ACKNOWLEDGMENTS

The authors acknowledge with thanks the contributions of R. J. Manning who assisted in making many of the measurements, D. P. Miller who oriented the crystals, J. L. Rooke for valuable technical assistance, and of R. Stratton for helpful discussions.

PHYSICAL REVIEW VOLUME 132, NUMBER 6 15 DECEMBER 1963

Theory of the Superconducting Transition Temperature and Energy Gap Function of Superposed Metal Films

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(Received 5 August 1963)

A calculation is made of the transition temperature of a film sandwich composed of two thin superposed films of different metals, only one of which is superconducting in bulk. Good quantitative agreement is obtained with existing measurements of the dependence of the transition temperature on the thicknesses of the two component films. The problem is shown to be mathematically equivalent to the simple one of the energy levels of a particle in a one-dimensional square potential well.

I. INTRODUCTION

A NUMBER of experiments[1–5] have been reported recently measuring the superconducting transition temperature of metal film sandwiches. In these experiments, the sandwiches are composed of films of two different metals evaporated one on top of the other, only one of the metals being superconducting in bulk at laboratory temperatures. In summary, such experiments show that the transition temperature of a given film of superconducting material (s) is decreased by the superposition of a normal metal (n). The amount of the decrease depends on the thicknesses D_s and D_n of the two components. For D_s much greater than a certain characteristic length ξ_s, the transition temperature T_c of the sandwich drops with increasing D_n, but approaches a finite limiting value as D_n becomes greater than another characteristic length ξ_n; whereas for D_s much less than ξ_s, T_c drops rapidly below experimental detection as D_n approaches ξ_n. A representative plot of such behavior is given in Fig. 1. Values of ξ_s and ξ_n are typically 10^{-5}–10^{-6} cm. The various experiments[1–5] differ in details, such as in geometry and choice of metals, temperature of the substrate during evaporation, and range of thicknesses investigated, but all show the general effects indicated above.

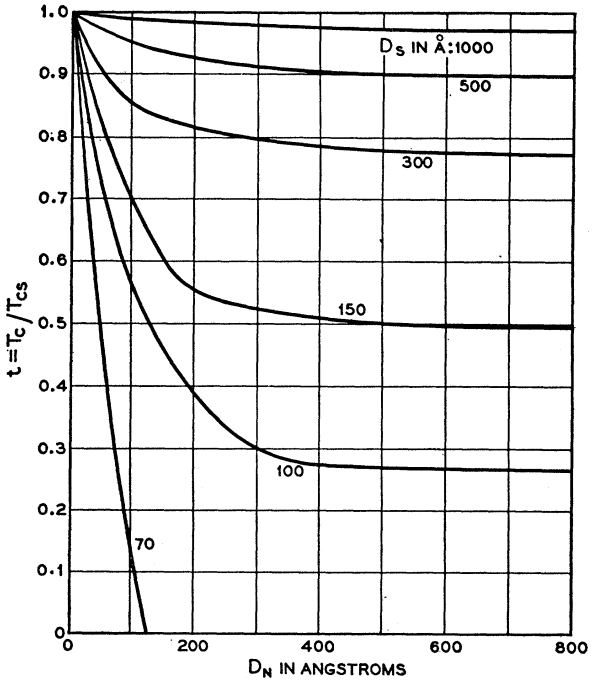

FIG. 1. Representative experimental curves taken from Hilsch (Ref. 5) showing reduction in transition temperature from that of bulk lead for a lead-copper film sandwich, as a function of the component film thicknesses.

Interspersed with the experimental publications, several authors[6–9] have attempted theoretical explanations of the phenomenon. Common to their approaches is the notion that superconductivity in the bulk is characterized by an electron pair correlation, with an associated coherence distance typically of order 10^{-4}–10^{-5} cm, and that therefore this correlation should also

