

Characterization of Ag Clusters Formed on AgBr Grains by Light and Reduction in Terms of Kubo Effect

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Abstract

Only one cluster of Ag atoms was formed on each fine AgBr grain by light regardless of exposure owing to the concentration principle, while as many as 200 clusters were formed on each grain by reduction. This result led to the proposal that a clusters of Ag atoms grew one by one under illumination, while it was formed by reduction as a result of the coagulation of dimmers of Ag atoms. These clusters gave rise to a conduction electron spin resonance (CESR) signal, whose intensity increased with increasing size. The intensity of the CESR signal of the clusters formed by light was significantly larger than that of the clusters formed by reduction when their size and number were the same. In accord with this result, the developability of the former was much higher than that of the latter. These results have indicated that the spacing of electronic energy levels in the former was much smaller than that in the latter. It is proposed that the electronic structure of a dimmer of Ag atoms remains in the electronic structure of a cluster formed by reduction in concert with its formation mechanism.

Introduction

The formation, property, and behavior of clusters of Ag atoms have ever been attractive subjects for photographic scientists, since they are irreplaceable for photographic processes, acting as latent image centers, reduction sensitization centers, fog centers, photolytic silver and developed silver[1-5]. In the previous paper[6], it was revealed by an electron microscope that as many as 200 clusters of Ag atoms were formed on each fine AgBr grain when the grains were treated by a reducing agent (dimethyl-amineborane). When the grains were exposed to light, only one cluster of Ag atoms was formed on each grain regardless of exposure owing to the concentration principle[1]. It is therefore considered that the formation of the clusters of Ag atoms by reduction takes place in the absence of the concentration principle, in which free electrons, interstitial silver ions, and single Ag atoms play important roles.

On the basis of the above-stated result, a proposal was made in the previous paper[6] for the mechanism of the formation of clusters of Ag atoms by the reduction of silver halides in contrtast with that of the formation of the clusters of Ag atoms by the photolysis of silver halides. Namely, it was proposed that dimers of Ag atoms, which were directly formed on a silver halide grain by reduction with contribution of neither a free electron nor a single silver atom, were stabilized at surface kink sites to form reduction sensitization centers, and that they coagulated with each other to form large clusters of Ag atoms acting as fog centers when surface kink sites were saturated with the dimmers.

Since it was anticipated that the difference in the formation mechanism would lead to the difference in the property and behavior between clusters of Ag atoms formed on AgBr grains by light and reduction, the present study was undertaken to examine their electronic structure by measuring their conduction electron spin resonance (CESR) and their catalytic activity by measuring their developability. Although Stevens, Symons, and Eachus measured and analyzed the CESR signals of clusters of Ag atoms formed by light on AgBr and AgCl grains, they did not measure the concentration and size of the clusters. The present authors measured the concentration and average size of the clusters of Ag atoms by means of an electron microscope, and analyzed the CESR signal and developability of the clusters with known concentration and average size under the light of the Kubo effect for metal clusters[8].

Conduction Electron Spin Resonance of Clusters of Ag Atoms

A study was made on the clusters of Ag atoms formed on cubic AgBr grains with average edge length of 0.18 μm. The number, average size, and characteristics of CESR signal of the clusters are shown in Table 1. Samples A, A', and B were prepared by exposing the emulsions containing the AgBr grains to light in a photochemical reaction vessel, and Samples C and D were prepared by digesting the same emulsions at 60℃ for 60 min in the presence of a reduction sensitizer, dimethylamineborane (DMAB). The clusters

were directly observed in the gelatinate shell of the grains by means of an electron microscope Model JEM-2000FX-Ⅱ (JEOL, Tokyo, Japan). It is noted that only one cluster per grain was formed in Samples A, A', and B owing to the concentration principle, while many clusters were formed on a single grain in Samples C and D.

Table 1. CESR of clusters of Ag atoms formed on cubic AgBr grains with edge length of 0.2 μ m..

Sample	Number	Size	g-Value	Intensity
A(Light)	1/grain	4.1 μ m	2.004	5.3(rel.)
A'(light)	1	5.3	2.005	10.5
B(light)	1	6.0	2.005	34.6
C(Red.)	90	2.7	No signal	No signal
D(Red.)	200	5.5	2.003	1.6

Silver bromide grains with clusters of Ag atoms in each sample were separated, dried, and subjected to ESR measurement at - 150℃ by means of an electron-spin resonance spectrometer Model JES-ME-3X made by Japan Electron Optics Laboratory Co., Ltd., with an X band and a magnetic field of 100 KHz.

