T_c oxides and we can also infer from this the expected behavior in other regimes (e.g., conventional superconductors) by suitable scaling. The intrinsic asymmetry parameter ν for this case is expected to be a few meV. We calculate the tunneling current using Eq. (28), with junction resistance $R = 1\ \Omega$.

In Fig. 4 we compare the effect of intrinsic asymmetry and energy-dependent transmission on tunneling characteristics. The results for $\nu = 1.5$ meV and constant $T(E)$ (solid lines) are almost indistinguishable from those for $\nu = 0$ and a $T(E)$ with $c = -10\ \mathrm{eV}^{-1}$ (Eq. 14), both giving rise to a larger peak for positive voltages (i.e., when the sample is negatively biased). In particular, as the temperature increases and the gap becomes smaller, both the intrinsic asymmetry and the asymmetry due to $T(E)$ are similarly reduced. This indicates that observation of a tunneling asymmetry that disappears as the system becomes normal (by either raising the temperature or applying a magnetic field) cannot by itself be interpreted as evidence for intrinsic electron-hole asymmetry in the superconductor. Conversely, observation of symmetric characteristics cannot by itself be interpreted as evidence against intrinsic electron-hole asymmetry, as they could arise from cancelling effects of intrinsic asymmetry and energy-dependent $T(E)$, as shown in Fig. 4(b).

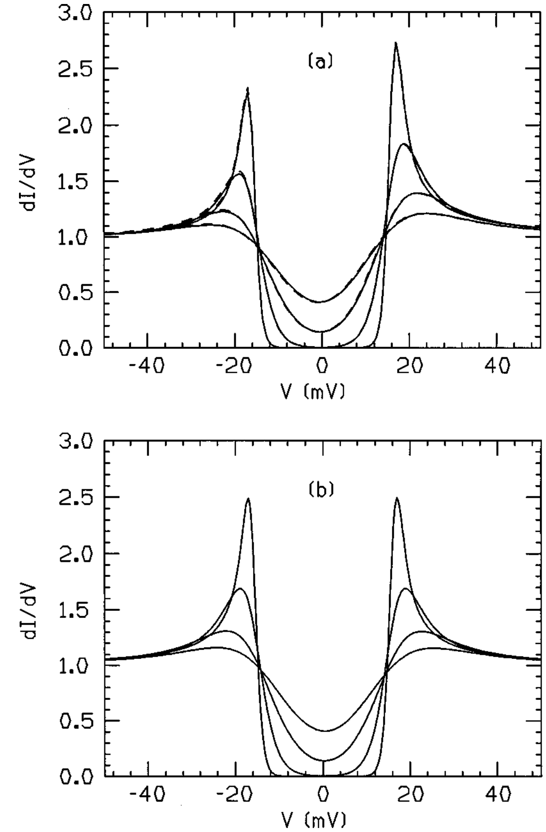

FIG. 4. Tunneling characteristics for a superconductor with zero temperature gap $\Delta_0 = 16$ meV and $T_c = 100$ K, for temperatures $T = 10$, 25, 50, and 75 K. The temperature dependence of the gap is usual BCS, and the asymmetry parameter ν is proportional to Δ_0^2. The degree of energy dependence of the tunneling probability on energy is given by the parameter c [Eq. (15)]. Here and in the following figures, positive current flows from N to S, and positive voltage denotes N is positive with respect to S. (a) Full lines: $c = 0$, $\nu = 1.5$ meV (at $T = 0$; at $T > 0$, ν decreases proportionally to Δ_0^2); dashed lines, $\nu = 0$, $c = -10\ \mathrm{eV}^{-1}$. Note that the dashed and solid lines closely agree at all temperatures; (b) $\nu = 1.5$ meV, $c = 11.5\ \mathrm{eV}^{-1}$: the energy-dependent transmission almost exactly cancels the intrinsic asymmetry effect.

Next we consider the effect of different temperatures in the normal and superconducting electrodes. Here, it is more useful to look at I versus V, as no appreciable effects appear in dI/dV in the presence of a temperature gradient. Figure 5(a) shows I versus V for a case of intrinsic asymmetry: the slope of I versus V is determined by the temperature of the normal electrode, and when the temperature of the superconductor is raised the curve shifts more or less rigidly down-

