the contributions of second order by a factor of $0.1|V(\vec{G})|_{max}/E_F$, where E_F is the Fermi energy. This factor is less than 0.01.

It should be noted that in the sums in Eqs. (19) the terms corresponding to the first two or three nearest-neighbor reciprocal-lattice vectors dominate. As it turns out, the contribution of the nearest-neighbor reciprocal-lattice vector comes in with a sign opposite to that of the next two nearest neighbors due to the factor $\sin(2\vec{G}\cdot\vec{\tau})$. Also, for each metal the magnitude of the nearest-neighbor reciprocal-lattice vector is close to the value of q at which $W(q)$ has its first zero. As a result, comparatively small changes in the bare-ion model potential can significantly affect the contributions to P and Q, even to the extent of changing the signs of these contributions, decreasing thereby the value of $|P+iQ|$.

The principal source of error in the present calculations is probably to be found in the choice of a bare-ion model potential. It is possible that a different choice from that made here could lead to an improvement in the agreement between theory and experiment. Nevertheless, it is still gratifying that the simple calculation described here is capable of yielding values of the Raman tensors of Be, Mg, and Zn which are in order-of-magnitude agreement with such experimental values as exist.

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Effect of Weak Surface Autocorrelation on the Size Effect in Electrical Conduction

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Correlation between points on a conductor surface may be important in explaining the relatively large specularity parameters attributed to measurements in single-crystal samples. An expression for the size effect in the electrical conductivity is obtained that takes into account the effect of weak surface autocorrelation. The expression shows that, as expected, the correlation increases the electrical conductivity. It also shows that even an angle-dependent specularity parameter may not be an adequate description in the sense of the Fuchs model. Numerical estimates are given for the size effects due to surface roughness and autocorrelation. These are explained in terms of the competing effects of flux conservation and surface asperity slopes.

Most descriptions of the effect of surface scattering of conduction electrons have employed the constant specularity parameter p as introduced by Fuchs.[1] It has generally been recognized that a constant p is not likely to provide a realistic description of this process, except under simplifying conditions.[2] If the surface scattering is due to random surface charges, the specularity parameter may depend on the angle of incidence of the electron's wave vector and the surface and may also differ from the magnitude expected on the basis of the reflection coefficient.[3] Surface roughness also is expected to produce an angle-dependent specularity parameter.[4] In addition, the degree of correlation between the heights of various points on the surface should have an effect on the detailed nature of the portion of the scattered flux usually described as "diffuse." With increasing autocorrelation of the surface heights, the "diffuse" flux should have a narrower distribution about the specular beam. This leads to a finite, increasing contribution of this flux to the current, as correlation increases. Because of this, the effect of surface-height variation in increasing the electrical resistivity should be diminished.

Recently methods for observing the effect of angular dependence of p have been proposed.[5–7] It seems appropriate to consider the effect of finite correlation at this point. This might be important in explaining observations of apparently nondiffuse scattering in metals, especially in single crystals, even though the deBroglie wavelengths of electrons at the Fermi surface are of the order of interatomic spacings.[8] It is hard to believe that the surface height will not vary by more than atomic dimensions, even in a single crystal. However, it seems likely that, on single-crystal or even polycrystalline or abraded crystalline sample surfaces, there may be sufficient short-range, or even long-range, order for correlation to be an important factor. (An experimental test of this might be the use of an amorphous surface.)

The purpose of this paper is to give estimates of the effect of surface autocorrelation on the electrical conductivity size effect and to consider the question of the existence of an angle-dependent p in the presence of correlation.

The basic theory has been given in Ref. 4. The solution of the boundary-value problem involves solving a Fredholm integral equation and appears to be quite difficult in the general case. However, in the presence of weak correlation, $L \ll \lambda$, where L is the correlation length and λ the deBroglie wavelength, the problem is not as formidable. This case is considered here.

We summarize the boundary condition for a sample filling all space between planes at $z=0$ and $z=t$, for the surface at $z=0$. The distribution function deviates from the Fermi distribution f_0 by $f_1^{\pm}(\vec{v}, z)$ where the $+(-)$ sign is for electrons leaving (approaching) the surface. The boundary condition is

$$f_1^{+}(\vec{v}, 0) = \int d\Omega_0 P(\Omega_0, \Omega) f_1^{-}(\vec{v}_0, 0), \tag{1a}$$

$$f_1^{\pm}(\vec{v}, z) = f_1^{b}(\vec{v})[1 + \Phi^{\pm}(\vec{v}) e^{-z/lu}], \tag{1b}$$

