INTERACTIONS BETWEEN MOLECULES AND SUPERCONDUCTORS

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To my Father, Mother

and Brothers

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ABSTRACT

Recently, the possibility has been raised that interactions favorable to superconductivity might occur in molecules. Although most molecules or molecular aggregates are not even potentially superconducting, it has occurred to us that molecules can be coupled to metals through various kinds of bonds, and that such systems may then have interesting superconducting properties. Our approach to the preparation of such systems involves the deposition of selected molecules on thin metal films.

We first present a discussion of the theory of superconductivity, including a review of some of the interaction mechanisms appropriate to molecules. The experimental apparatus is described. Our results are then reported and discussed. We have found compounds that increase the superconducting transition temperature and critical current of thin vanadium films, as well as others which decrease them, and we have found that the sign of this effect can be correlated in a simple way with the electronic structure of the molecules. The nature of these effects is partially clarified by comparison to similar experiments with indium films.

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I. INTRODUCTION (1)

Superconductivity was discovered in 1911 by Kammerlingh Onnes (2) during investigations of the changes in resistance of metals as they are cooled. The resistance of most metals he studied decreases rapidly with temperature until some limiting value is reached, and then remains constant with further cooling. However, the resistance of mercury behaves in this manner only down to 4.15°K. At this temperature, and within an interval of a fraction of a degree, mercury loses all of its resistance. At that time, this state exhibiting infinite conductivity was only one mystery among the many which puzzled investigators of the properties of metals. The discovery of quantum mechanics and its rapid application to solid state physics (3) permitted a basic understanding of many metallic properties, such as the value of the specific heat magnetic susceptibility and normal electronic conductivity, but left the nature of superconductivity still a mystery.

For many years after its initial discovery, the superconducting state was assumed to be basically a state of infinite conductivity, and theoretical efforts were devoted to explaining this phenomenon. An important step forward came in 1933, with the discovery by Meissner and Ochsenfeld (4) that a superconductor is a perfect diamagnet. That is, a magnetic B field is completely excluded from the interior of a massive superconductor, the field penetrating only a distance of ~ 500 Å. Since perfect

conductivity alone would only prevent a change in B inside of a superconductor, the Meissner effect definitely shows that a superconductor is more than a perfect conductor. It also shows that there is a unique state of a simply connected superconducting body for given values of the variables temperature, pressure and externally applied B field; the transition from normal to superconducting state is reversible, and thermodynamics may therefore be applied to the system (5).

The general features that a microscopic theory of superconductivity must embody were first described by F. London in 1935 (6). The unique properties of a superconductor arise because it has an ordered ground state which is to be regarded as a single quantum state extending throughout the material. A superconductor is "a quantum structure on a macroscopic scale" which is a "kind of a solidification or condensation of the average momentum distribution." He further stated that his successful phenomenological equations could be interpreted by assuming that "the electrons are coupled in such a way that the lowest state be separated by a finite interval from the excited states"--in other words, there is an energy gap in the excitation spectrum (7).

Until 1957, however, all attempts to construct a microscopic theory proved to be inadequate. It is perhaps less surprising that forty-six years had to elapse before the solution of this problem if its complexity is considered. Whereas the correlation energy due to the coulomb interaction between electrons is of the order of 1 eV/electron, and self-energies associated with the

electron-phonon interaction are of the order of 10^{-4} eV/ electron,

the energy difference between normal and superconducting states

of a metal is only of the order of 10^{-8} eV/ electron (8). Since

there is no hope of calculating the energy of either state with

an accuracy of 10^{-8} eV, all that can be done is to attempt to

focus on the terms in the energy which cause the difference

between superconducting and normal phases and to directly calcu-

late this difference as accurately as possible.

In 1950, Frohlich (9) suggested that the basic force

responsible for superconductivity was an attractive interaction

between electrons arising from their interactions with the crystal

lattice vibrations (phonons). Although his theory as a whole was

inadequate, it predicted an isotope effect in which the transition

temperature, T_c, varied as

$$T_c \propto M^{-\alpha}$$

with $\alpha = 1/2$. The discovery by Maxwell (10) and by Reynolds (11)

in the same year of an isotope effect in tin, thallium and mer-

cury, with $T_c \propto M^{-1/2 \pm 10\%}$ gave strong support to the importance

of an electron-lattice interaction. It is hard to imagine how

an isotope effect could fit into a theory based solely on

electron-electron interactions, one in which the Born-Oppenheimer

approximation is employed.

But even with attention focused on the important inter-

action, a complete theory did not immediately appear. For one

thing, the early theories based on the electron-phonon inter-

action considered primarily the resulting electron self-energy,

rather than the true interaction between electrons (12). Another significant reason is that simple perturbation theory cannot be used. As Schafroth proved (13), the Meissner effect cannot be obtained in any finite order of perturbation theory beginning with the uncoupled electron lattice system. Later, Migdal (14) showed that within the perturbation theory there is no energy gap in the electronic excitation spectrum.

The present amazingly successful microscopic theory of superconductivity was proposed by J. Bardeen, L. N. Cooper, and J. R. Schrieffer (15) (BCS) in 1957. It is based on the fact, established by Cooper (16), that the Fermi sea is unstable in the presence of a net attraction between electrons. It employed a variational calculation in which the critical term in the hamiltonian was such an attraction; all interactions except this one were assumed to be the same in both normal and superconducting states. The trial wave function for the superconducting ground state is described in terms of a linear combination of normal state-like configurations in which the individual electron states are occupied in pairs of opposite spin and momentum. This function gives a long range spatial correlation between electrons of opposite spin so as to take advantage of the attractive interaction. The resulting state has an energy gap in the excitation spectrum and has the correct thermal and electromagnetic properties to display superconducting behavior. Soon after this, Bogoliubov (17) and Gorkov (18) obtained the BCS results using different formulations. The elegance of their approaches "made

the field of superconductivity extremely attractive to a great
number of theoretical physicists, whose exponentially increasing
number of contributions have now flooded the literature" (19).

Paralleling the theoretical activity has been a similar
burst of experimental work. One indication of this is that in
1962 a compilation of known superconductors contained nine
hundred entries, as compared with more than 500 entries in a
list prepared in 1960 (20). In the past four years efforts
have not slackened. Among the more exciting occurrences has
been the discovery that superconductivity can occur in a semi-
conductor, GeTe being the first such material found (21).

The search for new materials has largely been made for
two different, though relatable reasons. The first has been
that by systematically studying the conditions under which
superconductivity appears, empirical rules can be set up which
correlate the occurrence of superconductivity with the properties
of a material. Notable is the work of Matthias (22) who has given
general rules for the appearance of superconductivity as related
to the number of valence electrons of a metal or alloy. These
studies were first undertaken long before the discovery of the
BCS theory, in the hope that empirical rules might suggest the
basis for a microscopic theory. There are sufficient limitations
to the present theory that such experimental studies can still
suggest modifications and extensions. Theory has not yet com-
pletely reached from the general to the particular, from the
idealized superconductor to the particular metal.

An important instance of this concerns some elements which show a reduced, or even vanishing isotope effect (Ru, Os, Mo, Nb_3Sn) (23). This has been interpreted to mean that mechanisms other than electron-phonon interactions can lead to an effective electron-electron attraction. The issue is still unresolved, although more realistic calculations than BCS have been performed. Morel and Anderson (24) do find a reduced isotope effect; however, their results are now too low, with the exponents α at least 15% lower than the experimental values for non-transition metals. Garland (25) achieves good agreement with the values of α without invoking a new attractive interaction, and has therefore shown that the vanishing isotope effects do not preclude the importance of phonons, but he also has elaborated on one of the alternative mechanisms that have been suggested for producing an attractive interaction between electrons in transition metals (25).

In addition, what seem to be anomalously high transition temperatures in certain dilute alloys, particularly iron in titanium (26), and in the elements lanthanum and uranium (27), have also been interpreted as evidence that other mechanisms operate in addition to phonon coupling. Thus, extending the study of superconductivity into different materials is still a legitimate and necessary test for the existence of alternative mechanisms, since the theory is not sufficiently precise to distinguish quantitatively between the many possible mechanisms which might lead to a similar qualitative result--namely, the appearance of superconductivity.

A second reason for an intensive search for new superconducting materials is technological. At present there exists a class of materials which can remain superconducting in high magnetic fields, and which have become very useful in the production of superconducting magnets.

> The prospects of further utilization of superconductors in engineering would seem to be unlimited, were it not for the lamentable circumstance that in all the cases known to date the superconducting state is realized at very low, and therefore difficult to attain, temperatures. Thus the question of the future of superconductivity is connected primarily with the problem of increasing the critical temperatures, if this is at all possible. (28) .

Now, the highest transition temperature presently known is 18.6 K for Nb_3Sn. Why the cutoff should come at this temperature is completely unknown. However, it is reasonable that there should be some kind of cutoff if the attractive interaction arises from interactions of the conduction electrons with the lattice. One would expect T_c to increase as this interaction increases, but only up to a point, for strong electron-lattice interactions can lead to a phase transformation to a new crystal structure with smaller interactions. Something along these lines is suggested in an examination of the compounds with the highest transition temperatures, most of which crystallize in the β-W crystal structure. Several materials which "should" crystallize in this structure and exhibit very high values of T_c, instead crystallize in a different structure and have lower values of T_c than expected. As Matthias said about one of these, Zr_3Sb, "And yet to date it has not been possible to form this compound in the β-W structure by any technique. Perhaps the reason that it cannot

be made is simply that if this material could be made, its transition temperature would be too high."

Thus, it is conceivable that the extension of superconductivity to higher temperatures, if that is possible at all, will rest on the occurrence of other mechanisms for establishing an effective attraction between electrons, and perhaps on the discovery of new kinds of material in which some such mechanism, perhaps already seen in one of the anomalous situations mentioned previously, can be optimized.

The work we have done was undertaken in the belief that electronic and vibronic interactions favorable to superconductivity could arise in appropriate molecules, and that if the conduction electrons of metal could experience these interactions by coupling of the molecules to a superconducting metal through various kinds of bonds, such systems should have interesting superconducting properties. We have studied this proposal in a series of experiments in which a chemical is deposited on a thin superconducting film. We have found compounds which increase the transition temperature of superconducting vanadium films, as well as others which decrease it, and we have found that the sign of this effect can be correlated in a simple way with the electronic structure of the molecules. Compounds with low electronegativity increase T_c, while those with high electronegativity decrease it. The nature of these effects is partially clarified by comparison to similar experiments with indium films.

In section II, a discussion of the microscopic theory of superconductivity is given, with an emphasis on those aspects which have guided our efforts and are relevant to our experiments. Section III contains a description of the experimental apparatus, procedure, and results. Section IV is a discussion of these results, and considers in some detail the correlation between molecular properties and effects on superconductivity.

II. THEORY OF SUPERCONDUCTIVITY

Dynamics

Superconductivity occurs because the normal state of a metal is unstable in the presence of an attractive interaction between particles. The ground state of a free electron gas (a usual starting point in the study of metals) corresponds to the complete filling of the one-electron states of wave vector $\underline{k}$ and energy $\hbar^2 \frac{k^2}{2m}$ up to a certain energy $E = \hbar^2 k^2 F$, the Fermi energy. However as was first shown by Cooper (16), if there is a net attraction, no matter how weak, between a pair of electrons near the Fermi surface this state becomes unstable and the pair can form a bound state. This important result led directly to the BCS analysis of the superconducting ground state. Although Cooper's result is not in itself a theory of superconductivity, for it does not handle the far more complex many-electron problem, it will be reproduced here because it embodies many of the ideas of the full theory in a transparent form. This is then followed by a discussion of the BCS theory.

A. Cooper's Problem

We consider two interacting electrons above a noninteracting Fermi sea. The effect of the other electrons is to prevent our two electrons from occupying states with $k < k_F$ because of the exclusion principle. Since momentum is conserved in the scattering processes due to electron interactions, the wave function of

the two electrons, Ψ , can be expanded as plane wave product functions with identical center of mass momentum, $\underline{K}$. Considering only states where $\underline{K}$ = 0, Ψ is then only a function of $\underline{r}_1$ - $\underline{r}_2$:

$$\Psi(r_1-r_2) = \sum_{k>k_F} g(\underline{k}) \, e^{i\underline{k}\cdot(r_1-r_2)} \tag{1}$$

where g($\underline{k}$) is the probability amplitude for finding one electron in the plane wave state of momentum $\overline{h}\underline{k}$ and the other in the state ($-\overline{h}\underline{k}$). The restriction on k in the summation arises from the exclusion principle. Thus we see that the pair wave function is a superposition of configurations in each of which a definite pair state ($\underline{k}$,$-\underline{k}$) is occupied. The calculation is thus an infinite order configuration interaction treatment, with all possible excited pair states included.

The Schrödinger equation for the two electrons is

$$-\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right)\Psi(r_1-r_2) + V(r_1,r_2)\,\Psi(r_1-r_2) = \left(E+2E_F\right)\psi(r_1-r_2) \tag{2}$$

where E measures the energy of the pair relative to a state with both electrons at the Fermi level. Inserting our expression for ψ gives

$$\left(\frac{\hbar^2 k^2}{m} - 2E_F-E\right) g(\underline{k}) = -\sum_{k>k_F} V_{kk'} \, g(\underline{k}') \tag{3}$$

where

$$V_{kk'} = \langle \underline{k},-\underline{k} \mid v \mid \underline{k}',-\underline{k}'\rangle = \frac{1}{L^3} \int V(r)\, e^{i(\underline{k}'-\underline{k})\cdot r}\, d^3r$$

is the matrix element of the interaction in which the electrons ($\underline{k}'$, $-\underline{k}'$) scatter off each other into the state ($\underline{k}$, $-\underline{k}$). L^3 is the volume of the system. For $E > 0$ this equation has a continuous spectrum of nearly plane-wave solutions. However, if the interaction V is attractive there may also be bound state solutions with $E < 0$ and a finite spatial extent. This is demonstrated by considering a simplified interaction which is attractive and constant in an energy band $\hbar\omega$ above the Fermi level

$$V_{kk'} = \begin{cases} -\dfrac{V}{L^3} & \dfrac{\hbar^2 k^2}{2m}, \ \dfrac{\hbar^2 k'^2}{2m} < E_F + \hbar\omega = \dfrac{\hbar^2 k_m^2}{2m} = \dfrac{\hbar^2 (k_F + \delta)^2}{2m} \\[2ex] 0 & \text{otherwise} \end{cases} \quad (4)$$

Then equation 3 becomes,

$$\left(\frac{\hbar^2 k^2}{m} - 2E_F - E \right) g(k) = \frac{V}{L^3} \sum_{k>k'}^{k_m} g(k') = C \quad (5)$$

where $C = \frac{V}{L^3} \sum g(k')$ is a constant, independent of $\underline{k}$, giving

$$g(k) = \frac{C}{\frac{\hbar^2 k^2}{m} - 2E_F - E} \quad (6)$$

Substituting the value for g(k) into the definition of C gives the self-consistency equation

$$1 = \frac{V}{L^3} \sum_{k'>k_F}^{k_m} \frac{1}{\left(\frac{\hbar^2 k'^2}{m} - 2E_F \right) - E} \quad (7)$$

Changing the sum to an integral over energy by defining $\xi = \frac{\hbar^2 k^2}{2m} - E_F$ and by introducing the density of states per unit energy interval $N(\xi)$ equation 7 becomes

$$I = V \int_{0}^{\hbar\omega} N(\epsilon') \, \frac{d\epsilon'}{2\epsilon' - E} \tag{8}$$

If $\hbar\omega \ll E_F$, $N(\epsilon)$ can be replaced over the small energy range involved by the constant $N(0)$, the value at the Fermi level. For a bound state, $-E = \Delta$, a positive quantity, and equation 8 can be simply integrated

$$I = V N(0) \int_{0}^{\hbar\omega} \frac{d\epsilon}{2\epsilon + \Delta}$$

$$= V N(0) \, \ln \frac{2\hbar\omega + \Delta}{\Delta}$$

For a weak interaction $N(0)V \ll 1$ and

$$\Delta = 2\hbar\omega \, e^{-\frac{2}{N(0)V}} \tag{9}$$

This is the binding energy of a pair with respect to the Fermi level.

Therefore, in the presence of an attractive interaction we can lower the energy of the system by exciting a pair of electrons above the Fermi level. We would expect from this that in a real system more pairs would go into such a state, causing the normal state to be unstable.

The following observations may be made about the above results:

(1) There is a bound state solution for an attractive V of any magnitude. Furthermore, the binding energy Δ cannot be

expanded in powers of V as V → 0, which shows that this result could not be obtained in any finite order of perturbation theory.

(2) The wave function for the pairs is a true bound state with a large mean square radius and nonexponential dependence for large $r = r_1 - r_2$

$$\Psi(r) = \sum_{k > k_F}^{k_m} g(k)\, e^{i \underline{k}' \cdot \underline{r}}$$

$$= \left(\frac{2\pi}{L}\right)^3 \int d^3k' \; \frac{e^{i \underline{k}' \cdot r}}{\epsilon(k) + \Delta} \underset{r \to \infty}{\propto} \frac{\sin k_F r \, \sin \delta r}{r^2}$$

$$\rho = \left[\langle r^2 \rangle\right]^{1/2} = \left[\frac{\int |\Psi(r)|^2 r^2 d^3 r}{\int |\Psi(r)|^2 d^3 r}\right]^{1/2} \sim 10^{-4}\, cm.$$

$$\text{for} \quad \frac{\Delta}{k_B} \sim 1^\circ K$$

(10)

From several considerations, Pippard concluded that the superconducting state is characterized by a long-range coherence such that large changes cannot occur over distances less than $\sim 10^{-4}$ cm in pure metals. The extent of these "Cooper Pairs" is of the right order of magnitude to account for this coherence length.

(3) Despite the fact that this is a two-electron calculation, the existence of a localized bound state is nevertheless a direct result of the presence of the other electrons through the exclusion of states with $k < k_F$ by the Pauli principle. If the integration could be extended to $\frac{h^2 k^2}{2m} = 0$, for small V there would be no bound state.

(4) With our simplified interaction, $g(\underline{k})$ depends only on
ϵ. It therefore depends only on $/k/$, and the function Ψ is sym-
metric with respect to the interchange of the two electrons.
Thus it must be associated with the antisymmetric (singlet) spin
function. Although a potential $V_{\underline{k}\underline{k}'}$ which is strongly dependent
on the angle between k and k' could give rise to bound triplet
states, in actuality this appears not to be important.

(5) Recognizing that an instability exists does not neces-
sarily tell what the new state will be. Cooper's treatment is
not yet a true explanation of superconductivity for it does not
treat all electrons equally. In fact, it is found that the
formation of a "Cooper pair" in the BCS theory depends critically
on the presence of other pairs, and the energy gap and most of
the observed properties of the superconducting state would be
absent were it not for the strong correlations between pairs.

Nevertheless, the concept of the correlated occupation of
pairs of states with opposite momentum and spin led directly to
the BCS theory to be discussed below. The concept of Cooper pairs
with a large spatial extension is still an exceedingly useful
guide in attempts to understand how superconductors behave.

B. Theory of Bardeen, Cooper, and Schrieffer

The BCS theory follows the direction pointed by Cooper.
The basic mechanism responsible for superconductivity is assumed
to be an effective attractive interaction between electrons; the
crucial assumption is made that all interactions except this

contribute equally in the superconducting and normal ground states. The many-electron trial function for the superconducting ground state is formed from a linear combination of nearly degenerate normal state-like configurations in which particles are excited to low energies above the Fermi sea. Their method is to choose a subset of configurations whose phases are such that the matrix elements of the interaction between any two configurations i and j are predominantly negative. Then the trial function for the ground state can be chosen as a linear combination of these configurations with coefficients of the same sign. That is, we can write

$$\Psi = \sum_j a_j \Psi_j$$

where each Ψ_j, can be thought of as a particular Slater determinant and the a_j are to be determined variationally. The energy can then be written, in obvious notation

$$E = \sum_j a_j^2 \varepsilon_j + \sum_{i \neq j} a_i a_j H_{ij}$$

If the H_{ij} vary randomly in sign, the second term gives little. But if they can be made predominantly negative, then the combination of many configurations can give a net lowering of the energy.

Now, the effective pair interaction considered by BCS has non-vanishing matrix elements between configurations which differ in the occupation of two particles, for instance with k_1 and k_2 going to k_1' and k_2' with conservation of wave vector:

$$k_1 + k_2 = k_1' + k_2' = Q$$

Because of the Fermi statistics of the electrons, the sign of the matrix element for this scattering depends on the occupation of the other states which are unchanged in the transition. If a definite ordering of all states is chosen, k_α, k_β, k_γ, . . . , then

$$\langle k_\alpha, k_\beta, \cdots k_1' \cdots k_2' \cdots k_\delta | U | k_\alpha, k_\beta \cdots k_1 \cdots k_2 \cdots k_\delta \rangle = (-1)^{N+N'} \langle k_1' k_2' | U | k_1 k_2 \rangle \quad (11)$$

(Spin variables are not indicated)

where N and N' are the total number of occupied states between k_1 and k_2 in the initial state and k_1' and k_2' in the final state, respectively. Thus, the relative sign for the matrix element is $(-1)^{N+N'}$. Since, for general configurations, N and N' are equally likely to be even or odd, the sign of these off-diagonal matrix elements will alternate, and they will not add to produce a net lowering of the energy as in the illustration above. Furthermore, since there are many more matrix elements than configurations, it is not possible to get consistent signs by changing the signs of the coefficients of the various configurations.

The step taken by BCS is to select a subset of configurations (of negligible statistical weight) between which the matrix elements are predominantly negative for an attractive interaction. This is done by associating the states in pairs (k_1, k_2), and requiring that in any configuration with one member of a pair occupied, the other is also. Thus N + N' must always be even, and the matrix elements all have the same relative sign. To get

the maximum number of matrix elements, any pair should be able
to scatter into any other pair. Since the interaction conserves
momentum, all pairs should then have the same total momentum
$k_1 + k_2 = Q$. By analogy to the Cooper pairs we take the anti-
parallel spin state. Thus, for the ground state, where $Q = 0$,
we pair states $(k\uparrow, -k\downarrow)$. We have therefore again arrived at the
concept of pairs with opposite momentum and spin.

