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CONDUCTION ELECTRON SPIN RESONANCE OF ULTRAFINE PARTICLES OF MAGNESIUM(1)

Keisaku KIMURA* and Sanshiro SAKO†
Instrument Center, Institute for Molecular Science,
Myodaiji, Okazaki 444
†Department of Physics, Faculty of Education, Mie University,
Tsu, Mie 514

Two resonance lines were observed in the conduction electron spin resonance of ultrafine particles of magnesium prepared in tetrahydrofuran. From the microwave frequency and the power dependencies of the resonance lines, it was found that the broader line was attributed to the quantum size effect which appears only in small particles, whereas the narrower line was due to a surface impurity.

We have recently(2) developed a new preparation method for ultrafine particles of metals in organic solvents. This technique was applied to several metals dispersed in ethanol in order to observe optical spectra of metal colloids. It was found that Pb, Sn, Ca, and Cu were unstable in ethanol. The time course of the optical absorption spectra of Cu sols in ethanol was analyzed and it was found that this instability is caused by a surface reaction of small particles in the sol.(3) It was also found that this reaction was suppressed in hexane. Therefore, the control of the surface conditions of ultrafine particles is very important to the stability of the sols. In metal ultrafine particles, moreover, it is well known that the physical properties change owing to the effect of the separation of the continuous energy levels of conduction electrons. This so-called quantum size effect(4) has been reported in Al(5) and in Mg(6,7) produced by the gas evaporation technique. Hence, it is necessary to compare the volume and the surface properties of metal fine particles prepared by our method with those produced by other techniques.

Here we report the conduction electron spin resonance(CESR) data of ultrafine particles of Mg produced by the matrix isolation method.(2) Magnesium has been taken as a sample for three reasons: 1)moderate chemical activity of metal surface, 2)its strong ESR signal, and 3)much previous work on its CESR. ESR measurements were made with a Varian E-112 spectrometer at the X-band(9.1 GHz) and at the Q-band(35 GHz) with a magnetic field modulation of 100 kHz. The temperature was controlled from 2 K to room temperature with an Oxford ESR 9 liquid helium flow cryostat for X-band measurements.

Figure 1 shows the CESR spectra of ultrafine particles of magnesium in tetrahydrofuran(THF). It can be clearly seen in this figure that there are two peaks with different linewidths. The linewidths(ΔH) of these lines are 6.0 G and 1.6 G (1G = 10^{-4}T), respectively. In the fine particles produced by the gas evaporation method, the resonance line(ΔH$\sim$14G at the X-band and room temperature$^{7)}$) was related to the quantum size effect, and so this line was thought to be intrinsic to ultrafine particles. It was confirmed that the observed broad line(ΔH = 6.0 G) had the same behaviours in the temperature and frequency dependences as those for the line of the quantum size effect. But the origin of the narrow center line(ΔH = 1.6 G, g = 2.0012) remains unclear. In order to distinguish whether the origin of these lines is the same or not, the power saturation method$^{8)}$ was applied. Figure 2 shows the CESR derivative lines at two different powers, namely 128 mW and 0.25 mW at 9 K. The narrow central line at 0.25 mW was saturated and a single broad line remained at the power of 128 mW. This shows that the relaxation time T_1 of the narrow line is much longer than that of the broad line. Therefore, it was proved that the origins of these lines were quite different.

The intensity of the broad line increased monotonously with increasing power up to 160 mW at 9 K. The conclusion that the broad line arises from the quantum size effect but not from a localized spin is consistent with this finding. No such effect is expected of the localized spin in organic radicals in which the signal is easily saturated even at a microwave power of 0.1 mW at very low temperatures like this experiment. This, in turn, suggests that the central narrow line may come from free radicals produced in the solvent, because of the narrow linewidth(ΔH = 1.6 G) and its long relaxation time. However, we observed no ESR signal in the solvent part of the sample tube(Mg fine particles were deposited on the bottom of the tube). In addition, we observed identical CESR spectra after keeping the sample for more than one month at room temperature, although the intensities of both the broad and the narrow lines lowered. It is known that the lifetime of free radicals at room temperature is very short for many organic

