Quantum size effect in copper: NMR in small particles*

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Nuclear-magnetic-resonance line shifts are measured for copper particles of diameters between 25 and 450 Å at temperatures between 0.4 and 77 K in magnetic fields between 2 and 9 kG. At temperatures such that kT is small compared to the average electronic level spacing, effects attributable to the predicted spin pairing in even particles and Curie-type paramagnetism in odd particles are observed for diameters of 100 Å or less. Residual shifts, indicating imperfect spin pairing at $T = 0$ in even particles, are attributable to spin-reversing scattering by spin-orbit coupling in analogy to superconducting small particles with comparable energy gaps. It is estimated that the conduction-electron spins in copper particles flip once per approximately 150 boundary scatterings. The spin-orbit coupling is thus relatively weak, which is consistent with the experimental dependence of spin pairing with temperature, indicating that the smallest copper particles are describable by Dyson's orthogonal case.

I. INTRODUCTION

The thermal broadening of electronic levels in a large piece of metal effectively produces a continuous spectrum. The energy levels, however, are expected to separate[1,2] for small particles when the average spacing δ between nondegenerate levels is less than the thermal energy kT. This should occur for particles of diameter less than 100 Å and temperatures below 10 K. This paper represents an experimental study of the effects of electronic level structure on the electronic spin susceptibility as measured by the nuclear-magnetic-resonance (NMR) shift in copper metal particles.

Previous reports on lithium[3] have noted the effects of level separation on the NMR shift and magnetic susceptibility, but only for a limited range of particle sizes and over limited temperature ranges. Other work on small particles on nonsuperconducting aluminum[4] at low temperatures gave a similar result, namely, a vanishing susceptibility for even particles. Evidence was also seen for the Curie-type paramagnetism of the odd particles. On the other hand, previous reports on copper[5] indicate a broadened NMR line with an enhanced low-field tail associated with odd-particle paramagnetism, but no indication of a vanishing susceptibility for even particles. We report here[6] on several samples of copper with mean diameters between 25 and 450 Å. The smallest samples contain particles with a narrow distribution of sizes and show a reduction in susceptibility at low temperatures, with a residual NMR shift at zero temperature which depends on particle size. The apparently different results[5,6] for copper can be understood in terms of the difference in size distributions.

II. THEORETICAL BACKGROUND

The phenomenon of level separation in small particles was first considered by Fröhlich,[1] who proposed in 1937 that it be used as a test of quantum mechanics. Recent theoretical interest in the electronic spin susceptibility of small particles was revived by Kubo,[2] who argued that small particles at low temperatures remain electrically neutral, lacking sufficient energy to become charged. The constancy of electron number then implies that particles can be categorized as being even or odd, depending on whether they contain total even or odd numbers of conduction electrons. The even and odd particles are supposed to exhibit different electronic spin susceptibilities and are treated separately. In the limit of low temperatures, the current model has the susceptibility of even particles approaching zero because of spin pairing, while the odd particles become Curie-like in their magnetic properties.

In order to calculate the spin susceptibility one must find the appropriate partition functions, but this procedure is complicated by the fact that the wavelengths of the conduction electrons, and consequently the energy levels, will depend critically on surface imperfections which may easily be of atomic dimensions. Kubo therefore considered an ensemble of particles and solved the statistical problem, treating the level structure as a random variable with neighbor spacings following the Poisson distribution. Subsequently, Gor'kov and Eliashburg[7] solved a similar problem, with the particle sizes and shapes as random variables, and with an energy level system described in terms of eigenvalues of a random matrix, in analogy to problems in nuclear physics[8] involving a high density of levels with intermixing. The solution of the problem of random matrices was further considered by Dyson,[9] who showed that general symmetry requirements provided for a classification into three groups corresponding to respective ensembles of Hamilto-

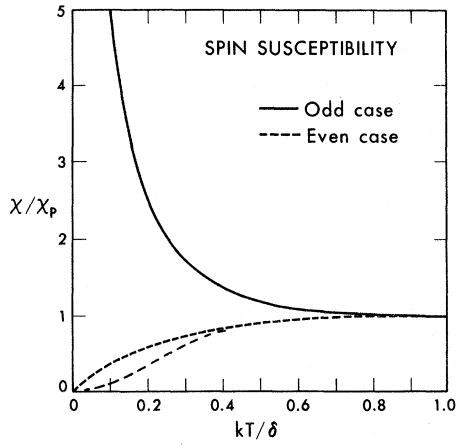

FIG. 1. Conduction-electron spin susceptibility, after Denton *et al.* (Ref. 10). For even particles in the orthogonal regime the susceptibility is proportional to T at low temperatures. For even particles in the symplectic regime the susceptibility varies as T^4 at low temperatures. The odd particles are Curie-like. All values are normalized to the Pauli value.