$$f_1^{b}(\vec{v}) = eEl \frac{v_x}{v} \frac{\partial f_0}{\partial \epsilon}, \tag{1c}$$

where the integration is over $\frac{1}{2}\pi < \theta_0 < \pi$, allowed angles of incidence with the inward-pointing surface normal, $u = \cos\theta$, l is the bulk mean free path, and the electric field E in the $-x$ direction is parallel to the surface. $f_b^1(\vec{v})$ is the bulk deviation from f_0. The transition probability between incident angles $\Omega_0(\theta_0, \varphi_0)$ and emerging angles $\Omega(\theta, \varphi)$, $0 < \theta < \frac{1}{2}\pi$ is given by

$$P(\Omega_0, \Omega) = [\epsilon(\Omega_0)]^{-1} \delta(\alpha)\delta(\beta) + [1 - p_s(\theta_0)] \times c(\Omega_0, \Omega)/c(\Omega_0), \tag{2a}$$

$$c(\Omega_0, \Omega) = (L^2/4\pi) e^{-\langle\phi^2\rangle\gamma^2} \sum_{n=1}^{\infty} \frac{(\langle\phi^2\rangle\gamma^2)^n}{n!\,n} \times e^{-(L^2/4n)(\alpha^2+\beta^2)}, \tag{2b}$$

$$c(\Omega_0) = \int d\Omega\, c(\Omega_0, \Omega), \tag{2c}$$

$$\epsilon(\Omega_0) = \int d\Omega\, \delta(\alpha)\, \delta(\beta), \tag{2d}$$

$$\langle\phi^2\rangle = (2\pi h/\lambda)^2, \tag{2e}$$

$$p_s(\theta_0) = e^{-4\langle\phi^2\rangle u_0^2}, \tag{2f}$$

where

$$\alpha = (2\pi/\lambda)(\sin\theta_0 \cos\varphi_0 - \sin\theta \cos\varphi), \tag{3a}$$

$$\beta = (2\pi/\lambda)(\sin\theta_0 \sin\varphi_0 - \sin\theta \sin\varphi), \tag{3b}$$

$$\gamma = \cos\theta - \cos\theta_0 = u - u_0. \tag{3c}$$

Here h is the rms surface-height variation and L is the correlation length from the normal distributions assumed for the height distribution and autocorrelation functions in Ref. 4. For like surfaces, we have

$$\Phi^{-}(\vec{v}_0) = \Phi^{+}(\vec{v}_0) e^{K/u_0}, \tag{4}$$

where $K = t/l$. Substitution of Eq. (1b) into (1a) using (4) gives a Fredholm equation for $\Phi^{+}(\Omega)$:

$$\Phi^{+}(\Omega) = F(\Omega) + \Gamma \int d\Omega_0 K(\Omega_0, \Omega) \Phi^{+}(\Omega_0). \tag{5}$$

Writing all quantities in the form $Q = Q^{(0)} + Q^{(L)}$, where $Q^{(0)}$ is evaluated in the absence of correlation and $Q^{(L)}$ is the lowest-order correction caused by correlation, upon subtracting the zero-order solution $\Phi^{+(0)}(\Omega)$, we get to lowest order

$$\Phi^{+(L)}(\Omega) = F^{(L)}(\Omega) + \Gamma \int_{(\theta_0 > \pi/2)} d\Omega_0 \times [K^{(L)}(\Omega_0, \Omega)\Phi^{+(0)}(\Omega_0) + K^{(0)}(\Omega_0, \Omega)\Phi^{+(L)}(\Omega_0)]. \tag{6}$$

Explicitly, we find

$$F^{(0)}(\Omega) = -[1 - p_s(\theta)]/[1 - p_s(\theta)e^{-K/u}] + \{f_1^{b}(\Omega)[1 - p_s(\theta)e^{-K/u}]\}^{-1} \times \int_{(\theta_0 > \pi/2)} d\Omega_0 f_1^{b}(\Omega_0)[1 - p_s(\theta_0)] R^{(0)}(\Omega_0, \Omega), \tag{7a}$$

$$F^{(L)}(\Omega) = \{f_1^{b}(\Omega)[1 - p_s(\theta)e^{-K/u}]\}^{-1} \int_{(\theta_0 > \pi/2)} d\Omega_0 f_1^{b}(\Omega_0)[1 - p_s(\theta)] R^{(L)}(\Omega_0, \Omega), \tag{7b}$$

