

PROGRESS IN INORGANIC CHEMISTRY

EDITED BY

STEPHEN J. LIPPARD
DEPARTMENT OF CHEMISTRY
COLUMBIA UNIVERSITY
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INORGANIC CHEMISTRY

Volume 20

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Contents

One-Dimensional Inorganic Complexes

By Joel S. Miller and Arthur J. Epstein, *Webster Research Center,
Xerox Corporation, Webster, New York* 1

The Study of Electron Distributions in Inorganic Solids: A Survey of Techniques and Results

By B. C. Tofield, *Bell Telephone Laboratories, Holmdel,
New Jersey* 153

The Temperature-Dependence of the Apparent Energy of Activation

By Berta Perlmutter-Hayman, *Department of Physical Chemistry,
The Hebrew University of Jerusalem, Jerusalem, Israel* 229

Applications of Carbon-13 NMR in Inorganic Chemistry

By M. H. Chisholm and S. Godleski, *Department of Chemistry,
Princeton University, Princeton, New Jersey* 299

Subject Index 437

Cumulative Index, Volumes 1-20 455

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One-Dimensional Inorganic Complexes

by **JOEL S. MILLER** and **ARTHUR J. EPSTEIN**

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One-Dimensional Inorganic Complexes	2
Part I: Physics of One Dimension	4
I. Electrical Properties in One Dimension	4
A. Band Theory	5
1. Tight-Binding Band Theory	6
2. Properties of Electron Energy Band Systems	11
3. Peierls Transition	16
B. Limitations of Band Theory	20
1. Electron-Electron Coulomb Repulsion—Mott Transition	20
2. Disorder in One-Dimensional Systems	25
3. Interrupted Strand Model	26
C. Polaron and Exciton	27
1. Polarons	27
2. Excitons	28
D. Superconductivity	29
1. BCS. Phonon Mechanism for Superconductivity	29
2. W. A. Little. Exciton Mechanism for Superconductivity	30
3. H. Fröhlich. Nonpairing Model for Superconductivity	31
E. Design of a One-Dimensional Conducting System	33
II. Magnetic Properties in One Dimension	34
A. The Dimer Pair. Singlet-Triplet Behavior	35
B. Magnetic Chains	35
C. Three-Dimensional Effects	38
Part II: One-Dimensional Inorganic Systems	40
I. Columnar Inorganic Systems	40
A. Highly Conducting One-Dimensional Systems	42
1. Tetracyanoplatinate Complexes	43
a. Chemical Properties	43
b. Physical Properties	49
2. Bis(oxalato)platinate Complexes	72
3. Iridium Halocarbonyl Complexes	75
a. Halotricarbonyliridate complexes	76
b. Derivatives of the Halotricarbonyliridate complexes	78
c. Dihalodicarbonyliridate Complexes	79
4. Multidimensional One-Dimensional Systems	83
a. Mixed Valent Platinum Oxides	83
b. Polymercury Cations	87

B. Poorly Conducting One-Dimensional Materials	90
1. Metal Halide and Haloamine Complexes	90
a. Metals in the Same Oxidation State	90
b. Metals in Different Oxidation States	93
c. Miscellaneous Platinum Haloamines	97
2. Rhodium and Iridium Dicarbonyl Acetylacetonates	97
3. α -Diimine Metal Complexes	99
4. Dithiolene Complexes	104
5. Complexes with Macrocyclic Ligands	108
C. Potential One-Dimensional Systems	110
1. Polyplatinum Anions	110
2. Metal Isocyanide Complexes	112
3. Metal Fulminate Complexes	113
4. Platinum Blue	113
5. Miscellaneous Materials	114
D. Conducting Inorganic Polymers	115
1. Polydentate Ligand Metal Polymers	115
2. Ferrocene Polymers	115
3. Metal-Cyano Polymers	118
4. Poly(sulfurnitride)	118
II. One-Dimensional Magnetic Systems	124
A. Antiferromagnetically Coupled Systems	125
B. Ferromagnetically Coupled Systems	131
Summary	132
Acknowledgement	135
References	135

ONE-DIMENSIONAL INORGANIC COMPLEXES

In the past decade there has been considerable interest in the chemical and physical properties of one-dimensional materials. Activity has recently increased due to the demonstration of the existence of a one-dimensional metallic state and the observation of phenomena such as metal-insulator transition, and cooperative magnetic interaction. This has led to a large impact on concepts utilized in chemistry and in solid state physics. The chemistry of mixed valent and partially oxidized complexes has come under extensive study. The physical properties of one-dimensional conducting and magnetic systems have been critically examined both theoretically and experimentally.

Both inorganic and organic examples of one-dimensional materials have been studied. They have been the subject of a number of recent excellent reviews covering specific aspects of this field. The physics of organic one-dimensional materials, generally based on 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ), has been reviewed by Shchegolev (375) and Zeller (433). The design and synthesis of organic metals have been detailed by Garito and

Heeger (153) and Yagubskii and Khidekel' (429). A classification scheme for organic charge transfer complex has been presented by Soos (563). Heeger and Garito (496) have detailed the physical properties and current interpretation of the highly conducting tetrathiofulvalenium 7,7,8,8-tetracyano-*p*-quinodimethanide (TTF)(TCNQ) salts. One-dimensional inorganic systems have been reviewed by Krogmann (238) and Thomas and Underhill (398) from a chemistry viewpoint as well as by Zeller (433) and Shchegolev (375) from a physics viewpoint. Recently several short reviews on one-dimensional inorganic complexes by Underhill (569), Gomm (487) and Aderjan et al. (441) have appeared. General reviews on mixed valent complexes have been comprehensively detailed by Robin and Day (355), Hush (198a) and Allen and Hush (198b). Recently Day has written a pair of reviews pertaining to mixed valency and one-dimensional complexes (471). Miller (537) has summarized the properties associated with one-dimensional inorganic complexes. The properties of one-dimensional systems which exhibit ferro- and antiferromagnetic couplings have been the subject of two recent reviews (439, 498).

In light of the recent rapid advances in the field, we feel that a broad review of those inorganic materials that form a columnar structure in the solid state is useful at this time. Both chemical and physical properties of these materials are described. This review is divided into two parts. Part I introduces physical concepts useful in describing electrical and magnetic properties of one-dimensional systems, with emphasis on the former. One electron band theory is reviewed as a framework for discussing cooperative phenomena. The potential effects of electron correlation, crystallographic disorder, and crystal morphology are introduced as are the concepts of polarons and excitons. Known and proposed mechanisms for superconductivity are reviewed including the concept of charge density waves and its potential applications to one-dimensional metals. The necessary conditions, as currently understood, for the design of a one-dimensional metal are summarized at various points. The potential cooperative behaviors of insulating one-dimensional magnetic systems are surveyed.

Part II surveys the inorganic materials which exhibit or potentially exhibit a columnar structure. Emphasis is placed on square planar third-row transition metal complexes which exhibit the properties of anisotropic electrical conductivity and the first-row transition metal complexes which exhibit anisotropic cooperative magnetic behavior. The measured chemical and physical properties of the known one-dimensional inorganic complexes are summarized and a number of potentially one-dimensional materials are surveyed. The known one-dimensional magnetic systems are then presented. An extensive reference list including citations through the beginning of 1975 is included to make it easy for the reader to go further into areas of his particular interest.

PART I: PHYSICS OF ONE DIMENSION

Classification of materials as "one-dimensional" is somewhat arbitrary. The materials included in this review are crystalline solids that are considered to have one-dimensional properties because there is a gross anisotropy in the value of at least one intensive variable of the system, for example, conductivity (resistivity) or magnetic susceptibility. In this context "gross" implies a factor of order 100 or greater between the value of a variable along and orthogonal to a preferred direction. Because this anisotropy factor is never infinite, three-dimensional effects may modify the dominant one-dimensional behavior. This is particularly true in the case of one-dimensional insulating magnetic chains that show three-dimensional magnetic ordering at sufficiently low temperatures. The presence of anisotropic behavior in a parameter does not imply that a system is anisotropic in all variables. For example, lattice vibrations usually retain their three-dimensional behavior even when one-dimensional electrical behavior is present.

There are several different types of solid state one-dimensional systems. One large category of such materials is covalently bonded polymers. Organic examples such as polyethylene or polystyrene are numerous. Inorganic examples such as poly(sulfurnitride) are fewer in number and are generally not as well characterized. Therefore they do not receive a prominent place in this review. The physics of one dimension will be discussed in terms of the more common configuration of well-defined molecules stacked in linear parallel rows or strands to form one-dimensional columns or chains. The shape of these molecules, their electronic structure, and their overlap with their neighbors determine the electrical and magnetic properties of the one-dimensional solid. Emphasis will be placed on the electrical properties of these materials. Section I introduces physical concepts useful in describing one-dimensional conducting systems. Section II briefly discusses magnetic effects in one dimension.

I. ELECTRICAL PROPERTIES IN ONE DIMENSION

The recent experimental confirmation of the existence of one-dimensional metallic systems has led to a rapid increase in the experimental and theoretical study of these conducting systems. The objective of this section is to acquaint the reader with the physical basis of the concepts currently being used to explain the experimental results. Emphasis is given to the development of one electron band theory because of its central importance in the description of metals and understanding the effects of lattice distortion (Peierls transition), electron correlation, disorder potentials, and interruptions in the strands. It

is becoming increasingly clear, however, that the one electron models are not sophisticated enough to represent the detailed behavior of these materials and that cooperative interactions (e.g., electron-phonon interaction and electron-electron correlation) need to be included. Polarons, excitons, charge density waves, and superconductivity are introduced to illustrate cooperative phenomena. Finally, the necessary conditions, as currently understood, for the design of a one-dimensional metal are summarized at various points.

