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DISCRETENESS OF ENERGY LEVELS IN SMALL METALLIC PARTICLES

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Résumé. — Dans une petite particule métallique les niveaux d'énergie électroniques ont une structure discrète. Si l'espacement des niveaux est comparable ou supérieur aux paramètres d'énergie intervenant dans un phénomène physique, la discontinuité des niveaux peut donner lieu à un comportement tout à fait différent de celui du métal massif. On discute ici des idées de base et des récents progrès accomplis dans ce domaine.

Abstract. — In a small metallic particle, the quantized electronic energy levels make a discrete structure. If the level spacing is comparable to or larger than relevant energy parameters in a physical phenomenon, the discreteness of levels may give rise to some anomalies quite distinct from the normal behaviour in a bulk metal. In this review the basic ideas and recent progress are discussed.

1. — If we take the familiar picture of free electrons, the one-electron levels in a piece of metal are considered as quantized states. In the bulk limit, however, these levels are quasi-continuous and a sum over these states is replaced by an integral with a properly defined density of states, which is independent of the boundary condition imposed on the wave function as known by the Weyl-Laue theorem. In thermal equilibrium, each state is occupied with a probability given by the well-known Fermi distribution function. Thermodynamic properties of metallic electrons are thus easily calculated. Dynamic properties, such as electronic conduction, spin relaxation and so forth, are governed by the scattering processes of electrons by phonons or defects perturbing the ideal periodicity of the lattice.

This standard picture of metallic electrons may have to be drastically modified when we deal with small particles. The finiteness of extension brings about two distinct effects on the electronic states in a particle. The first is the real discreteness of the energy levels and the second is the surface effect due to the boundary conditions. As the surface-to-volume ratio increases, the latter effect gives a correction to the effective density of states. For example, in the tight binding picture the band width will be narrowed around the center and the effective density of states may increase. Certainly the surface effect of this sort may become significant under circumstances, but here we shall be mainly concerned with the first effect, namely that of the discreteness of energy levels.

A small particle is indeed a giant molecule composed of many thousand atoms. The one-electron levels in a given particle will be denoted as ... ε_{-2} , ε_{-1} , ε_0 , ε_1 , ε_2 ... At the absolute zero of

temperature electrons in the particle fill these levels up to ε_0 , leaving the levels ε_1 , ε_2 , ... empty. If the number of electrons is even the level ε_0 is occupied by a pair of plus and minus spins; if it is odd, the level ε_0 is occupied by an electron with free spin.

In practice we observe a collection of large number of particles. Since the size and shape of particles can be controlled only within a limited accuracy, the set of electronic levels (... ε_{-2} , ε_{-1} , ε_0 , ε_1 , ε_2 , ...) is considered as a statistical object defined by the statistical ensemble of particles. Consequently, the spacing Δ for a pair of successive levels is also statistical; its distribution function will be denoted by $P(\Delta)$; namely

$$P(\Delta) d\Delta = \text{Pr}(\Delta, \Delta + d\Delta) \quad (1)$$

is the probability to find Δ in the interval Δ and $\Delta + d\Delta$. The average spacing

$$\delta = \int \Delta P(\Delta) d\Delta$$

is easily estimated to be

$$\delta \sim D(\zeta)^{-1} = 0(\zeta/N) \quad (2)$$

where $D(\zeta)$ is the density of states at the Fermi level in a bulk metal converted to the average volume of a particle and N is the average number of metallic electrons in a particle. For a free electron model ζ is the maximum kinetic energy at 0 K and for a band model ζ is measured from the bottom of the band. This estimation shows that δ is inversely proportional to the size of particles (¹). Since ζ is a few electron volts in most metals, δ amounts to 10^{-4} eV if the size is, say 50 Å in diameter.

(¹) In a very small particles, δ may be smaller than this estimation because of the narrowing of band width at the surface.

