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Deviation of spin susceptibility of small metallic particles as predicted by the random-matrix theory

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The spin susceptibility of small metallic particles is studied with the contribution of the clustering of particles, size distribution of the sample, shape effect on the electronic-energy distribution, spin-orbit coupling interaction, and magnetic field effects taken into account within the framework of random-matrix theory. It is found that each of these effects contributes to enhance the spin susceptibility. From the analyses stated above of the Cu Knight-shift data, the spin-orbit coupling energy is derived and compared with those derived from ESR measurements. The two-level correlation function that is proportional to the spin susceptibility given by Efetov is used to analyze both the Knight-shift data of Cu and Al small particles under a strong magnetic field which gives the orthogonal energy-level distribution rather than the symplectic one (corresponding to the symmetry of the electron Hamiltonian with regard to space and time).

I. INTRODUCTION

In a finite-size metallic particle, the energy levels of the electrons are no longer continuous but are discrete exhibiting remarkable deviation of electronic properties from those in bulk as is known by the quantum size effect (QSE). This effect is prescribed by the energy-level statistics of electronic states of conduction electrons. Well-known Fermi-Dirac distribution cannot be applied for small metallic particles because of the constraint of electric neutrality for the electron distribution. The level statistics so far proposed in small particles are Poisson (random level-spacing distribution), orthogonal (weak spin-orbit coupling and weak magnetic field), and symplectic (strong spin-orbit coupling and weak magnetic field) cases depending on the symmetry of the electron Hamiltonian with regard to time and space. The odd-even characteristic for the number of electrons is also essential to the magnetic properties of small particles. For a small particle with an even number of electrons (hereafter, we call it an even-electron-number particle), the ground spin state is singlet and the Pauli paramagnetism will decrease with decreasing temperature and particle size. This inclination is apparent in the very-low-temperature region and the standard theory for the electronic state of small particles based on the random-matrix theory (RMT) qualitatively predicts this deviation.[1,2] However, a quantitative treatment based on the above theory failed to give an estimate of this deviation as a function of size and temperature. It has been always observed that the measured magnetic susceptibility is larger than estimations derived from RMT (named as the paramagnetic enhancement). Apart from the fact that this paramagnetic enhancement is due to the impurity effect[3] or surface effect[4] in some experiments, sometimes this discrepancy was ascribed to the inaccuracy of the measurement of the size of particles due to particle clustering and the size distribution of particles, which is inevitable for practical samples. However, a detailed analysis of these effects on the magnetic properties of small size materials has not been studied so far.

In this report, we quantitatively examine the effect of size distribution and clustering of particles on the magnetic susceptibility of small metallic even-electron-number particles. At the same time we will discuss the effect of the shape of the particles, spin-orbit contribution, and the magnetic field interaction on this paramagnetic enhancement. All these terms contribute to enhance the spin susceptibility. Hence the observed magnetic susceptibility χ_{obs} can be expressed simply as

$$\chi_{obs}=\chi_{RMT}+\Delta\chi_{shape}+\Delta\chi_{s.o.}+\Delta\chi_{Zeeman} . \tag{1}$$

Here χ_{RMT} is the spin susceptibility given by the RMT postulate and taken as a standard, $\Delta\chi_{shape}$ is the paramagnetic enhancement due to the shape effect, $\Delta\chi_{s.o.}$ is from the spin-orbit interaction, and $\Delta\chi_{Zeeman}$ is from the contribution of Zeeman effect. The latter effect can be easily isolated through the experiment with changing the strength of magnetic field. Since the spin-orbit interaction is not large for light metal elements, the shape effect will be highlighted in Mg and Al if it exists under a weak magnetic field, while it is complicated in heavy elements such as Cu and Sn. Through the careful examination of the data of these materials, all factors given in Eq. (1) can be separately obtained as will be done in the present paper.