A. Band Theory

The important physical properties of simple metals and, in particular, the alkali metals can be understood in terms of a free electron model in which the most weakly bound electrons of the constituent atoms move freely throughout the volume of the metal (231). This is analogous to the free electron model for conjugated systems (365) where the electrons are assumed to be free to move along the bonds throughout the system under a potential field which is, in a first approximation, constant (the particle-in-a-box model). The free electron approach can be improved by replacing the constant potential with a periodic potential to represent discrete atoms in the chain (365). This corresponds to the nearly free electron model (231) for treating electrons in a metal.

If the delocalized electrons interact strongly with atomic sites, both of these approaches for calculation of molecular energy levels are inadequate. In this case, a better representation for the electrons on the molecule is obtained if a linear combination of atomic orbitals (LCAO) is used to describe the electron wavefunction (330). Tight-binding band theory is the analogous approach for crystalline solids (155a). When the electron-site interaction is large, the atomic (or molecular) orbitals localized on each site are combined to represent an electron delocalized throughout the crystal. This method has been applied with particular success to the d bands of transition metals (437).

The highly conducting one-dimensional inorganic materials are generally based on third-row transition metal complexes stacked with collinear metal atoms [e.g., $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}(\text{H}_2\text{O})_3$]. Many of their properties are evaluated in terms of conduction electrons in a delocalized energy band formed by overlap of the d_{22} orbitals. One-electron tight-binding band theory has been used as a starting point for evaluating measurements on both the highly conducting one-dimensional inorganic and organic systems (8, 349). This theory is reviewed to illustrate and emphasize the dependence of electron energy bandwidth on the distance between molecules and the role of the electron wavevector k (155a, 543). In individual systems, if the band formed through molecular overlap is sufficiently wide and the electron density sufficiently uniform in space (e.g., sigma type overlap giving almost constant electron

density), the electronic properties may be better described by the free electron model. Some of the characteristic properties of free electron metals are enumerated in Section I.A.2.

1. Tight-Binding Band Theory

Tight-binding band theory is described first for the case of distinct molecules uniformly stacked with equivalent separation, \mathbf{a} , between each site, Fig. 1. The potential in which the electron moves, $V(\mathbf{r})$, is periodic, $V(\mathbf{r} + \mathbf{a}) = V(\mathbf{r})$. Here \mathbf{r} is the vector coordinate for electrons and \mathbf{a} is the vector length between equivalent sites in the chain. Vector notation is used because of the three-dimensional extent of the individual molecules. Assuming the chain axis is parallel to the z -axis, $\mathbf{a} = a\mathbf{z}$ (\mathbf{z} is a unit vector along the z -axis).

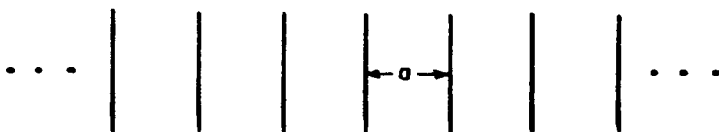


Fig. 1. Uniform chain of molecules with separation a .

The periodic potential may be viewed as a sum of the potentials at each site in the chain, $V(\mathbf{r}) = \sum V'(\mathbf{r} - n\mathbf{a})$ where $V'(\mathbf{r} - n\mathbf{a})$ is the potential of a single molecule at site $n\mathbf{a}$ (n is an integer). The Hamiltonian for the electrons in such a system is

$$H = -\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \quad (1)$$

where \hbar is Planck's constant divided by 2π , m the electron mass and ∇^2 is the Laplacian operator. The first term on the right is the kinetic energy of the electrons moving through the lattice. The second term, $V(\mathbf{r})$, is the periodic potential mentioned above. The electrons are represented by the wavefunction, ψ , which is a solution to the Schrödinger equation, Eq. 2:

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) - E \right) \psi(\mathbf{r}) = 0 \quad (2)$$

The operator within the parentheses remains the same if $(\mathbf{r} + n\mathbf{a})$ is substituted for \mathbf{r} . The Bloch theorem (231, 437) states that because of this periodicity, $\psi(\mathbf{r} + \mathbf{a})$ must be the same as $\psi(\mathbf{r})$ to within a phase factor, that is $\psi(\mathbf{r} + \mathbf{a}) = e^{i\mathbf{k} \cdot \mathbf{a}} \psi(\mathbf{r})$. Each eigenfunction that satisfies Eq. (2) has a wavevector \mathbf{k} associated with it such that translation by a lattice vector $n\mathbf{a}$ is equivalent to multiplying the eigenfunction, $\psi_{\mathbf{k}}(\mathbf{r})$, by the phase factor $\exp(i\mathbf{k} \cdot n\mathbf{a})$.

For an isolated molecule, electrons are assumed to be in molecular orbitals, $\varphi_{\alpha}(\mathbf{r})$, of energy E_{α} . If the molecule is located at site \mathbf{l} , then the electrons are in orbitals $\varphi_{\alpha}(\mathbf{r} - \mathbf{l})$. Now consider N of these molecules to be stacked into a uniform chain with a separation, \mathbf{a} , between each site (i.e., $\mathbf{l} = n\mathbf{a}$), Fig. 1. Movement of the electrons along this chain is described by the Schrödinger equation, Eq. 2. It is seen that

$$\psi_{\alpha\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{N}} \sum_{\mathbf{l}} e^{i\mathbf{k}\cdot\mathbf{l}} \varphi_{\alpha}(\mathbf{r} - \mathbf{l}) \quad (3)$$

is an electron wavefunction that satisfies the Bloch theorem. This function extends over the entire chain and is a sum of localized molecular orbitals multiplied by a phase factor $\exp(i\mathbf{k}\cdot\mathbf{l})$, Fig. 2. While $\psi_{\alpha\mathbf{k}}(\mathbf{r})$ is not an exact eigen-

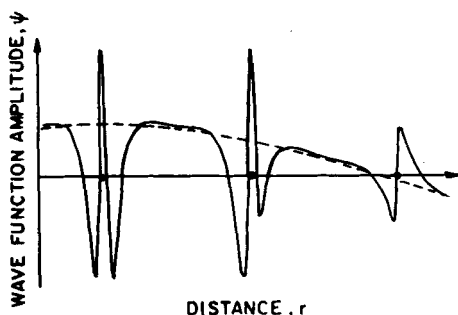


Fig. 2. Electron wavefunction in a tight-binding solid (solid line). The dashed line is the multiplicative phase factor used in obtaining ψ (437).

function of Eq. 2, it is often a good approximation and, as such, may be used to calculate the energy levels for electrons in the periodic chain. This may be done for each value of \mathbf{k} . As shown below, each isolated molecular energy level leads to a band of allowed energies in the solid. In this approximation, the energy $E_{\alpha}(\mathbf{k})$ of an electron of wavefunction $\psi_{\alpha\mathbf{k}}$ is

$$E_{\alpha}(\mathbf{k}) = \frac{\int \psi_{\alpha\mathbf{k}}^*(\mathbf{r}) H \psi_{\alpha\mathbf{k}}(\mathbf{r}) d^3r}{\int \psi_{\alpha\mathbf{k}}^*(\mathbf{r}) \psi_{\alpha\mathbf{k}}(\mathbf{r}) d^3r} \quad (4)$$

where H is the total Hamiltonian (energy) for an electron in the periodic chain Eq. 1. The denominator of Eq. 4 is the normalization factor and is approximately equal to one, assuming the molecular orbitals centered at different sites have very small overlap.

Using Eq. 3, the integrals in Eq. 4 may now be written as:

$$E_{\alpha}(\mathbf{k}) = \frac{1}{N} \sum_{\mathbf{l}, \mathbf{l}'} e^{i\mathbf{k}\cdot(\mathbf{l}-\mathbf{l}')} \int \varphi_{\alpha}^*(\mathbf{r}-\mathbf{l}') H \varphi_{\alpha}(\mathbf{r}-\mathbf{l}) d^3r \quad (5)$$

or

$$E_{\alpha}(\mathbf{k}) = \sum_{\mathbf{h}} e^{i\mathbf{k}\cdot\mathbf{h}} E_{\alpha}(\mathbf{h}) \quad (6)$$

where $\mathbf{h} = (\mathbf{l} - \mathbf{l}')$ and $E_{\alpha}(\mathbf{h})$ is given by

$$E_{\alpha}(\mathbf{h}) = \int \varphi_{\alpha}^*(\mathbf{r} + \mathbf{h}) H \varphi_{\alpha}(\mathbf{r}) d^3r \quad (7)$$