In treating bulk properties, the spacing δ is considered to be smaller than any of relevant energy parameters; this is in fact what is meant by the quasi-continuous spectrum of energy levels. On the other hand, for particles small enough, the spacing δ may no longer be small in comparison to the relevant energy parameters. Thus, thermal properties of particles, the heat capacity or the magnetic susceptibility for example, may be quite different from those of bulk if we work at such low temperatures as $\delta \gtrsim kT$ or at weak field $\delta \gtrsim \mu_B H$. Dynamical responses of particles at a frequency ω so low as to satisfy the condition $\hbar\omega \lesssim \delta$ may be completely different from those of a bulk system.

Thermodynamic anomalies of this sort was first discussed by Fröhlich [1] many years ago. He assumed energy levels to be equally spaced and showed naturally that the electron heat capacity should decrease exponentially at very low temperatures in contrast to the Sommerfeld linear law. Later, Brout, Greenwood and Krumhansl [2] pointed out the anomaly of the spin susceptibility at low temperatures. Independently the present author published a paper [3] on this subject, which seems to have attracted attention of experimentalists as well as of theorists to this rather unusual physics of small particles. As was discussed in this work, there is another peculiar feature of metallic particles which is very important but had not been clearly realized before. That is the neutrality condition of each single particle.

If just one electron is added to or is lost by a particle of radius R , the work required in the process amounts to about $e^2/2R$. For R equal to the hydrogen radius, this energy is 13.5 eV; for $R \sim 50 \text{ \AA}$ or 500 \AA , it is 0.13 eV or 0.013 eV. This energy is considerably larger than the thermal energy kT at room temperature. This means that, if particles are separated, each particle keeps the number of electrons in it very strictly constant and remains electrically neutral. In fact, the presence of this energy is seen in conduction properties of thin metallic films in which evaporated atoms form islands with some tunnelling contacts [4]. For a certain range of effective thickness the conduction is of activation type, the activation energy increasing with decrease in thickness or the size of islands. Competition between the contact and the localization of electrons is a very popular subject in related fields of physics, for example in the metal-insulator transition.

The reason why the neutrality condition is so important is seen from the following consideration. If this condition needs not be forced on each particle, electrons are freely exchanged between different particles. Then the whole sets of random levels for a great number of particles just make a continuum spectrum; there is nothing left to discriminate a collection of particles from a bulk

metal and accordingly there is no thermodynamic anomalies. On the other hand, if the neutrality condition should be strictly kept, the statistical mechanics of a single particle is that in which the electron number is kept constant, namely the *canonical* statistics rather than the *grand-canonical* statistics. Usually the difference of the two is ignored because fluctuation of electron number in a grand-canonical ensemble is considered to be negligible. It should be clearly recognized that the condition for this is that

$$\delta \ll kT$$

and not simply that the electron number is large.

Therefore, the thermodynamics of small particles is properly treated by applying the canonical statistics for a single particle and then averaging thermodynamic quantities over the statistical ensemble of the sets of energy levels. Calculations of this sort is generally pretty hard.

In order to make the problem simpler and to look into the effects of the discreteness of energy levels, one sometimes uses the constant spacing model, in which every particle is assumed to have levels with a constant spacing δ as was first treated by Fröhlich. The adequateness of this simplification depends on what one would like to see. Thermodynamic anomalies appearing in this model are not quite the same as those in the models with statistical level schemes, but a great advantage is that it allows rigorous mathematical treatments [5]. It is interesting, for example, to note the difference between canonical and grand-canonical treatments of this model; the occupation probability of the levels is discontinuous in the canonical statistics in contrast to the familiar continuous Fermi distribution function.

2. — Let us now consider the heat capacity at very low temperatures. Figure 1 shows electronic configurations of a particle with an even number of electrons at the ground state and the lowest excited states. The partition function is given by

$$Z_{\text{even}} = 1 + 4e^{-\beta(\epsilon_1 - \epsilon_0)} + \dots \quad (3)$$

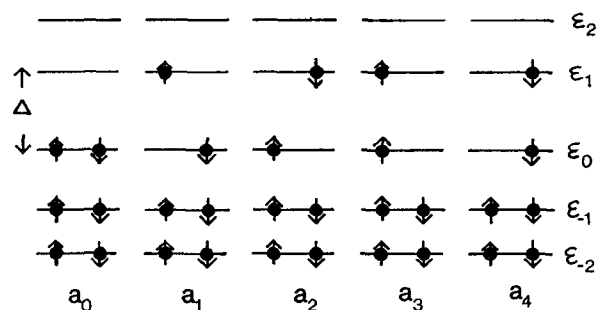


FIG. 1. — Electronic configurations in a particle with an even number of electrons; a_0 is the ground state and a_1, a_2, a_3 and a_4 are excited states.