[1] H. Meissner, Phys. Rev. **117**, 672 (1960); IBM J. Res. Develop. **6**, 71 (1962); Eighth International Congress on Low Temperature Physics, London, 1962 (to be published).
[2] P. H. Smith, S. Shapiro, J. L. Miles, and J. Nicol, Phys. Rev. Letters **6**, 686 (1961).
[3] A. C. Rose-Innes and B. Serin, Phys. Rev. Letters **7**, 278 (1961).
[4] W. A. Simmons and D. H. Douglass, Jr., Phys. Rev. Letters **9**, 153 (1962).
[5] P. Hilsch, Z. Physik **167**, 511 (1962); P. Hilsch, R. Hilsch, and G. v. Minnigerode, Eighth International Congress on Low Temperature Physics, London, 1962 (to be published).
[6] R. H. Parmenter, Phys. Rev. **118**, 1173 (1960).
[7] L. N. Cooper, Phys. Rev. Letters **6**, 89 (1961).
[8] D. H. Douglass, Jr., Phys. Rev. Letters **9**, 155 (1962).
[9] P. G. de Gennes and E. Guyon, Phys. Letters **3**, 168 (1963).

extend a similar distance into a normal metal in contact with a superconductor. It then becomes plausible that superconducting films of thickness less than or comparable to a coherence distance will have their transition temperature lowered by superposition of the normal metal, and that this lowering should be independent of normal metal thickness for D_n larger than a coherence distance.

The argument of Cooper[7] then, is that the correlation introduces a nonlocality into the electron pair wave function, so that pairs sample an effective attractive potential which is simply the spatial average of the potentials on the two sides of the interface. Assuming for simplicity the normal metal to have BCS coupling constant $[N(0)V]_n=0$, Cooper is led to write

$$[N(0)V]_{\text{eff}}=D_s[N(0)V]_s/(D_s+D_n)$$

as the effective coupling constant, and

$$T_c=1.14\theta_D \exp\{-[N(0)V]_{\text{eff}}^{-1}\}$$

as the transition temperature for the film complex. If it is kept firmly in mind that these formulas can be valid only for D_s and D_n both much less than the coherence distance, that is (as we shall see) only for the thinnest films, reasonable qualitative agreement with the existing data can be obtained.

Douglass,[8] on the other hand, chooses to regard the normal film rather as a superconductor with free energy higher than the normal state, and hence an "imaginary critical field." By making guesses as to the temperature dependence of such a quantity, and minimizing a phenomenonological total free energy expression for the film complex, he arrives at a formula which can be fitted to the data of Simmons and Douglass.[4] Several objections can be raised to this analysis, however. The most serious is that fundamentally no such free energy minimum exists corresponding to the continuation of the superconducting state above the normal state (in the absence of a magnetic field). If the minimum did exist, the transition itself could not be of second order as observed. Douglass also confuses a metal which is at a temperature above its transition temperature and hence in the normal state, with a metal having a repulsive electron-electron interaction and hence incapable of superconductivity at any temperature no matter how low.

The calculation of de Gennes and Guyon[9] proceeds in a more basic manner by generalizing Gor'kov's[10] Green's function treatment of superconductivity to the case of a position-dependent electron-electron interaction, with a consequent spatial variation to the energy gap function $\Delta(\mathbf{r})$. These authors construct the linear homogeneous integral equation satisfied by $\Delta(\mathbf{r})$ at the transition temperature T_c of the film complex. Although they do not pursue the task of including the boundary conditions on $\Delta(\mathbf{r})$ at the n-s interface so as to obtain explicitly the eigenvalue of the integral kernel (the eigenvalue in this case being T_c), they are able to draw some general qualitative conclusions which reproduce certain features of the experimental data, in particular those of Hilsch.[5]

In the present paper, we adopt the point of view of de Gennes and Guyon,[9] and extend their treatment so as to obtain a complete solution for $\Delta(\mathbf{r})$ and T_c. By transforming their integral equation into a differential equation and including the proper boundary conditions, we are able to make a simple one-to-one correspondence between the superposed film problem and the quantum mechanics textbook example of the energy levels and wave functions of a particle in a one-dimensional potential well. All the observed features of the film sandwich sketched in the opening paragraph can then be intuitively understood from the well-known results for the analog. Detailed calculations can easily be carried out, however, for quantitative comparison, and for those experiments where sufficient data is supplied,[5] good agreement is obtained without the use of adjustable parameters.

To make the analysis tractable, we have resorted to an idealized model of the film sandwich. The chief assumption is that the two metals are identical in the normal state, that is, have the same Fermi velocity v_F and density of states at the Fermi level $N(0)$, the same residual resistivity, and the same Debye temperatures θ_D. All differences between the metals we assume to be contained in the BCS electron-electron interaction parameter V, which we take to be a uniform constant throughout a given metal. As a corollary assumption, we take no explicit account of possible surface scattering, except in so far as it is included in the measured mean free path.