II. PARTICLE CLUSTERING AND SIZE DISTRIBUTION

Practically, the samples for the measurement of magnetic properties (NMR, ESR, Mössbauer, or static magnetic susceptibility measurement) are always an assembly of particles which is supported on a substrate or embedded in a matrix. Therefore, it should be taken into account that there is an accidental clustering among particles and this obscures the electronic properties of particles as a function of size. One possibility of the results of the clustering is electron transfer between particles. In a simplest case, the clustering effect can be accounted for increasing the effective size of a particle. Given the average number of particles in a cluster N, the mean level spacing at the Fermi level of a particle, δ, becomes δ/N.

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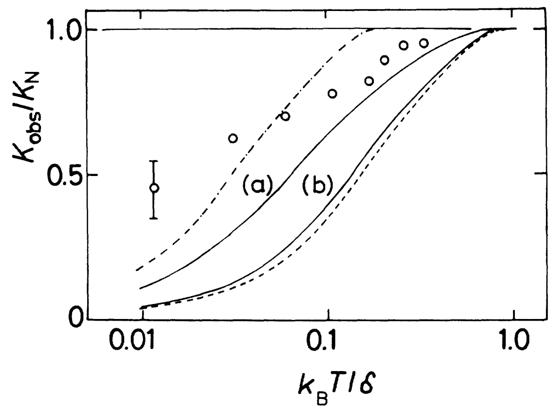

FIG. 1. Clustering and size distributions of particles. Temperatures are normalized to the average level spacing at E_F. Knight shifts are represented in the unit of the bulk value K_N. Circles for experimental data of the Knight shift for 4-nm Cu small particles (Yee and Knight). Dashed line for RMT with 4 nm diameter, dot-dashed line for RMT with the clustering of five particles. Solid lines for (a) RMT with variance $2\sigma^2=0.4$, (b) RMT with observed variance of 0.04.

Hence, the temperature profile of the susceptibility shifts towards the side of low temperature. Superficially, the spin paramagnetism seems to be enhanced at a given temperature. Figure 1 shows the effect of clustering in case of N being 5 together with the Knight-shift data of small Cu particles.[5] Upon contacting the particles the original RMT curve (dashed line) shifts to a lower-temperature region (dot-dashed line) as evident from the figure. However it has no effect on the temperature profile of the susceptibility and shifts only the position of the line to the left leaving the curvature of the line unchanged. We could not fit the curve to the experimental plots in any way by this procedure. Thus the particle clustering is not crucial to the discrepancy between the experiment and the RMT estimation.

Next we examine the influence of the size distribution of particles to the observed magnetic susceptibility. Fortunately, Yee and Knight[5] had precisely studied the size distribution of their Cu sample which is reproduced in Fig. 2. They fitted the measured histogram by the Gaussian distribution with the variance of 0.04 corresponding to the Gaussian half-width 0.6 nm. Using the observed parameters (size and variance), we numerically calculated the spin susceptibility for the orthogonal ensemble which is shown in Fig. 1, curve (b). It is evident from Fig. 1 that the contribution of the size distribution is not significant. The susceptibility reveals a slight enhancement due to the contribution of larger particles in the size distribution. K_{obs}/K_N of this fraction is almost constant (≈ 1) in the wide temperature range. When we assume a very large size distribution with the variance of 0.4 as shown in Fig. 2, the enhancement of the spin susceptibility is obvious as seen in Fig. 1, curve (a). Still the calculated susceptibility is lower than the observed value even assuming unrealistically large size distribution. As a conclusion, the enhancement of the observed Knight shift as a function of temperature cannot be explained by clustering and size distribution of particles.

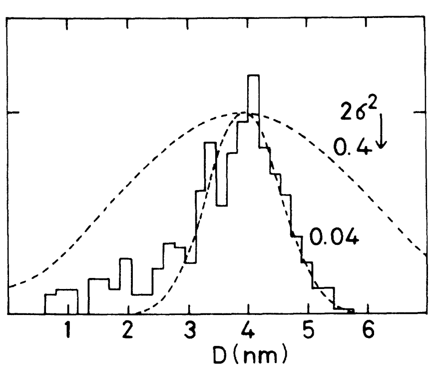

FIG. 2. Size distribution of 4-nm Cu ultrafine particle (UFP) after Yee and Knight. Solid line for a measured histogram. Dashed lines with two variances 0.04 and 0.4 are calculation curves for the Gaussian distribution.

