

*MINUTE METALLIC PARTICLES IN AN ELECTROMAGNETIC FIELD*

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We consider some properties of metallic particles with dimensions so small that the spectrum of the electronic excitations becomes discrete. The existence of microscopic roughnesses on the particle surfaces makes it impossible to calculate the detailed level distribution in the spectrum of each individual particle. At the same time, the mean level density is still determined by the macroscopic characteristics of the metal. This circumstance allows us to describe the level distribution statistically, in a manner similar to that employed in nuclear physics to find the distribution of the highly excited levels of the atomic nucleus. The formulas obtained for the electric polarizability in a high-frequency field, especially the part of the polarizability responsible for the absorption, contain explicitly the binary correlation function introduced in Dyson's well-known papers. It is shown that all three types of level statistics proposed by Dyson are realized in the objects under study under different conditions. It therefore becomes possible to observe in the level scheme of a random system a long-range order that leads to strong oscillations of the absorption when the field frequency is varied. Formulas are also obtained for the specific heat and for the paramagnetic-resonance intensity in minute metallic particles. The possibility of experimentally observing the phenomena in question is discussed.

**1. STATEMENT OF PROBLEM**

A system of many particles in a finite volume has discrete levels, the distances between which, generally speaking, decreases exponentially with increasing number of particles. The systematics of the low-excitation levels, to which it is sufficient to confine oneself at low temperatures, has a unique character. As is presently well known from statistics, it is possible to use at low temperatures the notion of excitations or quasiparticles obeying a definite dispersion law (which as a rule is phenomenological). The energy of the entire system is represented by the sum of the energies of the individual quasiparticles.

Of special interest for what follows are excitations of the Fermi type or, more accurately speaking, electronic excitations in metals. The density of the number of states per unit energy interval does not vanish in this case at zero excitation energy, but is equal to a constant, whose values for an isotropic dispersion law is

$$\nu = Vm^*p_0 / 2\pi^2, \quad (1)$$

where  $V$  is the volume of the system,  $m^*$  the effective mass, and  $p_0$  the limiting momentum of the Fermi surface ( $\hbar = 1$ ). The reciprocal  $\Delta = \nu^{-1}$

is thus the average distance between the levels near the Fermi surface. Usually the level systematics of particles in a large volume is obtained by considering the system in a large cube with periodic boundary conditions, with the final levels corresponding to the values of the momentum quantized in intervals  $\Delta p \sim 1/a$ , where  $a$  is the dimension of the system. This is perfectly adequate for a description of a macroscopic system, but becomes incorrect if we consider seriously the levels of sufficiently minute metallic particles. Imperfections in the shapes of such particles, which cannot be controlled at all, and which arise when the metal is sputtered, cause the distances between levels to be mainly of the order of  $\Delta$ , and certainly not of the order  $p_0/m^*a$ .

This circumstance was already pointed out by Kubo<sup>[1]</sup>, who introduced the phenomenological level-distribution probability density, on the basis of which he investigated the thermodynamic properties of such systems, namely the specific heat and the magnetic susceptibility. We shall show below that Kubo's phenomenological function leads to incorrect relations for these quantities, but the most interesting from our point of view is a study of the properties of minute particles in an alternating field, where the concepts developed below

lead to non-trivial consequences.

It is important to note that the distribution of the levels should remain random even if the particles have the same volume and a good shape, say spherical particles of equal size. The point is that electrons in the metal have a wavelength on the order of atomic dimensions. Therefore surface irregularities of atomic size are sufficient to make the level distribution perfectly random. This distribution ceases to be random if the electron reflection is not diffuse but specular.

Thus, if the quasiparticle concept is valid in this range of dimensions and temperatures, then the quasiparticle levels are determined by the perfectly random interactions with the walls, and the average distance between levels is  $\Delta = \nu^{-1}$  with  $\nu$  given by (1).

The situation is therefore completely analogous with that which takes place for the distribution of high-excitation levels of the nucleus in nuclear physics. The complexity of the real interactions in the nucleus leads to the possibility of considering the distribution of the levels statistically. In the nucleus, the averaging is carried out over different nuclei with respect to the average density of the levels of the nucleus, or over different sections of the spectrum of the nucleus. In our problem, the averaging reduces to a study of a large assemblage of metallic particles of equal size.

The concepts of nuclear-level statistics based on complete randomness of the interactions were apparently first developed by Wigner<sup>[2]</sup>. Recent papers by Dyson<sup>[3]</sup> and Dyson and Mehta<sup>[4]</sup> presented a mathematical formulation of these concepts and formulas for the correlation functions between these levels, which we shall henceforth simply borrow from these papers.

According to<sup>[3]</sup>, the level distribution coincides with the distribution on the unit circle of the eigenvalues of matrices from different ensembles.