Equation 7 is the matrix element of the full Hamiltonian, Eq. 1, between the molecular orbitals centered about sites $(\mathbf{l} - \mathbf{l}') = \mathbf{h}$ and $(\mathbf{l} - \mathbf{l}') = \mathbf{0}$ ($\mathbf{l} = \mathbf{l}'$). Because the molecular orbitals $\varphi_{\alpha}(\mathbf{r} + \mathbf{h})$ fall off exponentially with distance from site \mathbf{h} , $E_{\alpha}(\mathbf{h})$ becomes exponentially small for all but the on-site [$\mathbf{h} = \mathbf{0}$, $E_{\alpha}(\mathbf{h} = \mathbf{0}) \equiv E_{\alpha}^0$] and nearest neighbor [$\mathbf{h} = \pm \mathbf{a}$, $E_{\alpha}(\mathbf{h}) \equiv E_{\alpha}^1$] integrals. Therefore, including only nearest neighbor interactions, Eq. 6 becomes

$$E_{\alpha}(\mathbf{k}) = E_{\alpha}^0 + E_{\alpha}^1 e^{i\mathbf{k}\cdot\mathbf{a}} + E_{\alpha}^1 e^{-i\mathbf{k}\cdot\mathbf{a}} = E_{\alpha}^0 + 2E_{\alpha}^1 \cos(\mathbf{k}\cdot\mathbf{a}) \quad (8)$$

This is analogous to the simple Hückel approximation in molecular orbital calculations (365). Since it is assumed that the electrons are constrained to a single chain, i.e., \mathbf{k} is parallel to \mathbf{a} , $\mathbf{k}\cdot\mathbf{a}$ is equal to ka . Vector notation is therefore discontinued. Because of the very small overlap assumed it is seen from Eq. 7 (with $\mathbf{h} = \mathbf{0}$) that

$$E_{\alpha}^0 = E_{\alpha} \quad (9)$$

where E_{α} is the energy associated with the isolated molecular orbital φ_{α} . The transfer integral or transfer matrix element t_{α} associated with molecular orbital φ_{α} is defined as

$$t_{\alpha} \equiv -E_{\alpha}^1 \quad (10)$$

Equation 8 can now be written as

$$E_{\alpha}(k) = E_{\alpha} - 2t_{\alpha} \cos(ka) \equiv \varepsilon_{\alpha}(k) \quad (11)$$

This is the fundamental result of this tight-binding band theory calculation. Hence, as N molecules are brought together, their orbitals overlap and the allowed energy levels spread out from that of the isolated molecule E_{α} . A band of N states is formed from each molecular orbital φ_{α} with energies given by Eq. 11. As each state can accommodate up to two electrons (of opposite spin), each band may accommodate up to $2N$ electrons. The width of this band of electron states, W_{α} , is equal to $4t_{\alpha}$ and is directly related to and very sensitive to the degree of overlap of the molecular orbitals. Figure 3 schematically illus-

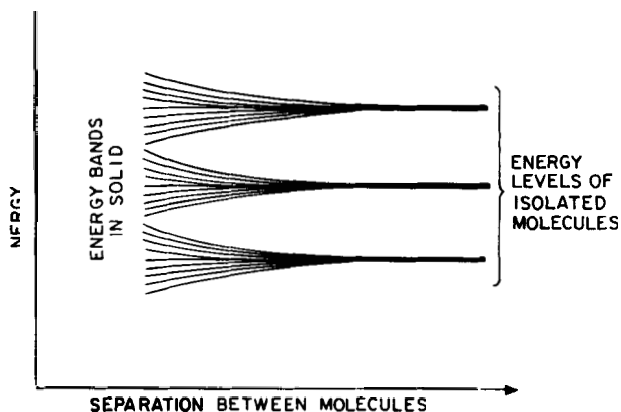


Fig. 3. Schematic illustration of the energy levels of isolated molecules spread into bands as the molecules are brought closer together.

trates the energy bands forming in the solid from the molecular levels as isolated molecules are brought closer together.

The energy versus wavevector k curve for a single energy band in the solid is shown in Fig. 4. The allowed values of k are quantized, limited to N values

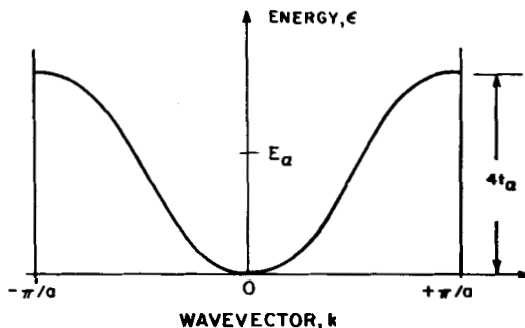


Fig. 4. Energy versus wavevector for electrons in a one-dimensional tight-binding band (from Eq. 11).

(because there are N molecules in the chain) evenly distributed between $-\pi/a$ and $+\pi/a$, and have a density, $\rho(k) = Na/2\pi$, called a density of states in k space per spin. (The Pauli exclusion principle allows only one electron of each spin value to have a particular k value.) The density of states per unit energy per spin, $\rho(\epsilon)$, is obtained from $\rho(k)$ through

$$\rho(\varepsilon)d\varepsilon = \rho(k) \left(\frac{\partial k}{\partial \varepsilon} \right) d\varepsilon \quad (12)$$

Using Eq. 11 one can evaluate the density of states per unit energy per spin for a tight-binding energy band of width $4t$:

$$\rho(\varepsilon) = \frac{N}{2\pi} (4t^2 - \varepsilon^2)^{-1/2} \quad (13)$$

The energy, ε , is measured with respect to the center of the band (E_α defined as zero). This is schematically shown in Fig. 5. The value of $\rho(\varepsilon)$ for the highest occupied energy in a partially filled band is directly related to measurable parameters (e.g., susceptibility).

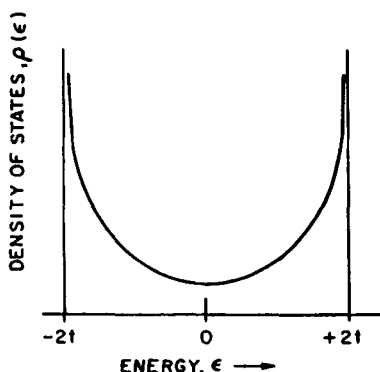


Fig. 5. Schematic illustration of the density of states per unit energy for a one-dimensional tight-binding band. $\rho(\varepsilon)\Delta\varepsilon$ is the number of electrons of the same spin which can be accommodated in an energy range $\Delta\varepsilon$ centered at ε_1 . The bandwidth, W , is $4t$.

A tight-binding calculation (570) of the allowed energy bands may be performed for the case where the molecules in the chain have alternate spacings (dimerized chain) of a_1 and a_2 ($a_1 < a_2$), Fig. 6. In this case one derives two allowed energy bands from each molecular orbital φ_α . Referring to Eqs. 7 and 10, one may now distinguish two transfer matrix elements $t_{\alpha 1}$ and $t_{\alpha 2}$, given by

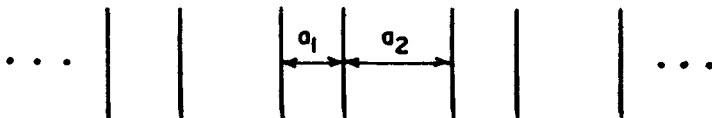


Fig. 6. Dimerized chain of molecules with alternate separation a_1 and a_2 .

$$t_{\alpha i} = - \int \varphi_{\alpha}^*(\mathbf{r} + \mathbf{a}_i) H \varphi_{\alpha}(\mathbf{r}) d^3r \quad (14)$$

Assuming $E_{\alpha} = 0$, the allowed electron energies are now given by

$$E_{\alpha}(k) = \pm \{t_{\alpha 1}^2 + t_{\alpha 2}^2 + 2t_{\alpha 1} t_{\alpha 2} \cos[(a_1 + a_2)k]\}^{1/2} \quad (15)$$

$E_{\alpha}(k)$ is shown in Fig. 7 in a reduced zone scheme (231). There are a total of $N/2$ states in each of two bands of width $E_b = 2|t_{\alpha 2}|$ and an energy gap between them of $E_g = 2(|t_{\alpha 1}| - |t_{\alpha 2}|)$. Each state may accommodate two electrons (of opposite spin), allowing N electrons per band or $2N$ electrons for both bands together. Examining Eq. 15, when a_1 equals a_2 (or equivalently, when $t_{\alpha 1}$ equals $t_{\alpha 2}$), the energy bands for the "dimer" case become identical with the results derived for the uniform chain, Eq. 11.

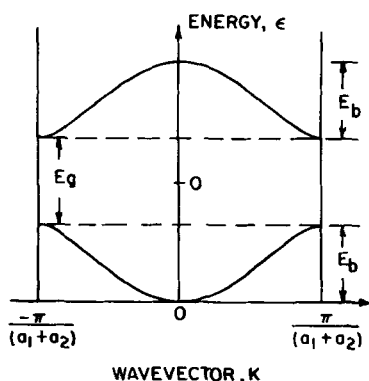


Fig. 7. Energy bands for a dimerized chain in a reduced zone scheme (231);

$$E_b = 2|t_{\alpha 2}|, E_g = 2(|t_{\alpha 1}| - |t_{\alpha 2}|).$$

Summarizing these tight-binding band theory results, when N molecules form a uniform chain, each molecular orbital φ_{α} of energy E_{α} forms a band of states of width $4t_{\alpha}$ capable of holding $2N$ electrons; if these N molecules formed a dimerized chain, two bands of states would be formed with each band capable of holding N electrons. Similarly if the N molecules in the chain group as N/z z -mers, each molecular orbital φ_{α} will form z bands of states capable of holding $2N/z$ electrons. The z bands are separated from each other by energy gaps.

