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D I A M A G N E T I S M*

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ABSTRACT

DIAMAGNETISM is the phenomenon by which a given substance or body repels or expels magnetic flux from its interior. A diamagnet increases its free energy when placed in a magnetic field, and thus experiences a repulsive force away from regions of space where the magnetic field is high. Diamagnetism is a purely quantum-mechanical phenomenon and can only be understood in quantum-mechanical terms. Examples of diamagnets are closed-shell systems -- atoms and molecules with no unpaired electrons -- in their gaseous, liquid or solid form, and superconductors, the perfect diamagnets. Metallic electrons also provide, through their orbital quantization in the presence of a magnetic field, a diamagnetic contribution to the susceptibility, even though -- in most metals -- the paramagnetic contribution of the electron spin dominates. The orbital diamagnetism of metallic electrons also contains a part which oscillates as a function of the intensity of the applied static magnetic field. This phenomenon -- known as the de Haas - van Alphen effect -- pro-

vides a very precise experimental tool to determine the quantum-mechanical electronic structure of pure metals.

April 6, 1990

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TABLE OF CONTENTS

5.3.6 Quantum Interference Phenomena

6. CONCLUSION

GLOSSARY

antiferromagnetic (antiferromagnetism)

A substance in which local magnetic moments are arranged in alternating orientations, resulting in no net macroscopic moment.

Bardeen, Cooper and Schrieffer theory

See BCS theory.

BCS theory

A microscopic theory of superconductivity formulated by Bardeen, Cooper and Schrieffer in 1957.

Bohr-Sommerfeld quantization rules

Rules by which the energy of bound electronic states were quantized in the "old" quantum mechanics.

Brillouin zone

The polyhedron in reciprocal space over which the wave vector **k** is allowed to vary.

coherence length

The distance over which the coherence of the quantum-mechanical phase of the superconducting order parameter is preserved.

yclotron resonance

Resonance absorption of electromagnetic radiation obtained when the electromagnetic frequency is equal to the cyclotron frequency of electrons moving in a magnetic field; it is also sometimes called diamagnetic resonance.

de Haas - van Alphen effect

Oscillatory contribution to the magnetic susceptibility, periodic in $1/B$, caused by the interrelationship of the quantized energy levels and the Fermi surface.

diamagnetic (diamagnetism)

A substance or body that repels or expels magnetic flux.

diamagnetic resonance

See cyclotron resonance.

Fermi-Dirac statistics

The thermal-equilibrium statistics that applies to particles which satisfy the Pauli exclusion principle, electrons among them.

Fermi level

The value of the energy that separates occupied from empty states in the limit $T \rightarrow 0$ of the Fermi-Dirac statistics.

Fermi surface

The surface of constant energy in **k**-space corresponding to the Fermi level.

ferrimagnetic

An arrangement of local magnetic moments which exhibits both a uniform value -- a macroscopic moment -- and a spatially oscillatory component.

ferromagnetic (ferromagnetism)

An arrangement of magnetic moments all parallel to each other that results in a macroscopic moment.

fluxoid

The quantum of magnetic flux in multiply connected superconductors (see flux quantization)

flux quantization

The property of multiply connected superconductors that restricts the values of the magnetic field inside the sample to integral multiples of a fixed quantity, called the fluxoid.

Ginzburg-Landau theory (Ginzburg-Landau equations)

A phenomenological quantum theory that describes the electromagnetic properties of superconductors and which allows for spatial variations and coherence effects.

Josephson effect

Coherent tunneling of electrons between two superconductors separated by a thin non-superconducting -- normally insulating -- layer.

London theory (London equation)

A macroscopic classical theory which describes the electromagnetic properties of superconductors.

Meissner effect

The complete exclusion of magnetic flux (perfect diamagnetism) from the body of a superconductor at low enough values of the applied magnetic field.

paramagnetic (paramagnetism)

A substance that exhibits neither permanent magnetic moment nor long-range order of local moments and which attracts magnetic flux.

penetration depth

The distance over which an outside magnetic field decays into the bulk of a superconductor.

reciprocal lattice

The discrete, infinite set of points in reciprocal space which defines the vectors used in the Fourier series for a given periodic structure in three-dimensions.

reciprocal space (k-space)

A mathematical space, with the dimension of inverse length, over which wave vectors and periodicities of Fourier series are defined.

1. INTRODUCTION

The word DIAMAGNETIC was introduced -- originally as a noun, later as an adjective -- by Michael Faraday in 1846. In the *Philosophical Transactions* **I** , 2, page 2149, one reads: "By a DIAMAGNETIC I mean a body through which lines of magnetic force are passing, and which by their action does not assume the usual magnetic state of iron or loadstone". It was constructed from the Greek prefix δια (which means by, through, across) and the word *magnetic* -- from the Latin word *magneticus* -- which described, at that time, the special forces inherent in naturally occurring iron, iron oxides, and other substances.

The operational definition of DIAMAGNETISM, quoted in most electromagnetism and materials sciences textbooks for a century and a half, is still valid. A substance shaped in the form of a bar or needle and suspended freely between the poles of a magnet is called paramagnetic or magnetic if it orients itself longitudinally with the magnetic lines of force, *i.e.* pointing towards the poles; it is called diamagnetic if it orients itself equatorially, *i.e.* perpendicular to the lines of force. Already in 1849 Mrs. Sommerville [*Connect. Phys. Sc. xxiii* , 369] wrote "Substances affected after the manner of bismuth (when suspended between the poles of an electromagnet) are said to be diamagnetic": To the present day the semimetal bismuth is taken as the prototype of a diamagnetic substance.

Although the concept of magnetism of materials predated Quantum Mechanics by some eighty years, magnetism is a purely quantum-mechanical effect. Strictly classical systems in equilibrium cannot display a magnetic moment, even in the presence of a magnetic field. Understanding diamagnetism, therefore, requires a complete quantum-mechanical treatment.

2. THERMODYNAMIC ARGUMENTS

In the presence of an applied external magnetic field **B**, the free energy $F(T,\mathbf{B})$ of a given system at a given temperature T can be expanded in a Taylor series of the form

$$F(T,\mathbf{B}) = F_0(T) - \mathbf{M}_0(T)\cdot\mathbf{B} - (1/2\mu_0)\sum_{ij} B_i\,\chi_{ij}(T)\,B_j \quad . \tag{2.1}$$

In (2.1) the vector $\mathbf{M}_0(T)$ is called the temperature-dependent intrinsic magnetization, and the second-rank $\boldsymbol{\chi}(T)$ is the magnetic susceptibility tensor. The magnetization $\mathbf{M}(T)$ is defined by

$$\mathbf{M}(T) = \mathbf{M}_0(T) + (1/\mu_0)\,\chi\cdot\mathbf{B} \quad . \tag{2.2}$$

Materials for which $\mathbf{M}_0(T)$ is non-zero at a particular T are called *ferromagnets* or *ferrimagnets* at that temperature, irrespective of the properties of $\chi(T)$. Such is the case, for instance, of the metals *Fe, Co, Ni,* and *Gd* and the compounds CrO_2, *EuS*, and Fe_3O_4, *inter alia,* at low enough temperatures.

If, on the other hand, $\mathbf{M}_0(T) = 0$, then the magnetic properties are dominated by $\chi(T)$. In particular, for isotropic systems where χ is a diagonal tensor, $\chi_{ij}(T) = \chi(T)\,\delta_{ij}$, if $\chi(T)$ is positive, then the substance is said to be *paramagnetic* , whereas if $\chi(T)$ is negative, then it is labelled *diamagnetic*. The definitions can be extended to particular directions of anisotropic systems.

Examples of paramagnets are *Fe, Co, Ni,* and *Gd* at high temperatures, most rare-earth compounds and gaseous molecular oxygen. Examples of diamagnets include the noble gases *He, Ne, Ar, Kr,* and *Xe,* most molecular gases, liquids and solids, and the semimetals *As, Sb, Bi,* and graphite.