where $\beta = 1/kT$, and the free energy by

$$F_{\text{even}} = -kT \log Z_{\text{even}} = -4kT e^{-\beta(\epsilon_1 - \epsilon_0)} + \dots \quad (4)$$

The ground state and excited states of a particle with an odd number of electrons are shown in figure 2. The partition function and the free energy are

$$Z_{\text{odd}} = 2 + 2e^{-\beta(\epsilon_1 - \epsilon_0)} + 2e^{-\beta(\epsilon_0 - \epsilon_{-1})} + \dots \quad (5)$$

$$F_{\text{odd}} = -kT \log 2 - kT(e^{-\beta(\epsilon_1 - \epsilon_0)} + e^{-\beta(\epsilon_0 - \epsilon_{-1})}) + \dots \quad (6)$$

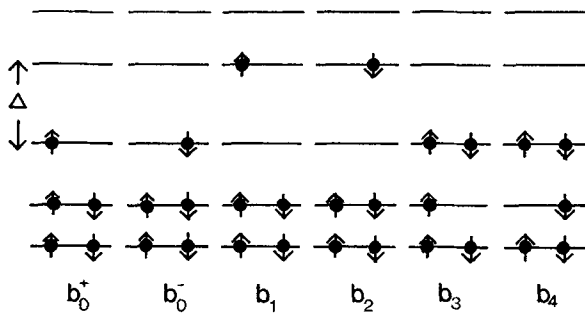


FIG. 2. — Electronic configurations in a particle with an odd number of electrons; b_0^+ and b_0^- are the ground states and b_1 , b_2 , b_3 and b_4 are excited states.

For a statistical ensemble of particles, we must average the free energy for even and odd particles and also over the possible distribution of the level spacing $\epsilon_1 - \epsilon_0$ and $\epsilon_0 - \epsilon_{-1}$. Thus we have, for the averaged free energy per particle,

$$F = \frac{1}{2} (\langle F_{\text{even}} \rangle + \langle F_{\text{odd}} \rangle) = -\frac{1}{2} kT \log 2 - 3kT \langle e^{-\beta\Delta} \rangle + \dots \quad (7)$$

As will be discussed later, the distribution function $P(\Delta)$ has the form

$$P(\Delta) = \text{const.} \Delta^n \quad (8)$$

for small values of Δ with possible values of n equal to 1, 2 or 4. As the result the heat capacity behaves as

$$C \propto T^{n+1} \quad (9)$$

at low temperatures satisfying the condition $kT \ll \delta$. There the heat capacity should be suppressed below the Sommerfeld linear law (?). Experimental verification of this prediction seems to have been unsuccessful up to date.

In the presence of a weak magnetic field satisfying the condition, $\mu_B H \ll \delta$, namely that the electronic Zeeman energy is much smaller than the average spacing, the electron spin paramagnetism of an even particle should be totally quenched at

(?) More rigorously, in eqs. (3) and (5) we have to include excitations to higher levels or from lower levels. Because of this complication, the proportionality constant in the relation (9) is obtained by fairly complicated calculations [3, 5].

low temperatures, $kT \ll \delta$, whereas that of an odd particle should be enhanced to a free spin paramagnetism obeying the Curie law. It should be noted that this exceeds the normal Pauli paramagnetism at such low temperatures. So much can be predicted without any calculation. More detailed behaviour of quenching or enhancement from the Pauli paramagnetism can be obtained with elaborate calculation [5].