There are three such ensembles: 1) orthogonal, which describes systems that are invariant against time and space inversion, or with integer spin; 2) symplectic—for random interactions, invariant against time reversal; the total spin of the system is half-integer; 3) unitary—for systems that are not invariant against time reversal.

In nuclear physics, apparently, only the first ensemble is realized. If we employ this approach to describe the spectrum of an individual Fermi excitation in the field of a random potential, then the orthogonal ensemble pertains to the case of small spin-orbit coupling, when the spin is a quantum number; the symplectic ensemble is realized when the spin-orbit coupling is sufficient to mix

levels with different spins. Finally, the unitary ensemble is obtained from the symplectic one when the magnetic field is turned on and  $\mu H \gg \Delta$ .

The value of  $\Delta$  is inversely proportional to the volume of the particle and for a linear law of electronic specific heat it is connected with the coefficient by

$$\Delta = 1.1 \cdot 10^{-20} \frac{A}{a^3 \rho \gamma} [^\circ K] \sim \frac{\epsilon_F}{N} \quad (2)$$

( $A$  is the atomic weight,  $\rho$  is the density, and  $\gamma$  is expressed in mJ/mole-deg<sup>2</sup>). For aluminum with  $a = 4.2 \times 10^{-7}$  cm we have  $\Delta \approx 1^\circ$ . In general, it is seen from (2) that when  $N \sim 10^4 - 10^5$  the average distance is  $\Delta \sim 1 - 0.1^\circ$ , that is, it is quite large when the system dimensions are still sufficiently large to be able to use the macroscopic characteristics of the metal.

To conclude this section, let us discuss the main question: to what extent is the excitation concept applicable to the case of such small dimensions or such low temperatures (as  $\Delta \rightarrow 0$ ). We note immediately that acoustic oscillations, both volume and surface, can be excluded from consideration, since long-wave sound has a strictly discrete set of frequencies, starting with low values of  $\omega \sim u/a$  ( $u$ —speed of sound). The ratio

$$\omega / \Delta \sim u(p_0 a)^2 / v_F$$

can always be made sufficiently large. For example, when  $a \sim 10^{-6}$  we have  $\omega / \Delta \sim 10$ . For this reason, at sufficiently low temperatures  $T \sim \Delta$ , the sound oscillations are not excited at all, and at higher temperatures the interaction between the electrons and the phonons is less effective because of the discreteness of the spectrum.

The reason why the excitation concept may turn out to be incorrect is the attenuation connected with the interaction between the electrons themselves. In bulk metal at frequency  $\omega$ , the attenuation is on the order of  $\omega^2 / \epsilon_F$  or  $T^2 / \epsilon_F$ . It is therefore clear that at temperatures

$$T \ll \sqrt{\Delta \epsilon_F} \sim 10 - 100^\circ K \quad (3)$$

the attenuation becomes smaller than the level spacings  $\Delta$ . Finally, heat exchange with the medium is also too weak to lead to a noticeable broadening of the levels. By virtue of these considerations, we assume that it is meaningful to speak of Fermi excitations in the objects of interest to us.

## 2. PARTICLES IN AN ELECTROMAGNETIC FIELD

So long as the frequencies  $\omega$  of the field are small compared with the reciprocal of the time the

electron travels from wall to wall ( $\sim v/a$ ), and the field intensities are small compared with the internal fields

$$eEa \ll \Delta,$$

the interaction of a "metallic" small particle with the field can be considered by using perturbation theory for a quantum system. In this range of fields the particle behaves like an atom with a certain polarizability and does not manifest its metallic properties at all. Inasmuch as the field changes little over the dimensions of the particle, the interaction reduces to the term

$$\hat{U} = -E\hat{d},$$

where  $\hat{d}$  is the dipole moment of the system.

The average dipole moment

$$\langle d_\alpha \rangle = i \int_{-\infty}^{\infty} \langle [d_\alpha(t), d_\beta(t')] \rangle E_\beta(t') dt',$$

( $[, ]$ —commutator) can be easily expressed in terms of matrix elements of the coordinates of the excitations and the occupation numbers of the individual levels  $n_k$ :

$$d_{\alpha\omega} = -e^2 E_{\beta\omega} \sum_{k,l} \frac{n_k - n_l}{\epsilon_k - \epsilon_l + \omega + i\delta} \mathbf{r}_{kl}^\alpha \mathbf{r}_{lk}^\beta. \quad (4)$$

In the last formula we have changed over to the Fourier components of all the quantities in accordance with

$$d(t) = \frac{1}{2\pi} \int_{-\infty}^{\infty} d_\omega e^{-i\omega t} d\omega.$$