It should be pointed out that the free energy of a diamagnet increases in the presence of a magnetic field, and therefore the system evolves so as to avoid high-field regions of space; there is a net repulsive force, caused by the magnetic field, acting on the diamagnet. Conversely the free energy of a paramagnet decreases in the presence of a magnetic field, with an attendant attractive force.

3 . DIAMAGNETISM OF ATOMS, MOLECULES AND MOLECULAR SOLIDS

Lenz's law in electromagnetism {see 05-01-5-124 and 05-01-5-127} establishes that when the magnetic flux through an electrical circuit is changed, an induced current appears so as to oppose the flux change. In classical systems that current rapidly decays through dissipation, and a new state of equilibrium is achieved with no current flowing through the circuit, and with the new value of the magnetic flux permanently established. In quantized systems with a discrete, non-degenerate energy spectrum, such as a closed-shell atom or molecule, the induced current persists for as long as the applied field is present, and the net magnetic field -- the sum of the applied field and the internal one generated by the electronic current in the atom -- is always smaller than the applied field.

In addition, closed-shell systems, because of their non-degenerate ground state, possess no intrinsic magnetic moment and are therefore diamagnetic. (It should be remembered that intrinsic magnetic moments are caused by non-vanishing orbital or spin angular momenta which are able to reorient themselves in the presence of a magnetic field; that capability of reorientation requires degeneracy of the ground-state manifold.)

3.1 Hamiltonian of Electrons in a Magnetic Field

A well established result, valid in both classical and quantum mechanics, states that a system of electrons in a magnetic field **B**, defined by a vector potential **A**, such that

$$\nabla \times \mathbf{A} = \mathbf{B} \quad , \tag{3.1}$$

is described by the following Hamiltonian:

$$H = \frac{1}{2m} \sum_i \left[\mathbf{p}_i + e\,\mathbf{A}(\mathbf{r}_i) \right]^2 + V - \sum_i e\,\phi(\mathbf{r}_i) + \frac{e}{m} \sum_i \sigma_i \cdot \nabla \times \mathbf{A}(\mathbf{r}_i) \quad . \tag{3.2}$$

In (3.2) m is the mass of the electron, e is the (positive) charge of the proton, V is the internal electrostatic energy of the electronic system, ϕ is the electrostatic (scalar) potential, and $\mathbf{r}_i$, $\mathbf{p}_i$, and $(e/m)\,\sigma_i$ are the position, the momentum and the spin magnetic moment of the i th electron, respectively.

For a single *atom* or *ion* in a uniform magnetic field of magnitude B oriented in the z direction, it is convenient to choose the so-called symmetric gauge

$$\mathbf{A} = \tfrac{1}{2}\,\mathbf{B} \times \mathbf{r} \quad , \tag{3.3}$$

where the origin of the gauge is located at the nucleus. Under such conditions the Hamiltonian (3.2) reduces to

$$H = \sum_i \left[\frac{1}{2m} p_i^2 + e\,\phi(\mathbf{r}_i) + \frac{eB}{2m} (L_{zi} + 2\,\sigma_{zi}) + \frac{e^2 B^2}{8\,m} (x_i^2 + y_i^2) \right] + V \quad . \tag{3.4}$$

The terms in the summation correspond, for each electron, to the kinetic energy, the outside potential energy, the coupling of the magnetic moments arising from the orbital (L_{zi}) and the spin (σ_{zi}) magnetic moments of the electrons to the magnetic field, and the weak quadratic term, proportional to B^2.

3.2 Langevin Theory for Closed-Shell Systems

Diamagnetism arises in systems where the contribution from the third term in (3.4), linear in B vanishes, *i.e.* for atoms and molecules with a closed-shell structure. The magnetic-field dependence to the energy originates then exclusively from the term quadratic in B. For a system of N *atoms* or *ions* per unit volume, each consisting of n electrons which have an average square radial distance from the nucleus equal to $\langle r^2 \rangle$, the summation

$$\sum_i (x_i^2 + y_i^2)$$

in (3.4) can be replaced by ($2Nn < r^2 > / 3$). This substitution results in an excess magnetic energy per unit volume of

$$\frac{e^2 B^2}{12\, m} n\, N < r^2 > \quad ,$$

and, consequently, in a diamagnetic susceptibility

$$\chi = -\frac{\mu_0\, e^2}{6\, m} n\, N < r^2 > \quad . \tag{3.5}$$

If the system (solid, liquid or gas) consists of N_α atoms or ions of the α-type per unit volume, and all these species are closed electronic shells, then the diamagnetic susceptibility of the system is given by

$$\chi = -\frac{\mu_0\, e^2}{6\, m} \sum_\alpha n_\alpha N_\alpha < r_\alpha^2 > \quad , \tag{3.6}$$

where n_α and $< r_\alpha^2 >$ are, respectively, the number of electrons on the α atom or ion and the mean value of r^2 for the electrons from their nucleus, for that particular species.

It should be noted that the diamagnetism of closed-shell systems is essentially a very weak perturbation of the non-degenerate ground state caused by the presence of the applied magnetic field. It is therefore a pure quantum-mechanical phenomenon -- since it requires a discrete, non-degenerate lowest energy state in the spectrum, a feature that can only be achieved quantum-mechanically -- and an effect that depends extremely weakly on the temperature. This virtual temperature independence is, once again, caused by the same features of the spectrum: only at inaccessible temperatures are the excited states appreciably populated, the only way in which the various $< r_\alpha^2 >$ in (3.6) can be affected by the temperature.

4. ORBITAL DIAMAGNETISM OF METALLIC ELECTRONS

Metallic electrons are, by their very nature, itinerant. Their wave functions extend essentially over the entire crystal and their energy spectrum is in the form of bands separated, in some cases, by forbidden energy gaps. The single-electron wave functions {see 12-00-4-296} are in the form of Bloch states, *i.e.* a product of a plane wave of vector **k**, a periodic function with the full periodicity of the crystal lattice, and a spinor. Each Bloch function is thus labelled by a **k**-vector, a band index ν (a positive integer), and a spin index σ ($\uparrow$ or $\downarrow$). The vector **k** is restricted to a finite region in reciprocal space (**k**-space), a polyhedron known as the Brillouin zone. The energy ε of each state is given by the band-structure function $\varepsilon_\nu(\mathbf{k},\sigma)$, which is continuous in **k**-space. These features arise from the solution of the Schrodinger equation in a periodic potential, and from the properties of periodic functions and Fourier series in three dimensions.

The occupation of the one-electron energy bands follows FERMI-DIRAC STATISTICS {see 08-01-5-215}, with no more than one electron occupying each state. At very low temperatures, $T \to 0$, the Fermi-Dirac distribution is a step-function, with all electronic states with energy $\varepsilon < \varepsilon_F$ being occupied by one electron, and all states with $\varepsilon > \varepsilon_F$ being empty. The energy ε_F is called the Fermi level and, in a metal, falls in the middle of one or more bands, *i.e.* not in the middle of a forbidden energy gap. The equation

$$\varepsilon_\nu(\mathbf{k},\sigma) = \varepsilon_F \tag{4.1}$$

defines, for a metal, a surface in **k**-space called the FERMI SURFACE {see 12-00-4-297}. This surface consists of one or more sheets -- one or more for each band ν which crosses the Fermi level --, is defined within the Brillouin zone, and has all the symmetry and periodic properties of the Brillouin zone and **k**-space.

Metallic electrons do not form closed electronic shells, and therefore do not fall in the category discussed in the previous section. The fact that the Fermi level falls in the middle of a continuous energy band guarantees that the ground state of the many-electron system is not part of the discrete spectrum, *i.e.* the ground state is the lowest of a set of continuum states. The response of metallic electrons to an applied magnetic field is in general very complex, and contains several contributions of various characteristics which must be treated separately:

(i) If the bands of different spin are not identical and are occupied differently then the system develops a spontaneous local magnetization which, depending on the way it distributes itself, results in MAGNETIC ORDERING {see 13-00-4-329}; these ordered states include ferromagnets, ferrimagnets, antiferromagnets, spiral spin arrangements, etc.