nians. For small particles the orthogonal ensemble applies when spin-orbit coupling of the conduction electrons is weak and time-reversal invariance holds. The symplectic ensemble describes the case of strong spin-orbit coupling with time-reversal invariance. The unitary ensemble is used for the case of large spin-orbit coupling with no time-reversal invariance, i.e., in large magnetic fields.

Gor'kov and Eliashberg solved for the spin susceptibility of small particles in the limit of low temperature, using the orthogonal ensemble, which specifically requires that the spin-orbit coupling energy of the conduction electrons is smaller than the average energy spacing δ. More recently Denton, Mühlschlegel, and Scalapino[10] have calculated the spin susceptibility as a function of temperature by numerical methods and an interpolation scheme. (They and others have also calculated thermal properties, which we omit here as not being of direct relevance to our problem of susceptibility.) In the zero-order approximation one assumes equal spacings between levels. For even particles one averages over the lowest excited level above the Fermi level according to the appropriate statistical distribution (in the low-temperature limit the density of levels is proportional to a variable level spacing Δ in the orthogonal case; to Δ^4 for the symplectic case), with all other levels equally spaced. For odd particles a similar procedure is followed but the level just below the Fermi level is included as well as the first level above the Fermi level.

The results of Denton *et al.* for spin susceptibility are plotted in Fig. 1 for the orthogonal and symplectic cases, assuming small magnetic field. The lower curves represent the even particles, with spin pairing reducing the susceptibility (and consequently the NMR shift) to zero at $T=0$. The low-temperature behaviors are proportional to T and T^4 for orthogonal and symplectic cases from the respective level densities. The upper curve represents odd particles, in which the odd electron produces a Curie-like behavior. For values of kT exceeding the average level spacing δ, the susceptibility for both odd and even particles assumes the normal Pauli value. It is to be noted that a distribution of particle sizes will produce corresponding distributions of χ and NMR shift for any given temperature. Thus the NMR line will have a width and shape which depends on the details of the size distribution, and in principle one could observe two resolved lines at low temperatures for the odd and even particles, respectively. It is found in practice that the particle size distributions usually prevent the observation of resolved lines.

With the foregoing as a brief qualitative summary of the theoretical situation we turn to the present experiments.

III. EXPERIMENTAL METHODS

As we have indicated, the experimental determination of magnetic susceptibility in these experiments is made in terms of the NMR shift,[11] depending directly on the zero-frequency electronic spin susceptibility, which takes on the Pauli value χ_P in large particles or at high temperatures. We prepared small particles of copper by vacuum evaporation and also by chemical reduction.

In the first method[11] small bits (each with a mass of a few milligrams) of copper wire were evaporated from a resistance-heated boat, where the size of the particles was controlled by varying the mass of the bit and the temperature of the substrate. The quantity of copper evaporated and the source-substrate separation were adjusted so that the primary centers of nucleation were widely separated and there was no overlapping of the fully grown particles, as may be seen in Fig. 2. Each sample consisted of up to 400 layers of copper interleaved with evaporated silicon oxide on Mylar, which was folded over and over into a small package a few millimeters in diameter, and on which the rf coil was wound. Silicon monoxide was chosen as the insulating matrix because it is easily evaporated and because it inhibits oxidation of the copper particles after they are formed. Uniformity of particle size is achieved by limiting the amount evaporated in each bit to prevent overlap and coalescence of neighboring particles and by cutting the bits to be of equal weight. One sees from Fig. 2 that the average separation between particles is at least one average diameter. The density of par-

