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ELECTRICAL RESISTANCE OF THIN METALLIC FILMS: DIRECT SCATTERING OF CONDUCTION ELECTRONS BY ADSORBED ATOMS

By

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Abstract

In order to interpret changes in the electrical resistance of thin metallic films due to adsorption of gases, Fuchs' form specularity parameter derived by Greene in the Boltzmann-Fuchs transport equation is represented and calculated by scattering probabilities of the conduction electrons at the surface. The metal surface is approximated by the jellium model with a step surface potential barrier and standing wave functions of the conduction electrons. Scattering potentials of neutral adatoms are assumed as $V(r)=-z^*e^2/r\exp(-2r/r_0)$, where z^* and r_0 are determined by Slater's rule. The calculation is based on the premise that the conduction electrons are scattered by geometrical surface roughness and additionally by potentials of adatoms after adsorption takes place. The theory is applied to oxygen and hydrogen adsorbed on thin evaporated nickel films and compared with experiments observed by Suhrmann *et al.*, and Mizushima. The theoretical direct scattering cross section of adsorbed oxygen and hydrogen are about 1.2×10^{-16} cm^2 and 4.8×10^{-18} cm^2, respectively, depending upon incident angles of the conduction electrons to the surface. The theoretical resistance change agrees well with the experiment for Ni-O system but does not for Ni-H system. This discrepancy seems to suggest that the assumed scattering potential is not suitable for hydrogen and second order processes of the scattering play a role in Ni-H system. So-called scattering mechanism is confirmed to explain the resistance change due to chemisorption.

1. Introduction

The behavior of the conduction electrons at or near solid surfaces has gradually become distinct, although our understanding is insufficient even now. In particular, the band bending and electronic states near semiconductor surfaces have been investigated intensively because of close connections with devices. It is important to understand surface scatterings of the conduction electrons (abbreviated as CE's) at metal surfaces or surfaces of partially degenerated semiconductors from the following stand points: first,

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studies of the two dimensional quantization of CE's near semiconductor surfaces, second, adsorption phenomena and catalytic reactions on solid surfaces; and third, the possibility of superconductive solid surfaces. The existence of scattering mechanisms of CE's on metal surfaces is experimentally evident, which is typically shown by a large electrical resistance of thin evaporated films and increases in the resistance due to adsorption of various gases[1]; recent presentations further confirm scatterings of CE's by adsorbed atoms.[2] Based on an idea of the scattering, experimental results of the resistance have been analyzed first by Toya in 1960 in his discussion on adsorbed states of hydrogen.[3] Recently, the present author has proposed a more quantitative method of analysis,[4] in which the cross sections of adatoms for CE's are evaluated and changes in the resistance due to adsorption are understood in more detail.

However, there are a few theoretical points which can be improved, and detailed processes of the calculation are insufficiently delineated in previous papers.[4,6] In the present paper, previous calculations and related problems are first reviewed (Sections 2 and 3. 1), and then an improved calculation (Sections 3. 2, 3. 3) and an application of the theory to chemisorption of gases on nickel films (Section 4) are presented.

2. Statement of Problems

We are going to consider the resistance of thin evaporated films and changes in it due to adsorption of gases. The analysis starts with a solution of the Boltzmann-Fuchs transport equation:[5] the conductivity of a thin metallic film σ referred to its bulk conductivity σ_0 is given in terms of parameter $x=d/l$, and the specularity p_{up} of the upper surface, *viz.*,

$$\frac{\sigma}{\sigma_0}=\frac{\rho_0}{\rho}=1-\frac{3}{4x}\left[\int_0^1 du\,(u-u^3)\,(1-e^{-x/u})\left\{2-p_{up}(1-e^{-x/u})\right\}\right]$$
$$=1-F(x,p_{up}), \qquad (1)$$

where d is the thickness of the film, l is the mean free path of CE's in the film, and u is cosine of an incident angle of CE's measured from the surface normal; p_{up} is originally defined by

$$f_1^+(v_z,z_s)=p_{up}f_1^-(-v_z,z_s), \qquad (2)$$

where $f_1^\pm(\pm v_z,z_s)$ is a small deviation of the Fermi distribution function of incident or reflected electrons, respectively, at the surface z_s due to an applied electric field, *i. e.*, a CE's distribution function f is assumed to be $f=f_e+f_1$, where f_e is the equilibrium distribution function. Equation (2) is well known

as Fuchs's boundary condition. As is understood in Eq. (1), effects of scattering of CE's at the upper surface are totally included in p_{up}, while the specularity of the lower surface, which usually contacts with a substrate, is assumed to be zero in this case.[4] Using Eq. (1), one obtains the relative change in the resistance caused by adsorption as

$$\frac{\delta R}{R}=\frac{\delta\rho}{\rho}=\frac{F(x,p_{up}(\text{ad.}))-F(x,p_{up}(\text{clean}))}{1-F(x,p_{up}(\text{ad.}))}, \tag{3}$$

which is well observable in experiments.

Subsequently, a main problem is to connect p_{up} with particular scattering mechanisms on the surface. In the previous papers,[4,6] two mechanisms were assumed to be the most important on the surface, *i. e.*, the scattering by a geometrical roughness on the surface and the scattering by impurity potentials produced by adatoms: CE's are scattered by the roughness when the surface is clean, and after adsorption, CE's are additionally scattered by adatom potentials. It seems that these assumptions are appropriate for surfaces of thin evaporated films and thin wires, though some other scattering mechanisms, such as surface lattice defects, surface phonons, can be assumed; a reflection of CE's by a finite potential barrier at a metal surface may cause a diffuse reflection, in particular, when the Fermi surface is not spherical. However, those seem to be minor effects on the scattering because of the fact that clean and atomically smooth surfaces generate large specularities.[7,8,9]

As seen in Eq. (2), specularity p_{up} is statistical mechanically defined and a phenomenological parameter, which requires a more basic definition to be connected with the quantum mechanical scattering theory. The first attempt was done by Greene[10,11] in 1966. He introduced a new boundary condition for surface distributions of CE's from a kinetic viewpoint, where a scattering probability of CE's, generally consisting of specular and diffuse reflections at the surface, appears explicitly. His new boundary condition corresponding to Fuch's boundary condition is

$$f_1(u_+\phi_+)=\frac{\{W_0(u_+\phi_+)f_1(-u_+\phi_+)+(1-W_0(u_+\phi_+))\langle f_1(u_-\phi_-)\rangle\}}{(1+f_eW_e(u_+\phi_+))}, \tag{4}$$

followed by

$$W_0(u_+\phi_+)+(1-f_e)W_s=1,$$

$$W_s(u_+\phi_+)=\int_{-1}^{0}du_-\int_0^{2\pi}d\phi_-\left(\frac{-u_-}{u_+}\right)w_s(u_-\phi_-|u_+\phi_+),$$

$$\langle f_1(u_-\phi_-)\rangle\equiv W_s(u_+\phi_+)^{-1}\int_{-1}^{0}du_-\int_0^{2\pi}d\phi_-\left(\frac{-u_-}{u_+}\right)w_s(u_-\phi_-|u_+\phi_+)f_1(u_-\phi_-).$$

In above equations, $u_+=\cos\theta_+$, ϕ_+ or $u_-=\cos\theta_-$, ϕ_- are the angle coordinates of an electron leaving or going to the surface, respectively. W_0 and w_s are defined by the following total scattering probability w at a surface:

$$w(u_-\phi_-\,|\,u_+\phi_+)=W_0(u_+\phi_+)\,\delta(u_-+u_+)\,\delta(\phi_--\phi_-)+(1-f(u_+\phi_+))\,w_s(u_-\phi_-\,|\,u_+\phi_+)\,. \tag{5}$$