2. Properties of Electron Energy Band Systems

Figure 8 schematically illustrates the distinction between various electrical behaviors possible for ideal materials where a band description applies:

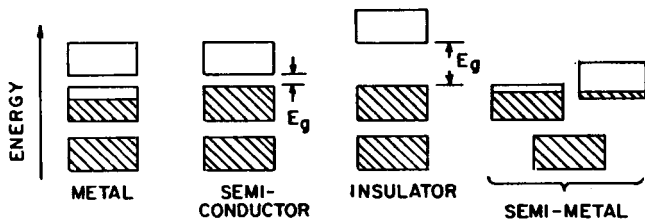


Fig. 8. Schematic illustration of the occupation of the allowed energy bands (rectangles) for a metal, semiconductor, insulator, and semimetal.

1. Metal: A material with a partially filled energy band.
2. Semiconductor and Insulator: A material with filled and empty energy bands (at $T = 0^\circ\text{K}$), and an energy gap E_g between highest filled and lowest empty bands.
3. Semimetal: A material which formally has only completely filled and completely empty bands, but which has, due to overlap of a formally filled and a formally empty band, two or more partially filled bands and behaves as a metal instead of as a semiconductor or insulator.

Note that these formal definitions do not involve the conductivity (\equiv resistivity⁻¹) of the materials, only their energy bands and relative occupation. A short description of the distinguishing properties (231, 232, 436, 437) of each follows:

a. Metals and Semimetals. It is the partially filled electron energy band that gives a metal its distinguishing features. A partially filled energy band implies that there are unoccupied energy levels infinitesimally separated in energy and wavevector k from the occupied levels. This allows a net change in electron momentum ($\hbar k$) when an electric field is applied. Hence, metals are good conductors. Their conductivity is limited by scattering of the electrons with lattice vibrations (phonons) and impurities, defects, and surfaces. In an ideal metal the resistivity decreases as the temperature is lowered (fewer lattice vibrations are present to scatter the electrons) until a residual value of the resistivity due to imperfections and impurities is reached. This is clearly seen for the three-dimensional metal, sodium, in Fig. 9. For such one-dimensional metals as the partially oxidized tetracyanoplatinate systems, the resistivity is also seen to drop as the temperature is lowered from room temperature, but a transition to an insulating state occurs because of effects not included in the one-electron band picture presented above.

Simple (free electron theory) metals have a number of other characteristic properties, including:

1. Pauli spin susceptibility. Unlike free spin systems, the magnetic suscep-

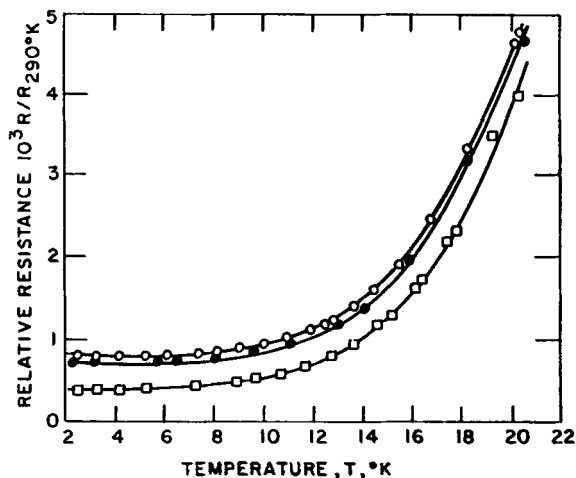


Fig. 9. Temperature dependence of the relative resistance of sodium (278), a three-dimensional metal. The three curves are for three different samples. The plots show how the residual resistivity may vary from sample to sample.

tibility of ideal metals is temperature independent and is given by $\chi = 2\mu_B^2 \cdot \rho(\epsilon_F)$, where μ_B is the Bohr magneton and $\rho(\epsilon_F)$ is the density of states per unit energy per spin at the maximum occupied energy (Fermi energy, ϵ_F).

2. A specific heat C that includes a term linear in temperature in addition to the T^3 lattice term, that is, $C = \alpha T + \beta T^3$. This term is most readily observed at liquid helium temperatures ($< 4.2^\circ\text{K}$) by plotting C/T versus T^2 and evaluating the intercept at $T = 0^\circ\text{K}$.

3. A characteristic frequency dependence of reflectivity, conductivity, and dielectric constant. Each of these quantities is dependent in turn upon the plasma frequency ω_p ,

$$\omega_p = \left[\frac{4\pi N e^2}{\epsilon_c m} \right]^{1/2} \quad (16)$$

where N is the electron density per unit volume, e the charge on an electron, m the electron mass and ϵ_c the frequency independent core dielectric constant ($\epsilon_c = 1$ for ideal free electron metal with no core electrons). An electron effective mass m^* determined by the details of the electron energy band replaces m in Eq. 16 for nonfree electron metals. The response of the conduction electrons to an applied alternating electric field can be calculated using a Drude model where the electrons are presumed to have a single frequency independent collision time or relaxation time τ . Within the simple model the frequency dependent electrical conductivity, $\sigma(\omega)$, and dielectric constant, $\epsilon(\omega)$, are

$$\sigma(\omega) = \frac{\epsilon_c \omega_p^2 \tau}{4\pi(1 - i\omega\tau)} \quad (17)$$

and

$$\epsilon(\omega) = \epsilon_c \left[1 - \frac{\omega_p^2}{\omega^2 + i\omega/\tau} \right] \quad (18)$$

These expressions can be used to derive the nearly total reflectance of metals below their plasma frequency. A similar characteristic frequency dependence of $\sigma(\omega)$ and $\epsilon(\omega)$ may be seen in semiconductors where ω_p depends the electron density in the filled valence band. The conduction electrons can oscillate as a collective mode (plasma oscillation). A *plasmon* is a quantized plasma oscillation. The frequency and wavevector dependence of plasmons in one-dimensional metals have been predicted (458, 576) to be qualitatively different from those of three-dimensional metals. Recent direct measurements (552) of plasmons in the one-dimensional organic metal tetrathiofulvalinium-tetracyanoquinodimethanide (TTF)(TCNQ) are qualitatively consistent with some of the predictions assuming a tight-binding band (576).

b. Semiconductors and Insulators. Semiconductors and insulators are materials with an energy gap E_g between filled and empty energy bands. If this energy gap is small enough to allow thermal excitation of a significant number of "free" electrons into the lowest empty band, the material is characterized as a semiconductor; otherwise it is termed an insulator. Semiconductors are understood (231) to have electrical conductivities at room temperature of 10^2 to $10^{-9} \Omega^{-1} \text{ cm}^{-1}$. At the upper end the conductivity is of the order of that of a poor metallic conductor. Systems with conductivities below this range are usually termed insulators. Conductivity in insulators is frequently interpreted in terms of models other than the band model.

Semiconductor properties are dominated by the number of free charge carriers. Intrinsic semiconductors are those whose free carriers are predominantly electrons thermally excited across the energy gap from the filled valence band and holes (empty states in the otherwise filled valence band) thereby created. In the simplest approximation the conductivity, σ , is a function of E_g :

$$\sigma \propto \exp \left[\frac{-E_g}{2k_B T} \right] \quad (19)$$

where k_B is Boltzman's constant. A plot of $\log \sigma$ ($-\log \rho$) versus T^{-1} may be used to determine E_g . Equation 19 is often used to phenomenologically parametrize the measured conductivity of a material with an activation energy, $E_a \equiv E_g/2$.

Changes in free electron and hole concentrations can arise from impurities, defects, and variations in stoichiometry. When the number of free carriers from

these contributions exceeds the number of "intrinsic" free electrons and holes, the material is termed in *impurity* or *extrinsic* semiconductor. The more general expression for conductivity is then used:

$$\sigma = (n_e e \mu_e + n_h e \mu_h) \quad (20)$$

where e is the electron charge, n_e and n_h are the concentration of free electrons and holes, respectively, and μ_e and μ_h are their respective mobilities. (The mobility is the drift velocity per unit electric field.) Semiconductor properties can be dominated by intrinsic free carriers at high temperatures and determined by other free carrier contributions at low temperatures, as shown in Fig. 10. In the region where the intrinsic free carriers dominate, the number of free carriers is a function of $\exp(-E_g/2k_B T)$. This exponential factor usually

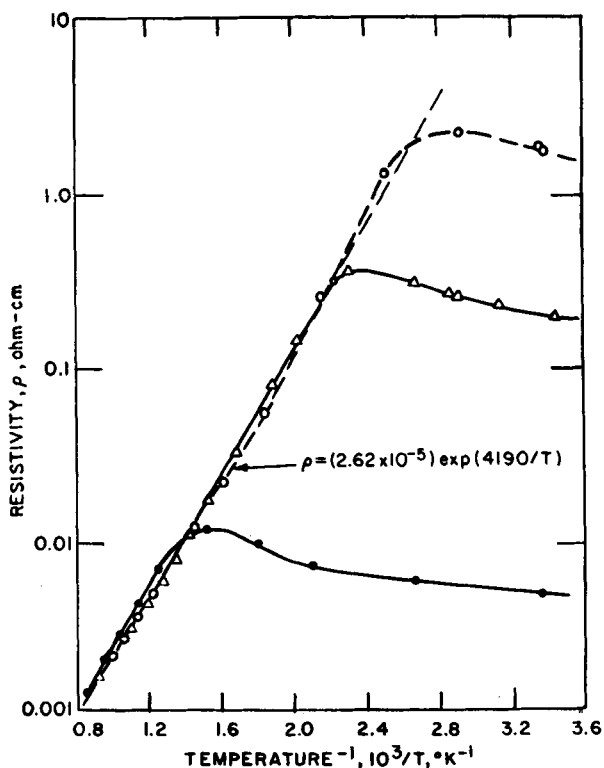


Fig. 10. Log resistivity versus inverse temperature for three crystals of germanium with different impurity concentrations. The conductivity is intrinsic at high temperatures (at the left) and impurity dominated at low temperatures (at the right). From the slope in the intrinsic regime, $E_g \approx 0.72$ eV (230).