(ii) If the bands of different spin are identical -- and identically occupied -- in the absence of an applied magnetic field, then the electron spin and its associated magnetic moment are responsible for a rearrangement of the band occupation when a magnetic field is applied; the imbalance in the spin distribution results in a temperature-independent positive susceptibility known as PAULI PARAMAGNETISM {see 13-00-4-328}. For simple metals of columns I, II, III and IV of the periodic table that contain only fully occupied and/or fully empty d and f atomic shells, a commonly used approximation is the so-called *free-electron* model. This model replaces the periodic potential of the lattice by a constant, *i.e.* the periodic oscillations of the potential are completely smoothed out. As a consequence the periodic factor in the Bloch state reduces to a plane wave of vector $\mathbf{G}_\nu$; the set of $\mathbf{G}_\nu$'s is infinite but discrete and constitutes the so-called the reciprocal lattice. The energy spectrum for the Bloch states in the free-electron model is given by

$$\varepsilon_\nu(\mathbf{k},\sigma) = \frac{\hbar^2}{2m}(\mathbf{k}+\mathbf{G}_\nu)^2 \quad . \tag{4.2}$$

In this model the Pauli contribution to the (paramagnetic) susceptibility per unit volume is equal to

$$\chi_{Pauli} = \mu_0 \frac{\mu^2 m}{\pi^2 \hbar^2} (3 \pi^2 N n)^{1/3} \quad . \tag{4.3}$$

In (4.3) μ is the Bohr magneton, N is the number of metal atoms per unit volume, and n is the number of metallic (conduction) electrons per atom.

(iii) There is, in addition, an orbital diamagnetic contribution to the susceptibility, known as LANDAU DIAMAGNETISM, discussed below. For the free-electron model this contribution is

$$\chi_{Landau} = - \mu_0 \frac{\mu^2 m}{3 \pi^2 \hbar^2} (3 \pi^2 N n)^{1/3} \quad , \tag{4.4}$$

i.e. $\chi_{Landau} = - (1/3) \chi_{Pauli}$, which yields a total *paramagnetic* susceptibility

$$\chi_{free-electrons} = (2/3) \chi_{Pauli} \tag{4.5}$$

for the free-electron model. The free-electron model, however, has only a very restricted range of applicability. For some substances -- the semimetals *As, Sb, Bi,* and graphite being the most notable examples -- real band-structure effects, caused by the periodic potential, produce a large enhancement of the Landau diamagnetism, by factors of up to several hundred. The diamagnetic contribution thus overwhelms the paramagnetic Pauli term; the net result is a negative χ and a diamagnetic solid.

(iv) The orbital contribution of metallic electrons also includes a diamagnetic term which oscillates with the magnetic field, and is periodic in ($1/B$). This oscillatory contribution is called the DE HAAS - VAN ALPHEN effect. Its periods and amplitudes give very precise information on the geometrical and differential properties of the Fermi surface.

4.1 Quantization of Itinerant Electrons in a Magnetic Field

To study diamagnetic effect in metals the effect of the electron-electron interaction can be neglected, and the electrons may be treated as independent particles. Independent electrons moving in a crystal lattice in a magnetic field are described by (3.3), with the electron-electron interaction made to vanish, $V = 0$, and with the electrostatic term $[-e\,\phi(\mathbf{r}_i)]$ representing the periodic potential acting on electron i and caused by the lattice of nuclei and ionic cores. The solution of the Schrodinger equation under these conditions is still a very complex and difficult process. The difficulty arises from conflicting periodicities imposed separately by the lattice and the magnetic field. The problem is simple only in the free-electron case, $\phi = 0$. The solution was obtained by L. D. Landau in 1930, the early days of Quantum Mechanics. Landau chose the field $\mathbf{B}$ along the z-axis and an asymmetric gauge

$$\mathbf{A} = [\,0\,, Bx\,,\,0\,] \quad . \tag{4.6}$$

The resulting spectrum is

$$\varepsilon(\nu, k_z) = (\,\nu + \tfrac{1}{2}\,)\,\hbar\,\omega_c + [\hbar^2/2m]\;k_z^2 \quad , \tag{4.7}$$

where ν is a non-negative integer, k_z is the wave vector for motion along the direction of the magnetic field, and ω_c, the so-called cyclotron frequency, is given by

$$\omega_c = e\;B\;/\;m \quad . \tag{4.8}$$

This spectrum for three-dimensional electrons, which depends only on two-quantum numbers (a discrete ν and a continuous k_z), is highly degenerate -- each energy is shared by very large number of states. There is a "hidden" quantum number, k_y, necessary to define completely the wave function. The energy ε does not depend on k_y and all wave functions with the same ν and k_z -- no matter the value of k_y -- have the same energy. For each fixed value of the set (ν, k_z), there are

$$\frac{L_x\,L_y\;e\;B}{2\pi\,\hbar} \tag{4.9}$$

different k_y states, where $(L_x L_y)$ is the macroscopic area of the crystal -- assumed to be prismatic -- perpendicular to the direction of the magnetic field.

Each integer ν defines for the perpendicular motion in the (x,y) plane and for fixed k_z a discrete energy level, called a LANDAU LEVEL.

From this spectrum, (4.7) - (4.9), its degeneracy and its dependence on the magnetic field intensity B, all thermodynamic quantities can be calculated for the free-electron model. Some of these quantities are discussed explicitly in the next two subsections.

Extension of equations (4.7) - (4.9) to the case of a non-vanishing periodic potential was proposed by L. Onsager and I. M. Lifshitz, who based their method on a semi-classical approach. This approach consists of determining electron trajectories and applying to them the Bohr-Sommerfeld "old" quantum-mechanical quantization rules, *i.e.*

$$\int_{closed\ orbit} \mathbf{p} \cdot d\mathbf{r} = (\nu + \gamma)\, 2\pi\hbar \quad , \tag{4.10}$$

where ν is a non-negative integer, γ is a (positive) phase correction which takes the value ½ in the free-electron case, the position $\mathbf{r}$ follows the closed semi-classical trajectories of the electron in the (x,y) plane, $\mathbf{p}$ is the *canonical* momentum

$$\mathbf{p} = \hbar\mathbf{k} - e\mathbf{A} \quad , \tag{4.11}$$

$\hbar\mathbf{k}$ is interpreted as the *kinetic* momentum, and $(-e\mathbf{A})$ is the contribution of the field to the canonical momentum.

The semi-classical equations of motion of electrons in a periodic potential and a magnetic field are given by

$$k_{parallel} = constant \quad , \tag{4.12}$$

where $k_{parallel}$ is the component of $\mathbf{k}$ parallel to $\mathbf{B}$,

$$\varepsilon_\nu(\mathbf{k},\sigma) = constant \quad , \tag{4.13}$$

and

$$\hbar \dot{\mathbf{k}} = -e \, \dot{\mathbf{r}} \times \mathbf{B} \quad , \tag{4.14}$$

which integrated and with proper choice of the origin yields

$$\hbar \mathbf{k} = -e \, \mathbf{r} \times \mathbf{B} \tag{4.15}$$

for the motion perpendicular to **B** .

