neck[12] is not effective. The minimum may then be attributed to a Korringa relation between the g shift and the linewidth, and will occur where $\Delta g = 0$.

In summary, we have shown that suppression of the Zeeman splitting by the spin-orbit interaction produces an anisotropically enhanced local susceptibility. This anisotropy is reflected in the g value of the impurity resonance. In our model it is the cancelation of the molecular fields from the various bands in Sc rather than the disappearance of the local-moment–conduction-electron coupling which allows the g shift to pass through zero. Since the anisotropic orbital moment will remain, and since the cancelation need not extend beyond the impurity cell, the presence of an excess moment at all angles does not seem to be in contradiction with our results.

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Electronic Heat Capacity and Susceptibility of Small Metal Particles*

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Detailed calculations of the temperature dependence of the heat capacity and magnetic spin susceptibility of small metal particles are presented. The results depend sensitively upon the symmetries or near symmetries of the dynamics, and exhibit the usual thermodynamic behavior only as the particle size becomes sufficiently large.

The electronic properties of an assembly of small metal particles are determined by and reflect the distribution of the electronic energy levels. This distribution may contain strong correlations arising, for example, from the presence of localized impurities or surface states. Alternatively, if such correlations are absent, one has a more universal problem in which it becomes reasonable to treat the level distribution statistically. The statistical characteristics of the energy level distribution are then determined by (1) the particle size distribution, (2) a mean single-electron-level spacing δ for particles of a particular size, and (3) the symmetry of the dynamics. The problem of a statistical level distribution was first considered by Kubo[1] who assumed a random distribution and calculated the electronic heat capacity and spin susceptibility for the limiting cases $\delta \ll kT$ and $\delta \gg kT$. Subsequently Gor'kov and Eliashberg[2] showed that the correlations between levels could lead to qualitatively different results for these quantities at low temperatures.

In this Letter we present detailed calculations of the heat capacity and magnetic spin susceptibility of metal particles for the whole temperature range and for different statistical assumptions. Our special aim is to encourage experi-

mental comparison.[3] This would be very interesting not solely in view of the unusual properties of small particles, but at the same time such a comparison could test the fundamental assumptions made for both the thermal ensemble and the level distribution ensemble.

"Small" particle size implies that the typical electronic level spacings are of order rather than infinitesimal compared to other energies such as thermal, kT, Zeeman, $g\mu H$, or electromagnetic, $\hbar\omega$. Here we have in mind particles with level spacings of order 1 to 10 K. For these initial calculations we use a noninteracting electron scheme so that the total electronic energy levels of a particle are obtained by adding up the excitation energies of the single-electron states consistent with the symmetry properties of the system. First, of course, the Pauli principle must be obeyed, and second, as emphasized by Kubo, the large electrostatic energy enforces charge conservation. This latter near symmetry is particularly important since it implies that the appropriate partition function corresponding to the allowed electronic energy levels is the canonical and not the more familiar grand canonical one. We will see that this leads to distinct differences for small particles. Given these two basic symmetry requirements, the distribution of total electronic levels is determined by the distribution of the single-electron energy levels ϵ_i. As pointed out by Kubo, irregular variations among the particles on an atomic scale lead to a single-level distribution which has a mean level spacing δ given by the inverse of the density of states for one spin direction $N(0)$ at the Fermi energy. For particle size a of order 100 Å this implies $\delta/k \sim 1$ K and δ varies as a^{-3}. If the irregular potential merely had diagonal matrix elements among the perfect small-particle crystal states, the resulting electron-level distribution would be random. Then the probability density $P_n(\epsilon)$ for finding a level an energy ϵ away from a given level with n levels in between is just the Poisson distribution,

$$P_n(\epsilon) = \frac{1}{n!}\left(\frac{\epsilon}{\delta}\right)^n \frac{e^{-\epsilon/\delta}}{\delta} \tag{1}$$

which for $n=0$ reduces to an exponential nearest-neighbor spacing. However, as discussed for nuclear level statistics by Wigner,[4] if there are off-diagonal matrix elements of the irregular potential, the familiar energy-level repulsion effect suppresses the probability of small level spacings. For this reason, Wigner suggested that a more appropriate nearest-neighbor level distribution was

$$P_W(\epsilon) = (\pi\epsilon/2\delta^2)\exp[-\tfrac{1}{4}\pi(\epsilon/\delta)^2]. \tag{2}$$