Therefore, W_0 stands for a specular reflection probability in a kinetic sense and w_s describes scattering processes. When we use a well-known bulk solution of the Boltzmann transport equation,

$$f_1=e\tau\,\mathbf{v}\cdot\mathbf{E}\left(-\frac{\partial f_e}{\partial\varepsilon}\right)=g(v^2)\cos\phi_-\sqrt{1-u_-^2}\,, \tag{6}$$

in the relaxation time approximation, Eq. (4) is shown to be approximately converted to Fuch's boundary condition resulting in[10,11]

$$p(u_+\phi_+)=\frac{1}{(1+f_eW_s)}\left\{1-(1-f_e)\,W_s\left(1-\cos\Delta\phi\sqrt{\frac{1-u_-^2}{1-u_+^2}}\right)\right\}, \tag{7}$$

where $\Delta\phi=\phi_--\phi_+$. Conditions imposed in Eq. (7) are that the band of the solid is flat near the surface and the bulk relaxation time of CE's can be used right up to the surface, so that Eq. (7) is more properly applied to metal surfaces because of flat bands near the surfaces. Using the approximation of $f_e=1/2$ at the Fermi level, we have from Eq. (7),

$$p(u_+\phi_+)=p_{ad}=1-\frac{W_s+W_p}{2+W_s}\,, \tag{8}$$

for the specularity to be determined by adatom scatterings, where

$$W_s=\int_{-1}^{0}du_-\int_0^{2\pi}d\Delta\phi\left(\frac{-u_-}{u_+}\right)w_s(u_-,\Delta\phi\,|\,u_+,\Delta\phi)\,, \tag{9 a}$$

$$W_p=\int_{-1}^{0}du_-\int_0^{2\pi}d\Delta\phi\left(\frac{-u_-}{u_+}\right)w_s(u_-,\Delta\phi\,|\,u_+,\Delta\phi)\times\left(1-\cos\Delta\phi\sqrt{\frac{1-u_-^2}{1-u_+^2}}\right). \tag{9 b}$$

It is seen that p_{ad} can be not zero, even if $W_s=1$. This is mainly caused by the crude approximations in transforming Eq. (4) into Eqs. (7) and (8). Equation (8) is accordingly faultless when W_s is small. The calculations of W_s and W_p were performed by Greene and O'Donnell[12] in the case that CE's are scattered by localized surface charges on semiconductor surfaces. Reasonable results were obtained with use of the free electron and the Born approximations, in which a plane and infinite potential barrier is as-

sumed at the surface. Other related problems such as the interference in the scattering from different surface scatterers and effects of the dielectric image force were also discussed by Greene and coworkers along the same category of the calculation.[16,17]

On the other hand, the scattering of CE's by a geometrical surface roughness was studied by Ziman[13] and Soffer,[14] who succeeded in expressing the specularity p in terms of a roughness scattering mechanism, employing a statistical superposition of scattered waves from various parts of a bumpy surface and the autocorrelation function formulation. This problem will be briefly discussed in Section 4.

The points in the present paper are as follows. Greene and O'Donnell's theory (it is abbreviated as the GO theory or calculation in what follows) is concerned with point charges on semiconductor surfaces, while we intend to study neutral adatoms on metal surfaces. In this case, adatom potentials interact with CE's in a short range as compared with point charges on semiconductors, so that the CE's density at surface has to be more properly taken, and further the metal-adatom distance has to be changed for each of adatoms. The method of Born approximation is the first step to deal with this kind of problems. Adatoms may interact strongly with d- electrons and weakly with s, p conduction electrons on surfaces of the transition metals, so that the Born approximation is roughly rationalized. Another improvement is an adequate estimation of the mean free path of CE's in evaporated nickel films, when the theory is applied to the resistance change due to adsorption, which results in producing a significant conclusion.

3. Calculation of the direct scattering probability of CE's

3.1. The Greene and O'Donnell method.

Let us assume that the surface is ideally smooth, on which CE's are specularly reflected and after adsorption of gases a small part of CE's are diffusely scattered by adatoms. It is useful in the following arguments to review the calculation of $w_s(u_-, \Delta\phi | u_+, \Delta\phi)$ in the GO theory. The obtained results are most appropriately applied to charged (polarized) adatoms on semiconductors and semimetals. They used the assumptions that CE's being free electrons inside the metal have standing wave functions in z direction, and an infinite step potential barrier is placed at $z=0$ for the sake of simplicity, *i. e.*, the one electron wave function is assumed as

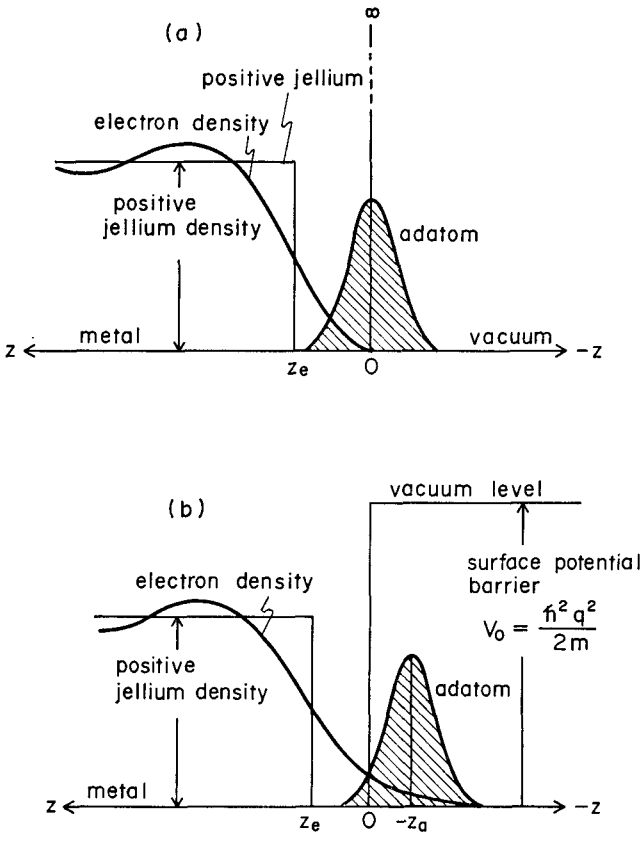

Fig. 1. Schematic representation of models for the surface. (a) infinite surface barrier model used in the GO calculation, (b) step surface barrier model used in the present calculation. The V_0 stands for the barrier height.

$$\phi_{\mathbf{k}}(\mathbf{r}) = \frac{2\mathrm{i}}{\sqrt{\Omega}} e^{\mathrm{i}(k_x x + k_y y)} \sin k_z z$$

$$= \frac{1}{\sqrt{\Omega}} (e^{\mathrm{i}\mathbf{k}\cdot\mathbf{r}} - e^{\mathrm{i}\mathbf{k}_\mathrm{i}\cdot\mathbf{r}}), \qquad z \geq 0 \tag{10 a}$$

$$\phi_{\mathbf{k}}(\mathbf{r}) = 0, \qquad z < 0 \tag{10 b}$$

where Ω is the volume of metal and $\mathbf{k}_\mathrm{i} = (k_x, k_y, -k_z)$ is the image momentum of $\mathbf{k} = (k_x, k_y, k_z)$. The used model of the surface is schematically shown in Fig. 1a. When a weak scattering potential of an adatom formed

$$V(r)=\frac{-z^*e^2}{r}\,\mathrm{e}^{-2r/r_0}\,, \tag{11}$$

is located at $z=0$, a new wave function of the system can be assumed to be

$$\Psi_{\mathbf{k}}(\mathbf{r})=\Phi_{\mathbf{k}}(\mathbf{r})+u_{\mathbf{k}}(\mathbf{r})\,,\qquad \Phi_{\mathbf{k}}(\mathbf{r})\gg u_{\mathbf{k}}(\mathbf{r})\,. \tag{12}$$

The Born approximation leads from the Schrödinger equation to

$$(\nabla^2+k^2)\,u_{\mathbf{k}}(\mathbf{r})=\left(\frac{2m}{\hbar^2}V(r)\right)\Phi_{\mathbf{k}}(\mathbf{r})\,,\qquad z\geq 0\,. \tag{13}$$