dominates the temperature dependence of the mobility so that for intrinsic semiconductors Eq. 20 often reduces to Eq. 19. The properties of semiconductors have been extensively studied and have led to the development of a large number of interesting and useful devices (532).

c. Design of a Metallic Band System. Utilizing the band theory presented above, a system with an even number of electrons per repeat unit has filled electron energy bands and will be a semiconductor or insulator unless there is an overlapping of filled and unfilled bands (semimetals). The approach to preparing a one-dimensional metal is therefore to obtain partially filled bands by using a system that has a noneven number of electrons per crystallographic repeat unit along the direction of interest. An example is $\text{K}_2\text{Pt}(\text{CN})_4$ where without partial oxidation there is an even number of electrons per repeat unit and thus no metallic state. After partial oxidation to $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}(\text{H}_2\text{O})_3$, a partially filled band is formed and a metallic state (at least at room temperature) is observed. An example where the overlapping of energy bands possibly is important in obtaining a more highly conducting system is observed in the high pressure study on $[\text{PtBr}_2(\text{NH}_3)_2][\text{PtBr}_4(\text{NH}_3)_2]$, see Part II.

Equations 7, 10, and 11 show that overlap of the molecular orbitals of adjacent molecules determines the bandwidth. A very narrow bandwidth may lead to the breakdown of the one-electron band theory and the formation of poorly conducting systems as discussed in Section I. B. 1. Therefore, to obtain a metallic system, one requires molecules that stack in one-dimensional chains, have a close approach to their nearest-neighbors in the chain (for large overlap), and possess as well a noneven number of electrons per crystallographic repeat unit. This is best accomplished with planar molecules that can attain a close approach to nearest neighbors. In addition, partial occupation of the π -molecular orbital and/or the d_{z^2} orbital would greatly benefit one-dimensional band formation for two reasons: (1) larger extension of the molecular orbital in the chain direction, increasing the value of the transfer matrix element t , and (2) small molecular orbital extension in directions perpendicular to the chain, reducing overlap in the transverse direction and enhancing the anisotropy. These favorable features are illustrated by the highly conducting partially oxidized $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}(\text{H}_2\text{O})_3$ system. Here it is believed that the orbital from which an electron is removed through partial oxidation is of mostly d_{z^2} character. A delocalized electron energy band, based on the overlap of this molecular orbital throughout the chain, is then believed to be formed.

3. Peierls Transition

In 1955, R. E. Peierls (334) pointed out the inherent instability of a one-dimensional metal such as $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}(\text{H}_2\text{O})_3$. In analogy with the Jahn-

Teller effect (102), distortion of the symmetry (periodicity) of a chain which has a partially filled electron energy band lowers the total energy of the system. For example, consider a linear chain of equidistant sites of separation a , as in Fig. 1. Band theories yield a range of electron energy levels as a function of the wavevector k (cf. Eq. 11 and Fig. 4 for the tight-binding result). If the chain is now distorted by displacing groups of r sites in the same manner, a new unit cell of the chain containing r sites is formed. The new energy spectrum has gaps introduced at $k = \pm s\pi/ra$ ($s = 1, 2, \dots, r$). The effect of a lattice distortion with $r = 3$ on the energy bands is illustrated in Figs. 11a and 11b. The effect is to separate the energy values near $k = \pm s\pi/ra$ ($s = 1, 2, \dots, r$) leaving the mean of the energies above and below the energy gaps essentially unchanged. If such a gap coincides exactly or very nearly with the wavevector of the highest occupied state determined by the number of electrons in the band, k_F (the Fermi wavevector), the occupied states are displaced

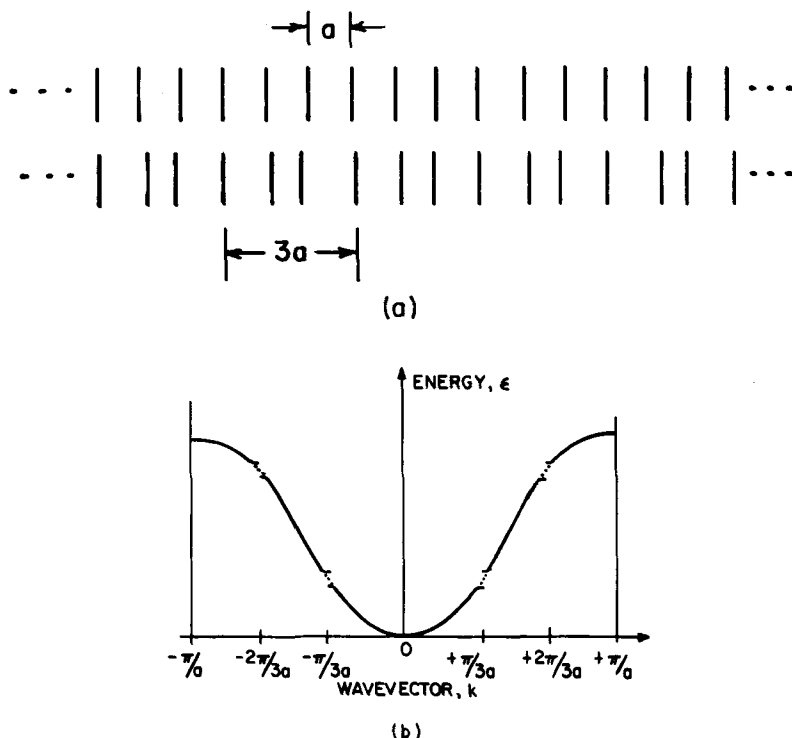


Fig. 11. (a) Uniform chain (upper line) and distorted chain for $r = 3$ (lower line). The new repeat unit is $3a$. (b) Allowed energy levels for the uniform chain (dashed line) and the distorted chain (solid line) for $r = 3$. The energy bands for the distorted chain are in the extended zone scheme.

downwards and the empty states are raised upwards in energy, resulting in a net reduction of energy. The reduction in energy is greatest when r is small. This distortion of the lattice is known as a Peierls distortion.

Theoretical studies of the Peierls distortion show that within mean field theory its presence can be a function of temperature (261, 347, 349). This leads to a transition from a band metal to a band semiconductor/insulator as the temperature is lowered below the transition temperature, T_p , termed the Peierls transition. The characterization of the metal-insulator transition in $\text{K}_2\text{Pt}(\text{CN})_4\text{-Br}_{0.3}(\text{H}_2\text{O})_3$ as a Peierls transition has triggered much of the increased work on the theory of the Peierls transition.

The transition arises dynamically through the interaction between the electrons and the quantized lattice vibrations of the solid, phonons (437). The phonons, in a manner similar to electrons, are assigned a wavevector $q = 2\pi/\lambda$ where λ is the wavelength of the lattice vibration. There is an energy associated with each phonon of wavevector q , $\hbar\Omega_q$, as indicated schematically in Fig. 12. The actual dispersion relation is a function of the mass of the atoms in a

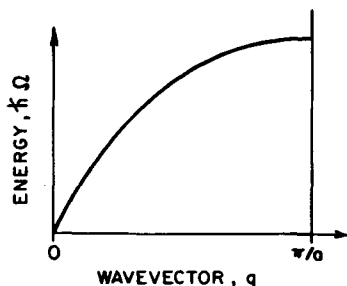


Fig. 12. Schematic phonon energy versus reciprocal lattice wavevector for a linear chain. The actual dispersion curve depends upon the masses of and forces between the constituent atoms.

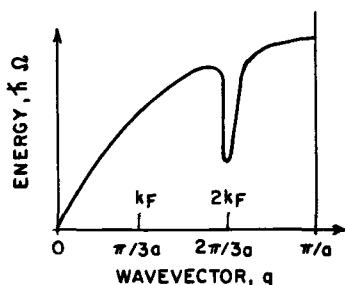


Fig. 13. Phonon energy spectrum with soft mode (Kohn anomaly) at $q = 2\pi/3a$ ($k_F = \pi/3a$).

unit cell and the restoring forces which arise for small displacements in the relative positions of the atoms. W. Kohn (236) in 1959 pointed out that phonons of wavevector $q = 2k_F$ strongly interact with the electrons of wavevector k_F . This strong interaction results in a reduction in the energy of the $q = 2k_F$ phonons in a metal. Figure 13 schematically shows the phonon energy spectrum for the case where $k_F = \pi/3a$. The presence of the dip in the phonon spectrum of a metal is termed the Kohn anomaly (236); the phonons of lowered energy are termed soft phonon modes. A Kohn anomaly in the phonon spectrum has been observed at $2k_F$ in $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}(\text{H}_2\text{O})_3$ using neutron scattering (342), Fig. 14.