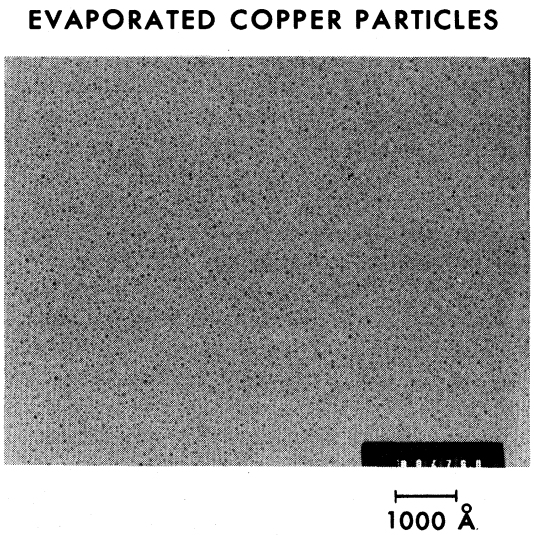

FIG. 2. Electron micrograph of 40-Å copper particles. The particle density is of the order of $2\times10^{12}/cm^2$, with average separation greater than the average particle diameter, which is quite uniform.

ticles is of the order of 10^{12} per cm^2.

In the second method,[12] copper ions are spread over a porous alumina powder with high surface area and chemically reduced. The alumina is agitated in a solution of copper fluoride for several hours. Fluorine ions in solution break the aluminum oxygen bonds in the alumina and form stable Al-F bonds. The remaining unsatisfied oxygen bonds capture copper ions from solution, resulting in a monolayer of copper ions spread over the surface of the alumina. On heating the alumina, on which the copper ions have been chemisorbed in a hydrogen atmosphere, the copper is reduced and water is evolved. The particle size is controlled by varying the concentration of copper ions chemisorbed on the alumina surface and by changing the temperature and duration of the reduction process. The finished product is encapsulated in paraffin, before it is removed from the hydrogen atmosphere, in order to prevent oxidation.

The impurity content of the samples is of concern primarily insofar as paramagnetic effects broaden the NMR linewidth. The copper and SiO used in the evaporations contained less than 10 ppm significant impurities, although it was found that[13,14] samples of evaporated SiO with or without the copper particles contained up to 10^{19} paramagnetic spins per cm^3. These could be partially annealed out, but some remain as an undesirable source of NMR line broadening. The copper fluoride contained less than 50 ppm iron, plus traces of tin, arsenic, and lead, none of which is expected to cause serious trouble. Note, for example, that 10 ppm averages to one impurity per hundred particles, for particles containing 10^3 atoms. As was true for the evaporated samples, the important impurities come, not from the starting ingredients, but rather as a result of the particle manufacturing process. The alumina support contained 160-ppm sodium and no other significant impurities. However, a spin resonance study[14] of the samples showed that, after the copper was chemisorbed onto the alumina, paramagnetic spins appeared in concentrations up to 10^{18} per cm^3, associated with the formation of some as yet unidentified compound. We must conclude that, depending somewhat on particle size and the conditions of preparation and annealing, either type of sample contained impurities which averaged to one or more paramagnetic spins per copper particle. Whether these impurity spins are concentrated near the particle surfaces is not yet known. They may therefore be sources of line broadening, but are not expected to affect the center position of the resonance lines, which is the important quantity in determining the spin susceptibility of the conduction electrons of the particles themselves at low temperatures.

The low-temperature and resonance equipment was conventional and will not be discussed. The experimental ranges for magnetic field and temperature were 2–9 kG and 0.4–77 K, respectively.

Particle size distributions for some samples were determined with the electron microscope. For others the broadening of x-ray diffraction lines served as a measure of average size. Table I gives a summary.

IV. EXPERIMENTAL RESULTS

We studied six samples of copper with average diameters ranging between 25 and 450 Å as listed in Table I. Sample No. 2 was particularly useful, because of the narrowness of the size distribution, because the average size facilitated the observation of quantum size effects at temperatures above 4 K, and because the concentration of particles provided for quite adequate signals (which was hardly true of the smallest sample). The result of extensive analysis of the particle sizes for sample No. 2 (40 Å) is shown in Fig. 3, which gives both a histogram of observed particle diameters and also a Gaussian fit to the histogram with

TABLE I. Summary of sample characteristics.

