Physics Vol. 2, No. 4, pp. 153-163, 1966. Physics Publishing Co. Printed in Great Britain.

SURFACE SUPERCONDUCTIVITY AT HIGH TEMPERATURES*

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(*Received* 9 *August* 1965)

Abstract

The possibility that surface superconductivity of the Ginzburg type might occur at high temperatures is investigated. The most likely effect is seen to be surface ordering brought about by resonance coupling through the impurity surface states. A mechanism is described by which the localized coherence which this requires can occur, giving transition temperatures orders of magnitudes higher than any now known.

Introduction

THE possibility that the interaction between electrons at the surface of a superconductor might be strong enough to give rise to a new type of superconductivity was originally proposed by Ginzburg and Kirzhnits [1], who dealt primarily with the possibility that superconductivity might occur in the surface band alone. A distinction was made between this type of two-dimensional effect and the phenomenon of "surface ordering" proposed simultaneously by Bulayevskiy and Ginzburg [2], in which surface coupling between Bloch waves occurs. Subsequently, Ginzburg [3,4] suggested that the presence of impurity atoms on the surface might be a contributing mechanism for both effects. The present author [5] has since then shown that two distinct types of surface ordering can occur in thin films, one of which depends on thickness and one of which does not. In addition, a number of different mechanisms have been studied, and there is reason to believe that surface superconductivity might appear at remarkably high temperatures [3,6].

A year preceding the initial work of Ginzburg *et al.*, Saint-James and de Gennes [7] described the possibility that a superconductor in a high magnetic field might be superconducting only in a thin surface layer. This effect, which has also been referred to as "surface superconductivity", is quite unrelated to those mentioned above and might better be referred to as "type III" superconductivity. It occurs because the translational symmetry of the system is broken by the surface, so that the superconducting wave function can respond to an imposed field with an additional degree of freedom; however, the transition temperature is unchanged in the field-free case. We shall not consider type III superconductivity in this paper, but rather concentrate on an exciting feature of the Ginzburg effect, the prospect of superconductivity at room temperature and above.

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* Supported by the National Science Foundation.

Theory of Surface Coherence

The original suggestion of Ginzburg and Kirzhnits [1], that superconductivity of just the surface band might be possible, is particularly challenging, since it involves the topological question of two-dimensional superconductivity. The idea that superconductivity might occur in other than three-dimensional systems was first proposed by Little [8], who examined the possibility that organic polymers might become superconducting at room temperature. It was then shown by Ferrell [9] that the zero-point energy associated with compressional modes in a one-dimensional system is sufficient to disrupt long-range coherence. While Ferrell's calculation does not rule out the possibility of two-dimensional superconductivity, it might do so if collective excitations with non-linear dispersion were included [9a]. On the other hand, ascribing less than three dimensions to any object in the real world is a risky approximation, and superconductivity in these special systems may occur as coherence in the transverse degrees of freedom.

Although the question of two-dimensional superconductivity involves this interesting fundamental issue, from an experimental viewpoint it is not promising. The fraction of electrons on the surface which are in surface states is believed to be small, and Auger emission studies of clean surfaces suggest that it may be on the order of 10^{-3} [10]. Because of the short lifetimes of these states, it is difficult to envision their forming a stable coherent system. Two-dimensional superconductivity, if it exists, might better be looked for in systems where virtually all the electrons are in long-lived states with only two accessible translational degrees of freedom. Such a system might be a monolayer, where the level spacing for motion perpendicular to the plane of the film approaches the Fermi energy [11].

The concept of "surface ordering" [2], on the other hand, admits of the possibility that all the electrons on the surface contribute to a coherent state. Since most of these electrons are in Bloch states of real momentum, this does not mean a correlation between electrons in localized surface states, but rather a localized correlation between orbits which pass through the entire volume. This can occur in different ways, depending on how strongly the interaction modifies the unperturbed electron states. If the interaction is weak or is spread over a fairly thick surface layer, the Bloch waves are essentially unmodified, and the superconductive properties are affected only to the extent that the average of the interaction over the entire volume is changed. This effect involves only a slight generalization of the principles which apply to bulk superconductors, and we shall refer to it as "surface enhancement". If, on the other hand, the electron-electron interaction is sharply peaked in the surface region, the Bloch waves will then be significantly altered and localized correlation effects can occur.