In the trial function chosen by BCS they follow a Hartree-
like approximation in which they assume that the probability with
which a specific configuration of pairs appears can be expressed
as a product of the probability that each indivual pair state is
occupied. If v_k is the probability amplitude that the state
$(k, -k)$ is occupied, and u_k the amplitude that it is unoccupied,
their values are related by the normalization condition

$$v_k^2 + u_k^2 = 1 \tag{12}$$

The energy difference between the superconducting and normal
states is then

$$W_s - W_n = 2 \sum_k \epsilon_k v_k^2 - 2 \sum_{k < k_F} |\epsilon_k| + \sum_{kk'} V_{kk'} u_k v_k u_{k'} v_{k'} \tag{13}$$

where ϵ_k is the single particle energy for an electron in the
state k measured from the Fermi surface and $V_{k'k}$ is the matrix
element

$$\left\langle --; k'\uparrow, -k'\downarrow; \cdots \left| V \right| k\uparrow, -k\downarrow; --\cdots \right\rangle$$

The interaction term is of this form because in the initial state pair k must be occupied, amplitude v_k, and pair k' unoccupied, amplitude $u_{k'}$; in the final state k must be occupied (u_k), and state k' occupied ($v_{k'}$). The coefficients u_k and v_k, and thus the energy, can be obtained by variational calculation:

$$v_k^2 = \frac{1}{2}\left(1 + \frac{\epsilon_k}{[\epsilon_k^2 + \Delta_k^2]^{1/2}}\right)$$

$$u_k^2 = \frac{1}{2}\left(1 - \frac{\epsilon_k}{[\epsilon_k^2 + \Delta_k^2]^{1/2}}\right)$$

(14)

where Δ_k, the energy gap parameter, is given by the integral equation

$$\Delta_k = \sum_{k'} \frac{V_{kk'}}{2} \frac{\Delta_{k'}}{[\epsilon_{k'}^2 + \Delta_{k'}^2]^{1/2}}$$

(15)

For the special case $V_{kk'} = -V$ for $/\epsilon_k/ < \hbar\omega$ and zero otherwise, Δ_k is a constant Δ for $/\epsilon_k/ < \hbar\omega$ and zero for $/\epsilon_k/ > \hbar\omega$. In this case, equation 15 becomes

$$1 = N(0) V \int_0^{\hbar\omega} \frac{d\epsilon_k'}{[\epsilon_k'^2 + \Delta^2]^{1/2}}$$

where $N(\epsilon)$ has been approximated as the constant $N(0)$, upon taking $\hbar\omega \ll E_F$. Integrating gives

$$\Delta = \frac{\hbar\omega}{\sinh(1/N(0)V)}$$

$$\Delta \approx 2\hbar\omega\, e^{-\frac{1}{N(0)V}} \qquad , \quad N(0)V < .5$$

(16)

The simplest excitation from the BCS ground state consists of a state in which, for example the state $\underline{k}$ is surely occupied and the state $-\underline{k}$ is surely unoccupied, but otherwise is identical to the ground state. The energy for this excitation is

$$\varepsilon_k = [\epsilon_k^2 + \Delta^2]^{1/2} \tag{17}$$

and therefore the single particle excitation spectrum has an energy gap, with minimum excitation energy Δ occurring at the Fermi surface where $\epsilon_k = 0$.

Extension of the theory to finite temperatures gives for the transition temperature, T_c,

$$k_j T_c = 1.14 \, \hbar\omega \, e^{-\frac{1}{N(0)V}} \tag{18}$$

This relationship combined with equation 16 gives a general relationship between the energy gap at $0°K$, $\Delta(0)$, and T_c:

$$2\,\Delta(0) = 3.52 \, k_B T_c \tag{19}$$

The range of experimental values for the ratio $2\Delta(0)/k_j T_c$ for all superconductors is 3.2-4.6, with most lying near 3.5, affording quite satisfactory agreement.

Again, certain comments are in order:

(1) This _is_ a theory of superconductivity. In addition to the energy gap and its relation to T_c, the BCS theory accounts for a second order phase transition at T_c, for the Meissner effect and probably for persistent currents. A striking prediction of the theory, completely verified by experiment, is the influence

of coherence effects associated with the pairing on transition
probabilities for such phenomena as absorption of ultrasonic or
electromagnetic waves and for nuclear spin relaxation times (30).

(2) Since 1957 an intensive study of the mathematical
structure of the theory has occurred. Reformulations (17,18),
more suitable to calculation have led to a wide increase in the
number and kinds of problems considered. However, this brief
discussion of the kinematics of the theory, as first discovered
by BCS, is sufficient for our purposes, and in fact subsequent
theoretical work to be mentioned in later sections was often
couched in BCS terms.

(3) As in the Cooper problem, the value of the energy gap,
and also of T_c, cannot be expanded in powers of V for V → 0.

(4) From equation 13 we see that the contribution of pair
state k to the energy of condensation is (for $k > k_F$)

$$W_k = 2 \epsilon_k v_k^2 - V \cdot u_k v_k \sum_{k'} u_{k'} v_{k'}$$

Thus, the decrease in energy for a given pair is a result of the
interaction with all other pairs, as was stated previously.

(5) If, as was discussed in the introduction, the attrac-
tive interactions arise indirectly from a coupling of the elec-
trons to the phonons, the cutoff energy, $\hbar \omega$, should be equal to
$k_B \theta_D$, where θ_D is the Debye temperature, since this is the energy
of the most energetic longitudinal phonon. Since $\theta_D \propto M^{1/2}$, and
N(0)V is expected to be independent of isotopic mass, equation
18 gives $T_c \propto M^{-1/2}$, and the general existence of the isotope

effect is explained. Furthermore, the presence of the exponential accounts for the fact that $T_c \ll \theta_D$.

(6) However, it is not necessary to assume any particular mechanism for the attractive interaction. As long as a net attraction exists, equation 15 has a solution, and a superconducting state is predicted. It is this fact, when buttressed with considerations of the anomalous cases mentioned in the introduction, which have led people to consider alternative attractive interactions.

Interaction Mechanisms

Suggestions of non-phonon coupled attractive interactions have been advanced as explanations of certain experimental results, mentioned previously, and also as elements in proposals of unusual synthetic superconducting materials, often predicted to show unusually high transition temperatures (31, 32). Since the experiments described in later sections were undertaken because of our belief that favorable interactions might result from the binding of molecules to metals, the nature of such suggestions is of central importance. In this section we first describe the nature of the phonon-mediated interaction, and then discuss several suggested alternatives, emphasizing how they might occur in metal-molecule systems.

It should be pointed out, however, that proposing a mechanism is considerably easier than proving its existence in an actual material. Even in the pure metals with small or zero isotope effect, the presence of an alternative mechanism is by no means universally accepted. In alloys, there are many variables which can affect T_c. As the percentage of alloying component is increased from zero, there is always an initial decrease in T_c caused by elastic impurity scattering (33). At higher concentrations, changes in number of valence electrons, density of states, lattice parameters, and in θ_D all can lead to changes in T_c. For example, when titanium is alloyed with vanadium, the transition temperature increases from $\sim5°K$ for pure vanadium to $\sim7°K$ for 80%

vanadium, 20% titanium (34). These changes in T_c correlate quite

well with changes in N(0) and θ_D when equation 18 is employed.

A. Phonon-Coupled Interactions (9)

The physical origin of an attractive interaction between

electrons, mediated by the lattice, is easily understood. As an

electron moves through a lattice in which the ions are not rigidly

fixed or infinitely heavy, the lattice will polarize in its wake,

producing a temporary excess of positive charge by attempting to

crowd nearer to the electron. A second electron traveling with

the appropriate phase relative to the first will not see the

original lattice potential, but rather the more attractive

potential of the distorted lattice, with its excess of positive

charge. Thus, the polarizability of the lattice produces an

effectively attractive force between two electrons, V_{ph}.

To this force must be added their mutual coulomb repulsion.

In systems with high densities of freely moving electrons the

long-range coulomb interaction between two electrons is "screened"

by the correlated motions of the electrons. A simple model in

which screening occurs is a dense free-electron gas with a uniform

background charge. Then, by using a linearized form of the

Thomas-Fermi equation, a quantum analog to the linearized Poisson-

Boltzman equation of the Debye-Hückel theory, the interaction

between two electrons is found to be, not the "bare" interaction

$V_c \propto \frac{1}{r}$, but the screened interaction $V_c^s \propto \frac{e^{-\lambda r}}{r}$. This is a

short-range interaction, with range $\lambda^{-1} = \left(\frac{6\pi n e^2}{\varepsilon_f} \right)^{-\frac{1}{2}} \sim .5 A^{\circ}$.

Much more complete treatments of screening have been developed

by Bohm and Pines (35), and extended by others (35), but the

above discussion is qualitatively correct.

Combining these two interactions and taking an average over

those states near the Fermi level which might contribute to the

BCS superposition, of configurations, we have an effective matrix

element

$$-V = \langle V_c + V_{ph} \rangle$$

The criterion for superconductivity in the BCS theory is that

$-V < 0$.

Quantum mechanically, the lattice-mediated interaction is

calculated as a second-order process in which a virtual phonon

is emitted by one electron and absorbed by another, resulting

in an interaction between the two electrons.

The Hamiltonian for the conduction electrons has a term (36)

$$H_{e-I} = \sum_{ij} v(x_i - X_j) \tag{20}$$

where v is the electron-ion interaction, x_i is the position of

the i'th electron and X_j that of the j'th ion. In the Born-

Oppenheimer approximation, $X_j = X_j^O$, the equilibrium position.

If motions of the ions are included, $X_j = X_j^O + \delta X_j$ and the

term H_{e-I} can be expanded to first order in δX_j. This gives

a coupling which is first order in the ion displacements, and

which can be written as terms linear in phonon operators. The

processes caused by these terms are the scattering of an electron
from state k to state k + q with either the absorption of a phonon
with wave vector q, or the emission of a phonon with -q. The
value of the matrix element for momentum transfer q, D_q, can be
taken for convenience as a constant, D.

The influence of the phonons on the electrons can be studied
by a canonical transformation on the Hamiltonian

$$\tilde{H} = e^{iS} H e^{-iS} \tag{21}$$

where S is an hermitian operator chosen so that the transformation
eliminates terms linear in the phonon variables--terms linear in
D. This was first done by Fröhlich (9,36), who found that the
transformation produced a term corresponding to an interaction
between electrons. For a process which can be indicated schemati-
cally
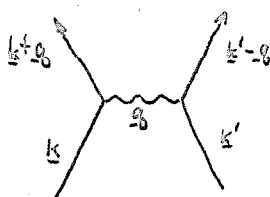
the matrix element is

$$\langle k+q, k'-q | \tilde{H} | k, k' \rangle = \frac{2 D^2 \hbar \omega_q}{\left(\epsilon_k - \epsilon_{k-q} \right)^2 - \left(\hbar \omega_q \right)^2} \tag{22}$$

It can be seen that for energy differences $|\epsilon_k - \epsilon_{k-q}| < \hbar \omega_q$,
the interaction is attractive (negative). This attractive

interaction is the result of an exchange of a virtual phonon of wave vector q. It is a virtual process because the condition for an attraction shows that the change in electronic energies is not sufficient to create a real phonon of energy hw_q. This means that the energy of the intermediate state containing the virtual phonon must be uncertain to approximately $\Delta E \sim hw_q$, and that therefore, by the uncertainty principle, its lifetime must be $\tau \lesssim \frac{1}{w_q}$, the period of oscillation of the phonon.

Since most longitudinal phonons have energies $hw_q \sim k\Theta_D$, the approximation of treating the interaction as a constant $-V$ in the energy shell for which the interaction is attractive leads to the condition $/\varepsilon_k - \varepsilon_{k-q}/ < k\Theta_D$. Then, since the ε_k of importance are of the order $\varepsilon_k \sim kT_c$, whereas Θ_D is usually greater than $100°K$, it is a good approximation to simplify the energy condition to $/\varepsilon/, /\varepsilon_{k-q}/ < k\Theta_D$, giving a cutoff $hw = k\Theta_D$ in equation 18, and to approximate the attractive interaction by the constant

$$V_{ph} = \frac{2 D^2}{k\Theta_D} \qquad |\varepsilon_k|, |\varepsilon_{k-q}| < k\Theta_D \qquad (23)$$

To this must be added some average value for the coulomb repulsion.

B. Dynamic Charge Transfer

One of the first departures from the simplified model of a metal used by BCS was made by Suhl, Matthias, and Walker (37). In an attempt to discuss transition metals, they discussed a two-band model of a metal, with phonon-coupled interactions. Kondo (38) later considered a similar two-band model, but he suggested

a new mechanism. In the presence of inter band scattering due to s-d exchange interactions, a process independent of phonons, he showed that T_c is always raised over that of a single attractive band, _even_ when the net interaction between electrons in the second band is repulsive. If both phonon and exchange mechanisms contribute, he finds that V in the exponent for the transition temperature (equation 18) is augmented by a term V' due to exchange, increasing T_c. In the limit that the phonon interaction disappears, he still finds a superconductive solution caused solely by the interband interaction, with

$$k_B T_c = 1.14 \, \Delta \, e^{-\frac{1}{N_s \, J^2/U}} \qquad (24)$$

where Δ is a quantity related to the width and position of the superconducting s-band and N_s is its density of states, J is the exchange interaction, and U is the repulsive interaction in the second band (d).

Kondo interprets this result in terms of a second-order virtual process in which a pair in the first band is transferred to the second band and then returns. "The second order process always acts as an attraction in the s-band, regardless of the sign of J. The effective interaction is quite naturally expressed by J^2/U." Thus he arrives at a mechanism for superconductivity depending only on the coulomb interaction between electrons.

He further considers the case where a narrow d-band is empty, but very close to the Fermi level. If the band is infinitely sharp and located a distance Γ above the Fermi level,

then the transition temperature is given by

$$k_B T_c = 1.14 \, \hbar \omega \, exp\left(- \frac{1}{N_s\left[V + \frac{J^2}{U' + \frac{\Gamma}{2}}\right]}\right)$$

(25)

where U' is a modified d band repulsion and Z is the total number of electrons per atom which can be accommodated in the d-band. Thus, the interaction with an empty, but accessible band can enhance superconductivity.

Kondo advances his mechanism as an explanation for the reduced isotope effect, and for the unusually high transition temperature of lanthanum (empty f-band near the Fermi level). The same process might operate in a system containing appropriate molecules bonded to a metal. The most promising class of molecules is the planar aromatics because of their ability to form π-bonds to metal atoms as in the metallocenes (39). If there were unoccupied orbitals of the molecules at energies near the Fermi level, "dynamic charge transfer" processes could occur, in which pairs of conduction electrons are virtually transferred to the molecule and then return, giving rise to an enhancement of superconductivity.

C. Electron-Coupled Interactions

A critical extension of the two-band model was made by Garland (25). He assumes a model with one band of nearly free, s-electrons, and a second, tightly bound d-band. His calculation shows that under certain conditions this model admits superconductivity <u>without</u> the inclusion of electron-phonon interactions or

of interband scattering terms. His theory, which is based on the Hamiltonian for coulomb interactions screened by a frequency dependent dielectric constant $\epsilon(q,w)$, generates an attractive interaction between conduction electrons. The "heavy" d-electrons are apparently polarized by the s-electrons and tend to antishield-- change the sign of--the interactions of the s-electrons with one another. Thus, he arrives at the possibility of the occurrence of an attractive interaction between electrons caused by the mediation of a distinct second group of electrons, rather than by phonons.

An interaction of this type, viewed in terms of the virtual excitation of a localized electronic state by one electron and its deexcitation by a second, has been a basic motivating idea in our experiments; we consider it possible that, if a finite concentration of molecules can be coupled to a metal, molecular electronic states can form the second system which antishields the conduction electrons.

In a metal-molecule system, it is also possible to consider intermediate virtual states other than those associated with an isolated molecule. If the molecule is strongly bound to a metal atom, or atoms, there may be low-lying excited states of this combined system, including charge-transfer states, which can be virtually excited by the conduction electrons. Such considerations are again applicable to aromatic molecules, but may be most important in those molecules which can function as chelating agents for metals atoms in low-valence states (40) through

"synergic" bonds (41), such as phenanthrolines, bipyridines, and aromatic arsines.

In addition, McConnell (31) has proposed a variation of the electron-coupling mechanism which should be particularly effective in certain metal-molecule systems. He envisages a situation in which some of the molecular orbitals are "conductively conjugated" to the metal. That is, they are quantum mechanically mixed with the conduction band of the metal, allowing conduction electrons to flow through the molecule. At the same time, other orbitals remain largely localized; these supply the system of states for the virtual excitation.

An idealized example is pyrazine bonded in a vanadium lattice:
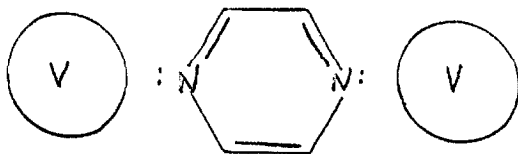
Of the six π-orbitals of pyrazine, the highest and the lowest are considered to be too far from the Fermi level to be important. Of the remaining four, two are symmetric with respect to reflection in the plane perpendicular to the ring and containing the nitrogen atoms; these have large amplitudes on the nitrogen atoms. Since it is well known that pyridine-type nitrogen atoms form strong bonds to transition metals, these orbitals should be conductively conjugated with the metal. The two antisymmetric orbitals, however, have a node at the nitrogen atoms, and should

remain largely localized. These latter two states form the system necessary for the electron-coupled attractive mechanism.
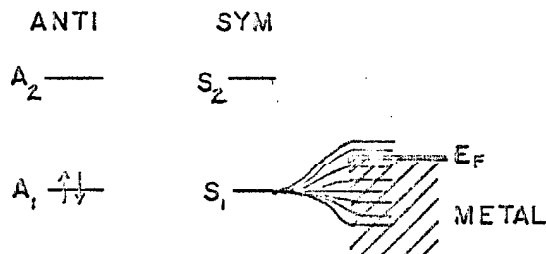
The coupling between conduction electrons and localized states should be very strong because both have finite amplitudes on the carbon atoms of the molecule, giving rise to one-center terms in any matrix element between them. A rough numerical calculation by McConnell indicates that a T_c of the order of room temperature might occur when the volume fraction of such a molecule is roughly 9-10%.

It is obvious that a real situation will probably not be so simple--localized antisymmetric orbitals with infinitely sharp energies. Perhaps more important, the mechanism is critically dependent on the relation of the molecular energy levels to E_F. The states important to superconductivity lie within several kT_c of the Fermi level. If the band of conduction states to which S_1 conjugates does not approach this closely to E_F, this mechanism cannot operate. Then, redrawing part of the above energy diagram,
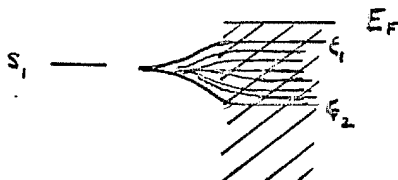
conductive conjugation, to be effective, requires approximately
that $E_F-\epsilon_1 \lesssim 4kT_c$, and will work best if S_1 is nearly degenerate
with the Fermi level.

It should be pointed out that under this condition, the
density of states, $N(0)$, is increased by the addition of states
near the Fermi level. This will increase T_c through equation 18
independently of any virtual electron-coupling. On the other
hand, if $E_F-\epsilon_1 \gg 4Tc$ and if S_z is far above the Fermi level,
then considerations by M. H. Cohen, in a paper to be discussed
again below (42), suggest that a large increase in the density
of states can arise below the d-band of a transition metal, and
that this can be accompanied by a decrease of the density of states
at the Fermi level. Under these conditions, mixing of molecular
orbitals with conduction band states might cause a decrease of
T_c.

The mechanism of virtual electronic coupling has been dis-
cussed in detail as part of a proposal, made by W. A. Little (32),
which has excited the imagination of much of the scientific com-
munity. His idea is relatively simple. He considers a linear
conjugated polyene with alternating single and double bonds.
Attached to this spine are regularly spaced, highly polarizable
side-chains with a low-lying excited level of excitation energy
hw. The spine electrons are considered to be nearly free. The
side-chain electrons are tightly bound, since they are not conju-
gated to the spine, nor to one another. Little derives an inter-
action between spine and side-chain in which a spine electron is

scattered, either creating or absorbing an electronic excitation (exciton) in the side-chain system. The operators for side-chain excitations appear in the same manner as do phonon operators in the first order interaction between electrons and the lattice. Terms linear in the exciton operators can then be eliminated by the same type of Fröhlich canonical transformation, leading to an interaction between electrons of the spine. If the matrix element for this interaction is taken to be an average constant, as in the phonon case, we arrive at an attractive interaction with matrix element

$$-V_e = - \frac{2\langle V(\hat{Q})^2\rangle}{\hbar\omega_e} \quad ; \quad |\epsilon_k|, |\epsilon_{k+q}| < \hbar\omega \qquad (26)$$

where $V(Q)$ is the interaction between spine and side-chain corresponding to D_q for phonons. This attractive interaction is caused by the fact that one electron moving near the side chain polarizes it in such a way that a considerable positive charge is induced near the spine. This induced charge is experienced by a second electron as an attraction for the first. Quantum mechanically, the interaction is caused by a virtual exchange of excitons.

If this term dominates the screened coulomb interaction, then within the framework of the BCS theory, the model is predicted to exhibit superconductivity, with T_c given by

$$k_B T_c = 1.14 \, \hbar\omega_e \, e^{-\frac{1}{N(0) V_e}}$$

The excitement over Little's proposal is largely due to the result of a numerical calculation on a particular model. He finds that the attractive interaction does dominate, and that the polymer might have a transition temperature as high as 2,200 K! This large transition temperature results as does McConnell's because the pre-exponential factor, $\hbar w$, in equation 18 is no longer $\sim 10^{2 \circ} K$, but is a molecular excitation energy $\frac{\hbar we}{k_B} \sim 10^{4 \circ} K$. Or, more glibly, we have replaced a lattice oscillator by an electronic oscillator. The isotope effect for a phonon-coupled superconductor gives $T_c \sim M^{-1/2}$, where M is the isotopic nuclear mass. Then, for an electron-coupled superconductor, T_c should be higher by about the ratio $\sqrt{M/m} \sim 300$, where m is the electronic mass.

One reaction to Little's proposal has been the appearance of several papers utilizing variants of it (43). Another reaction has been the appearance of papers criticizing his results. A fundamental objection has been raised as to the possibility of superconductivity in one dimension (44). This we will not discuss, for our experiments are concerned with the possible occurrence of the electronic coupling mechanism in a three dimensional system. Objections have been raised, however, which do concern us, for they question the very possibility of utilizing an electron-coupled interaction and are therefore often equally applicable to our system as to Little's.

Keldysh (28) points out that Little's estimates of V are based on perturbation theory, but that the energy of interaction

between spine electron and polarized side-chain is much greater

than the excitation energy of the side-chain excited level.

> It is quite clear that this circumstance should lead to
> a considerable shift of those levels, and to a cardinal
> realignment of the side chain, and perhaps of the entire
> molecule as a whole. Therefore, Little's calculations
> show that the molecular model proposed by him is apparently
> unstable and should rearrange itself spontaneously into
> some other state. It is not at all obvious here that this
> new state will be superconducting, and not dielectric. (28)

Merrifield (45) believes that, for a one-dimensional system, the

new state may be semiconducting and ferroelectric, rather than .

superconducting.