Sample number	Average diam. (Å)	Method of preparation	Temp. of substrate (or reduction) (°C)	Method of size determination
1	25±5	Evap.	25 °C	x ray
2	40±5	Evap.	25 °C	*E* micr.
3	100±10	Red.	(350 °C)	x ray
4	110±10	Evap.	325 °C	*E* micr.
5	150±10	Evap.	325 °C	*E* micr.
6	450±50	Red.	(680 °C)	x ray

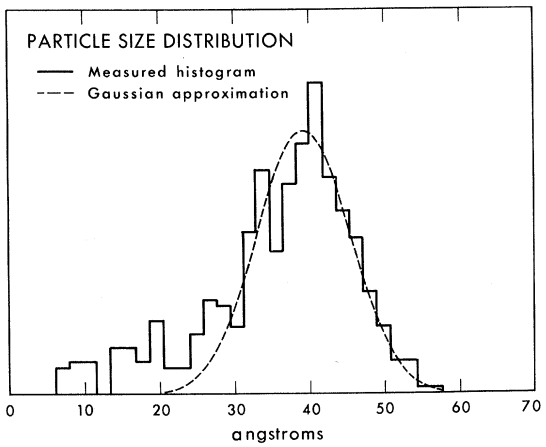

FIG. 3. Size distribution of 40-Å sample of copper particles. Solid curve: distribution of average diameters. Dashed curve: Gaussian fit to experimental distribution curve; Gaussian half width 6 Å. The average particle is estimated to contain approximately 3000 atoms, assuming a spherical shape. Actually the particles are probably slightly flattened (see Ref. 19).

a half-width of 6 Å. It will appear in a subsequent discussion that the narrow distribution in particle size for this sample permits observations of the shift of resonance line center which are obscured in samples containing broader size distributions.

It is instructive to examine Fig. 4, which shows the resonance line for sample No. 3 (100 Å) taken at 0.4 K and 8.8 kG. It will be seen[15] that the NMR shift is reduced, the line is broadened, and the low-field tail is slightly enhanced. The reduction in NMR shift is attributed to spin pairing in the even particles, and the low-field tail is associated with the Curie paramagnetism of the odd particles. The width is partly accounted for in terms of a distribution of shifts arising from the variations in particle size. Predictably, no quantum size effects are seen for the larger particles, since the level spacings would be less than kT for one degree. Figure 5 gives the normalized susceptibility (i.e., NMR shift) as a function of temperature for the four smallest samples. It is clear that the susceptibility decreases with decreasing temperature and that the limiting value is lower for smaller particles. The susceptibility had value χ_P at 77 K for all samples.

The density of particles in sample No. 1 (25 Å) was not sufficiently great to produce signals adequate for drawing conclusions from the shape of the line, although its center was easily determined. For sample No. 2, which is known to have a very narrow distribution of sizes, no significant line asymmetries were observed, and a computer simulation based on Figs. 1 and 3 verified that the low-field tail from the odd particles would not have been evident in these experiments. Intensity measurements indicated a loss of a factor of 2 at low temperatures, consistent with the loss of the contribution of the odd particles. Thus the measurements from samples 1 and 2 are considered to apply to the even particles only, and the reduction in NMR shift should result directly from spin pairing.

V. DISCUSSION

The experimental curves of NMR shifts vs temperature fall toward the residual values at low temperature in the same general way as predicted by the curves for even particles in Fig. 1. The experimental precision is not adequate for distinguishing orthogonal from symplectic behavior from a simple inspection of the shape of the curves. However, the data for the smallest samples may be interpreted in the following way. Sample 2 is estimated to contain particles of approximately 3000 atoms, implying a level separation of 36 K. The NMR shift has fallen one half of the way to the residual value at 3 K. The ratio of these temperatures is 0.08, which is to be compared with 0.17 taken directly from the curve for the orthogonal case in Fig. 1. The corresponding theoretical figure for the symplectic case would be 0.28, which is considerably out of range of the experimental result. A similar result is obtained for sample 1. Thus, although the smallest samples are probably orthogonal, for the larger samples it is likely that the spin-orbit coupling energy is comparable[5] to the level spacing, and the orthogonal case is no longer applicable in the accessible temperature range. The present data for the larger samples are not useful for distinguishing among the possible statistical ensembles.