In order to see how "surface ordering" can occur in a superconductor, we must investigate the microscopic structure of the superconducting state when the Hamiltonian is a rapidly changing function of position. To do so we consider the likelyhood that two electrons will combine to form a "Cooper pair" [12], which can be expressed in terms of the "anomalous Green's function" $F(\mathbf{r}, \mathbf{r}') = < \psi_\uparrow(\mathbf{r})\psi_\downarrow(\mathbf{r}') >$ [13]. This matrix element gives the amplitude for transition from a state containing two electrons of opposite spin above an N-particle condensed phase into a state in which the condensed phase contains $N + 2$ electrons. The "condensate" to which we refer is similar to the macroscopically-occupied ground state of a Bose-Einstein system, and may be viewed as a many-body wave function for which the only "good" quantum numbers are collective ones, and of those, the important ones have the same value as they do for the real vacuum, i.e. zero. The pairing interaction can be treated by field theoretic methods similar to those commonly used in perturbation theory [14], and the anomalous Green's function can be expressed in the form $F(\mathbf{r}, \mathbf{r}') = \int G_0(\mathbf{r}, \mathbf{r}'') \Sigma(\mathbf{r}'', \mathbf{r}''')G_0(\mathbf{r}''', \mathbf{r}')d\mathbf{r}''d\mathbf{r}'''$; here G_0 is the Green's function,

$G(\mathbf{r}, \mathbf{r}') = - < \psi_\uparrow(\mathbf{r})\psi_\uparrow^+(\mathbf{r}') >$ evaluated for the normal state, and Σ is a self-energy term. Since Σ can itself be expressed in terms of F's, this expression constitutes an integral equation for the anomalous Green's function. In particular, we shall be interested in the "pair correlation amplitude", $\chi(\mathbf{r}) = F(\mathbf{r}, \mathbf{r})$, which is the excess probability amplitude for finding two electrons of opposite spin at the point $\mathbf{r}$. Near the transition temperature the self-energy reduces to $\Sigma(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')\Delta(\mathbf{r})$, where $\Delta(\mathbf{r}) = V(\mathbf{r})\chi(\mathbf{r})$ is the "energy gap function", so called because it reduces to the BCS [15] energy gap for the case of translational invariance. Finally, we obtain for $\chi(\mathbf{r})$ the integral equation

$$\chi(\mathbf{r}) = V(\mathbf{r}) \int K(\mathbf{r}, \mathbf{r}')\, \chi(\mathbf{r}')d\mathbf{r}', \tag{1}$$

where $K(\mathbf{r}, \mathbf{r}') = < G_0(\mathbf{r}, \mathbf{r}')G_0(\mathbf{r}', \mathbf{r}) >_{\text{imp}}$ is the square of the normal Green's function averaged over impurities. This equation, which relates the amplitude for pair condensation at a point, $\chi(\mathbf{r}) = < \psi_\uparrow(\mathbf{r})\psi_\downarrow(\mathbf{r}) >$, to the one-electron Green's function of the normal state, is the limiting form $(T \sim T_c)$ of the BCS energy gap equation, or "consistency condition" as it is often called. Since superconductivity is possible only when this equation has a non-zero solution, we look for the highest temperature at which solutions of equation (1) exist, which is the transition temperature [16].

We now wish to investigate the properties of the kernel occurring in the above expression for the correlation amplitude. A very useful sum rule is due to de Gennes [17], who has shown that

$$\int K(\mathbf{r}, \mathbf{r}')d\mathbf{r}' = N(\mathbf{r})\ln(\hbar\omega(\mathbf{r})/kT),$$

where $N(\mathbf{r})$ is the local density of states at the Fermi surface and $\omega(\mathbf{r})$ is a local characteristic cutoff frequency, assumed to be much larger than $kT/\hbar$ [19]. If $\rho(\mathbf{r}) \equiv N(\mathbf{r})V(\mathbf{r})$ is a slowly varying function of position, as is the case in a bulk superconductor, the transition temperature is given by the BCS expression [15]:

$$kT_c = \hbar\,\omega\, e^{-1/\rho}. \tag{2}$$

We are, however, going to be concerned with systems in which N, V, and ω are rapidly varying functions of position.