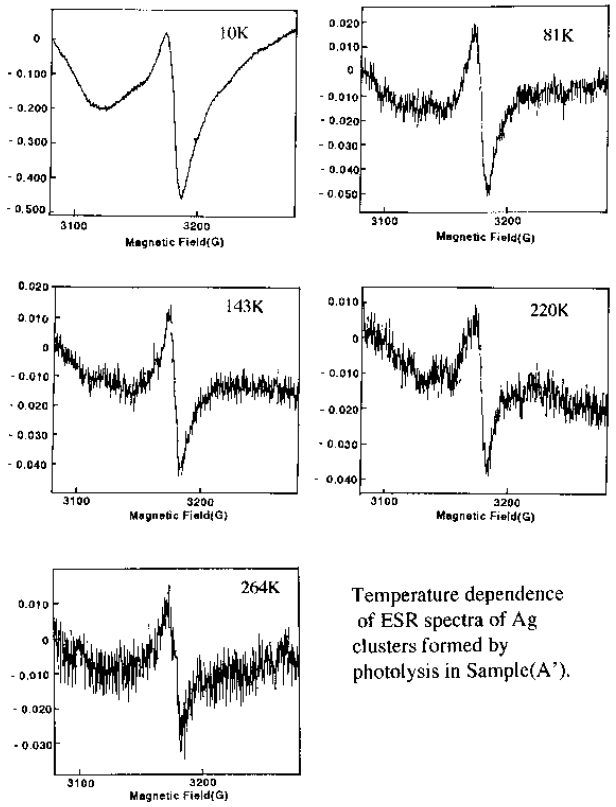

Figure 1.

A structureless signal was observed at g-value of 2.003-2.005 for the AgBr grains with clusters of Ag atoms. As shown in Table 1, the signal intensity increased with increasing the average size of the clusters. It was also noted from the result in Table 1 that the magnetic susceptibility of the clusters of Ag atoms formed on AgBr grains by light was much larger than that of the clusters by reduction under the light of the fact that the concentration of Ag clusters in the former samples was much smaller than that in the latter samples.

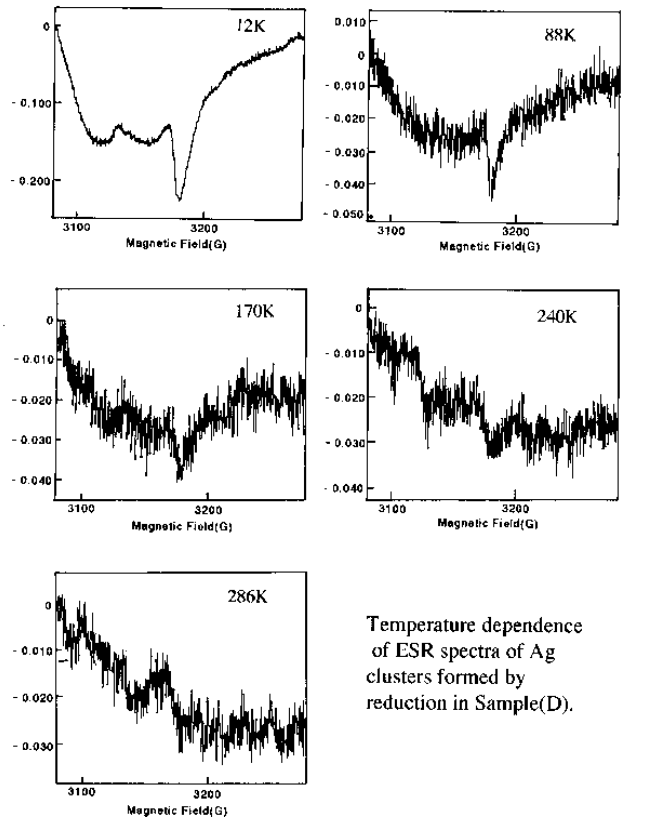

Figure 2.

It was recognized that the average size of the clusters was nearly the same between Samples A' and D, and that the concentration of the clusters in Sample D was larger by 200 times than that in Sample A'. Then, the temperature dependences of the ESR signals of Samples A' and D were measured in the range from 10 K through 300K, and are shown in Figures 1-3. It was noted that the signal intensity of Sample A' was larger by several times than that of Sample D over wide range of temperature. By taking into account of the difference in the concentration of the clusters between them, it is considered that the magnetic susceptibility of the clusters of Ag atoms in Sample A' was larger by three order of magnitude than that in Sample D. It was confirmed that the signal intensities of both Samples A' and D increased with decreasing temperature.