Separating in (4) the static part of the polarizability  $\alpha$ , we obtain

$$\alpha_\omega = \alpha_0 - \frac{e^2\omega}{3} \sum_{k,l} \frac{n_k - n_l}{\epsilon_k - \epsilon_l} \frac{\mathbf{r}_{kl}\mathbf{r}_{lk}}{(\epsilon_k - \epsilon_l)^2 - (\omega + i\delta)^2}, \quad (5)$$

$$\alpha_0 = -\frac{e^2}{3} \sum_{k,l} \mathbf{r}_{kl}\mathbf{r}_{lk} \frac{n_k - n_l}{\epsilon_k - \epsilon_l} = \frac{2}{3} v e^2 \sum_l \mathbf{r}_{k_0 l} \mathbf{r}_{l k_0}. \quad (6)$$

As will be shown below, the sum over  $l$  in (6) converges when  $\epsilon_k - \epsilon_l \sim v/a$ , that is, near the Fermi surface. As a result,

$$\alpha_0 = \frac{2}{3} e^2 v \langle r^2 \rangle = \frac{4e^2 a^5 m p_0}{15\pi} = \frac{4a^5 e^2 \gamma}{5\pi},$$

where  $\gamma$  is the coefficient in the linear law of specific heat:  $C_e = V\gamma T$ . The order of this quantity is

$$\alpha_0 \sim a^3 (p_0 a)^2 \sim \alpha_{met} (p_0 a)^2,$$

where  $\alpha_{met} = a^3$  denotes the polarizability of the equivalent metallic particle in the field.

For the objects considered, a polarizability  $\alpha \sim \alpha_{met}$  is attained in fields  $eEa \gg \Delta$ , suffi-

ciently strong to mix the levels of the system. In these fields the system will have the usual metallic properties. As far as we know, no one has called attention to the anomalously large values of the polarizability of minute metallic particles in weak fields. Yet, apparently, this circumstance uncovers a possibility of producing artificial dielectrics with large controllable dielectric constants.

In formulas (4) and (5)  $n_k$  are the equilibrium occupation numbers for which, however, we cannot in general use the known formulas with a chemical potential for the Fermi distributions. When  $T \sim \Delta$  the number of excitations is very small and it is therefore necessary to take into account the well known premise of the Fermi-liquid theory concerning the conservation of the total number of quasiparticles. An analysis for  $T = 0$  and for large values of the temperatures (3), when we can write

$$n_k = \{\exp [(\epsilon_k - \mu) / T] + 1\}^{-1}$$

yields the same result. That the results which follow from (5) are completely independent of the temperature can be demonstrated by using the more general method of Fowler and Darwin<sup>[5]</sup>, in which the conservation of the number of excitations is explicitly taken into account. Without dwelling on this proof, we present a derivation for the case of high temperatures (3), since it is of greatest experimental interest.

Let us average (5) over the level distribution. To this end we multiply each term in the sum (5) by the probability

$$R(\epsilon_1 - \epsilon_2) v d\epsilon_1 v d\epsilon_2 \quad (7)$$

that two levels will be in the interval of values  $d\epsilon_1$  and  $d\epsilon_2$ , and integrated with respect to  $\epsilon_1$  and  $\epsilon_2$ :

$$\alpha_\omega - \alpha_0 = -\frac{e^2\omega^2}{3} v^2 \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} d\epsilon_1 d\epsilon_2 \frac{n_1 - n_2}{\epsilon_1 - \epsilon_2} \frac{(\mathbf{r}_{12}\mathbf{r}_{21}) R(|\epsilon_1 - \epsilon_2|)}{(\epsilon_1 - \epsilon_2)^2 - (\omega + i\delta)^2}. \quad (8)$$

The integral over the energy difference converges when  $\epsilon_1 - \epsilon_2 \sim \omega$ . If  $\omega \ll v/a$ , as assumed, then  $\mathbf{r}_{21} \cdot \mathbf{r}_{12} \approx (\mathbf{r}_{21} \cdot \mathbf{r}_{12})_0$  is constant. Replacing  $(n_1 - n_2)/(\epsilon_1 - \epsilon_2)$  by  $\partial n / \partial \epsilon$  for  $\epsilon \sim \omega \ll T$ , we obtain

$$\alpha_\omega = \alpha_0 + \frac{1}{3} e^2 (\mathbf{r}_{21}\mathbf{r}_{12})_0 v A(\omega), \quad (9)$$

$$A(\omega) = \omega^2 v \int_{-\infty}^{\infty} \frac{R(|\epsilon|) d\epsilon}{\epsilon^2 - (\omega + i\delta)^2}. \quad (10)$$