The above mentioned prediction can be tested by experiments. The first successful experiment was done by Taupin [6] for very small platelets of lithium produced in LiF by irradiation of neutrons and following heat treatments. An unshifted Li [7] line was attributed to even particles. More recent observations for copper by Kobayashi *et al.* [7] and by Yee *et al.* [8] also demonstrate the anomalous spin susceptibility by an asymmetric shape of the NMR line, which is composed of a unshifted line due to even particles and a broad line with large shift due to odd particles. Also a direct evidence of the Curie law has been obtained by Borel *et al.* [9] for small part particles of lithium embedded in a matrix of CO_2 or Xe.

In the first paper of the present author [3], the distribution $P(\Delta)$ was assumed for simplicity to be purely random, namely

$$P(\Delta) = e^{-\Delta/\delta} / \delta. \quad (10)$$

This is a Poisson distribution and corresponds to the $n = 0$ case in eq. (8). Someone immediately pointed out to the author that this will not generally be the case because two crossing eigenvalues tend to repel each other so that $n = 0$ is to be expected. Later Gor'kov and Eliashberg [10] discussed this point employing the theory of random matrices first introduced by Wigner [11] for a nuclear problem and developed further by Dyson and others [12].

Corresponding to an ensemble of particles, we may suppose an ensemble of random Hamiltonians. We can take two different points of view; One is the many-electron picture and the other is the one-electron picture. From the first point of view we consider many-electron Hamiltonians, each defining electronic states of a particle as a whole. From the second point of view we consider one-electron Hamiltonians, each defining one-electron states in a particle. The former is more general than the latter, which is based on an approximation but, on the other hand, gives more information within its framework. In either picture, we distinguish the following three classes of statistical ensembles which are characterized by different values of the zero-limit power n in eq. (8).

a) *Orthogonal Ensemble*; $n = 1$. If the Hamiltonians have time reversal symmetry and the matrix elements can be made real by suitable choice of representation, an ensemble of such random Hamiltonian is called orthogonal, because it is invariant

under orthogonal transformations. In many-electron picture, particles with even numbers of electrons, and accordingly with integer spins, in zero magnetic field make this ensemble. In one-electron picture, this is an ensemble of orbital Hamiltonians with real random potentials in zero magnetic field.

b) *Symplectic Ensemble*; $n = 4$. This corresponds to Hamiltonians which can be represented by matrices having elements in quaternions. The basic transformations is a symplectic group. Thus the orbital and the spin states are inseparably coupled to Kramers doublets by spin-orbit interactions, the time reversal symmetry being preserved. This applies to many-electron Hamiltonians for odd numbers of electrons, or to one-electron Hamiltonians with strong spin-orbit coupling, both in zero magnetic field.

c) *Unitary Ensemble*; $n = 2$. If the time-reversal symmetry is lost, Hamiltonians are generally represented by hermitian matrices, which are subject to unitary transformations. This applies to many-electron as well as one-electron Hamiltonians in the presence of a magnetic field.

It is easy to see how the power n in eq. (7) comes about for these different ensembles. In an orthogonal ensemble, two levels are close each other when the relevant part of the Hamiltonian matrix take the form

$$\begin{pmatrix} x & y \\ y & -x \end{pmatrix} \quad (11)$$

for which the eigen value are

$$\varepsilon = \pm \sqrt{x^2 + y^2}. \quad (12)$$

Therefore the spacing $\Delta = 2\varepsilon$ is a random variable having two independent real random numbers, x and y . The probability to find Δ in a ring between the radii Δ and $\Delta + d\Delta$ in the x - y plane is obviously proportional to $\Delta d\Delta$ for small values of Δ . Thus we have $n = 1$. For an unitary ensemble, the offdiagonal elements of (11) are replaced by $y = y' + iy''$ and $y^* = y' - iy''$, so that the eigenvalues are

$$\varepsilon = \pm \sqrt{x^2 + y'^2 + y''^2}.$$

Since there are three independent real random variables, x , y' , y'' , the power n is equal to 2. For a symplectic ensemble the Hamiltonian is composed of quaternions, or more explicitly the relevant part is of the form

$$\begin{pmatrix} x & 0 & y & iz \\ 0 & x & iz^* & y^* \\ y^* & -iz & -x & 0 \\ -iz^* & y & 0 & -x \end{pmatrix} \quad \begin{aligned} y &= y' + iy'' \\ z &= z' + iz'' \end{aligned}$$

which has the eigenvalues

$$\varepsilon = \pm \sqrt{x^2 + y'^2 + y''^2 + z'^2 + z''^2}$$

and the corresponding pair of doublets. Since the number of independent variables is now five, the power n is 4.