The solution of this equation is, as is well known,

$$u_{\mathbf{k}}(\mathbf{r})=\int G(\mathbf{r},\mathbf{r}')\left(\frac{2m}{\hbar^2}V(r')\right)\Phi_{\mathbf{k}}(\mathbf{r}')\,\mathrm{d}\mathbf{r}'\,, \tag{14}$$

where

$$G(\mathbf{r},\mathbf{r}')=\sum_{\mathbf{k}}\frac{\Phi_{\mathbf{k}}(\mathbf{r})\,\Phi_{\mathbf{k}}^*(\mathbf{r}')}{\varepsilon-\varepsilon_{\mathbf{k}}}\,. \tag{15}$$

The calculation of Eq. (15) is a version of the free particle Green's function with the image property given in Eq. (10a). For the calculation, the following image relations play an important role, *i. e.*,

$$\mathbf{k}_{\mathrm{i}}\cdot\mathbf{r}'=\mathbf{k}\cdot\mathbf{r}_{\mathrm{i}}'\,,\qquad \mathbf{k}\cdot\mathbf{r}'=\mathbf{k}_{\mathrm{i}}\cdot\mathbf{r}_{\mathrm{i}}' \text{ and } \int\mathrm{d}\mathbf{r}_{\mathrm{i}}'=\int\mathrm{d}\mathbf{r}'\,. \tag{16}$$

The result is

$$G(\mathbf{r},\mathbf{r}')=\frac{\exp[ik|\mathbf{r}-\mathbf{r}'|]}{-4\pi|\mathbf{r}-\mathbf{r}'|}-\frac{\exp[ik|\mathbf{r}-\mathbf{r}_{\mathrm{i}}|]}{-4\pi|\mathbf{r}-\mathbf{r}_{\mathrm{i}}'|}\,, \tag{17}$$

The substitution of Eq. (17) into Eq. (14) makes its integration possible, in which the image relations of Eq. (16) are again used. The asymptotic wave function of scattering waves becomes consequently,

$$u_{\mathbf{k}}(\mathbf{r})=g(\mathbf{k}',\mathbf{k})\frac{\mathrm{e}^{ikr}}{r}\,, \tag{18}$$

where

$$\begin{aligned} g(\mathbf{k}',\mathbf{k})&=\left(\frac{-2m}{2\pi\hbar^2}\right)\left[V(\mathbf{k}'-\mathbf{k})-V(\mathbf{k}'-\mathbf{k}_{\mathrm{i}})\right]\\ &=\left(\frac{-m\sqrt{\Omega}}{2\pi\hbar^2}\right)<\mathbf{k}'|\,V(r)|\mathbf{k}>\,, \end{aligned} \tag{19}$$

followed by

$$V(\mathbf{k}'-\mathbf{k})=\frac{1}{\sqrt{\Omega}}\int d\mathbf{r}'\,V(r')\,e^{i(\mathbf{k}-\mathbf{k}')\cdot\mathbf{r}'}=\frac{-2\pi z^*e^2}{\sqrt{\Omega}}\left\{\frac{2}{(2/r_0)^2+(\mathbf{k}'-\mathbf{k})^2}\right\}$$
$$=\frac{-2\pi z^*e^2}{\sqrt{\Omega}}\frac{1}{k_f^2}\left\{\frac{1}{2/(r_0k_f)^2+(1+u_+u_--\cos\Delta\phi\sqrt{(1-u_-^2)(1-u_+^2)})}\right\}, \tag{20}$$

and

$$V(\mathbf{k}'-\mathbf{k}_i)=\frac{1}{\sqrt{\Omega}}\int d\mathbf{r}'\,V(r')\,e^{i(\mathbf{k}_i-\mathbf{k}')\cdot\mathbf{r}'}=\frac{-2\pi z^*e^2}{\sqrt{\Omega}}\left\{\frac{2}{(2/r_0)^2+(\mathbf{k}'-\mathbf{k}_i)^2}\right\}$$
$$=\frac{-2\pi z^*e^2}{\sqrt{\Omega}}\frac{1}{k_f^2}\left\{\frac{1}{2/(r_0k_f)^2+((1-u_+u_--\cos\Delta\phi\sqrt{(1-u_-^2)(1-u_+^2)})}\right\}. \tag{21}$$

In each of the last two equations, $(\mathbf{k}'-\mathbf{k})^2$ or $(\mathbf{k}'-\mathbf{k}_i)^2$ is converted into the incident and scattering angles u_+, u_- and $\Delta\phi=\phi_--\phi_+$. For the resistance problems we evaluate only the contribution from k_f electrons on account of the factor $f_k(1-f_{k'})\delta(E_k-E_{k'})$ in the transition. From Eqs. (19), (20) and (21), we have

$$|V_{k'k}|^2=|\langle\mathbf{k}'|V(r)|\mathbf{k}\rangle|^2$$
$$=\left(\frac{4\pi z^*e^2}{\Omega k_f^2}\right)^2\left[\frac{1}{2/(r_0k_f)^2+(1+u_+u_--\cos\Delta\phi\sqrt{(1-u_-^2)(1-u_+^2)})}\right.$$
$$\left.-\frac{1}{2/(r_0k_f)^2+(1-u_+u_--\cos\Delta\phi\sqrt{(1-u_-^2)(1-u_+^2)})}\right]^2, \tag{22}$$

which is to be substituted into Eqs. (9a) and (9b) according to the relation $w_s=N_a/(-u_-)\cdot(m\Omega/2\pi\hbar^2)^2|V_{k'k}|^2$, (see Eq. (29)). The present author attempted to apply this matrix element to Eqs. (9), (8) and (3).[4] Experimental changes in the resistance of thin evaporated Ni films due to adsorption of hydrogen were analyzed with a consideration of the roughness scattering. Adjustable parameters are z^* and r_0. For adsorbed hydrogen, $z^*=1$ is used (see Section 3.3) and r_0 is varied to fit the calculated values to experimental ones. When r_0 is 1.4 to 1.1A, the theory coincides with the experiment. Since r_0 is considered as an atomic radius of the adsorbed atom, these values are too large. It is obviously rough assumptions for neutral adatoms that CE's density is terminated at $z=0$, and besides adatom potentials are located there.

3.2. Improved Calculation

Let us approximate the surface potential barrier as a step and finite

barrier, which is shown in Fig. 1b. The potential $V_0=\hbar^2q^2/2m$ stands for the height of barrier, so that $-V_0$ is the energy level of the bottom of conduction band. When CE with momentum $\mathbf{k}$ collides with this potential barrier, it is subjected to a phase shift $\delta(\mathbf{k})$, and its wave function dumps with an exponential form in the potential. The wave functions of CE's can be assumed as,

$$\Phi_{\mathbf{k}}(\mathbf{r})=\frac{2ie^{-ik_z\delta}}{\sqrt{\Omega}}e^{i(k_xx+k_yy)}\sin k_z(z+\delta)$$

$$=\frac{1}{\sqrt{\Omega}}(e^{i\mathbf{k}\cdot\mathbf{r}}-e^{-2ik_z\delta}e^{i\mathbf{k}_z\cdot\mathbf{r}}),\qquad z\geq 0, \tag{23 a}$$

$$\Phi_{\mathbf{k}}(\mathbf{r})=\frac{2ie^{-ik_z\delta}}{\sqrt{\Omega}}\sin(k_z\delta)\,e^{i(k_xx+k_yy)}\exp[(q^2-k_z^2)^{1/2}z],\qquad z<0, \tag{23 b}$$

where $\mathbf{k}_i$ is the image momentum of $\mathbf{k}$ as before. This form of the wave function was originally used by Huntington.[18] The continuity condition for Eqs. (23a) and (23b) requires the relation

$$\sin(k_z\delta)=k_z/q, \tag{24}$$

between the phase shift $k_z\delta$ and q. In addition, the requirement that charge be conserved determines the position of the edge of positive jellium, which is denoted by z_e (see Fig. 1b), as a function of q and the Fermi momentum k_f :[18,19,20]

$$\frac{2}{3}k_f^3z_e=\frac{\pi}{4}k_f^2+\frac{1}{2}(q^2-2k_f^2)\sin^{-1}\left(\frac{k_f}{q}\right)-\frac{1}{2}k_f(q^2-k_s^2)^{1/2}. \tag{25}$$

From Eq. (25), z_e is 0.37 A for Ni with use of $k_f=1.18\times10^8\,\mathrm{cm}^{-1}$ and $D=(q/k_f)^2=1.85$ (see Section 3.3).

