Paramagnetic Enhancement in the Magnetic Susceptibility of Ultrafine Magnesium Particles

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The static magnetic susceptibility of ultrafine Mg particles with various diameters of less than 10 nm has been measured in the temperature range from 2 to 240 K. We show for the first time that the temperature-independent paramagnetism is enhanced for smaller particles relative to bulk materials. This finding is compatible with the recent study on Os multinuclear cluster compounds that revealed a size-dependent paramagnetic enhancement. The coexistence of the quantum size effect and the enhancement of paramagnetism has also been observed at low temperatures.

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There have been many reports on metal clusters and small metal particles with respect to their potential as catalyst and to understand their nucleation process in crystal growth. These studies have also been triggered by the question as to the size at which a metallic element displays metallic character. There are two approaches to this question in the literature. One is the so-called atom-to-bulk approach. In this approach, physical properties of metal clusters are measured under a contact-free condition. However, it is difficult to observe magnetic properties of a small particle in the cluster beam, especially for clusters with large sizes.[1] The same difficulty is encountered with multinuclear-cluster complexes because of the difficulty of synthesizing the compounds composed of several tens of metal atoms and also because of the instability of such large clusters. The second, called the bulk-to-atom approach, is advantageous for the study of giant clusters with a size greater than 1 nm in which a sufficient amount of large clusters is available for measurement regardless of a weak point of a size distribution. Therefore, we have employed the gas-evaporation technique[2] known to yield ultrafine particles (UFP's) and we have used an organic liquid to reduce the particle-contact problem and undesirable air oxidation. In this report, we describe the magnetic susceptibility of Mg UFP as a function of particle size ranging from 1.4 to 40 nm in line with the bulk-to-atom approach.

In order to get a sharp particle-size distribution, small metal particles were carefully prepared resulting in the very small amount of particles that is required for high-sensitivity measurements of magnetic susceptibility. Careful attention was also paid to the sample handling to avoid air oxidation. Mg UFP's were prepared by the matrix-isolation method combined with the gas-evaporation techniques described elsewhere.[3] Gaseous hexane was introduced *in vacuo* to a Pyrex Dewar cooled by liquid nitrogen to make the cryogenic matrix. A Mg tip (of 99.99% purity) was then sublimed in an atmosphere of 99.9999%-pure He gas and the UFP's produced were trapped on the matrix of hexane. In order to avoid a particle-contact problem, gaseous hexane was introduced again giving a new surface of the cryogenic hexane matrix. These procedures were repeated several times until a sufficient amount of particles accumulated in the matrix for magnetic-susceptibility measurements. After warming of the Dewar at room temperature, nitrogen gas (of purity >99.9995%) was introduced to the Dewar. Through a SEPTA rubber cap, a colloidal solution containing Mg UFP's was then transferred to a storage bottle by a syringe with a metal Luer lock. A sample solution for magnetic-susceptibility measurements was transferred from a storage bottle to a quartz cell in a glove box. Hexane in the quartz cell was removed in a dry nitrogen gas stream and the degassed paraffin liquid was added to the sample in an atmosphere of nitrogen or helium in a glove box. Paraffin liquid was effective to reduce oxidation and also particle clustering.[4] Sample treatment and weighing were always conducted in a glove box. The size distribution of UFP's was determined directly from electron micrographs of the samples prepared by dropping the sample solution onto a Cu mesh covered with an evaporated carbon film. The full width at half maximum (FWHM) of smaller particles was about one-half of the average diameter (D), as determined by the size histogram prepared by an image analyzer.