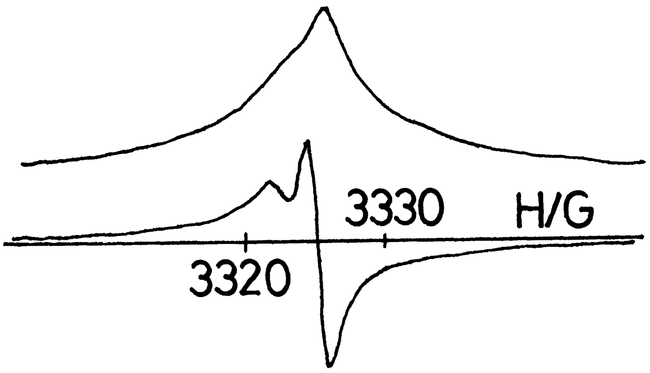

Fig. 1. X-Band CESR and its derivative spectra of ultrafine particles of magnesium in THF. Microwave power 1mW, temperature 35 K.

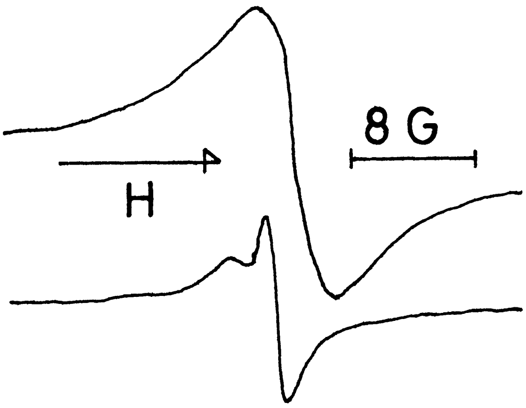

Fig. 2. X-Band CESR derivative spectra in THF at different microwave powers. Upper 128 mW, lower 0.25 mW, temperature 9 K.

compounds. These facts rule out the possibility of the narrow line being arisen from radicals in THF. As for the origins of the impurities other than radicals in THF, there are two possibilities; the one which is homogeneously dispersed in the volume of fine particles and the other which is localized at the surface of fine particles. The purity of the magnesium used(99.9999%) and the result of the magnetic susceptibility$^{9)}$ of the bulk magnesium rule out the former possibility. We thus tentatively assign the narrow line coming from the impurity trapped at the surface of the fine particles. The influence of solvents on this "surface impurity" is described in the following paragraph, because solvent affects only the surface of the particles. The lowering of the CESR spectral intensity in a sample that has been kept for a long time, may be related to the ageing of the metal colloids. The change in color of the sample from black to grayish black in the same period also indicates the ageing of the sample.

The difference in character of the two lines, the broad one originating from the quantum size effect and the narrow one from surface localized spins, should reflect the dependence of their linewidths on the microwave frequency. The reason is that the resonance position of the CESR, which is due to quantum size effect, depends strongly on the diameter of particles.$^{10-12)}$ The sample used is an ensemble of particles with different diameters(with an average diameter of 20 Å as determined by electron microscope). Hence the distribution of resonance lines with different g-values results in the broadening of the apparent linewidth at higher field(Q-band). On the other hand, the linewidth of the resonance line coming from the surface impurity probably depends weakly on the observation frequency. Figure 3 shows the CESR derivative spectra of ultrafine particles of Mg in THF at the X- and Q-bands. The linewidths of the narrow and the broad lines are about 1.5 G and 5.6 G for the X-band, and about 1.5 G and 13 G for the Q-band, respectively. The ratio of the linewidths of the broad component at the X- and Q-band is 2.3, which is comparable to the ratio of the two frequencies at the X- and Q-band, viz, 3.8. The value for the narrow line is 1, indicating independence of frequency. These findings also support the assignment of these lines as described above.