The impurity-averaged kernel, $K(\mathbf{r}, \mathbf{r}')$, can be obtained by the method of Abrikosov and Gor'kov [20]. Werthamer [18] has derived the result for the case of short-range isotropic scattering, and a generalization of the Werthamer calculation gives the following result for a bulk superconductor, valid for all values of the mean free path:

$$K(\mathbf{r} - \mathbf{r}') = 2kT \sum_{n=0}^{\hbar\omega/2\pi kT} \int K_n(q)e^{iq\cdot(\mathbf{r}-\mathbf{r}')}dq,$$

where

$$K_n(q) = \frac{2N}{\hbar v}\left\{\frac{q}{\arctan \zeta_n q} - \frac{1}{l}\right\}^{-1};$$

v is the Fermi velocity, l the mean free path, and $\zeta_n^{-1} = [2(2n + 1)\pi kT/\hbar v] + l^{-1}$ [21].

This result can be simplified by expanding the factor $q/\arctan \zeta_n q$ in the denominator, which gives

$$K_n(q) = \frac{2N}{\hbar v}\left\{\frac{1}{\zeta_n} - \frac{1}{l} + \frac{1}{3}\zeta_n q^2 - \frac{4}{45}\zeta_n^3 q^4 + \dots\right\}^{-1}$$

$$= \frac{N}{(2n+1)\pi kT}\left\{1 + \xi_n^2 q^2 - \frac{4}{15}\xi_n^2\zeta_n^2 q^4 + \dots\right\}^{-1},$$

where $\xi_n = [\zeta_n \hbar v/6(2n+1)\pi kT]^{1/2}$ is a generalized coherence length. By dropping powers of q greater than the second, we obtain a kernel of the diffusion type; letting $R = |\mathbf{r} - \mathbf{r}'|$ this gives $K_n(R) \sim K_n^{\rm diff}(R) \propto R^{-1}\exp\{-R/\xi_n\}$.

The diffusion approximation, as introduced originally by de Gennes and Guyon [22] and subsequently used by the Gennes [17] and Werthamer [18], involves two assumptions: (i) that K can be set equal to $K^{\rm diff}$ for all values of R of interest, and (ii) that ζ_n can be replaced by l in the above expression for ξ_n. Assumption (i) is not valid when we consider the surface region, since it holds only when $R \gg l$, a condition seldom met by the characteristic distances associated with surfaces. Assumption (ii) is not necessary; the diffusion law in this case is a result of mathematical convenience, not of physical behavior, and the characteristic $l^{1/2}$ dependence of the correlation lengths need not appear. In fact, we need only retain the exact form of the ξ_n given above to obtain a "diffusion approximation" applicable to systems in which the mean free path is not at all short [23].

In order to avail ourselves of the conveniently simple form of the diffusion equation without using either of the above assumptions, we define the correction term $K^{\rm corr} \equiv K - K^{\rm diff}$, with $K^{\rm diff}$ derived as above, and investigate its properties. Since both K and $K^{\rm diff}$ obey the de Gennes sum rule, which is equivalent to the obvious fact that $K_n^{\rm corr}(q = 0) = 0$, and since $K^{\rm corr}(q)$ is an even function of q, we see that $K^{\rm corr}$ is an oscillating real function of R, with a wavelength λ small compared to the mean free path. It is singular at the origin, as evidenced by the $1/q$ dependence for large q; recalling the definition of K as the square of the Green's function, it is evident that $K(R) \sim R^{-2}$ as $R \to 0$.

From the fact that $K^{\rm corr}$ is rapidly oscillating, we see that it will affect the correlation amplitude $\chi(\mathbf{r})$ only when the interaction changes equally rapidly; however, because of the R^{-2} singularity, it is possible for a localized interaction to make a major contribution to the correlation amplitude. If, for example, we investigate the contribution of a small spherical well of depth V and radius a in a superconductor to the transition temperature, we see that the relevant parameter of the well in the diffusion approximation is Va^2, as seen from the integral $V\int R^{-1}\,d\mathbf{r} \sim V\int R^{-1}\cdot R^2 dR \sim Va^2$, while for R^{-2} dependence the factor is $\sim\lambda Va$, where the wavelength λ is the characteristic range of $K^{\rm corr}$ and does not depend on the geometry of the well. This means that the contribution of a very narrow deep well will be much greater when the correction term in the kernel is taken into account than when only the diffusion term is considered. A similar situation holds for the one-dimensional kernel appropriate to surface problems, where the diffusion kernel is bounded ($K_n^{\rm diff}(z) \sim \exp\{-|z|/\xi_n\}$), but $K^{\rm corr}$ has a logarithmic singularity which can greatly amplify the effect of a thin surface layer on the superconducting properties.