We now calculate the quasiclassical matrix element  $(\mathbf{r}_{12} \cdot \mathbf{r}_{21})_0$ . For the case of diffuse re-

flection of the electrons from the surface, Shapoval<sup>[6]</sup> developed a general method of calculating such quantities, which we shall use with slight modification. The average of two quantities  $\hat{f}(t)$  and  $\hat{g}(t)$  at different instants of time, taken over the state  $|ni\rangle$ , is

$$\langle ni | \hat{f}(t) \hat{g}(t + \tau) | ni \rangle = \sum_{j'k} \langle ni | \hat{f}(t) | kj' \rangle \langle kj' | \hat{g}(t) | ni \rangle e^{-i\omega_{kn}\tau},$$

where  $n$  and  $k$  denote the energies, while  $i$  and  $j$  are the other quantum numbers. It follows therefore that the matrix element averaged over  $i$  and  $j$ , which we shall denote by  $f_{nk}g_{kn}$ , is

$$f_{nk}g_{kn} = \frac{1}{2\pi\nu} \int_{-\infty}^{\infty} e^{i\omega_{kn}\tau} \langle f(t)g(t + \tau) \rangle d\tau.$$

Going over to the quasiclassical approach, we obtain

$$f_{nk}g_{kn} = \frac{1}{2\pi\nu} \frac{1}{2T_1} \int_{-T_1}^{T_1} dt \int_{-T_1}^{\infty} d\tau e^{i\omega_{kn}\tau} f(t)g(t + \tau).$$

Here the integration with respect to  $t$  corresponds to averaging along the given trajectory, and the bar over the integral denotes averaging over all the quasiclassical trajectories of the particle. For the quantity of interest to us, using the fact that the correlations with respect to  $\tau$  are even, we obtain

$$\mathbf{r}_{hi}\mathbf{r}_{lk} = \frac{1}{\pi\nu} \frac{1}{2T_1} \int_{-T_1}^{T_1} dt \int_0^{\infty} d\tau \cos(\omega_{hi}\tau) (\mathbf{r}(t)\mathbf{r}(t + \tau)). \quad (11)$$

As can be seen, expression (11) is actually cut off at  $\omega_{kl}l \sim v/a$ .

Let  $0, t_1, t_2, \dots, t_n \dots$  be the times of collisions of the particles with the wall. Let the time  $t$  lie in the interval  $0 < t < t_1$ , and then  $t + \tau$  can lie either in the same interval or in the next interval, corresponding to one, two, etc. reflections. It is therefore sufficient to calculate the integrals

$$\int_0^{t_1} \mathbf{r}(t) dt \left\{ \int_0^{t_1-t} \mathbf{r}(t + \tau) d\tau + \int_{t_1-t}^{t_2-t} \mathbf{r}(t + \tau) d\tau + \dots \right\} \quad (12)$$

and to average them over all the reflection angles and the initial point of the trajectory  $\mathbf{r}_0$ . Total integration with respect to  $t$  reduces to multiplication of (12) by a number of segments of the trajectory  $N$  equal to the number of collisions of the particle with the surface during the time  $2T_1$ :

$$N = 2T_1\nu S / 4V.$$

The probability of a given trajectory is

$$d\Sigma_{\text{traject}} = \frac{dS}{S} \prod_i \frac{\cos \vartheta_i}{\pi} dO_i,$$

where  $\vartheta_i$  is the angle of reflection of the particle after the  $i$ -th collision. Finally,

$$\begin{aligned} (\mathbf{r}_{hi}\mathbf{r}_{lk})_0 &= \frac{\nu}{4\pi\nu V} \int dS \int \dots \int \prod_i \frac{\cos \vartheta_i}{\pi} dO_i \int_0^{t_1} \mathbf{r}(t) dt \\ &\times \left\{ \int_0^{t_1-t} \mathbf{r}(t + \tau) d\tau + \int_{t_1-t}^{t_2-t} \mathbf{r}(t + \tau) d\tau + \dots \right\}. \end{aligned} \quad (13)$$

For a sphere we obtain after elementary calculations

$$(\mathbf{r}_{hi}\mathbf{r}_{lk})_0 = \frac{139}{150} \frac{1}{2\pi\nu} a^2 \frac{a}{v}. \quad (14)$$

A somewhat different approach is necessary if the range of the electrons in the sample is smaller than the sample dimensions. In the integration with respect to  $\tau$ , the characteristic time in formula (11) is determined by the diffusion from the point  $\mathbf{r}(t)$  to the point  $\mathbf{r}(t + \tau)$ :

$$\tau_{\text{eff}} \sim a^2 / D \sim a^2 / lv.$$

In this case we always have  $\Delta \cdot \tau_{\text{eff}} \sim a p_0 l p_0 \gg 1$ . The matrix element of interest to us can be written in the form

$$(\mathbf{r}_{hi}\mathbf{r}_{lk})_0 = \frac{1}{\pi\nu V} \int d^3\mathbf{r}_0 \int d^3\mathbf{r}(\mathbf{r}_0\mathbf{r}) \int_0^{\infty} W_{\mathbf{r}_0}(\mathbf{r}, t) dt, \quad (15)$$

where  $W_{\mathbf{r}_0}(\mathbf{r}, t)$  is the probability of finding the particle in the point  $\mathbf{r}$  at the instant  $t$ , if its position at  $t = 0$  is  $\mathbf{r}_0$ :

$$\frac{\partial W_{\mathbf{r}_0}(\mathbf{r}, t)}{\partial t} = D \Delta W_{\mathbf{r}_0}(\mathbf{r}, t), \quad W_{\mathbf{r}_0}(\mathbf{r}, t = 0) = \delta(\mathbf{r} - \mathbf{r}_0).$$