III. SHAPE EFFECT

The statistical nature of the electronic-energy-level separation in small metallic particles have been discussed by several authors.[1,2,6] Theoretically, the orthogonal distribution is derived when both spin-orbit coupling and the external magnetic field are small compared with δ. The numerical calculation shows that the level distribution becomes orthogonal when the shape of a particle has a maximum randomness contrast to the Poisson one when the shape is regular. These two cases were unified with the use of Brody distribution by Tanaka and Sugano.[7] The shape effect of a particle on the spin susceptibility was precisely treated by the present author[8] and applied to Mg small particles in which the contribution from spin-orbit interaction is negligible. The spin susceptibility incorporated with the shape effect is expressed as

$$\chi_s(\rho)=\chi_{\rm Poisson}^{2-\rho}\chi_{\rm RMT}^{\rho-1} \tag{2}$$

in which ρ is the exponent representing the contribution of shape effect, $\chi_{\rm Poisson}$ is the spin susceptibility for the Poisson distribution, and $\chi_{\rm RMT}$ for the orthogonal case as stated above. The calculated χ_s for various values of ρ is depicted in Fig. 3. Since the contribution of the shape effect to spin susceptibility $\Delta\chi_{\rm shape}$, is defined as the deviation from $\chi_{\rm RMT}$ in Eq. (1), it can be given by

$$\Delta\chi_{\rm shape}=\chi_{\rm RMT}[(\chi_{\rm Poisson}/\chi_{\rm RMT})^{2-\rho}-1]\ . \tag{3}$$

$\Delta\chi_{\rm shape}$ thus defined is also shown in Fig. 3. It should be noted that for the larger ρ value, the shape of the particles is more irregular, i.e., the more QSE is prominent, the less the effect of $\Delta\chi_{\rm shape}$ becomes. Hence QSE itself strongly depends on the state of the samples such as size, shape, and surface conditions. It was reported by Kobayashi *et al.*[11] that Al small particles coupled with oxide surfaces revealed a clear QSE in NMR Knight shift. This is keen contrast to the fact that QSE is absent in the sample encapsuled in vacuum.[12] When the particle surface is oxidized, the surface becomes more irregular which causes the promoted QSE as indicated in the above reports and the findings can be interpreted in terms of the shape effect. The first convincing experiment understood

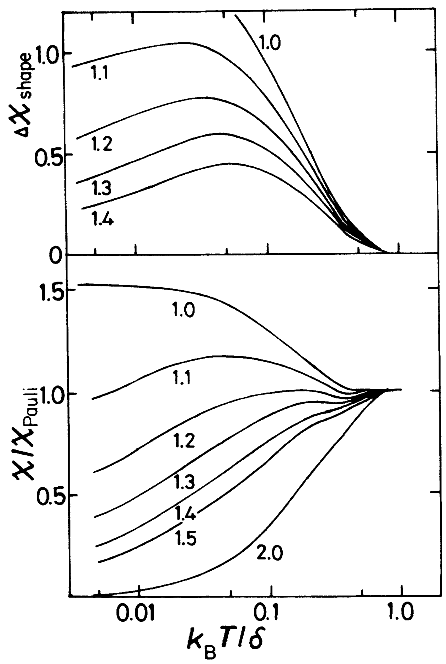

FIG. 3. Spin susceptibility of even-electron-number particles as a function of absolute temperature normalized to a Kubo gap at E_F. The numbers in the figure are the exponent for shape effect ρ. $\rho=1$ for Poisson, $\rho=2$ for orthogonal, and others are the exponents used for the calculation of Eq. (2). Bottom, calculated spin susceptibility (Ref. 9). Top, paramagnetic spin enhancement, $\Delta\chi_{\text{shape}}$, from the RMT case due to the shape effect. The susceptibility is normalized by the Pauli paramagnetic one.