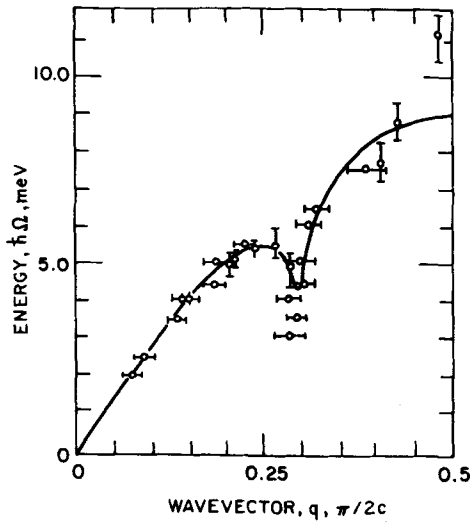


Fig. 14. The Kohn anomaly in the phonon spectrum of $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.30}(\text{H}_2\text{O})_3$ as observed by neutron scattering (342).

The value of $\hbar\Omega_{q=2k_F}$ decreases as the temperature is lowered resulting in greater thermal occupation of this mode (more phonons of $q = 2k_F$). A temperature, T_p , is ultimately reached at which $\Omega_{q=2k_F} = 0$. Within mean field theory there then occurs a periodic distortion of the previously uniform lattice of period $\lambda = 2\pi/q = \pi/k_F$. In turn, Peierls energy gaps Δ appear in the electron energy bands at $k = \pm k_F$ and multiples of k_F . The energy gap Δ increases from $\Delta = 0$ at T_p to a fixed value at $T = 0^\circ\text{K}$. The insulating state is termed a Peierls insulator. Figure 15 is a schematic illustration for a one-dimensional system of the mean field temperature dependence of Δ and $\hbar\Omega_{q=2k_F}$.

There has been speculation that anomalous electrical behavior may accompany a Peierls transition. In particular, the presence of a soft phonon mode at

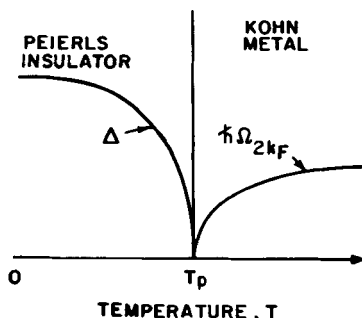


Fig. 15. Schematic illustration of the temperature dependence of the Peierls transition in mean field theory for a one-dimensional metal. Above T_p the temperature dependence of the energy of the $2k_F$ phonon is illustrated. Below T_p , the temperature dependence of the energy gap Δ is illustrated. The energy scale above and below T_p is not the same.

$q = 2k_F$ has been discussed as a mechanism for enhancing the BCS-type superconducting transition temperature (97, 494). Other recent theoretical work challenges this (11a, 348, 522). In a separate approach, Bardeen (28) and co-workers (8) have indicated that a new type of superconductivity may be introduced via the soft phonon mode whereby the formation of charge density waves can lead to collective charge transport. This theory, based on work initially published by Fröhlich (152) in 1954, is described in Section I. D. 3.

There has been some speculation (97) concerning the means of forestalling a Peierls transition and stabilizing the one-dimensional metallic state down to very low temperatures. The ideas include (1) making it very difficult for the uniform one-dimensional structure to distort because of the presence of bulky side groups, (2) introducing a controlled amount of disorder into the system (e.g., utilizing asymmetric molecules) to remove the exact periodicity, and (3) intentionally generating some two- or three-dimensional character to the system to make a Peierls transition less energetically favorable. These approaches have not been fully explored (97).

B. Limitations of Band Theory

The tight-binding band theory and the accompanying Peierls instability discussion assumed that all electrons move independently of each other in a perfect uniform lattice. Electron-electron Coulomb repulsion, disorder, and interruptions in the strands alter the band theory results. These effects are important for the understanding of one-dimensional metals and are now introduced.

1. Electron-Electron Coulomb Repulsion—Mott Transition

In 1949, Sir Neville Mott (15, 320) addressed himself to a paradoxical result

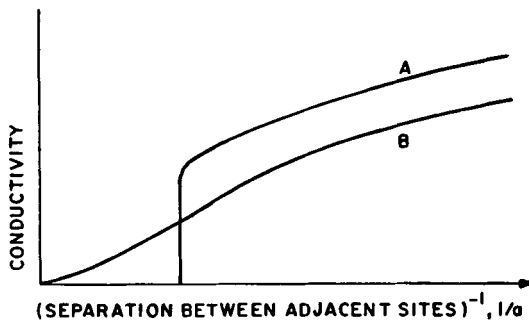


Fig. 16. The Mott metal-insulator transition as a function of separation between lattice sites, a . Curve A is the conductivity versus the inverse of the lattice spacing predicted by Mott. Curve B is conductivity versus the inverse of the lattice spacing predicted by one electron band theory, assuming a finite mean free path for electrons in the metallic phase.

of the one electron band theory. Suppose a large number of equally spaced molecules, each with an odd number of electrons, were brought together from infinity. One electron band theory predicts that the electron wavefunction on each molecule would overlap, electron energy bands would be formed, and the solid would immediately become a conductor, no matter how far apart the molecules might be, Fig. 3. Mott pointed out the crucial role of electron-electron interaction (Coulomb repulsion). The determinantal wavefunction of all the occupied band states places two electrons on some sites and leaves other sites empty. The excess Coulomb repulsion resulting from two electrons on a single site may more than outweigh the energy gained in band formation (an amount of order t per site, see Eq. 11), especially for narrow energy bands. The electron-electron Coulomb repulsion and the resulting electron correlation have been shown to have a major role in the conducting one-dimensional organic material, *N* methylphenazinium-tetracyanoquinodimethanide (NMP)-(TCNQ) (138).

As originally conceived by Mott, a transition (the Mott transition) would occur from a localized to a delocalized electronic state as the molecules were brought closer together than some critical value (320). This is illustrated schematically in Fig. 16. Later work suggested that such a transition could also occur for a fixed intersite spacing as a function of temperature, from a localized low temperature state to a delocalized high temperature state (126). The importance of Coulomb repulsion between electrons and the reduction of this effect through electron correlation is illustrated by reviewing the familiar "simple" two electron systems, atomic helium, He, and molecular hydrogen, H₂ (330).

For atomic helium, the total Hamiltonian, H , is given by

$$H = H_1 + H_2 + V_I \quad (21)$$

where

$$H_1 = -\frac{\hbar^2}{2m} \nabla_1^2 - \frac{Ze^2}{r_1}; \quad H_2 = -\frac{\hbar^2}{2m} \nabla_2^2 - \frac{Ze^2}{r_2} \quad (22a)$$

and

$$V_I = +\frac{e^2}{r_{12}} \quad (22b)$$

H_1 and H_2 are the one-electron energies for electrons one and two, Z the nuclear charge in units of the electron charge e ($Z = 2$ for helium), and V_I is the interaction potential (Coulomb repulsion) between two electrons separated by $r_{12} = |\mathbf{r}_1 - \mathbf{r}_2|$.

The experimental value for the total ground state energy of the two electrons in helium is given in Table I, along with the values calculated by various theoretical techniques. A comparison of (1) and (2) shows the extreme importance of V_I , the Coulomb repulsion. Techniques (2) through (4) are increasingly sophisticated means of treating V_I in the calculation. In particular, the Hartree-Fock technique (4) assumes that each electron responds to the average position of the other electron. However, none of these methods take into account the ability of two electrons to actively correlate to stay apart. The energy gained through correlation E_{corr} is defined as

$$E_{corr} \equiv E_{exp} - E_{H-F} = 1.13 \text{ eV/per pair of electrons}$$

where E_{exp} is (1) and E_{H-F} is (4). The electrons can gain a significant amount of energy through correlation.

A similar result is obtained for the H_2 molecule. In this case $E_{corr} \equiv E_{exp} - E_{H-F} = 1.1 \text{ eV per pair of electrons}$, again indicating the importance of correlation. It is convenient, within the framework of the hydrogen molecule, to illustrate the difference between an uncorrelated (band picture) and a correlat-

TABLE I
EXPERIMENTAL AND CALCULATED VALUES OF THE
TOTAL GROUND STATE ELECTRON ENERGY FOR He (330)

Technique	Ground State Energy (eV)	$E - E_{exp}$ (eV)
(1) Experiment	-78.98	—
(2) Ignoring V_I	-108.80	-29.82
(3) Variational	-77.47	+1.51
(4) Hartree-Fock Effective Field	-77.85	+1.13

ed (localized picture) electron state. The molecular orbital (MO) formulation assumes no correlation between electrons and delocalizes them over both sites:

$$\begin{aligned}\psi_{MO} &= C_1[\phi^A(1) + \phi^B(1)][\phi^A(2) + \phi^B(2)] \\ &= C_1[\phi^A(1)\phi^B(2) + \phi^B(1)\phi^A(2) + \phi^A(1)\phi^A(2) + \phi^B(1)\phi^B(2)].\end{aligned}\quad (23)$$

Wavefunction $\phi^A(1)$ represents electron 1 in the atomic orbital centered at site A and so on; C_1 is a normalization constant. Each electron is assumed delocalized over both nuclei thereby lowering its kinetic energy and allowing it to strongly interact with both positive charges. The disadvantage of this uncorrelated picture is that there is a large ionic contribution when both electrons are centered at the same nucleus [terms $\phi^A(1)\phi^A(2)$ and $\phi^B(1)\phi^B(2)$ in Eq. 23].

