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Optical absorption of 4d fcc transition-metal particles: Study of the contribution of the conduction-electron density to the correlation interaction

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Optical absorption of 4*d* fcc transition-metal particles: Study of the contribution of the conduction-electron density to the correlation interaction

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Optical plasma-resonance absorption of Rh island films consisting of Rh particles larger than about 15 Å in diameter has been measured in the photon energy region from 0.5 to 6.5 eV. Comparison of the broadening and the location of this absorption with those of Pd island films shows that the correlation interaction between conduction electrons is stronger in Pd than in Rh, and that the conduction-electron density n is lower in Pd than in Rh. The difference in the correlation interaction shows that there are factors contributing to the correlation interaction besides the d character of conduction electrons. Assuming that n contributes to the correlation interaction as in a well-known electron-gas model, in which the correlation interaction is strong at low electron density, we can qualitatively attribute the difference in the correlation interaction to the fact that the correlation interaction due to the contribution of n is stronger in Pd than in Rh because Pd has lower n than Rh. This suggests that n also contributes to the correlation interaction.

I. INTRODUCTION

In fundamental studies of electronic properties of transition metals, interactions between electrons are of considerable importance.[1] Although these interactions have been extensively investigated,[2] a detailed understanding is still lacking. In particular, very little is known about interactions in the dynamical state.

Optical plasma-resonance absorption (OPRA) of metal island films, consisting of small metal particles, results from the plasma oscillation of conduction electrons, and reflects the motion of these electrons.[3] Information about OPRA is thus useful in understanding interactions between conduction electrons in the dynamical state due to the incidence of light. For example, previous studies of the OPRA of transition-metal [Ni and Pd (Ref. 4) and fcc Co (Ref. 5)] island films have shown that the broadening of OPRA reflects the correlation interaction between conduction electrons, and that the d character of the conduction electrons contributes to the correlation interaction.

In an electron-gas model,[6] accepted to be very useful for the study of the correlation interaction between electrons, the electron density is an important factor contributing to the correlation interaction; e.g., this interaction is shown to be strong at low electron density.

From this model, also in transition metals, the study of the relation between the correlation interaction and the conduction-electron density is considered to be very important for the understanding of the correlation interaction. At present, very little is known about this relation.

The location of the OPRA is concerned with the conduction-electron density.[3,5,7] Thus, for transition metals, we can study the above relation by analyzing the broadening and the location of the OPRA.

In this study, the differences in the correlation interaction and the conduction-electron density between Rh and Pd are investigated from the broadening and the location of the OPRA of Rh and Pd island films.[4] On the basis of the electron-gas model, the difference in the correlation interaction is related to the difference in the conduction-electron density, and it is suggested that, in addition to the d character, the conduction-electron density contributes to the correlation interaction.

II. EXPERIMENTAL

In conditions similar to those described in a previous paper,[4] the samples were prepared by vacuum evaporation. Rh (purity 99.9%) was deposited both on a SiO_2-coated fused-quartz substrate and on SiO_2-coated carbon meshes, which were heated to about 500 °C during deposition. The island films were then annealed at the same temperature for 1 h. After annealing, the films were coated with SiO_2 to prevent adsorption or chemical reactions on exposure to air. The weight thickness and the deposition rate were monitored with a quartz-crystal oscillator. In the spectral region of interest here, the transmittance of the evaporated SiO_2 film without Rh particles was almost constant.

Optical and electron-microscopic investigations were carried out after exposure of the samples to air. In the photon energy region from 0.5 to 6.5 eV, transmittance spectra for normal incidence and their derivatives were measured within experimental accuracies of $\pm 0.1\%$ and $\pm(0.001-0.01)$ eV at room temperature, and -193 °C with a double-beam spectrophotometer. The derivative was measured at a wavelength difference of about 4 nm. The particle size and the electron-diffraction pattern were investigated with an electron microscope operating at 200 kV. In the spectra in this paper, the scale of the derivative is the same, and the inset shows the particle-size distribution in vol %.