A second objection, raised by Paulus (46), is concerned

with the use of a screened coulomb repulsion between conduction

electrons when one is considering an electron-coupled interaction.

Since the virtual electronic oscillator excited by the first

electron has a much shorter lifetime than would a lattice oscil-

lator, the second electron must "follow" the first more closely.

If it must be closer than approximately a screening length, use

of the full coulomb interaction is claimed to be necessary. This

question is of crucial importance, for the assumptions about

screening completely determine the sign of the total interaction;

a screened repulsion can be dominated by the attractive inter-

action, an unscreened repulsion cannot. Unfortunately, Paulus

makes little effort to justify his assumption that the inclusion

of screening is not appropriate.

The nature of the problem can perhaps be clarified as

follows. A virtual excitation of a level with energy $\hbar w$ must

occur for a time $\tau \lesssim \frac{1}{\omega}$. For a lattice oscillator, $\hbar w_L \sim 10^{-2}$ eV

and $\tau_L \lesssim 10^{-13}$ seconds; for an electronic oscillator, $\hbar w_e \sim 2$eV

and $\tau_e \lesssim 10^{-15}$ seconds. Now an electron at the Fermi level moves

with a velocity v_F, where $E_F = \frac{v_F^2}{2 m^*}$. If $E_F = 5$eV, and the free

electron mass is used, then $v_F \sim 10^7$ cm/sec. Therefore, an

electron can move roughly a distance $d_F = v_F \tau$ in the lifetime

of a virtual excitation. For a lattice oscillator, $d_L \sim 10^{-6}$

cm. which is much greater than the screening length. However,

for an electronic oscillator, $d_e \sim 10^{-8}$ cm., which is greater

than, but of the same order as a screening length. Thus, if

these considerations are appropriate, it would seem that the

question of screening in this case lies in the difficult inter-

mediate region in which only a careful analysis can decide the

proper interaction, and in which individual cases must be con-

sidered. Aluminum, indium and tin all have $v_F \sim 10^8$ cm/sec;

Nb_3Sn, Nb_3Ga, with large effective masses, have $v_F \sim 10^6$ cm/sec.

It should be remembered, however, that Garland's work (25) using

a _self-consistent_ treatment of the frequency dependent dielectric

constant, indicated that in transition metals an attractive inter-

action in one group of electrons _could_ be caused by a second

group.

Perhaps an even stronger indication of the subtleties

involved in attempting to invent new superconductive mechanisms

is seen in a paper by Morrel Cohen (42), considering the four

combinations of transition metals and simple metals as solute

and solvent in dilute alloy systems. For the case of a transition

metal dissolved in a simple metal, he considers a solute atom
with two levels, excitation energy $h\nu$, and allows the conduction
electrons to interact with the solute. Since the only solute
property of importance is the fact that it has two levels, the
situation is identical to that proposed by us for molecules in
metals, and is very similar to that in Little's polymer. A
straightforward treatment of the conduction electron-impurity
interaction would lead to an attractive interaction between the
conduction electrons (47).

However, Cohen, treating the impurity interaction as a
perturbation on the metal states obtains <u>two</u> new interaction
terms. One term is an antishielding of the coulomb interaction,
as expected. Taking an average constant, as before,

$$\Delta V_c \sim -\frac{C_D C}{h\nu} V_c < 0$$

where C_D is the impurity concentration, and C an "uninteresting"
(sic) constant. But the second term is an antishielding of the
attractive phonon interaction, giving rise to a repulsion:

$$\Delta V_{ph} \sim -2\frac{C_D C'}{h\nu} V_{ph} > 0$$

Since $/V_{ph}/ > /V_c/$ for an ordinary superconductor, and since
Cohen claims that $C \sim C'$, the new repulsive term is stronger
than the new attractive term. The result is a decrease in the
net attractive interaction and a lowering of T_c.

This second, and dominating term is absent in all other
treatments of similar models. It will not arise if both electron-

phonon and electron-impurity (or electron-exciton) interactions are treated equally as first order interactions and are straight-forwardly eliminated by a canonical transformation. It apparently arises when the phonon interaction is treated first, and then the impurity is used to modify the resulting interaction. Once again, this seems to be a situation where the particular system must be considered; the order in which interactions are to be treated can only be justified by very careful, and probably very complex, analyses.

In summary, several plausible mechanisms have been described for producing an attractive interaction between electrons, but their theoretical justifications have been questioned. The situation is resolvable either by more detailed calculations, or by successful experiments. It is hoped that the experiments that we will describe offer some pertinent data for such a resolution.

III. EXPERIMENTS

Preliminaries

Our experimental goal, motivated by a consideration of the various mechanisms which have been discussed, is the preparation of a material in which a metal is coupled to a finite concentration of molecules of an appropriate type. If this can be done in such a way that the metallic state is not destroyed by the molecules, while the molecules retain their individual identity, the material is expected to exhibit interesting properties, both in the superconducting, and presumably also in the normal state.

An ideal method for preparing such a material would be vapor codeposition of a metal and of a small concentration of alloying molecules. This is quite analogous to the matrix isolation techniques of preparing molecules in rare gas solids (48); in the present case, the matrix would be the chosen metal. This procedure, however, involves too many parameters whose importance cannot be weighed in advance. The exact molecular properties which are desirable, and those molecules which best embody them, cannot be unambiguously predicted. The concentration range of interest must be exceedingly narrow; for instance, there must certainly be some concentration of molecules, beyond which the metallic character of the matrix will be lost. The possibility of molecular decomposition during deposition must be considered. In addition, there are all the other factors mentioned at the

beginning of Section II which can affect T_c, possibly masking the presence of a new mechanism.

For the first exploratory experiments designed to measure the effects of organic molecules on the superconductivity of metals, we chose a less ambitious, but workable technique. From adsorption and catalysis studies it is known that strong electronic interactions, strong bonds, can occur between molecules and clean metal surfaces (49). We therefore decided to study thin films of metallic superconductors and to look for changes. in superconductive properties produced by the deposition of selected chemicals on clean film surfaces. For our films, $<$ 100 Å thick, the number of molecules per metal atom can be appreciable. For these films the coherence length of a Cooper pair in the transverse direction should essentially equal the film thickness, and therefore there should be a good opportunity for "volume" superconducting electrons to interact effectively with strongly bound surface molecules.

What we actually measure is the dc-critical current of a film as a function of temperature, both before and after deposition of the chosen chemical. The critical current is taken to be that required to restore a small, fixed, resistance to a superconducting film (50). This is not an ideal measurement for two reasons. Since the value of the resistance restored is very low, we are essentially looking at the very first portions of the film to be driven normal. This initial resistance will generally arise at flaws, unusually thin areas, or edges--the poorest portions of the film (51).

Second, current-induced transitions are plagued by the joule-heating which begins when resistance develops (52). Newhouse (53) has shown that if a film element goes normal at relatively high currents, the joule heat generated can exceed a critical value and can drive adjacent areas normal, an effect which can propagate as a thermal wave through the film. Such a process can start outside of the film area being studied--perhaps at the contact areas, which may be contaminated by the contact material.

However, these problems can at least be minimized. The effect of the edges is probably reduced because the films are thin enough, and the temperature close enough to T_c, that the current is nearly uniformly distributed, instead of being concentrated near the edges as would be the case with thick films and temperatures much less than T_c (54). There is no escaping the problem of flaws. However, by choosing always to restore a given resistance, we are presumably always driving the same element of film normal (50). As shown in section III (Results), the changes in T_c produced by a deposited chemical are independent of the value of restored resistance as this value is varied by more than a factor of ten; this means that the effect of the chemical is the same over at least some small region of the film, and not merely at one flaw.

Choosing a small value of restored resistance also minimizes the problem of thermal propagation. Resistance first appears at a flaw, thin region, or distribution of such. As long as the

power generated, I^2R, is too small to cause a thermal wave, these regions will act independently of one another and the transition is called "isothermal." That is, the joule heating of a region already gone normal cannot raise the temperature of other regions, which will remain at the bath temperature T_o and exhibit critical currents characteristic of that temperature, $I_c(T_o)$. Since we typically work with a restored resistance $\sim 5 \times 10^{-3}\Omega$, and with critical currents $\lesssim 10$ ma., the power generated, $\sim 5\mu W$ is indeed small.

The use of the geometry recommended by Newhouse (53), in which the contact areas are much wider than the film strip being studied, eliminates the possibility of a thermal wave originating outside of the strip. Since the critical current increases with

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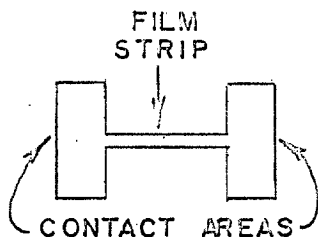
CONTACT AREAS

film width (53), the strip will become resistive while the wider areas remain superconducting. This ensures that contaminated regions at the contacts do not affect the measurements.

For our experiments, the apparatus shown in Fig. 1 was constructed. It is essentially the union of an all-metal liquid helium dewar with an all-metal ultra-high vacuum (UHV) evaporation chamber; a detailed description is given in the next section. Ultra-high vacuum techniques are absolutely essential for experiments which are meant to study clean surfaces. Kinetic theory
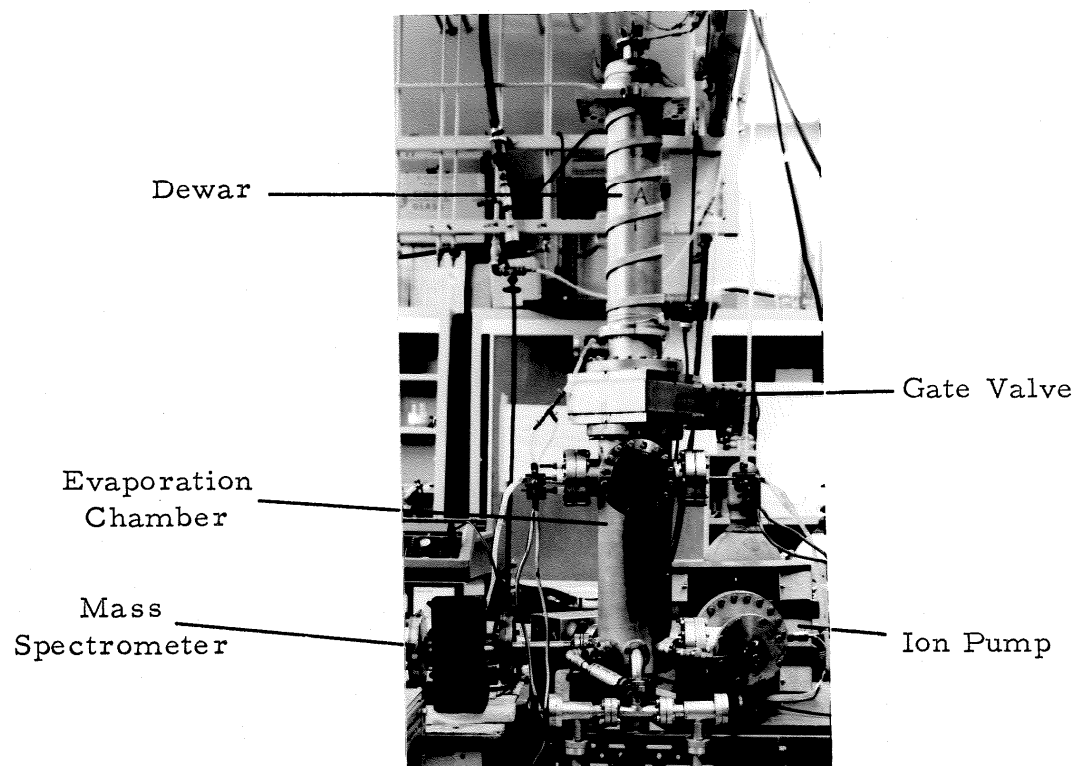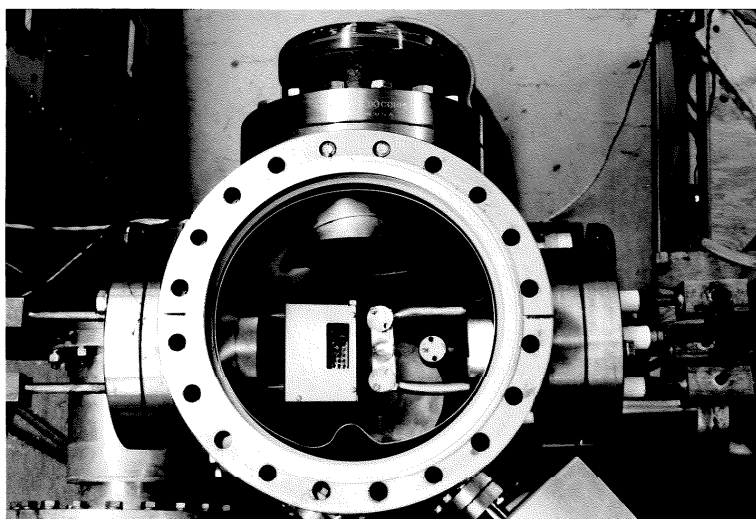
Fig. 1. Experimental Apparatus

Fig. 2. Looking into evaporation chamber
with evaporation sources in place

calculations predict, and surface experiments verify, that at
$\sim 10^{-6}$ torr. a surface becomes covered with a monolayer of
adsorbed gases in a matter of seconds (55). Since this time is
inversely proportional to the effective pressure, it is obvious
that the vacuum at a freshly deposited film must be $\sim 10^{-9}$ torr.
or better in order to permit critical current measurements to
be performed and a desired chemical deposited before surface
contamination can occur.

It is unfortunately true, that the very nature of the
experiment performed increases the difficulty of obtaining ade-
quately low pressures. First, into a vacuum system carefully
designed to eliminate all gassy structural materials, we must
introduce an organic compound which by UHV standards has an
enormous vapor pressure; anthracene has a vapor pressure of .1 μ
at 35°C (56). Moreover, the compound is usually a powder, with
a large surface area for gas adsorption.

A second difficulty is a limitation on bakeout temperatures.
It is standard UHV procedure to bake a system under vacuum to
250°C, if the elastomer Viton-A is present, and to $\sim 350°C$ or
more if the system is entirely metal (57). This is done to desorb
gases from the walls, since the slow desorption of these gases
would constitute the primary gas source in an unbaked system. We
are limited to $\sim 100°C$ for the system as a whole because of the
necessity of using indium cryogenic vacuum seals in the dewar
assembly. Indium melts at 156°C, and at somewhat lower tempera-
tures softens to the point that a seal can be ruptured by atmos-
pheric pressure.

Despite these obstacles, UHV can be obtained. In our experiments, metal films are evaporated in UHV onto a substrate in direct contact with liquid helium. Critical currents can be determined without exposing the film surface to contamination. An appropriate chemical can then be deposited, and the properties of metal film plus chemical overlayer can be directly compared to those of the film itself. This differential measurement of the effects of a chemical on a given film allows the reliable detection of effects much smaller than possible variations between films (58).

Description of Apparatus

The liquid helium dewar was designed by A. Kwiram and is described in his thesis (59). The primary responsibility for the design of the evaporation and substrate systems belonged to D. D. Thomas; because of this, and because apparatus not vastly different from ours is commercially available (60), an attempt will be made to discuss mainly those details of construction which are either unique to our apparatus or critical to our particular experiments.

A. General Description of Vacuum System (see Fig. 1)

The evaporation chamber made by the Ultek Corporation, is an upright stainless steel cylinder, 6" in diameter and 20" tall, with ports for admitting the various vacuum components. All static seals to the chamber are obtained by compressing annealed copper o-rings between stainless steel flanges. Around the bottom is a ring of ports of various sizes to which are connected fore pumps, ion pump, thermocouple gauge, ionization gauge, mass spectrometer, and up-to-atmosphere (UTA) valve. At other times the feedthroughs for a copper liquid nitrogen (LN) coil (Meissner trap) were attached here. A titanium sublimation pump is admitted through a port at the bottom of the chamber.

About two-thirds of the way up are three additional ports. Two opposed 3" ports admit the vacuum evaporators, one for the experimental film and one for the chosen organic compound. A

Pyrex window is sealed to the third, 4" port. Figure 2 is a view

into the chamber showing the evaporators in place and the port.

The chamber is capped by a 6" gate valve. Atop the gate

valve, a reducing collar mates to the liquid helium dewar. A

Viton o-ring is used because the dewar was originally designed

with elastomer seals for EPR experiments. In addition, Viton

o-rings are used with blank-off flanges on the ports through which

the dewar had originally been evacuated. Compressed indium seals

are used for the liquid helium temperature and UHV seals in the

substrate assembly at the bottom of the helium well. When the

gate valve is open, the vacuum chambers of the dewar are continu-

ous with the evaporation chamber. If desired, the mass spectrome-

ter tube can also be mounted on a port in the reducing collar,

bringing it closer to the film surface.

The helium dewar was modified for this study by a brass

substrate holder (SH) which bolts to the open bottom of the

liquid helium well. The vacuum seal is made with compressed

indium. A quartz substrate is sealed to the SH, forming the

bottom of the helium well. The seal is again compressed indium.

A brass compression flange ("presser-downer", PD) supplies the

necessary pressure. An 0.005" stainless steel evaporation mask,

cut to the desired form shape, fits onto the PD and masks the

substrate. Over the stainless steel mask is an appropriately cut

1/10" copper plate. Because of the thermal conductivity of copper,

the mask acts as a helium temperature heat shield. Another helium

temperature heat shield is bolted to the periphery of the substrate

holder. A liquid nitrogen heat shield is bolted to the bottom of
the LN well.

The substrate assembly is shown in cross-section in Fig. 3.
The heat shields, PD, and substrate holder are shown in Fig. 4.
The mask and a substrate with an evaporated film are shown in
Fig. 5.

B. Pumps

(a) Fore pumps.--The roughing system consists of two Ultek
sorption pumps filled with Linde #5X molecular sieves. The pumps
open to their common, 1", tube into the chamber through separate
Ultek model #40-131 1" right-angle vacuum valves. When cooled
by LN they can rapidly reduce the system pressure to less than
one micron Hg. The pumps are regenerated by baking them at high
temperatures to drive off adsorbed gases.

The advantage of sorption pumps over mechanical forepumps
is their cleanliness. It is difficult to prevent backstreaming
of pump oil from a mechanical pump. Since our experiments are
designed to detect the effects of organic chemicals on clean film
surfaces, the introduction of appreciable amounts of pump oil
into the system would be intolerable.

The chief disadvantage of sorption pumps is their finite
capacity. If the system is pumped down more than once without
the sorption pumps having been warmed, they can reach saturation
and adequate roughing pressures can no longer be obtained. This
is particularly likely if the pumps have pumped on a leak during
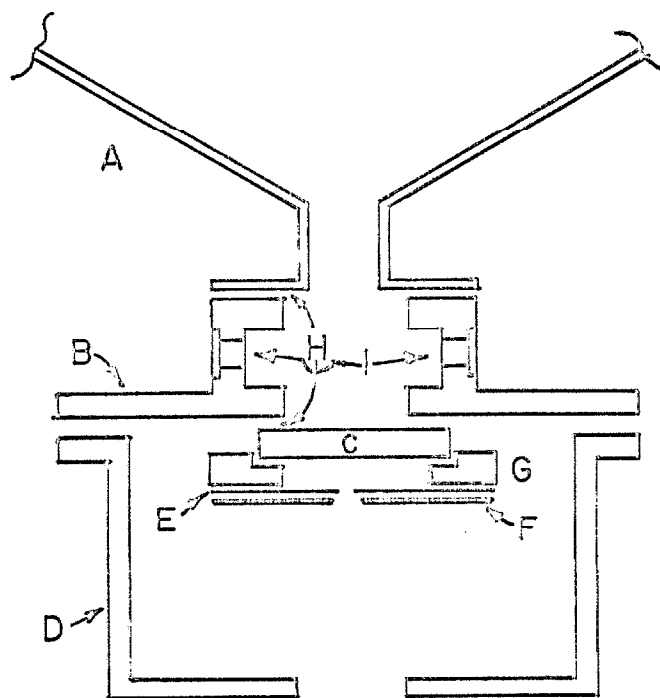
Fig. 3. Schematic Cross-Section of Substrate Assembly (approximately actual size). (A) Dewar helium well; (B) Substrate holder; (C) Substrate; (D) Heat shield; (E) Evaporation Mask; (F) Copper Over-mask; (G) Compression Flange; (H) Indium cryogenic vacuum seals; (I) Feed-through wells.

Fig. 4. Back, left: helium heat shield; right: LN heat shield
Front, left: substrate holder; right: compression flange

Fig. 5. Evaporation mask and substrate with evaporated film

the first pump-down. Such a failure of the sorption pumps necess-
itates either an appreciable delay while they are baked out, or
else the "exasperation" method of attaching a mechanical forepump
through the UTA valve.

(b) The primary pump is a Ultek 100L/S titanium getter-ion
pump. It is connected to the evaporation chamber by an Ultek 3"
right angle vacuum valve (#40-311). The principles and advantages
of ion pumping are explained elsewhere (57) and will not be
repeated here.

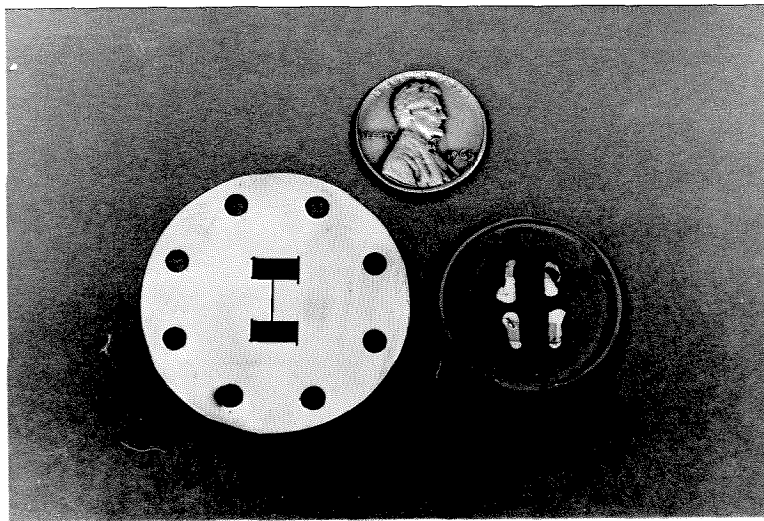An important disadvantage for the present application is
that the getter-ion pump can be contaminated by high molecular
weight organic vapors such as benzene, toluene and any of the
organic compounds with which we have experimented (57). The
cathodes build up a carbonaceous deposit which is difficult to
sputter. These areas do not pump efficiently and therefore, the
pumping speed is decreased. Such contamination has required that
the ion pump be chemically cleaned three times in a year and a
half. The principal problem seems to be that occasionally some
of the experimental compound sublimes during bakeouts and ends
up in the pump. However, the high vapor pressures of these com-
pounds means that they must be continuously evolving small amounts
of vapor which enter the pump, causing eventual contamination.