In Sec. II, we treat the general problem of the transition temperature of a system with a spatially-varying electron-electron interaction, obtaining the equations in a particularly transparent form from which the simple physical analog presents itself. Section III then specializes to the case of two superposed thin films and presents detailed comparisons with the experimental data. An Appendix supplies an alternative and more detailed derivation of the integral kernel than that of de Gennes and Guyon.[9]

II. GENERAL FORMULATION AND PHYSICAL ANALOGUE

As our starting point we adopt the linear homogeneous integral equation of de Gennes and Guyon[9] for the gap function at the transition temperature of the sandwich,

$$\Delta(\mathbf{r})=\int d^3r' K(\mathbf{r},\mathbf{r}')\Delta(\mathbf{r}'), \tag{1}$$

[10] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **34**, 735 (1958) [translation: Soviet Phys.—JETP **7**, 505 (1958)].

where the kernel is

$$K(\mathbf{r},\mathbf{r}')=N(0)V(\mathbf{r})[\ln(1.14\theta_D/T_c)\delta^3(\mathbf{r}-\mathbf{r}')-X(\mathbf{r}-\mathbf{r}')], \tag{2}$$

and

$$X(\mathbf{r})\equiv(2\pi)^{-3}\int d^3k e^{i\mathbf{k}\cdot\mathbf{r}}\chi(\hbar v_F l k^2/6\pi k_B T_c), \tag{3}$$

$$\chi(z)\equiv\psi(\tfrac{1}{2}+\tfrac{1}{2}z)-\psi(\tfrac{1}{2}), \tag{4}$$

with ψ being the digamma function.[11] An alternative derivation of Eqs. (1)–(4) is given in the Appendix. We proceed by rewriting Eq. (1) as

$$\Delta(\mathbf{r}')\ln[T_c(\mathbf{r}')/T_c]=\int d^3r''X(\mathbf{r}'-\mathbf{r}'')\Delta(\mathbf{r}''), \tag{5}$$

where a local bulk transition temperature $T_c(\mathbf{r})$ has been defined by

$$[N(0)V(\mathbf{r})]^{-1}\equiv\ln[1.14\theta_D/T_c(\mathbf{r})]. \tag{6}$$

We next introduce the function $\tilde{X}(\mathbf{r})$,

$$\tilde{X}(\mathbf{r})\equiv(2\pi)^{-3}\int d^3k e^{i\mathbf{k}\cdot\mathbf{r}}\chi^{-1}(\xi^2k^2), \tag{7}$$

with $\xi^2\equiv\hbar v_F l/6\pi k_B T_c$. Multiplying Eq. (5) on both sides by $\tilde{X}(\mathbf{r}-\mathbf{r}')$ and integrating over $\mathbf{r}'$, we find

$$\Delta(\mathbf{r})=\int d^3r'\tilde{X}(\mathbf{r}-\mathbf{r}')\ln[T_c(\mathbf{r}')/T_c]\Delta(\mathbf{r}'). \tag{8}$$

But since $\chi(0)=0$ from Eq. (4), the definition (7) is ambiguous in that no specification has been given for integrating around the pole of the integrand. However, when we recognize that $\tilde{X}(\mathbf{r})$ is just the Green's function for the differential operator $\chi(-\xi^2\nabla^2)$, it is clear that specifying the contour of integration is equivalent to choosing the boundary conditions satisfied by $\Delta(\mathbf{r})$. More importantly, the identification of $\tilde{X}$ as a Green's function enables us to cast Eq. (7) into the differential form

$$\chi(-\xi^2\nabla^2)\Delta(\mathbf{r})=\ln[T_c(\mathbf{r})/T_c]\Delta(\mathbf{r}), \tag{9}$$

again plus boundary conditions.

Since Eq. (9) looks very much like a Schrödinger equation, we can now make a direct mathematical correspondence with the quantum motion of a particle of energy E in a potential $U(\mathbf{r})$. We immediately identify $\ln\theta_D/T_c(\mathbf{r})$ with $U(\mathbf{r})$, $\ln\theta_D/T_c$ with E, and $\chi(\xi^2k^2)$ with the free particle kinetic energy $k^2/2m$. Also $\Delta(\mathbf{r})$ corresponds to the particle wave function, although we will see shortly that they obey different boundary conditions. The superconducting film problem, where we expect $T_c(\mathbf{r})|_{\min}<T_c<T_c(\mathbf{r})|_{\max}$, is thus analogous to that of the lowest bound level of a "Bloch electron" in a specified potential well. The observed behavior of T_c with varying film thicknesses as sketched in the introduction can readily be understood in terms of the well-known dependence of a bound level on the width of the well.