III. RESULTS AND DISCUSSION

For the Rh island films, only the fcc structure could always be identified in electron-diffraction patterns. The spectra of the Pd island films, prepared by the same method as that in this study, have almost agreed with the simulated

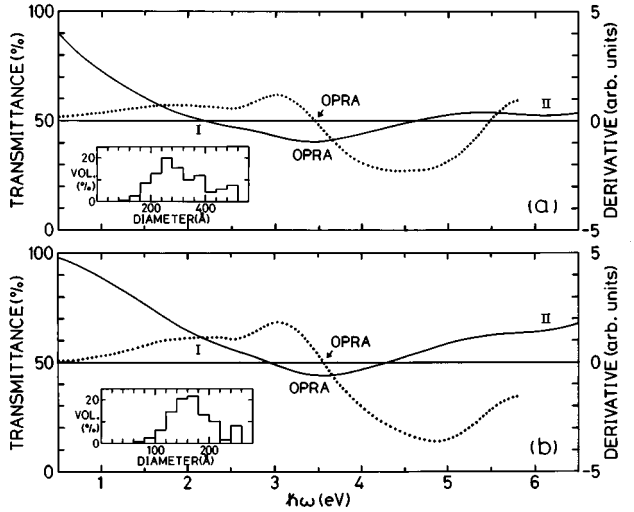

FIG. 1. Transmittance spectra (solid curves) and their derivatives (dotted curves) for Rh island films with particle diameters of about (a) 280 and (b) 160 Å. The weight thickness and the deposition rate are (a) 55.4 Å and 0.11 Å/s and (b) 41.6 Å and 0.11 Å/s. The half-width of the OPRA is (a) 3.48 and (b) 2.62 eV.

spectra based on bulk optical constants.[4] These results show that chemical reactions such as oxidation hardly occur for Rh and Pd particles. Thus, in this study, the formation of a compound layer (such as oxide layer) on the particle surface is not taken into account.

A. Spectrum of Rh island films

Two examples of the transmittance spectrum of Rh island films at room temperature are shown in Fig. 1 (about 280 and 160 Å in diameter). Referring to experimental[8] and theoretical studies[9,10] of the optical absorption of bulk Rh, we see that dip I is the interband-transition absorption due to transitions from middle *d*-like states into uppermost *d* states and empty *s*,*p*-like states just above the Fermi level, and that dip II is the interband-transition absorption generated by transitions between lowest-lying *d* states and empty *s*,*p*-like states just above the Fermi level.

The broad absorption (labeled OPRA) appearing at about 3.5 eV is the OPRA. As shown in Fig. 1 and the following figures, the broad absorption is shifted to the higher-energy side with decreasing weight thickness. Such a shift is characteristic of the OPRA.[3,11,12]

The OPRA and dips were well defined in the transmittance spectrum of the island films with particle sizes larger than about 160 Å in diameter [Fig. 1(b)]. Figures 2(a), 2(b), and 2(c) show the transmittance spectrum of the Rh island film with particle diameters of about 120, 80, and 55 Å at room temperature, respectively. The OPRA and dip II are well defined as in Fig. 1, but dip I is ill defined compared to that in Fig. 1, and becomes weak with decreasing particle size.

The above difference in dip I between Figs. 1 and 2 is not due to the change of the particles into compounds because, as mentioned above, chemical reactions hardly occur. The weakening of the dip with decreasing particle size has also been reported for noble-metal island films,[13] in which the weakening occurs below about 100 Å in diameter.

