$$F(z,z,x = y = t = 0) = (2\pi)^{-1}\int_{-\infty}^{\infty} d\omega$$
$$\times F(z,z,x = y = 0,\omega) = (2\pi)^{-1}\int_{-\infty}^{\infty} d\omega$$
$$\times \int_0^{k_F} KdK \exp\left[i(2m|\omega|z/K)\right]\frac{2m\Delta_\infty}{4\pi K(\omega^2 - \Delta_\infty^2)^{\frac{1}{2}}}$$
$$= \frac{2m\Delta_\infty k_F}{4\pi^2}\int_0^{\infty}\frac{d\omega}{(\omega^2 - \Delta_\infty^2)^{\frac{1}{2}}} B\left(\frac{2m\omega z}{k_F}\right), \qquad (20)$$

where

$$B(x) = ie^{ix}\int_0^{\infty}\left(\frac{t}{t+x}\right)e^{it}dt = e^{ix} - ix\,\mathrm{Ei}^{+}(ix)$$
$$\backsim -e^{ix}/x, \qquad x \gg 1. \qquad (21)$$

In the limit we obtain

$$F(z,z,x = y = t = 0) \propto B(2m\Delta_\infty z/k_F) \propto 1/z,$$
$$z > k_F/2m\Delta_\infty \approx 10^{-4}\text{cm}. \qquad (22)$$

In calculating the z dependence of (20) at smaller distances, we must remember that by using the bulk value of F for $F(0^+,0^+)$ we neglect the effect of the change in energy gap near the edge of the superconductor.

This nonexponential falloff has been commented on by Falk.[5] It should be pointed out that this result is a consequence of choosing $V = 0$ in the normal metal. Since the pairing energy is zero, we have the limiting case of class II wave functions and the corresponding $1/z$ falloff.[6] In a metal having a repulsive interaction between electrons the positive potential energy might be expected to give rise to the exponential falloff characteristic of class I functions.

It might be added that metals having a repulsive electron–electron interaction will exhibit an energy gap in the neighborhood of a superconducting contact, following from (3) and the continuity of the wave function. This has been observed experimentally in tunneling experiments.[7]

This method is easily generalized to finite temperatures by the use of thermal Green's functions.[1] The above results are being extended to thin films and samples in which $V(r)$ takes both positive and negative values.

I am most thankful to Professor Leon Cooper for suggesting the above problem and for his many helpful suggestions.

[5] D. S. Falk, University of Maryland, Physics Department, Technical Report No. 315 (unpublished).
[6] E. C. Kemble, *Quantum Mechanics* (Dover Publications, Inc., New York, 1958), p. 85.
[7] P. H. Smith, S. Shapiro, J. L. Miles, and J. Nicol, Phys. Rev. Letters 6, 686 (1961).

The Effect of Quasiparticle Damping on the Ratio between the Energy Gap and the Transition Temperature of Lead

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According to the BCS theory the ratio between the energy gap at zero temperature and the transition temperature (multiplied by the Boltzmann constant) is 3.5 in the weak coupling limit. However, experiments show that it increases to $\simeq$4.1 (for Pb) and $\simeq$4.6 (for Hg) as the electron–phonon coupling strength increases. Since nonresonant processes have been shown to decrease this ratio with increasing coupling strength,[1] we suggest that the quasi-particle damping gives rise to this phenomenon. Since the damping rate is greater at higher temperature, it reduces the transition temperature much more than the energy gap, thereby increasing the ratio.

In the calculation for lead, the electron–phonon interaction is written as

$$H' = \sum_{\substack{kK\\ q\lambda}} \frac{1}{(2\omega_{q\lambda})^{\frac{1}{2}}} v(\mathbf{q}+\mathbf{K})(\mathbf{q}+\mathbf{K})\cdot\mathbf{e}_{q\lambda}c^*_{k+q+K}c_k a_{q\lambda}$$
$$+ \text{Hermitian conjugate},$$

where c_k annihilates an electron of quasi-momentum $\mathbf{k}$ and $a_{q\lambda}$ annihilates a phonon of momentum $\mathbf{q}$ (restricted to first Brillouin zone), polarization λ, and frequency $\omega_{q\lambda}$. The unit polarization vector $\mathbf{e}_{q\lambda}$ is as-