Let us now consider the simple model of the surface of a superconductor shown in Fig. 1. The interaction parameter V' is constant in a thin surface layer of thickness d', then falls abruptly to the bulk value V (we assume for simplicity that the density of states is constant).

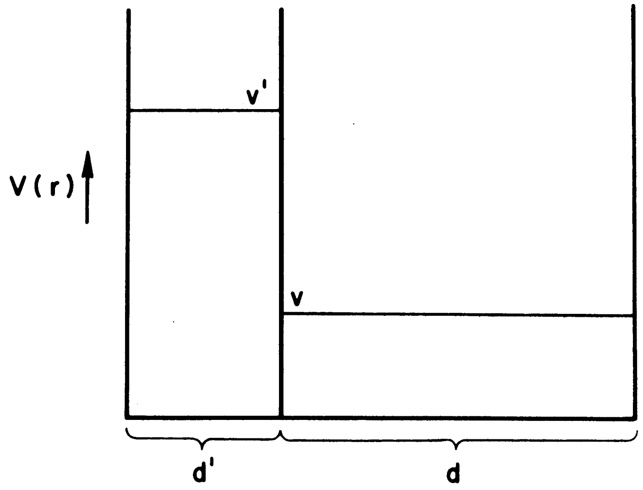

FIGURE 1.

Layer model of the superconducting surface. After Strongin *et al.* (ref. [25]).

The two cases of interest are $d' > \lambda$, $d' < \lambda$ where λ is the characteristic range of K^{corr} and is closely related to the mean free path in dirty specimens. In the first case, where $d' > \lambda$, the contribution from the correction term vanishes, and $\chi(\mathbf{r})$ is governed by the diffusion equation. If the film thickness d is small enough to satisfy the Cooper limit [24], the result is $kT_c = \hbar\omega \exp\{-1/NV_{av}\}$, where $V_{av} = (V'd' + Vd)/(d' + d)$ [25]. Since d' is typically much less than d, the effect of the surface layer is considerably diluted. In addition, the contribution of high-frequency components of the surface interaction, which may be looked for when $\omega' >> \omega$, will tend to be cancelled by the repulsive high-frequency components of the electron-phonon interaction. We do not, therefore, expect drastic changes in the transition temperature to occur in this case.

There is some evidence that this situation has been observed, and that changes in the transition temperature on the order of a degree or so can occur [25-29]. Because these experiments have generally fallen within the region of validity of the Cooper limit and are described by the above result, it is reasonable to conjecture that $d' > \lambda$ for these systems; this is consistent with the likelihood that the mean free paths involved are short. Since this effect does not actually involve surface coherence (in fact, in the Cooper limit $\chi(\mathbf{r})$ is essentially constant throughout the system), but arises only from the modified volume average of the interaction, we refer to this effect as "surface enhancement".

If d' is less than λ, the oscillations in K^{corr} will not average out the contribution of this term to the correlation amplitude. On the contrary, if we let d' go to zero while changing V so that the product Vd' remains constant, the amplitude of the correlation function at the surface increases as $|\log d'|$, and the transition temperature becomes in the limit inversely proportional to d'. The surface enhancement effect meanwhile remains unchanged. This phenomenon, which we shall henceforth designate "surface superconductivity", may provide the greatest likelihood of realizing high-temperature superconductivity, and we shall discuss it at greater length. The actual situation which prevails at the surface of a superconductor is of course far more complex then the simple layer model which we have used indicates, so we shall first investigate the actual mechanisms which may give rise to a greatly increased surface interaction, and then we shall see that transition temperatures are actually within the range of possibility.