Subsequently Dyson[5] and others[6,7] studied the distributions of eigenvalues of ensembles of random matrices constrained to satisfy various symmetries. For the small-particle problem, the relevance of these ensembles depends upon the strength of the spin-orbit coupling energy[8] η relative to the level spacing δ: (1) The orthogonal ensemble is appropriate for $\eta/\delta \ll 1$; (2) the symplectic ensemble applies for $\eta/\delta \gg 1$; and (3) the unitary ensemble applies when $\mu H \gg \delta$ and $\eta/\delta \gg 1$.[2,8] For the orthogonal ensemble, it was found[6] that the nearest-neighbor distribution is closely approximated by the Wigner distribution (2).

Before averaging over the level distribution one must solve the fixed-level problem. The combined restrictions of electron-number conservation and the Pauli principle complicate this seemingly simple noninteracting-electron problem. If however, there is no spin-orbit coupling and the energy levels are equally spaced by δ, the projection of the canonical partition function Z from the grand canonical one by means of a contour integration,

$$e^{-\beta E_0(N)} Z(N,\beta) = \frac{1}{2\pi i}\oint \frac{d\lambda\, Q(\lambda,\beta)}{\lambda^{N+1}}, \tag{3}$$

can be performed without the use of steepest descents or other approximations. Here $E_0(N)$ is the ground-state energy with no magnetic field. Integrating over the unit circle $\lambda = e^{i\varphi}$, θ functions of the type $\theta_2(\frac{1}{2}\varphi|i\beta\delta/2\pi)$ will appear in the integrand and allow a direct evaluation of the canonical partition functions for even and odd total electron number N:

$$\begin{aligned} Z_{\text{even}} &= \{1 + 2\sum_{n=0}^{\infty} \exp[-\beta\delta(n+1)^2] \\ &\qquad \times \cosh[(n+1)g\beta\mu H]\} Z_B^{\,2}, \\ Z_{\text{odd}} &= 2\sum_{n=0}^{\infty} \exp[-\beta\delta n(n+1)] \\ &\qquad \times \cosh[(n+\tfrac{1}{2})g\beta\mu H] Z_B^{\,2}, \end{aligned} \tag{4}$$

with

$$Z_B = \prod_{n=1}^{\infty} (1 - e^{-\beta\delta n})^{-1} \tag{5}$$

being the canonical partition function of spinless fermions. Notice that the "Bose" partition function (5) reflects the fact that the number-conserv-