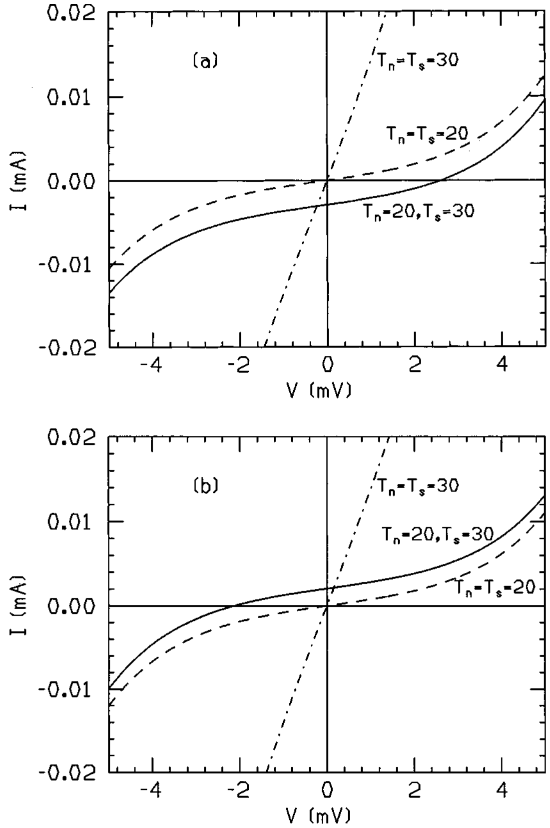

FIG. 5. Current versus voltage for an *NIS* tunnel junction with the normal electrode colder than the superconducting one (solid line) and for both electrodes at the same temperature, as indicated (dashed and dash-dotted lines). (a) $\nu=1.5$ (at $T=0$), energy-independent transmission ($c=0$). (b) No intrinsic electron-hole asymmetry ($\nu=0$) and energy-dependent transmission, $c=4.5\ \mathrm{eV}^{-1}$, with the transmission probability of an *electron* increasing with energy.

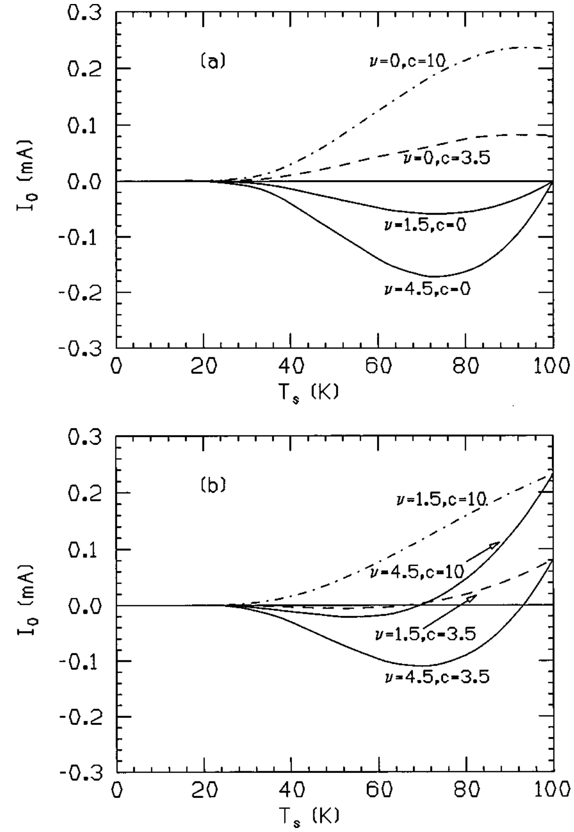

FIG. 6. Zero-voltage thermoelectric current I_0 versus temperature of the superconducting electrode for fixed temperature difference $T_s-T_n=10$ K. (a) Full lines: intrinsic asymmetry, energy-independent transmission. Dashed lines: no intrinsic asymmetry, energy-dependent transmission. (b) Some cases with both intrinsic asymmetry and energy-dependent transmission.

wards; a zero-voltage current I_0 exists from the superconductor to the normal metal and a zero-current voltage V_0 where N is positive with respect to S. Similarly in Fig. 5(b) the same behavior (with opposite sign) is found with no intrinsic asymmetry but energy-dependent $T(E)$. Note however that the magnitude of c required to give the same magnitude effect as $\nu=1.5$ is smaller than that required to give symmetric tunneling characteristics [Fig. 4(b)]. In other words, if intrinsic asymmetry and $T(E)$ effects are of a magnitude such as to cancel each other in dI/dV, the thermoelectric effect due to $T(E)$ would dominate.

As seen from Fig. 5(a), a temperature gradient where T_s is larger than T_n causes less current to flow from N to S than when $T_s=T_n$ for the same T_n for small voltages, so that $|I|$ is smaller for positive than for negative voltages. For voltages somewhat larger than shown in Fig. 5(a), however, the asymmetry in the density of states takes over and both I and dI/dV are larger for positive than for negative voltages. On the scale of Fig. 4, the temperature gradient does not change the dI/dV behavior shown in Fig. 4.

From the results presented so far, we conclude that it is not possible to distinguish effects due to intrinsic electron-hole asymmetry versus energy-dependent $T(E)$ neither in the voltage and temperature dependence of dI/dV nor in the voltage dependence of I in the presence of a temperature gradient across the barrier. As we will see in what follows, distinction does become possible when we consider dependence of thermoelectric current and voltage on temperature, magnetic field, or barrier thickness.