Surface Interaction Mechanisms

We turn now to a discussion of the mechanisms for the greatly modified surface interaction which, as we have suggested in the previous section, might be responsible for surface superconductivity. The interaction processes occur through intermediate boson excitations of various types, and the relevant features are the spectra of these excitations and the strength with which they couple to the electrons. One main characteristic of the spectrum is the effective cutoff, or band width, since this provides an upper limit to the exchange energy of the electrons and to the critical temperature; this can be seen directly from the BCS formula, which tells us that $T_c < \hbar\omega/k$. While the structure of the spectrum, including its dispersion in both time and space, must be considered in any detailed theory of superconductivity (e.g., tunnelling) a suitably defined one-parameter model suffices for the crude calculations to follow. The coupling strength is the other important feature of the interaction, and plays the greatest role in the weak-coupling limit. We shall indicate briefly how strong-coupling can occur at the surface of a superconductor, and then, emphasizing the cases where $e^{-1/NV}$ may be close to unity, we shall look at band-widths. The reason that the cutoff is of prime importance in the strong-coupling case is that the transition temperature depends mainly on the relationship between kT and the binding energy of a Cooper pair, not on the rate at which pairs are formed; while the reason that the dependence on V is dominant in the weak-coupling case is that the competing real phonon processes are of lower order in the electron-phonon coupling constant. The situation is similar to that described by the law of mass action; if the stoichiometric coefficients balance, then the equilibrium point depends only on temperature and is independent of kinetic factors.

An immediate question is whether or not the interaction is attractive. This is difficult to answer for a complex interaction mechanism, but in most cases the formal nature of the coupling is similar to that of the electron-phonon system, and the following considerations are valid: the general interaction is of the form $-V(\mathbf{r},\ t;\ \mathbf{r}',\ t') \sim |g^2|\ D(\mathbf{r} - \mathbf{r}',\ t - t')$, where g is a coupling constant, D is the Green's function of a boson excitation, and the minus sign arises from our convention that a positive interaction is attractive. The Fourier transform of the boson Green's function, $D(\mathbf{q},\ \omega)$ is generally negative in some finite region about ($\mathbf{q} = 0,\ \omega = 0$), and in this region the interaction will be attractive. Beyond this region V may be repulsive, but the electrons can apparently adjust to this and avoid the energetically unfavorable portion of the spectrum. For a retarded interaction, the characteristic cutoff is defined (within a numerical factor of 1.14) as the frequency at which the Green's function of the excitation changes sign.

The electron-phonon interaction, which provides a satisfactory explanation of the bulk superconductivity of most substances, is modified in two ways at the surface [30]. Because of the lessened constraint to which the surface atoms are subject, the normal frequencies are shifted downwards and the effective cutoff is lowered. There is also the possibility of coupling to large-amplitude evanescent modes, and this, as well as the enhancement of the usual coupling through the resonance mechanism to be discussed below, can increase the magnitude of the interaction to well within the strong-coupling regime. This suggests that transition temperatures close to the Debye temperature are possible through the electron-phonon interaction alone. There are, however, other interactions associated with impurity surface states which feature both high cutoffs and large interaction parameters.

An impurity atom in a crystal adds its energy levels to those already present, and the presence of a large number of impurities can give rise to an impurity band lying close to the regular conduction band. This effect is particularly significant in the surface region, partly because of the high impurity concentrations (e.g., oxide, substrate, adsorbed gasses) usually present, partly because the presence of these impurities creates a localized impurity band without affecting the bulk electronic properties of the crystal. Because of the large amplitudes of these localized states, the exchange integral between them and the Bloch states is magnified. Assuming a falloff of roughly 5 atomic spacings for the surface state [31], this means that a large surface interaction can exist within a layer whose thickness is a good bit less than the mean free path, which is what surface superconductivity requires.

The surface levels couple to a number of excitation modes. There is of course the vibrational mode discussed previously, with a cutoff determined by the Debye frequency. Ginzburg has pointed out that transitions between electronic states of the impurity atoms involve energies on the order of electron volts, and with values of $\hbar\omega$ of this magnitude it should be possible to arrive at transition temperatures between 10^2 and 10^4 °K [3]. However, the internal coupling may be weak and the effective density of states can be sharply reduced if the width of the transition is small. A more serious restriction is that Cooper pairs have the same net quantum numbers as the vacuum, which imposes strict selection rules on the excitation process. Atomic transitions are as likely to destroy superconductivity as to help it, the $\Delta L \neq 0$ and $\Delta L = 0$ excitations interfering in the same way that spin waves and phonons compete in magnetic materials.

If the surface is in contact with a dielectric material, such as a substrate or oxide layer, there is the additional possibility that the impurity surface states can couple to exciton modes. The magnitude of this effect is difficult to determine, but if it were significant one might also expect to find structure in tunneling data related to the exciton spectrum. Interaction with the surface dipole layer arising from the contact potential has been suggested as an interaction mechanism in some cases [32].