Integrating the diffusion equation with respect to  $t$ , expanding  $W_{\mathbf{r}_0}(\mathbf{r}, t)$  in Legendre polynomials and using the fact that  $W_{\mathbf{r}_0}(\mathbf{r}, t = \infty) = 1/V$ , we obtain

$$\frac{1}{V} - \delta(\mathbf{r} - \mathbf{r}_0) = D \sum_l \left\{ \frac{1}{r^2} \frac{d}{dr} r^2 \frac{d}{dr} - \frac{l(l+1)}{r^2} \right\}$$

$$\times \int_0^{\infty} W_{\mathbf{r}_0}{}^l(r, t) P_l(\cos \vartheta) dt.$$

Putting

$$\frac{f(r)}{r} = \int \frac{d^3\mathbf{r}_0(\mathbf{r}_0\mathbf{r})}{V} \int_0^{\infty} W_{\mathbf{r}_0}(\mathbf{r}, t) dt,$$

we obtain for  $f(r)$  the elementary equation

$$-\frac{r}{V} = D \left( \frac{f''}{r} - \frac{2}{r^3} f \right), \quad \left. \frac{d}{dr} \frac{f(r)}{r} \right|_{r=a} = 0,$$

from which, after calculations, we finally obtain

$$(\mathbf{r}_{hi}\mathbf{r}_{lk})_0 = \frac{48}{175} \frac{1}{2\pi\nu} \frac{a^4}{D}. \quad (16)$$

We note here that whereas for a pure sample

the frequency-dependent part of the polarizability (including  $\text{Im } \alpha$ , which determines the absorption) is of the order of  $\alpha - \alpha_0 \sim \alpha_{\text{met}}$ , in the case of a small mean free path we have

$$\alpha - \alpha_0 \approx \alpha_{\text{met}} a / l \gg \alpha_{\text{met}}.$$

We now proceed to expression (10) for  $A(\omega)$ . As already mentioned, the orthogonal ensemble is realized in the case when the spin-orbit interaction can be neglected, that is, for light metals. According to [3], we have in this case

$$R^{\text{ort}}(\pi\nu\varepsilon) \equiv R^{\text{ort}}(x) = 1 - \frac{\sin^2 x}{x^2} + \int_0^1 \frac{\sin xt}{t} dt \times \frac{d}{dx} \left( \frac{\sin x}{x} \right) - \frac{\pi}{2} \frac{d}{dx} \left( \frac{\sin x}{x} \right). \quad (17)$$

Breaking up the part of (17) that is symmetrical in  $x$  into two branches  $f_+ + f_-$ , which are analytic in the upper and lower half planes respectively, we can calculate the integral in (10) in explicit form

$$A(\omega\nu) \equiv A(z) = 2 - \frac{\sin 2z}{z} - \frac{2 \text{Ci}(z)}{z} (\sin z - z \cos z) + i \left[ 2z - \frac{1}{z} + \frac{\cos 2z}{z} - \frac{\text{Si}(z)}{z} (\sin z - z \cos z) \right], \quad (18)$$

where  $\text{Ci}(z)$ , and  $\text{Si}(z)$  are the integral sine and cosine, respectively. [7]

In Fig. 1 is shown a plot of the real and imaginary parts of the ratio  $A(z)/2z = [A_1(z) + iA_2(z)]/2z$ . This dependence is far from trivial. In particular, we see that when  $\omega \lesssim \Delta$  the absorption acquires essentially a quantum character. As  $\omega \rightarrow 0$  we get

$$A(z) \approx \frac{2}{3}z^2(2 - \ln(\gamma z)) + \frac{1}{3}i\pi z^2.$$

In the opposite limiting case, as  $z \rightarrow \infty$ , we have

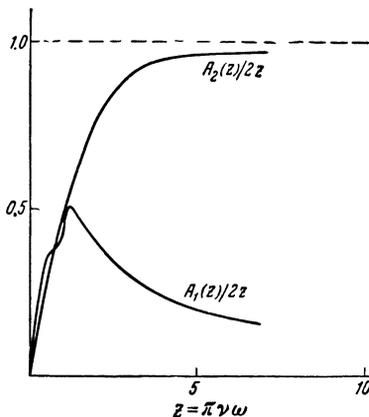


FIG. 1.

$$\frac{A(z)}{2z} \approx i \left( 1 - \frac{1}{z^2} + \frac{3}{2z^4} + \frac{\cos 2z}{2z^4} \right) + \frac{1}{z} - \frac{1}{z^3} - \frac{\sin 2z}{2z^4}.$$

The oscillating term denotes the presence of a long-range correlation in the arrangements of the levels—the effect of “repulsion” between levels, that is, the existence of an appreciable probability of a periodic arrangement of the levels [2,3]. Unfortunately, these oscillations are too small to be observed experimentally. We therefore proceed now to discuss the results for heavier metals or for larger particles, where the spin-orbit interaction cannot be neglected, and which we therefore describe by the so called “symplectic ensemble” [4].