A. Temperature dependence of thermoelectric effect

We consider the zero-voltage thermoelectric current I_0 for a fixed temperature difference $T_s-T_n=10$ K, as a function of T_s. Figure 6(a) shows the behavior for two cases with intrinsic asymmetry and energy-independent transmission, and two cases with no intrinsic asymmetry and energy-dependent $T(E)$. The behavior is qualitatively different as T approaches T_c, as the current due to intrinsic asymmetry vanishes and that due to energy-dependent $T(E)$ saturates at a nonzero value. Thus, this measurement provides a clear qualitative difference of the consequences of both effects. In the presence of both effects together they add, and I_0 versus temperature can change sign, as shown in some examples in Fig. 6(b). Note also that even if it does not change sign, evidence for a nonzero ν in Fig. 6(b) is that $I_0(T)$ has finite slope as T approaches T_c, in contrast to Fig. 6(a). Thus, if it is found that the thermoelectric current goes to zero as $T\rightarrow T_c$, we would conclude that $T(E)$ is energy independent and intrinsic asymmetry exists, otherwise one would calculate the expected $I_0(T)$ for various values of ν and c until a

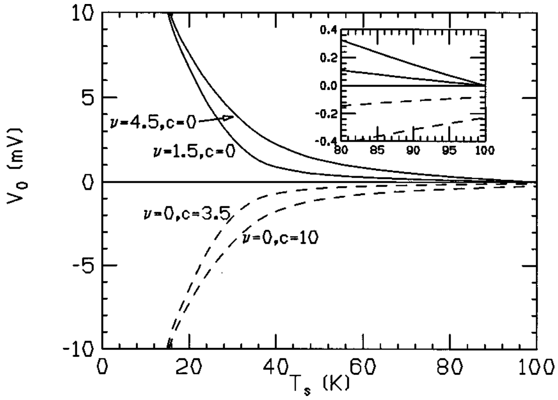

FIG. 7. Zero-current thermoelectric voltage for the same cases as in Fig. 6(a). The inset shows the region of temperature close to T_c amplified.

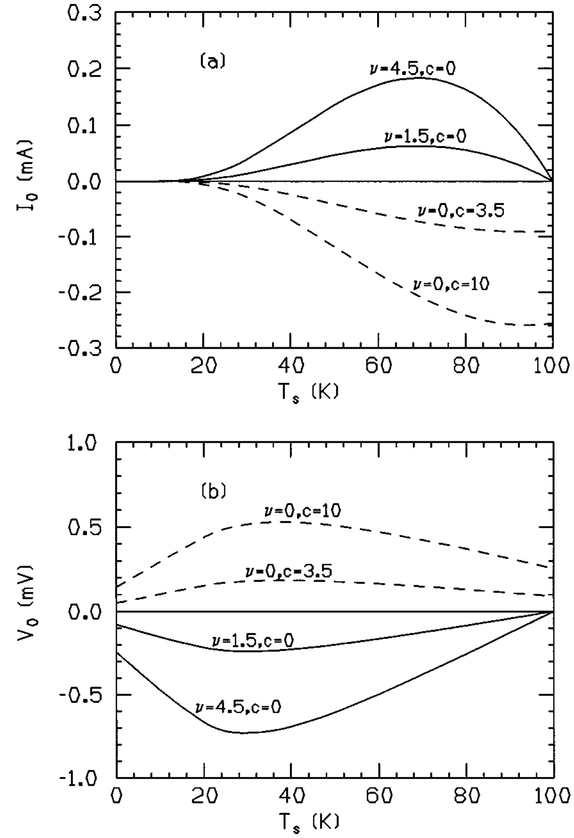

FIG. 8. Dependence of current and voltage on temperature when the normal metal is at higher temperature than the superconductor: $T_n - T_s = 10$ K. (a) Zero-voltage thermoelectric current, (b) zero-current thermoelectric voltage. The parameters are indicated in the figure.

best fit is found. Because of the qualitative difference in the two effects as $T \to T_c$, the fitting procedure would allow determination of ν and c given sufficiently accurate experimental results for I_0.

The zero-current thermoelectric voltage is shown in Fig. 7 for some cases. At low temperatures, the thermoelectric voltages become rather large when the normal metal is colder than the superconductor, as described by Eq. (30). As T approaches T_c, V_0 goes to zero if only intrinsic asymmetry exists and remains finite for energy-dependent transmission (inset).

For the case where the superconductor is colder than the normal metal, the behavior of the zero-voltage thermoelectric current is similar, as shown in Fig. 8(a). However, the voltages at low temperatures are much smaller in this case, as shown in Fig. 8(b). This is to be expected from Eq. (30).

B. Magnetic-field dependence

In the presence of a magnetic field large enough to suppress the gap in the superconductor, the intrinsic asymmetry is also suppressed, while the asymmetry due to $T(E)$ persists. Figure 9 shows the zero-voltage thermoelectric current versus energy gap for fixed transmission and various values of intrinsic asymmetry (a) and for fixed intrinsic asymmetry and varying transmission energy dependence (b). Here, $T_n = 20$ K, $T_s = 50$ K. Note that the curves are nonmonotonic in most cases. For example, a decreasing energy gap can cause I_0 (in absolute value) first to increase and then decrease both for $\nu = 0$ as well as for $c = 0$. Again, as the gap goes to zero, I_0 remains finite only if energy dependence in $T(E)$ exists. If I_0 changes sign as a function of Δ_0, it indicates that both intrinsic asymmetry and energy dependence in $T(E)$ exist. For large energy dependence of $T(E)$ and small intrinsic asymmetry, no change in sign occurs; nevertheless, even in that case a small intrinsic asymmetry would be detectable as it makes the maximum in I_0 versus Δ_0 disappear.