Magnetic susceptibility was measured by a high-sensitivity Faraday-type magnetic balance unit with a superconducting magnet (an operating magnetic field was 1 T) and with a microprocessor-aided data-logging system. The separate magnet unit, composed of a main coil and a pair of reverse Helmholtz coils for the field gradient, was used to ensure absolute magnetic-susceptibility measurements. The overall accuracy of the magnetic measurements was one part in 10^{-3}. Details of the experiments have been described in the previous paper (spin state of only 18 μg of organic radicals was determined by our magnetic balance unit).[5] Samples (typically 5 mg Mg UFP's in 100 μl paraffin liquid) in a cylindrical Suprasil-grade quartz cell were suspended by a 0.2-mm-diameter quartz fiber from the arm of an electrobalance in the atmosphere of He-gas stream. The samples were rapidly frozen at about 100 K in a cryostat and evacuated for 2 h to remove oxygen completely, and the samples were then gradually cooled to 4.2 K under a helium atmosphere (10^3 Pa). A control experiment was performed with use of the same quartz cell carrying the same amount of paraffin liquid for each measurement. The magnetic susceptibilities of the samples were obtained after subtraction of the control values. No ferromagnetic impurities were detected in all samples measured at 4.2 K by the field dependence of magnetization up to 5 T.

After we measured magnetic susceptibilities, a Cu $K\alpha$ x-ray powder diffraction of 5.2-nm particles was taken under aerobic conditions several days later. The diffraction trace showed only four strong metal Mg peaks in addition to one very broad pattern of amorphous MgO in the 2θ range from 50° to 30°. We concluded that the MgO was distributed over the surface of Mg UFP and that about 20% of the total Mg atoms were oxidized, on the basis of the ratio of the peak areas of Mg to MgO. Since analysis was conducted under aerobic conditions after the susceptibility measurements, it may be concluded that most of the oxygen detected by x-ray diffraction was introduced after the measurements. A surface analysis by x-ray photoelectron spectroscopy of 3-nm Mg UFP prepared under the same condition but without paraffin liquid showed that one-half of the surface Mg atoms were oxidized. Therefore, oxidation of one-half of the surface (25% oxidation of total atoms for 3-nm particles and 16% oxidation for 5.2-nm particles) is consistent with the observed value (20% oxidation) by x-ray diffraction. However, this calculation is based on oxidized samples after magnetic measurements, so that actual samples hardly suffer from oxidation. If oxidation exists—or perhaps not—we have to take account of the local spins over MgO.[6] The content of paramagnetic impurities which follow the Curie law was determined by ESR. The magnetic susceptibility due to these spins at 2 K was roughly estimated as being less than 1×10^{-7} emu/g. This did not affect the static magnetic susceptibility for the whole region measured. Figure 1 shows the mass magnetic susceptibilities (in cgs electromagnetic units per gram) of several kinds of Mg UFP's with different diameters. The largest particles ($D=40$ nm) yielded $x_b=0.68\times10^{-6}$ emu/g, which is comparable to the bulk value reported (0.55×10^{-6} emu/g).[7] No increase in magnetic susceptibility was observed in the low-temperature region in this sample, reaffirming that contribution from paramagnetic impurities is less than 1×10^{-7} emu/g. A constant Pauli paramagnetism, characteristic of the bulk material, was observed only in this sample, in sharp contrast to the smaller size particles that showed anomalous temperature dependence, as seen in Fig. 1. With the small particles, we note a marked enhancement of magnetic susceptibility in the higher-temperature region and a sudden decrease in magnetic susceptibility in the lower-temperature region. A decrease in magnetic susceptibility at very low temperature is known as the quantum size effect,[8] as has been observed in the Knight shift of NMR by Yee and Knight[9] and by Kobayashi and co-workers.[10] We have also reported on the same effect on the basis of the static magnetic susceptibility.[11] It should also be noted that the magnetic susceptibility slightly increases in the intermediate-temperature region for all smaller particles. We will not discuss further the behavior in the intermediate- and low-temperature regions in this paper, and focus our attention instead on the magnetic property at high temperature where it is nearly constant above 200 K. We define this constant susceptibility ($\chi_{\rm UFP}$) as the mass magnetic susceptibility of Mg at 240 K, which is the maximum temperature available in the present experiments. No correction was made for the contribution of MgO.[12]