[11] See, e.g., H. T. Davis, *Tables of Higher Mathematical Functions* (Principia Press, Inc., Bloomington, Indiana, 1935), Vol. I.

III. SPECIAL CASE OF AN *n-s* FILM SANDWICH

A. Solution and Eigenvalue Equation

We next specialize to the case of two superposed thin films, one of a known superconductor,

$$T_c(\mathbf{r})=T_{cs},\quad 0<x\leq D_s; \tag{10a}$$

and one of a metal which is not superconducting at presently available laboratory temperatures, but which we assume to have a nonvanishing attractive electron-electron interaction and thus a small but nonvanishing transition temperature,

$$T_c(\mathbf{r})=T_{cn},\quad -D_n\leq x<0. \tag{10b}$$

Solutions of Eq. (9) can immediately be written down:

$$\begin{aligned}\Delta(\mathbf{r})&=e^{\pm ik_s x}, && 0<x\leq D_s,\\ &=e^{\pm k_n x}, && -D_n\leq x<0,\end{aligned} \tag{11}$$

where $k_{s,n}$ satisfy

$$\chi(\xi^2k_s^2)=\ln T_{cs}/T_c,\quad -\chi(-\xi^2k_n^2)=\ln T_c/T_{cn}. \tag{12}$$

We must now pick the appropriate boundary conditions. As discussed by de Gennes and co-workers[9,12,13] we require that $d\Delta(\mathbf{r})/dx$ vanish at metal-insulator or metal-vacuum surfaces, here at $x=D_s$ and $x=-D_n$. This condition insures that a single superconducting film no matter how thin has virtually the same transition temperature as the bulk material. At the metal-metal interface, however, we cannot choose $\Delta(\mathbf{r})$ to be continuous and have a continuous first derivative, as we would for a Schrödinger wave function. This is because $\Delta(\mathbf{r})$ is proportional to $V(\mathbf{r})$ [Eqs. (1) and (2)] and is thus discontinuous. On the other hand, $\Delta(\mathbf{r})/V(\mathbf{r})$ is directly proportional to the Gor'kov Green's function $\langle\psi(\mathbf{r})\psi(\mathbf{r})\rangle$, which can be interpreted as the wave function of a correlated pair and which should obey the standard continuity conditions of Schrödinger wave functions. Thus $d\Delta/\Delta dx$ is continuous, even though Δ and its first derivative themselves are not. Applying all boundary conditions leads to the final solution

$$\begin{aligned}\Delta(x)&\propto V_s\cos k_s(x-D_s)/\cos k_sD_s, && 0<x\leq D_s,\\ &\propto V_n\cosh k_n(x+D_n)/\cosh k_nD_n, && -D_n\leq x<0,\end{aligned} \tag{13}$$

and

$$k_s\tan k_sD_s=k_n\tanh k_nD_n. \tag{14}$$

Equations (4), (12), and (14) are sufficient to determine T_c.

[12] C. Caroli, P. G. de Gennes, and J. Matricon, J. Phys. Radium **23**, 707 (1962).

[13] P. G. de Gennes, Phys. Letters **5**, 22 (1963).

B. Comparison with Experiment

Of the various experimental investigations, the only one to supply mean free path information is that of Hilsch,[5] using lead and copper evaporated at liquid He temperatures. Thus, we can attempt a quantitative comparison of our predictions with these measurements only. Other investigators[1–4] find qualitatively similar results.