Figure 10 shows the behavior of the zero-current thermoelectric voltage versus Δ_0 for various cases for $T_n = 20$ K, $T_s = 50$ K. Here again the qualitative difference occurs as $\Delta_0 \to 0$, while for large Δ_0 the dependence of V_0 on gap for both intrinsic asymmetry and energy-dependent $T(E)$ is similar.

C. Barrier thickness dependence

The parameter c that gives rise to the thermoelectric effect due to the barrier is directly proportional to the barrier thickness, as discussed in Sec. III [Eq. (15)]. Hence, in the presence of both intrinsic asymmetry and energy-dependent transmission, measuring the thermoelectric effect for different barrier thicknesses should be useful in sorting out the two effects. In particular, as the barrier thickness approaches zero, the intrinsic effect will dominate. However, when the barrier becomes very thin the tunnel junction will no longer be ideal and the effect due to intrinsic asymmetry is also weakened, as discussed in Ref. 3. Here we assume that the barrier remains ideal in the range of thicknesses considered.

Figure 11 shows the zero-voltage thermoelectric current (a) and the zero-current thermoelectric voltage (b) versus c, which is proportional to the barrier thickness for various values of the intrinsic asymmetry parameter ν in the presence of a fixed temperature gradient. The zero-voltage current is given by

$$I_0 = \frac{2}{eRa} \int_{\Delta_0}^{\infty} dE \frac{E}{\sqrt{e^2 - \Delta_0^2}} \left[\frac{\nu}{E} - cE \right] [f_n(E) - f_s(E)], \tag{32}$$

so that it is linear in c. Hence, even if the intrinsic asymmetry is small and the barriers are not very thin, extrapolation

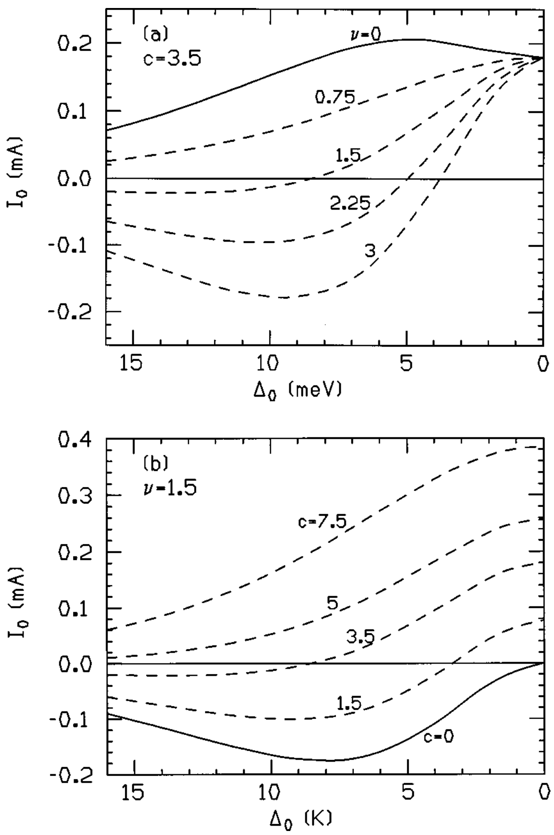

FIG. 9. Zero-voltage thermoelectric current versus gap Δ_0 for (a) fixed transmission and various degrees of intrinsic asymmetry and (b) fixed intrinsic asymmetry and varying energy-dependence of transmission. $T_n = 20$ K, $T_s = 50$ K. The curves are labeled by the value of the asymmetry parameter ν at zero temperature with zero-temperature gap $\Delta_0 = 16$ meV; as Δ_0 is reduced, ν is reduced proportionally to Δ_0^2.

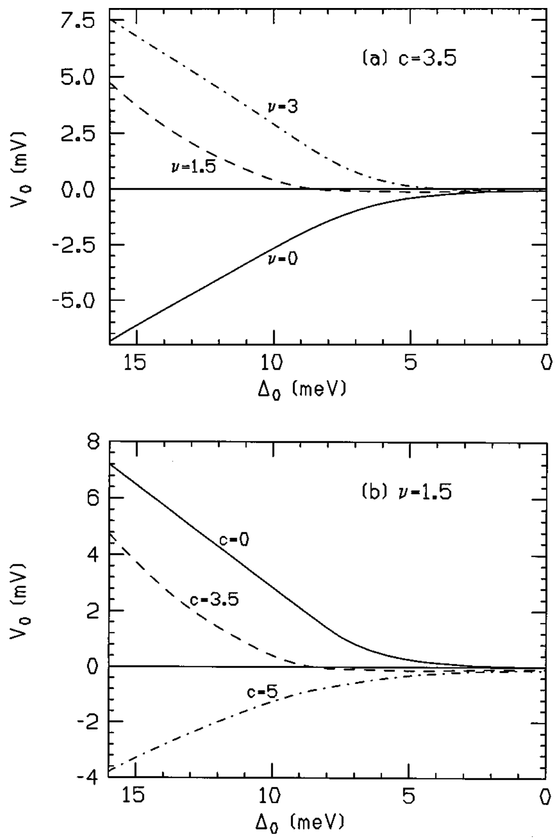

FIG. 10. Zero-current thermoelectric voltage versus gap for (a) fixed transmission and various degrees of intrinsic asymmetry and (b) fixed intrinsic asymmetry and varying energy dependence of transmission. $T_n = 20$ K, $T_s = 50$ K.

of $I_0(c)$ to $c = 0$ should not be too difficult, and would provide direct information on the intrinsic asymmetry ν.