The principal unanticipated result is the residual shift at $T=0$ which varies with particle size and which reflects an incomplete spin pairing even in

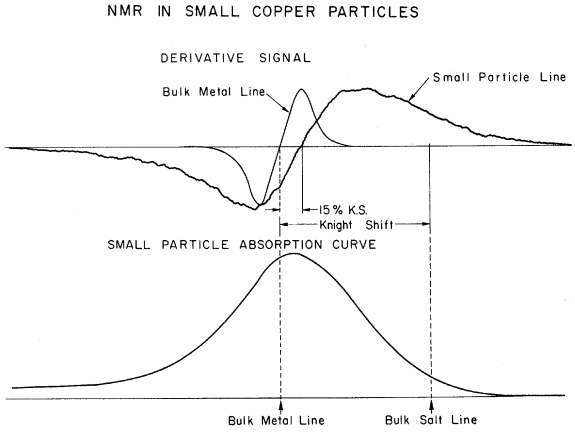

FIG. 4. NMR in 100-Å sample. Experimental derivative signal and integrated absorption curve for sample 3 taken at 0.4 K and 8.8 kOe. Note small shift of line center plus broadening and enhanced low-field tail.

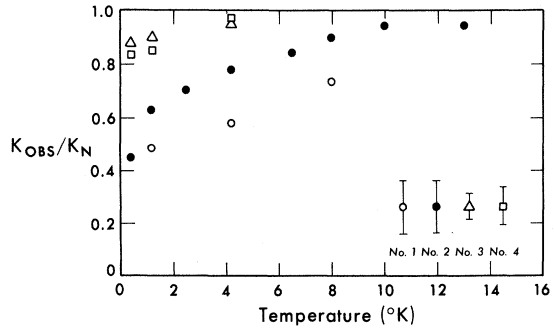

FIG. 5. Observed NMR shift vs temperature for samples Nos. 1–4. Note residual shift at lowest temperature increases with particle size. For sample 2 the level separation expected from the measured particle size is approximately 36 K. The NMR shift is normalized to the measured value in bulk copper.

the limit $kT \ll \delta$. We believe that the residual shift is attributable to spin-reversing scattering effects in analogy to the behavior of superconducting particles.[16] Thus Abrikosov and Gor'kov[17] developed an expression for the residual NMR shift in superconductors as a function of the parameter $\rho_0 = 2\hbar/3\tau_s\epsilon_0$, where ϵ_0 is one half the superconducting energy gap and τ_s is the mean spin lifetime. As was pointed out by Anderson,[18] the effect of spin-reversing scattering at surfaces or impurities is to change the shape of the frequency-dependent susceptibility $\chi''(\omega) \sim (1+\omega^2\tau^2)^{-1}$, the integral of which gives the static susceptibility χ_p. The superconducting energy gap removes the components of $\chi''(\omega)$ which are less than $\omega \sim 2\epsilon_0/\hbar$. For large particles with relatively long spin lifetimes we have that $\chi''(\omega)$ is negligible for frequencies larger than the energy-gap frequency, resulting in a vanishing static susceptibility. Conversely, for small particles and short lifetimes, the contributions to $\chi''(\omega)$ are important above the energy gap frequency and the susceptibility remains finite. In the full treatment of Abrikosov and Gor'kov, the residual susceptibility is one half the Pauli value when the parameter $\rho_o = 1$, i.e., when the spin lifetime is of the order of $\hbar/\epsilon_o$.

This treatment may be applied to nonsuperconducting particles at low temperatures, because in even particles for $kT \ll \delta$ the lowest excited state above the Fermi level is the only important one with a significant probability of being occupied, and it assumes the role of the energy gap. However, while the small-particle energy-gap treatment can be patterned on the superconductor theory, there are some important differences. In the superconductor the energy gap is a function of temperature, while in the normal small particle the level spacing δ varies inversely as the volume of the particle. The electron spin lifetime should be directly proportional to the average particle radius in both cases. Thus the parameter ρ_o should vary as $1/r$ for the superconductor and as r^2 for the normal particle. Observations on superconducting[19] and normal particles confirm the respective dependences on radius.