The contamination problem, incidentally, cancels one apparent
advantage of ion-pumps. In principle, the pump current should be
a measure of the pressure; the ion pump itself should therefore
eliminate the necessity of an ionization gauge. However, an ion

pump has some leakage current which is independent of pressure and which creates a low-pressure limit (usually $\sim 10^{-9}$ torr.) to the pump's usefulness as a gauge. Contamination can increase the leakage current to such an extent that despite a true system pressure of $< 10^{-9}$ torr, the pump will indicate as high at 10^{-7} torr, thus making an independent pressure measurement essential.

Another disadvantage of ion pumps is the reluctance to pump large quantities of gas. This is important during initial pump-down and during pressure surges in the course of a metal-film evaporation.

(c) The system also contains a titanium sublimation pump (TSP), consisting of a filament holder containing four titanium filaments. A stainless steel shield is mounted atop the holder to prevent titanium from being sublimed onto the vacuum evaporators or substrate. The assembly is admitted through a port in the bottom of the evaporation chamber. Fresh titanium surfaces, thermally sublimed onto the chamber wall from the TSP filaments, pump neutral reactive gases by combining with them to form stable compounds. Such surfaces have pumping speeds of the order of $10^{L}/s/in.^{2}$ at 20°C, and are especially effective in combination with an ion pump (61).

This additional pumping speed is important at relatively high pressures; it greatly decreased pumpdown town from roughing pressure ($\sim 1\ \mu$) to $\sim 10^{-7}$ torr, at which pressure leak testing is done and bake out is begun. The TSP is most important, however, during vanadium evaporation. Often large quantities of gas are

evolved which the ion pump alone cannot handle without momentary, but disastrous increase in system pressure from $\sim 5 \times 10^{-10}$ torr. to $\sim 10^{-7}$ torr. The TSP limits the pressure rise to less than 3×10^{-8} torr. and decreases the time during which it obtains.

Unfortunately, the design of the evaporation chamber limits the efficiency of the TSP. It is narrow, and as a consequence, the walls get quite hot during titanium sublimation. The pumping efficiency of a titanium film decreases with increasing temperature. One solution to this problem is cooling coils brazed to the chamber's exterior. This was not done in construction, and is not feasible now that the flanges are attached.

An even more efficient solution is to sublime the titanium onto a LN coil (Meissner trap), combining titanium gettering with LN cryopumping. However, the narrow chambers cannot fit both the TSP and Meissner trap. We had in fact installed a Meissner trap prior to the addition of the TSP. The LN cryopumping was capable of maintaining acceptably low pressures during evaporations, but the coil was difficult to clean in place, and could not be readily removed because it was difficult to make vacuum-tight connections inside the chamber.

During pumpdown, the reduced efficiency of the TSP is accepted; the only countermeasure taken is a small fan. During an actual experiment, maintenance of the ultimate pressure is critical. Therefore the evaporation chamber is surrounded by a styrofoam jacket filled with dry ice.

C. Pressure Measurement

(a) Roughing pressures are measured by an NRC thermocouple
gauge and box. This gauge is isolated from the system by closing
a Whitey #1GM4 poppet valve after the pressure is below 1 micron.
The UTA valve is also a Whitey #1GM4 valve.

(b) Pressures below 1 micron are measured by a hot-filament
Bayard-Alpert ionization gauge (Ultek model #60-722). The tube
has a glass envelope and is externally mounted on a 1 1/2" flange
by a tube 2" x 3/4". Because of the relatively low conductance
of this tube, it is likely that at indicated gauge pressures of
$\sim 5 \times 10^{-10}$ torr. or better, the gauge tube may have the highest
pressure in the system. As a result, pressures are generally
quoted without a gauge correction which is in principle calculable
using the mass spectrometer, and was estimated to be ~ 1.4 on one
occasion.

(c) An Associated Electronics Industries model MS-10 mass
spectrometer is also incorporated in the vacuum system. This is
an 180° magnetic deflection instrument. It has m/e ranges of 2,
3, 4, 12-45 and 18-100 using an 0.020" slit. With this slit we
can easily resolve peaks one mass unit apart below m/e $\sim$ 80; the
stated detection limits are 6×10^{-12} torr. for N_2 and $\sim 10^{-11}$
torr. for O_2. The stainless steel (SS) analyzer tube is con-
nected to the evaporation chamber by an SS tube 6" x 1".

The mass spectrometer was added to the system after we dis-
covered that oxygen deposited on the surface of a vanadium film
can increase its T_c (see section III, Results, A). Without knowing

the composition of the gases released during a chemical deposition, it is not possible to unambiguously attribute an effect to the selected chemical, and not to some other evolved gas.

We found that in general, hydrogen was the gas responsible for most of the pressure increase during evaporation of the chemical overlayer. Hydrogen has been seen to be the principle gas during experiments in which T_c was increased, and also in others during which it was decreased. The hydrogen presumably is dissolved by the tantalum boat which holds the chemical, and is released by heating.

The influence of oxygen can safely be discounted since its partial pressure during a chemical evaporation may only rise from $\sim 10^{-11}$ torr. to $< 5 \times 10^{-10}$ torr., while the system pressure is increasing from $\sim 5 \times 10^{-10}$ torr. to $\sim 3 \times 10^{-9}$ torr., due to the release of hydrogen. Other gases, such as CO_2 ($m/e = 44$) and N_2 or CO (both $m/e = 28$), have been monitored during organic chemical evaporations, and have only displayed small variations.

Hydrogen is also the principal gas released during vanadium evaporations and during titanium sublimation from TSP.

The mass spectrometer performs two other valuable functions. First, by giving the residual gas spectrum it serves as an indicator of general system cleanliness. In particular, the dewar had originally been used for EPR experiments in a diffusion-pumped system and was found to be contaminated, as indicated by the presence of high mass peaks ($m/e > 45$). After chemical cleaning of the dewar and successive experiments involving cleaning of the

evaporation chamber plus overall system bakeouts, peaks of m/e
> 45 almost completely disappeared. The cleanliness of the system
is indicated by the fact that, often, most of the residual gas is
water, carbon monoxide and carbon dioxide--the vapors evolved by
Viton A (62). In one, rather clean, experiment these three gases
comprised $\sim$ 82% of the residual gases; hydrogen, argon and helium
comprised $\sim$ 9%. Methane, which is synthesized in the ion pump
from water and carbon dioxide, made up most of the remainder.

Second, and of supreme practical importance, is the ability
of the mass spectrometer to function as a leak detector. Ion
pumps are extremely efficient at removing reactive gases. There-
fore, at low pressures with no leaks there is almost no peak at
m/e = 32 (oxygen). The presence of an appreciable peak at this
mass is therefore characteristic of a leak. By the use of the
mass spectrometer and a probe gas (usually helium), it has been
possible to pinpoint, and occasionally correct, leaks at pressures
as low as $\sim 2 \times 10^{-9}$ torr.

D. Vacuum Evaporation System

(a) Evaporation sources.--Helical tungsten coils are used
as vanadium evaporation sources. Since vanadium alloys with
tungsten, the coils eventually fail. We could not reliably
evaporate vanadium from even the thickest commercially available
sources, made from 3 x .030" braided tungsten wire (R. D. Mathis,
#B1-3x0.030W), and several experiments were ruined because of
such coil failures.

Home-made coils were therefore wound to approximately the same dimensions, from 4 x 0.30" W. No experiment has failed (completely) because of a failure of such a coil. Nevertheless, a second coil is often mounted on the metal evaporator, as insurance.

Indium and tin are evaporated from tungsten or molybdenum dimple boats (Mathis, ME 4, .005" W or Mo).

The chemical overlayer is evaporated from a covered tantalum boat (Mathis, #ME-2, cover #ME-2B). The boat is two to three times as wide as the metal source to ensure that the metal film can still be completely covered, despite minor misalignments of the two sources.

(b) <u>Source supports</u>.--Separate flanges, each with water-cooled OFHC copper supports brazed to the hollow metal-ceramic vacuum electrical feed-throughs (Ceramaseal Corporation #804B2779-2) mounted on them, carry the two evaporation sources. Figure 6 shows the two flanges with sources in place. Water-cooling the mount for the metal source is important because of the high temperatures ($\sim 2000°C$) necessary to evaporate vanadium. Three supports are presently mounted on this flange, capable of mounting three metal sources.

The flange for the organic chemical evaporator mounts only one source. This source has been completely enclosed by copper heat shields, apart from a 1" x 1/2" hole for evaporation. The water cooling and the heat shields are necessary to prevent the source from being heated during bakeouts or metal evaporations;
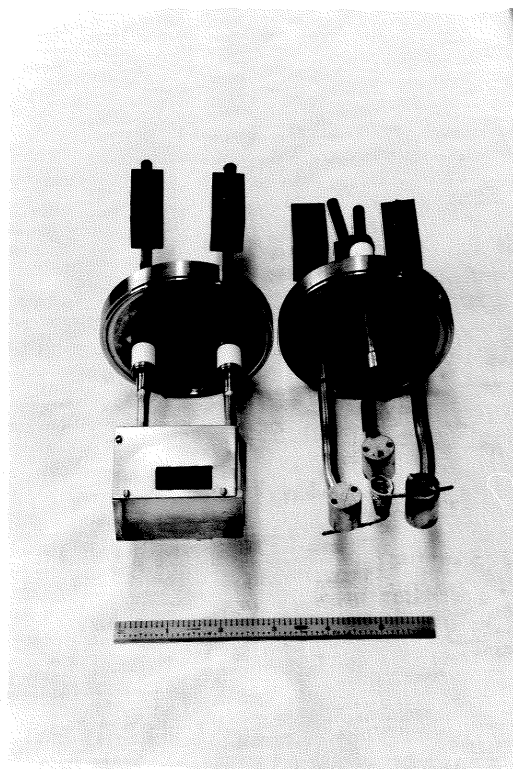
Fig. 6. Vacuum Evaporators. Left, organic
chemical; right, metal evaporator

such heating can cause the chemical to sublime prematurely, contaminating the system.

Because the problem of contamination during bakeouts was not anticipated, the present organic evaporator was originally used for the metal source; the original organic evaporator was not water-cooled, but merely had solid supports. The change was effected because cooling the organic evaporator flange during bakeouts by a stream of air proved marginally effective, at best. At worst, it once proved disastrous when the fan burned out, the organic source heated up and the entire system was contaminated by chloranil, the chemical in the boat.

(c) Current source.--The currents necessary for the resistance-heated sources come from a 120 volt line, using a step-down transformer controlled by Variacs. The source for the metal evaporator is a 115/11 volt transformer and a 10 amp. Variac. That for the organic evaporator is a 115/5 volt transformer and 5 amp. Variac.

E. Chemicals

Vanadium used in early experiments (Table I, #5; II, #1; III) was nominally 99.8% pure. Spectroscopic analysis revealed the following impurities: Cu, 1 ppm; Cr, 47 ppm; Fe, 344 ppm; Mg, 25 ppm; Mn, 178 ppm; Si, 1400 ppm. All other vanadium experiments were done with zone refined, nominally 99.999% pure vanadium from Research Inorganic Chemicals. Spectroscopic analysis could detect no impurities. Film properties for the two purities are essentially the same.

The _indium_ experiments were done with nominally 99.999%
pure metal. Spectroscopic analysis revealed less than 5 ppm
copper.

The _organic compounds_ used were either zone refined (anthra-
cene) or recrystallized and then sublimed, usually two or more
times. Paramagnetic impurities were not always removed by this
procedure. They were sometimes found in very low concentration,
but in both "enhancers," molecules which increased T_c, and
"depressors," those which decreased it.

In the experiment involving the deposition of _oxygen_, the
oxygen was generated in the vacuum chamber by the thermal decom-
position of silver oxide.

F. Substrate Assembly

(a) A cross-section of the substrate assembly has been
shown in Figure 3, and the various components pictured in Figures
4 and 5. The substrate holder is machined from brass, and the
only critical feature is the mounting of the vacuum electrical
feed-throughs, to be discussed below. The PD is also machined
from brass.

The two heat shields are machined OFHC copper cans. They
prevent room temperature radiation from reaching the film, except
in the small solid angle through which the chemicals are evapo-
rated. The small aperture in the heat shields should serve an
additional function. Since the standard kinetic theory calcula-
tion for the number of molecules striking a plane surface involves

integrations over the full solid angle of 2π at the surface, at any given system pressure the shields should reduce the rate of surface contamination by a factor of 5 or 10.

(b) <u>Masks</u>.--The geometry of evaporated films is determined by the pattern cut in a 0.005" stainless steel mask, located 1/8" from the substrate. Two different four-point probe geometries have been used. The initial pattern
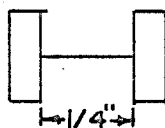
$\vdash$1/4"$\dashv$
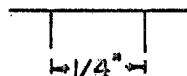
was soon changed to the "H" pattern recommended by Newhouse (53):

$\vdash$1/4"$\dashv$

The defining slit width has been 0.010" and 0.006".

(c) <u>Substrates</u> are optically flat, y-axis cut single-crystal quartz disks, 1" in diameter x 1/8" thick, from Valpey Corporation. At helium temperatures, single crystal quartz has a thermal conductivity in the y direction slightly greater than that of copper (63). This makes it the best available substrate material, since thermal gradients across the substrate must be minimized.

(d) <u>Film leads</u>.--In order to make electrical contact to a film, four islands of electrically conducting paint are put onto the substrate before it is mounted on the SH. Silver paint is spread with a thin metal wire, and care is taken to make the edges toward the film very thin and smooth. Although the paint

is initially air-dried, it then sits in vacuum for a minimum of four days in the evaporation system. This includes ~ 48 hours of being vacuum baked to ~ 90°C during the system bakeout.

Superconducting Pb contacts have also been used. These are precvaporated onto a clean quartz dish at ~ 10^{-5} torr. in a separate evaporation chamber. They are defined by an 0.005" stainless steel mask held flush with the quartz surface. This prevents lead atoms from "bouncing" onto the area to be used for the experimental film.

Although there have been literature reports that silver paint contacts can contaminate evaporated metal films (64), we have found that the lead contacts produced no significant differences. This probably results from the fact that the portion of a film whose properties are being studied is quite far removed from the contacts. The vacuum bakeout may also contribute significantly to the benign behavior of our silver paint contacts.

Connections to the silver paint contact islands are made using #40 nyclad copper wire stripped of its insulation by Strip-X and tinned with In-Sn solder. The wires are soldered to four binding posts of thicker wire epoxied (Resinweld) into radial holes in the PD. They are attached to the contacts by "gluing" them down with drops of the same silver paint used for the contacts. No experimental failures have ever been traced to a wire pulling away from its contact.

Wires from the binding posts of the PD are soldered to four heavy wires epoxied to the substrate holder. From these binding

posts, wires are soldered to the four glass-metal vacuum electrical feedthroughs (Glass Instruments Inc. #1207) mounted in the substrate holder. These carry the electrical leads from the vacuum chamber into the helium well.

Inside the helium well wires from the feedthroughs terminate in a modified transistor socket. Since the helium well is pumped to as low as several torr., the wires from the mating socket go through a simple vacuum seal in the cap.

(e) Cryogenic, vacuum-electrical feedthroughs.--Bringing the electrical leads into the vacuum through the liquid helium prevents them from acting as heat leaks. This procedure is necessary because we assume the film temperature to equal that of the helium bath, although the film is not immersed in helium. Inefficient thermal grounding of the leads could raise the film temperature. Unfortunately, these feedthroughs are probably the most critical vacuum element in the entire apparatus. Repeated thermal cycling between room and helium temperatures can cause them to fail, presumably because of fatiguing due to differential thermal expansion.

However, the previous set of feedthroughs was completely leak-free for many months--many helium transfers and even more cyclings between I and II--before they eventually failed. The replacement has performed similarly well for several experiments, and should last as long. The critical features in mounting these feedthroughs seem to be avoiding thermal shock during the soldering process and keeping solder out of the hole through the SH in

which the feedthrough sits. The latter is made difficult because
of the small clearances dictated by the size of the feedthrough
and the maximum possible size of a transverse hole in the substrate
holder. Capillary action tends to draw liquid solder into the
narrow annulus between feedthrough and well. An attempt is made
to minimize this by counterboring the well for the lip of the
feedthrough.
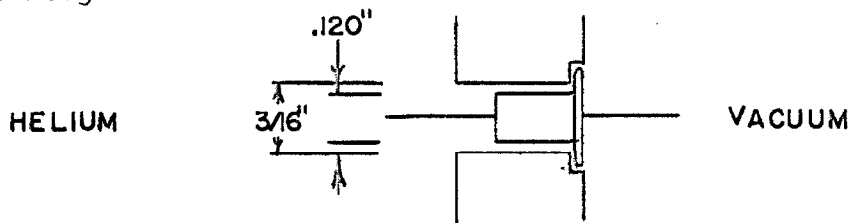
The procedure for soldering the feedthroughs is as follows.
They are placed in their wells in the SH and are held in place
by the tension of a cylindrical brass strip which pressed against
the wire of the feedthrough. This assembly is then placed in an
oven and heated slowly to a temperature above the melting point
of soft solder. It is then removed and placed on a hotplate to
maintain the necessary temperature. A minimal amount of solder
is then applied, using Lloyd's stainless steel soldering flux.
Turning down the hotplate temperature allows the assembly to cool
slowly.

G. Critical Current Measurement

The four leads brought out of the helium well are connected
by a shielded cable to a simple apparatus designed to measure the
voltage drop across two voltage contacts of an "H"-shaped film as

a function of an impressed current supplied through a separate

set of two current contacts. This well-known four-point probe

technique allows the voltage-drop to be measured in a circuit

which carries no current. Thus, contact resistances do not

affect the measurement.

The circuit diagram for the apparatus is given by Figure 7.

The resistance of a film can vary from 0 ohms, when it is super-

conducting, to more than 10,000 ohms, when fully normal; the

source is of moderately high impedance, and can maintain an

approximately constant current as a superconducting film goes

normal. (A rigorously constant current source is not necessary.)

The current through the film is determined by the voltage drop

across a 1 K ohm resistor. This current-measuring voltage is

displayed on the y-axis of a Moseley x-y recorder. The voltage

developed across the film is directly displayed on the x-axis of

the recorder. The maximum instrumental sensitivity, 0.1 mv/inch,

is adequate without prior amplification. Thus, the primary

experimental data are curves displaying the voltage developed

across the film as a function of impressed current. (See Fig. 8.)

H. Liquid Helium Temperature

Helium is transferred with a Supairco transfer tube. Helium

levels in the dewar are determined by three carbon resistors

suspended at different heights in the dewar. We use 300 ohm

Allen-Bradley resistors with the porcelain coat ground off. When

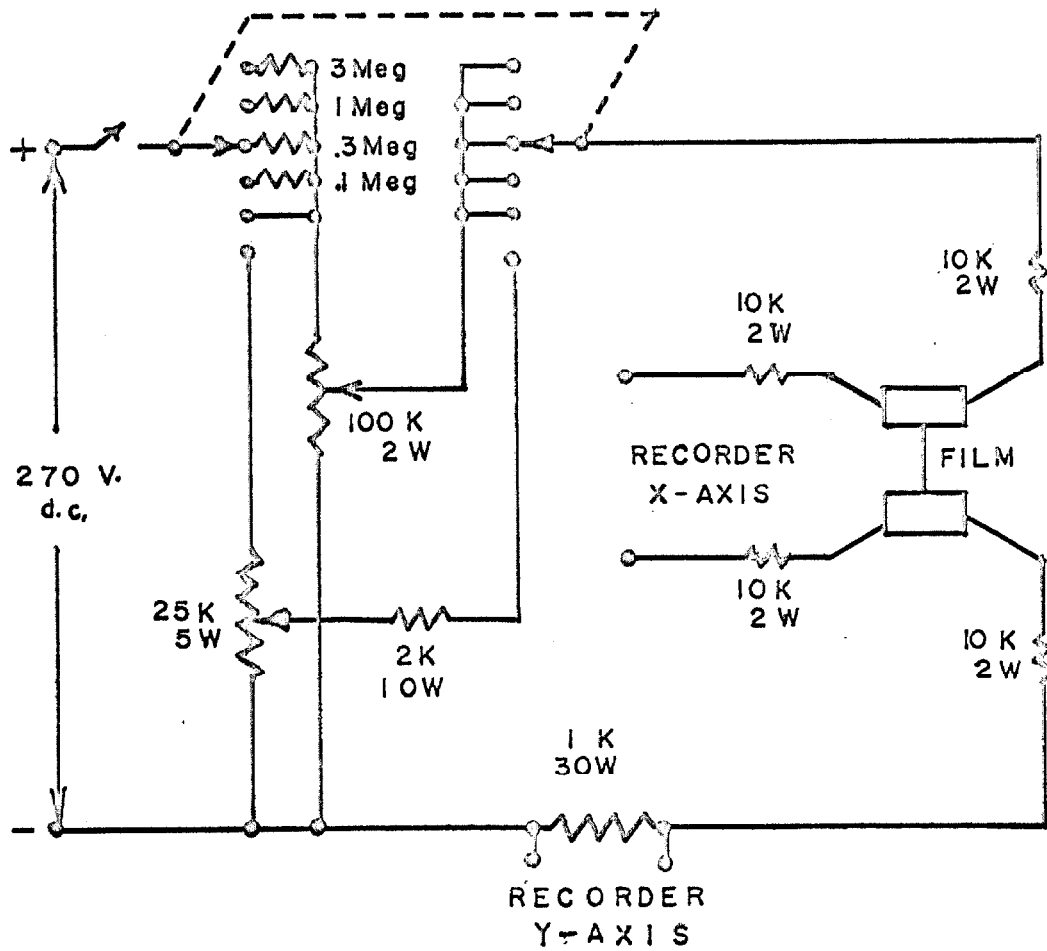~ 9 v is put across such a resistor the current drawn will change

Fig. 7. Critical Current Measuring Circuit

from $\sim$ 8 ma to $\sim$ 4 ma as the liquid helium level rises past it.
Wires to the resistors are simply epoxied into a hole in the
helium well cap.

Temperatures are determined from the vapor pressure of the
pumped helium. The pressures are measured with a precision
manometer via a tube which terminates near the substrate. Except
for the actual measurement of T_c, experiments are usually done
entirely below the λ-point in order to eliminate thermal gradients
in the liquid helium. These precautions are taken to ensure that
the temperature at the helium side of the quartz substrate should
be very close to the temperature derived from the helium vapor
pressure curve. Thermal gradients across the substrate caused
by room temperature radiation should be quite small because of
the high thermal conductivity of the quartz at these temperatures
and because of the shielding provided by one liquid nitrogen and
two liquid helium temperature heat shields. The effectiveness
of this arrangement is demonstrated by the fact that films held
at $\sim$ 1.8°K (indicated), later shown to have transition tempera-
tures only 0.2°K higher, were superconducting during the latter
part of the metal evaporation, while hot metal atoms were striking
the surface, and the source at approximately 2000°K was only ten
inches away.