The thermoelectric voltage, Fig. 11(b), shows a rapid crossover from intrinsic asymmetry dominated for thin barriers to barrier dominated for thicker barriers; observation of this crossover would provide direct information on the existence of these competing effects. If however the intrinsic asymmetry is very small, it would be difficult to extract information on ν from V_0 if only a limited range of thick barriers was available. Nevertheless, except for this caveat, the fact that the thermoelectric voltage can become very large at low temperatures suggests that measurement of V_0 versus barrier thickness may be the most direct way to extract information on the intrinsic asymmetry.

VI. EXPERIMENTAL FEASIBILITY

We consider the circuit shown in Fig. 12. As discussed by Leivo, Pekola, and Averin,[5] a *SINIS* structure provides a more efficient way of cooling than the original *NIS* structure considered by Nahum, Eiles, and Martinis,[4] because it avoids heat leakage through the *SN* contact used to bias the junction. Leivo, Pekola, and Averin used two additional ''thermometer'' *SIN* junctions to measure the temperature drop in the *N* electrode through a floating voltage measurement at constant bias current. In Fig. 12 we show instead a $S'IN$ and a $N'IN$ junction; these should serve the purpose of both measuring the temperature drop as well as detecting the thermoelectric voltage.

The entire system in Fig. 12 should be at temperature T_s, and when the current I_{refr} flows the electrode N will be cooled to a lower temperature T_n. The normal metal N' may be the same metal as N, but will be at temperature T_s. We use a tunnel junction $N'IN$ rather than a metallic contact to avoid heat losses. The superconductor S' should have a lower critical field than S, so that it would be possible to suppress the superconductivity in S' with a magnetic field while maintaining the refrigerating power of the *SINIS* system.

If there is no energy dependence in the transmission across the $S'IN$ and $N'IN$ junctions, the voltage V_0 measured between electrodes N' and S' will be the zero-current thermoelectric voltage due to intrinsic asymmetry in the superconductor S', provided the junctions $S'IN$ and $N'IN$ are exactly opposite each other. To average over geometric asymmetry, the voltage V_0 should be measured with positive and negative I_{refr}, and averaged. If the junction's transmission has energy dependence, the effects of $T(E)$ in the $S'IN$ and $N'IN$ junctions should come in with opposite signs and nearly cancel out if the junctions are of similar nature and thickness; the residual effect should be representable by a small ''effective'' value of the parameter c in the tunneling characteristics discussed in the previous section.

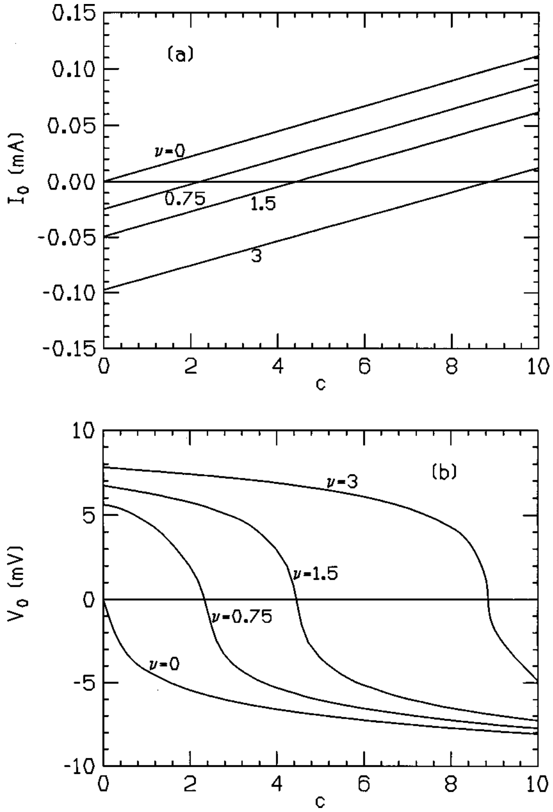

FIG. 11. Dependence on magnitude of transmission parameter c, which is proportional to barrier thickness, of (a) zero-voltage thermoelectric current and (b) zero-current thermoelectric voltage. $T_n=20$ K, $T_s=50$ K.