$$\Gamma K^{(0)}(\Omega_0, \Omega) = \{f_1^b(\Omega)[1 - p_s(\theta)e^{-K/u}]\}^{-1} f_1^b(\Omega_0)[1 - p_s(\theta_0)] R^{(0)}(\Omega_0, \Omega) e^{-K/|u_0|}\,, \tag{7c}$$

$$\Gamma K^{(L)}(\Omega_0, \Omega) = \{f_1^b(\Omega)[1 - p_s(\theta)e^{-K/u}]\}^{-1} f_1^b(\Omega_0)[1 - p_s(\theta_0)] R^{(L)}(\Omega_0, \Omega) e^{-K/|u_0|}\,, \tag{7d}$$

where

$$c(\Omega_0, \Omega)/c(\Omega_0) = R^{(0)}(\Omega_0, \Omega) + R^{(L)}(\Omega_0, \Omega). \tag{8}$$

Using the expansion to lowest order in L/λ, we obtain

$$\exp[-(L^2/4n)(\alpha^2+\beta^2)] = 1 - (\eta/n)$$
$$\times[(\sin\theta_0 \cos\varphi_0 - \sin\theta \cos\varphi)^2$$
$$+ (\sin\theta_0 \sin\varphi_0 - \sin\theta \sin\varphi)^2]\,,$$

where

$$\Gamma \to \eta \equiv (\pi L/\lambda)^2 \tag{9}$$

is a natural parameter for the strength of the correlation.

If Eqs. (7) and (8) are evaluated explicitly, there is considerable simplification due to the vanishing of several of the integrals over azimuthal angles:

$$\Phi^{+(L)} = [1 - p_s(u)e^{-K/u}]^{-1} \int_0^1 du'(1-u'^2)[1 - p_s(u')]$$
$$\times\{(1 - e^{-K/u'})/[1 - p_s(u')e^{-K/u'}]\}\mathcal{L}(u, u')\eta\,, \tag{10a}$$

$$\mathcal{L}(u, u') = S_2[\langle\phi^2\rangle^{1/2}(u+u')]/\int_0^1 du''$$
$$\times S_1[\langle\phi^2\rangle^{1/2}(u'+u'')]\,, \tag{10b}$$

$$S_m(\chi) \equiv e^{-\chi^2} \sum_{n=1}^{\infty} \frac{\chi^{2n}}{n!\,n^m}\,; \tag{10c}$$

without correlation,

$$\Phi^{+(0)}(\Omega) = -[1 - p_s(u)]/[1 - p_s(u)e^{-K/u}]. \tag{11}$$

Substitution into the expression for conductivity σ relative to bulk σ_0:

$$\sigma/\sigma_0 = 1 - (\tfrac{3}{2}K)\int_0^1 du(u-u^3)\Phi^+(u)[e^{-K/u} - 1] \tag{12}$$

gives the result

$$\frac{\sigma}{\sigma_0} = \left(\frac{\sigma}{\sigma_0}\right)^{(0)} + \left(\frac{\sigma}{\sigma_0}\right)^{(L)} = 1 - (\tfrac{3}{2}K)\int_0^1 du(u-u^3)$$
$$\times \frac{(1-e^{-K/u})}{[1 - p_s(u)e^{-K/u}]}\int_0^1 du'[1 - p_s(u')]$$
$$\times\left(\delta(u-u') - \eta\frac{(1-u'^2)(1-e^{-K/u'})}{[1 - p_s(u')e^{-K/u'}]}\mathcal{L}(u, u')\right)\,. \tag{13}$$

From this expression two things are immediately apparent. To this order, at least (and presumably to any order), one gets the expected increase of conductivity due to the correlation term. Also, although in the absence of correlation the Fuchs conductivity appears, with p depending on angle as $p_s(u)$, this is no longer true under the influence of correlation. That is, the factor $[1 - p_s(u)]$ is replaced by a more complicated expression, but the factor $[1 - p_s(u)e^{-K/u}]^{-1}$ is not. Physically, the "diffuse" scattering is contributing, as described above; this is quite different from a simple lowering of the amplitude of the specular beam.