by virtue of QSE is the Knight shift of Cu particles prepared by the vacuum evaporation on a SiO matrix.[5] There were two origins in the Knight shift. The low-field tail was ascribed to the odd-electron-number particles and the high-field shift to spin pairing in the even-electron-number particles. The data for the even-electron-number particles are reproduced in Fig. 4 together with the calculation curves from Fig. 3 with $\rho=1.4$ and with the observed diameter. Obviously the RMT curves (dashed lines in the figure) lie much lower than the observed values. On the contrary, for every sample with a different diameter, the calculation based on Eq. (2) is in good agreement with the experiments in the high-temperature region, but slightly deviates in the low-temperature region. The deviation is due to the spin-orbit interaction neglected in the preceding treatment and is discussed in Sec. IV. For metals like Mg, the spin-orbit coupling is weak. Therefore one might expect that the spin susceptibility can be understood exclusively by the shape effect. The analysis for Mg particles in line with the above treatment was done in the previous report.[10] The observed spin susceptibility derived from the static magnetic susceptibility measurement completely agreed with the calculation of $\rho=1.2$. Concerning the exponent of shape effect ρ, the observed value for Cu ($\rho=1.4$) is larger than that of Mg ($\rho=1.2$), i.e., the shape of Cu particles is suggested to be more irregular than Mg. This may be due to the difference of the preparation technique engaged in these small particles; Cu by vacuum evaporation on the SiO substrate, on the other hand Mg by gas evaporation in free gaseous space. The latter gives a regular shape of the particles.[8,13]

IV. SPIN-ORBIT INTERACTION

When there is a large spin-orbit interaction, the Knight shift no longer reduces to zero in the low-temperature limit.[14] This is quite different from the behavior depicted in Fig. 3 where the spin susceptibility goes to zero even when the contribution of the shape effect is taken into account. Therefore it is reasonable to regard the deviation found in the low-temperature region of Fig. 4 as due to the spin-orbit interaction. The spin-orbit interaction energies were calculated using the residual Knight shift of Cu particles assuming all the deviation from bulk value at low temperature being due to the spin-orbit interaction and were compared with those from ESR g value by Kobayashi and Katsumoto.[15] Since the spin susceptibility also enhances in the low temperature when the shape effect is incorporated into QSE as seen in Fig. 3, this contribution cannot be disregarded in analyzing the temperature dependence of the spin susceptibility. However, they neglected the shape effect and took all the nonzero Knight shift, K_{obs}/K_N, to be a residual Knight shift.

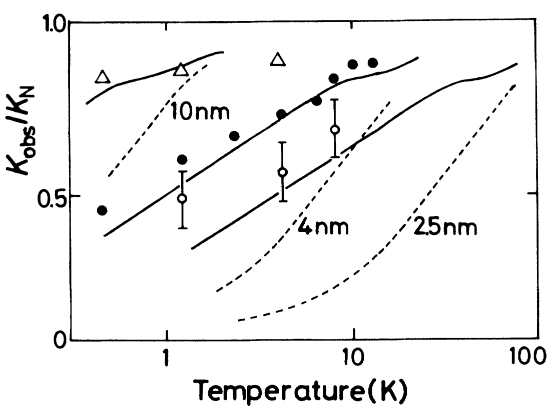

FIG. 4. Observed NMR Knight shift of Cu small particles (after Yee and Knight, Ref. 5) as a function of temperature and particle size. Dashed lines are calculated curves for RMT. Solid lines for the curve with $\rho=1.4$ in Fig. 3. Triangle, 10 nm; solid circle, 4 nm; open circle with error bar, 2.5 nm.