[1] G. J. Culler, B. D. Fried, R. W. Huff, and J. R. Schrieffer, Phys. Rev. Letters 8, 399 (1962).

sumed to be parallel to $\mathbf{q}$ for $\lambda = 1$, and perpendicular to $\mathbf{q}$ for $\lambda = 2, 3$. The vector $\mathbf{K}$ is any reciprocal lattice vector; $\mathbf{K} = 0$ for normal processes, $\mathbf{K} \neq 0$ for umklapp processes. $\omega_{q\lambda}$'s are assumed to have simple spherically symmetrical forms described in Fig. 1. The initial slopes at small q are determined

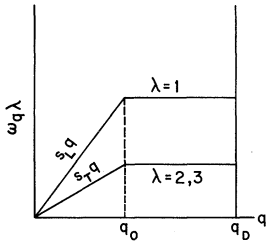

FIG. 1. Phonon energies, $\omega_{q\lambda}$ which simulate Brockhouse's data. s_L and s_T are the sound velocities, and q_D is the Debye cutoff.

by the angular averages of measured longitudinal and transversal sound velocities s_L and s_T, respectively, which are $s_L = 2.42 \times 10^5$ cm/sec, $s_T = 1.07 \times 10^5$ cm/sec at $T = 10°\text{K}$.[2] q_0 is determined so as to give an over-all agreement with Brockhouse's data[3] and we use

$$q_0 = 0.45\, q_D ,$$

where q_D is the Debye cutoff. This choice gives a fairly good agreement for $\omega_{0L} = s_L q_0$ and $\omega_{0T} = s_T q_0$ with those determined from the tunneling experiments.[4,5]

According to Harrison,[6] $v(\mathbf{q} + \mathbf{K})$ can be approximated by a linear function of $|\mathbf{q} + \mathbf{K}|$ at $|\mathbf{q} + \mathbf{K}| < 2k_F$ for zinc and some other metals. It seems to increase more sharply for lead at small $|\mathbf{q} + \mathbf{K}|$, and at large $|\mathbf{q} + \mathbf{K}|$ near to $2k_F$ it might be a better approximation to regard it as a constant, otherwise we can not obtain the measured value of electrical resistivity at high temperature. Therefore, $v(\mathbf{q} + \mathbf{K})$ is assumed to be

$$v(\mathbf{q}) = v(0)(1 - \alpha q/k_F) , \qquad \text{for normal processes,}$$

$$v(\mathbf{q} + \mathbf{K}) = v(0)\delta , \qquad \text{for umklapp processes,}$$

where α and δ are constants, k_F is the Fermi momentum, and

$$v(0) = -\frac{4\pi Z e^2}{k_s^2}\left(\frac{N}{M}\right)^{\frac{1}{2}},$$

where Z is the number of conduction electrons per ion ($Z = 4$ for lead), k_s is the inverse Fermi–Thomas screening length, N is the number density of ions, and M is the mass per ion. If we require the extrapolation of $v(q)$ to become $v(0)\delta$ at a large momentum transfer, say, at $q = K_1$, the nearest reciprocal lattice vector, we can find the values of α and δ by calculating the high-temperature electrical resistivity along the line discussed by Rothwarf and Cohen[7] making use of the effective electron mass $m^* = 2.1$ m. Those are

$$\delta^2 = 7.28 \times 10^{-3} , \qquad \alpha = 0.781 , \qquad (1)$$

which correspond to

$$I(K_1)^2 = 3.2 \times 10^{-53}\,\text{erg}^2\,\text{cm}^4$$

in Rothwarf and Cohen's notation. Their value is 6.1×10^{-52} erg^{2}cm^4. SSW derived the energy gap equation using the Nambu formalism at absolute zero temperature taking into account the quasiparticle damping. The same method is applied to our model at a finite temperature. Neglecting the small nondiagonal elements of the electron self-energy part with respect to the electron momentum due to the umklapp processes, and using the fact that the diagonal elements are essentially independent of the momentum, we calculate the energy gap function $\Delta(\omega)$ by including both electron–phonon and Coulomb interactions and it turns out to be