Next, we introduce adatoms in the system, whose potentials are also assumed as Eq. (11). The z coordinate of an adatom is denoted by $-z_a$ (see Fig. 1b) measured from the edge of the potential barrier. The metal-adatom distance is hence defined by $L=z_e+z_a$. The perturbed wave function is again assumed to be

$$\Psi_{\mathbf{k}}(\mathbf{r})=\Phi_{\mathbf{k}}(\mathbf{r})+u_{\mathbf{k}}(\mathbf{r}),\qquad \Phi_{\mathbf{k}}(\mathbf{r})\gg u_{\mathbf{k}}(\mathbf{r}).$$

Using the Born approximation, we obtain, from the Schrödinger equation,

$$(\nabla^2+k^2)u_{\mathbf{k}}(\mathbf{r})=\left(\frac{2m}{\hbar^2}V(r)\right)\phi_{\mathbf{k}}(\mathbf{r}),\qquad z\geq 0, \tag{26 a}$$

$$(\nabla^2+k^2-q^2)\,u_{\mathbf{k}}(\mathbf{r})=\left(\frac{2m}{\hbar^2}\,V(r)\right)\phi_{\mathbf{k}}(\mathbf{r})\,,\qquad z<0\,. \tag{26 b}$$

The solution is again

$$u_{\mathbf{k}}(\mathbf{r})=\int \mathrm{d}\mathbf{r}'\,G(\mathbf{r},\,\mathbf{r}')\left(\frac{2m}{\hbar^2}\,V(r')\right)\phi_{\mathbf{k}}(\mathbf{r}')\,.$$

In this case, the calculation of the Green's function is rather complicated, but $G(\mathbf{r},\mathbf{r}')$ in the asymptotic form may become in general

$$G(\mathbf{r},\mathbf{r}')\xrightarrow[\mathbf{r}\to\infty]{}\left(\frac{-m\sqrt{\Omega}}{2\pi\hbar^2}\right)\left(\frac{\mathrm{e}^{ikr}}{r}\right)\phi_{\mathbf{k}}(\mathbf{r}')\,,$$

irrespective of free electrons or electrons in a potential.[27] Then the asymptotic scattering wave function becomes

$$u_{\mathbf{k}}(\mathbf{r})=g(\mathbf{k}',\mathbf{k})\,\frac{\mathrm{e}^{ikr}}{r}\,,$$

with

$$g(\mathbf{k}',\mathbf{k})=\left(\frac{-m\sqrt{\Omega}}{2\pi\hbar^2}\right)\int \mathrm{d}\mathbf{r}\,\phi^*_{\mathbf{k}'}(\mathbf{r}')\,V(r)\,\phi_{\mathbf{k}}(\mathbf{r}')=\left(\frac{-m\sqrt{\Omega}}{2\pi\hbar^2}\right)\langle\mathbf{k}'|\,V(r')|\mathbf{k}\rangle\,, \tag{27}$$

similar to Eqs. (18) and (19). This result is directly verified by Fermi's golden rule for the transition probability, *i. e.*,

$$T(\mathbf{k}'-\mathbf{k})=\left(\frac{2\pi}{\hbar}\right)|\langle\mathbf{k}'|\,V(r)|\mathbf{k}\rangle|^2\rho(\mathbf{k}')\,, \tag{28}$$

which is known to be equivalent to that obtained from the first order Born approximation, where $\rho(\mathbf{k}')$ is the density of the final states given by

$$\rho(\mathbf{k}')=\left(\frac{\Omega}{8\pi^3}\right)\frac{mk_{\mathrm{f}}}{\hbar^2}\,\mathrm{d}\Omega'\,.$$

The flux of incoming wave is $-v_{\mathrm{f}}u_-|\Omega^{-1/2}\exp(i\mathbf{k}\cdot\mathbf{r})|^2$, and we assume further that there are N_{a} atoms cm^{-2} of independent and equivalent scatterers on the surface. Then we have the scattering probability w_{s}:

$$w_{\mathrm{s}}(\mathbf{k}',\mathbf{k})\,\mathrm{d}\Omega'=\frac{1}{-u_-}\left(\frac{1}{v_{\mathrm{f}}/\Omega}\right)N_{\mathrm{a}}\,T(\mathbf{k}'-\mathbf{k})\,,$$

and

$$w_{\mathrm{s}}(\mathbf{k}',\mathbf{k})=\left(\frac{N_a}{-u_-}\right)\left(\frac{m\Omega}{2\pi\hbar^2}\right)^2|\langle\mathbf{k}|\,V(r)|\mathbf{k}\rangle|^2\,. \tag{29}$$

The calculation of matrix element $\langle\mathbf{k}'|\,V(r)|\mathbf{k}\rangle$ is given in Appendix A. The result is,

$$V_{\mathbf{k}'\mathbf{k}}=\langle\mathbf{k}'|V(r)|\mathbf{k}\rangle=\int d\mathbf{r}\,\phi^*_{\mathbf{k}'}(\mathbf{r})\left\{\frac{-z^*e^2}{2\pi^2}\int d\mathbf{Q}\,\frac{e^{i\mathbf{Q}\cdot\mathbf{r}}}{(2/r_0)^2+Q^2}\right\}\phi_{\mathbf{k}}(\mathbf{r})$$
$$=\left(\frac{-2\pi z^*e^2}{\Omega k_f^2}\right)(V_1+V_2)\,, \tag{30}$$

followed by

$$V_1=e^{-S_0x}\left(\frac{4u_+u_-}{D^2}\right)\frac{(u_-+i\sqrt{D-u_-^2})(u_+-i\sqrt{D-u_+^2})}{(S_0-T)}$$
$$\times\left\{\frac{e^{(S_0-T)x}}{T}-\frac{2}{(S_0+T)}\right\}, \tag{31}$$

where

$$D=\left(\frac{q}{k_f}\right)^2,\qquad x=z_ak_f\,,\qquad S_0=(\sqrt{D-u_-^2}+\sqrt{D-u_+^2})$$
$$T=\left\{\left(\frac{2}{r_0k_f}\right)^2+2-2\cos\Delta\phi\sqrt{(1-u_-^2)(1-u_+^2)}-u_-^2-u_+^2\right\}^{1/2},$$

and

$$V_2=\left\{\frac{e^{-Tx}}{T^2+(u_--u_+)^2}\right\}\left[e^{i(u_--u_+)x}\left\{\left(1+i\frac{u_--u_+}{T}\right)\cos(u_--u_+)\,x\right.\right.$$
$$\left.-\left(\frac{u_--u_+}{T}-i\right)\sin(u_--u_+)\,x\right\}$$
$$+R_+R_-e^{-i(u_--u_+)x}\left\{\left(1-i\frac{u_--u_+}{T}\right)\cos(u_--u_+)\,x\right.$$
$$\left.\left.-\left(\frac{u_--u_+}{T}+i\right)\sin(u_--u_+)\,x\right\}\right]$$
$$-\left\{\frac{e^{-Tx}}{T^2+(u_-+u_+)^2}\right\}\left[R_-e^{-i(u_-+u_+)x}\left\{\left(1-i\frac{u_-+u_+}{T}\right)\cos(u_-+u_+)\,x\right.\right.$$
$$\left.-\left(\frac{u_-+u_+}{T}+i\right)\sin(u_-+u_+)\,x\right\}$$
$$+R_+e^{i(u_-+u_+)x}\left\{\left(1-i\frac{u_-+u_+}{T}\right)\cos(u_-+u_+)\,x\right.$$
$$\left.\left.-\left(\frac{u_-+u_+}{T}-i\right)\sin(u_-+u_+)\,x\right\}\right], \tag{32}$$

where

$$R_+=\left\{1-\frac{2u_+^2}{D}+i\frac{2u_+\sqrt{D-u_+^2}}{D}\right\},$$
$$R_-=\left\{1-\frac{2u_-^2}{D}-i\frac{2u_-\sqrt{D-u_-^2}}{D}\right\}.$$

V_1 stands for the contribution in $z<0$, and V_2 in $z\geq0$. When $D=(q/k_f)^2=\infty$ and $z_a=0$, Eq. (30) reduces to

$$V_{k'k}=\left(\frac{2\pi z^*e^2}{\Omega k_f^2}\right)\left\{\frac{2}{T^2+(u_--u_+)^2}-\frac{2}{T^2+(u_-+u_+)^2}\right\},$$

which is equal to the matrix element obtained in the GO theory (Eq. (22)).