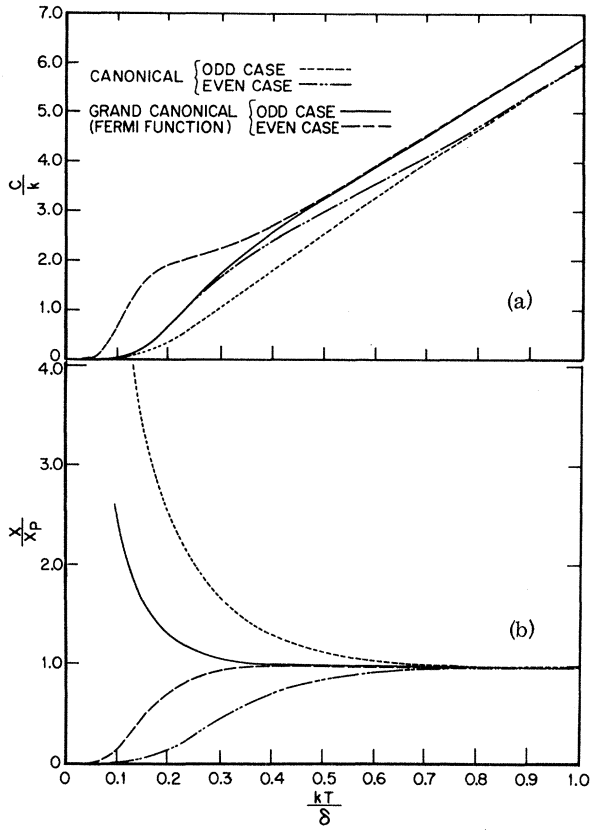

FIG. 1. (a) Electronic heat capacity C and (b) spin susceptibility χ for a system with equal level spacing δ. χ is normalized to the Pauli susceptibility $\chi_P = 2(\frac{1}{2}g\mu)^2/\delta$.

ing particle-hole excitations can be described by bosons as in Tomonaga's model.[9] Furthermore, introducing spin to this model and classifying the excitations according to S_z leads in a natural way to the rotational-like partition functions. With strong spin-orbit coupling, Eq. (4) applies if H is set equal to zero. If, in addition, the magnetic field is strong, Eq. (5) is appropriate with δ replaced by $\frac{1}{2}\delta$.

Heat capacities computed from (4) are shown in Fig. 1 together with the grand-canonical results obtained 33 years ago by Fröhlich,[10] who was the first to treat the problem of small metal particles. Note that the grand canonical ensemble gives rise to a larger heat capacity because there are more excitations allowed when the electron number is not conserved. This is clearly evident both at low temperatures and asymptotically where the canonical heat capacity is $\frac{1}{2}k$ lower than the grand-canonical result. Similarly, the canonical and grand-canonical susceptibilities differ; both are shown in the lower part of Fig. 1.

With this equal-level case in mind we turn next

Table I. Leading low-temperature behavior of the electronic heat capacity and spin susceptibility for different ensembles, with even and odd electron number.

Ensemble	Even	Odd
	C/k	
Poisson	$5.02kT/\delta$	$3.29kT/\delta$
Orthogonal	$(3.02\times 10)(kT/\delta)^2$	$(1.78\times 10)(kT/\delta)^2$
Symplectic	$(3.18\times 10^4)(kT/\delta)^5$	$(1.64\times 10^4)(kT/\delta)^5$
Unitary	$(5.88\times 10^2)(kT/\delta)^3$	
	χ	
Poisson	$3.04(\frac{1}{2}g\mu)^2/\delta$	$(\frac{1}{2}g\mu)^2/kT$
Orthogonal	$7.63(\frac{1}{2}g\mu)^2kT/\delta^2$	$(\frac{1}{2}g\mu)^2/kT$

to the problem of treating the single-level distributions for an assembly of particles of equal size. For $kT \ll \delta$ Kubo has calculated C and χ in the random (Poisson) case. In Table I, the leading low-temperature behavior of C and χ for the random case is listed along with our results for the three correlated ensembles. Unfortunately the leading behavior given in Table I is only good for $kT/\delta \lesssim 0.1$, and the calculation of higher order terms is very tedious.[1] Therefore it is necessary to find another approach.

When $kT \gtrsim \delta$, the distribution averages rapidly approach the canonical equal-level-spacing results shown in Fig. 1. Therefore, a useful interpolation scheme for the entire region is to expand either the distributed-level C or χ about the equal-level-spacing results. The first level strongly influences the behavior of either C or χ only for $kT \ll \delta$, the second level becomes important as kT/δ increases, etc. Thus with the equal-level-spacing results forming the zeroth-order approximation, the contribution of the closest electronic levels is removed and averaged over the appropriate level-spacing distribution to give the first-order approximation.[11] This procedure removes the exponential decrease in C for $kT/\delta < 1$ and gives the leading low-temperature dependence while still retaining the correct high-temperature behavior. In the next approximation the terms containing the next-closest contributing levels are removed and appropriately averaged. Except for the random case the distributions have their spacings strongly peaked about δ, which guarantees rapid convergence of our results as we go to higher approximations.[12]