The helium vapor pressure is regulated by a diaphragm mano-
stat built by A. L. Kwiram (59) with a more flexible diaphragm
installed by D. D. Thomas. This manostat seems to function better
as the vapor pressure is decreased and the helium is more nearly

continuously pumped. Pressure stability is quite acceptable by 350 mm., $\sim 3.5°K$. Below ~ 250 mm. (3.2°K), the pressures can be kept steady to within 0.1 or 0.2 torr., the reading accuracy of the manometer, during a measurement.

Procedure

Our experimental procedure is as follows:

(a) The system is thoroughly cleaned of metal and organic compounds from the previous experiment. The evaporation chamber and gate valve are wiped with methanol-soaked Kimwipes. Deposits which have flaked off the chamber walls are removed with a vacuum cleaner. Copper pieces--evaporators, heat shields and over-mask-- are polished with steel wool and/or dipped in acid. Nitric acid may be used to remove vanadium deposits, but usually hydrochloric acid is used to remove copper oxide. To ensure that no grease, "finger juice," or errant chemical from the previous experiment is returned to the clean system, all components, however cleaned, are given a final methanol rinse.

Because it is tedious and time-consuming to clean the evaporation chamber and gate-valve, removable copper shields have recently been made. They largely protect these areas during depositions, and can be easily cleaned upon removal. Despite the fact that these shields triple the number of surfaces which must be degassed, they still effect a net savings in effort and time, with no apparent sacrifice in ultimate pressure.

The surface of the vanadium chunks used for evaporation is cleaned by etching in dilute nitric acid.

Tungsten coils and "dimple" boats are cleaned either by following the directions in Guthrie's book (57b), or by using sodium peroxide.

The organic source is simply boiled several times in the appropriate solvent to remove the previous chemical.

A dirty quartz substrate is cleaned as follows:

(i)   An organic solvent (usually trichloroethylene) is used to remove most of the dried silver paint and previous organic material.

(ii) Concentrated nitric acid removes the metal films. (Sometimes aqua regia is used and step (i) is eliminated.)

(iii) The above two steps do not generally remove all traces of the previous experiment. The quartz disk is next rubbed gently between clean fingers, using Lava soap as a cleaning agent. Careful studies by electron microscopy and other techniques have verified that this simple procedure is better than such extensive techniques as ultrasonic cleaning etc. (65) (which we couldn't do anyway).

(iv) The disk is next rinsed in tap water and then rinsed in distilled water for several minutes.

(v)   A methanol rinse completes the procedure. The disk is allowed to air dry.

(b)   The evaporation chamber is then reassembled with a new metal source, a new (organic) chemical, and new titanium filaments for the TSP, if necessary. The dewar, with the clean substrate mounted in the substrate assembly, is placed atop the reducing collar, closing the vacuum system.

(c) The system is then evacuated to $\stackrel{<}{\sim} 1$ micron. At this
time the TSP is degassed, as recommended by Ultek (60). The
forepumps are then valved out and the ion pump plus TSP reduce
the pressure to $< 10^{-7}$ torr. A preliminary leak test is then
made, using the mass spectrometer with helium as a probe gas.
It is not unusual at this point to find a flange that has to be
further tightened.

(d) After leaks have been corrected, the system is baked
to $\sim 100°C$. The evaporation chamber is usually heated by infra-
red lamps, although sometimes heating tapes are used; the dewar
is heated by tapes. Infrared lamps are always used for heating
the odd places on which it is impossible to put a tape. The mass
spectrometer and ion pump have their own heaters.

The bakeout is usually continued for about 48 hours, or
until the pressure while hot is $\sim 10^{-6}$ to 10^{-7} torr. During this
time the vanadium is given a preliminary degassing.

(e) The bakeout is stopped and, as the system cools, the
pressure falls to less than a few times 10^{-9} torr.--usually to
$< 6 \times 10^{-10}$ torr. The system is again leak tested to verify that
no leaks have developed during bakeout. At some time during the
final pumpdown, the vanadium and organic chemical are degassed,
and small amounts of both are evaporated. The surface of the
substrate is protected by closing the gate valve.

(f) When a satisfactory base pressure has been achieved,
the liquid nitrogen well of the dewar is filled. This usually
done the evening before an experiment is to be run, to allow the

helium well and substrate assembly to slowly cool overnight. The liquid nitrogen level is maintained by a Harvey Control Co. level controller. The helium well is kept at a small positive pressure of helium gas during this period to prevent the condensation of water vapor or liquid oxygen.

(g) The actual experiment begins with the transfer of liquid helium into the helium well of the dewar. The helium temperature is then usually reduced to ~ 1.8°K, well below the λ-point at 2.17°K. Both metal and organic films are evaporated through the fixed helium temperature mask onto the quartz substrate in direct contact with superfluid helium. Pressures during vanadium evaporations are $< 3 \times 10^{-8}$ torr., during the indium and organic evaporations are $< 3 \times 10^{-9}$ torr. and are generally $< 6 \times 10^{-10}$ torr. at all other times.

Metal is usually evaporated until the film superconducts. However, the existence of an approximate relationship between the resistance of a vanadium film, freshly deposited on a helium surface, and its transition temperature (Fig. 12) allows us to evaporate to a predetermined resistance while holding the temperature somewhat above the expected T_c. The critical current, I_c, is then measured as a function of temperature over some limited range below the λ-point. The critical current at a particular temperature is taken to be that current necessary to restore a certain fixed resistance to the film, generally between 10^{-3} and 10^{-2} ohms. Figure 8 shows a typical current-voltage curve; I_c can be taken as that current which restores any given value of
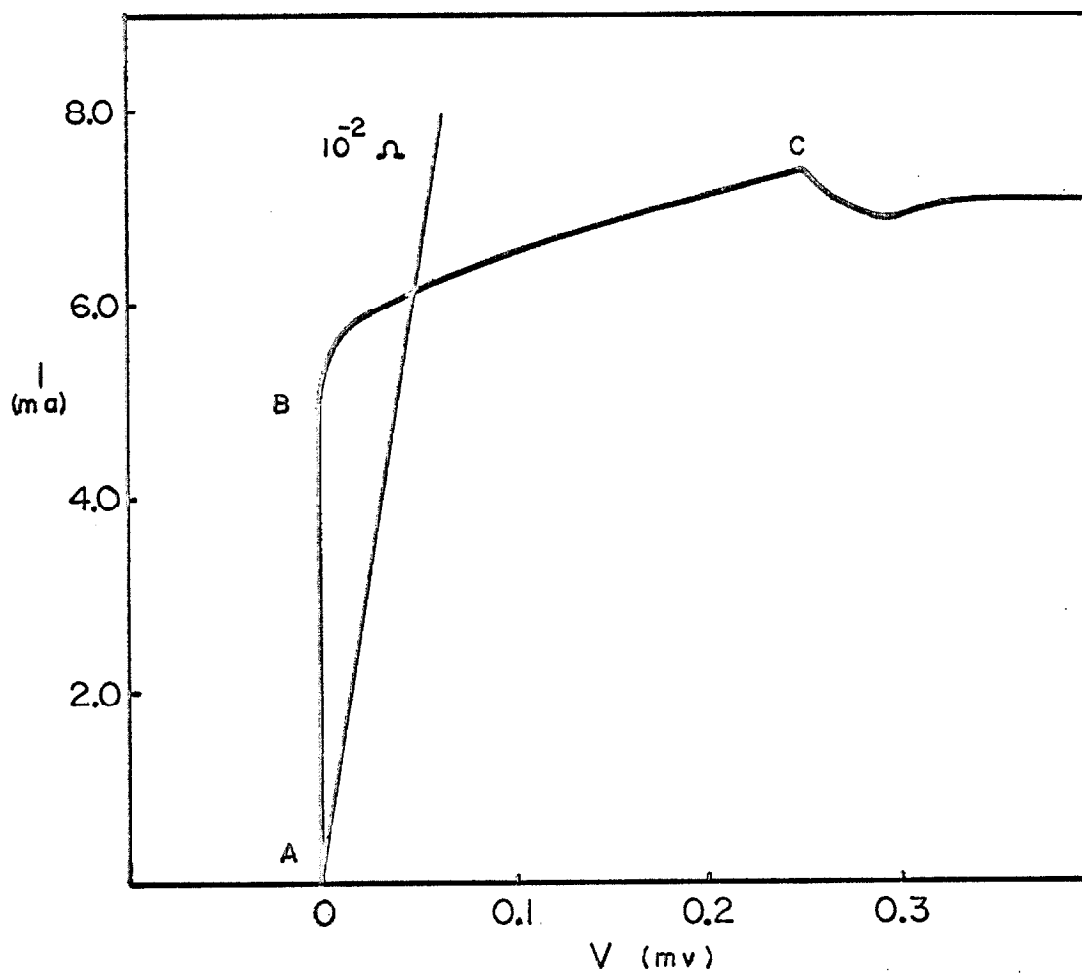
Fig. 8. Typical current-voltage curve for a superconducting vanadium film. Region A-B, the film has zero resistance. B-C is a region of "isothermal" transition to the normal state. Point C, the film is driven normal by a propagating thermal wave. At the intersection with the straight line the restored resistance is 10^{-2}

resistance within the "isothermal" region. I_c at a particular

temperature does not change with time at a system pressure of

$\sim 6 \times 10^{-6}$ torr. as it would if surface contamination by residual

gases were important (66). Nevertheless, to ensure that the sur-

face remains clean, the measurements are generally taken within

fifteen minutes of the film deposition, and always within thirty

minutes.

The portion of the film being studied is then completely

covered with an evaporated layer of the selected compound. This

produces a change, often dramatic, in the critical current, which

is monitored during the evaporation. The new I_c versus T curve

is then measured. Over the small temperature range usually

studied, the new curve is identical in shape to that of the clean

film, but is displaced along the temperature axis. This displace-

ment is assumed to equal ΔT_c, the change in the superconducting

transition temperature produced by the compound. Both the sign

and the magnitude of ΔT_c are insensitive to the precise definition

definition of I_c (see Figure 9). In experiments no. 3 and 11,

Table I, the validity of equating curve displacement with ΔT_c was

tested by actually measuring T_c both before and after the chemical

deposition. The resulting curves for no. 3 (see Figure 10), show

that the lateral displacement of the two curves varies between

+0.06 and +0.08°K as the critical current changes by more than

three orders of magnitude. This displacement agrees with the

measured change in T_c of +0.076°K. The differential nature of
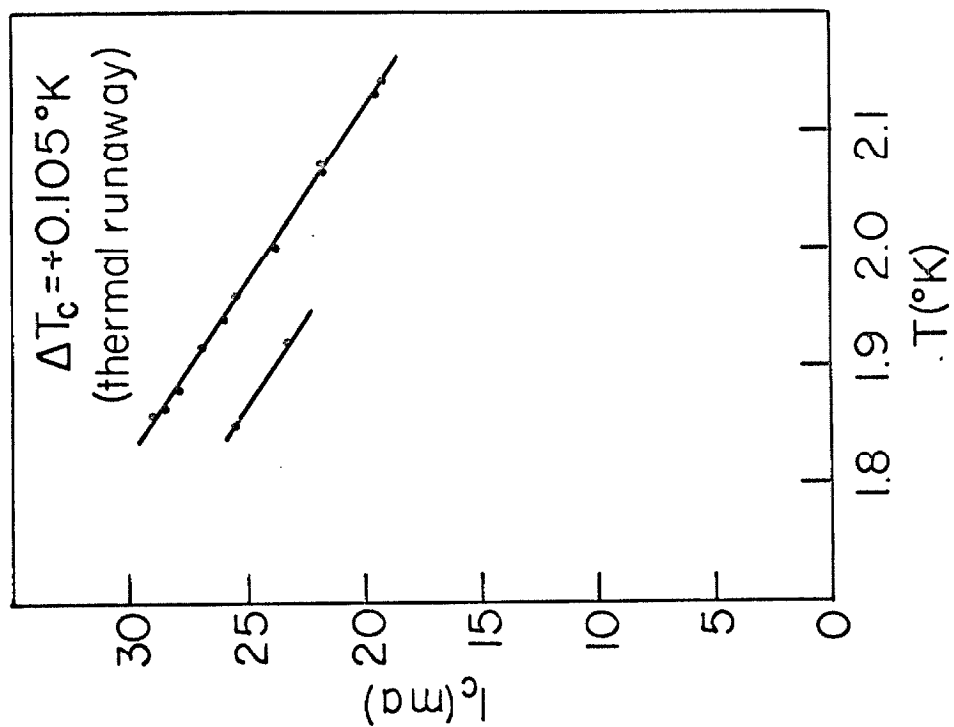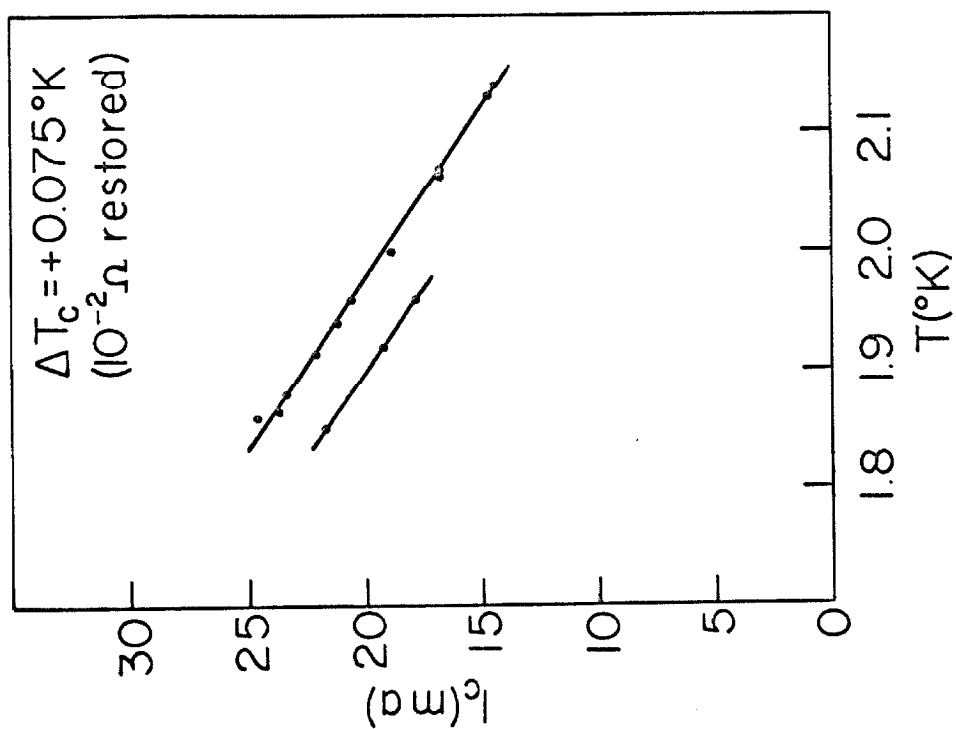
Fig. 9. ΔT_c as determined at the point of thermal
runaway and at 3 values of restored resistance.
Lower curves are before, upper curves after, the
deposition of tetracene.
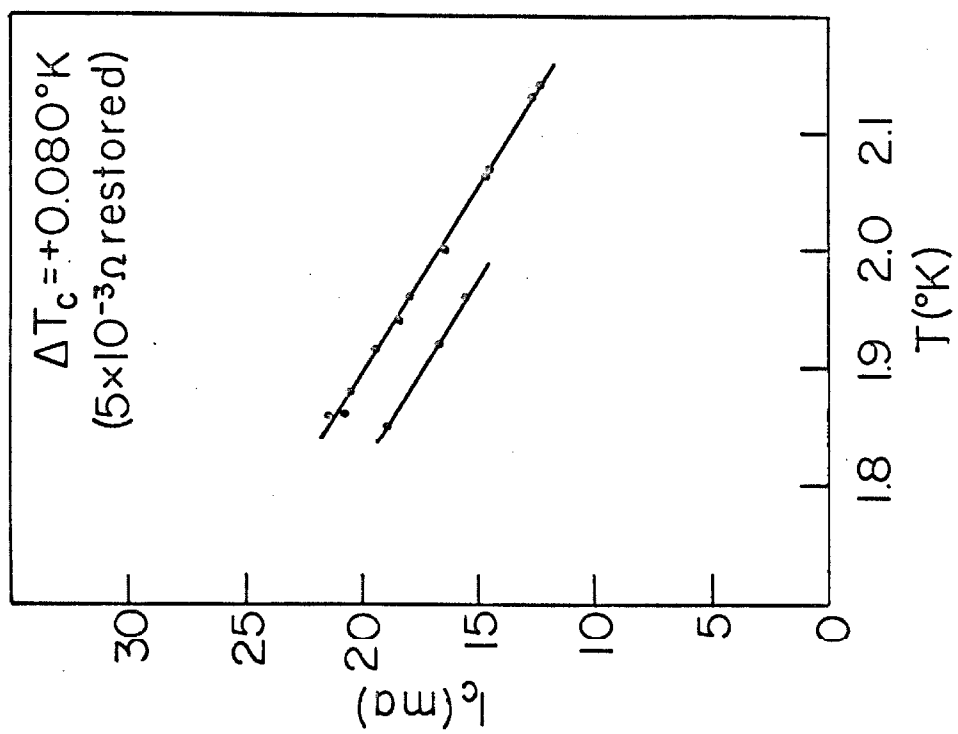
Fig.
9c
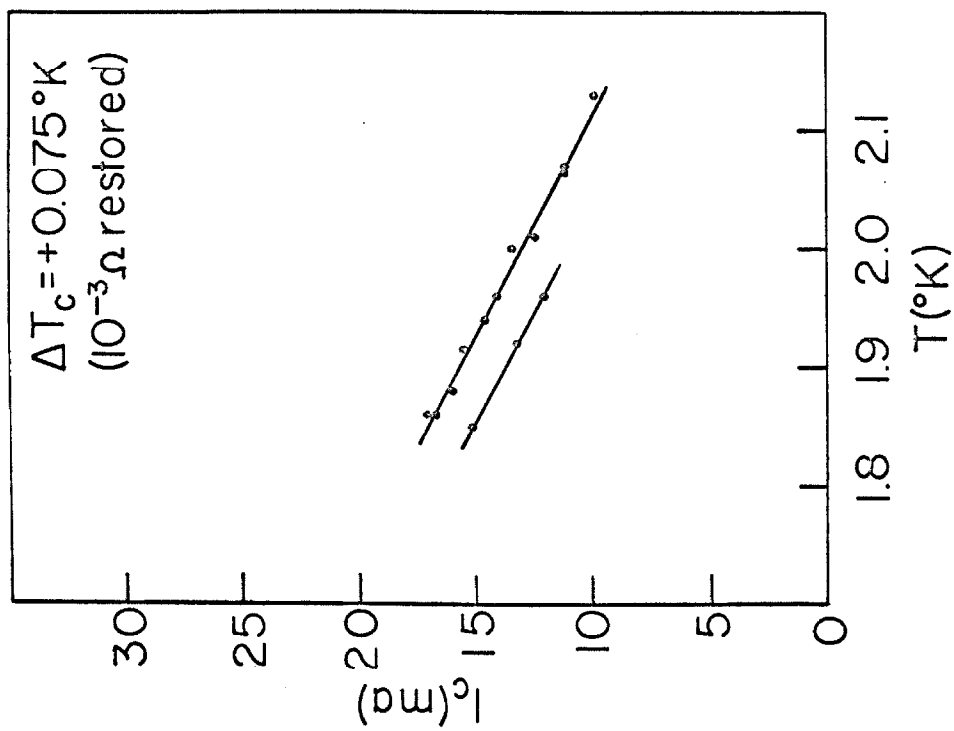
Fig.
9d
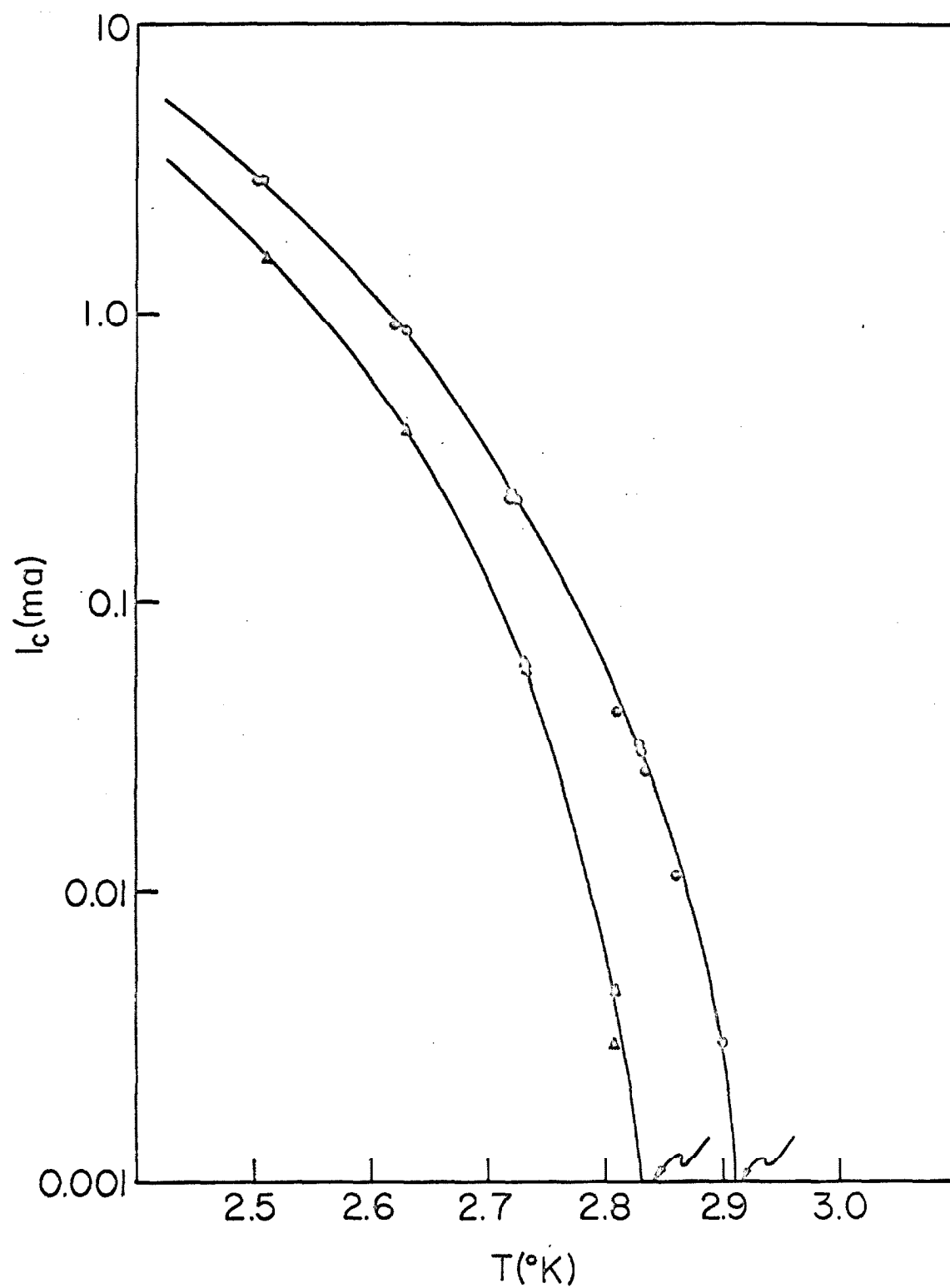
Fig. 10. Data from expt. 3, Table I. Arrows indicate measured values of T_c. Lower curve is before, upper curve is after, deposition of perylene.

the experiment allows changes in T_c as small as $0.025°K$ to be measured easily; it also allows a reliable determination of a zero effect.