If the randomness is a resultant of a number of random causes, the matrix elements of a random Hamiltonians may be assumed to be nearly Gaussian. If further the variances were all the same, we would have

$$P(\Delta) = C\Delta^n e^{-\alpha\Delta^2} \quad (13)$$

to generalize eq. (8) to larger values of Δ . This corresponds to Wigner's surmise [11]. However, this law is not generally true, because the variances may be different for different types of random elements in the Hamiltonian matrices. For example, if for some reason y in the expression (11) has a much smaller variance than the diagonal elements, the power n in eq. (13) would be zero except for very small values of Δ . This case is not exactly Poisson but is close to it. If the applied field is weak, an orthogonal ensemble is more adequate than a unitary ensemble, into which the ensemble goes over when the magnetic field becomes strong enough to mix states with different characters with respect to time reversal. For a non-degenerate band, the orthogonal ensemble is suitable to describe the real situation as long as the spin-orbit interaction is not so strong as to admix the higher bands into the conduction band. For degenerate bands the situation is more complex and depends on energy and effective momenta.

Gor'kov and Eliashberg [10] pointed out that the infrared absorption of small metallic particles should reflect the effect of level repulsion by showing some sort of wriggles in the absorption curve. Experimental verification of this interesting prediction is, however, very difficult and a recent experiment [13] seems to indicate a strange discrepancy between theory and experiment with regard to the intensity of absorption.

At the beginning of this section, we have briefly discussed anomalies in the heat capacity and the magnetic susceptibility. This was based on a simple one-electron picture for orbital states. Since there are other possibilities of random energy levels as we have seen in the above, it is desirable to make the theory more precise. A very careful study was made by Denton *et. al.* [5], who calculated in a good approximation the heat capacity for the three ensembles and the spin susceptibility for orthogonal and symplectic ensembles taking account of distribution laws as predicted by the theory of random matrices. Differences between different ensembles are interesting, but they are not easily detectable by experiments.

3. — To conclude this short review, some diverse points should be further commented on.

It has been pointed out by Shiva [14] and Sone [15] that even a weak spin orbit interaction

can significantly affect the anomalous spin paramagnetism of small particles. We consider here, for simplicity, a metal with a non-degenerate band. A degenerate band case is somewhat complicated. In an infinite crystal, a Bloch function with wave number k and spin polarization along a chosen direction is written as

$$\psi_{\hat{k}} = \{ a_k | + \rangle + b_k | - \rangle \} e^{ikr} \quad (14)$$

where a_k and b_k are appropriate periodic functions, a_k belonging mainly to the conduction band and b_k mainly to upper bands coupled to the lower band through spin orbit interaction. If the spin orbit interaction is weak compared with band gaps, the amplitude of b_k is much smaller than that of a_k . The function $\psi_{\hat{k}}$ is predominantly with plus spin. The ratio of b_k to a_k is a measure of the *intrinsic* mixing of spin states by spin orbit interaction.

In the presence of a perturbation destroying the periodicity of a perfect crystal, the above-mentioned intrinsic mixing of spin states gives rise to non-vanishing matrix elements between Bloch functions with different k 's and different spin orientations. This is the Elliott mechanism [16], by which an electron flips its spin when it is scattered at impurities or at a surface. Elliott estimates the spin flip rate $1/\tau_s$ as

$$\frac{1}{\tau_s} \sim \frac{1}{\tau_R} (g - 2)^2 \quad (15)$$

except for a numerical factor. The momentum relaxation rate $1/\tau_R$ is roughly given by