For all high energy excitation processes, an upper bound on the cutoff is imposed by the width of the surface band. This will generally depend on a number of factors, but it seems reasonable to use the values of a few tenths of an eV suggested by Auger emission data [10]. For strongly coupled modes this would admit the possibility of room temperature superconductivity. We shall now investigate the structure of the surface layer in detail to see how realistic this possibility is.

Structure of the Surface Layer

The surface layer is not a uniform homogeneous sheath, nor can it be represented by a continuum of impurity atoms. The actual interaction seen by an atom on the surface will be due not solely to the impurity scattering mechanisms described above, but rather to the net excitation spectrum of the entire surface, for which the impurity density is likely to be small (it is conceivable that localized superconductivity due to K^{corr} could occur at an isolated impurity site, which need not be on the surface, but the cost in kinetic energy would be severe). Therefore, if we are to make a realistic estimate of the probable transition temperature of such a system, we must generalize the BCS formula in such a way that the parameters N, V, and ω are appropriately averaged over the surface. This can most easily be done by calculating the free energy density in the Cooper limit, meaning that the energy=gap function is taken to be constant, and finding the highest temperature at which the total free energy is negative [33]. This is determined by the vanishing of the integral $\int[y(\mathbf{r}) - V(\mathbf{r})y^2(\mathbf{r})]d\mathbf{r}$ over the surface region, where

$y(\mathbf{r}) = N(\mathbf{r})L(\hbar\omega(\mathbf{r})/kT)$ and L is the difference of two digamma functions, $L(z) = \psi(\frac{1}{2}[\pi z e^{-\gamma} + 1]) - \psi(\frac{1}{2})$, and where γ is Euler's constant and the factor $\frac{1}{2}\pi e^{-\gamma} = (1.14)^{-1}$ arises from our definition of the cutoff frequency. For a homogeneous system this reduces to $NVL(\hbar\omega/kT_c) = 1$; since $L(z) \sim \ln z$ for large z, this agrees with the BCS weak-coupling limit, equation (2), $kT_c = \hbar\omega e^{-1/NV}$. Since, however, we are looking for transition temperatures on the order of the Debye temperature, this approximation must be used with caution. If the concentration of impurity atoms on the surface, x, is small, the logarithmic approximation can be used to find the exponential dependence $T_c = T_0 e^{ax}$, where $a = \ln(\hbar\omega_{\text{imp}}/kT_0)[\rho_{\text{imp}} \ln(\hbar\omega_{\text{imp}}/kT_0) - 1]$ and T_0 is the bulk transition temperature. It can readily be confirmed that in the case $\omega_{\text{imp}} = \omega_0$ this reduces to the Cooper limit, $kT_c = \hbar\omega \exp\{-1/[\rho_0 + x(\rho_{\text{imp}} - \rho_0)]\}$. For $\omega_{\text{imp}} > \omega_0$ the repulsive tail of the electron-phonon interaction will tend to inhibit the high-frequency modes, as occurs in surface enhancement, but the components with frequencies close to ω_{imp} will only be suppressed for small values of x. At higher concentrations the effect of impurity trapping will saturate, and the limiting value of T_c will correspond to $kT_c^{\text{lim}} = \hbar\omega_{\text{imp}} \exp\{-1/\rho_{\text{imp}}\}$.

Since the high-frequency modes are most heavily suppressed in the case of surface enhancement, this effect can be used to estimate the strength of the surface coupling. The data of Strongin *et al.* [25,26] indicate that $\rho_{\text{imp}} > \rho_{\text{Al}}$, and the other data on Al agree if we assume that the surface enhancement mechanism applies [27-29]. There is some evidence that the transition temperatures of strong-coupled superconductors are depressed by surface effects [34], and if we take this to be a case of negative surface enhancement we arrive at the estimate $\rho_{\text{imp}} \sim 0.3$-$0.35$ suggested by Strongin, Kammerer, and Paskin [25]. This value is smaller than might be expected from the preceding arguments, but, in view of the sensitivity of ρ_{imp} to the relationship between the impurity surface band and the bulk conduction band, the consistency of these results for different metals suggests that mean free path or strain effects may be the determining factors [29].