3.3. Numerical Computations.

The present matrix element, Eq. (30) is compared with GO's one, Eq. (22). Equations (9a) and (8), that is,

$$W_s=\int_{-1}^{0}du_-\int_0^{2\pi}d\Delta\phi\left(\frac{-u_-}{u_+}\right)w_s(u_-,\Delta\phi|u_+,\Delta\phi), \tag{9 a}$$

$$p_{ad}=1-\frac{W_s+W_p}{2+W_s}, \tag{8}$$

are numerically calculated for adsorption of H, O, C and N on Ni. Para-

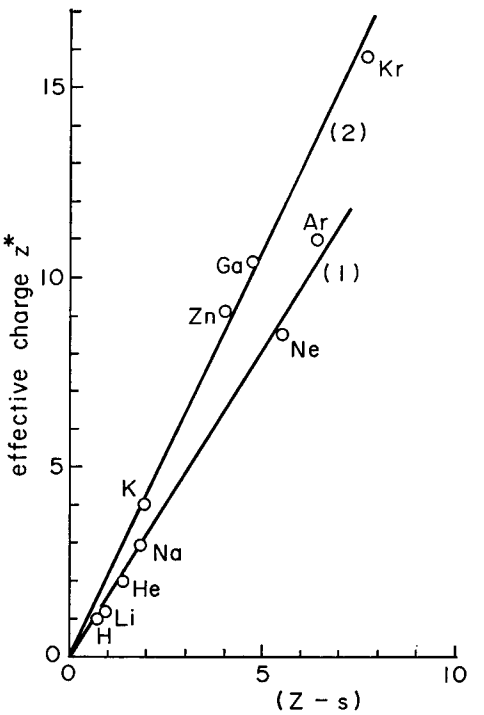

Fig. 2. Relation between the effective charge z^* and the effective nuclear charge $(Z-s)$ defined by Slater. This is obtained from the result calculated by Allis and Morse. Line (1) is applicable to atoms with the atomic number less than 18, and line (2) to atoms with the atomic number from 19 to 36.

meters D and z_a are determined as follows: $D=(q/k_f)^2=(E_f+\Phi)/E_f=(5.3\ \mathrm{eV}+4.5\ \mathrm{eV})/5.3\ \mathrm{eV}=1.85$, where E_f is the Fermi energy and Φ is the work function; metal-adatom distance is assumed to be $L=z_e+z_a=r_0$, so that $z_a=r_0-0.37$ A for nickel. This assumption means that an adatom with atomic radius r_0 contacts just with the metal (the positive jellium). The parameters z^* and r_0 defined by Eq. (11) are determined by Slater's rule. The values of r_0 are tabulated by Slater.[21] Determination of z^* has been discussed by Allis and Morse[22] for scatterings of slow electrons by gaseous atoms. Note that z^* differs from the effective nuclear charge $(Z-s)$ (in Slater's notation). The values of z^* is not determined straightforwardly from Slater's effective nuclear charge but closely related to it as shown by Allis and Morse, who determined it by averaging the effective nuclear charges in different atomic shells. The values thus determined explained satisfactorily the scattering of slow electrons. Though their method is not simple, we can find a linear relation between z^* and the effective nuclear charge $(Z-s)$ in their result as shown in Fig. 2, by which we can directly determine z^*'s for many atoms. Used values of the parameters and resulting W_s are given in Table I. Figure 3 demonstrates calculated p_{ad} for adsorption of hydrogen on nickel with r_0 being parameterized, in which the present results are compared with GO's ones. Here it is noticed that though p_{ad} is given as a function of the scattering angle u_+ in Eq. (8), it is plotted with the incident

TABLE I Scattering probabilities of the conduction electrons by H, O, N and C adsorbed on Ni, and values of r_0 and z^* determind by Slater's rule and Allis and Morse's method, respectively. Parameters for Ni are: $E_f=5.3$ eV, $k_f=1.18\times10^8\ \mathrm{cm}^{-1}$, $D=(q/k_f)^2=1.85$ with 4.5 eV of the work function.

atoms	z^*	r_0(A)*)	L(A)	z_a(A)	W_s(for $N_a=0.2\times10^{15}$ atoms cm^{-2}) $u_+=0.20$	0.50	0.80
H	1.0	0.53	0.53	0.16	8.34×10^{-4}	1.91×10^{-3}	2.65×10^{-3}
O	7.0	0.47	0.47	0.10	2.02×10^{-2}	4.78×10^{-2}	7.01×10^{-2}
C	4.7	0.65	0.65	0.28	4.28×10^{-2}	9.23×10^{-2}	1.15×10^{-1}
N	5.9	0.55	0.55	0.18	3.32×10^{-2}	7.54×10^{-2}	1.03×10^{-1}

*) The atomic radii are calculated from $r_0=(n^*)^2/(Z-s)$ according to Slater's rule, in which $(Z-1)$ electrons contribute to the evaluation of $(Z-s)$, where Z is the atomic number of atom considered, because the radius of the outermost electron is to be calculated as r_0. However, Z electrons contribute to $(Z-s)$ for the determination of z^*, because z^* is an effective charge seen by incident conduction electrons.

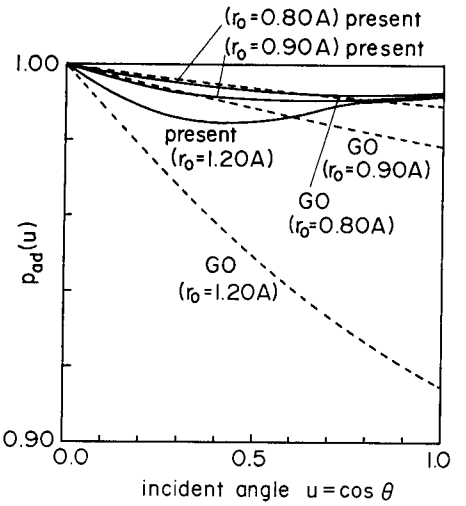

Fig. 3. Comparison of the present specularity parameter $p_{ad}(u)$ with that obtained by the GO calculation for hydrogen adsorbed on nickel. The number of adsorbed hydrogen is fixed at $N_a=0.2\times10^{15}$ atoms/cm^2.

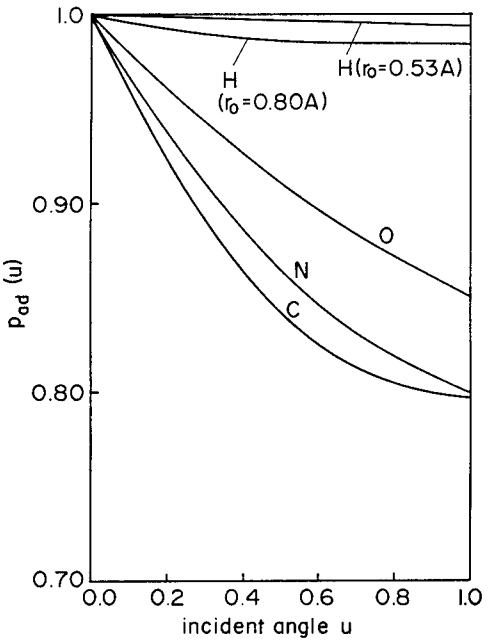

Fig. 4. Specularity parameter $p_{ad}(u)$ for adsorption of H, O, C and N on Ni. $N_a=0.4\times10^{15}$ atoms/cm^2 and other used parameters are given in Table I.

angle u in Fig. 3, because Fuch's boundary condition imposes the relation of $u_+=|u_-|=u$. It is seen in Fig. 3 that when r_0 is small, the present results are similar to those of the GO calculation, but r_0 becomes large, GO's matrix element becomes much larger than the present one. This is because the position of adatom is fixed at $z=z_a=0$ in the GO calculation, so that overlapping of the wave function with the scattering potential becomes large with r_0 being large, while in the present calculation, the position of adatom shifts outside with r_0 enlarged resulting in a small increase in the overlap. In Fig. 4, p_{ad}'s for adsorption of C, N, and O are compared with that of H. The change in p_{ad} for C is the largest among them due to the largest value of r_0 as seen in Table I. Note in Figs. 3 and 4 that the grazingly incident electrons are less scattered because of the termination of the wave functions of CE's at the surface. Therefore, grazing electrons behave in a more specular reflection than normally incident electrons.