Insertion of (4.15) and (4.11) into (4.10), use of Stokes's theorem and application of (3.1) yields Onsager's famous result for the quantization of itinerant electron orbits in a uniform magnetic field,

$$\int_{closed\ orbit} \mathbf{p} \cdot d\mathbf{r} = e \, \Phi = (\nu + \gamma) \; 2\pi \hbar \quad , \tag{4.16}$$

for the motion of the electrons perpendicular to **B**. In (4.16) Φ is the magnetic flux encircled by the electron in its trajectory in the plane perpendicular to **B**. In other words the only trajectories that are (quantum-mechanically) allowed are those that, in the plane perpendicular to **B**, encirle a magnetic flux Φ which takes the discrete values

$$\Phi_\nu = (\nu + \gamma) \; \frac{2\pi \hbar}{e} \quad . \tag{4.17}$$

Because the magnetic flux is quantized, and the value of the magnetic field B is externally determined, the areas of the allowed orbits in real space, A_ν, must take well defined, discrete values. In addition (4.12) , (4.13) and (4.15) state that the orbits in real space in the plane perpendicular to **B** are proportional to -- and rotated by an angle of $(\pi / 2)$ from -- the corresponding trajectories in **k**-space. The cross sections (4.12) at a constant $k_{parallel}$ of the surface of constant energy in **k**-space, (4.13), are therefore proportional to the areas A_ν of the allowed orbits in real space. The constant of proportionality between areas in **k**-space and real space, as given by (4.15), is proportional to B^2, *i.e.* equal to $(e \; B \; / \; \hbar)^2$. Therefore the allowed cross-sectional areas S_ν of the surfaces of constant energy in **k**-space are given by

$$S_\nu = (\nu + \gamma)\ \frac{2\pi\, e}{\hbar}\, B \quad . \tag{4.18}$$

Because the cross-sectional areas in **k**-space S_ν perpendicular to **B** are quantized -- take only the discrete values given by (4.18) -- the energies for the motion perpendicular to **B** are also quantized. Two successive levels, which differ by $\Delta\nu = \pm 1$, are separated by an energy $\Delta\,\varepsilon$, which defines, for that particular value of the energy and that particular value of k_z, a cyclotron frequency $\omega_c{}^*$ and an effective cyclotron mass $m_c{}^*$:

$$\Delta\varepsilon\ =\ \hbar\,\omega_c{}^*\ =\ \frac{\hbar\, e\ B}{m_c{}^*} \quad . \tag{4.19}$$

When the Onsager rules (4.18) are applied to the free-electron model, the results (4.7) - (4.9) are obtained if $\gamma = ½$. For this particular case $\omega_c{}^* = \omega_c$, as given by (4.8), and $m_c{}^* = m$, *i.e.* the cyclotron mass is equal to the electron mass.

It should be mentioned that transition between two adjacent Landau levels, with conservation of $k_{parallel}$ can be induced, for electrons near the Fermi level, by microwave or far infrared radiation; when the frequency ω of that radiation is in the vicinity of ω_c, a resonance -- the so-called CYCLOTRON RESONANCE or diamagnetic resonance -- is observed.

4.2 Landau Diamagnetism

For non-interacting electrons, the total energy of the system -- the metal -- is obtained by adding the individual energies of each electron. Since electrons satisfy Fermi-Dirac statistics {see 08-01-5-216}, in the limit $T \to 0$ that total energy is obtained by summing one-electron energies for all states with energy below the Fermi level ε_F.

The term (½) in the factor (ν + ½) in (4.7) -- or equivalently the term γ in the factor ($\nu + \gamma$) in (4.17)-(4.18) --, which is ordinarily called the zero-point energy, guarantees that although upon the application of a magnetic field some states increase their energy and other decrease it, the energy sum over states of contiguous occupation up to the Fermi level always shows an *increase* by an amount proportional to B^2, thus yielding a diamagnetic contribution to the susceptibility. This is the Laundau diamagnetic contribution to the susceptibility of metallic electrons.

The summation is in general difficult to perform. It can be done numerically -- and laboriously -- for some specific cases, where the number of carriers is small, *i.e.* for the semimetals. For the free-electron model the summation can be accomplished in closed form. The result is that quoted in (4.4).

4.3 The de Haas - van Alphen Effect

The de Haas - van Alphen effect is an oscillatory variation in the magnetic susceptibility of metals as a function of the magnitude of the *static* magnetic field intensity B. It is an effect observed in strong magnetic fields, for pure specimens, and at low temperatures. These three conditions arise from the necessity to have the Landau levels widely separated, not blurred by electron collision effects with impurities, and populated with a sharp discontinuity at the Fermi level, *i.e.* a discontinuity in occupation of essentially 1 between the last "occupied" and the first "empty" levels. These conditions may be summarized by two inequalities

$$k_B\, T \ll \hbar\, \omega_c^* \quad , \quad \omega_c^*\, \tau \gg 1 \quad , \tag{4.20}$$

where ω_c^* is the cyclotron frequency defined by (4.19), k_B is Boltzmann's constant and τ, the relaxation time, is the median time between electron collisions {see 08-01-5-212 and 08-01-4-214}.

The *locus* of allowed quantum states -- in **k**-space -- for itinerant electrons in a periodic lattice and a magnetic field are "tubes", *i.e.* cylindrical shells of well determined, discrete cross sections, given by (4.18). The cylinders, nor necessarily of circular cross section, are inside each other in order of either increasing or decreasing energy. For the free-electron model the tubes are concentric circular cylinders of axis parallel to **B**. These highly degenerate tubes, when the conditions (4.20) are satisfied, are populated by electrons if the energy of their states is lower that ε_F, *i.e.* states are occupied for that part of those tubes that lies inside the Fermi surface (4.1). Only *some* parts of *some* tubes are populated by electrons. The rest -- the states for which $\varepsilon > \varepsilon_F$ -- are allowed but empty states. This distribution is illustrated in Figure 1.

As the magnitude B of the field increases the tubes get more widely separated and contain more states -- as indicated by (4.18) and (4.9). The tubes get thus repopulated at each increasing value of the field. For each orientation (θ , ϕ) of the magnetic field **B** there are discrete values of the field intensity, B_ν , for which a given tube gets completely depopulated, *i.e.* it "leaves" the Fermi surface and lies completely outside. These values of the field B_ν satisfy the condition

$$S_\nu = (\nu + \gamma) \frac{2\pi e}{\hbar} B_\nu = S_{Fermi\ surface}(\theta , \phi) \quad , \tag{4.21}$$

where $S_{Fermi\ surface}(\theta , \phi)$ is the *extremal* cross-sectional area of the Fermi surface in the direction perpendicular to **B**. This phenomenon of allowed-energy tubes "peeling off" the Fermi surface results in a contribution to the free energy, the magnetization, and the susceptibility of the sample which is periodic in $(1/B)$, with period

$$\Delta \left[\frac{1}{B} \right] = \frac{2\pi e}{\hbar \ S_{Fermi\ surface}(\theta , \phi)} \quad , \tag{4.22}$$

i.e. a $(1 / B)$ period inversely proportional to the extremal cross-sectional area of the Fermi surface in the direction (θ , ϕ) perpendicular to **B**.

If the Fermi surface is complex and exhibits several sheets and/or several extremal cross-sectional areas for a given sheet, the magnetization becomes a very complicated oscillatory function. The analysis of the various periods in $(1/B)$ permits the determination of the corresponding cross-sectional areas. Studies of the variation of the oscillations with orientation (θ , ϕ) of the magnetic field lead to accurate determination of the geometry and topology of the Fermi surface of the metal under consideration.

The amplitude of the oscillations and its variation with temperature yield information about the separation between the levels -- the cyclotron mass $m_c{}^*$ at the Fermi level for a particular orientation, (θ , ϕ), an intrinsic property of the metal -- as well as the relaxation time τ, a specific property of the sample under study. The de Haas - van Alphen effect provides the most useful tool to investigate the electronic properties of metals. It yields extremely accurate information on the structural and dynamical properties of itinerant-electron states in solids.

5. DIAMAGNETISM IN SUPERCONDUCTORS

Superconductors are perfect diamagnets for a given range of intensities of applied magnetic fields. They are also perfect conductors, *i.e.* they have zero resistivity. Although the zero resistivity is a necessary condition for perfect diamagnetism -- since it is required for the induced currents in Lenz's law not to decay -- by itself it only implies that the magnetic field in the bulk of a superconductor cannot be changed, whatever its value. The expulsion of the field from the bulk of a superconductor is an additional property, known as the MEISSNER EFFECT. It is illustrated in Figure 2.

SUPERCONDUCTIVITY (see 11-00-4-287) is a phase, a state of matter (in the sense that ice and steam are phases of water and diamond and graphite are phases of pure carbon) observed *only* in some solids, mostly metals.

The superconducting state has several characteristic properties:

(i) When it exists for a given substance, it exists only at temperatures below a so-called transition temperature T_c, and in general down to the absolute zero of the temperature scale $0\ K$.