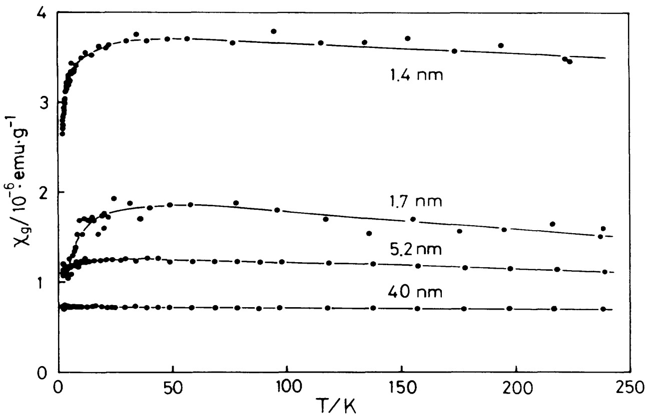

FIG. 1. Magnetic susceptibilities of Mg UFP as a function of temperature. Numbers in the units of nanometers stand for average diameters of UFP's determined by electron micrograph. The plots of 2.5-nm particles are omitted in this figure to avoid overlap with the points for particles of other diameters.

In Fig. 2, we plot the constant paramagnetic susceptibility normalized to the bulk value (χ_b) as a function of the inverse of the number of atoms in a particle. From this figure, we can deduce an empirical relationship between the number of atoms in a particle and $\chi_{\rm UFP}$, although our results are approximate and plots are rather scattered because of the difficulty controlling the distribution of particle diameters (size distribution is represented by a horizontal error bar in Fig. 2). The magnetic susceptibility is given by

$$\chi_{\rm UFP}=\chi_b+(200/n)\chi_b.$$

Since the contribution of diamagnetism due to Mg ions to the magnetic susceptibility is independent of particle size, the above relation can be rewritten in terms of con-

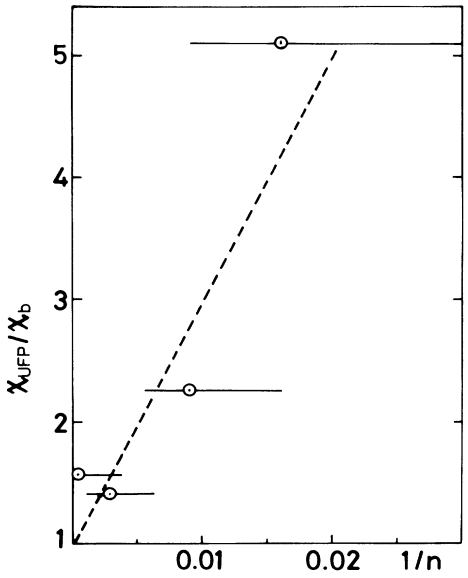

FIG. 2. Normalized magnetic susceptibilities of UFP as a function of the inverse of the number of atoms in a particle. Horizontal bars in the figure reflect the particle-size distribution.

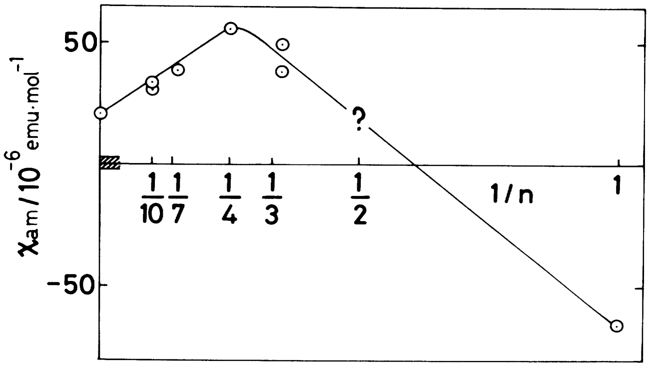

FIG. 3. Magnetic susceptibilities of osmium cluster complexes as a function of the inverse of cluster size. The excess molecular magnetic susceptibility, $\chi_{\rm ems}$, from Ref. 16 was converted to atom normalized molar susceptibility, i.e., $\chi_{\rm am} = \chi_{\rm ems}/n$, where n is the number of Os atoms per cluster. Datum at $n=2$ was not reported. For $n=1$, i.e., atomic susceptibility, the value of -66×10^{-6} emu/mol was from Ref. 17 and for $n=\infty$, i.e., bulk, the value $+20\times10^{-6}$ emu/mol was from Ref. 7 after correction for diamagnetic susceptibility due to the ion core (Ref. 17). The hatched region on the left-hand side of the abscissa corresponds to the number of Mg atoms per UFP from the present study.