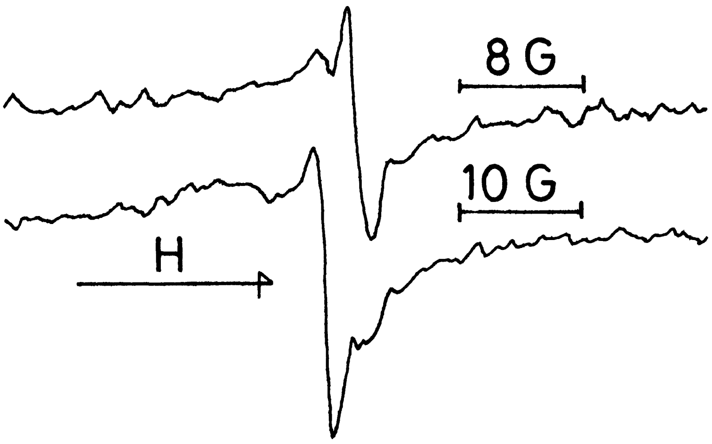

Fig. 3. CESR derivative spectra of particles in THF at different microwave frequencies. Upper X-band at 16 mW, lower Q-band at 10 mW. Both spectra were taken at room temperature.

The surface condition of the particles may be strongly affected by the surrounding materials, in contrast to the case of volume state. The difference of surface conditions in the two matrices, THF and hexane, is seen in the CESR lines shown in Fig. 4. It is noteworthy that the narrow central line(ΔH = 1 G) is missing in the spectrum of ultrafine particles in hexane. Since hexane is chemically more inactive than THF, the surface reaction may be suppressed in the Mg/hexane system. A similar behavior was found also in the optical spectrum of Cu/ethanol sols, the 213 nm peak of which, due to the product of a surface reaction, disappeared if hexane was used instead.[3)] Therefore, the 1.5 G line observed both at the two frequencies is due to the impurity at the surface. It was also observed that the central narrow line was enhanced even in the sample prepared in hexane when the ultrafine particles were produced under bad vacuum conditions. This finding suggests that traces of oxygen are involved with the surface reaction of the particles in the solvent.

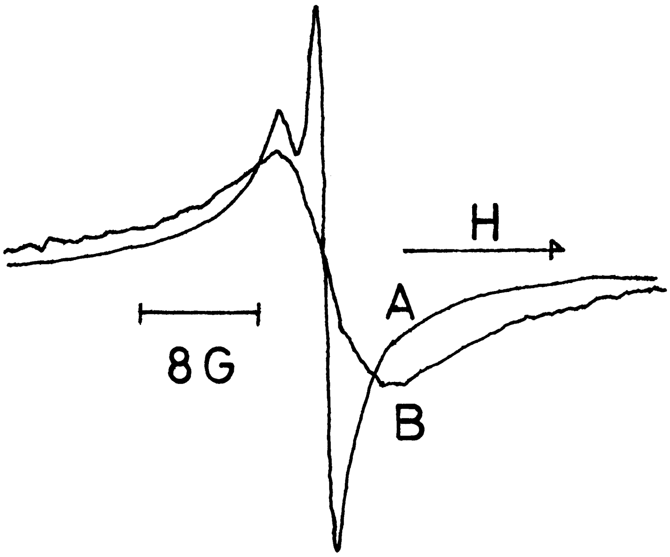

Fig. 4. X-Band CESR derivative spectra in THF and in hexane at 9 K and 8 mW. The linewidth of the broad line is 6 G for both samples and that of the narrow line is 1 G.

In this Letter, we have reported that the surface condition of ultrafine particles was affected by the surrounding solvent which is reflected in its CESR spectra. This, in turn, provides a possible means to controlling the surface state of particles by changing the surrounding materials. As for the qauntum size effect, we need more comprehensive studies including on the dependences of the particle size and metal species.

The detailed report will be published in the near future.

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