The scattering cross section of an adatom is useful to understand the nature of scattering, which is defined by

$$W_s=(N_a/u)\,Q_s\,, \tag{33}$$

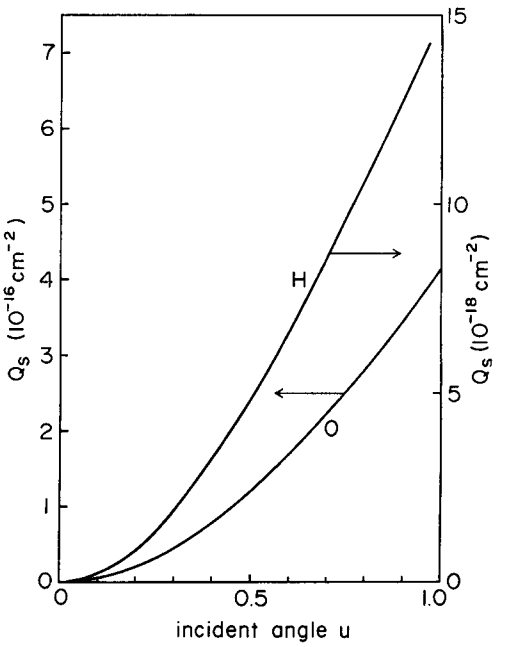

Fig. 5. Calculated scattering cross sections of H and O adsorbed on Ni. Used values of the parameters are those given in Table I.

where N_a is the number of randomly adsorbed scatterers per cm^2, Q_s is the total cross section,*) and factor (N_a/u) represents the asperity effect.[11] From Eqs. (9a), (29), (30) and (33), we have

$$Q_s(u) = (z^*/a_0 k_f^2)^2 \times \int_{-1}^{0} du_- \int_0^{2\pi} d\Delta\phi |V_1 + V_2|^2 , \tag{34}$$

where a_0 is the Bohr radius. Note that Q_s depends on the incident angle of CE's which is a feature of surface scattering problems. Calculated cross sections are shown in Fig. 5 for O and H plotted with the incident angle, where the cross section of O is much larger than that of H.

4. Application of the theory to changes in the resistance of Ni films due to adsorption of O_2 and H_2.

In this section, the present theory is compared with experiments. There are many experimental results of changes in the resistance of thin evaporated films due to adsorption. However, the most of them can not be compared with the theory because of being lack of some basic imformations, *i. e.*, the mean free path l of CE's, thickness of films, the resistance absent of adsorbate or number of adatoms per cm^2. Here the theory is compared with experimental results obtained by Suhrmann *et al.*[23,24] and Mizushima.[25]

4.1. Scattering by surface roughness and the mean free path of CE's in evaporated Ni films.

We have considered the impurity scattering of CE's on an ideal metal surface, where gas atoms are assumed to be adsorbed on a smooth and plane surface. This assumption implies that CE's with wave length λ being much larger than an average asperity h_0 of a real surface feel the surface smooth. However, it is well known that there is a large scale roughness or bumpyness ($h_0 \geq 10$ A) on actual surfaces of evaporated films. It must be taken into account to understand the resistance of films. Many experiments have actually shown small values of p_{up} before adsorption takes place, which signifies a prior existence of scattering mechanisms. Therefore, we have postulated a geometrical surface roughness being the most important mechanism on clean surfaces. Significant theories for this problem are presented by Ziman[13] and Soffer,[14] who represented the specularity as a function of phase differences of waves reflected from a bumpy surface whose averaged height deviation is h_0 measured from a plane base surface, *viz.*,

*) It is noted that in Refs. 6 and 12, the cross section is defined by $Q = \pi (z^* r_0/a_0 k_f)^2$, which represents a strength of the scattering of each adatom independent of nature of metal surfaces.

$$p_r(u)=f\left(\frac{4\pi h_0}{\lambda}u\right).$$

When a Gaussian distribution for the height deviation and an autocorrelation function for the deviation parallel to the base surface are assumed, it becomes,

$$p_r(u)=\exp\left\{-\left(\frac{4\pi h_0}{\lambda}\right)^2 u^2\right\} \tag{35}$$

at a limit of no correlation length,[14] which satisfies Fuchs' boundary condition. Since this result is based on an extremely simplified case of the theories, it should be qualitatively understood. When we intend to apply Eq. (35) to thin evaporated polycrystalline films, where $h_0/\lambda>1$, we notice that $(4\pi h_0/\lambda)^2$ factor becomes unrealistically large, so that Eq. (35) is substantially zero. As we have no criterion for knowing what forms are more plausible, we assume the same form of the specularity,

$$p_r(u)=\exp\left(-c\left(\frac{4\pi h_0}{\lambda}\right)^2 u^2\right)=\exp\left(-Cu^2\right), \tag{36}$$

with putting correction c to obtain a reasonable value of $p_r(u)$. In the case of roughness scattering, grazingly incident electrons should behave in a specular fasion just like the surface impurity scattering shown in Fig. 3, because grazing electrons have apparently long wave lengths given by λ/u. The assumption of Eq. (36) is hence reasonable.

Constant C can be determined from observed resistance R of thin evaporated films. Let us write the resistance as $R=\gamma\rho/d$, where γ is a constant determined by experimental conditions. From Eq. (1) and R, we obtain

$$\frac{R(T_2,d_1)}{R(T_1,d_1)}=\frac{l(T_1)}{l(T_2)}\times\frac{1-F(x=d_1/l(T_1),p_r(u))}{1-F(x=d_1/l(T_2),p_r(u))}, \tag{37}$$

for d_1 and also another similar equation for d_2, where T is temperature of films. By using the resistance measured by Mizushima[22] (see Fig. 12 of Ref. 22) and parameterizing C and $l(T_1)/l(T_2)$ to obtain best fit of Eqs. (37) to the experiment for d_1 and d_2, the following values are obtained: $l(90\text{ K})=350\pm20$ A, $l(273\text{ K})=180\pm20$ A; $C=3.8$ for $d_1=100$ and $d_2=200$ A and $l(90\text{ K})=410\pm30$ A, $l(273\text{ K})=210\pm30$ A; $C=4.2$ for $d_1=300$ and $d_2=400$ A. These mean free paths are not so different from the values evaluated by Toya:[26] $l(90\text{ K})=270$ A and $l(273\text{ K})=150$ A, but much smaller than the bulk values: $l(90\text{ K})=1280$ A and $l(273\text{ K})=266$ A. It is noted that $C=3.0$ is experimentally determined for thin Pt wires,[6] of which roughness is supposed to be smaller than that of evaporated nickel films.