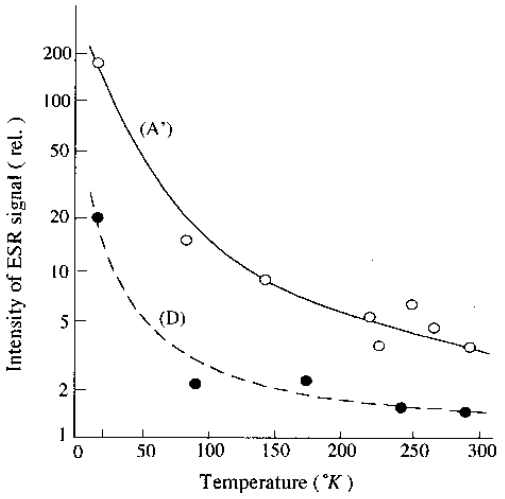

Figure 3. Temperature dependence of ESR signal intensities of clusters of Ag atoms in Samples A' and D.

All the above-stated results indicate that the observed ESR signal is ascribed to the conduction electron spin resonance of clusters of Ag atoms on the basis of the Kubo effect[8], and that the spacing between electronic energy levels in the clusters of Ag atoms formed by light was much smaller than that in the clusters by reduction. This result could support the proposed mechanism that a clusters of Ag atoms grows one by one on a silver halide grain under illumination, while it is formed by reduction as a result of the coagulation of dimmers of Ag atoms.

Developability of Clusters of Ag Atoms

It was then expected that the difference in the electronic structure between clusters of Ag atoms formed by light and reduction resulted in the difference in catalytic activity between them. The rate of development of coatings of Samples A' and D were given by measuring the changes of their optical densities at 1090 nm as a function of time when they were immersed in various developers. The developers used and results are shown in Table 2. The driving force of a developer is expressed by the difference between its redox potential and silver potential (Δ) in mV. The rate of development (r), as given by the maximum slope (rel.) in a curve of the density as a function of time, was measured with variation of temperature for the determination of its activation energy by the Arrhenius plot.

Table 2. Rate of development (r) initiated by clusters of Ag atoms in Samples A' and D with various developers..

Dev.	Δ	r(A')	r(D)	Δ(A')	Δ(D)
D8:2+1	-395	1020	1400	7.3	7.6
MAA-1	-314	166	282	8.9	9.4
DK-50	-305	145	204	10.9	11.1
D19	-300	295	475	11.1	12.4
D76	-245	28	58	11.0	12.4

As seen in this table, there was a general trend that the rate of development increased and its activation energy decreased with increasing the driving force of developers. Although the rate of development of Sample D was a little larger than that of Sample A', it is considered that the developability of a cluster of Ag atoms in Sample A' was much larger than that of an cluster in Sample D, since the number of the clusters per grain in Sample D was larger by 200 times than that in Sample A' and the activation energy of the rate of development of Sample D was larger than that of Sample A'. The difference in the developability between clusters of Ag atoms in Samples A' and D resulted in the difference in the shape of developed silver between them, as was observed by an electron microscope.

The distinct difference in the magnetic susceptibility and developability between clusters of Ag atoms in Samples A' and D has clearly indicated that the spacing between electronic energy levels in clusters of Ag atoms formed on silver halide grains by reduction is much larger than that in the clusters formed by light, and has supported the proposed mechanism in the previous paper[6] that a cluster of Ag atoms grows one by one under illumination, while it is formed by reduction as a result of the coagulation of dimmers of Ag atoms. It is proposed that the electronic structure of a dimmer of Ag atoms remains in the electronic structure of a cluster of Ag atoms formed on a silver halide grain by reduction.

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Biography

Tadaaki Tani received his B.S. degree in Synthetic Chemistry from the University of Tokyo in 1963 and a Ph.D. in Industrial Chemistry from the same university in 1968. Since 1968 he has worked in Ashigara Research Laboratories, Fuji Photo Film Co., Ltd.. His work has primarily focused on fundamental research on photographic sensitivity including the mechanisms of latent image formation, its chemical and spectral sensitization. He is a member of the IS&T and the SPSTJ.