(ii) It exhibits *d.c.* zero resistivity i.e. infinite conductivity for zero-frequency measurements (an effect discovered in mercury by Kamerlingh Onnes in 1911),

$$\rho(\omega = 0\, ; T < T_c) = 0 \ . \tag{5.1}$$

(iii) It exhibits, for weak magnetic fields, perfect diamagnetism, *i.e.* its magnetic susceptibility is given by

$$\chi = -1 \tag{5.2}$$

which means that magnetic flux lines are completely expelled from the superconductor and that there is a force pushing superconductors away from magnetic fields. This is the Meissner effect discovered by Meissner and Ochsenfeld in 1933.

(iv) In addition to the effect of high temperatures, superconductivity can be destroyed (with a return to the normal metallic state) by either a large enough electric current $I > I_c$, or a large enough applied magnetic field $B > H_c$. The quantities I_c, and H_c are called the critical current, and the critical magnetic field, respectively.

(v) Superconductivity is a macroscopic quantum phenomenon with amplitudes and phases associated with an order parameter ψ. Therefore interference and diffraction effects can be achieved, in particular the Josephson effect. These effects can be fruitfully employed in processing, storing, and retrieving information, i.e. in computer technology {see 11-00-1-291}.

5.1 The Meissner Effect

Meissner and Ochsenfeld discovered that, when a superconductor is cooled below T_c in the presence of a magnetic field, at the transition the lines of induction **B** are completely expelled from the bulk of the sample. In other words, inside the superconductor (5.2) is obtained or, equivalently,

$$\mathbf{B} = 0 \ . \tag{5.3}$$

This result holds up to a given value of the applied field B. In the so-called type I superconductors there is only one critical field H_c. For $B > H_c$ superconductivity is destroyed, the flux fully penetrates the sample, and the metal returns to its normal state.

In type II superconductors there is no field penetration for $B < H_{c1}$ and the superconductors acts as a perfect diamagnet. For intermediate field strengths $H_{c1} < B < H_{c2}$, the magnetic flux lines partially penetrate the superconductor but do not destroy the superconducting state. Since in general H_{c2} is very large, this feature of type II superconductors make them useful as materials for magnets {see 11-00-1-294}. Finally for $B > H_{c2}$ superconductivity is again destroyed with a return of the substance to its normal state. This behavior is illustrated in Figure 3.

5.2 The London Theory

The London theory is completely classical. It incorporates into Maxwell's equations, phenomenologically, the electrodynamic characteristics of superconductors. The zero resistivity property (5.1) requires that, since

$$\rho\, \mathbf{j} = \mathbf{E} \quad ,$$

the electric field **E** should vanish everywhere in a superconductor. The Meissner effect (5.2)-(5.3) implies vanishing magnetic field **B** in the bulk. These two conditions led F. London, in 1950, to *postulate* that in a superconductor the current density **j**, instead of being proportional to **E**, as is the case in other media, is proportional to the vector potential **A**

$$\mathbf{j} = -\left[\frac{1}{\mu_0\, \lambda_L^2}\right] \mathbf{A} \quad , \tag{5.4}$$

where the constant of proportionality defines the length λ_L, the *London penetration depth*. The London equation (5.4), by taking the curl on both sides, may also be expressed as

$$\nabla \times \mathbf{j} = \left[\frac{1}{\mu_0 \ \lambda_L^2} \right] \mathbf{B} \quad . \tag{5.5}$$

Since the vector potential **A** *is not,* in general, a physically measurable quantity, and the current density **j** *always is,* equation (5.4) in effect selects a particular gauge, the so-called London gauge. Equation (5.4) must be consistent with Maxwell's equations. Therefore it implies that, in the absence of charges $\nabla \cdot \mathbf{A} = 0$, and that the normal components of **A** are zero on any external surface through which no external current is fed. Additional conditions on the gauge, compatible with the physical boundary conditions, should be imposed on problems with multiply connected geometries.

It is easily seen that the London equation implies the Meissner effect, and that λ_L is the characteristic length describing the penetration and exponential decay of the magnetic field **B** into a superconductor. From Maxwell's equation,

$$\nabla \times \mathbf{B} = \mu_0 \ \mathbf{j} \quad , \tag{5.6}$$

when the curl is taken on both sides and use is made of (5.5) and of Maxwell's other equation, $\nabla \cdot \mathbf{B} = 0$, one obtains

$$\nabla^2 \mathbf{B} = \mathbf{B} \ / \ \lambda_L^2 \quad . \tag{5.7}$$

Equation (5.7) does not allow a constant **B** solution, unless $\mathbf{B} = 0$. In addition (5.6) guarantees that $\mathbf{j} = 0$ wherever **B** vanishes. In a superconductor extending over the half-space $x \geq 0$, if the field at the boundary $x = 0$ is parallel to the surface and of magnitude B_0 , solution of (5.6) yields

$$B(x) = B_0 \ \exp\left(-x \ / \ \lambda_L\right) \quad , \tag{5.8}$$

i.e. the field decays exponentially into the superconductor, a perfect diamagnet, with characteristic length given by the *London penetration depth.*

5.3 The Ginzburg-Landau Theory

5.3.1 General Formulation

In 1950 Ginzburg and Landau (GL) proposed a macroscopic, phenomenological theory of superconductivity, which was independent of the microscopic aspects of the phenomenon. The theory is quantum-mechanical, in the sense that includes coherent, macroscopic quantum effects. It is a pioneering theory which, independently of the mechanisms responsible for superconductivity, is still valid today. It contains such diverse phenomena as magnetic-field penetration depths, coherence lengths, magnetic-field flux quantization, magnetic-field dependence of the superconducting order parameter, and the Josephson effect. It can be applied to all superconductors, as well as to superfluid ^{3}He, and has become the prototype theory to study a whole class of phenomena related to spatial dependence in second-order phase transitions.

The GL theory introduces a complex order parameter ψ which is allowed to vary in space. Originally GL interpreted ψ as an amplitude, and $|\psi|^2$ as the density of the "superconducting" electrons (they envisioned a superconductor as two interpenetrating electron fluids, the non-dissipative, non-resistive "superconducting" electron fluid, and the dissipative, resistive "normal" electron fluid). In 1959, however, Gor'kov proved that for temperatures below and close to T_c, equations identical to those of GL could be obtained from the Bardeen-Cooper-Schrieffer (BCS) microscopic theory of superconductivity, and that the GL parameters ψ could be interpreted (except for a trivial constant of proportionality) as what in the BCS theory is known as the energy-gap parameter.

The starting point of the GL theory is the introduction of a magnetic Helmholtz free energy F_{SH} for the superconductor, derived from plausibility arguments

$$F_{SH} = \int_{superconductor} d^3r \left[F_{N0} + \Delta F(|\psi|^2) + \left(\frac{1}{2m}\right) \left| -i\hbar\nabla\psi - e^*\mathbf{A}\psi \right|^2 + \left(\frac{1}{2\mu_0}\right) B^2(\mathbf{r}) \right] .$$

(5.9)

Here F_{N0} is the free-energy density of the normal state in the absence of a magnetic field; ΔF is the difference of free-energy densities between the superconducting and the normal states (also in the absence of a field) and is a function of $|\psi|^2$. The third term is the gauge invariant "superconducting kinetic energy", and the last term is the magnetic-field energy in the superconductor. The vector potential is **A**, **B** is the magnetic field, and $e*$ is an effective charge, known now to be $(-2e)$, twice the charge of the electron (the charge of a "Cooper pair" in the BCS theory). All terms in (5.9) are functions of the position **r**, and change with the magnitude and direction of the magnetic field.