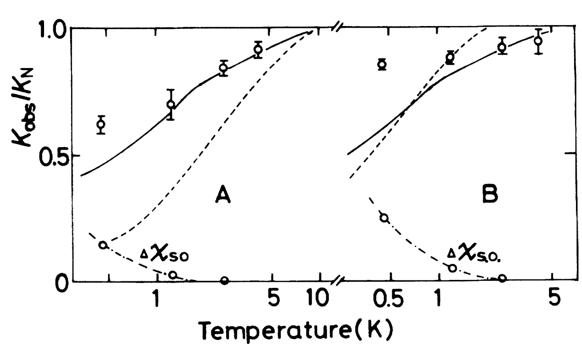

FIG. 5. NMR Knight shift vs temperature for Cu particles (after Kobayashi and Katsumoto, Ref. 15) in a low-temperature region. Dashed line for RMT. Solid line for Fig. 3 with $\rho=1.5$. Dot-dashed line for the enhancement due to the spin-orbit interaction, $\Delta\chi_{\text{s.o}}$.

TABLE I. Spin-orbit coupling energies of several Cu samples.

	D (nm)	δ (K)	ρ	η	$\hbar/\tau_{s.o}$ (K) NMR	ESR
Yee and Knight (Ref. 5)	4	39	1.4	0.1	3.9	2.9
Kobayashi and	6	9.3	1.5	0.33	3.1	1.9
Katsumoto (Ref. 15)	10[a]	4.8	1.5	0.55	2.6	1.6

[a]Fitting parameters are derived assuming the diameter being 7.5 nm. $\Delta g = 0.031$ was used for the calculation of $\hbar/\tau_{s.o}$ (ESR).

Here we reevaluate their data taking into account the shape effect along with those by Yee and Knight and compare them with the ESR results. In Fig. 5, the data for Cu particles under a weak field by Kobayashi and Katsumoto are reproduced. The dashed curves from RMT calculated with the observed diameter are far below the observed Knight shifts in the low-temperature region indicating that the shape and spin-orbit interaction are crucial to this sample. The solid lines are from Fig. 3 with $\rho = 1.5$. In Fig. 5 (curve B), we assume the diameter of particles being 7.5 nm instead of the observed one, 10 nm on account of surface oxidation. If not, we could not fit the data in any way. The Knight shifts after subtraction of the contribution of the shape effect, $\Delta\chi_{s.o.}$, are also drawn in Fig. 5 (curves A and B) by a dot-dashed line. From the corrected residual Knight shift, the spin-orbit interaction energy, $\hbar/\tau_{s.o.}$ can be obtained according to the procedure by Kobayashi and Katsumoto[15] and shown in Table I together with those shown in Fig. 4 by Yee and Knight.[5] The values of the interaction energies and the tendency as a function of particle size obtained by both methods, NMR and ESR, roughly coincided with each other in the size range from 4 to 10 nm. The large ρ value, 1.4–1.5, reflects the preparation method (vacuum evaporation) engaged in their experiments as

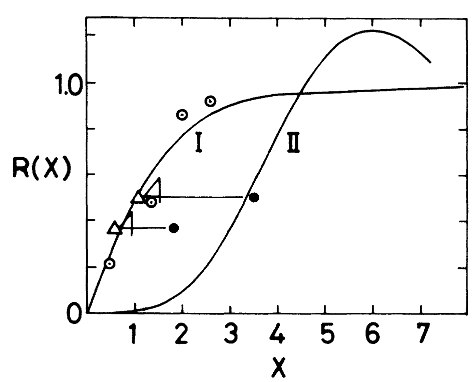

FIG. 6. Two-level correlation function $R(x)$ for orthogonal and symplectic cases as a function of $x = 2\pi\mu_B H/\delta$ after Halperin. I, orthogonal ensemble; II, symplectic ensemble. ● for Cu UFP's from Ref. 15. Δ after using $x = 2\mu_B H/\delta$ instead of $2\pi\mu_B H/\delta$. Arrows stand for this change in the x axis. Other circles ⊙ for Al UFP's by Kobayashi *et al.* (Ref. 19) using $x = 2\mu_B H/\delta$.