The cooling power of the refrigerating junctions is determined by the heat current that flows when an electric current circulates. For energy-independent transmission and no intrinsic asymmetry, the heat current is given by[4]

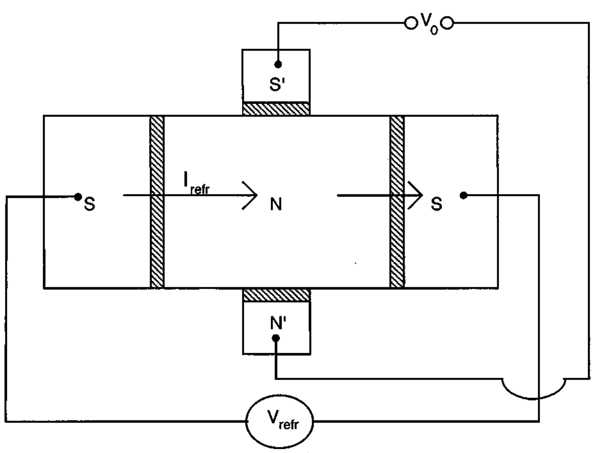

FIG. 12. Schematic circuit for measurement of thermoelectric effect. The entire system is at temperature T_s, and when the current I_{refr} circulates the electrode N will be cooled to a lower temperature T_n if $V_{refr}\sim\Delta_0/2$. The electrodes S' and N' will remain at temperature T_s. If the barriers $S'IN$ and $N'IN$ are similar, the voltage V_0 will measure the intrinsic asymmetry parameter of the superconductor S'. The junctions $S'IN$ and $N'IN$ can also be used to measure the temperature drop in N as in the case of Leivo, Pekola, and Averin.

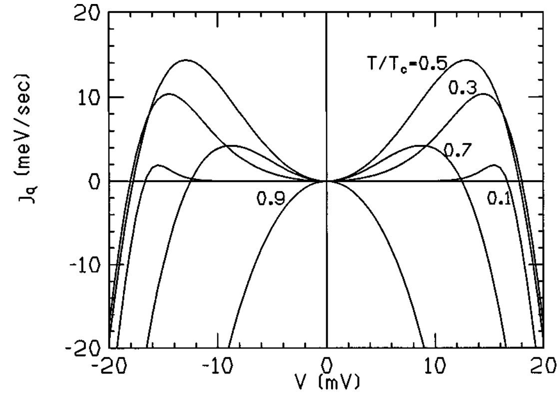

FIG. 13. Cooling power of an SIN junction with zero-temperature gap $\Delta_0=16$ meV and $T_c=100$ K. The numbers next to the curves give the value of T_s/T_c.

$$j_q=\frac{1}{e^2R}\int_{\Delta_0}^{\infty}dE\frac{E}{\sqrt{E^2-\Delta_0^2}}(E-\mathrm{eV})[f_n(E-\mathrm{eV})-f_s(E)]. \tag{33}$$

In the presence of intrinsic asymmetry or of energy-dependent transmission, the magnitude of j_q will be slightly different for positive and negative junction polarity. However, in the *SINIS* geometry these effects will average out and we will not consider them in what follows.

The cooling power is largest when the bias voltage of the refrigerating junctions is close to Δ_0/e, as shown in Fig. 13. As a function of temperature, the cooling power first increases as T is lowered below T_c and the gap opens up, and decreases again at lower temperatures as the number of excited quasiparticles becomes small. Figure 14 shows the maximum cooling power as function of T_s for $T_s=T_n$ and for $T_s-T_n=0.1T_c$, as assumed for the results in Figs. 6 and 7. In that case, the maximum cooling power occurs for $T_s\sim0.43T_c$.

The electronic temperature that can be reached in the N electrode depends on the coupling between electrons and phonons, which is expected to be proportional to the 5th power of the temperature, as discussed in Ref. 5. The energy transfer from electrons in the normal electrode to phonons is given by[5]

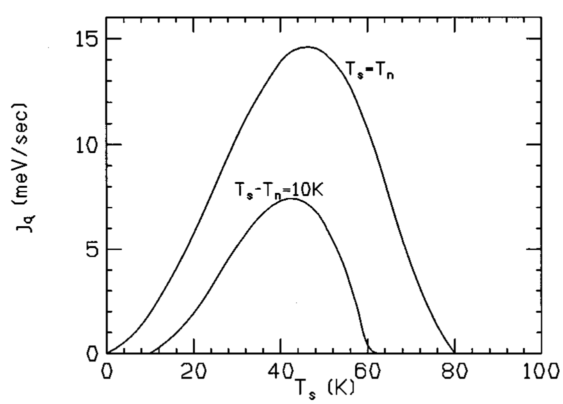

FIG. 14. Maximum cooling power versus T_s for $T_s=T_n$ and for $T_s-T_n=10$ K for the case of Fig. 13.

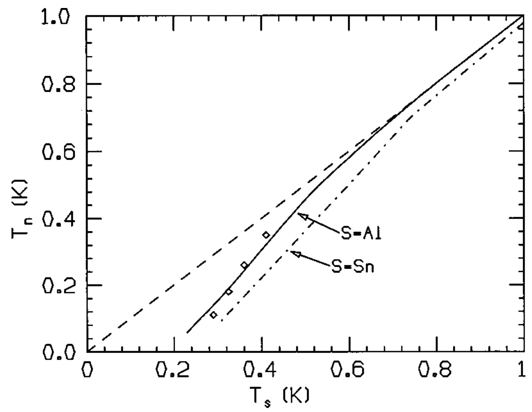

FIG. 15. Temperature of normal electrode T_n versus temperature of superconducting electrode for a junction of dimensions and parameter Σ [Eq. (31)] as in the case of Leivo, Pekola, and Averin for $S=$Al ($T_c=1.14$ K) and for S=Sn ($T_c=3.72$ K). The resistance of the refrigerating junction is assumed to be 1 K Ω.

$$j_l=\Sigma\Omega(T_s^5-T_n^5), \tag{34}$$

where we assume that the lattice is at temperature T_s. Here, Ω is the volume of the normal electrode and Σ is a constant that depends on the strength of electron-phonon coupling. In the experiment of Leivo, Pekola, and Averin, Σ was estimated to be

$$\Sigma=4 \ \text{nW}/K^5 \ \mu\text{m}^3, \tag{35}$$

and the normal electrode dimensions were 0.5 μm, 0.3 μm, and 35 nm for length, width, and thickness, respectively.