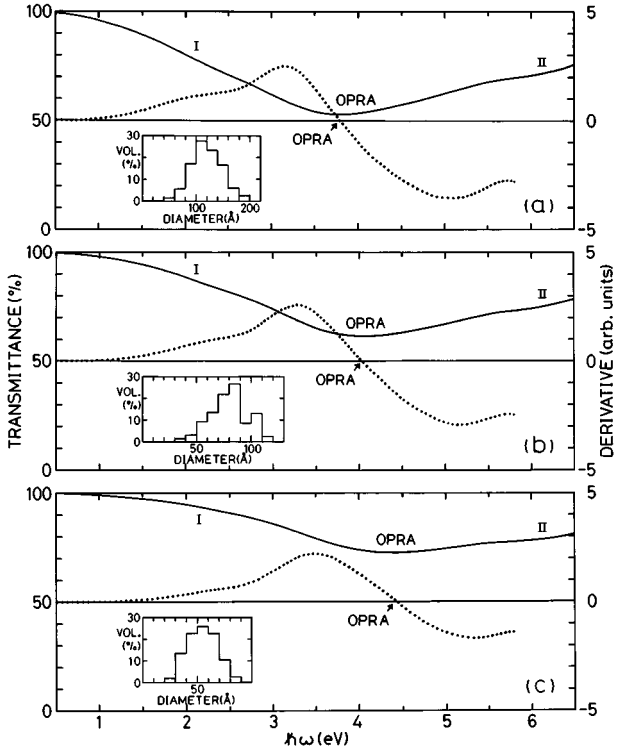

FIG. 2. Transmittance spectra (solid curves) and their derivatives (dotted curves) for Rh island films with particle diameters of about (a) 120, (b) 80, and (c) 55 Å. The weight thickness and the deposition rate are (a) 27.7 Å and 0.09 Å/s, (b) 20.8 Å and 0.08 Å/s, and (c) 13.9 Å and 0.07 Å/s. The half-width of the OPRA is (a) 2.38, (b) 2.36, and (c) 2.40 eV.

The weakening in the noble-metal island films has been explained by the decrease in the density of states (DOS) due to lattice contractions. That is, the lattice has been reported to contract with decreasing particle size. This contraction causes the *d*-band broadening, which is accompanied by a decrease in the DOS of *d* bands. Because of such a decrease in the DOS with decreasing particle size, interband transitions become weak, i.e., the dips become weak.

Presumably, the weakening of dip *I* is also caused by a decrease in the DOS due to the lattice contraction. In the derivative, the sloped part for the OPRA appears clearly, and thus the OPRA could be labeled. However, the sloped part for dip I is not clear, and the sloped part for dip II could not be measured. Thus the dips were not labeled in the derivative.

B. Broadening of the OPRA of Rh island films

In transition metals, since *s* and *d* bands are hybridized (*s*-*d* hybridization) and the Fermi level intersects the *d* bands,[1,14] the *d* character of conduction electrons is strong. In the dynamical state due to the incidence of light, strong correlation interaction acts between the conduction electrons because of such *d* character.[4] The broadening of the OPRA of Ni and Pd (Ref. 4) and fcc Co (Ref. 5) island films has been shown to arise from the damping of the plasma oscillation due to this strong correlation interaction. Evidence of such broadening is the fact that the half-width of the OPRA

is almost constant irrespective of the particle-size distribution and the variety of particle shapes, and that the OPRA is temperature independent.[4]

Also for the Rh island films, to understand the broadening, the OPRA and its half-width were investigated in relation to the particle-size distribution, the variety of particle shapes, and the temperature. As previously,[4,5] the half-width was obtained from the OPRA, not separated from the dips, because the separation method is not yet established, and this width was defined by $2\Gamma_{1/2}$, where $\Gamma_{1/2}$ is half of the half-width at the low-energy flank.

In island films with increasing weight thickness d_W, particles grow through the agglomeration of smaller particles. In this growth, the particle size increases, the particle shape, which is spherical at an initial stage of the growth, becomes flat and irregular, and the spacing between the particles becomes large.[11,12] These changes in the size and shape are attended with the particle-size distribution and the variety of particle shapes, respectively. As is well known, the OPRA shifts with d_W. This shift is caused by the above changes in the size, shape, and spacing.[11,12] Thus the particle-size distribution and the variety of particle shapes are sure when the OPRA shifts with d_W.

In Figs. 1 and 2, the OPRA shifts with d_W, and the particle-size distribution is found. Thus the variety of particle shapes is sure for the island films in these figures, though the observation of three-dimensional particle shapes was difficult in this study.

If the overlap of the OPRA and the dips is large and significantly affects the half-width, the half-width must change when the OPRA shifts with d_W. This is the case for Fig. 1, where the difference in the half-width between Figs. 1(a) and 1(b) is large. Because of the large overlap, the half-width in Fig. 1 must be larger than the actual half-width. The half-width in Fig. 1 is thus unreliable data, and does not give reliable information about the relation between the half-width and the particle-size distribution and the variety of particle shapes. Thus the half-width in Fig. 1 is not adopted here.

Below about 160 Å in diameter [Fig. 1(b)], the half-width was almost constant down to about 55 Å in diameter [Fig. 2(c)], irrespective of the particle-size distribution and the variety of particle shapes. For example, in the particle-size region in Fig. 2 (about 120–55 Å in diameter), the half-width is almost constant (2.36–2.40 eV).

In the above particle-size region, on the basis of the almost constant half-width, it is presumed that the overlap of the OPRA and the dips is small at the low-energy flank, and thus has little effect on $\Gamma_{1/2}$. Thus the almost constant half-width is considered to be reliable data.