To get some idea of the effect of correlation, approximate numerical evaluations of the zero-order and first-order terms in Eq. (13) were carried out. The quantity $(\sigma/\sigma_0)^{(L)}/\eta$ was evaluated by using the Gaussian integration procedure and a three-point interpolation scheme for $S_m(x)$, which is plotted in Fig. 1. [Four (and occasionally as a check, six) points were used. The third figure may not always be fully significant, although in most cases it is.] $(\sigma/\sigma_0)^{(L)}/\eta$ and $1 - (\sigma/\sigma_0)^{(0)}$ are plotted in Fig. 2. These quantities represent the increase and decrease of the relative conductivity due to finite and zero correlation, respectively. The resultant resistivity size effect

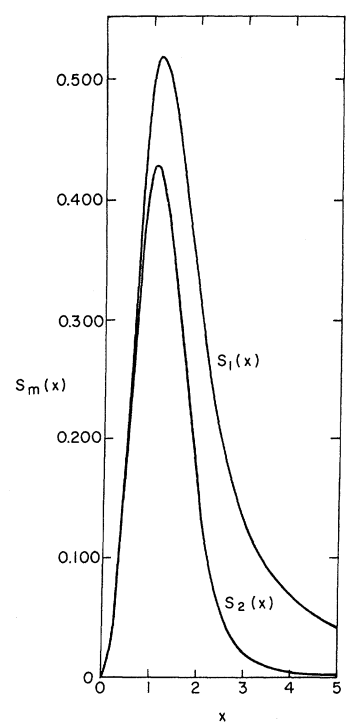

FIG. 1. Plots of the universal functions $S_m(x)$ for $m=1$ and 2.

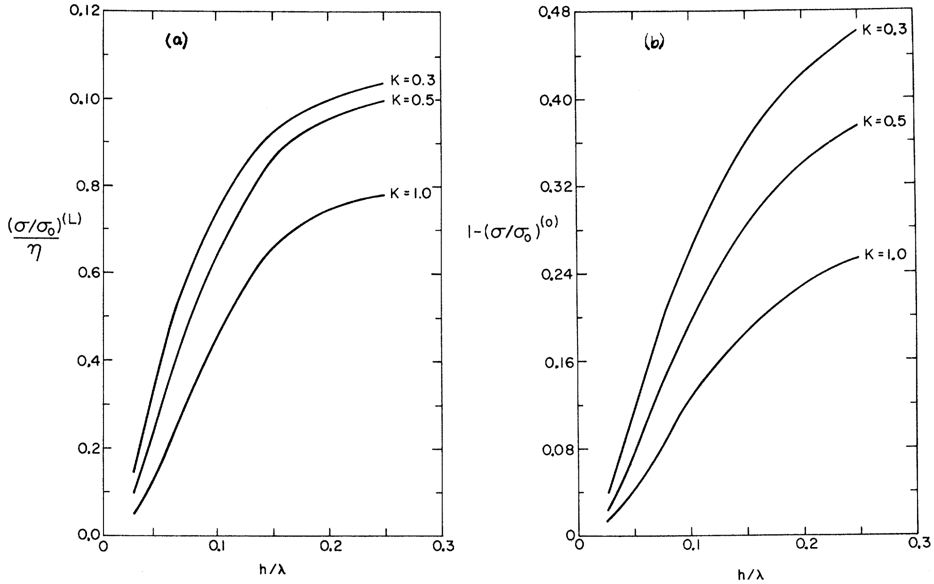

FIG. 2. (a) Contribution of correlation to the conductivity size effect is plotted against roughness h/λ for various t/l; (b) for comparison, the decrease of relative conductivity in the absence of correlation is shown.

$(\rho-\rho_0)/\rho_0$ is plotted in Fig. 3 for the thinnest case considered, $K=0.3$. (This is done only up to $\eta=0.1\approx L/\lambda$, since for higher values the next-order term is likely to be significant.)

From Fig. 2, it is seen that the correlation effect $(\sigma/\sigma_0)^{(L)}$ for fixed η rises with increasing roughness and starts to level off. This leveling off is more noticeable than in the zero correlation effect. An explanation offered for this behavior of the correlation effect is that there are two opposing effects contributing to its roughness dependence. One is that, as roughness is increased, the amount of flux in the "diffuse" channel increases, roughly as some average of $1-p$. This was included in the original model by imposing flux conservation.[4] Eventually, this saturates at about unity, since most of the electrons which reach the surface without internal scattering (which produces the size effects) are at angles nearer the normal, in which p becomes rapidly smaller, as h/λ is raised. Since the "diffuse" channel contributes to an increase in conductivity, this causes an increase in this effect. As saturation occurs, another effect takes over. This is the effect of increasing asperity slope as h/L is increased. The quantity should be more significant than L/λ itself. As h/L is raised, the "diffuse" flux should become more nearly isotropic. (It is shown in Ref. 4 that in this limit the flux density does not become truly isotropic, but rather becomes symmetric about the normal, as well as smaller, which still leads to no contribution to the current in the Fuchs case.) This means its contribution to raising the conductivity is diminished. Thus, it would appear that the roughness dependence of the correlation contribution to the conductivity can be explained as an increasing contribution of the "h/L" or slope effect as the "$1-p$" or flux-conservation effect saturates.