Equating the heat current Eq. (33) to the heat loss Eq. (34) yields an estimate for the temperature that will be attained in the normal electrode. Figure 15 shows T_n versus T_s estimated this way versus T_s and the experimental data of Leivo, Pekola, and Averin, where S is aluminum and N is copper. We also show the cooling power for the case where $T_c=3.72$ K, as it would be if the superconducting electrodes S were Sn. The sample dimensions and strength of electron-phonon coupling were taken to be as for the case of Leivo, Pekola, and Averin.

For the case of Leivo, Pekola, and Averin, the critical field of S (Al) would be $H_c=105$ G. For S', one should use a superconductor with lower critical field, to be able to suppress superconductivity in S' with a magnetic field while maintaining it in S. For example, one could use Ga or Zn, with critical temperatures $T_c=1.091$ K and $T_c=0.875$ K and critical fields $H_c=51$ G and $H_c=53$ G, respectively. To measure the ν parameter of Al one could use Al for S' and Sn for S, with $H_c=309$ G. The refrigerating junction's resistance assumed for Fig. 15 is 1 $K\,\Omega$; better results would be obtained with smaller junction resistance and smaller sample dimensions.

To estimate the magnitude of the expected thermoelectric effect for these cases, the critical temperature needs to be scaled by a factor of approximately 100 from the cases discussed in Sec. V. However, we expect the asymmetry parameter ν to be reduced even more, perhaps by a factor of 1000, i.e., $\nu=1.5$ μV. Then, the thermoelectric voltages that will be measured corresponding to a few mV in the graphs in Sec. V will be a few μV. Concerning the currents, for the results in Sec. V we assumed a resistance for the $S'IN$ junction of $R=1$ Ω. Assuming a more realistic value, $R\sim100$ Ω, we conclude that currents will be scaled down by a factor of approximately 10^5 from those shown in the figures in Sec. V, hence we expect measured thermoelectric currents for these cases to be of order nA. We conclude that the expected values for thermoelectric voltages and currents are well within what can be detected in the laboratory. In the experiment of Smith, Tinkham, and Skocpol[8] with a Pb-I-Al tunnel junction, a superconducting quantum interference device galvanometer was used to measure thermoelectric currents down to a few pA.

One should also consider possible thermoelectric effects that could arise from temperature gradients in the normal electrodes N and N'. Let us assume as an upper bound that the temperature drop occurs entirely in the electrodes rather than at the barrier. Assuming the normal electrodes are Cu, at a temperature of 1 K its thermoelectric power is approximately $S\sim-0.01$ μV/K; thus, this contribution should be substantially smaller than the expected thermoelectric voltage from intrinsic asymmetry in S' and from barrier effects.

Finally, let us estimate the voltage that could arise due to geometric asymmetry in the location of the junctions $S'IN$ and $N'IN$. For refrigerating junctions of resistance 1 K Ω, the refrigerating current will be of order $I_{refr}\sim0.2$ μA if the bias voltage is of order $V\sim0.2$ mV, the magnitude of the energy gap in Al. Assuming a Cu sample of resistivity ratio of 10^3 (about 20 ppm impurities) and a geometric asymmetry corresponding to a relative displacement of 2.5 μm between the junctions $S'IN$ and $N'IN$ would yield a voltage drop of approximately 1 nV. Thus the effect of geometric asymmetry can be expected to be much smaller than the expected thermoelectric voltage; in addition, it can be largely eliminated by circulating I_{refr} in positive and negative directions.

VII. DISCUSSION

We have studied the feasibility of measuring the intrinsic electron-hole asymmetry expected to occur in all superconductors according to the theory of hole superconductivity by measuring a thermoelectric effect across tunnel junctions. The recent developments in achieving refrigeration with such junctions open up the possibility of measuring this effect. Even in the presence of energy dependence of transmission across the barriers, we have seen that it should be possible to detect the intrinsic electron-hole asymmetry in the superconductor. Essentially, the reasons are that the intrinsic asymmetry is expected to be strongly dependent on the existence of the superconducting gap, while thermoelectric effects due to the barrier are expected to remain even when the superconducting gap is suppressed; also, thermoelectric effects due to barrier will be strongly dependent on the thickness of the barrier. Furthermore, they can be largely eliminated with the geometry of Fig. 12 with similar junctions $S'IN$ and $N'IN$. We have also seen that other sources of thermoelectric effects as well as voltages arising from geometric asymmetries are not expected to be significant.