The OPRA of the Rh island films did not change as the temperature was decreased from room temperature to about −193 °C; i.e., this OPRA was temperature independent. The almost constant half-width and the temperature independence of the OPRA of the Rh island films agree with the above evidence, and show that in the Rh island films also, the broadening of the OPRA arises from the damping of the plasma oscillation due to the correlation interaction.

For the OPRA of metal island films, it has been reported theoretically that in addition to the damping of the plasma oscillation, the disorder in the particle distribution induces

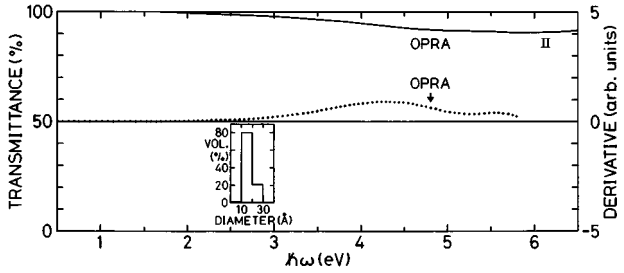

FIG. 3. Transmittance spectrum (solid curve) and its derivative (dotted curve) for a Rh island film with a particle diameter of about 15 Å. The weight thickness is 3.5 Å. The deposition rate was 0.03 Å/s.

the broadening of the OPRA.[15] As shown for Ni and Pd island films,[4] the almost constant half-width (i.e., broadening) agrees well with the half-width (the broadening) of the simulated OPRA based on bulk optical constants. Since the broadening of the simulated OPRA is due to the damping, the agreement shows that the almost constant half-width is caused mainly by the damping, which is the same as that for the simulated OPRA.[4] Thus the disorder seems to have little effect on the almost constant half-width in this study.

For Ag particles embedded in the SiO_2 matrix, the broadening of the OPRA due to the interaction between the particles and the matrix has been theoretically reported.[16] Under this interaction, the motion of conduction electrons in the particles is different from that in bulk. The damping of the plasma oscillation reflects the motion of electrons. As mentioned above, the damping for the almost constant half-width (i.e., for the particles) is the same as that for the simulated OPRA based on bulk optical constants, which shows the motion of conduction electrons in the particles to be almost the same as that in bulk.[4] This indicates that at least when the half-width is almost constant, the above interaction hardly occurs for the SiO_2-coated particles in this study.

Below about 55 Å in diameter [Fig. 2(c)], the OPRA was broadened with decreasing particle size. As an example, the spectrum at about 15 Å in diameter at room temperature is shown in Fig. 3. Dip I is not found. The measurement of the half-width was difficult because the OPRA is very broad.

As suggested for Ni island films,[4] in which the broadening of the OPRA with decreasing particle size is found below about 80 Å in diameter, the above broadening below about 55 Å in diameter may be due to the fact that the *d* character is strengthened by the *s*-*d* hybridization enhancement due to the lattice contraction, and this strengthening enhances the correlation interaction (i.e., enhances the damping).

In Ni and Pd island films,[4] comparison of the experimental OPRA with the simulated OPRA based on bulk optical constants was useful for the study of the broadening of the OPRA. Data for optical constants of bulk Rh are very scarce. Thus, in this study, such a comparison was difficult.

C. Correlation interaction in Rh and Pd

Previous studies[4,5,17] have shown that the *d* character, which depends on the *s*-*d* hybridization and on the position of the Fermi level relative to *d* bands, is the important factor

for the correlation interaction: when the *d* character is strong, the correlation interaction is also strong and the damping (i.e., the half-width) is large.

For example, the *d* character is stronger in fcc Co than in Ni because the *s*-*d* hybridization is larger in fcc Co than in Ni.[18] In this case, the half-width for fcc Co island films is larger than that for Ni island films because the correlation interaction in fcc Co is stronger than that in Ni.[5] Furthermore, in cases where the *d* character is very strong, such as in Fe and Cr, in which the Fermi level intersects the middle part of *d* bands, the strong correlation interaction causes the localization of conduction electrons, and the OPRA does not occur in island films.[17]

The Fermi level is closer to *d* bands in Rh than in Pd, and the *s*-*d* hybridization is larger in Rh than in Pd.[9,10,19,20] This shows that the *d* character in Rh is stronger than that in Pd. This is similar to the above case of fcc Co and Ni. However, in contrast to the above-mentioned difference in the half-width between the fcc Co and Ni island films, the almost constant half-width (about 2.36–2.40 eV) for the Rh island films is smaller than that (about 2.50–2.60 eV) for the Pd island films in the previous study.[4] That is, although the *d* character is stronger in Rh than in Pd, the correlation interaction is stronger in Pd than in Rh.

