Effect of surface state on the spin susceptibility of ultrafine metallic particles

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We have calculated the spin susceptibility of small metallic particles as a function of temperature, taking into account both effects of the finite energy-level spacing and the surface state allowing the electron tunneling among these electronic levels. The calculated magnetic susceptibility at low temperatures shows large enhancement due to the surface state in comparison with Pauli paramagnetism. This behavior is in good agreement with the peculiar temperature dependence of the susceptibilities of the reported divalent small metallic particles measured by the electron-spin-resonance method.

In small metallic particles, we must consider two effects which are negligible in metals composed of an infinite number of atoms. One is the volume effect which arises from the fact that an average energy difference between successive electronic levels, δ, is no longer small compared to other energies such as the thermal energy kT and the electronic Zeeman energy $\mu_B H$. The other is the surface effect which arises from surface states or defect states. We can imagine several origins of these states: the surface irregularities of the clean surface, surface chemical species, or the influence from supporting materials inevitable for real particle ensemble. The surface effect is greatly enhanced for ultrafine particles (UFP's) because of the finite surface-to-volume ratio, and yet its contribution to the quantum size effect has not been treated theoretically so far.

The volume effect appears in the thermodynamical properties and the spin relaxation processes at low temperatures.[1] We can most vividly see this effect in the spin susceptibility. The charge-neutrality condition for UFP's (Ref. 1) leads us to distinguish two cases according to the number of electrons in the particle; let us call an UFP comprising an even number of electrons and an odd number of electrons an "even particle" and "odd particle," respectively. At such low temperatures where $\delta > kT$, the spin susceptibility of an odd particle shows the Curie-like susceptibility as was confirmed by the nuclear magnetic resonance (NMR) shifts in Li,[2] while that of an even particle approaches zero because of spin pairing. This was confirmed by our recent static magnetic susceptibility measurements on Mg UFP's (Refs. 3 and 4) and by the NMR Knight shifts in Cu UFP's.[5,6] However, there are many controversial reports concerning an even particle. Mg, Zn, and Be UFP's measured by electron-spin resonance (ESR) showed an abrupt increment in the magnetic susceptibility at very low temperature.[7–11] Millet and Borel[7] measured the spin susceptibility of Mg UFP's by conduction-electron-spin resonance (CESR). They observed the increase of the susceptibility below a certain temperature depending on the particle size, and carefully checked that this temperature dependence could not be fitted to pure-Curie behavior. A similar result to this work was obtained by the present author[8] and by Pasche and Borel[9,10] for Mg UFP's. Sako observed the enhancement of the ESR absorption intensity at the low-temperature region in small Be particles and pointed out the possibility of surface species as the origin of this Curie-like component.[11] Very recently we have found that there was no such signal in the Mg UFP's when the measurement was conducted under an ultrahigh vacuum condition.[12] Therefore it is strongly suggested that these phenomena arise from extrinsic origins. In all cases, however, it was impossible to fit the temperature dependence of the ESR intensity of these species as pure-Curie behavior normally expected in the isolated impurity.

The purpose of the present paper is to explain the peculiar temperature dependence of the spin susceptibility mentioned above as a manifestation of the surface effect. In order to describe the volume effect, we adopt a model of equal energy-level spacings δ for the description of the bulk electronic states of UFP's. Because this model qualitatively reproduces the results of random-matrix theory,[13] it is an adequate approximation to the actual case.[14] It should be mentioned that the electronic states near the Fermi level are crucial to the determination of the thermodynamical properties at low temperatures. If there is an electronic level just above the Fermi level which has a different origin from that of the volume states and which is not affected by level repulsion, it greatly influences the spin susceptibility at such a temperature where $kT < \delta$. Such a state is called a "surface state" hereafter. We take into account only one surface state nearest to the Fermi level, because the introduction of many surface states does not change the essential result. Our picture for the level distribution of UFP's is summarized in Fig. 1.

We will start by calculating the partition function of a system represented by the level scheme in Fig. 1. The charge-neutrality condition compels us to use the canonical ensemble in the calculation of the partition function.[1] We will restrict ourselves to the case of an even particle in which conduction electrons can transfer to the surface level via tunneling. Following the method of Denton *et al.*,[14] the canonical partition function is given by

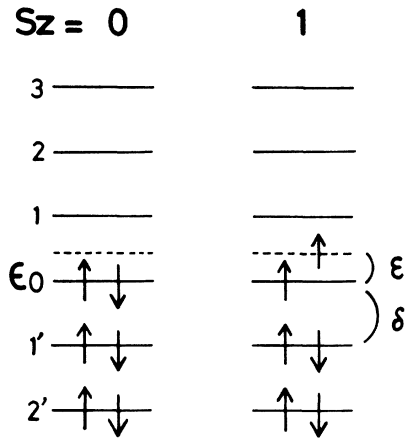

FIG. 1. Electron configuration for ground and first excited states of a metallic UFP. δ, level spacing; ε, gap between the Fermi level (ε_0) and the surface energy level.