$$\begin{aligned}\Delta(\omega) = \frac{1}{Z(\omega)}\int_{\Delta_0}^{\omega_c} d\omega' \,\mathrm{Re}\left[\frac{\Delta'}{(\omega'^2 - \Delta'^2)^{\frac{1}{2}}}\right]\Bigg[\frac{m^*}{16\pi^3 k_F} \\ \times \sum_{K\lambda}\int d^3q \,\frac{|v(\mathbf{q}+\mathbf{K})|^2}{2\omega_{q\lambda}|\mathbf{q}+\mathbf{K}|}\,((\mathbf{q}+\mathbf{K})\mathbf{e}_{q\lambda})^2 \\ \times \theta(2k_F - |\mathbf{q}+\mathbf{K}|) \\ \times \{D_{q\lambda}(\omega'+\omega) + D_{q\lambda}(\omega'-\omega)\} - U\Bigg] \\ \times \tanh(\tfrac{1}{2}\beta\omega') . \qquad (2)\end{aligned}$$

where some small terms are neglected, $Z(\omega)$ can be expressed by an integral which involves only $\Delta(\omega)$, $D_{q\lambda}(x) = (x + \omega_{q\lambda} - i0^+)^{-1}$, $\Delta_0 \equiv \Delta(\Delta_0)$ the gap parameter at the edge of the energy gap, $\theta(x) = 1$ if $x > 0$ and zero otherwise, and the screened Coulomb interaction is replaced by a pseudopotential U defined to include interactions between electrons outside a band of energies $|\omega| < \omega_c$, which is large in comparison with the Debye energy.

The simplest way to estimate the effect of quasiparticle damping is to use the "effective interaction"

[2] D. L. Waldorf and G. A. Alers, J. Appl. Phys. **33**, 3266 (1962).
[3] B. N. Brockhouse, T. Arase, G. Caglioti, K. R. Rao, and A. D. B. Woods, Phys. Rev. **128**, 1099 (1962).
[4] J. M. Rowell, P. W. Anderson, and D. E. Thomas, Phys. Rev. Letters **10**, 334 (1963).
[5] J. R. Schrieffer, D. J. Scalapino, and J. W. Wilkins, Phys. Rev. Letters **10**, 336 (1963). This is denoted as SSW, hereafter.
[6] W. A. Harrison, Phys. Rev. **129**, 2503 (1963); **129**, 2512 (1963).
[7] A. Rothwarf and M. Cohen, Phys. Rev. **130**, 1401 (1963).

approximation, that is, to simulate the kernel in the integral equation (2) by a separable form $\gamma(\omega)\gamma(\omega')$, then the equation is reduced to

$$1 \simeq \langle\gamma(\omega)^2\rangle \int_{\Delta_0}^{\omega_0} d\omega \, \mathrm{Re}\left\{\frac{1}{Z(\omega)(\omega^2-\Delta^2)^{\frac{1}{2}}}\right\} \tanh\left(\tfrac{1}{2}\beta\omega\right), \tag{3}$$

where γ^2 is replaced by some average since it is a slowly varying function within $\omega < \omega_0$, which is of the order of magnitude of the Debye energy. At $\omega > \omega_0$, it is a good approximation to regard γ^2 as small. That is suggested by the fact that $\Delta(\omega)$ is sharply decreasing at $\omega \simeq \omega_0$ according to the zero temperature calculation by SSW. Under the effective interaction approximation it is consistent to regard Δ as a real constant and to write $Z(\omega)$ as

$$Z(\omega) = 1 + i\Gamma(\omega)/\omega, \tag{4}$$

in terms of the damping rate of the quasi-particle $\Gamma(\omega)$, at $\Delta_0 < \omega < \omega_0$. Equation (3) becomes

$$1 = \langle\gamma(\omega)^2\rangle \int_{\Delta_0}^{\omega_0} \frac{d\omega}{(\omega^2-\Delta_0^2)^{\frac{1}{2}}} \cdot \frac{\omega^2}{\omega^2+\Gamma(\omega)^2} \tanh\left(\tfrac{1}{2}\beta\omega\right). \tag{5}$$