Experimental Results

A. Film Properties

Thin vanadium films deposited at liquid helium temperatures are quench-condensed in a high resistivity, presumably highly disordered or even amorphous form which exhibits a T_c considerably below 5.3°K, that of bulk vanadium (67). These films can be annealed. After the liquid helium is exhausted, the temperature rises slowly. Annealing begins at approximately 35°K, and the . resistance decreases until 75°K. After $\sim$ 75°K, films show a positive temperature coefficient of resistance. The films can also be annealed to varying degrees of resistance heating with helium still present. Upon annealing, transition temperatures rise; normal film resistances drop by factors of as much as 15 to 20. We have also found that it is possible to prepare vanadium films in a low resistivity form. This can be done by first depositing a thin layer of organic compound on the helium-temperature substrate, and then depositing the vanadium film. One thick film (d $\sim$ 250Å) deposited directly onto the quartz was also largely annealed in formation.

Our film thicknesses were usually estimated from the room temperature resistance, R(300°K), using a bulk resistivity, ρ_B = 25 x 10^{-6} ohm-cm (68). The use of ρ_B is consistent with the data for Little's films (69), which have an average room-temperature resistivity of 21.2 x 10^{-6} ohm-cm. In addition, some high-resistivity films could apparently be nearly fully

annealed at 4°K by resistance heating. This is indicated by a
large decrease from the unannealed low-temperature resistance,
R(U), to the annealed, residual resistance, R(A), and by the
large resistance ratio $\frac{R(300°K)}{R(A)}$ (particularly Table I, films
no. 8 and 12, but also no. 6). In these cases the thicknesses
determined using the differences R(300°K) - R(A) and the tempera-
ture dependent resistivity ρ = 18.5 x 10^{-6} ohm-cm of van Beelen
et al. (70) are in excellent agreement with those determined
from R(300°K) and ρ_B.

For the vanadium films we have studied, a linear relation-
ship between R(U) and R(300°K) can be formulated

$$R(300°K) = 0.196 \ R(U) + 0.153K\text{-ohms}. \tag{28}$$

This line is plotted on Figure 11, along with the experimental
data. The constants are obtained by the method of least squares,
and the standard error of estimate is 0.053K-ohms. This formula
is used with measured values of R(U) to approximate R(300°K), and
from this the thickness for those films for which R(300°K) could
not be measured.

For unannealed films of the order of 100 A$^{\circ}$ thick, transi-
tion temperatures are generally between 2.2° and 2.6°K. There
is a nearly linear increase in T_c with increasing film thickness
for unannealed films as shown in Figure 12. The transition tem-
peratures of annealed films also increased with thickness; T_c for
some of the thicker annealed films was greater than 4.2°K.
Little (69) has observed transition temperatures of 3.95 to
4.68°K for annealed vanadium films 170 to 1000 A$^{\circ}$ thick, the
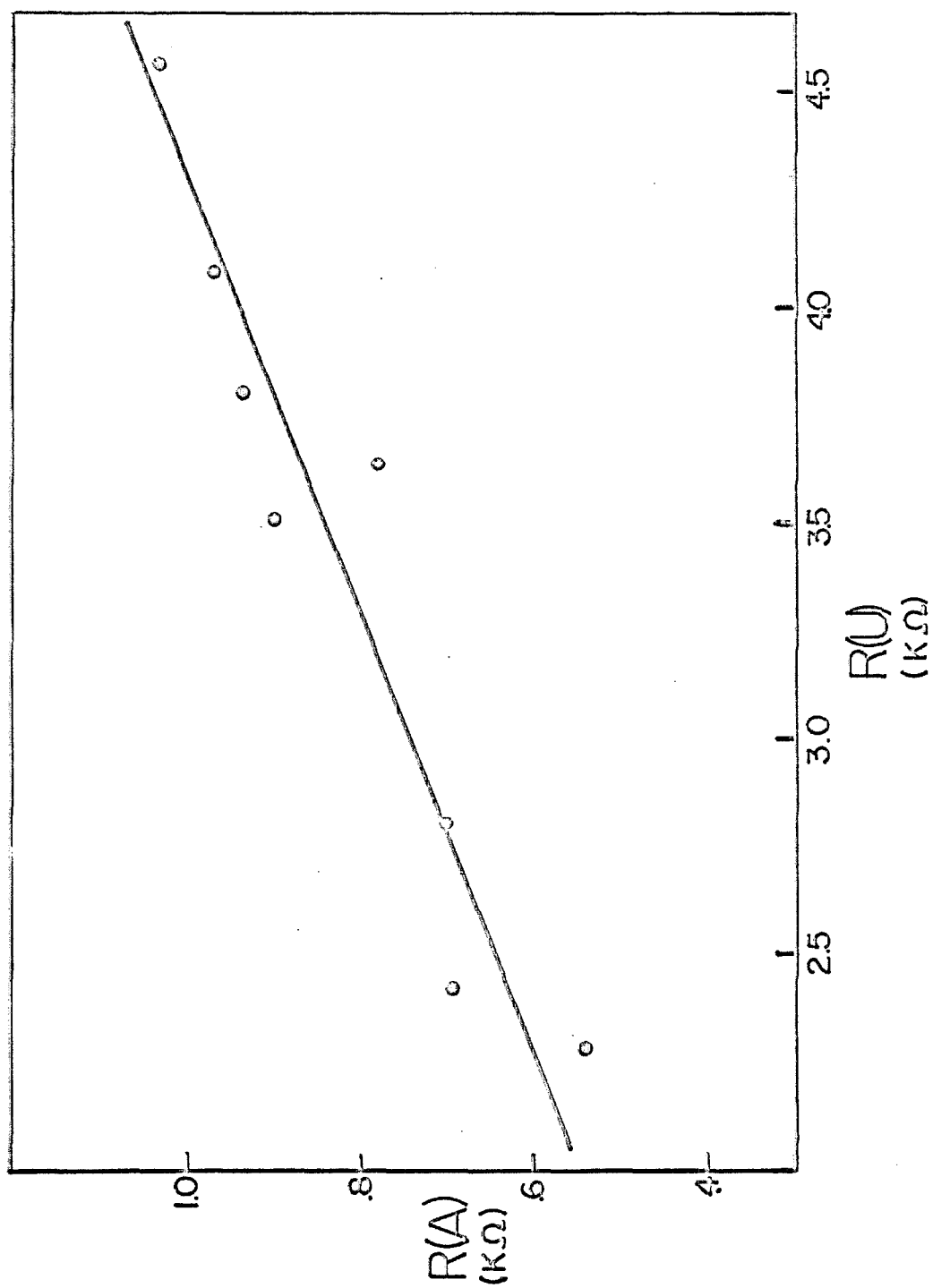
Fig. 11. R(U) versus R(A) for unannealed vanadium films. The straight line corresponds to equation 28.
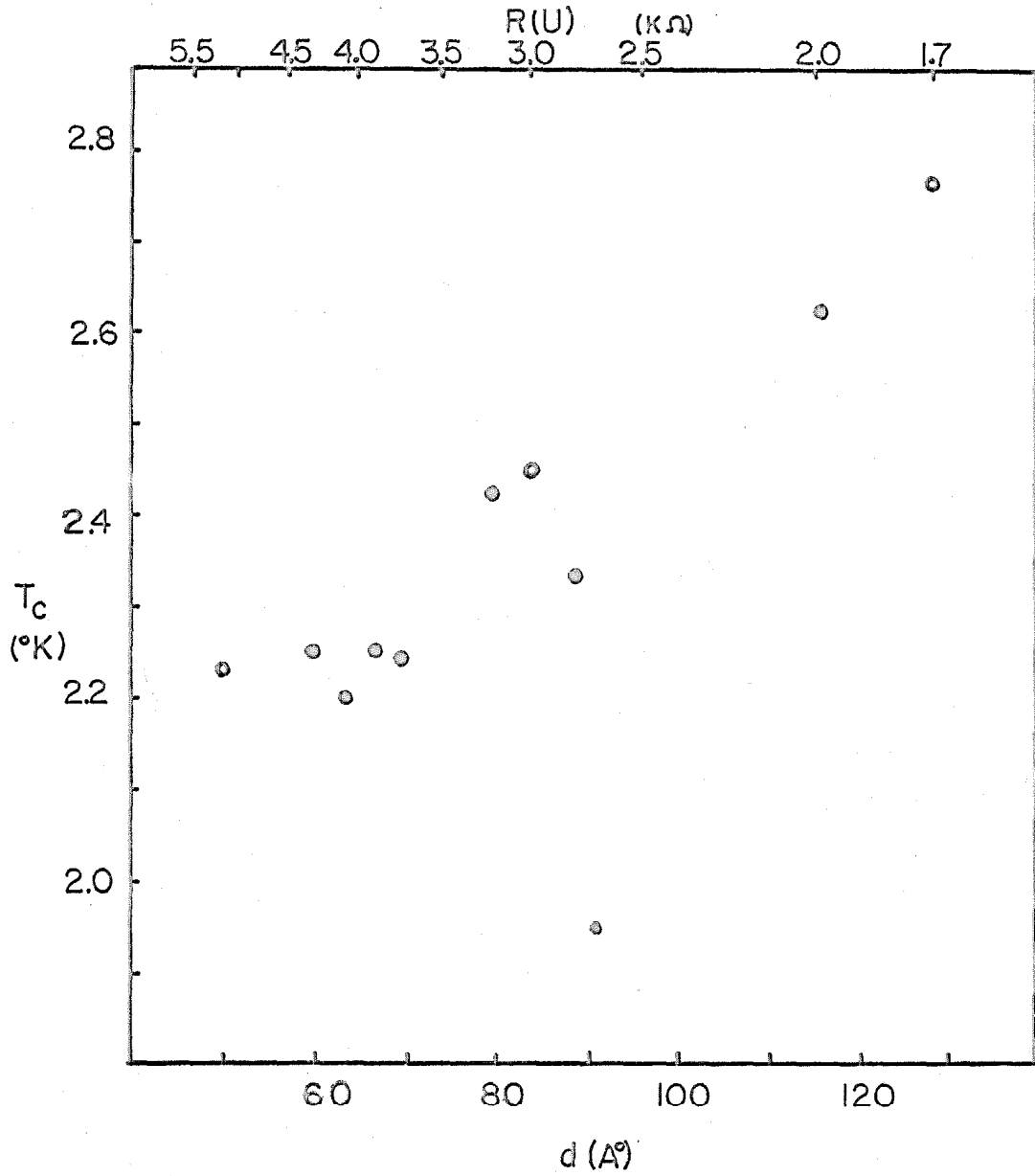
Fig. 12. T_c versus thickness (d) for unannealed vanadium films. The R(U) scale is determined from d using equation 28 and the room temperature resistivity.

●   d calculated from R(A).

○   d calculated from R(U) and equation 28.

thicker films having generally higher T_c. Van Beelen et al. (70)
have seen transition temperatures from 1.8 to 4.6°K for thick-
nesses between 130 and 800 A°.

Indium films quench-condensed on a 4°K quartz surface were
superconducting above the bulk transition temperature (3.4°K), as
expected (71). The normal resistance of these films was reduced
by a factor less than four on annealing.

Measurements of dc critical currents have been adequate to
establish the existence of the effects we were seeking. We have
been able to study "isothermal" transitions (Fig. 8) and the
results are independent of restored resistance (Fig. 9). There
have been several attempts to determine critical currents for
thin films from theory. Ginzburg (72) found that

$$I_c(T) \propto (T_c - T)^{3/2} \tag{29}$$

for T very close to T_c. Since this relationship has been veri-
fied in other investigations (73) it is worthwhile to test our
critical current measurements against it. In particular, if
joule heating is important, critical currents should increase
less rapidly than predicted by equation 29, since the heating
will tend to drive the film normal before the "true" critical
current. Figure 13 is a log-log plot of $I_c(T)$ versus $(T_c - T)$ for
the two experiments on which such a test can be performed. The
curve for experiment 11 has a slope of ~1.8, slightly greater than
the value predicted by equation 29. That for experiment 3
approaches 3/2 as $(T_c - T) \to 0$, but at larger values the slope
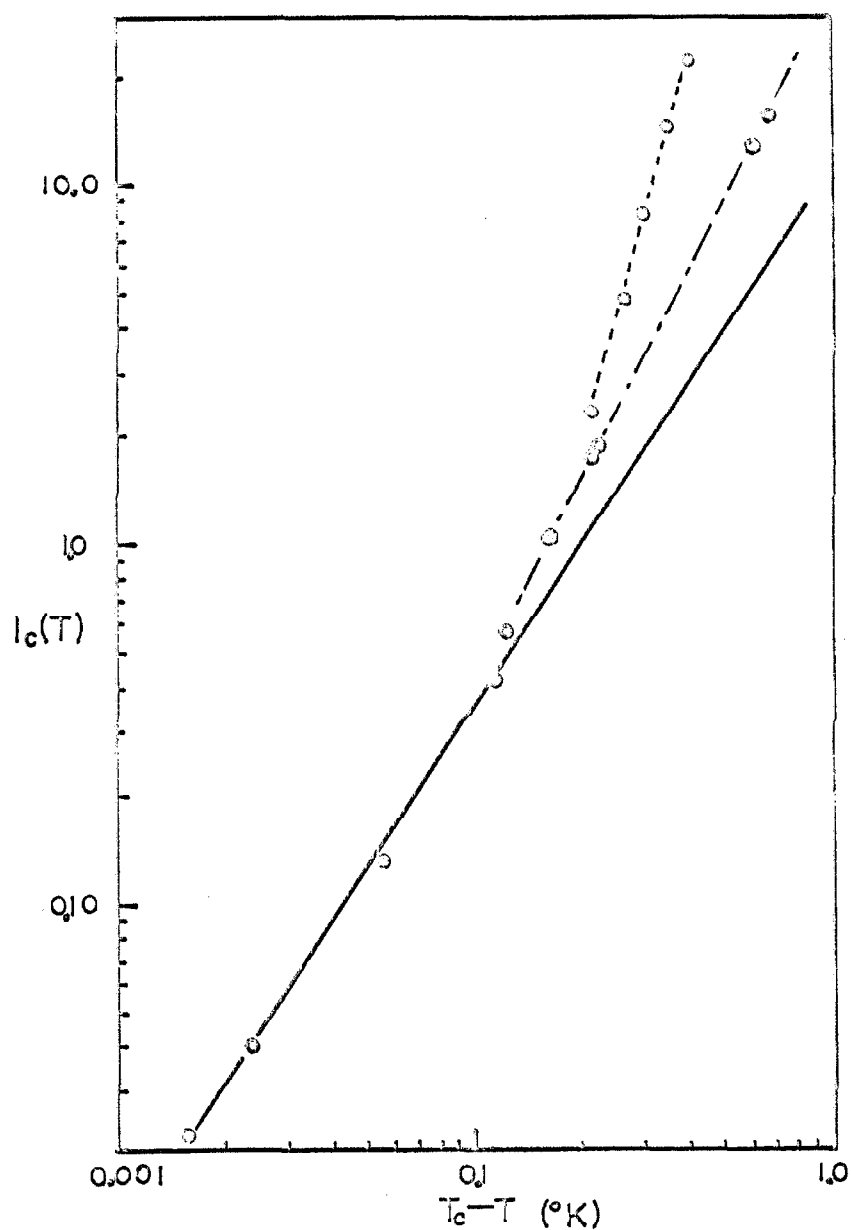
Fig. 13. Log-log plot of temperature variation of critical current. Currents are normalized so that lowest points fall on solid line of slope 3/2.

    o   Expt. 3, Table I.   o   Expt. 11, Table I.

    - - - -   Straight line of slope 7/2 for expt. I

    — - — -   Straight line of slope 1.87 for expt. 11 large values of T_c - T

increases to 7/2, instead of decreasing as might be expected if heating were becoming important. Whether these unexpectedly large slopes result from the fact that our films are much thinner than those used in previous comparisons to equation 29, or from some peculiarity of thin vanadium films can only be decided by further experiments. In any event, it is gratifying that the slopes approach to the expected value in the region where the theory is most applicable, $(T_c-T) \to 0$, and that deviations are not in the direction indicative of joule-heating difficulties.

It must be pointed out, however, that $I_c(T)$ versus T curves generally show discontinuities at the λ-point. These have also been observed by others (74), and are due to the large increase in the thermal conductivity of liquid helium as it becomes super-fluid. Their existence indicates that heating of some kind still plays a role in determining I_c. We believe that this heating is the result of that small amount of room temperature radiation reaching the sample, rather than of the impressed currents.

B. Chemical Effects

Experimental results for the organic chemicals studied are displayed in Table I. It can be seen that the values of ΔT_c for vanadium films fall into two groups which are approximately symmetric about $\Delta T_c = 0$; most enhancers increase T_c by 0.06° to 0.11°K and depressors decrease T_c by ~ 0.05° to 0.10°K, for films with T_c generally between 2.2 and 2.6°K. A correlation of the sign of ΔT_c with the properties of the molecules studied is dis-cussed in section IV. The two experiments with indium films

Table I

Expt.	Compound	ΔT_c (°K)	T_c (°K)	film[b] Width (mm × 10)	R(U) (KΩ)	R(A) (KΩ)	R(300) (KΩ)	$\frac{R(300)}{R(A)}$	Thickness (Å)[i] from R(300)	Thickness from R(300)-R(A)	I (eV)	A[l] (eV)
	Vanadium Films											
1	Anthracene	+0.10	2.33	2.54	2.80	(.400)[e]	.70	1.75	89		7.23[g]	.42
2	Tetracene	+0.075	2.76	2.54	1.70				128[f]		6.88[g]	1.0
3	Perylene	+0.08	2.92	1.52	2.48	.22	.51	2.32	204	265	7.15[g]	.85
4	Phenothiazine	+0.09	2.2	1.52	6.80	(.01)[e]	1.63	1.62	64		7.28[h]	
5	3,4,7,8 tetramethyl-1,10-phenanthroline	+0.09	2.45	2.54[c]	3.02				84[f]		8.65[i]	
6	2-aninoanthra-quinone	+0.06	2.62	1.52	3.80	.285	.900	3.16	116	125		<.5[i]
7	1,4,5,8-tetrachloro-anthraquinone	+0.025	2.23	1.52	9.25				50[f]	≥9.34[j]	.66[i]	
8	Pyromellitic dian-hydride	-0.11	2.25	1.52	6.33	.445	1.56	3.5	67	69		1.37
9	Chloranil	<0[a]		2.54[c]							≥9.68[k]	.85
10	Tetracyanoquino-dimethan	-0.10	2.25	1.52	7.6	.600	1.72	2.87	60	68		1.7
11	Tripyridyl-s-triazine	+0.05	3.6	1.52	(.750)[d]	.655	1.67	2.58	62	78		
12	Dicyclopentadienyl-titanium dichloride	-0.05	2.42	2.54	3.63	.222	.780	3.5	80	83		
	Indium Films											
13	3,4,7,8 tetramethyl-1,10-phenanthroline	0.00	4.1	1.52	4.58						11.7[j]	
14	Tetrocyanoquino-dimethan	-0.23	4.09	1.52	3.28	.843					1.38[j]	

Legend to Table I

(a) Film was destroyed after the initial critical current depression was observed, but before ΔT_c could be measured.

(b) All films, 6.35 mm. long.

(c) Newhouse geometry not used.

(d) Vanadium was deposited in an essentially annealed form. Experiments with this compound on unannealed films were similar.

(e) Not fully annealed.

(f) Estimated from R(U) as described in text.

(g) From "Introduction to Mass Spectrometry" by Robert W. Kiser (Prentice-Hall, Englewood Cliffs, N. J., 1966), Appendix IV.

(h) From M. Kinoshita, Bull. Chem. Soc. Jap., 35, 1609, 1962.

(i) Estimated in this laboratory from charge-transfer absorption spectra.

(j) Ionization potential of unsubstituted anthraquinone = 9.34.

(k) Ionization potential of unsubstituted quinone = 9.68.

(l) From G. Briegleb, Angew. Chem. Internat. Edit., 3, 617 (1964), except where noted.

were primarily performed as tests of suggestions which were advanced about the mechanism producing changes in T_c, and are also discussed.

Experiments for two organic compounds, metal-free pthalo-cyanine ($\Delta T_c \sim -0.05°K$) and 5-nitro-1,10-phenanthroline ($\Delta T_c \sim +0.05°K$) are not included in the table because poor vacuums during those experiments made it likely that the chemicals were deposited onto highly contaminated surfaces, making the results suspect.

Table II contains the data for the two inorganic compounds, oxygen and thallium chloride, whose effects have been studied.

Table III presents the data for four experiments with 3,4,7,8-tetramethyl-1,10-phenanthroline (TMP) deposited on vanadium films, including experiment 5 of Table I. Since experiments 1-3 were done with rather poor vacuum conditions, a superfluid helium leak required that experiment 3 be carried out above the λ-point, and none of these experiments employed the Newhouse geometry, we consider this spread in values to give an upper limit to our experimental error. With the improved experimental conditions that have obtained since these, our very first experiments, much better films, with more nearly uncontaminated surfaces, can now be studied. Experiments with such films should allow better reproducibility for a given compound, and quantitative comparisons between results for different compounds. In the present results, the variation in film properties and experimental conditions between experiments makes the variations in magnitude

Table II

Vanadium Films Compound	ΔT_c (°K)	T_c (°K)	Width (mm. x 10)	R(U) (KΩ)	R(A) (KΩ)	R(300) K(Ω)	Thickness (A°) per R(300)
1. Oxygen[a]	+0.07	2.24	2.54[b]	3.5		.898	70
2. Thallous Chloride	+0.05	2.4	1.52	4.75	.375		87

Table III[a],[b]

	ΔT_c (°K)	T_c (°K)	Width (mm. x 10)	R(U) (KΩ)	R(A) (KΩ)	R(300) K(Ω)	Thickness (A°) per R(300)
1. 3,4,7,8-tetramethyl-9,10-phenanthroline	+0.07	2.1	2.54	3.4			76
2. "	+0.04	2.35	"				100
3. "	+0.06	1.95	"	2.42		690	91
4. "	+0.09	2.45	"	3.02			84

(a) 3N5 Vanadium.