For superconductors with higher critical temperatures, and in particular for high-T_c oxides, the much larger magnitude of heat transfer from electrons to phonons [Eq. (34)] would preclude the possibility of achieving much lower electronic than lattice temperatures, as was achieved in the experiment of Leivo, Pekola, and Averin.[5] However, it may still be possible in that case to achieve a substantial temperature drop in the normal electrode (electrons and lattice) by thermally insulating it from the environment, as was achieved to some degree in the experiment of Manninen, Leivo, and Pekola.[6] In that case, thermal conduction across the tunnel barrier would limit the magnitude of gradients that can be achieved, making it desirable to use tunnel barriers of low thermal conductivity. Also, the possibility of achieving large temperature gradients across tunnel junctions by heating rather than cooling, e.g., by laser irradiation[8] or by joule heating, should be further explored.

The thermoelectric effect due to intrinsic asymmetry would also occur when both electrodes in a tunnel junction are superconducting,[3] in which case the effects of the parameter ν in each electrode would add. Furthermore, in that case the cooling power of an SIS' junction (with different gaps for S and S') would be even larger in certain parameter ranges due to the diverging density of states in both electrodes. Thus, a setup where all electrodes are superconducting could provide an even more efficient way to measure the parameter ν of a superconductor.

The intrinsic thermoelectric effect discussed here will arise in any superconductor where the gap function as function of energy has a finite slope at the Fermi energy. Just as it is of interest to measure variations of the superconducting gap on different points on the Fermi surface (e.g., s wave versus d wave) it should be of interest to measure variations of the gap in directions *perpendicular* to the Fermi surface. Quite generally, this information should provide clues on the nature of the pairing mechanism. In other theoretical frameworks one might expect the slope of the superconducting gap to be zero or of random sign and to not correlate with the magnitude of T_c. In contrast, the theory of hole superconductivity predicts the slope to be of universal sign and to increase with the critical temperature.

In conclusion, we believe that an experimental effort to measure the parameter ν of superconductors (i.e., the slope of the superconducting gap function at the Fermi energy), should be pursued. In addition to the technique discussed here, there may be other more direct ways of doing this without involving tunnel junctions. Such ways should be investigated. Finding a single superconductor where ν is negative or zero would invalidate the theory of hole superconductivity. More generally, knowledge of the value of ν of superconductors, in addition to other fundamental properties such as energy gap and critical field, is likely to add valuable insight into the systematics of superconductivity in nature.

ACKNOWLEDGMENT

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[1] J. E. Hirsch and F. Marsiglio, Phys. Rev. B **39**, 11 515 (1989); F. Marsiglio and J. E. Hirsch, *ibid.* **41**, 6435 (1990).

[2] J. E. Hirsch, Phys. Lett. A **134**, 451 (1989); Physica C **158**, 326 (1989); Phys. Rev. B **43**, 11 400 (1991); **48**, 3327 (1993); J. Phys. Chem. Solids **54**, 1101 (1993).

[3] J. E. Hirsch, Phys. Rev. Lett. **72**, 558 (1994); Phys. Rev. B **50**, 3165 (1994).

[4] M. Nahum, T. M. Eiles, and J. M. Martinis, Appl. Phys. Lett. **65**, 3123 (1994).

[5] M. M. Leivo, J. P. Pekola, and D. V. Averin, Appl. Phys. Lett. **68**, 1996 (1996).

[6] A. J. Manninen, M. M. Leivo, and J. P. Pekola, Appl. Phys. Lett. **70**, 1885 (1997).

[7] M. G. Blamire, E. C. G. Kirk, J. E. Evetts, and T. M. Klapwijk, Phys. Rev. Lett. **66**, 220 (1991); D. R. Heslinga and T. M. Klapwijk, Phys. Rev. B **47**, 5157 (1993).

[8] A. D. Smith, M. Tinkham, and W. J. Skocpol, Phys. Rev. B **22**, 4346 (1980).

[9] W. A. Harrison, Phys. Rev. **123**, 85 (1961).

[10] R. Micnas, J. Ranninger, and S. Robaszkiewicz, Rev. Mod. Phys. **62**, 113 (1990); J. Appel, M. Grodzicki, and F. Paulsen, Phys. Rev. B **47**, 2812 (1993); G. Japaridze and E. Muller Hartmann, Ann. Phys. (Leipzig) **3**, 163 (1994); L. Arrachea *et al.*, Phys. Rev. B **50**, 16 044 (1994); M. Airoldi and A. Parola, *ibid.* **51**, 16 327 (1995); M. Quaisser, A. Schadschneider, and J. Zittartz, Europhys. Lett. **32**, 179 (1995).

[11] F. Marsiglio and J. E. Hirsch, Physica C **159**, 157 (1989).

[12] J. Frenkel, Phys. Rev. **36**, 1604 (1930); T. E. Hartman, J. Appl. Phys. **35**, 3283 (1964); W. F. Brinkman, R. C. Dynes, and J. M. Rowell, J. Appl. Phys. **41**, 1915 (1970).

[13] K. H. Gundlach, J. Appl. Phys. **44**, 5005 (1973).

[14] M. Tinkham, Phys. Rev. B **6**, 1747 (1972).