We calculate the right-hand side of (5) in two cases, at zero and transition temperatures, assuming the superconductor at $T = 0$, curve C is for normal metal at the transition temperature and for the sake of reference curve A is drawn for normal metal at $T = 0$. Curve A has two discontinuities at $\omega = \omega_{0T}$ and $\omega = \omega_{0L}$. This is because it becomes energetically possible for a quasi-particle to emit a phonon of every momentum when its energy surpasses these values. And we see the two square root singularities of the curve B at $\omega_{0T} + \Delta_0$ and $\omega_{0L} + \Delta_0$ due to the density of states effect. By making use of these results, the integral in (5) is calculated and it gives

$$1/\langle\gamma(\omega)^2\rangle = 2.39, \quad \text{at} \quad T = Tc, \quad (\Delta_0 = 0) \tag{6}$$

and

$$1/\langle\gamma(\omega)^2\rangle = 2.62, \quad \text{at} \quad T = 0, \quad (\beta = \infty), \tag{7}$$

where ω_0 is assumed to be $\omega_0 = 20\kappa T_c = 1.39\ \omega_{0L}$. The difference $1/\langle\gamma(\omega^2)\rangle_0 - 1/\langle\gamma(\omega)^2\rangle_{Tc}$ is almost independent of cutoff ω_0. If ω_0 is decreased by 10%, the difference increases only by 2%. We can see what this difference means for the gap–transition temperature ratio by rewriting Eq. (5) as

$$\int_{\Delta_0}^{\omega_0} \frac{d\omega}{(\omega^2-\Delta_0^2)^{\frac{1}{2}}} = \frac{1}{\langle\gamma(\omega)^2\rangle} - \int_{\Delta_0}^{\omega_0} \frac{d\omega}{(\omega^2-\Delta_0^2)^{\frac{1}{2}}} \times \left(\frac{\omega^2}{\omega^2+\Gamma^2} - 1\right), \tag{8}$$

and substituting (6) and estimating the right-hand-side integral assuming the experimental gap–κT_c ratio as above. The right-hand side of (8) corresponds to the inverse coupling strength of BCS theory modified by the quasiparticle damping and we can obtain the modified energy gap from the left-hand side. The ratio turns out to be

$$2\Delta_0/\kappa T_c = 5.2.$$

This is fairly large in comparison with the experimental value 4.1. Although the numerical agreement is poor within the effective interaction approximation, it is certain that the damping effect plays the essential role in gap–κT_c ratio problem. We can tentatively estimate the effect of the imaginary part of Δ making use of knowledge obtained for it by SSW. It increases the quantity (7) a little, a worse direction for gap–κT_c ratio. Finally the electron phonon coupling strength obtained from (1) is compared with that used by SSW. They obtained their coupling strength by adjusting it so as to give a right Δ_0. One can make the comparison by calculating $\Gamma(\omega)$ in normal metal at $T = 0$ and $\omega > \omega_{0L}$.

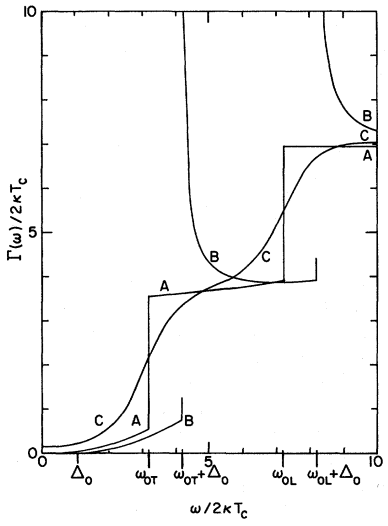

FIG. 2. The damping rate of the quasi-particle, $\Gamma(\omega)$, in the unit of $2\kappa T_c$. (A) Normal metal at $T = 0$; (B) Superconductor at $T = 0$; (C) Normal metal at $T = T_c$.

experimental value for the gap, $2\Delta_0/\kappa T_c = 4.1$, in order to see whether the same value can be obtained for $\langle\gamma(\omega)^2\rangle$.

The function $\Gamma(\omega)$ is computed from the expression for $Z(\omega)$ and (4) within 13% error and illustrated in Fig. 2 in the unit of $2\kappa T_c$. Curve B is for the

From Fig. 2 it is found

$$\Gamma(\omega_{0L} + 0) = 6.96 \times 2\kappa T_c = 8.68 \times 10^{-3}\ \text{eV}.$$

On the other hand, according to SSW strength,

$$\Gamma(\omega_{0L} + 0) = 9.45 \times 10^{-3}\ \text{eV},$$

in good agreement with the experimentally determined value. It may be worthwhile to remark that the gap–κT_c ratio is a rather sensitive quantity to the details of electron–phonon interaction. To obtain a numerical agreement more elaborate calculations would be necessary.