tribution from conduction electrons only, i.e.,

$$\chi^e_{\rm UFP} = \chi^e_b + {\rm const}/n,$$

which can also be converted to the following equation:

$$\chi^e_{\rm UFP} = \chi^e_b + {\rm const} \times \delta,$$

where δ stands for an average level spacing at the Fermi level. Two types of contribution are probably responsible for this enhancement. One is the surface state contribution of an enhanced spin paramagnetism (as in the cases of V and Cr metals where the density of state drastically changes at the surface[13]). However, for a quantitative estimate of the surface contribution, we need precise knowledge of the density of states at the surface of "small" Mg particles, because this mechanism is not plausible for the "bulk" density of states for Mg.[14]

Second is a contribution from the orbital paramagnetism. In this case, the spin contribution is considered to be independent of particle size at higher temperatures because the quantum size effect diminishes at higher temperatures. The above relation leads to

$$\chi^{\rm orb}_{\rm UFP} = \chi^{\rm orb}_b + {\rm const}/n.$$

This emphasizes the importance of the contribution from the wave function to the size effect in UFP, which has been neglected in the existing theories. As $\chi^{\rm orb}_b$ is negative and the coefficient of $1/n$ is positive, $\chi^{\rm orb}_{\rm UFP}$ is negative for large particles but becomes large and positive for very small particles It is known that the orbital motion of a perfectly free electron produces Landau diamagnetism, but does not show paramagnetism within the framework of the single-band model. However, when there is an overlapping of the bands, as in the case of divalent metals, an applied magnetic field induces a nonzero interband matrix element. This term adds a paramagnetic contribution to the intraband Landau diamagnetism.[15] However, we are not aware of any theoretical prediction that suggests an enhanced orbital paramagnetic effect in small metal particles.

Experimentally, Johnson *et al.*[16] have recently reported that an enhanced paramagnetism was observed in an Os polynuclear complex. In order to compare their data with our results, the excess molecular susceptibility used in their paper was converted to the atom-normalized molar susceptibility, $\chi_{\rm am}$, i.e., molar susceptibility is divided by the number of atoms per cluster, giving a direct measure of the magnetic susceptibility per atom. The newly defined susceptibility is useful to examine the cluster complex that develops a metallic character successively from atom to bulk through a multinuclear cluster. Figure 3 shows the atom-normalized molar susceptibility of the Os cluster compound versus the inverse of cluster size. An interesting conclusion can be drawn from Fig. 3 that an incremental increase in paramagnetism appears in the multinuclear cluster. A maximum magnetic susceptibility appears with the tetranuclear complex and the magnetic susceptibility approaches its bulk value with increase in cluster size. The hatched section in Fig. 3 represents the corresponding size region in Mg from the present study. It should be noted that the increase in paramagnetism with decreasing particle size near the bulk region is the same for both systems. The enhanced paramagnetism observed in the Os cluster has been explained by Van Vleck's temperature-independent paramagnetism. In spite of differences in electronic structure between Os and Mg atoms, the resemblance of Van Vleck's temperature-independent paramagnetism in the cluster compounds to the orbital paramagnetism in the divalent metals is noteworthy. The former originates from a second-order perturbation of a localized electron orbital, and the latter from the same contribution due to itinerant electrons.[18]

A detailed analysis of the behavior of the spin susceptibility at the lower-temperature region will be reported in a forthcoming paper.

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[18] We are aware of these explanations as not completely compatible with the $1/n$ dependence of χ_{UFP}.