The function

$$R^{\text{simpl}}(2\pi\nu\varepsilon) \equiv R^{\text{simpl}}(x)$$

is given by

$$R^{\text{simpl}}(x) = 1 - \frac{\sin^2 x}{x^2} - \int_0^1 \frac{\sin xt}{t} dt \frac{d}{dx} \left( \frac{\sin x}{x} \right).$$

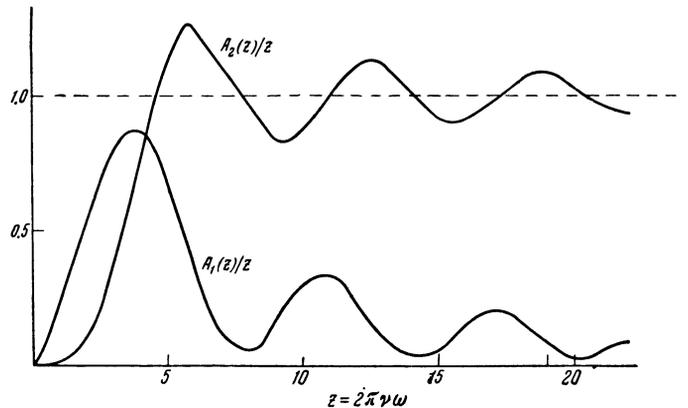


FIG. 2.

Figure 2 shows the behavior of the ratio  $A(z)/z$ :

$$A(2\pi\nu\omega) \equiv A(z) = 2 - \frac{\sin 2z}{2z} - \left( \frac{\pi}{2} + \text{Si}(z) \right) \frac{\cos z + z \sin z}{z} + i \left[ z - \frac{\sin^2 z}{z} + \left( \frac{\pi}{2} + \text{Si}(z) \right) \frac{z \cos z - \sin z}{z} \right]. \quad (19)$$

We see here the strongly pronounced oscillations of both the real and the imaginary parts of  $A(z)/z$ . Indeed, as  $z \rightarrow \infty$  we have

$$\frac{A(z)}{z} \approx \frac{2}{z} - \frac{\pi}{2z} \sin z + i \left( 1 + \frac{\pi}{2z} \cos z \right), \quad (20)$$

that is, the oscillations have a much larger amplitude than in lighter substances. The physical rea-

son for this effect, as is well known, is that the spin-orbit interaction lifts all but the Kramers degeneracy. Therefore a random appearance of two closely-lying levels is even less probable than in an orthogonal ensemble, and accordingly a stronger "repulsion" is produced between levels.

We present also an asymptotic expression for low frequencies:

$$A(z) \approx 2/9z^2 + 1/45z^5,$$

from which we see that absorption is very small in this case and has a very steep variation with increasing frequency.

To conclude this section we present formulas describing the absorption of electromagnetic radiation, when, on the one hand, the spin-orbit interaction is sufficiently strong, and on the other there is an external constant magnetic field sufficient to mix the levels ( $\mu H \gg \Delta$ ) and to produce a "unitary ensemble"<sup>[3,4]</sup>:

$$A^{unit}(2\pi\nu\omega) \equiv A^{unit}(z) = 2 - \frac{\sin 2z}{2z} + i \left[ z - \frac{\sin 2z}{2z} \right]. \quad (21)$$

Although the oscillations here are weaker than in the symplectic ensemble, they are also quite noticeable.

### 3. SPECIFIC HEAT AND SINGULARITIES OF THE BEHAVIOR IN A MAGNETIC FIELD

At high temperatures  $T \gg \Delta$ , all the thermodynamic quantities, naturally, have the same form as for bulk metal. We confine ourselves therefore here only to the case of low temperatures  $T \ll \Delta$ . The situation is the simplest with specific heat, for at such low temperatures the appearance of more than one excitation per system has little likelihood. For the orthogonal and symplectic ensembles, which both have doubly degenerate levels, the level filling scheme is shown in Fig. 3. The dashed line denotes the free levels, the solid line with circle the occupied levels.