Following Elliott,[20] the spin lifetime τ_s may be related to the resistivity mean free time τ_R by $\tau_s = f\tau_R$, where the constant f is an average number of transit times between spin flips and depends on the spin-orbit coupling. Elliott estimates $f \sim \alpha(\Delta E/\lambda)^2 \sim \alpha/(\Delta g)^2$, where ΔE is the separation between nearest bands with the same transformation properties, λ is the spin-orbit coupling constant, Δg is the electronic g shift in the metal, and α is an undetermined constant. For superconducting tin, Appel[21] estimates theoretically that $f \sim 70$, with $\Delta E = 3$ eV and $\lambda = 0.36$ eV, while Wright[19] found experimentally that $f \sim 8$ by making best fits of residual shift data with the Abrikosov–Gor'kov curves. Further work on superconducting aluminum gave results consistent with this picture. Thus Appel estimates $f = 2 \times 10^4$ with $\lambda = 0.22$, and Hammond and Kelly[22] find f to be unmeasurably large since the residual shift is approximately zero. For superconducting lead[23] with a large spin-orbit coupling, the number f appeared to be approximately 2, and for a number of superconducting alloys of tin[11] with impurities of varying spin-orbit strength, the f number was reduced according to the concentration of the impurity and its atomic spin-orbit coupling. For example, 1% of lead reduced the f number from 8 (pure tin) to 4, indicating that the impurity effect in that sample was equivalent to surface scattering in limiting the spin lifetime.

Now we turn to a consideration of the effective f number in normal copper particles, expecting on the basis of the above arguments that it will lie somewhere between 10 and 10^4. Using Schultz's value[24] for $g = 2.033$ and Elliott's expression with $\alpha = 1$, we find $f \sim 10^3$. For comparison we have determined the best fit (see Fig. 6) to the Abrikosov–Gor'kov relations, taking τ_R as the mean transit time between surface encounters and taking $\frac{3}{2}\epsilon_0$ as the Fermi energy divided by the average number of conduction electrons in the particle. The residual shifts were taken by extrapolating the curves in Fig. 4. We have assumed that the NMR shift in copper has no appreciable contributions from orbital or core polarization effects. The result $f = 150$ is consistent with the above arguments and implies a reasonable value for Elliott's $\alpha = 0.15$.

It appears, then, that the theoretical predictions for quantum size effects are realized in small particles of copper, provided one allows for the inhibition of spin pairing by spin-reversing scattering. It is worth noting that these results are not inconsistent with previous reports on copper,[5]

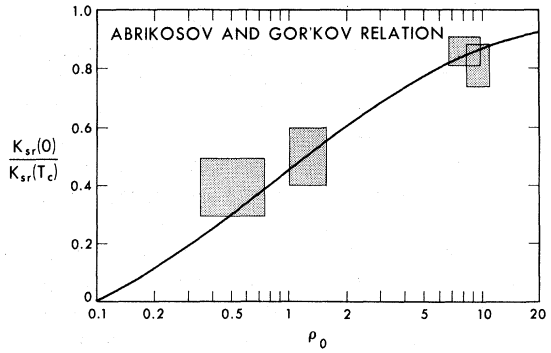

FIG. 6. Residual NMR shift vs spin reversing scattering parameter $\rho_0 = \hbar N/f\tau_R E_F$. The solid line is the curve of Abrikosov and Gor'kov (see Ref. 17). The squares represent experimental points for samples 1–4, with N the number of atoms in the average particle, E_F the Fermi energy of copper, τ_R the average time between surface encounters for the conduction electrons, and the factor $f=150$ for best fit.

which differed mainly in the manner of preparation and in the breadth of the particle size distribution. The sample 1 of Kobayashi *et al.* had an average particle size of 40 Å (which is equal to that of our sample 2), but their sample contained an appreciable number of particles of double that diameter which contained the predominant fraction of the total volume of copper in the sample. It is not surprising then that the low-field tail became evident as the odd-particle paramagnetism set in. The larger even particles would have large residual shifts, and the smaller even particles would contribute only a small part of the intensity, resulting in little shift of the line peak and showing up as a slight broadening of the high-field side of the line. As for the methods of preparation, both appear to result in undesired paramagnetic impurities, possibly from oxides in the particles prepared in helium gas, or as dangling bonds in the SiO matrix. These impurities affect the nuclear spin relaxation time and linewidth, but are not important for the NMR shift measurements. The same is true for the paramagnetic centers that develop in the chemical reduction processes.

VI. CONCLUSIONS

The existing evidence supports the view that Kubo's basic ideas are correct and that quantum size effects occur in small systems. The indications of reduced low-temperature susceptibility in even particles of lithium, aluminum, and copper as obtained via NMR shifts are consistent with the theoretical picture,[10] providing some assumptions are made concerning the dynamic behavior of the electrons. However, it must be remembered that the detailed mechanism for the boundary and spin-reversing scattering[25] of the electrons in particles are not known independently.