As a preliminary step, we replace the function $\chi(z)$ of Eq. (4) by the simple expression

$$\begin{aligned}\psi(\tfrac{1}{2}+\tfrac{1}{2}z)-\psi(\tfrac{1}{2}) &\to \ln[1+(\pi^2 z/4)], \quad z\geq 0,\\ &\to (\pi^2/4)\ln(1+z), \quad z\leq 0,\end{aligned} \tag{15}$$

the two being identical for $z\ll 1$. The functions are both plotted in Fig. 2, and in the region of interest $|z|\lesssim 1$, the approximation is seen to be adequate for present purposes. Since the final results are comparatively sensitive to this approximation, the correct expression (4) should be used when more precise data becomes available, especially for lower values of T_c. This replacement, however, enables us to solve Eqs. (12) explicitly and find

$$\begin{aligned}k_s&=(2/\pi\xi)[(T_{cs}/T_c)-1]^{1/2},\\ k_n&=\xi^{-1}[1-(T_{cn}/T_c)^{4/\pi^2}]^{1/2}.\end{aligned} \tag{16}$$

We will also assume throughout that the "normal" metal has a transition temperature sufficiently below the conventional laboratory range that $(T_{cn}/T_c)^{4/\pi^2}\ll 1$. Although accurate measurements should be capable of determining T_{cn}, or at least setting an upper limit, satisfactory agreement with present experiments is found by neglecting T_{cn} altogether.

The first situation we investigate is that of the normal metal film being very thick, $k_n D_n\gg 1$, so that T_c no longer depends on D_n. We can then combine Eqs. (14) and (15) to write

$$d_s=(\pi/2)(1-t)^{-1/2}\cot^{-1}[(2/\pi)(t^{-1}-1)^{1/2}], \tag{17}$$

where we define the reduced variables

$$d_s\equiv D_s(\hbar v_{Fs} l_s/6\pi k_B T_{cs})^{-1/2}, \quad t\equiv T_c/T_{cs}. \tag{18}$$

Using the value $v_{Fs}=0.50\times 10^8$ cm/sec for Pb, and extracting values for l_s from Fig. 8 of Ref. 5a, expression (17) is plotted in Fig. 3. Data points are taken from Fig. 5 of Ref. 5a on quartz-Cu-Pb sandwiches; the observed differences in T_c between these and Cu-Pb-Quartz sandwiches remain unexplained. Error flags are assigned by the present author, solely on the basis of scatter and uncertainty in reading data from the published graphs; no estimate of uncertainty in D_s or l_s is made in Ref. 5. Under the circumstances, agreement between theory and experiment must be considered good.

To make similar comparisons at finite D_n and fixed D_s, we need not go to the trouble of numerical computations. Hilsch states that his data are well-fitted by the formula

$$t=1-(1-\theta)(1-e^{-D_n/a}), \tag{19}$$

where $\theta\equiv t(D_n\to\infty)$, and $a\sim 100$ Å. Rearranging Eqs. (14) and (15) into the form

$$t=\left[1+\frac{\pi^2}{4}\frac{k_s\tanh D_n/\xi}{\tan k_s D_s}\right]^{-1}, \tag{20}$$

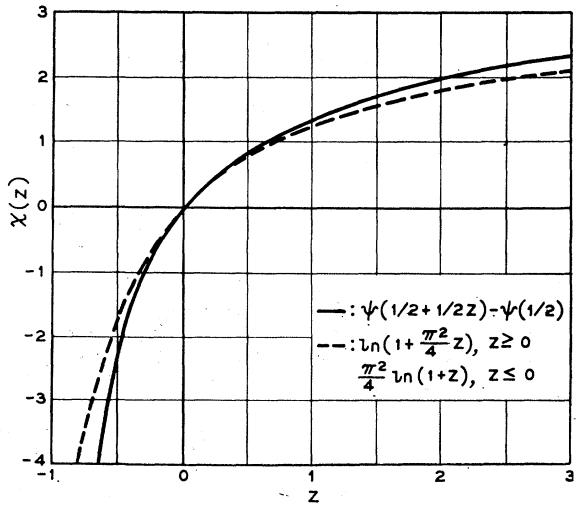

FIG. 2. The function $\chi(z)=\psi(\frac{1}{2}+\frac{1}{2}z)-\psi(\frac{1}{2})$ and the approximation $\chi(z)\cong\ln[1+(\pi^2 z/4)]$, $z\geq 0$; $(\pi^2/4)\ln(1+z)$, $z\leq 0$; plotted versus z.