$$\frac{1}{\tau_R} \sim \frac{R}{v} \quad (16)$$

for the case of surface scattering in a particle with a linear dimension R . This is the frequency for an electron with velocity v bouncing back and forth within a particle. We may write the spin flip rate as

$$\frac{1}{\tau_s} \sim \frac{2\pi}{h} \bar{H}_{so}^2 / \delta \quad (17)$$

in terms of an effective spin orbit interaction \bar{H}_{so} , which may be called the Elliott interaction for convenience, and the density of states, $1/\delta$. Considering that

$$\delta \propto 1/R^3$$

we find

$$\bar{H}_{so} \propto 1/R^2.$$

For a large particle, in which electronic levels make a quasi-continuous spectrum, the Elliott interaction acts as an agency for spin relaxation. On the other hand, for very small particle, we expect the inequality

$$\delta \gg \bar{H}_{so}$$

to hold. In the latter case, the Elliott interaction is a weak perturbation to the discrete one-electron quantum states in a particle. Given a particular kind

of metal, there may or may not be a certain range of size of particles where the discreteness effect is still pronounced and yet the Elliott interaction \bar{H}_{so} is comparable to or even larger than the level spacing δ . In such a range of size, the anomaly of spin susceptibility depends on the parameter

$$\rho \sim \frac{h}{\tau_s} / \delta \sim (\bar{H}_{so} / \delta)^2. \quad (18)$$

As this parameter increases, the anomaly will be suppressed.

Taking the axis of spin quantization along an applied magnetic field, we write the wave functions of a Kramers doublet in a particle as

$$\phi_n^{\uparrow} = u_n | + \rangle + v_n | - \rangle \quad (19)$$

$$\phi_n^{\downarrow} = u_n^* | - \rangle - v_n^* | + \rangle$$

including the effect of the boundary. For the matrix elements of spin operators, we have

$$\begin{aligned} \langle \phi_n^{\uparrow} | \sigma_z | \phi_n^{\uparrow} \rangle &= 1 - \gamma_n, \quad 1 > \gamma_n > 0 \\ \langle \phi_n^{\downarrow} | \sigma_z | \phi_n^{\downarrow} \rangle &= -1 + \gamma_n \\ \langle \phi_n^{\uparrow} | \sigma_z | \phi_n^{\downarrow} \rangle &= 0, \quad \langle \phi_n^{\uparrow} | \sigma_z | \phi_m^{\downarrow} \rangle \neq 0, \text{ etc.} \end{aligned} \quad (20)$$

Spin magnetization induced by a magnetic field generally consists of two contributions; one is the orientation part and the other is the polarization part. The orientation part is due to the diagonal elements of σ_z and gives rise to the anomalous spin paramagnetism of small particles as we have discussed before. The spin orbit interaction tends to reduce the effective Bohr magneton as seen in eq. (19), so that the Curie constant for odd particles will decrease as the parameter ρ increases. The polarization part is due to the off-diagonal elements of σ_z and is a perturbational effect in second order, an analogue to the Van Vleck term in atomic magnetism. This is independent of temperature and also of the odd-even parity of the electron number in a particle. It increases as ρ increases and approaches the normal Pauli paramagnetism in the limit of a large ρ , where the diagonal elements tend to zero and the orientation part vanishes. The qualitative feature is illustrated in figure 3.

The line shape of ESR by conduction electrons in small particles is a subject closely related to the above-mentioned topics. This problem has been treated by Kawabata [17] some years ago. As eq. (19) indicates, the Elliott interaction produces different splits for different Kramers doublets in a magnetic field, so that the ESR signal should consist of a number of discrete lines, if there is no other cause for broadening, but the envelope of these lines is the effective shape of ESR. On the other hand as was mentioned already, the Elliott interaction causes spin relaxation and the accompanying broadening in large particle. An interesting question is how to bridge these two seemingly different pictures.