Figure 3a corresponds to "even" filling. The total partition function is equal to

$$Z_{\text{even}} = 1 + 4 \exp \left[ -\frac{\epsilon_1 - \epsilon_0}{T} \right] + \exp \left[ -\frac{2(\epsilon_1 - \epsilon_0)}{T} \right].$$

The state on Fig. 3b is doubly degenerate. Leaving again in the partition function only those excitations which affect only one level, we obtain

$$Z_{\text{odd}} = 2 + 2 \exp \left[ -\frac{\epsilon_0 - \epsilon_{-1}}{T} \right] + 2 \exp \left[ -\frac{\epsilon_{+1} - \epsilon_0}{T} \right].$$

Averaging  $F = -T \ln Z$  over both possibilities, and also integrating over the probability  $P(\Delta)$  of

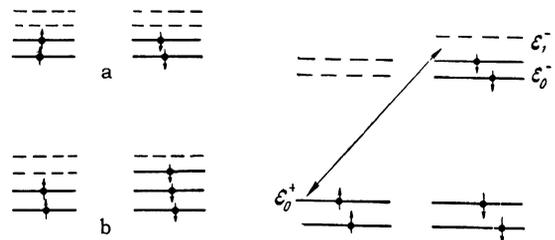


FIG. 3.

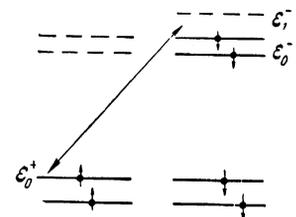


FIG. 4.

a given spacing  $\Delta$  between neighboring levels, we obtain

$$F = -\frac{T}{2} \ln 2 - 3T \int_0^\infty e^{-\Delta/T P(\Delta)} d\Delta - \frac{T}{2} \int_0^\infty e^{-2\Delta/T P(\Delta)} d\Delta.$$

The last formula leads to the results of Kubo<sup>[1]</sup>, if we use for  $P(\Delta)$  his expression which, however, does not take into account the repulsion of the levels. The correct functions lead to a specific heat which is proportional at low temperatures to  $T^2$ ,  $T^5$ , and  $T^4$  for the orthogonal, symplectic, and unitary ensembles, respectively.

We proceed to the magnetic susceptibility. For the symplectic ensemble, as expected, the susceptibility always coincides with the value for the bulk metal. Curious results can be obtained, however, for the orthogonal ensemble when the spin-orbit coupling is small and the spin remains a good quantum number. In this case we can speak separately of electronic excitations in which the spin is directed with and against the field. Let the field  $H$  have an arbitrary value ( $\mu H$  comparable with  $\Delta$ ). Figure 4 shows the level scheme of an individual particle in the field. Let  $\epsilon_0^+$  and  $\epsilon_0^-$  be respectively the last filled levels having spin parallel and antiparallel to the field, respectively.

Let us increase the field to a value  $H + dH$ . It may turn out that following this it is energetically easier for the excitation to go from the level  $\epsilon_0^+$  to the level  $\epsilon_1^-$ . The condition for this is

$$\epsilon_1^- - \epsilon_0^+ - 2\mu H - 2\mu dH < 0.$$

The moment of the entire system changes by an amount  $-2\mu$ . The probability of such an event is equal to the probability of two levels being separated by a distance  $2\mu H$  in the energy interval  $2\mu dH$ . Therefore

$$\chi_{\parallel} = dM / dH = 4\mu^2 \nu R^{ort}(2\pi\nu\mu H). \quad (22)$$

In weak fields

$$dM / dH \approx \chi_{\infty}^1 / 3\pi^2 \nu \mu H$$

vanishes. Of course, when  $\mu H \gg \Delta$ , Eq. (22) goes over to the value of the paramagnetic susceptibility of the bulk metal. In this case  $\chi_{\parallel}$  experiences

small oscillations of the same nature as described in Sec. 2:

$$\frac{dM}{dH} \approx \chi_{\infty} \left\{ 1 - \left( \frac{1}{2\pi\nu\mu H} \right)^2 + \frac{1 + \cos^2(2\pi\nu\mu H)}{(2\pi\nu\mu H)^4} \right\}.$$

The smaller the role of the spin-orbit interaction, the more accurately these relations are satisfied for the orthogonal ensemble. In particular, it can be thought that paramagnetic resonance would become observable, with good accuracy, in minute particles made of light metals. It is easy to obtain in the usual manner an expression for the perpendicular component of the paramagnetic susceptibility

$$\chi_{\perp} = -\mu^2 \sum_{k,p} \frac{n_k - n_p}{\varepsilon_k - \varepsilon_p + \omega + i\delta} \sigma_{kp}^{\perp} \sigma_{pk}^{\perp}.$$