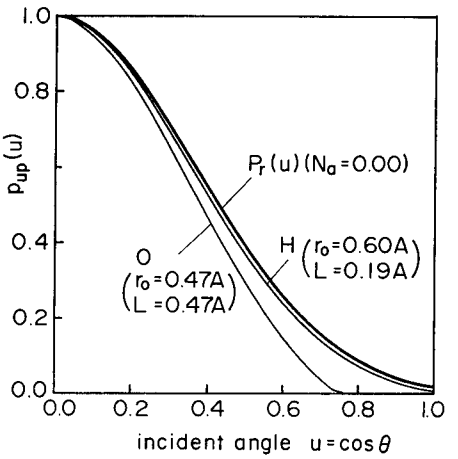

Fig. 6. Specularity parameter $p_{up}(u)$ defined by Eq. (38) for O and H adsorbed on Ni. $N_a=0.4\times10^{15}$ atoms/cm^2. $p_r(u)$ denotes the specularity for the roughness scattering.

It is finally assumed that the impurity scattering and the roughness scattering occur independently on the surface just as the assumption in problems of the bulk resistance, *viz.*,

$$p_{up}=1-\left\{(1-\exp(-Cu^2))+\frac{W_s+W_p}{2+W_s}\right\}$$
$$=\exp(-Cu^2)-\frac{W_s+W_p}{2+W_s}\geq 0\,, \tag{38}$$

which is to be substituted to Eq. (1). The above assumption implies that adatoms placed on a bumpy part of the surface do not contribute to resistance change, because CE's are always scattered by the roughness. Figure 6 results from the numerical computation of Eq. (38) for adsorption of hydrogen and oxygen on nickel.

4.2. Comparison of the calculation with the experiments.

Equation (38) and the mean free paths obtained in section 4.1 are substituted into Eq. (1), and it is numerically integrated, where $x=d/l=0.286$ at 90 K and 0.556 at 273 K. The relative change in the resistance is obtained from Eq. (3) as a function of N_a. Experimental results for Ni-O[24] and Ni-H systems[23,25] are shown in Fig. 7 along with the theoretical ones. The theory can not discuss the resistance change at the higher coverage, since randomly distributed and independent adatoms are assumed. Figure 7 demonstrates that the theory agrees with the experiment for Ni-O system but does not for Ni-H system with assuming the atomic values of r_0 and

$L=r_0$. The variation of r_0 from 0.53 to 0.80 A can not explain the experimental result of hydrogen. Therefore, we attempted to vary L for Ni-H system. In the present calculation, no surface structure parallel to the surface is considered. However, a wavy electronic surface can be assumed for rough surfaces. When we take L being close to zero, the adatom may be crudely approximated to be located at a valley of the wavy surface. We varied L with fixing $r_0=0.53$ or 0.60 A, and calculated the resistance change, which is found to increase rapidly with decrease in L. These results are shown by broken and dotted lines in Fig. 7. When $L=0.02$ A, the theory agrees with the experiment. However, such a small distance may not be allowed for adsorbed hydrogen due to large repulsions from the positive jellium and CE's. This inconsistency is possibly caused in part by the assumed scattering potential Eq. (11) which is of less suitability for light atoms, since this potential is similar to that derived from the Thomas-Fermi statistical model, in which the potential is accurate and has an approximately exponential dumping for heavy atoms. Another explanation of the inconsistency is that the second order processes such as $\mathbf{k}\rightarrow 1s\rightarrow\mathbf{k}'$ may contribute

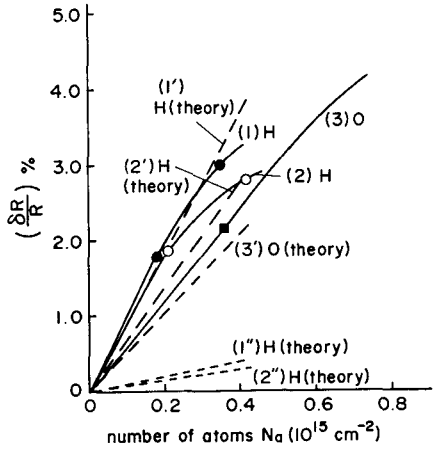

Fig. 7. Experimental changes in the resistance (solid lines) of evaporated Ni films ($d=100$ A) due to adsorption of H and O, and theoretical changes in the resistance (broken and dotted lines). (1) adsorption of H at 90 K, (2) adsorption of H at 273 K, (3) adsorption of O at 90 K, (1') adsorption of H at 90 K ($r_0=0.60$ A, $L=0.02$ A), (2') adsorption of H at 273 K ($r_0=0.60$ A, $L=0.02$ A), (3') adsorption of O at 90 K ($r_0=0.47$ A, $L=0.47$ A), (1'') adsorption of H at 90 K ($r_0=0.60$ A, $L=0.19$ A), (2'') adsorption of H at 273 K ($r_0=0.60$ A, $L=0.19$ A).

to the resistance change. This is probable as shown by Toya[3] because of deeper 1s level compared with negative of the work function.

It should be further noted in Fig. 7 that the theoretical temperature dependence of the resistance increase agrees with the experiment in Ni-H system, which indicates that the temperature dependence is caused by the change in l, and further the scattering mechanism we are adopting can only explain this temperature dependence.

5. Conclusion.

A quantitative analysis of changes in the resistance of thin Ni films due to adsorption of O_2 and H_2 has been attempted. It has been shown that the specularity parameter p_{up} is a function of incident angles and energy of conduction electrons. Hence, constant p's which have been often assumed to explain experimental results are very crude asumptions. The present results are summarized as follows. (1) The present scattering probability is similar to GO's one when r_0 is small, but much smaller than GO's one when r_0 is large. (2) The theoretical scattering probability of adsorbed oxygen is 25 times larger than that of hydrogen, while the experimental changes in the resistance due to them are about the same. (3) The theory agrees with the experiment for Ni-O system but does not for Ni-H system. Though a part of this discrepancy may be caused by the scattering potential of Eq. (11), it is probable that the second order scatterings such as $\mathbf{k}\rightarrow 1s\rightarrow\mathbf{k}'$ contribute considerably in Ni-H system. (4) The specularity parameter for surface roughness of Ni films is expressed by $p_r(u)=\exp(-3.8\,u^2)$, in which factor 3.8 is determined from the experimental resistance of films. (5) It is confirmed that when thin metallic films are continuous and thicker than about 50 A where changes in CE's number due to adsorption are negligible, the cause of resistance increase due to adsorption is generally scatterings of the conduction electrons at the surface.

Acknowledgement

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Appendix A: Calculation of matrix element $V_{\mathbf{k}'\mathbf{k}}$

$$V_{\mathbf{k}'\mathbf{k}} = \langle \mathbf{k}' \mid V(r) \mid \mathbf{k} \rangle = \int \mathrm{d}\mathbf{r} \psi^*_{\mathbf{k}'}(\mathbf{r}) \left(\frac{-z^* e^2}{r} \mathrm{e}^{2r/r_0} \right) \psi_{\mathbf{k}}(\mathbf{r})$$
$$= \left(\frac{-z^* e^2}{2\pi^2} \right) \int \mathrm{d}\mathbf{r} \psi^*_{\mathbf{k}'}(\mathbf{r}) \left[\int \mathrm{d}\mathbf{Q} \frac{\mathrm{e}^{\mathrm{i}\mathbf{Q}\cdot\mathbf{r}}}{(2/r_0)^2 + Q^2} \right] \psi_{\mathbf{k}}(\mathbf{r}), \tag{A 1}$$

where $\alpha = 2/r_0$. The wave function in Eq. (23) is rewritten as,

$$\psi_{\mathbf{k}}(\mathbf{r}) = \frac{1}{\sqrt{\Omega}} \mathrm{e}^{\mathrm{i}(k_x x + k_y y)} \times f(k_z, z), \tag{A 2}$$

which leads Eq. (A 1) to

$$V_{\mathbf{k}'\mathbf{k}} = \left(\frac{-z^* e^2}{2\pi^2 \Omega} \right) \int \frac{\mathrm{d}\mathbf{Q}}{\alpha^2 + Q^2} \int_{-\infty}^{\infty} \mathrm{d}x \, \mathrm{e}^{\mathrm{i}(Q_x + k_x - k'_x)x} \int_{-\infty}^{\infty} \mathrm{d}y \, \mathrm{e}^{\mathrm{i}(Q_y + k_y - k'_y)y}$$
$$\times \int_{-\infty}^{\infty} \mathrm{d}z \, f^*(k'_z, z) f(k_z, z) \, \mathrm{e}^{\mathrm{i}Q_z z}$$
$$= \left(\frac{-2z^* e^2}{\Omega} \right) \int_{-\infty}^{\infty} \frac{\mathrm{e}^{\mathrm{i}Q_z z} \mathrm{d}Q_z}{\alpha^2 + K_x^2 + K_y^2 + Q_z^2} \times \int_{-\infty}^{\infty} \mathrm{d}z \, f^*(k'_z, z) f(k_z, z)$$
$$= \left(\frac{-2\pi z^* e^2}{\Omega} \right) \int_{-\infty}^{\infty} \frac{\mathrm{e}^{-\beta|z|}}{\beta} f^*(k'_z, z) f(k_z, z) \, \mathrm{d}z, \tag{A 3}$$

where

$$\beta^2 = \alpha^2 + K_x^2 + K_y^2, \qquad K_x^2 = (k_x - k'_x)^2, \qquad K_y^2 = (k_y - k'_y)^2. \tag{A 4}$$