The author would like to thank Professor Schrieffer for his valuable discussions throughout this work.

Discussion 39

W. A. LITTLE, *Stamford University:* I would like to make a comment on the Ginzburg–Landau theory which was referred to in connection with Sewell's paper. As most of you know, the formulation of this theory is based on a general formulation of second-order phase transitions by Landau and Lifschitz. There is an expansion which is made in order parameter ω, which is taken to second order. That such an expansion is possible is only true if all the thermodynamic properties and thermodynamic functions are finite at the transition temperature. In a different context this has recently been tested and has been found that in the second-order phase transition for the gas to liquid transition in argon this fails at the critical point. In order to reformulate this type of second-order phase transition, Prof. Yang has recently reconsidered what Landau and Lifshitz have done and found it is necessary to add another term to this expansion of the form $\omega^2 \log \omega$. The presence of such a term would lead then to an infinite contribution to the specific heat. In the superconducting state this is probably exceedingly small and a very small magnetic field perhaps of the order of mG might wash this out; you cannot get close enough to the direct transition temperature in order to see it. In some sense this refers to some type of long-range order which occurs in the superconducting state which is missing in any of the present formulations of the theory.

W. A. HARRISON, *General Electric Research Laboratory:* As Dr. Wada has indicated, I have shown [Phys. Rev. **129**, 2503 (1963)] that the electron–phonon interaction can be written in terms of single function of wavenumber, the "OPW form factor" characteristic of the metal in question. The function is in fact the matrix element of the electron Hamiltonian of a single ion between two OPW's, but may be thought of as the Fourier transform of a pseudopotential to be associated with each ion. I computed this OPW form factor for zinc [Phys. Rev. **129**, 2512 (1963)] and found it could be roughly approximated by a straight line with the value $-(2/3)F_F$ at zero wave number; this is the approximate form used by Wada.

Subsequently I have found a much more accurate fit, but one which also depends only upon a single parameter for each metal. I obtained this form after computing the OPW form factors self-consistently from the Hartree–Fock ion fields and wave functions for Li, Be, Na, Mg, Al, K, Ca, and Cu. [Phys. Rev. **131**, 2433 (1963)]. In all of these cases (except copper) the OPW form factor could be fit within about three-hundredths of a Ry by the Fourier transform of the Coulomb potential of the net ion charge $(-Ze/r)$ plus the Fourier transform of a delta-function repulsion of strength β arising primarily from orthogonalization to the core, all screened by the conduction electrons in the Hartree approximation; that is, the OPW form factor is approximated by $(-4\pi Ze^2/q^2 + \beta)/\Omega_0\epsilon(q)$, where Ω_0 is the atomic volume and $\epsilon(q)$ the Hartree dielectric function for wave number q. Thus if β is known for a given metal, we obtain directly the approximate OPW form factor which determines not only the electron–phonon interaction, but also the Fermi surface, the resistivity due to defects, and most other potential-dependent aspects of the electronic properties. Further, if we have β for a pair of metals, we may compute directly the resistivity of the corresponding alloys.

I have used this latter property to attempt to obtain values of β for most of the nontransition metals not included in my first principles calculation. That is, I took β values for the light metals by fitting earlier calculations, and then adjusted β for the heavier elements to give the best fit to the observed resistivities of alloy systems involving the various elements. This allowed rather extensive cross checking since many of the metals have been studied in several alloy systems. This cross checking indicated that the scheme only worked moderately well in accounting for observed resistivities; I don't know if the discrepancies are experimental or theoretical. However, it did lead to values of β which may be of some interest in the absence of any other information, keeping in mind that they are of very limited reliability. The values obtained are listed below in units of Ry atomic units of volume. The uncertainty in the elements of atomic number less than or equal to that of zinc (except copper) is roughly 5. In copper and the heavier elements it is significantly greater.