Figure 3 shows the over-all magnitude of the combined effects on the resistivity for $K=0.3$. In the roughest case considered, $h\approx\frac{1}{4}\lambda$, the effect of correlation is no more than about 3% of the size effect in the strongest correlation case considered, $L\approx\frac{1}{10}\lambda$. Of course, in a more general calculation, these effects could be much larger. In particular, as $L/\lambda\to\infty$, the correlation effect exactly cancels the zero correlation contribution, giving bulk resistivity.[4]

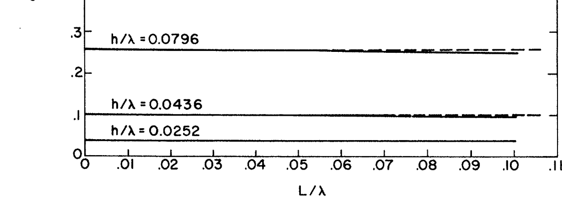

FIG. 3. Over-all effect of correlation and roughness on the resistivity size effect is shown for a range of correlation in which the model is assumed to be valid. Horizontal dashed lines denote the size effect in the absence of correlation.

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Many-Electron Theory of Nondirect Transitions in the Optical and Photoemission Spectra of Metals*

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The theory of the singular readjustment of a conduction band to a hole formed in an x-ray absorption event is extended to the case where the hole has finite mass, as in the *d* band of Cu. Although the resulting recoil removes the singularity, the effect may still be quite large, and results in an electron-induced Debye-Waller-factor reduction of the intensity of direct (*k*-conserving) optical or photoemission events. This reduction depends on the mass of the *d*-band hole, and is accompanied by inelastic contributions in which the photon energy is shared between an interband transition and a number of low-energy electron-hole pairs.

I. INTRODUCTION: HOLE PROPAGATOR

When an x ray is absorbed by a core electron in a metal, the consequent readjustment of the Fermi-gas conduction electrons to the hole potential has the singular character of an infrared divergence. This singularity was discovered by Mahan[1] and further investigated by Nozières and co-workers.[2,3]

In the present paper we suggest that a similar effect, though not singular as in the x-ray case, will occur when electrons in a narrow band (such as a *d* band) lying below the Fermi level are excited by some sort of radiation.

In the core-state case, Doniach and Sunjic[4] showed that the infrared singularity (suitably smeared by lifetime effects) would show up directly in the form of the low-energy tail in the line shape of emitted photoelectrons from the metal. In the present narrow-band case, too, we show that the relaxation of the Fermi sea of electrons around the narrow-band hole will lead to enhancement of weakly inelastic (1–2 eV)events during a uv photoemission process. The magnitude of this effect depends on the strength of the effective screened potential for conduction-electron-hole scattering, which is not known at the present time, but the effect possesses certain characteristic qualitative features which should allow it to be distinguished from other inelastic photoproduction mechanisms in the metal.

In the core-state case the infrared divergence is found theoretically from a study of the hole correlation function, or propagator (whose Fourier transform is directly related to the spectrum of photoelectrons in a photoemission experiment):

$$g(t) = i\langle b(t) b^{+}(0)\rangle , \qquad (1)$$

where b^+ is a creation operator for the core-state hole. The divergence shows up as a power-law behavior $g(t) \sim t^{-\alpha}$ for long times, which may be thought of as resulting from the fact that the production of zero-energy electron-hole pairs at the Fermi surface becomes infinitely probable; i.e., the lower the energy of the pairs, the more that will be produced. In the case of hole states in a narrow band, the hole creation operators are now labeled by a momentum suffix $b_K^\dagger$. The change in the physics is that the hole undergoes recoil during the emission and reabsorption of low-energy pairs, and the resulting recoil energy removes the zero-energy denominators, which lead to the divergence in the infinite-mass case. However, we suggest that the many low-energy pair scatterings will still be enhanced in the case of large hole mass (narrow hole band) relative to the perturbation-theory result (for a single electron-hole pair), leading to a propagator with spectral density of the form [Fourier transform of (1)]

$$\operatorname{Im} g_K(\omega) = A_K \delta(\omega - E_K) + \varphi_K(\omega) , \qquad (2)$$

where hole-lifetime effects due to recombination and scattering have been neglected.

The above result is based on a "pseudoharmonic" treatment of the perturbation of the electron-gas density by the hole potential. The reduction of the δ function part by the factor A_K is a kind of electron-