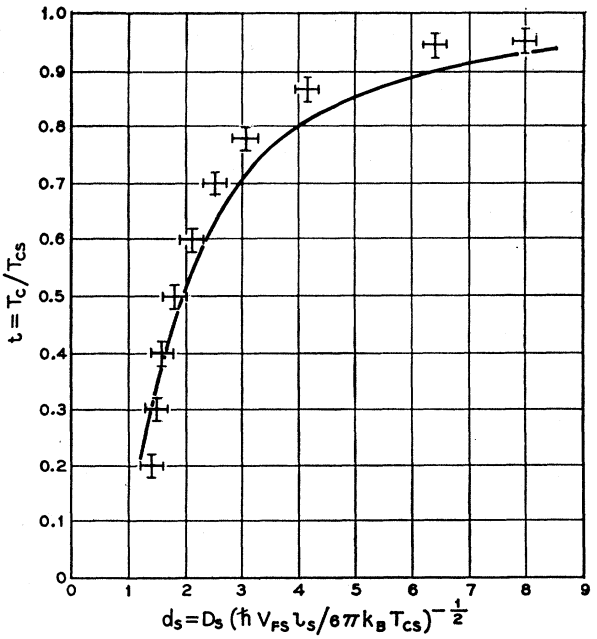

FIG. 3. The solid curve represents reduced transition temperature t of a lead-copper sandwich versus reduced lead film thickness d_s, as predicted theoretically from Eq. (17). Data points are taken from Hilsch (Ref. 5).

and introducing θ, which we have just found we can predict rather well, we arrive at

$$t\cong 1-(t/\theta)(1-\theta)\tanh D_n/\xi, \tag{21}$$

where here ξ is to be evaluated at $t=\theta$, and is roughly 150 Å. As also noted by de Gennes and Guyon, agreement between formulas (18) and (21) is reasonable, with the identification $a\rightarrow\frac{1}{2}\xi$.

We may also remark that all measurements[1-4] besides those of Hilsch were performed on films evaporated onto room-temperature substrates, a procedure which has been criticized in the past as possibly allowing interdiffusion of the two metals, which, in turn, would further alter the transition temperature and make interpretation ambiguous. In fact, Rose-Innes and Serin,[3] evaporating tin onto gold plates, noted that the T_c of certain of their samples was sharply reduced if they were later reexposed for a few minutes in the evaporator to the (empty) heated boat; this result they claimed to be the interdiffusion effect. Nevertheless, it is much more likely that the brief heating of the sample resulted in annealing of defects than in interdiffusion, and such an annealing would account, in our theory, for their observations. The particular samples they select for treatment are those with tin thickness D_s comparable to ξ according to our conclusions in Fig. 3, since slightly thinner samples have much lower T_c. Annealing so as to increase the mean free path would change the reduced thickness d_s, and hence T_c, in the same way as an actual decrease in D_s; this is precisely Rose-Innes and Serin's[3] result. It emphasizes the need for simultaneous T_c and resistivity measurements in future experiments; the temperature of the substrate during evaporation or subsequent storage is probably irrelevant except as a tool for varying l. Exposure to air, however, can be quite serious.[4,14]

Finally, we should make a comparison between our predictions when $D_{n,s}\ll\xi$ and those of Cooper.[7] In this limit, we find

$$t\cong[1+(\pi^2/4)(D_n/D_s)]^{-1}, \tag{23}$$

whereas Cooper's formulas can be rewritten as

$$t=(1.14\theta_D/T_{cs})^{-D_n/D_s}. \tag{24}$$

Although in both cases t decreases monotonically from one with increasing D_n/D_s, the initial decrease being linear, the differing functional dependence between Eqs. (23) and (24) should be resolvable experimentally. However, in a more exact treatment which includes the differences in v_F and l of the two metals, we feel that the coefficient of D_n/D_s in Eq. (23) would probably be modified to include these parameters.

ACKNOWLEDGMENTS

The author wishes to thank Dr. T. H. Geballe for initially stimulating his interest in this problem, and Dr. P. W. Anderson for several helpful conversations.

[14] J. L. Miles and P. Smith, J. Appl. Phys. (to be published).