Because the proper variables of the magnetic Helmholtz free energy are the temperature T and the magnetization **M**, where

$$\mathbf{M} = (1/\mu_0) \int_{all\ space} d^3r \left[\mathbf{B}(\mathbf{r}) - \mathbf{B}_a \right] \quad , \tag{5.10}$$

$$\mathbf{B}_a = applied \quad magnetic \quad field \quad ,$$

F_{SH} is not continuous at the critical fields. The function which is continuous at H_{c1} and H_{c2}, and whose proper variables are T and $\mathbf{B}_a$, is the Gibbs free energy G_{SH}, given by

$$G_{SH} = F_{SH} - \mathbf{M} \cdot \mathbf{B}_a \quad . \tag{5.11}$$

Substitution of (5.9) and (5.10) into (5.11) yields

$$G_{SH} = G_{NH} + \int_{superconductor} d^3r \left[\Delta F(|\psi|^2) + (1/2m) \left| -i\hbar\nabla\psi - e*\mathbf{A}\psi \right|^2 \right] +$$

$$\frac{1}{2\mu_0} \int \int_{all\ space} d^3r \left[\mathbf{B}(\mathbf{r}) - \mathbf{B}_a \right]^2 \quad , \tag{5.12}$$

where

$$G_{NH} = \int_{superconductor} d^3r \left[F_{N0} + \frac{B_a^2}{2\mu_0} \right] \quad .$$

It should be noted that the last term in (5.12) is to be integrated over *the whole space* (both in the superconductor and outside). Minimization of G with respect to the four functions ψ and **A** [or equivalently ψ and **B**] yields the GL equations:

$$\nabla^2 \mathbf{A} = \frac{ie*\hbar}{m}\left[\psi^*\nabla\psi - \psi\nabla\psi^*\right] + \frac{\mu_0 e*^2}{m}|\psi|^2 \mathbf{A} \quad , \tag{5.13}$$

$$\nabla \times \mathbf{A} = \mathbf{B}_a \quad on\ surface \quad , \tag{5.14}$$

$$\frac{\partial \Delta F}{\partial \psi^*} + \frac{1}{2m}\left[-i\,\hbar\nabla - e*\mathbf{A}\right]^2 \psi = 0 \quad , \tag{5.15}$$

$$\left[i\hbar\nabla\psi + e*\mathbf{A}\psi\right]_{perpendicular} = 0 \quad , \tag{5.16}$$

where the London gauge

$$\nabla \cdot \mathbf{A} = 0$$

has been chosen.

5.3.2 Penetration Length and Coherence Length

In singly connected samples with no penetration of the magnetic flux into the bulk superconductor, the phase of ψ can be chosen so that ψ is real throughout the sample. In particular for a one-dimensional, singly connected problem, with quantities varying along the x-axis, and with magnetic field and vector potential given by

$$\mathbf{B} = [\,0\,,0\,,B(x)\,] \quad ,$$

$$\mathbf{A} = [\,0\,,A(x)\,,0\,] \quad ,$$

the equations (5.13)-(5.16) become

$$(d^2A\ /\ dx^2) = (\mu_0\, e*^2/m)\,\psi^2 A \quad , \tag{5.17}$$

$$(dA\ /\ dx) = H_0 \quad on\ surface \quad , \tag{5.18}$$

$$\frac{\partial \Delta F}{\partial \psi} + \frac{e*^2}{m}A^2\psi = \frac{\hbar^2}{m}\frac{d^2\psi}{dx^2} \quad , \tag{5.19}$$

$$(d\psi / dx) = 0 \quad on\ surface \ . \tag{5.20}$$

For the free-energy difference ΔF, the original GL derivation used a power-series expansion in $|\psi|^2$, and neglected all terms higher than the second. That expansion is still commonly used, and is known to be valid for superconductors at temperatures close to T_c:

$$\Delta F = \frac{H_{cb}^2}{2\mu_0}\left[-2\left[\frac{\psi}{\psi_T}\right]^2 + \left[\frac{\psi}{\psi_T}\right]^4\right] , \tag{5.21}$$

where H_{cb} is the thermodynamic bulk critical field, and ψ_T is the equilibrium value of ψ in the bulk, at temperature T, in the absence of a magnetic field.

The problem of the superconducting half-space discussed above, (5.8) in connection with the London equation, can be solved in the GL theory. Integration of (5.17)-(5.21), under the assumption of small changes in ψ near the surface, yields for $x > 0$

$$\frac{\psi(x, B_a)}{\psi_T} = 1 - \frac{\kappa_o}{(2-\kappa_o^2)\sqrt{8}}\left[\frac{B_a}{H_{cb}}\right]^2 \left[e^{-\frac{\sqrt{2}\kappa_o x}{\lambda_L}} - \tfrac{1}{2}\kappa_o\, e^{-\frac{2x}{\lambda_L}}\right] , \tag{5.22}$$

and

$$B(x) \simeq B_0 \exp(-x/\lambda_L) \ . \tag{5.23}$$

Equation (5.23) reproduces, approximately, (5.8). In the GL equations λ_L, the London penetration depth, is given by

$$\lambda_L^2 = \frac{m}{\mu_0 e^{*2} \psi_T^2} \ . \tag{5.24}$$

In (5. 22) κ_o is a dimensionless constant

$$\kappa_o = (\sqrt{2}\, e^* / \hbar)\ \lambda_L^2\ H_{cb} \ . \tag{5.25}$$

Two remarks are necessary at this point. First, there are two length scales in the problem: (i) the decay length for magnetic fields, λ_L, and (ii) the decay length, $(\lambda_L / \sqrt{2}\kappa_o)$, for the order parameter ψ, given by the first exponent in (5.22). Second, Gor'kov has shown that

$$\kappa_o \approx 0.96\, \lambda_L\, \xi_o^{-1} \ , \tag{5.26}$$

where ξ_o is the coherence length introduced by Pippard in connection with the general electromagnetic properties of superconductors {see 11-00-4-287}. Values of κ_o are small (< 0.707) for the soft, type I superconductors [0.01 for Al; 0.3 for Pb], whereas it takes large values (> 0.707) for the hard, type II superconductors [~ 8 for V; extremely large for the new, high T_c materials {see 11-00-4-288}].

A type I superconductor excludes a magnetic field from its bulk completely. If the magnetic field B is increased there is a value, H_c for which the superconductivity is suddenly destroyed, the system returns to the normal state, and the magnetic field penetrates the specimen completely. A type II superconductor excludes the field completely up to a value H_{c1}. Above H_{c1} the field is partially excluded, although the specimen remains superconducting and exhibits zero resistivity. At a higher field, H_{c2} , the flux penetrates completely, superconductivity is destroyed and the specimen returns to its normal state.

5.3.3 Flux Quantization

In many applications (thin specimens, weak magnetic fields, etc.), the order parameter ψ can be considered to have a constant magnitude $n^{1/2}$, although its phase $\theta(\mathbf{r})$ can vary appreciably in space,

$$\psi = n^{1/2}\, e^{i\theta(\mathbf{r})} \ . \tag{5.27}$$

From standard quantum-mechanical arguments the electrical supercurrent is given in this case by the usual formula

$$\mathbf{j} = \frac{1}{2m}\left[\psi^* \left(-i\,\hbar\nabla - e^*\mathbf{A}\right)\psi + \psi\left(i\,\hbar\nabla - e^*\mathbf{A}\right)\psi^*\right]$$

$$= \frac{n\, e^*}{m}\left(\hbar\,\nabla\theta - e^*\mathbf{A}\right) \ . \tag{5.28}$$

Deep inside any superconductor the magnetic field **B** and the electric current **j** are zero and, therefore, from (5.28) one obtains

$$e* \mathbf{A} = \hbar \nabla\theta \ . \tag{5.29}$$

In a multiply connected sample one can find a closed path C which encircles a non-superconducting region where there may be a magnetic field. Line integration of (5.29) over that path, use of Stokes's theorem and knowledge that ψ must be single-valued yields

$$\int_{closed\ C} \mathbf{A} \cdot d\mathbf{s} = \int_{area\ C} \nabla\times\mathbf{A} \cdot d\boldsymbol{\sigma} = \int_{area\ C} \mathbf{B} \cdot d\boldsymbol{\sigma} = \Phi$$

$$= \frac{\hbar}{e*} \int_{closed\ C} \nabla\theta \cdot d\mathbf{s} = \frac{\hbar}{e*} \cdot 2\pi\nu \ , \tag{5.30}$$

where Φ is the magnetic-field flux, and ν is an arbitrary integer. In other words (5.30), taking $|e*| = 2e$, can be written

$$\Phi = \nu \ \Phi_0 = \nu \cdot 2.0678 \times 10^{-15} \ tesla \ m^2 \ , \tag{5.31}$$

i.e. if a closed path without currents can be established deep inside a multiply connected superconductor, then the magnetic-field flux encircled by that path is quantized in units of Φ_0. The unit of flux, Φ_0, is called a *fluxoid.*