The ionic contribution (Coulomb repulsion) can be reduced by dropping these last two terms. In the resulting formulation the electrons are highly correlated and remain apart. This is the Heitler–London or valence bond picture,

$$\psi_{H-L} = C_2[\phi^A(1)\phi^B(2) + \phi^A(2)\phi^B(1)] \quad (24)$$

The advantage of this description is the reduction of mutual Coulomb repulsion between the electrons. The disadvantage is that the electrons do not pile up between sites A and B in ψ_{MO} and hence do not feel the full Coulomb attraction of nuclei A and B.

The difference between experimental and calculated values for the total ground state energy of the two electrons in the hydrogen molecule is given in Table II for various theoretical approaches. The Hartree–Fock picture, which has each electron responding to an average of the Coulomb repulsion of the other electron, overestimates the total energy by 1.1 eV (E_{exp} is negative). The MO approach, which ignores correlation, gives an even poorer agreement with experiment. The Heitler–London wavefunction, which constrains the electrons to remain apart, comes closer to predicting the experimental energy value. A better approach is to continuously vary between localized (Heitler–

TABLE II
DIFFERENCE BETWEEN EXPERIMENTAL AND CALCULATED VALUES OF
THE TOTAL GROUND STATE ELECTRONIC ENERGY FOR H₂ (330)

Technique	$E - E_{exp}$ (eV)	Comment
(1) Hartree–Fock (H–F)	1.1	No correlation
(2) Molecular Orbital (MO)	1.3	No correlation (delocalized)
(3) Heitler–London (H–L)	1.0	High correlation (localized)
(4) Linear Combination, ψ'	0.7	Some correlation

London) and delocalized (molecular orbital) approaches. The wavefunction ψ' does this through a linear combination of the two extremes:

$$\psi' = a\psi_{H-L} + b\psi_{MO} \quad (25)$$

By adjusting a and b to minimize the energy, one can calculate a ground state energy for H_2 that differs from the experimental result by only 0.7 eV. This implies that some correlation between electrons is necessary to minimize the system energy. The important lessons gained from examining the He and H_2 systems are: (1) the central role of the Coulomb repulsion between the two electrons, and (2) the best approximation to the experimental energy is obtained by varying the amount of correlation in the electron wavefunction.

Hubbard (194–196) has postulated a model Hamiltonian to apply these physical concepts to electron motion in crystalline solids utilizing two adjustable parameters, the transfer matrix element, t , and the effective on-site Coulomb repulsion, U :

$$H = -t \sum_{\langle i,j \rangle} c_{i\sigma}^\dagger c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \quad (26)$$

where (in second quantized notation (232)) $c_{i\sigma}^\dagger$ is a creation operator for an electron of spin σ at site i , $c_{j\sigma}$ is a destruction operator for an electron of spin σ at site j , and $n_{i\uparrow}$ is the number of electrons of spin up (\uparrow) at site i and so forth. The first sum on the right extends over nearest neighbor pairs of sites and electron spin σ . This term lowers the total energy of the system by allowing the electron to transfer to its neighboring site when the Pauli exclusion principle allows it. The second term on the right of Eq. 26 adds an energy U to the total energy of the system for each doubly occupied site (a site with two electrons, one of spin up, one of spin down). A large number of calculations (37, 448, 467) have been performed using this Hubbard Hamiltonian, but few exact results are known (264). An important feature is that for $t \gg U$, the electrons will delocalize into a single band and act metallic. When $t \ll U$ and there is one electron per repeat unit, the electrons stay apart (one on each site to reduce the Coulomb repulsion) forming a semiconductor (Mott–Hubbard insulator). For those materials where $t \simeq U$, metal-insulator transitions may be observable as the temperature is lowered. Experimental systems for which observed metal-insulator transitions have been attributed to this effect include several transition metal oxides (4, 15) and the organic ion radical salt NMP-TCNQ (138). A Mott–Hubbard insulator with one unpaired electron per site behaves as an antiferromagnetically coupled insulator when $T \rightarrow 0^\circ\text{K}$ (138).

Though the Mott–Hubbard picture is still under theoretical and experimental investigation, it is clear that materials with an odd number of electrons per repeat unit may be either metals or semiconductors, depending on the relative size of the bandwidth ($\sim 4t$) and the effective on-site electron–electron

Coulomb repulsion, U . Therefore, to achieve a metallic state in a one-dimensional chain it is necessary to have: (1) Large overlap between repeat units. This is aided by using planar molecules which can closely approach their neighbors. The overlap is enhanced if the unpaired electron is in an orbital with a large extension perpendicular to the molecular plane (e.g., d_{z^2} , p_z , π). (2) Reduced on-site electron–electron Coulomb repulsion. This may be achieved by arranging strong electron-withdrawing groups, for example CN (153), at opposite ends of a planar molecule. This would tend to keep two excess electrons on a single molecule apart, reducing U . In addition, if the chain of molecules is imbedded in a highly polarizable medium, the polarization of the medium adjacent to a doubly occupied site may reduce the effective Coulomb repulsion (138, 153) through an attractive interaction with the polarization induced in the medium.

2. Disorder in One-Dimensional Systems

The lattice potential within which the electrons move has been assumed to this point to be rigorously periodic along the chain. However, the x-ray crystal structure of the highly conducting, partially oxidized tetracyanoplatinate systems and the structures of some of the highly conducting one-dimensional organic materials based on TCNQ indicate that all chain sites are not rigorously equivalent. In the $K_2Pt(CN)_4Br_{0.3}(H_2O)_3$ case, the bromide sites are not fully occupied. This leads to a random contribution to the potential within which the electrons move along the Pt chain.

Several authors (50, 51, 336) have noted that structural disorder is common to many of these conducting one-dimensional systems. They invoked exact theorems (61, 321) which state that in the presence of any disorder in the one-dimensional periodic potential, the electron wavefunctions will be localized to some finite length instead of extending throughout the chain. Using this *disorder model*, attempts were made to explain the experimental data available on these systems with the assumption that the electrons are “localized” in a state extending over several lattice sites by the disorder potential V_d (random potential introduced by the disorder). Electrical conductivity can then occur only by phonon assisted hopping (319) of electrons between these localized states. Three temperature regimes were then identified:

1. Low temperatures. The tunneling between electron states was predicted to dominate and be isotropic, and the conductivity, σ , to vary as

$$\ln \sigma \propto T^{-1/4} \quad . \quad (27)$$

2. Intermediate temperatures. Activated phonon assisted hopping was predicted to dominate, and the conductivity along the chain to vary as

$$\ln \sigma \propto T^{-1/2} \quad . \quad (28)$$

3. High temperatures. The conductivity along the chain was predicted to be diffusive:

$$\sigma \propto \frac{1}{T} \quad (29)$$

A plot of the early conductivity data available for a number of one-dimensional materials revealed some of these temperature dependencies (51). A more detailed comparison of the theoretical predictions of this model with experiments have shown major disagreements, especially with respect to more recent experimental work (96, 99, 132, 342, 343, 518). It has been suggested (132) that the physically relevant parameter is the ratio of the disorder potential V_a to the otherwise unperturbed, delocalized, one electron bandwidth W . Two important limits can then be distinguished. For $W/V_a \gg 1$, the electrons are delocalized over such a large number of sites that the disorder has only a peripheral role. In this limit, scattering of the band electrons by defects and phonons determines the electrons' mean free path and the system would appear as a delocalized band material without disorder. In the opposite limit, $W/V_a \ll 1$, the disorder potential is much greater than the one electron bandwidth and the electrons become localized over a few sites in the chain.

Recent experimental work indicates that the $W/V_a \gg 1$ regime is more relevant for many of the disordered materials. In particular, the observation (99, 342) of soft phonon modes in $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}(\text{H}_2\text{O})_3$ shows the dominance of the band formation in this partially oxidized material. In some of the organic materials, the previously published conductivity data used to demonstrate $\ln \sigma \propto T^{-1/2}$ behavior has been shown to be due to poor quality materials (60, 96). In addition, recent x-ray analysis (513a) of the organic ion radical salt (NMP)-(TCNQ) indicates that the potential exerted by the asymmetric cation on the TCNQ sites is not random as had been previously reported (513b). Thus it appears that structural disorder in the crystal structure does not dominate the electron transport properties for several structurally disordered materials although it may lead to a reduction in the Peierls transition temperature for a disordered one-dimensional conductor (97, 562). The implication for the design of a highly conducting one-dimensional system is that structural disorder may not destroy the metallic band formation but it is necessary that the disorder potential be small as compared with the bandwidth.

3. Interrupted Strand Model

A particular frailty of one-dimensional systems is the effect of a defect or impurity within the chain itself. The *interrupted strand model* was developed for the situation where the blockages dominate the electron motion (253, 345, 346). The model was originally applied to $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}(\text{H}_2\text{O})_3$ and was also

suggested for other systems (434). After the experimental establishment of a Kohn anomaly (342) and crystallographic distortion (99) in the $\text{K}_2\text{Pt}(\text{CN})_4\text{Br}_{0.3}(\text{H}_2\text{O})_3$ system, this model was deemphasized in favor of a delocalized band system exhibiting a metal-insulator transition. However, the model is useful for demonstrating the importance of sample purity and good crystal morphology.