In Fig. 2 we plot the simple average of the C^{odd} and C^{even} results obtained for the various level distributions. As previously noted, the temperature range over which the simple power-law

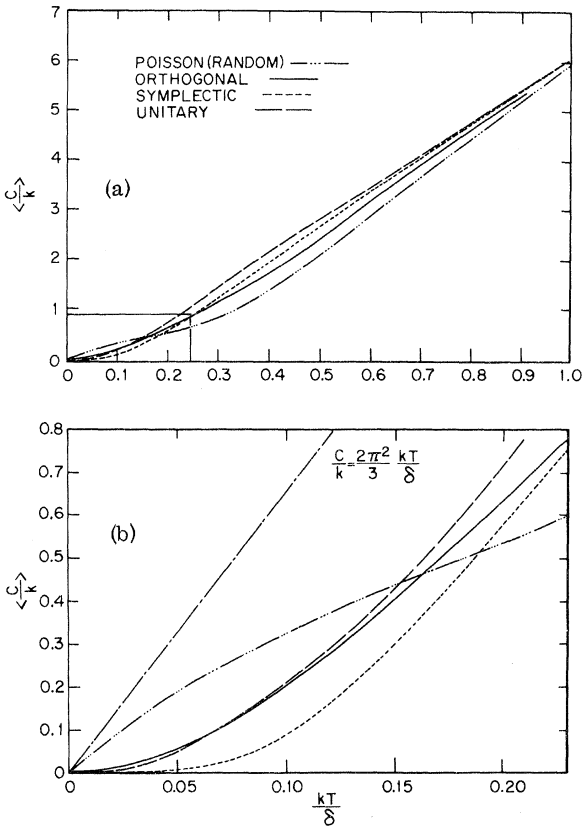

FIG. 2. (a) Electronic heat capacity after averaging over the level distributions with (b) a blowup of the region $kT/\delta \lesssim 0.25$.

forms are adequate is not δ/k but more nearly $0.1\delta/k$. Furthermore, for temperatures larger than δ/k the heat capacities for the various distributions converge to a linear behavior which is $\frac{1}{2}k$ lower than the familiar grand-canonical result. The blowup of the low-temperature region in Fig. 2 clearly shows the difference between the various single-level distributions. The large probability of small level spacings in the Poisson distribution gives rise to a low-temperature linear specific heat similar to that of the bulk metal. The energy-level correlations implicit in the other distributions are responsible for the higher power-law behavior at low temperatures, as first noted by Gor'kov and Eliashberg.[2] The level-repulsion effects are largest when spin angular momentum is not conserved and the Kramers degeneracy is present. This is evident in comparing the orthogonal and unitary results with those obtained from the sympletic ensemble.

The results obtained for the spin susceptibility using the random and the orthogonal level distributions are shown in Fig. 3. Just as in the equal-level-spacing case, the extra electron in the odd case gives rise to a Curie law behavior for $kT \ll \delta$. The difference between the distributions is clearly evident in the even case. Here the finite density of states at vanishing level spacing characteristic of the random distribution gives a finite value for χ_{even} when $kT \ll \delta$. However the level-repulsion effect contained in the orthogonal case leads to a spin susceptibility which is proportional to kT/δ for $kT \ll \delta$. Just as for superconductors we expect that spin-orbit coupling will wash out this level-correlation effect when $\eta \sim \delta$, so here we only consider the limiting case of negligible spin-orbit coupling in which the orthogonal ensemble is appropriate. Both the even and odd cases rapidly approach the Pauli expression as kT exceeds δ.