5.3.4 Phase-Current Relationship; the Josephson Effect

From the GL equations it can be easily seen that the order parameter ψ has an indeterminate *arbitrary, constant* phase. In a given superconductor (called 1) its phase θ_1 is completely arbitrary. If, however, there is nearby a second superconductor (called 2), which is *weakly* connected to the first one, although both phases, θ_1 and θ_2, are indeterminate by the *same* additive constant, the *phase difference* between the two,

$$\delta = \theta_2 - \theta_1 \ ,$$

is an observable meaningful quantity. As can be seen from (5.28) a variation of θ over space is responsible for the existence of a supercurrent. Similarly a phase difference between two weakly coupled, spatially close superconductors produces a current flow between them given by

$$J = J_0 \sin\delta \ , \tag{5.32}$$

where J_0, a constant, describes the maximum possible current which may flow between the two specimens. Equation (5.32) is Josephson's *d.c.* equation relating current and phase difference. It is implicit in the GL equations and applies to any system with a macroscopic, quantum-mechanical, complex order parameter. It can be interpreted in terms of the standard quantum-mechanical uncertainty relation between particle number and wave-function phase.

5.3.5. Magnetic-Field Dependence of the Order Parameter

Detailed solutions of (5.17)-(5.21) for thin films clearly exhibit a field dependence of the *amplitude* of the order parameter $|\psi|$ on the applied magnetic field strength B_a. As the field is increased the value of $|\psi|$ decreases, and there is a value H_f for which it goes (either continuously or discontinuously) to zero and the film becomes normal. It is found that H_f -- the film critical field -- depends on H_{cb}, the film thickness d, and the London penetration depth, and that the $|\psi|$ transition to zero at H_f is discontinuous if

$$d / \lambda_L > \sqrt{5} \ .$$

These results, and many others obtained from the solution of the GL equations for a variety of geometries and situations, have been confirmed by superconducting tunneling experiments.

5.3.6 Quantum Interference Phenomena

Given the following facts:

(i) the order parameter ψ is complex;

(ii) ψ must be single valued;

(iii) the magnetic field **B** couples to it in a gauge-invariant form and therefore is directly related to the phase θ of ψ; and

(iv) the GL equations are non linear;

it is possible to obtain a large number of interference and diffraction effects which can be fruitfully used in designing interesting electronic devices {see 11-00-1-291}. It can be said that, in understanding the origins of the diamagnetism in superconductors, scientists and engineers have promoted quantum mechanics to the macroscopic, everyday-use level.

6. CONCLUSION

All diamagnetic effects are quantum mechanical. The persistence of the currents induced by by Lenz's law is caused exclusively by the phase coherence of the quantum-mechanical wave functions, either at the microscopic level -- as evidenced in the diamagnetism of atoms, molecules and metallic electrons -- or in their macroscopic manifestations -- as in superconductors. One of the principal effects is the gauge-invariant way in which quantum-mechanical phases couple to magnetic fields. This coupling produces, in addition to steady currents that result in a screening of the magnetic field, *i.e.* normal diamagnetism, a wealth of refraction, interference and diffraction effects which are directly observable experimentally. The de Haas - van Alphen effect, discussed in Section 4, and the Josephson Effect and Flux Quantization in superconductors, presented briefly in Section 5, are all manifestations of the relationship between electrical current and quantum-mechanical phase, coherent coupling of magnetic fields to the phases of quantum-mechanical wave functions or order parameters, and the relationship between electrical currents and magnetic fields as given by Maxwell's equations.

FURTHER READING

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FIGURE CAPTIONS

Figure 1

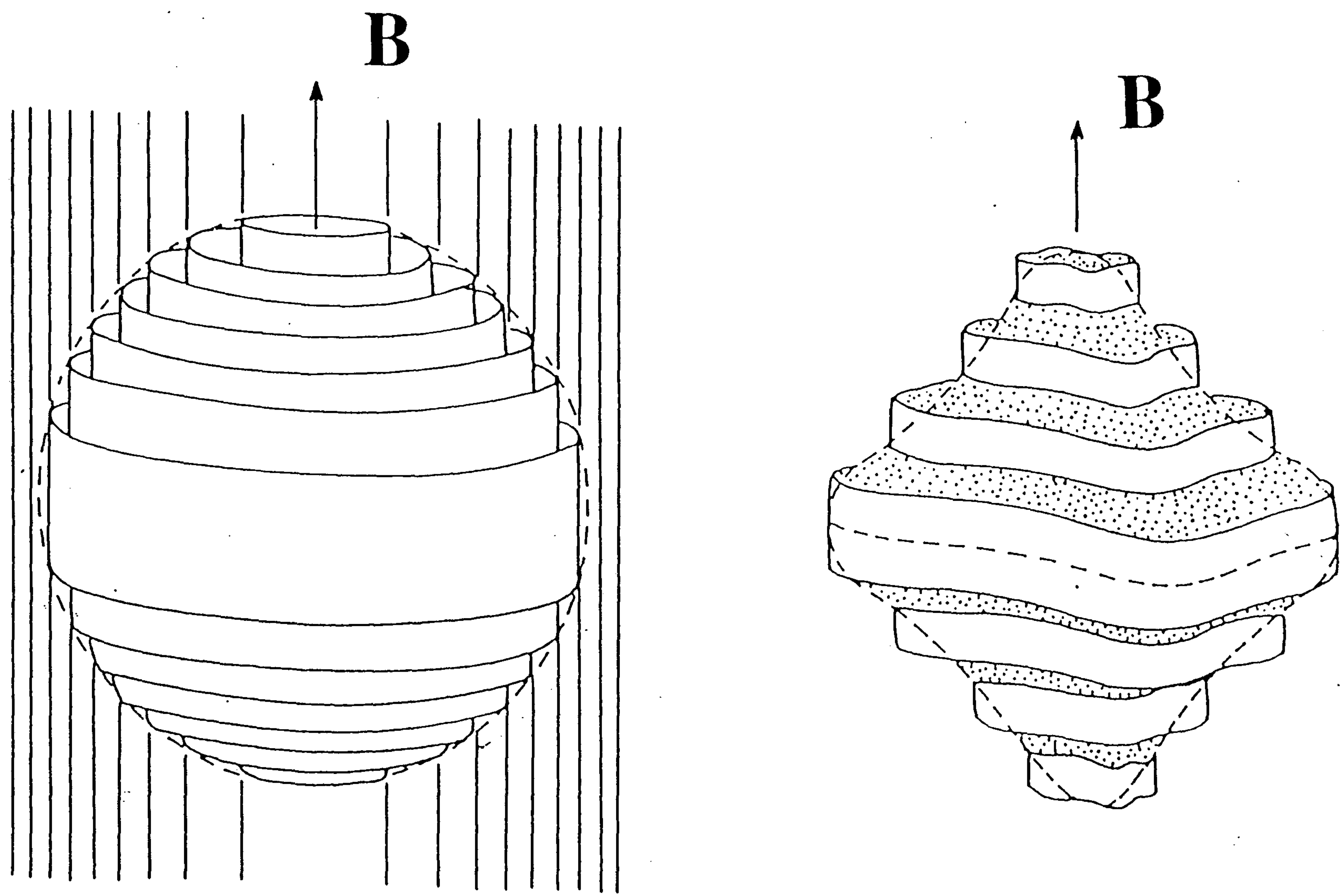
Schematic representation of the quantization of metallic electrons in a magnetic field. The depicted tubes are the *loci* of allowed states in **k**-space. Only the occupied portions of the tubes are drawn. (a) The free-electron model. (b) An arbitrary potential. [From Falicov, 1973]