It should be noted that surface superconductivity can occur even if $\rho_{\text{imp}} < \rho_0$, if the impurity cutoff is large enough so that $a = \ln(\hbar\omega_{\text{imp}}/kT_0)[\rho_{\text{imp}} \ln(\hbar\omega_{\text{imp}}/kT_0) - \rho_0 \ln(\hbar\omega_0/kT_0)]$ is positive. If we take $\rho = 0.3$ and $\hbar\omega_{\text{imp}}/kT_0 = 100$, for example, we get $T_c \sim T_0 e^{2x}$, which will give a small surface superconductivity effect whether or not the surface enhancement is negative. Which effect we observe depends of course on the thickness of the surface layer.

Conclusion

In our discussion of the possibilities for high-temperature surface superconductivity we have shown how a highly localized form of surface ordering can arise which is extremely sensitive to the nature of the electron-electron interaction in a thin surface layer. Impurity surface states provide a mechanism whereby the electrons can couple strongly to excitation modes having much higher cutoffs than the Debye frequency. Even for low impurity concentrations it should be possible to observe substantial increases in the transition temperature.

Certainly the introduction of virtually any new interaction mechanism will increase the cutoff parameter ω. The Debye spectrum cuts off at a frequency which is generally an order of magnitude less than other characteristic frequencies of the system [35]. Usually these non-acoustic excitation modes cut off at energies on the order of a few tenths of an eV, which corresponds to $\sim 10^3$ °K, and the main factor is the degree of coupling. If the coupling is strong, as we have suggested it may be when resonance scattering by impurity atoms is effective, room-temperature surface superconductivity should be possible.

To summarize, the existence of a surface layer with interaction different from that of the bulk material has been indicated for a number of superconductors by observation of the surface enhancement effect. Whether this surface layer can cause superconductivity to occur at high temperatures is as yet uncertain, but under ideal conditions, i.e. with an impurity surface band close in energy to the conduction band, transition temperatures as high as 10^3 °K are conceivable. How closely this conception approaches reality is difficult to say, as we cannot be sure even that we are justified in applying the BCS theory at temperatures of this magnitude; for, although we discuss the possibility of surface superconductivity at room temperature, we must remember that we can not as yet explain the rather surprising fact that superconductivity has never been observed above ~ 18°K.

Author's Note

The author regrets having failed to mention the work of W. Rühl (*Z. Phys.* **186**, 190, 1965, and previous work cited therein) on the effect of oxide layers on thin films. Rühl has observed both increases in the transition temperature (Al, Tl, In) and decreases (Sn, Pb, Ga) comparable in magnitude to those observed by Strongin *et al.* [25,26], although his results are somewhat different. McConnell and coworkers (*Proc. Natl. Acad. Sci. U. S.* **54**, 371, 1965) have reported changes in the transition temperatures of V films on which layers of various organic compounds were evaporated.

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16. The above argument is greatly simplified, and, in particular, all references to time-temperature variables has been suppressed. The reader interested in a fuller exposition of the application of the Gor'kov theory to this problem is referred to the papers of de GENNES (ref. [17]), WERTHAMER (ref. [18]), and AGD, Chapter 7. A comprehensive treatment of the theoretical methods used in this paper is contained in W. SILVERT and L.N. COOPER. *Phys. Rev.*, **141**, 336 (1966).

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18. N.R. WERTHAMER, *Phys. Rev.* **132**, 2440 (1963).

19. This cutoff arises from the spectrum of the interaction, which we have so far assumed has the form $V(\mathbf{r}, t; \mathbf{r}', t') = V(\mathbf{r})\delta(\mathbf{r} - \mathbf{r}')\delta(t - t')$. Real interactions are not this sharp, and if V, for example, is taken to be the retarded phonon interaction, the cutoff will be the reciprocal of the lattice relaxation time. In this case ω is approximately the Debye frequency.

20. AGD, pp. 325-341.

21. This result is not as arcane as it might appear; for a discussion of the use of field theoretic methods at finite temperatures, see AGD, Chapter 3.

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layer, and they point out that in both cases the dependence of the transition temperature on thickness is the same. Similar ambiguity exists for the data reported in refs. [27] and [28].

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31. V. HEINE, *Surface Sci.* 2, 1 (1964).

32. L. ESAKI and P.J. STILES, *Phys. Rev. Letters* 15, 152 (1965).

33. W. SILVERT and L.N. COOPER, *op. cit.* (ref. [16]).

34. J.J. HAUSER and H.C. THEUERER, *Phys. Rev.* 134, A198 (1964).

35. H. FROHLICH (*Phys. Letters* 7, 346, 1963) has pointed out that the width of the conduction band may be small enough to impose an upper limit on the cutoff in some cases.