In comparing the above results with experiment the effects of the particle-size distribution must be taken into account. For simplicity consider a "square" particle-size distribution $\mathcal{P}(a)$ centered at a_0 with width Δa. The size enters only in determining the average level spacing δ which varies as a^{-3}; so, for example, the average heat capacity is

$$\langle C\rangle = \int C(kT/\delta(a))\mathcal{P}(a)da. \tag{6}$$

Expanding this in powers of $(\Delta a/a_0)$ one finds that

$$\langle C\rangle \approx C(kT/\delta_0) + (\Delta a/a_0)^2[\tfrac{1}{4}(kT/\delta_0)C'(kT/\delta_0) + \tfrac{3}{8}(kT/\delta_0)^2C''(kT/\delta_0)], \tag{7}$$

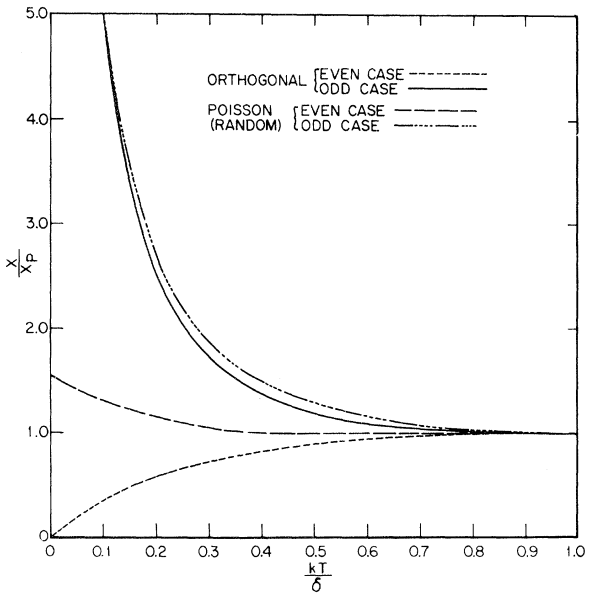

FIG. 3. Spin susceptibility after averaging over the level distributions.

where δ_0 is the level spacing for a particle of size a_0. In both the low- and high-temperature regions the particle-size distribution modifies only the coefficient of the leading temperature-dependent term and not the form of the power-law dependence.

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[11]In these calculations we approximate the n-level spacing distribution for Dyson's three ensembles by Wishart distributions (see Refs. 6 and 7). The Wigner function is just the single-spacing Wishart distribution corresponding to the orthogonal case.

[12]We estimate that the first-order approximation is good to within 10% for the Dyson ensembles and 20% for the Poisson case over the entire temperature range. Asymptotically at both low and high temperatures the error becomes completely negligible for our purposes and is caused by the small deviation of the finite-level-spacing Wishart distributions from the exact ones. See for example Fig. 1.3 of Ref. 7.

Interpretation of Low-Energy Electron-Diffraction Spectra for a Free-Electron Metal in Terms of Multiple Scattering Involving Strong Inelastic Damping*

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The multiple-scattering approach with strong inelastic damping has been used to formulate low-energy electron-diffraction intensity curves without the use of adjustable parameters. The results have been applied to the interpretation of spectra for the clean (001) face of aluminum with good agreement. Inclusion of energy-dependent higher order phase shifts obtained from a realistic potential, of energy-dependent strong inelastic damping, and of temperature effects contributes significantly to the agreement of the calculation with experiment.

The elastic and inelastic scattering of low-energy electrons provides a powerful approach to the study of the atomic structure and electron properties of crystal surfaces. Encouraging progress has been made recently in the development of theoretical approaches to the problem.[1-9] Recognition of the importance of strong inelastic damping contributed significantly to this development.[1-6] Duke and Tucker[1] were the first to provide effectively for this contribution in a phenomenological way in terms of the multiple-scattering approach. Using an s-wave model, they expressed the scattering and damping factors in terms of adjustable parameters, and they were able to interpret important qualitative features of the intensity profiles observed in low-energy electron diffraction (LEED).[1]

In this Letter, we wish to report on the first complete calculation of LEED spectra for a free-electron metal in terms of the multiple-scattering approach involving strong inelastic damping with no adjustable parameters. The significance of this work is that within the constraints inherent to the approach it produces spectral curves in meaningful agreement with specific details of experimental results obtained by Jona[10] for a relatively simple metal, aluminum, when we compare to the detailed conditions of his measurement. Specifically, resonance effects associated with strong intraplanar scattering were