Figure 2

Schematic representation of the Meissner effect. When a superconducting sphere is cooled in a constant applied magnetic field, below the transition temperature T_c the lines of induction **B** are ejected from the sphere. [From Kittel, 1986]

Figure 3

(a) Magnetization *versus* applied magnetic field for a type I superconductor exhibiting the Meissner effect (perfect diamagnetism) below H_c. (b) Magnetization *versus* applied magnetic field for a type II superconductor. [From Kittel, 1986]



(a) (b)

Figure 1

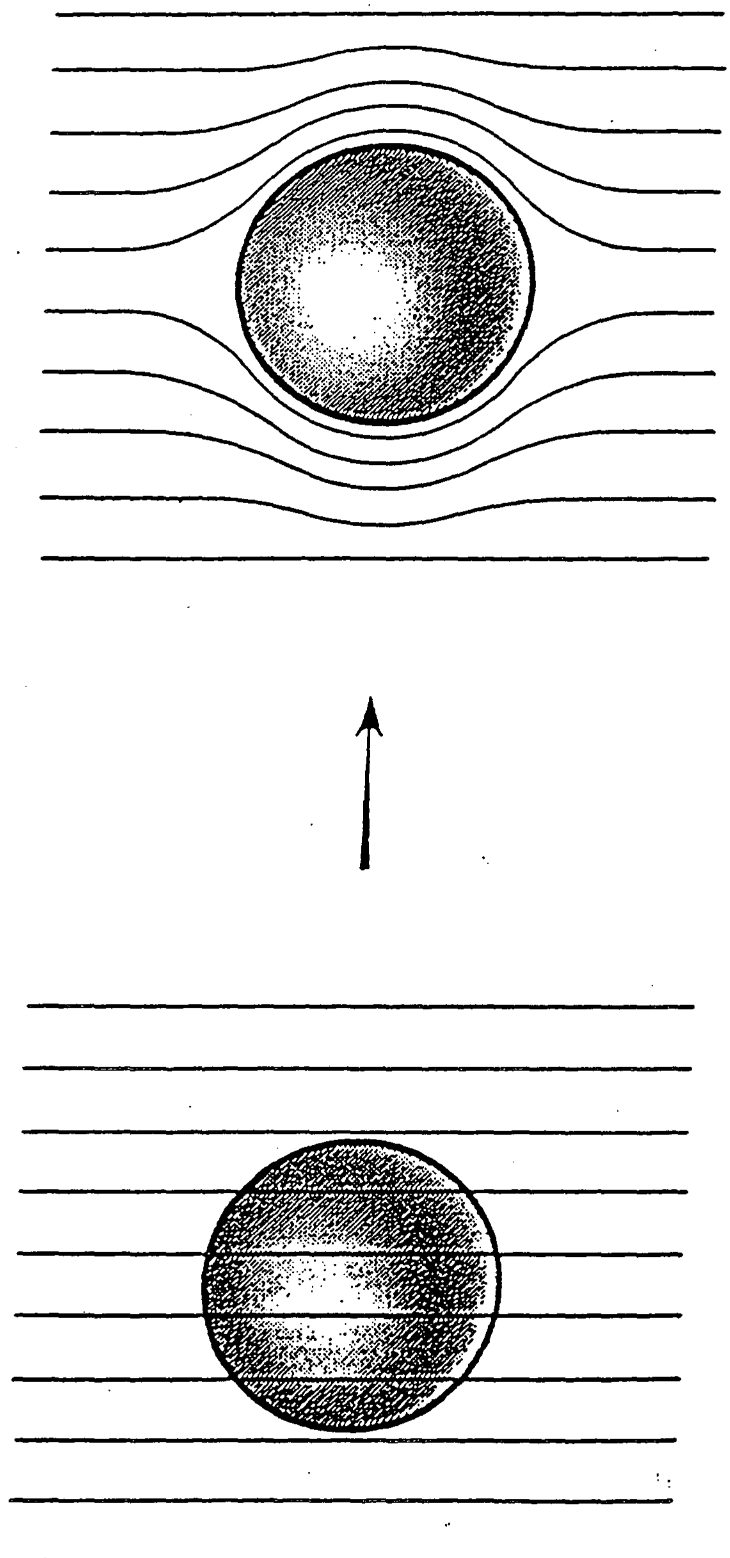
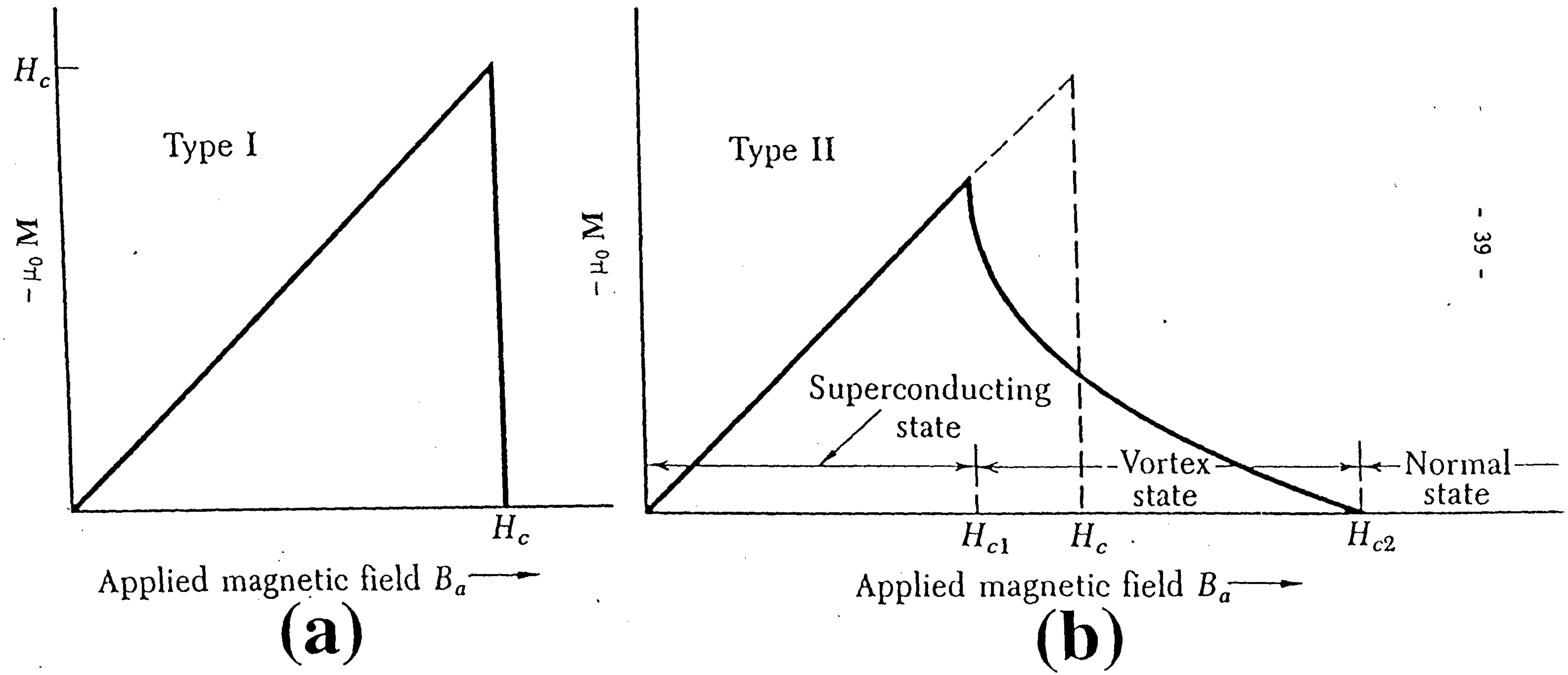


Figure 2



H_c
Type I
$-\mu_0$ M
H_c
Applied magnetic field B_a
(a)
Type II
$-\mu_0$ M
Superconducting state
Vortex state
Normal state
H_{c1}
H_c
H_{c2}
Applied magnetic field B_a
(b)

Figure 3

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