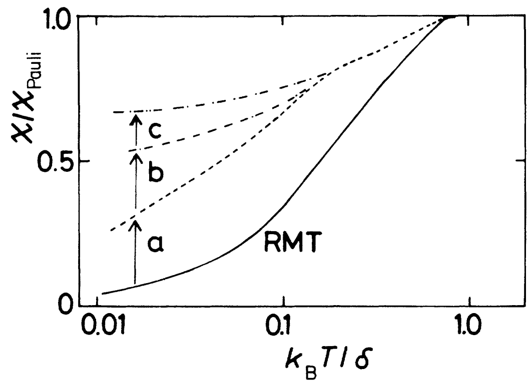

FIG. 7. Origin of the enhancement of spin susceptibility for the even-electron-number small metal particles. RMT for the orthogonal case. a, enhancement due to shape effect; b, enhancement due to the spin-orbit effect; c, enhancement due to the magnetic field effect. The example is taken for Cu 4 nm particles with the applied field of 5 T.

stated earlier (Sec. III, shape effect).

Shiba[16] numerically derived the temperature dependence of the susceptibility as a function of the spin-orbit coupling parameter. We tried to fit the present data in his theory by changing the coupling parameter, but it was unsuccessful. The reason may be due to his equal-level-spacing model.

V. ZEEMAN EFFECT

When under such a high magnetic field that the Zeeman energy exceeds the mean level spacing of conduction electrons, the up and down spin subbands are intermingled which results in the missed correlation between the levels near the Fermi level. Therefore, the level distribution approaches Poisson type, likewise does the case of the shape effect. This is another origin of the enhancement of the spin susceptibility. In the case of negligible spin-orbit coupling but with a large magnetic field, the two-level correlation function plays an essential role in the magnetic properties of small metallic particles. That is, the expected field dependence of the even-electron-number–particle susceptibility normalized to the bulk Pauli susceptibility is equal to the two-level correlation function $R(x)$ in the limit $T \rightarrow 0$. In Fig. 5 we have already shown the Knight-shift data under a weak magnetic field. Upon application of a high magnetic field, the observed Knight shift increased and approached the bulk value as described by Kobayashi and Katsumoto.[15] This enhancement as defined by $\Delta\chi_{\text{Zeeman}}$ was derived from their paper at 0.4 K and analyzed following the analytical form by Efetov[17] and recently graphically mapped by Halperin.[18] Figure 6 shows the two-level correlation function $R(x)$ as a function of energy separation $x = \pi\omega/\delta$ where ω is the separation of the successive two levels (which is equal to $2\mu_B H$ in the presence of external field). The function is thus equal to the probability for finding the two electronic levels in their respective intervals ω irrespective of the number of levels in between. The observed points (solid circles) do not fall both on the symplectic (the case of strong spin-orbit coupling and weak applied magnetic field) and orthogonal (the case of weak spin-orbit coupling and weak external magnetic field) cases. If we use $x = 2\mu_B H/\delta$ instead of $2\pi\mu_B H/\delta$ (namely, δ is replaced by $\pi\delta$), two points (triangles) fall just on the calculated line *I* as seen in Fig. 6. There are other Knight-shift data on aluminum small particles in high magnetic field.[19] They are also plotted against $x = 2\mu_B H/\delta$ by dotted circles at four different magnetic fields on the same figure. All these points seem to fall on the same line *I*, i.e., on the orthogonal case. However, the reason why δ changes to $\pi\delta$ is not yet clear.

In the literature we notice that the observed spin susceptibility always exceeds that obtained in random-matrix theory. We divide the observed susceptibility into four parts (the RMT component, the shape effect, the spin-orbit interaction, and the Zeeman effect), which are depicted in Fig. 7. In this figure, one can understand the contribution of each term to the *real* spin susceptibility measured.

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