Li	29	Be	31						
Na	27	Mg	42	Al	37				
K	32	Ca	51						
Cu	2	Zn	27	Ga	39	Ge	66		
Ag	5	Cd	26	In	31	Sn	55	Sb	85
Au	10	Hg	4	Tl	25	Pb	60	Bi	97

KUPER: I would like to report very briefly on some preliminary calculations which have been done by D. C. Hamilton, M. Jensen, and myself in connection with the superconductivity of Lanthanum and Uranium. Matthias' rule suggests that there should essentially be symmetry within the transition families about 6 valence electrons, with maxima in superconductivity at 5 and 7, and then a fairly rapid falloff at the larger and smaller numbers. One is faced with the anomaly that both Lanthanum and Uranium show superconductivity at much higher transition temperatures than one would estimate by looking at neighboring elements or at the other transition elements, the lanthanides and the actinides. Our suggested explanation of this anomaly in Lanthanum and Uranium is that they are in each case the last element before an f shell begins to fill and, therefore, there is an f band, presumably a very narrow f band very close to, but above the Fermi surface in these metals. Also, we know that cesium undergoes an antiferromagnetic phase transition at sufficiently low temperatures and we, there-

fore, presume that there is an antiferromagnetic exchange interaction between electrons in this f band. Under these assumptions we find that it is energetically favorable for some of the electrons in the Fermi sea to be promoted into the f band, and aligned in suitably ordered states. If we make a BCS ansatz for the wave function, including finite occupancy of the states in this f band, we find that this antiferromagnetic interaction in the f band can indeed assist superconductivity and the transition temperature can be much higher than one expects from the electron–phonon interaction alone. A typical assumption that we make of this band (which we treat as a completely degenerate single level) is that the height above the Fermi surface is less than the Debye temperature. Because of the assumption of a completely sharp level in the f band the BCS integral equation simplifies to an algebraic equation, and one can calculate the effect of the energy gap for the f band rather simply. It differs from the energy gap of the s band. One has to bring in an interband pairing interaction to produce an energy gap in the s band. Superconductivity will be enhanced in this case by the fact that the whole of the condensed f band is within the available distance of the Fermi surface. A firm prediction which one is able to make is that these elements should show no isotope effect if our model is applicable. I don't believe there are any available data on this point; unfortunately Lanthanum has only one stable isotope, but I hope some measurements can be made in Uranium. The second firm prediction is that the law of corresponding states should not hold; in particular, whereas the BCS value for $H_c^2/\gamma T_c$ is 5.9, we would predict a value somewhat larger. In fact, for all the superconductors for which data are available, with the exception of Lanthanum, the BCS value seems correct to within about 25%. For Lanthanum the data seem to indicate a value of 14 instead of 5.9. The third prediction (this is a less certain one) is that since there are two energy gaps for the s and f bands, one might hope to see in a tunneling experiment an f-band gap which might be rather bigger than the s-band gap (possibly even by a factor of 3 or 4). Whether this really is observable is a bit hard to say because of the large effective mass of f electrons.

ULTRASONICS

CHAIRMAN: *R. W. Morse*

Anisotropy of the Energy Gap in Niobium from Ultrasonic Measurements

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In its original formulation, the theory of Bardeen, Cooper, and Schrieffer[1] was based on a model superconductor, which had a spherical Fermi surface, an isotropic energy gap ($\Delta_k = \Delta$), and a simple, weak electron–electron interaction $-V$. This model led to a law of corresponding states for superconductors, in which the energy gap at 0°K, $\Delta(0) = 1.76\, kT_c$. At higher temperatures the BCS energy gap $\Delta(T)$ is given by the equation[2]

$$\frac{\Delta(T)}{\Delta(0)} = \tanh\left[\frac{T_c}{T}\cdot\frac{\Delta(T)}{\Delta(0)}\right]. \qquad (1)$$

The theory has been remarkably successful for most superconductors, in which the "weak coupling" approximation [$N(0)V \ll 1$ or $T_c \ll \theta_D$] is valid, although it is well known that their Fermi surfaces are far from spherical. For a few "strongly coupled" superconducting elements, such as niobium and lead, it is less successful and it is therefore possible, by studying the way in which they deviate from the law of corresponding states, to investigate the electron–electron interaction responsible for superconductivity in detail. We have used the ultrasonic method[3] to measure the energy gap in niobium as a function of temperature, and of orientation, in single crystals of resistivity ratio $R_{300}/R_4 = 300$.

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† Shell Scholar.
[1] J. Bardeen, L. N. Cooper, and J. R. Schreiffer, Phys. Rev. **108**, 1175 (1957).
[2] D. J. Thouless, Phys. Rev. **117**, 1256 (1960).
[3] R. W. Morse and H. V. Bohm, Phys. Rev. **108**, 1094 (1957).