In the absence of spin-orbit coupling, the spin precesses about the direction of the magnetic field with frequency  $2\mu H$ . From formulas of the type (11) it follows immediately that the only nonvanishing transitions are those with  $\omega_{kp} = 2\mu H \equiv \omega_0$ :

$$\chi_{\perp} = -2\mu^2 \frac{\omega_0}{\omega_0^2 - (\omega + i\delta)^2} \sum_k [n(\varepsilon_k + \mu H) - n(\varepsilon_k - \mu H)].$$

The meaning of this formula becomes perfectly clear if we look at Fig. 4:  $\chi_{\perp}$  is proportional to the number of places which are free on the left in this figure. Finally,

$$\chi_{\perp} = \frac{\omega_0^2}{\omega_0^2 - \omega^2} \frac{1}{H} \int_0^H \chi_{\parallel}(H) dH. \quad (23)$$

Thus, experiments will disclose that the intensity of the paramagnetic resonance lines experiences a quantum variation with varying magnetic field, changing in accordance with (22) and (23) from zero at small fields to a value characteristic of bulk metal when  $\mu H \gg \Delta$ .

We emphasize once more that all the formulas of this section, including (22) and (23), are valid only at low temperatures  $T \ll \Delta$ .

#### 4. CONCLUSION

We now discuss briefly the possibility of experimentally observing these effects. Measurements of the specific heat seem to us of little likelihood, primarily because of the smallness of the specific heat itself. It can be readily understood that when  $T \sim \Delta$  the specific heat is of the order of  $k$  per particle, that is, is comparable with the contribution made to the specific heat by the vibrations in the host matrix. For analogous reasons, it is difficult to measure the magnetic susceptibility di-

rectly. The point is that, when we considered the bulk properties we disregarded completely the existence of different surface centers with localized magnetic moments. Yet the contribution made to the susceptibility by such a center is of the order of  $\mu^2/T$ , and is much larger than (22) when  $T \ll \Delta$ . An analogous role is played by various paramagnetic impurities. Nevertheless, it seems to us that a direct measurement of the paramagnetic susceptibility is possible by determining the field dependence of the Knight shift of the frequency of the nuclear magnetic resonance. (We recall that only the conduction electrons are responsible for the Knight shift.) This dependence  $d\Delta\omega/dH$  is given directly by formula (22). When  $\Delta \sim 1^\circ$  the required temperature is  $0.1^\circ$  and the required field is  $H \sim 10^4$  Oe.

Of course, local centers can make a contribution to the paramagnetic resonance line, but in this case there is no field dependence of the line intensity. Therefore such measurements are also desirable.

The foregoing experiments necessitate, however, the use of low temperatures. Therefore, the most convenient for the confirmation of the proposed laws seem to be, in our opinion, the singularities of the behavior of small metallic particles in an electric field. We note, first, that it would be generally of interest to demonstrate the quantum character of such systems, and that even the observation of large polarizability of the systems in a weak static field is sufficient for this purpose. When  $a \sim 10^{-6}$  we have  $\Delta \sim 0.1^\circ$  and the permissible fields ( $eEa \ll \Delta$ ) are  $E \ll 10$  V/cm.

At low concentrations, the dielectric constant is

$$\varepsilon = 1 + 4\pi N\alpha, \quad (24)$$

where  $N$  is the number of particles per unit volume. Thus, a unique nonlinear effect exists even in relatively weak electric fields, in that the polarizability  $\alpha$ , the order of magnitude of which is  $(p_0 a)^2 a^3 \gg a^3$  when  $eEa \ll \Delta$  begins to decrease strongly when  $eEa \sim \Delta$ , and reaches finally the usual value  $a^3$  at  $eEa \gg \Delta$ . The field at which the nonlinear variation of  $\alpha$  begins decreases rapidly with increasing particle dimensions ( $\sim a^{-4}$ ). It is necessary to bear in mind here that the larger the particles the lower the temperature at which this effect can exist (see the end of Sec. 1).

Of fundamental interest, of course, is the quantitative verification of the formulas of Sec. 2, which follow from the general fundamental laws of the statistics of complex interactions. A principal factor here is the condition that the dispersed

particles be sufficient homogeneous in their dimensions and shapes. As can be seen from the diagram in Fig. 2, for a symplectic ensemble the absorption oscillations come into play when the volume or the frequency change by a factor 2 or 3. This imposes the condition that the dimension fluctuations not exceed several percent. In addition, the polarizability in (24) can, generally speaking, depend not only on the dimensionless quantity  $z = \omega/\Delta$ , but may contain, in accordance with (16), an extra power of  $a$  if the mean free path is shorter than the particle dimensions. It is difficult to control the mean free path and it would therefore be preferable to measure the frequency dependence of the dielectric constant (24). It can be assumed, however, that for dispersed particles of a sufficiently pure metal the mean free path will be of the order of the sample dimensions, and by virtue of this  $\alpha$  is a function of only the variable  $z = \omega/\Delta$ , which enters in  $A(\omega)$  (10).

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