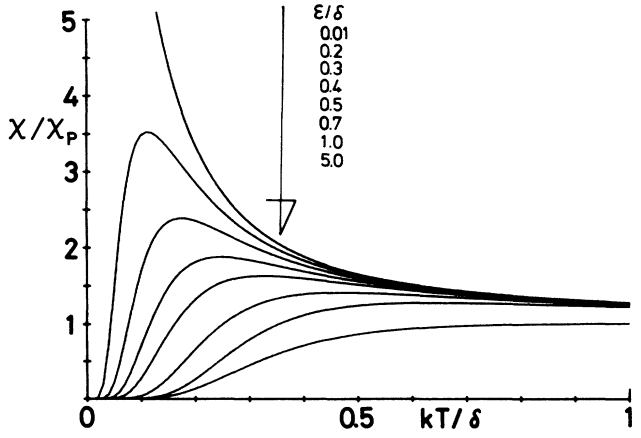

FIG. 2. Canonical spin susceptibilities as a function of temperature for several values of ε/δ.

$$Q(N,\beta,H)=\exp[-\beta E_0(N)]Z(H)\ , \tag{1}$$

with

$$Z(H)=\frac{1}{2\pi i}\oint\frac{dz}{z}\prod_{\substack{s=\pm1\\ n'=0}}^{N/2-1}\left[1+\frac{1}{z}e^{sh}e^{-\beta\delta n'}\right]\times\prod_{\substack{s=\pm1\\ n=1}}^{\infty}(1+ze^{sh}e^{-\beta\delta n})\times\prod_{s=\pm1}(1+ze^{sh}e^{-\beta\varepsilon})\ , \tag{2}$$

where $h=\frac{1}{2}\beta g\mu_B H$ and $E_0(N)=-\frac{1}{4}\delta N(N/2-1)$. In these formulas, $E_0(N)$ is the ground-state energy of N electrons in zero magnetic field and energies are measured from the topmost occupied level at $T=0$ K. The former two terms on the right-hand side of Eq. (2) represent the contribution from the volume energy levels and the last term comes from the surface state. Because of thermal degeneracy $\beta\delta(N/2-1)\gg1$, we can expand the limit in the products of the first term of Eq. (2), and after integrating around the unit circle we obtain

$$Z(H)=\frac{1}{G^2}\left[1+2\sum_{m=1}^{\infty}q^{2m^2}\cosh(2mh)+e^{-\beta\varepsilon}2\sum_{m=0}^{\infty}q^{2m(m+1)}\{\cosh[(2m+2)h]+\cosh(2mh)\}+e^{-2\beta\varepsilon}\left[1+2\sum_{m=1}^{\infty}q^{2m}\cosh(2mh)\right]\right]\ , \tag{3}$$

with $q=\exp(-\beta\varepsilon/2)$ and $G=\prod_{n=1}^{\infty}(1-q^{2n})$. The spin susceptibility normalized by the Pauli paramagnetic susceptibility $\chi_P=2\mu_B^2/\delta$ is given by

$$\chi/\chi_P=\frac{\beta\delta}{2}\left[\frac{\partial^2\ln Z}{\partial h^2}\right]\Bigg|_{h=0}\ . \tag{4}$$

The normalized susceptibilities are calculated for several ε/δ values and shown in Fig. 2. Note that the small ε/δ values lead to a great enhancement of the susceptibility at low temperatures. The curve with a large ε/δ value is similar to that of the even particle case of Denton *et al.*,[14] where no surface effect is incorporated.

In the following, we will compare several experimental data with our calculations. Figure 3 shows the fit using the experimental data of Millet and Borel for Mg UFP's (Ref. 7), where they have carefully checked that the increase of the susceptibility was not due to a paramagnetic impurity in the sample. We can get the best fit by using $\delta/k=25$ K and $\varepsilon/\delta=0.25$ for 1.2-nm particles, and by using $\delta/k=11$ K and $\varepsilon/\delta=0.27$ for 2.0-nm particles. We can also explain the Pauli-Curie transition proposed by Pasche and Borel[9] by our model as is easily seen in

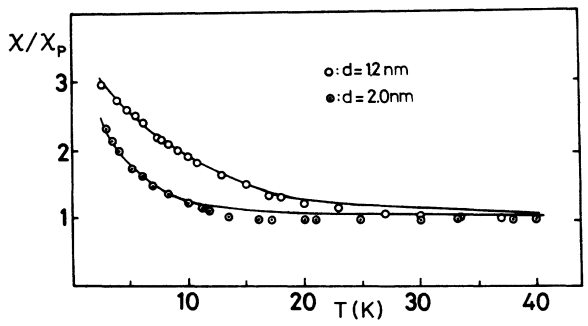

FIG. 3. Temperature dependence of spin susceptibility of Mg UFP. The data for different diameters, 1.2 and 2.0 nm, were taken from Ref. 7. The solid lines are calculated curves with $\delta/k=25$ K and $\varepsilon/\delta=0.25$ (for open circle) and with $\delta/k=11$ K and $\varepsilon/\delta=0.27$ (for dotted circle).

Fig. 2. Other divalent metal particles, Be UFP's, were also examined.[11] By the appropriate selection of δ and ϵ/δ, we could fit the observed increase of ESR intensity at low temperatures.

In conclusion, our model of the equal level spacing with the surface state explains the peculiar behavior of the spin susceptibilities at low temperature for various kinds of small divalent metal particles.

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