(b) Newhouse geometry not used.

(c) Except for #1, Table II, and #3, Table III, see comment f, Table I.

of ΔT_c within the enhancer and depressor groups of perhaps secondary significance.

There is an experimental observation which strongly supports the suggestion that there is a strong chemical interaction between these molecules and a metal surface, even at liquid helium temperatures. Deposition of the colorless compound, TMP, onto a vanadium film held at $4.2°K$ produced a reddish-purple color, indicative of a chemical reaction.

It should be mentioned that the occurrence of both positive and negative values of ΔT_c rules out most alternatives to the interpretation that the observed effects are chemical in nature. Since the physical properties of all the organic chemicals are so similar, any suggestion involving a physical change in film properties caused by the mere deposition of a chemical would predict only one sign for ΔT_c.

In addition, the fact that hydrogen is usually the primary gas released during the evaporation of both enhancers and depressors eliminates the possibility that it is the evolved gases, rather than the chosen chemical, that cause the observed effects.

IV. DISCUSSION

The experiments described in the preceding section have clearly demonstrated that it is possible to either raise or lower the critical temperature of thin metal films by the deposition of an appropriate chemical on the film surface; as suggested in part II, Interaction Mechanisms, the intimate association of molecules with a metal does influence the superconducting properties of the metal. What is more, the sign of ΔT_c for the aromatic compounds studied can be related to a simple division of the molecules by electronic properties. Molecules with low electronegativity, ψ , are enhancers, those with high electronegativity are depressors.

We use Mulliken's definition (75), $\psi = 1/2(I + A)$, where I is the first ionization potential and A the electron affinity. As can be seen in Table I, for many of these compounds I and A are not both known. However, if the compounds are divided into enhancers and depressors, it is seen that among the planar aromatic molecules all depressors act as acceptors in intermolecular charge-transfer complexes, while most of the enhancers are either well-known charge transfer donors (anthracene, tetracene, perylene, phenothiazine) (76) or can function as such (TMP) (77). Since acceptors characteristically have high ψ while donors have low ψ , the division of these enhancers and depressors on the basis of electronegativity is immediate.

Also among the enhancers are the substituted anthraquinones. These were chosen because it was expected that as ψ was

systematically decreased, the sign of ΔT_c would change at some point. They are weak charge transfer acceptors whose electron affinity values are less than those of tetracyanoquinodimethan (TCNQ), chloranil, and pyromellitic dianhydride (PMA) (78). If we consider the electronegativities for the charge-transfer acceptors to parallel their own A values, then all the planar aromatic compounds studied can be arranged according to ψ and a division made which separates enhancers from depressors, this division coming between PMA and 1,4,5,8-tetrachloroanthraquinone.

The two additional organic chemicals studied, tripyridyl-s-triazine (TPTZ) and dicyclopentadienyl-titaniumdichloride (DCT) are not _planar_ aromatics. They can, however, be reasonably arranged by electronegativity with the planar compounds, and the signs of ΔT_c correspond to the above division. The pyridine rings of TPTZ (ΔT_c = +0.05) are sterically prevented from all lying in the plane of the triazine ring, but the molecule should still be a weak electron donor with between that of TMP and the anthraquinones; thus it should be possible to place it by electronegativity with the other enhancers. DCT (ΔT_c = -0.05°K) is readily reduced, indicating the ease of the reaction $Ti^{(IV)} + e^{(-)} \rightarrow Ti^{(III)}$ and the correspondingly high electronegativity of the molecule; it can therefore reasonably be placed with the other depressors.

Despite our previously expressed doubts as to the significance of the relative magnitudes of ΔT_c, there is discernible a systematic variation of ΔT_c within the enhancers that should at

least be noted. Experiments 1-10 in Table I are arranged in order of increasing ψ for the organic chemical. Among the enhancers, there does seem to be a decrease of ΔT with increasing ψ (and I), particularly in experiments 4-7.

That such a simple correlation can serve to classify all the organic chemicals studied as enhancers and depressors should, perhaps, be surprising. As an indication of this, we might consider the first enhancer to be discovered, TMP. Vanadium atoms can occur in the zero valence state in $V°(TMP)_3$ complexes (40). It was therefore suggested that any observed effects with TMP might be attributable to chelation of surface atoms. Although a $V(TMP)_3$ complex would clearly be impossible, one could conceive of a surface vanadium complex $V(V)_X(TMP)$ where the remaining "ligands" are the neighbors of the surface vanadium atom. TPTZ, the second enhancer found, and also a potential chelating agent, might act similarly.

It is clear, however, that the aromatic hydrocarbons cannot be considered to act by chelation. It was only when we considered TMP, not as sitting perpendicular to a film surface, "biting" into a vanadium atom, but as lying flat on it, that the electron donor-acceptor behavior of these molecules and therefore their values, could be used to correlate their behavior.

It should <u>not</u> be surprising that, once the molecules are considered on the basis of electronegativity, the division between enhancers and depressors does not come at an obvious point in terms of intermolecular charge-transfer:

3,4,7,8-tetrachloroanthraquinone, an acceptor in charge-transfer complexes, is yet an enhancer. The qualitative division between donors and acceptors, low and high ψ , can only be made with respect to some arbitrary reference. In charge-transfer complexes benzene is frequently used as an implicit reference. In this study the division by electronegativity is made with a vanadium film surface as the reference.

Thus, the proposed division really suggests that the quantity which determines the sign of ΔT_c is $\Delta \psi = (\psi_{metal} - \psi_{mol.})$. Since it follows from the definition of ψ that $\psi_M = \phi_M$, the metallic work function, this can be rewritten $\Delta \psi = (\phi - \psi_m)$. Then the criterion for ΔT_c is as follows:

$$\Delta \psi > \alpha \Rightarrow \Delta T_c > 0$$
$$\Delta \psi < \alpha \Rightarrow \Delta T_c < 0 \tag{30}$$

where α is some constant which may be zero.

It is possible to relate $\Delta \psi$ to the properties of a molecule-metal surface bond by assuming a simple, three-configuration wave function to describe the bond (75);

$$|W\rangle = a|M^0 x^0\rangle + b|M^+ x^-\rangle + c|M^- x'\rangle$$
$$= a|a\rangle + b|b\rangle + c|c\rangle \tag{31}$$

The bond polarity is determined by $/b/^2 - /c/^2$, and the sign of this quantity is largely determined by $\Delta \psi$.

In an obvious notation the secular equations for the coefficients and energy are:

$$a(E_a - E) + b(H_{ab} - S_{ab}E) + c(H_{ac} - S_{ac}E) = 0$$

$$a(H_{ba} - S_{ba}E) + b(E_b - E) = 0 \qquad (32)$$

$$a(H_{ca} - S_{ca}E) + c(E_c - E) = 0$$

The off-diagonal elements involving two-electron transfer are assumed to be zero. The diagonal matrix elements are

$$E_a = 0$$

$$E_b = \phi - A_x - \varepsilon \qquad (33)$$

$$E_c = I_x - \phi - \varepsilon'$$

where I, A, and ϕ have been defined, and ε and ε' are stabilization energies for the negative and positive ions, respectively, at the metal surface.

The ground state solutions for b and c (energy E_0) are

$$b = -a \frac{(H_{ba} - S_{ba}E)}{E_b - E_0} \qquad c = -a \frac{(H_{ca} - S_{ca}E_0)}{E_c - E_0} \qquad (34)$$

If the simplifying assumption is made that the numerators are equal

$$H_{ba} - S_{ba}E_0 = H_{ca} - S_{ca}E_0$$

then b and c have the same sign and

$$|b| \gtrless |c| \quad \text{if} \quad \left(\frac{1}{\varepsilon_b - \varepsilon_0} \gtrless \frac{1}{\varepsilon_c - \varepsilon_0} \right) \tag{35}$$

which leads to

$$|b| \gtrless |c| \quad \text{if} \quad \Delta \psi \gtrless \left(\frac{\varepsilon - \varepsilon'}{2} \right) \tag{36}$$

The direction of this inequality, then determines the bond polarity. It is of course true that the magnitudes of a and b are determined by I, A, and ϕ individually, and that $\Delta \psi$ only determines which coefficient is larger.

The division by electronegativity does not, however, specify the detailed mechanism by which the changes in superconducting properties are produced. In particular, the obvious suggestion is that the effects in some way follow from simple electrostatic charging: thus, the molecule would donate or accept an electron from the metal and become a positive or negative ion at the surface. Fortunately, things seem to be more complicated, and therefore more interesting, than this.

Static charging experiments have been performed on indium and tin films by Glover and Sherrill (GS) (78), and by Stadler (79). GS prepared parallel plate capacitors with a superconducting thin film as one plate. By charging the capacitor, with the experimental film positive (or negative) electrons could be withdrawn (or added) and the effect on T_c could be observed. They found that adding electrons to an indium film lowers T_c, and that

subtracting electrons raises it. That is, if n is the electron concentration, $dT_c/dn < 0$. However, we observed that depositing TCNQ, a very strong electron acceptor, on an indium film gave $\Delta T_c = -0.23°K$ (Table I, expt. 14), the wrong sign for simple electron withdrawal. This result seems to unambiguously eliminate static charge transfer as the sole means by which TCNQ affects T_c of an indium film.

Further, although more indirect, evidence against the static charging hypothesis comes from considering Table II, expt. 2, in which oxygen deposited on the surface of a vanadium film increased T_c by 0.07°K. Rühl (80) has studied the effects of oxygen on the transition temperatures of films of metal from groups IIIa and IVa. Where his results could be compared with those of GS (In and Sn) they were completely interpretable on the basis of charge transfer. Electrons are withdrawn from the films by the activated reduction of molecular oxygen on the metal surface. Activation temperatures for the several metals ranged from 3°K to 25°K.

The reduction of molecular oxygen on transition metal surfaces is usually believed to be non-activated (81). Thus the increase of T_c of vanadium by oxygen is reasonably interpreted as a result of the withdrawal of electrons by the reduction of oxygen in a process with an activation temperature of less than about 2°K. This interpretation asserts that actual electron withdrawal from a vanadium film, as with an indium film, increases T_c. Since aromatic molecules of high electronegativity

decrease the T_c of vanadium and indium, this lends further support to the thesis that organic molecules do not change T_c by simple static charge transfer.

The results of the static charging experiments on the various metals can be understood simply. In Section II, Interaction Mechanisms, the BCS result was given, $T_c = 1.14 \, \theta_D \exp(-\frac{1}{N(E_F)V})$. Therefore, if electron addition or withdrawal changes E_F slightly, it will also in general change $N(E_F)$ and therefore T_c. The different sign of dT_c/dn for different metals can be understood by considering the simple density of states curves below:
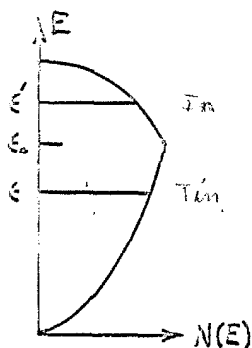
For an n-type metal, such as tin, with $E_F = \varepsilon < \varepsilon_o$, $\frac{dN(E)}{dE}/_{E_F} > 0$. Adding electrons will increase E_F, $N(E_F)$, and therefore $T_c (dT_c/dn > 0)$. For a p-type metal, such as indium $E_F = \varepsilon' > \varepsilon_o$, $\frac{dN(E)}{dE}/_{E_F} < 0$, and therefore $dT_c/dn < 0$.

Now low-temperature specific heat measurements on 3-d transition metals and their alloys have given a curve for the electronic specific heat coefficient versus the number of valence electrons in the alloy (34). If the simple one-electron picture is adopted and a rigid band assumed, a conversion of the electron concentration scale to an energy scale leads to the corresponding

density of states curve (84). It is found that $dN(E)/dE < 0$ at the fermi level of vanadium. The above explanation of static charging effects would then predict that electron withdrawal should increase T_c for vanadium, just as with indium. This is, again, consistent with the results for oxygen, but in opposition to those with organic donors and acceptors.

Up to this point, a correlation between molecular properties and the effects on superconductivity has been made, and arguments have been presented to indicate at least one microscopic mechanism that this correlation does <u>not</u> imply. There is one pair of experiments which <u>may</u> point in the direction of such a mechanism. TMP deposited on a vanadium film increased T_c (expt. 5, Table I), while deposited on an indium film it gave no effect (expt. 13, Table I). The bonds of molecules to transition metal surfaces are generally considered to be largely covalent and dependent on partially filled d-orbitals, as in the metallocene complexes of transition metals and aromatic molecules (40). The null effect of TMP on the non-transition metal indium, which has no unfilled d levels, may indicate that the enhancements seen on vanadium are related to d-π bonding between unfilled d-levels of the metal and the molecular π-orbitals.

Several mechanisms have been suggested in section II, Interaction Mechanisms, as being capable of enhancing supercon- ductivity in the presence of strong metal-molecule bonds. As to which--if any--of these are important, there is really little more that can be unambiguously drawn from this study.

It is still possible to speculate on the reason for the depressions. A simple suggestion is that the strong electron acceptors abstract an electron from the metal, forming radical anions on the surface. Magnetic interactions between the radical and the conduction electrons could overbalance the tendency of electron-withdrawal to increase T_c of these metals, causing a net reduction in T_c.

However, there are other suggestions which would involve strong, non-magnetic, coupling between molecule and metal. One was anticipated in the discussion of conductive conjugation, where it was suggested that interaction with a molecule might possibly lead to an increase in the density of states away from the Fermi surface of the metal, but a decrease at the Fermi surface. Both depressors and enhancers have ionization potentials greater than the work function of vanadium, and therefore would have their filled molecular orbitals located lower in energy than the Fermi level. Since the depressors have greater ionization potentials than do the enhancers, their filled molecular orbitals will lie farther below the Fermi surface than do those of the enhancers; they would thus be more likely to cause this unfavorable change in the density of states.

A second speculation is that the electrons in the molecules with high electronegativity may be less mobile, and therefore less capable of providing screening of electron-electron coulomb interactions. Thus, if the molecular orbitals of such a molecule were mixed with metallic conduction states, the interaction

would be less favorable, and possibly even repulsive, in the region of the molecule.

Two interesting observations may be made after the preceding remarks about ψ, screening, and ΔT_c. First, most of the enhancers are bigger molecules--more benzene rings--than are the depressors. This might be correlated with increasing shielding in the presence of bigger π-electron systems. The second observation is based on another, perhaps unwarranted, comparison of values of ΔT_c for different compounds. The compounds in experiments 1, 6, and 7, Table I, all have the three-ringed anthracene structure: anthracene, 2-aminoanthraquinone, and 1,4,5,8,-tetrachloroanthraquinone. There is a definite decrease in the magnitude of ΔT_c as ψ increases from one of these compounds to the next.

We have not succeeded in determining the microscopic nature of the effects we have observed. However, we feel that the possibility of correlating molecular properties with molecular effects on superconductivity in what is yet a preliminary investigation of a new phenomenon augurs well for an eventual understanding of the mechanisms involved, and for the profitable extension of these studies to other systems.

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-PROPOSITION I

Abstract

It is proposed that the method of photoselection be used
in studying the ESR of the triplet states of randomly oriented
molecules in rigid glasses.

The original observations of the ESR of organic molecules
in the lowest triplet state were made on single crystals of solid
solutions of naphthalene in durene. The spectra are due to tran-
sitions between sublevels of the triplet and are highly aniso-
tropic because of the zero-field splitting (1). This anisotropy
makes it very difficult to observe the ESR of a randomly oriented
sample of such molecules. The half-field, $/\Delta m/ = 2$ transitions
are comparatively isotropic and have been observed with non-
oriented molecules in rigid glasses (2). Recently, the $/\Delta m/ = 1$
transitions have also been seen in glasses, but the intensities
are much lower (3). However, observation of the higher field
resonance allows more ready calculation of the zero-field split-
ting parameters and is more sensitive to the values of these
parameters.

It is therefore proposed that the method of photoselection
be used for high field ESR experiments on triplet states (4).
Photoselection relies on selecting with polarized light a non-

random array of molecules from a randomly oriented sample. If
the light is chosen to correspond to an absorption band with
known polarization, the excited molecules produced now have a
known orientation in space. Although molecules not parallel
to the polarization axis can still absorb light with a probability
proportional to the square of the cosine of the angle between the
transition dipole and the electric vector, there is still an
important net orientation. This is most recently shown by
El-Sayed and Pavlapoulos in triplet-triplet absorption studies
using photoselection (5).

The normal high field spectrum from randomly oriented
molecules in a rigid glass is three pairs of lines (3). Each
pair arises from a group of molecules in which one of the three
principle axes of the zero-field splitting tensor is parallel to
the magnetic field. At these three canonical orientations the
zero-field splitting takes on a stationary value as a function
of orientation to the magnetic field. This is why the ESR
absorption can be seen despite the large anisotropy. However
in non-canonical orientations the splitting varies rapidly with
small changes in orientation. The signals from these molecules
therefore contribute to the noise level.

If the polarized light is oriented so that the absorbing
molecules are in a canonical orientation, the pair of lines that
correspond to that orientation should be effectively enhanced,
while the lines from the other two orientations should largely

disappear. If the direction of the electric dipole transition moment is parallel to one canonical direction, such a situation will be the case when the electric field is parallel to the magnetic field. Placing the electric field perpendicular to the magnetic field will then allow the observation of the other two pairs of lines, and the pair seen in the parallel case will be suppressed. Then if the orientation of the transition dipole moment with respect to the molecule is known, this makes it possible to relate a given splitting to the molecular orientation involved, and therefore to relate the axes that diagonalize the zero-field tensor to the molecular axes.

Added Note: This suggestion was originally submitted as a candidacy proposal in February, 1964. Since that time Kottis and Lefebvre [J. Chem. Phys. 41, 366 (1964)] published a note containing computer simulated spectra indicating that the effect of photoselection would indeed be to enhance the resonance of certain canonical orientations with respect to the others. They also point out that if the axes of the zero-field tensor are known with respect to the molecular axes, information about the transition-dipole moment can be obtained.

Very recently, Lhoste, Haug, and Ptak used the combination of photoselection and magnetic resonance and experimentally known orientations of the zero-field tensor to experimentally obtain information on the transition moments in phenoxazine [J. Chem. Phys. 44, 648 (1966)] and in coronene and phenanthrene

[_ibid._, p. 655]. Shortly thereafter, El-Sayed and Siegal [_ibid._, p. 1416] used the known directions of polarization of the electronic absorption bands of phenanthrene-d_{10} to assign the canonical directions for the zero-field tensor. In addition, they discuss in detail the method of making such assignments.

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PROPOSITION II

Abstract

We propose that low temperature optical absorption measurements be performed on crystalline 1:1 charge transfer complexes in order to determine experimentally the low temperature state of these crystals and how it develops with increasing temperature.

There have been extensive experimental and theoretical studies of the electrical and magnetic properties of crystalline 1:1 complexes DA between aromatic donor molecules D, and acceptor molecules A (1). Recently, McConnell (2) has proposed a treatment of the ground state and elementary excitations in the limit of low temperatures, although, as will be discussed, room temperature properties as determined by optical (3,4) spectroscopy seem to agree well with its predictions. We will propose here an extension of these measurements in order to explain the nature of this agreement, thereby obtaining the experimental results necessary for an extension of the present theory of these complexes.

On the basis of a simple molecular field model, McConnell predicts that at low temperatures the 1:1 DA crystalline complexes must divide sharply into two classes. Nonionic crystals (N) will be composed of essentially neutral components; ionic crystals (I)

will be composed of positive and negative ion radicals. Both classes should have a nonmagnetic ground state, the former because the neutral components are diamagnetic; the latter because the spin exchange interaction between radicals is expected to be anti-ferromagnetic. For both classes, the lowest energy excitations above the ground state are expected to be magnetic, being triplet excitions with large excitation energy in class N, and thermally accessible linear spin waves for class I.

Optical absorption and paramagnetic resonance experiments have indicated that at room temperature there does seem to be such a sharp division of these solids into diamagnetic, nonionic complexes and, at least partially paramagnetic, ionic complexes. Furthermore, the paramagnetism of the I complexes decrease exponentially with decreasing temperature, indicating that it is associated with a thermal excitation of the crystal (5).

These facts seem to be in good agreement with the theory. However, it must be stressed that the theory as formulated is only for low temperatures, whereas the IR and visible experiments which verify the division into classes are room-temperature measurements. In particular, the following questions may be asked. Are all those crystals which are ionic at room temperature also ionic at absolute zero, or is the room temperature ionic state, of at least some, the result of thermal excitations? If some complexes change from N to I, is this change continuous or abrupt? Extension of the theory to higher temperatures can

be made along the same lines as work by Chesnut (6) on triplet exciton systems. His results suggest that at high temperatures corresponding to high excitation concentrations, a rapid or even discontinuous change of the degree of ionization may occur. Finally, is the temperature dependence of the paramagnetism related to a corresponding change in ionization?

We propose that these questions can be answered by measuring the visible and/or IR spectra of several complexes down to cryogenic temperatures. Both techniques can differentiate ionic from nonionic crystals, and can tell whether, and in what manner, the degree of ionization of a complex changes with decreasing temperature. Furthermore, any changes in ionization can be compared to known, or measurable, changes in paramagnetism.

A preliminary IR experiment has been performed in collaboration with Mr. E. Weissberger. We measured the spectrum of the ionic 1:1 complex p-phenylenediamine-chloranil (7) from room temperature to $\sim 16°K$ and found no evidence for a decrease in the degree of ionization. However, the spectra were taken with the complex dispersed in a KBr pellet, and paramagnetic resonance measurements showed that this technique produced appreciable decomposition. The decomposition products are presumably D^+ and A^- radicals. Therefore, the results of this experiment are by no means conclusive. However, the use of Nujol as a dispersing medium should reduce decomposition as a problem.

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PROPOSITION III

Abstract

It is proposed that attempts be made to measure a Knight
shift for the alkali metall metals in alkali metal-graphite
intercalation compounds. Measurement of carbon-13 shifts are
mentioned as a possible alternative. Some suggestions are
offered for the study of other graphite intercalation compounds.