APPENDIX

We here supply a derivation of Eqs. (1)-(4) as an alternative to that of de Gennes and Guyon,[9] which makes clearer the nature and validity of the approximations used. The essential point is that we can borrow extensively from the analysis of Gor'kov[15] concerning the equation determining the gap function at the transition temperature in the presence of a dilute concentration of randomly distributed impurity scattering centers. We first define $G_\omega(\mathbf{r},\mathbf{r}')$ as the one-electron Green's function in the presence of a particular configuration of impurities, so that it satisfies

$$\left[i\omega+\frac{1}{2m}\nabla^2+\sum_j u(\mathbf{r}-\mathbf{r}_j)+\mu\right]G_\omega(\mathbf{r},\mathbf{r}')=\delta^3(\mathbf{r}-\mathbf{r}'), \tag{A1}$$

where $u(\mathbf{r}-\mathbf{r}_j)$ is the scattering potential of an impurity at site j, μ is the chemical potential, and $\omega=(2\nu+1)\pi T$ with ν an integer. Then Abrikosov and Gor'kov[15,16] have shown that the Green's function averaged over all impurity configurations is

$$\bar{G}_\omega(\mathbf{r},\mathbf{r}')=(2\pi)^{-3}\int d^3p e^{i\mathbf{p}\cdot(\mathbf{r}-\mathbf{r}')}\bar{G}_\omega(\mathbf{p}), \tag{A2}$$

$$\bar{G}_\omega(\mathbf{p})=[i\omega-\epsilon(\mathbf{p})+i\,\mathrm{sgn}\omega/2\tau]^{-1}. \tag{A3}$$

Here $\epsilon(\mathbf{p})\equiv(p^2/2m)-\mu$ and τ is the scattering time to be defined shortly.

Furthermore, at the second-order transition point, the impurity-averaged gap function is small and satisfies the equation[15]

$$\Delta(\mathbf{r})=\int d^3r' V(\mathbf{r})Q(\mathbf{r}-\mathbf{r}')\Delta(\mathbf{r}'), \tag{A4}$$

where

$$Q(\mathbf{r}-\mathbf{r}')=(2\pi)^{-3}\int d^3q e^{i\mathbf{q}\cdot(\mathbf{r}-\mathbf{r}')}Q(\mathbf{q}), \tag{A5}$$

$$Q(\mathbf{q})=T\sum_{\nu=-\infty}^{\infty}(2\pi)^{-3}\int d^3p Q_\omega(\mathbf{p},\mathbf{q}-\mathbf{p}). \tag{A6}$$

The kernel function Q_ω obeys the integral equation[15]

$$Q_\omega(\mathbf{p},\mathbf{q}-\mathbf{p})=\bar{G}_\omega(\mathbf{p})\bar{G}_{-\omega}(\mathbf{q}-\mathbf{p})$$
$$\times\left[1+n(2\pi)^{-3}\int d^3p'|u(\mathbf{p}-\mathbf{p}')|^2 Q_\omega(\mathbf{p}',\mathbf{q}-\mathbf{p}')\right], \tag{A7}$$

where n is the impurity concentration.

Since $u(\mathbf{r}-\mathbf{r}_j)$ is quite short-ranged, we make the simplifying approximation that $u(\mathbf{r}-\mathbf{r}_j)\rightarrow u\delta^3(\mathbf{r}-\mathbf{r}_j)$; then in Fourier space $u(\mathbf{p}-\mathbf{p}')$ is just the constant u, and the scattering time becomes

$$1/2\tau=\pi nN(0)|u|^2. \tag{A8}$$

[15] L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **37**, 1407 (1959) [translation: Soviet Phys.—JETP **10**, 998 (1960)].

[16] A. A. Abrikosov and L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **35**, 1558 (1958) [translation: Soviet Phys.—JETP **8**, 1090 (1959)].

Equation (A7) can then be solved algebraically, and Q_ω substituted into Eq. (A6) to obtain

$$Q(\mathbf{q})=T\sum_\nu R(\mathbf{q})/[1-n|u|^2R(\mathbf{q})], \quad \text{(A9)}$$

where

$$R(\mathbf{q})=(2\pi)^{-3}\int d^3p\bar{G}_\omega(\mathbf{p})\bar{G}_{-\omega}(\mathbf{q}-\mathbf{p}). \quad \text{(A10)}$$

Substituting expression (A3) into (A10), the integrations may be carried out, provided $q\ll p_F$, with the result that

$$R(\mathbf{q})=(2\pi N(0)/v_Fq)\tan^{-1}(v_Fq/[2|\omega|+(1/\tau)]). \quad \text{(A11)}$$