The interrupted strand model assumes the crystal to be comprised of parallel linear metallic strands with each strand being interrupted within itself by perfectly insulating defects. The electrons are assumed to be delocalized over and confined to each strand segment. This "particle in a box" arrangement leads to a discrete splitting of allowed energy values for electrons with a splitting of the order of 10^{-2} eV for electrons localized in a chain 300 Å long. The dc electrical conductivity for the crystal is then thermally activated with the activation energy related to the energy required to add another electron to a strand. The conductivity is given by

$$\ln \sigma \propto T^{-\mu} \quad \left(\frac{1}{3} \lesssim \mu \lesssim \frac{1}{2} \right) \quad (30)$$

This differs qualitatively from a conductivity increasing with decreasing temperature for uninterrupted strands. Similarly, it was shown (120, 342) that the specific heat and magnetic susceptibility for the interrupted strands can differ greatly both in magnitude and temperature dependence from that expected for continuous strands. The predicted optical conductivity and dielectric constant for the interrupted strand model (120, 173, 344) is more complicated than that for the continuous strands.

Thus good crystal morphology is of crucial importance for experimentally establishing the intrinsic nature of highly conducting one-dimensional materials. Impurities, disorder, and defects can drastically change the measured material properties.

C. Polaron and Exciton

The discussion so far has assumed that electrons are the quanta that move through the one-dimensional system. In materials where there are ions and/or low-lying electronic states available, the electron charge can distort the surrounding medium and propagate with its induced distortion through the crystal as a "quasiparticle". Two types of quasiparticles are now discussed, polarons and excitons (12, 192, 251). Their large role in the one-dimensional organic materials has been demonstrated (19, 85).

1. Polarons

The polaron concept was developed to treat the electron moving through an ionic crystal. The negatively charged electron attracts the positive ions and

repels the negative ions. These ions in their displaced positions change the periodic potential of the crystalline lattice and provide a potential well of lower energy for the electron. If this well is sufficiently attractive, the electron will be in a bound state of the well and thus "self-trapped." This combination of the electron with its induced lattice deformation is defined as a *polaron*. In its bound state, the electron cannot move to the next crystalline site without taking the well with it; that is, the polaron must move as a unit. The most immediate effect is that the electron moving through the crystal with the lattice deformation (the ions at each site distort as the electron passes) acts as if its mass were increased. Two physically meaningful limits are: (1) the large polaron, where the distortion extends over many lattice sites, and (2) the small polaron, whose dimensions are of the order of the lattice spacing. The small polaron, in particular, and its application to molecular crystals has been extensively studied (192, 193). Polarization of the solid by an electron has two contributions: distortion of the lattice and the electronic polarization (30, 85, 400). The latter effect can be especially large in molecular systems containing highly polarizable molecules where an excess electron can polarize the electrons on the individual molecules. The term *excitonic polaron* is applied in this case (85).

Studies (85, 448) of the effects of increased polarization on an electron moving in a narrow tight-binding electron band have shown two major features: (1) the tight-binding transfer integral t is reduced in value (the bandwidth decreases), and (2) the binding between electrons and the solid increases, reducing the effective Coulomb repulsion between two electrons.

This concept of polarons and, in particular, excitonic polarons has been used to explain observed features of the one-dimensional conducting organic materials based on 7,7,8,8-tetracyano-*p*-quinodimethane, TCNQ (85). It indicates that a way to reduce the Coulomb repulsion between electrons in the chain is to surround each chain by a highly polarizable medium. However, a limit may be reached beyond which, if the surrounding medium were made more polarizable, the effects due to band narrowing would outweigh the benefits of reduced Coulomb repulsion (85).

2. Excitons

A crystalline solid has a definite charge distribution throughout the crystal. When an electron is removed from a site, the site appears as if it has a net positive charge (hole). If the electron remains in close proximity to the hole, it may form a bound electron-hole pair (similar to the electron-proton pair of a hydrogen atom) called an *exciton*. The bound electron-hole pair may move through the crystal transporting excitation energy but not charge (251). As for polarons, there are two limiting types of excitons, one which is considered tightly bound, with the electron and hole separated by less than a lattice spacing (Frenkel exciton) (251), and the other in which the electron-hole separa-

tion is large in comparison to the lattice spacing (Mott or Wannier exciton) (251).

Molecular crystals frequently exhibit Frenkel excitons, a particular example being an isolated molecule with a singlet ground state and a low lying triplet excited state (triplet exciton). In some solids triplet excitons can migrate through a crystal and form energy bands. These excitons are important in understanding the physics of insulating systems. In particular, a number of the TCNQ anion radical salts (for example, triphenylmethylphosphonium⁺(TCNQ)₂⁻(87)) form one-dimensional magnetic insulators whose excitations are delocalized triplet excitons (19, 140, 227). Recently the optical excitation associated with the metallic luster of the poorly conducting rhodium and iridium dicarbonylacetylacetonates has been identified with the excitation of Frenkel excitons (474).

D. Superconductivity

Superconductivity was first discovered in mercury by H. Kamerlingh Onnes in 1911 (329) and eluded attempts at explanation until, in 1957, Bardeen, Cooper, and Schrieffer formulated the BCS theory (29) based on an electron-lattice-electron interaction. This theory and two others [by W. A. Little (268) and H. Fröhlich (152)] are briefly described; a full review is beyond the scope of this article. Interest in this area has been heightened by the report of superconducting fluctuations in the one-dimensional organic material, tetrathiofulvalenium tetracyanoquinodimethanide, (TTF)(TCNQ) (97).

1. BCS. Phonon Mechanism for Superconductivity

Extensive study of many three-dimensional superconductors has shown that the superconducting state is actually an ordered state of the conduction electrons in the metal (371) and not simply the absence of dc electrical resistivity due to a reduction in scattering of electrons. The order occurs through an association of pairs of electrons, with the lattice vibrations (phonons) providing the means of communication. Because the electronic state is different below (ordered) and above (unordered) the superconducting transition temperature T_c , other properties of the system, such as magnetic susceptibility and specific heat, also change at T_c (231). Experimentally, care must be taken to eliminate foreign magnetic impurities which can break the pairing of electrons. For example one atomic percent gadolinium in lanthanum lowers the transition temperature from 5.6 to 0.6° K (389). The presence of a sufficiently strong magnetic field will also suppress the onset of superconductivity (231, 371).

Many of the properties of the BCS superconductor are consequences of the formation of an energy gap E_g in the electron energy band at the Fermi energy ϵ_F when the temperature is reduced below T_c . The magnitude of this gap and T_c are related by $(E_g/k_B T_c) \leq 4$ where k_B is Boltzman's constant. This energy gap arises from an effective attractive interaction between paired elec-

trons (with the lattice acting as the intermediary in this mechanism) allowing the electrons to overcome their Coulomb repulsion. The attractive interaction occurs schematically as follows: A spin up (\uparrow) electron of wavevector $k\uparrow$ moves through the lattice and deforms it slightly (with a periodicity unique to k). The electron of wavevector $-k\downarrow$ can now adjust to the deformed lattice potential, reducing the system's energy. The superconducting transition temperature is related to the strength of the electron-phonon interaction V and the electron density of states per spin at the Fermi energy $\rho(\epsilon_F)$. The BCS model predicts that

$$T_c = 1.14 \Theta \exp \left\{ \frac{-1}{\rho(\epsilon_F)V} \right\} \quad (31)$$

The Debye temperature, Θ , (436) is a measure of the maximum energy of the allowed vibration (phonon) modes of the solid. It is related to an effective maximum frequency of lattice vibration, Ω_D , through $\Theta = \hbar\Omega_D/k_B$ and can be measured by evaluating the lattice contribution to the low temperature specific heat. For example, the Debye temperature for $\text{K}_2\text{Pt}(\text{CN})_4\text{Cl}_{0.32}(\text{H}_2\text{O})_x$ is 246°K (171), while the Debye temperature of the conducting one-dimensional tetracyanoquinodimethane salts is of order 90°K (141). The inorganic polymer $(\text{SN})_x$ has a Debye temperature of 170°K (490) intermediate between those of the organic ion radical salts and the platinum chain compounds. The BCS model provides a framework for more detailed treatment of specific types of superconducting metals (371).

Theoretically and experimentally the transition from a normal metal to superconductor is preceded (above T_c) by a rapid rise in the conductivity (13, 332), termed *paraconductivity* or *superconducting fluctuations*. The temperature dependence of the paraconductivity depends upon the system being one-, two-, or three-dimensional (392).

There has been considerable theoretical discussion concerning the role of the Peierls soft phonon mode with wavevector $2k_F$ in the indirect coupling of electrons into pairs to form the superconducting state in a one-dimensional metal. It has been suggested that this phonon could lead to an anomalously large attractive indirect electron-electron interaction (6, 97, 392). In contrast, some theoretical work shows that phonons of energy less than $k_B T_C$ (such as the soft phonon mode near the Peierls transition) tend to suppress the superconducting transition (6, 333, 348). Further theoretical and experimental work is necessary to fully resolve this point.

2. *W.A. Little. Exciton Mechanism for Superconductivity*

Equation 31 shows that the maximum superconducting transition temperature expected in the BCS theory is limited by the Debye temperature. This temperature plays a central role because the distortion of the lattice in response