It has been predicted[26] that the spin-flip rates will decrease in particles for which $\delta \gg kT$ and $\hbar\omega_e$, resulting in a narrowing of the conduction-electron-spin-resonance (CESR) line. Although reports[27] of this effect have appeared for particles around 10 Å in diameter in some metals, it has not yet been reported in either sodium or copper. In view of the fact that the present results appear to fit the Abrikosov-Gor'kov relations for all of our samples, we must conclude that either the effect would be seen only in particles of the order of possibly 10 Å or less, or that the theoretical predictions must be modified. Presumably for particles containing a very small number of atoms the electron spin relaxation rate must increase, since in the limit of the atomic beam the relaxation time is longer than the time of flight.

Thus, the interpretation of the NMR experiments depends importantly on knowledge of the electron spin lifetimes which are not known independently. Furthermore, remembering that the electron lifetimes may well depend on paramagnetic impurities in the matrix surrounding the particles or in surface oxide layers, we are not at present in a position to conclude that all of the observations refer uniquely to the metal particles and the atoms that constitute them. One might even question whether Kubo's assumptions of charge neutrality and constant electron number are valid for a metal particle with large surface-to-volume ratio interacting even weakly with the embedding matrix.

It therefore appears important to design complementary experiments which eliminate the problems of impurities and boundary interactions with the matrix at the surface of the particles under study. Such an experiment has been proposed[28] and is being carried out in this laboratory. Beams of freshly condensed particles are formed by an oven and collimating slits and pass through an inhomogeneous magnetic field, as in the Stern-Gerlach experiment, to a detector. The particles which have one Bohr magneton associated with the odd electron will suffer deflection, while the even particles will remain undeflected. Although schemes for acceleration and velocity selection may be employed in later experiments, preliminary estimates and experiments suggest that a collimated thermally effusing beam in the conventional atomic beam geometry will give deflections comparable to those found in atomic beam experiments for odd particles. It appears to be quite feasible to employ particles in the range from 10 to 10^3 atoms, thus making accessible a large range of measurements capable of elucidating the development of the electronic structure of the semi-infinite metallic lattice from the primordial metallic molecule. Refocusing and resonance experiments allow the possibilities in prin-

ciple of performing CESR, NMR, and quantum optical experiments on these particles as they fly in the uncontaminated state immediately following condensation. It is required that the electron spin lifetime be compatible with the time of flight in the beam, and that spin-rotation effects not interfere with the magnetic deflections. Ultimately, it should be possible to observe the effects of surface contamination and to measure the heat capacity of the particles. The method is applicable to nonmetallic particles, assuming that the technical problems of making and detecting the particles can be solved. Electric deflections should be possible.

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[27]M. Ya. Gen and V. E. Petinov, Zh. Eksp. Teor. Fiz. 48, 29 (1965) [Sov. Phys.—JETP 21, 19 (1965)]; K. Saiki, T. Fujito, Y. Shimizu, S. Sakoh, and N. Wada, J. Phys. Soc. Jpn. Suppl. 32, 447 (1972); R. Monot, C. Narbel, and J.-P. Borel, Nuovo Cimento B 19, 253 (1974). See Also Ref. 3 above. Negative results have been reported for sodium [M. A. Smithard, Solid State Commun. 14, 411 (1974)].

[28]W. D. Knight and D. A. Gordon (unpublished).

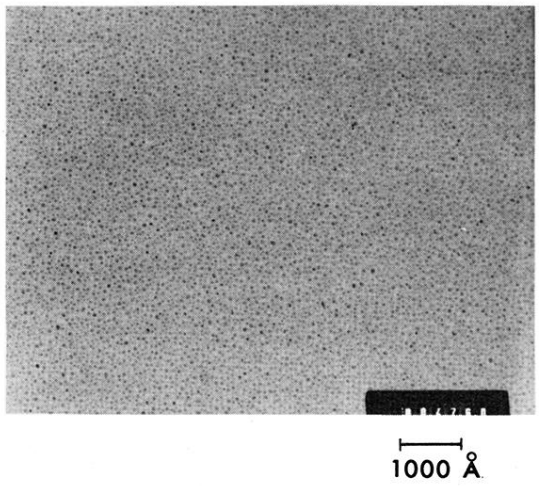

FIG. 2. Electron micrograph of 40-Å copper particles. The particle density is of the order of $2\times10^{12}/cm^2$, with average separation greater than the average particle diameter, which is quite uniform.