From Eq. (23),

$$f(k_z, z) = (\mathrm{e}^{\mathrm{i}k_z z} - \mathrm{e}^{-2\mathrm{i}k_z \delta} \mathrm{e}^{-\mathrm{i}k_z z}), \qquad z \geq 0,$$
$$= \left\{ 2\left(\frac{k_z}{q} \right)^2 + 2\mathrm{i}\left(\frac{k_z}{q} \right) \sqrt{1 - \left(\frac{k_z}{q} \right)^2} \right\} \mathrm{e}^{(q^2 - k_z^2)^{1/2} z}, \qquad z < 0.$$

The origin of coordinates of the wave function has to shifted to the position of the adatom, (0, 0, $-z_a$). Then we have,

$$f(k_z, z) = \mathrm{e}^{\mathrm{i}k_z z_a} \{ \mathrm{e}^{\mathrm{i}k_z z} - \mathrm{e}^{-2\mathrm{i}k_z(\delta + z_a)} \mathrm{e}^{-\mathrm{i}k_z z} \}, \qquad z \geq z_a$$
$$= \mathrm{e}^{(q^2 - k_z^2)^{1/2} z_a} \left\{ 2\left(\frac{k_z}{q} \right)^2 + 2\mathrm{i}\left(\frac{k_z}{q} \right) \sqrt{1 - \left(\frac{k_z}{q} \right)^2} \right\} \mathrm{e}^{(q^2 - k_z^2)^{1/2} z}, \quad z < z_z, \tag{A 5}$$

which is substituted into Eq. (A 3) and the integration is carried out:

$$V_{\mathbf{k}'\mathbf{k}} = (\mathrm{A}\ 3) = \left(\frac{-2\pi z^* e^2}{\Omega} \right) \left[\int_{-\infty}^{0} \frac{\mathrm{e}^{\beta z}}{\beta} f^*(k'_z, z) f(k_z, z) \, \mathrm{d}z \right.$$
$$\left. + \int_0^{z_a} \frac{\mathrm{e}^{-\beta z}}{\beta} f^*(k'_z, z) f(k_z, z) \, \mathrm{d}z + \int_{z_a}^{\infty} \frac{\mathrm{e}^{-\beta z}}{\beta} f^*(k'_z, z) f(k_z, z) \, \mathrm{d}z \right]. \tag{A 6}$$

The first and second integrals in the bracket are readily performed resulting in,

$$(1\text{st}) = \frac{C^*C}{\beta(\beta+S)}, \tag{A 7}$$

$$(2\text{nd}) = \frac{C^*C}{\beta}\left\{\frac{e^{(S-\beta)z_a}-1}{(S-\beta)}\right\}, \tag{A 8}$$

where

$$S = S(k_z, k_z') = \left\{(q^2-k_z^2)^{1/2}+(q^2-k_z')^{1/2}\right\},$$

$$C = C(q, k_z) = e^{(q^2-k_z^2)^{1/2}z_a}\left\{2\left(\frac{k_z}{q}\right)^2+2i\left(\frac{k_z}{q}\right)\sqrt{1-\left(\frac{k_z}{q}\right)^2}\right\} \tag{A 9}$$

In the third integral,

$$f^*f = e^{iK_-z_a}\left\{e^{iK_-z}+e^{-2iK_-(\delta+z_a)}\,e^{-iK_-z}-e^{-2ik_z(\delta+z_a)}\,e^{-iK_+z}\right.$$
$$\left.-e^{2ik_z'(\delta+z_a)}\,e^{iK_+z}\right\}, \tag{A 10}$$

where

$$K_- = k_z-k_z' \quad \text{and} \quad K_+ = k_z+k_z'. \tag{A 11}$$

The substitution of Eq. (A 10) into the third integral yields,

$$\begin{aligned}(3\text{rd}) = {} & e^{iK_-z_a}\left(\frac{e^{-\beta z_a}}{\beta^2+K_-^2}\right)\left[\left\{\left(1+i\frac{K_-}{\beta}\right)\cos K_-z_a-\left(\frac{K_-}{\beta}-i\right)\sin K_-z_a\right\}\right.\\
& \left.+e^{-2iK_-(\delta+z_a)}\left\{\left(1-i\frac{K_-}{\beta}\right)\cos K_-z_a-\left(\frac{K_-}{\beta}+i\right)\sin K_-z_a\right\}\right]\\
& -e^{iK_-z_a}\left(\frac{e^{-\beta z_a}}{\beta^2+K_+^2}\right)\left[e^{-2ik_z(\delta+z_a)}\left\{\left(1-i\frac{K_+}{\beta}\right)\cos K_+z_a\right.\right.\\
& \left.\left.-\left(\frac{K_+}{\beta}+i\right)\sin K_+z_a\right\}\right.\\
& \left.+e^{2ik_z'(\delta+z_a)}\left\{\left(1+i\frac{K_+}{\beta}\right)\cos K_+z_a-\left(\frac{K_+}{\beta}-i\right)\sin K_+z_a\right\}\right].\end{aligned} \tag{A 12}$$

We have thus accomplished the exact calculation of the matrix element. The result is

$$V_{k'k} = \left(\frac{-2\pi z^*e^2}{\Omega}\right)\left[(A\,7)+(A\,8)+(A\,12)\right]. \tag{A 13}$$

Since we are considering an electrical resistance problem, only $|k|=k_f$ should be taken into account for the assumed spherical Fermi surface. Therefore, Eqs. (A 4),(A 9) and (A 11) are transformed as follows:

$$\beta^2 = \alpha^2+K^2-K_z^2 = T^2k_f^2,$$

where

$$T^2 = \left\{\left(\frac{2}{r_0k_f}\right)^2+2-2\cos\Delta\psi\sqrt{(1-u_+^2)(1-u_-^2)}-u_+^2-u_-^2\right\}. \tag{A 14}$$

$$S(k_x, k_x') = \left\{\sqrt{D-u_+^2} + \sqrt{D-u_-^2}\right\} k_f = S_0 k_f , \tag{A 15}$$

where $D = \left(\frac{q}{k_f}\right)^2$.

$$C^*C = e^{-s_0 k_f z_a}\left(\frac{4u_+u_-}{D^2}\right)(u_- + i\sqrt{D-u_-^2})(u_+ - i\sqrt{D-u_+}) . \tag{A 16}$$

$$K_- = (u_- - u_+)\, k_f , \qquad K_+ = (u_- + u_+)\, k_f . \tag{A 17}$$

and

$$\begin{aligned} e^{2ik_z'\delta} &= \left\{1 - \frac{2u_+^2}{D} + i\,\frac{2u_+\sqrt{D-u_+^2}}{D}\right\} = R_+ \\ e^{-2ik_z\delta} &= \left\{1 - \frac{2u_-^2}{D} - i\,\frac{2u_-\sqrt{D-u_-^2}}{D}\right\} = R_- . \end{aligned} \tag{A 18}$$

The resulting form of the matrix element is given by Eq. (30).

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