If we only consider those values of q for which $q\ll(v_F/2\pi T)^{-1}+l^{-1}$, where $l=v_F\tau$ is the mean free path, then we can expand the $\tan^{-1}$ and find

$$Q(\mathbf{q})=N(0)\pi T\sum_\nu\left[|\omega|+\frac{1}{6\tau}\left(\frac{ql}{1+2|\omega|\tau}\right)^2\right]^{-1}. \quad \text{(A12)}$$

The divergence in the sum over integers ν can be cured by subtracting $Q(0)$ from both sides; a cutoff is then introduced into $Q(0)$ in the usual way.[15] We thus obtain

$$Q(\mathbf{q})-Q(0)=N(0)\sum_\nu\{[|2\nu+1|+(ql)^2(6\pi T\tau)^{-1}\times(1+2\pi T\tau|2\nu+1|)^{-2}]^{-1}-|2\nu+1|^{-1}\}, \quad \text{(A13)}$$

and

$$Q(0)=N(0)\ln 1.14\theta_D/T. \quad \text{(A14)}$$

When $2\pi T\tau\ll1$, the "dirty" limit which is almost always the situation in thin film experiments, the term $2\pi T\tau|2\nu+1|$ may be neglected in (A13), and so finally

$$Q(\mathbf{q})-Q(0)\cong-N(0)\{\psi[\tfrac{1}{2}+\tfrac{1}{2}(v_Flq^2/6\pi T)]-\psi(\tfrac{1}{2})\}, \quad \text{(A15)}$$

where ψ is the digamma function.[11] Combining Eqs. (A4), (A5), (A14), and (A15) just reproduces Eqs. (1)–(4) of Sec. II.

PHYSICAL REVIEW VOLUME 132, NUMBER 6 15 DECEMBER 1963

High-Temperature Dielectric Constant of Potassium Chloride*

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A dispersion of the dielectric constant of zone-purified potassium chloride has been observed at temperatures above 650°C and in the frequency range between one and ten megacycles/sec. The data are interpreted in terms of the Debye equations and the assumption that the dipoles are vacancy pairs. The activation energy for reorientation of a vacancy pair is found to be $1.04^{\pm0.05}$ eV and the heat of formation of a vacancy pair is found to be $1.34^{\pm0.07}$ eV. These quantities have been calculated by Tharmalingam and Lidiard as 1.15 and 1.28 eV, respectively. The dielectric data yield, however, an absolute number of vacancy pairs that is at least a factor of ten larger than is acceptable. Interfacial or Maxwell-Wagner types of polarization are excluded as explanations of the data.

INTRODUCTION

THE dielectric constant of pure potassium chloride at high temperature and in the frequency range between one and ten megacycles/sec exhibits a rather simple behavior. The real and imaginary parts of the dielectric constant, ϵ_1 and ϵ_2, are described by the Debye equations[1] and the expected contribution to ϵ_2 of the frequency-independent volume conductivity σ:

$$\epsilon_1=\epsilon_\infty+(\epsilon_s-\epsilon_\infty)/(1+\omega^2\tau^2), \quad (1)$$

$$\epsilon_2=\frac{4\pi\sigma}{\omega}+\frac{(\epsilon_s-\epsilon_\infty)\omega\tau}{1+\omega^2\tau^2}, \quad (2)$$

where τ is the relaxation time of the Debye dipoles and ω is the angular frequency. According to the simple Debye theory, the difference between the low-frequency dielectric constant ϵ_s and the high-frequency dielectric constant ϵ_∞ is given by

$$\epsilon_s-\epsilon_\infty=4\pi n\mu^2/3kT, \quad (3)$$

where n is the number of dipoles per unit volume and μ is the dipole moment.

EXPERIMENTAL PROCEDURE

The potassium chloride crystals were prepared from reagent grade powder by zone refining in an atmosphere of chlorine.[2] Twenty or more zones were passed through the salt which was contained in an open silica crucible. The zone speed was approximately 1 in./h. The dc conductivity of the zone-refined salt is illustrated in Fig.

* Partially supported by the U. S. Office of Naval Research and the U. S. Air Force Office of Scientific Research.

[1] H. Frohlich, *Theory of Dielectrics* (Clarendon Press, Oxford, 1949), p. 70.

[2] T. M. Srinivasan, Technical Note No. 3, AFOSR Contract 49(638)-529, University of Illinois, 1962 (unpublished).