Hannay et al. (1) have recently discovered that the
potassium, rubidium, and cesium intercalation compounds of
graphite in which graphite carbon layers alternate with layers
of metal atoms are superconductors. However, compounds in which
a metal layer alternates with two graphite layers show no signs
of superconductivity. These facts were related to theoretical
studies (2) which suggest that superconductivity cannot occur
in less than three dimensions. The implication is that the
addition of a second graphite layer between metal layers may
sufficiently restrict the conductivity to two dimensions to pre-
vent superconductivity.

After a brief discussion of the alkali metal intercalation
compounds, we suggest some measurements which should give infor-
mation about their electronic properties, and shed light on the
changes in conductivity and superconductivity with composition.

Graphite can form binary intercalation compounds with the alkali metals and with a large number of molecules. We here consider the spontaneous lamellar compounds as described in the review article by Hennig (3). These compounds can exist in several definite concentration states which differ in the number of graphite layers separating intercalated layers of reactant. Potassium graphite, for example, can exhibit ordered structures from stage 5, which has periodically arranged potassium layers separated by five carbon layers, through stage 1, in which carbon layers alternate with potassium layers.

The electrical resistivity of single crystals of graphite is about 4 to 6 x 10^{-5} Ω-cm. parallel to the planes (a-axis), which corresponds to that of a poor metal. Perpendicular to the planes (c-axis), the resistivity is much higher, being $\overset{<}{\sim}$ $.2$ Ω-cm. (4). The lamellar compounds are more "metallic" than graphite; They exhibit large decreases in resistivity as the reactant concentration is increased (2). The a-axis resistivity decreases steeply at the stage of dilute compound formation, where the intercalated reactant layers are widely separated, and then levels off; the resistance decrease for graphite potassium is about 1/10, and this value is reached at an approximate composition $C_{50}K$. The c-axis resistance decreases more slowly, but continues decreasing through the entire concentration range. By stage 1, corresponding to C_8K, the total change is a factor of .003.

Changes in the in-plane electrical properties can be quali-
tatively understood in terms of a two-dimensional band model (5).
There appears to be a transfer of electrons between graphite and
reactant, leaving the reactant partially or totally ionized.
Since the two-dimensional density of states is very low at the
top of the Fermi level and increases both above and below,
reactants which either add or withdraw electrons increase the
conductivity. A three-dimensional theory is clearly necessary ·
to explain the changes in c-axis conductivity.

The fact that there is a full order of magnitude decrease
in the c-axis resistivity of potassium graphite upon going from
stage 2 to stage 1, whereas the a-axis resistivity remains roughly
constant over this concentration range, might be used to support
the position that full three-dimensionality is a requisite to
superconductivity. The additional metal atoms in stage 1 may
merely add an additional, necessary number of carriers to the
graphite layers, but the constancy of the a-axis conductivity
from stage 2 to stage 1 must then be explained.

As a means of determining the electronic structure of the
alkali metal graphite compounds, we propose the application of
nuclear magnetic resonance techniques. In particular, if the
bonding between reactant and carbon layers is really "metallic"
the reactants should exhibit a Knight shift (6). This phenomenon
is a shift of NMR lines in metals (at fixed frequency) to fields
lower than those in the related ion. This shift is usually an
order of magnitude, or more, larger than ordinary chemical shifts.

It arises from the action of the Pauli paramagnetism of the conduction electrons on the nuclei <u>via</u> the electron-nuclear contact hyperfine interaction.

The fractional shift, $\Delta H/H_O$, is proportional to the average value at the Fermi level of the s-conduction electron wave functions taken at the nuclear position $\langle |u_k(0)|^2 \rangle_{av}$, and the Pauli susceptibility, χ_P. For a cubic environment

$$\frac{\Delta H}{H_o} = \frac{8\pi}{3} \langle |u_k(0)|^2 \rangle_{av.} \chi_P$$

Since the Knight shift is thus sensitive to the properties of the conduction electrons, its determination through the full alkali metal concentration range should tell how bonding changes with concentrations. In particular, any changes found as the stoichiometry is changed from that of stage 2 to that of stage 1 might bear on the superconductivity results.

Unfortunately, potassium, rubidium and cesium all have nuclear spins of greater than 1/2 and moderately large quadrupole moments. Ordinarily the presence of a large quadrupole *moment in* a non-cubic environment, as exists in these compounds, would broaden the NMR signal into indetectability. However, rapid motion will average the quadrupole interaction to zero. In the intercalation compounds, particularly at high temperatures, it is very possible that the metal atoms will be able to diffuse readily enough that their motion will provide the necessary averaging, particularly at higher dilutions. Support for this

is derived from X-ray diffraction studies which indicate that the metal atoms in stage 2 compounds are mobile. (7).

Because of the non-cubic environment, the Knight shift will be anisotropic, which will also cause broadening. Anisotropic Knight shifts have been observed (8), however, and this factor should be insignificant relative to quadrupole effects. .

An alternative (expensive) possibility is to prepare carbon-13 enriched graphite by the pyrolysis of enriched methane, having no quadrupole moment. The conduction electrons on the carbon atoms are primarily in p-type orbitals; this would reduce $\langle |\mu_k(0)|^2 \rangle_{av}$, and therefore the Knight shift. Nevertheless, the effects should still be separable from ordinary chemical shifts.

Although the alkali metal compounds are perhaps the most interesting, it should be mentioned that some of the molecules which form intercalation compounds have nuclei with spin 1/2, and therefore no quadrupole moment to interfere with NMR measurements (1). Other molecules, such as ferric chloride, have nuclei which exhibit Mossbauer resonance, which also exhibits shifts with changes in electron density.

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PROPOSITION IV

Abstract

The linear polyphenyls are considered as a model system
for the attractive electron-electron-interaction due to conduc-
tive conjugation. The system is not found to satisfy the
criterion for superconductivity.

The linear polyphenyls are an obvious model polymer for
calculating the attractive interactions between electrons due
to "conductive conjugation" (1). The plane of symmetry perpen-
dicular to the rings and parallel to the chain allows a classi-
fication into symmetric "conduction" orbitals and antisymmetric,
"localized" orbitals; the latter provide the states necessary
to produce an attraction between electrons in the former. After
solving in the Hückel approximation for the energies and wave
functions, we follow Little (2) in determining the criterion for
superconductivity and in evaluating the matrix elements for a
screened coulomb repulsion and for the attractive interaction.

We consider a polyphenyl of N units with cyclic boundary
conditions: ring N is bonded to ring 1. We chose the "natural"
unit of one phenyl ring as our unit cell, numbering the atoms
as follows:

Site $\underline{n}$
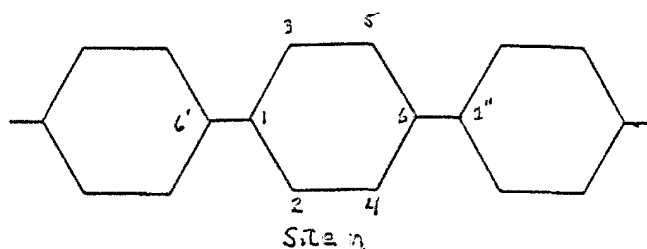
As a consequence of the cyclic boundary conditions the wave functions and energies can be characterized by the pseudo-momentum, k.

This, with the reflection symmetry through the center of the chain, allows us to form the symmetry-adapted orbitals

$$\phi_1^a(k) = \frac{1}{\sqrt{N}} \sum_n e^{-ik\left(n+\frac{1}{6}\right)} \frac{1}{\sqrt{2}} \left(\chi_2^n - \chi_3^n\right) \qquad\qquad \phi_3^s(k) = \frac{1}{\sqrt{N}} \sum_n e^{-ik\left(n+\frac{1}{6}\right)} \frac{1}{\sqrt{2}} \left(\chi_2^n + \chi_3^n\right)$$

$$\phi_2^a(k) = \frac{1}{\sqrt{N}} \sum_n e^{-ik\left(n+\frac{1}{3}\right)} \frac{1}{\sqrt{2}} \left(\chi_4^n - \chi_5^n\right) \qquad\qquad \phi_2^s(k) = \frac{1}{\sqrt{N}} \sum_n e^{-ik\left(n+\frac{1}{3}\right)} \frac{1}{\sqrt{2}} \left(\chi_4^n + \chi_5^n\right) \qquad (1)$$

$$\phi_1^s(k) = \frac{1}{\sqrt{N}} \sum_n e^{-ikn} \chi_1^n \qquad\qquad \phi_4^s(k) = \frac{1}{\sqrt{N}} \sum_n e^{-ik\left(n+\frac{1}{2}\right)} \chi_6^n$$

Here χ_i^n is a carbon 2p-π orbital on ring n, carbon i. The a-orbitals are antisymmetric, the s-orbitals symmetric with respect to reflection. We follow the procedure of measuring energies, ϵ_k, in units of β, the resonance integral, with respect to a zero of energy at α, the coulomb integral. To take into account the possibility of noncoplanarity of the benzene rings, or of longer bonds between them, the interring resonance integral is taken to be β', such that $\beta'/\beta = \delta < 1$.

The secular determinant for the antisymmetric orbitals is

$$\begin{vmatrix} \epsilon_k & e^{-ik/3} \\ e^{ik/3} & \epsilon_k \end{vmatrix} = 0 \qquad (2)$$

which gives

$$\epsilon_k = \pm 1 \qquad \text{(independent of k)} \qquad (3)$$

The antisymmetric orbitals on one ring do not have matrix elements to those on other rings, and therefore, as might have been expected, they have the same energies as would those on an isolated benzene ring. These two levels, separated by $\hbar w = 2\beta$, form the system which will couple electrons in the symmetric orbitals.

The secular determinant for the symmetric orbitals is

$$\begin{vmatrix} \epsilon_k & \delta e^{ik/3} & \sqrt{2}\, e^{-ik/6} & 0 \\ \delta e^{-ik/3} & \epsilon_k & 0 & \sqrt{2}\, e^{-ik/6} \\ \sqrt{2}\, e^{ik/6} & 0 & \epsilon_k & e^{-ik/3} \\ 0 & \sqrt{2}\, e^{-ik/6} & e^{+ik/3} & \epsilon_k \end{vmatrix} = 0 \qquad (4)$$

giving

$$\epsilon_k^4 - (5+\delta^2)\,\epsilon_k^2 + (4+\delta)^2 - 4\delta\cos k = 0 \qquad (5)$$

$$\epsilon_k^2 = \frac{5+\delta^2}{2} \pm 2\left[\left(\frac{\delta^2+3}{4}\right)^2 + \delta\cos k\right]^{1/2} \cdots \quad -\pi \le k \le +\pi$$

$$= 3 \pm 2\left[1 + \cos k\right]^{1/2} \quad \text{if } \underline{\delta = 1}$$

Thus, the two pairs of symmetric orbitals in benzene, one pair at $\epsilon = \pm 1$, the other pair at $\epsilon = \pm 2$, broaden into two pairs of bands as $N \to \infty$ in the polyphenyl. The lower two s-bands and the lower a-band are completely filled, the other bands completely empty, in the neutral molecule. The energy gap separating the filled and unfilled orbitals is

$$\gamma = 2\left\{ \frac{1+\delta^2}{2} - 2\left[\left(\frac{\delta^2+1}{4}\right)^2 + \delta\right]^{1/2}\right\}^{1/2} \beta$$

(6)

$$= 2(3 - 2\sqrt{2}) = .834\ \beta \quad \text{if } \delta = 1$$

If we simplify to $\delta = 1$, the lower two s-bands touch at $k = \pm \pi$, as do the upper two. Then, by using the extended zone scheme, we get two bands, separated by the energy gap γ, with limits on k, $-2\pi \leqslant k \leqslant + 2\pi$.

Reduced Zone Scheme

Extended Zone Scheme
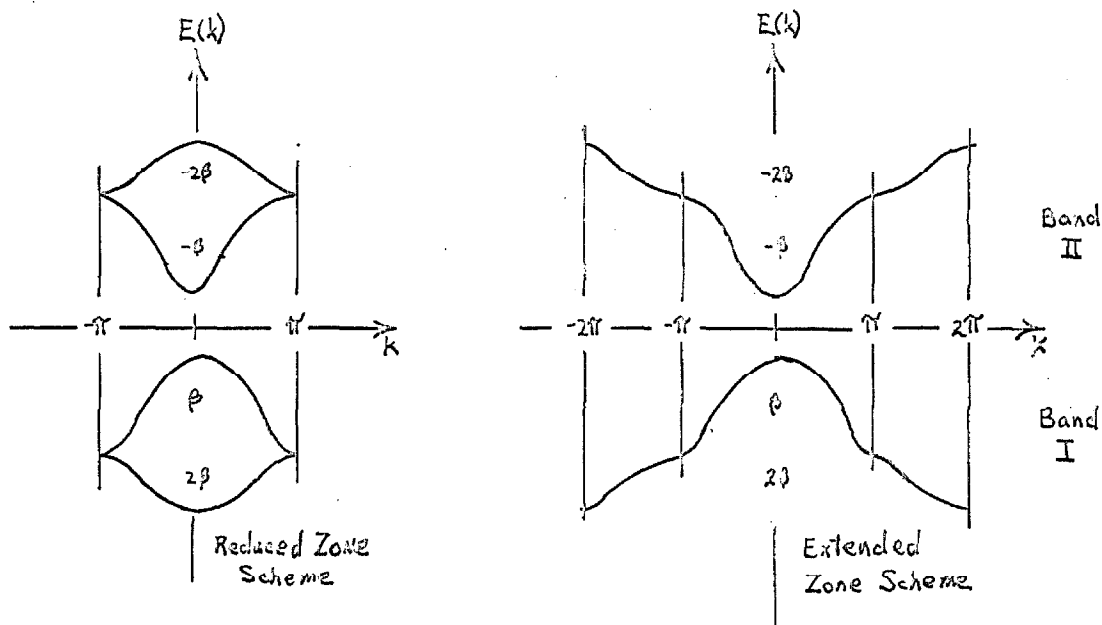
The energy can be rewritten

$$\epsilon(k) = \frac{\beta}{2} \left[2\sqrt{2} \, \sin^2 \frac{k}{4} + \left(\frac{\gamma}{2} \right)^2 \right]^{1/2} \tag{6}$$

Using this expression for the energy, we can either integrate Little's equation 3.1 without approximation, or use his equation 3.4 to give the criterion for superconductivity in the presence of the gap, γ . The integration, with the upper limit ℏw gives

$$|V| = |V_{coul.} + V_{attr.}| \gtrsim 1.29 \, \beta/N \tag{7}$$
$$\gtrsim 2.74 \, eV/N$$

where we take $\beta = -2.2$ eV. Of course the sign of V must be negative.

We must now calculate the coulomb repulsion and electron-coupled attraction terms for the s-states. The s-states of importance are those where the semiconducting gap is smallest, near k = 0, so that promoting an electron from the filled to the unfilled band costs the least energy. Therefore, matrix elements need only be calculated for s-states with k → 0. Then, since the interactions between s and a-states conserve momentum, only those a-states with k → 0 occur in matrix elements. For k = 0, the wavefunctions are just sums of the related benzene wave function for the individual sites. The s-band functions are

$$\psi_{II}(0) = \frac{1}{\sqrt{N}} \sum_n \frac{1}{\sqrt{12}} \left[\phi_3^5(0) - \phi_4^5(0) \right] + \frac{1}{\sqrt{3}} \left[\phi_1^5(0) - \phi_2^5(0) \right] \tag{8}$$

$$\psi_I(0) = \frac{1}{\sqrt{N}} \sum_n \frac{1}{\sqrt{12}} \left[\phi_3^5(0) + \phi_4^5(0) \right] - \frac{1}{\sqrt{3}} \left[\phi_1^5(0) + \phi_2^5(0) \right]$$

The a-band functions are

$$\psi_{A2}(0) = \frac{1}{\sqrt{2N}} \sum_n \left[\phi_A^1(0) - \phi_A^2(0) \right] \qquad \epsilon = -\beta$$

$$\psi_{A1}(0) = \frac{1}{\sqrt{2N}} \sum_n \left[\phi_A^1(0) + \phi_A^2(0) \right] \qquad \epsilon = +\beta \tag{9}$$

In evaluating the coulomb repulsions between s-state electrons we follow Little; we assume that only one-center terms contribute and that these are screened. In the one-center approximation all contributing coulomb matrix elements are equal:

$$V_{coul.} = (II|II)_{scr.} = (II|II)_{scr.} = (II|II)_{scr.} \tag{10}$$

$$= \int \psi_{(1)}^{I} \psi_{(1)}^{\mp} \frac{e^{-\lambda r_{12}}}{r_{12}} \psi_{(2)}^{\mp} \psi_{(2)}^{I} d^3r_1 d^3r_2 = \frac{1}{4N} \int |\chi_{(1)}|^2 \frac{e^{-\lambda r_{12}}}{r_{12}} |\chi_{(2)}|^2 d^3r_{12}$$

$$= 1.5 \; e^2/N$$

We have used Little's approximation in evaluating the one-center integral.

The matrix element for the attractive interaction involves the scattering of a "symmetric" electron from band I to band II with the excitation of an "antisymmetric electron from A1 to A2, and the transfer of wavevector Q. We again consider the limit k, Q = 0. We consider this interaction to be unscreened. We

take only one-center terms, and evaluate them in the same way that Little evaluated the screened integrals. Then,

$$\frac{U}{N} attr. = \int \psi_{A,2}(1) \psi_{A,1}(1) \frac{1}{r_{12}} \psi_{II}(2) \psi_{I}(2) \, d^3 r_1 \, d^3 r_2$$

$$= \frac{.083}{N} \int |\chi_i(1)|^2 \frac{1}{r_{12}} |\psi_i(2)|^2 \, d^3 r_{12}$$

$$= 1.41 \, eV/N$$

(11)

We recall the formula for the attractive interaction

$$V_{attr.} = \frac{1}{N} \frac{2\hbar\omega \, |U_{attr.}|^2}{(\Delta\epsilon)^2 - (\hbar\omega)^2}$$

(12)

Here $\hbar w = 2\beta$; because of the semiconducting energy gap, $\Delta\epsilon = .834\beta$. Thus the gap actually enhances the effectiveness of the interaction. Again using $\beta = -2.2$ eV, and using the result in equation 11, we get for equation 12

$$V_{attr} = -\frac{|U_{attr}|^2}{1.8 \, N} eV \geq -1.2 \, eV/N$$

(13)

Thus,

$$\langle V \rangle = V_{coul} + V_{attr}$$

(14)

$$= \frac{1.5}{N} - \frac{1.2}{N} = +.3 \, eV/N > 0$$

Therefore, our model does not merely fail to satisfy the necessary inequality, equation 7; the interaction is not even attractive. In fact, it can be seen that not even complete neglect of coulomb repulsions would be sufficient to satisfy equation 7.

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PROPOSITION V

Abstract

We propose to study the interaction of paramagnetic copper (II) ions with DNA by measuring the water proton relaxation enhancement and changes in phosphorous-31 nuclear magnetic resonance upon binding of the copper.

Eichhorn and Clark (1) have recently studied the effect of copper(II) ions on the thermal denaturation of DNA. They found that the presence of cupric ion causes the unwinding of the DNA helical structure, and that the unwound strands can apparently be totally rewound into the native double-helical configuration. We propose that nuclear magnetic resonance (NMR) measurements of the effects of binding copper ions to DNA on the relaxation rates of water protons (2) and of DNA phosphorous atoms (3) can give important information about the nature of the binding.

We first discuss briefly the nature of the measurements. A paramagnetic ion in water increases the longitudinal proton relaxation time for those molecules in its hydration sphere. (The hydration sphere can exchange with the bulk water.) Upon complexing of the ion, its immediate environment is changed, and the relaxation rate of the water will also change. A useful experimental parameter is the relaxation enhancement factor.

$$\varepsilon = \frac{R^*}{R}$$

R is the relaxation rate due to the ion in water and R^* the rate due to the ion in the presence of the binding agent. The observed value of ϵ will be a weighted average of the enhancement factors of the free and bound ions. Generally, $\epsilon > 1$ for binding at exterior sites (eg. phosphate groups of DNA) and $\epsilon < 1$ for binding to sites inaccessible to the water molecules (interior sites).

When a paramagnetic ion binds at a phosphate group, the relaxation rate of the phosphorous-31 nucleus is also changed. If this change is measured in conjunction with the proton enhancement factor it is possible to tell at what ion concentration binding to the phosphates becomes important.

We now discuss some of the characteristics of the DNA-copper (II) ion system, as studied by Eichhorn and Clark (EC). The addition of less than .4 moles of ion per mole of nucleotide increases T_m, the midpoint of the thermal denaturation curve of DNA. EC suggest this stabilizing effect at low concentrations results *from binding to the phosphates.* T_m is then drastically lowered by increasing concentrations of copper. There is a break in the slope of the curve of T_m versus copper concentration at a molar ratio of 1.5 copper/nucleotide. EC suggest that this may correspond to one copper bound to each phosphate, and an additional copper bound to two nucleotides. However, they reach no definite conclusions about the stoichiometry because they do not know if there exists any unbound copper.

The thermal denaturation (unwinding of DNA strands) of DNA in the presence of copper ions, in solutions of low electrolyte

concentration, cannot be reversed by cooling. However, upon

increase of the ionic strength, the DNA can be totally renatured.

The finding that the denaturation by copper (II) can be totally

reversed is contrary to usual experience; EC suggest that, while

the DNA is denatured, the single strands are held "in register"

by the copper ions.

Finally, the copper denatured DNA seems to be very

extensively aggregated; this is suggested by its very high sedi-

mentation velocity. Their picture of the copper-denatured state

contains copper ions coordinated to the bases and interposed

between complementary strands, breaking hydrogen bonds and

destroying the secondary structure.

We suggest that proton relaxation enhancement measurements

combined with phosphorous-31 NMR can supply important information

about the nature of the binding of copper (II) ions to DNA. By

studying the proton relaxation times for different copper/nucleo-

tide ratios it should be possible to determine the number of

different kinds of binding sites. Presumably there are at least

two, one at the phosphates and one at the base itself. If we

assume for simplicity that there are only two, then it should be

possible to estimate their binding parameters. In any case,

phosphorous NMR should show whether the phosphate site is the

first to bind, checking on the suggestion EC made about the

nature of the complex at low copper concentration.

It is also possible by use of the relaxation measurements

to estimate the fraction of bound copper ions. This information

permits a check of the stoichiometry of binding at the copper/ nucleotide ratio of 1.5, where the break in the T_m versus copper concentration curve occurs.

Finally, and perhaps of primary interest, the proton relaxation measurements might give information about the nature of the copper complex in the highly aggregated denatured state. If a large fraction of the copper ions bind the bases strands together and keep the bases in register, this fraction may be sufficiently isolated from the water that its enhancement factor would be less than unity, indicative of an interior site. Thus, if one of the binding sites is experimentally found to have $\varepsilon < 1$, this will be strong evidence for such binding.

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