The above discrepancy between the *d* character and the correlation interaction shows that there are factors contributing to the correlation interaction besides the *d* character, and that the correlation interaction is stronger in Pd than in Rh because of the contribution of such factors. Obviously, the correlation interaction due to the contribution of such factors must be stronger in Pd than in Rh. As a possible factor, the conduction-electron density is considered in the following.

D. Contribution of the conduction-electron density to the correlation interaction

In this section, at first (Sec. III D 1) the difference in the conduction-electron density between Rh and Pd is discussed, and then (Sec. III D 2), on the basis of this difference, the contribution of the conduction-electron density to the correlation interaction is qualitatively discussed.

1. Difference in the conduction-electron density between Rh and Pd

It has been known for island films that particles, which are flat and irregular, can be considered to be rotational ellipsoids.[11,12] In this case, the conduction-electron density n is related to the location $\hbar\omega_R$ of the peak of the OPRA as follows:[5,7]

$$\hbar\omega_R=\hbar\omega_P F^{1/2}/[F(1-\varepsilon_0)+\varepsilon_0]^{1/2},$$

$$\omega_P^2=4\pi ne^2/m,$$

where ω_P is the plasma frequency, F is the effective depolarization factor, ε_0 is the interparticle dielectric constant, e is the electron charge, and m is the optical mass of conduction electrons (i.e., the effective mass under the incidence of light).

ε_0 in this study is the dielectric constant of the evaporated SiO_2, and is constant. As previously,[5] the effective mass m_s of *s* electrons, calculated from the *d*-state radius and the atomic sphere radius,[21] is applied to m because data for m of Rh and Pd are very scarce. Since the m_s of Rh is almost comparable to that of Pd, the m of Rh and Pd is regarded to be almost comparable. Thus $\hbar\omega_R$ depends on F and n.

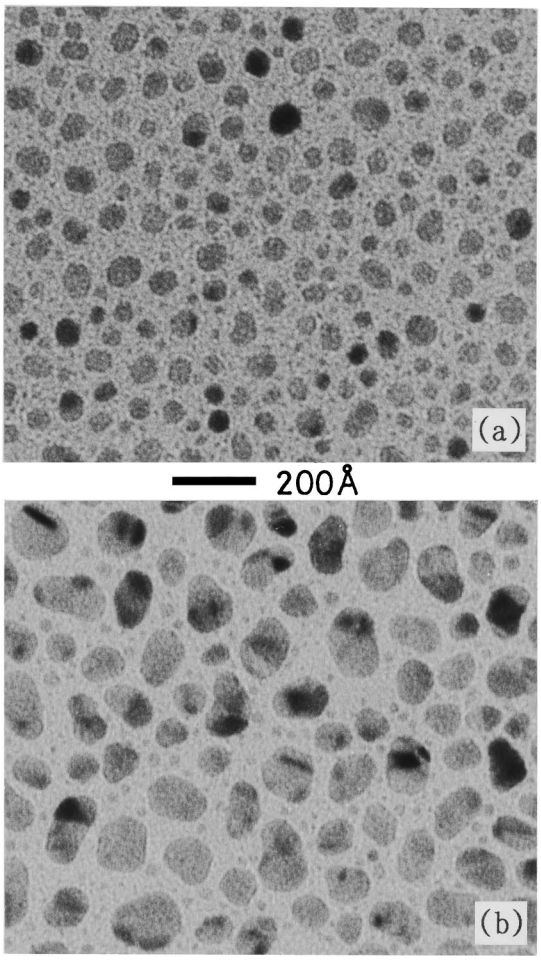

FIG. 4. Electron micrographs for (a) a Pd island film with a particle diameter of about 60 Å (Ref. 4), where the weight thickness and the deposition rate are 14.0 Å and 0.07 Å/s, and (b) the Rh island film of Fig. 2(a).

Factors for F are the weight thickness d_W, the spacing between particles, and the shape of particles (i.e., the shape of rotational ellipsoids).[11,12] When d_W and the spacing are large and when particles (rotational ellipsoids) are flat, F is small.[11,12]

It has been reported that particles (rotational ellipsoids) become flatter with increasing d_W.[11,12] As mentioned in Sec. III B, the increase in d_W causes the particle size and the spacing to be large. Thus particles (rotational ellipsoids) are flat when the particle size and the spacing are large.