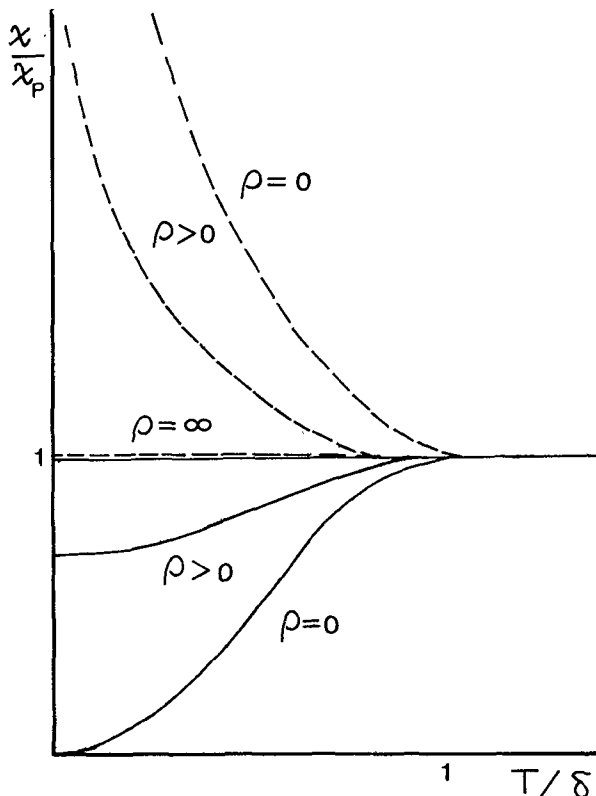


FIG. 3. — Spin paramagnetism of small metallic particles. The solid curves are for even particles and the dashed curves for odd particles. As the effective spin orbit interaction increases, the spin paramagnetism approaches the normal Pauli paramagnetism.

Another problem analogous to this is the broadening of plasma resonance absorption of small particles [18]. The classical picture of this is to attribute the broadening to resistance for electronic current in a particle, which is larger for smaller particles because electron mean free paths are limited by the size as is meant by eq. (16). However, this picture is not adequate for small particles in which the presence of boundaries is already incorporated in the structure of electron wave functions and so the boundaries are no longer agencies for scattering. A better picture then would be to interpret the broadening as a result of coupling of a plasma mode to the individual electronic motion through the interaction of electrons with the electric field produced by the plasma oscillation. A broadened resonance is the envelope of a number of resonance lines due to such coupled oscillations. Or, one can look the coupling as a

process of energy transfer from plasma oscillation to individual electrons. It is possible to formulate a unified theory in which the classical picture is one limit for large particles and the quantum picture is another limit for small particles [19].

Relaxation processes in small particles should also be greatly affected by the discreteness of electronic levels. In the relaxation process of electron spins in a bulk metal, the change of Zeeman energy is usually compensated by a change of kinetic energy of the electron. If the electronic levels are discrete, the matching for compensation is hardly realizable. Similarly, the Korringa mechanism hardly works for relaxation of nuclear spin. When a nuclear spin and an electron spin flip together by hyperfine interaction, the excess or the deficit of Zeeman energy can hardly be matched by a change of electron energy. This means that such relaxation mechanisms, which are effective in bulk materials, become ineffective in small particles, so that there may be a change in relaxation mechanism as the particle size diminishes. Quenching of spin lattice relaxation of conduction electrons in small particles of sodium was seen by Gordon [20]. Elongation of nuclear relaxation time in copper particles has been observed by Kobayashi [21]. It is difficult to decide what is the new mechanism of relaxation acting in small particles. This may be interactions with phonons within a particle coupled to those in the surrounding medium, or interactions between particles through some sort of contact or through electromagnetic coupling, or something else. The real mechanism is different in different situations.

Superconductivity in small particles is a very interesting subject [22], but unfortunately we have no time to discuss it here. It may be said, however, that very little is known at present about the effect of level discreteness on superconductivity. The problem remains for future studies.

The physics of small particles is certainly a rather peculiar field. It is neither quite macroscopic nor quite microscopic. Experimentally it is a difficult task to prepare good samples in this intermediate dimension. Theoretical tools have not well developed either for this peculiar area. In spite of these difficulties, a steady progress can be hoped in the future. The physics of small particles is interesting by itself just because of such intermediate nature of the problem and also it has broad contacts with other fields of science and technology.

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