Figures 4(a) and 4(b) show electron micrographs of a Pd island film with a particle diameter of about 60 Å in the previous study[4] and the Rh island film in Fig. 2(a), respectively. d_W and the spacing in Fig. 4(b) are appreciably larger in comparison with those in Fig. 4(a). Since the particles and the spacing in Fig. 4(b) are much larger than those in Fig. 4(a), the particles (the rotational ellipsoids) in Fig. 4(b) are presumably flat compared to those in Fig. 4(a).[11,12] Thus the Rh island film in Fig. 4(b) has a smaller F than the Pd island film in Fig. 4(a).

From the above m and F, if n of Pd is comparable to or higher than that of Rh, $\hbar\omega_R$ for the Pd island film in Fig. 4(a) must be high compared to that for the Rh island film in Fig. 2(a). However, $\hbar\omega_R$ (about 2.75 eV) (Ref. 4) for the Pd island film in Fig. 4(a) is not higher than that (about 2.80 eV) in Fig. 2(a). This shows that Pd has a lower n than Rh.

Based on the theoretical values of the number of conduction electrons per atom of bulk Rh and Pd (Rh:1.0989; Pd:0.3734),[22] and on the lattice constants of bulk Rh and Pd (Rh:3.8043 Å; Pd:3.8898 Å),[23] we estimate the n of Pd (2.5378×10^{22} cm^{-3}) to be about 30% of the n of Rh (7.9835×10^{22} cm^{-3}). This result shows that the n of Pd is very low compared to that of Rh.

2. Correlation interaction at different n

The correlation interaction between electrons has been studied based on an electron-gas model,[6] in which a large number of electrons move in a uniformly spread out positive charge having the density required to give the system charge neutrality. This model shows the electron density to be an important factor for the correlation interaction. For example, the correlation interaction is strong (i.e., the motion of electrons is strongly correlated) at low electron density because, when the electron density is low, in determining the wave function of electrons the Coulomb interaction energy is more dominant than the kinetic energy.

Considering the electron-gas model, the study of the influence of the electron density is essential to understand the correlation interaction. However, the correlation interaction in transition metals has not been studied in connection with n. For transition metals, there are thus very few data for the relation between the correlation interaction and n.

Here it is assumed for transition metals that n contributes to the correlation interaction as in the electron-gas model, i.e., assumed that the correlation interaction is strong at low n. Then, since the n of Pd is low compared to that of Rh, as mentioned above, the correlation interaction due to the contribution of n is stronger in Pd than in Rh. This tendency to be stronger in Pd than in Rh agrees with the above tendency that the correlation interaction due to the contribution of such factors must be stronger in Pd than in Rh (Sec. III C). This agreement suggests that, in addition to the d character, n contributes to the correlation interaction.

To show quantitatively the contribution of n to the correlation interaction, the correlation interaction due to the contribution of the d character must be separated from the correlation interaction reflected in the half-width of the OPRA. However, at present, the evaluation of these correlation interactions is difficult, and thus such a separation is also difficult.

In a previous study,[5] the n of Ni has been shown to be lower than that of fcc Co, but the difference in the half-width between fcc Co and Ni island films has reflected the difference in the d character, which is stronger in fcc Co than in Ni. This result seems to be because the difference in n is small, and the difference in the d character is large.

IV. SUMMARY

The OPRA of Rh island films has been measured. The half-width and the location of this OPRA have been compared with those of Pd island films in a previous study.[4] The comparison shows that the correlation interaction is stronger in Pd than in Rh, and that the conduction-electron density n is lower in Pd than in Rh. Since the d character of conduction electrons, which contributes to the correlation interaction, is stronger in Rh than in Pd, the difference in the correlation interaction shows that there are factors contributing to the correlation interaction besides the d character. The correlation interaction due to the contribution of such factors must be stronger in Pd than in Rh. Assuming that the correlation interaction is strong at low n as in the electron-gas model,[6] then the correlation interaction due to the contribution of n is stronger in Pd than in Rh because Pd has a lower n than Rh. This tendency to be stronger in Pd than in Rh agrees with the above tendency of the correlation interaction due to the contribution of such factors. This agreement suggests that, in addition to the d character, n contributes to the correlation interaction.

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