Henry and C. G. B. Garrett, Phys. Rev. 171, 1058 (1968).

[8] W. D. Johnston and I. P. Kaminow, Phys. Rev. 188, 1209 (1969).

[9] Unpublished index of refraction data of G. D. Boyd were used. See in addition, G. D. Boyd, F. R. Nash, and D. F. Nelson, Phys. Rev. Lett. 24, 1298 (1970); C. J. Johnson, G. H. Sherman, and R. Weil, Appl. Opt. 8, 1667 (1969).

[10] J. H. McFee, G. D. Boyd, and P. H. Schmidt, Appl. Phys. Lett. 17, 57 (1970).

[11] B. F. Levine and C. G. Bethea, Appl. Phys. Lett. 20, 272 (1972).

[12] Our measurement agrees with the work of C. C. Wang and N. W. Ressler, Phys. Rev. 132, 1827 (1970).

[13] C. Flytzanis, Phys. Lett. 31A, 273 (1970).

[14] D. E. Aspnes, Phys. Rev. Lett. 26, 1429 (1971).

[15] D. C. Haueisen and H. Mahr, Phys. Rev. Lett. 26, 838 (1971); D. Fröhlich, E. Mohler, and P. Wiesner, *ibid.* 26, 554 (1971).

Electronic Density of States at Transition-Metal Surfaces

R. Haydock, Volker Heine, M. J. Kelly, and J. B. Pendry
Cavendish Laboratory, Cambridge, England

(Received 7 August 1972)

A completely real-space solution of the tight-binding Hamiltonian has allowed a realistic interpretation of ion-neutralization spectroscopy and some ultraviolet photoelectron spectroscopy data in terms of the surface density of states at transition-metal surfaces. The rms width of the d-band density of states decreases as the square root of the coordination number of surface atoms. The extent to which this is observed depends on the surface sensitivity of the experimental technique.

Recent experimental results of Eastman,[1] using ultraviolet photoelectron spectroscopic techniques (UPS), show that with increasing energy of the incident photon the rms width of the optical density of states in Ni narrows from ~2.5 eV for 21.2-eV photons to ~2.0 eV for 40.8-eV photons. Measurements on Cr and Cu, but only for lower incident photon energy, show a similar but less marked narrowing for Cr, but no narrowing for Cu. Published data for ion neutralization spectroscopy (INS) from Ni and Cu surfaces[2] show a surface d-band density of states consistent with the same overall width as the bulk bands[3] but having a single central peak and smaller rms width [Fig. 1]. All these observations seem to us to be explicable in terms of the surface sensitivity of the experimental technique, and, in the case of INS results, can be compared with calculations performed to establish the effect of the surface environment on the density of states. By the latter we mean the local[4] density of states at the surface $\mathfrak{N}_s(E)$, namely, the density of levels $\mathfrak{N}(E)$ weighted by the probability density $|\psi|^2$ of the states of energy E at a surface atom.

The main qualitative effect, namely, the reduction in the rms width of the density of states at the surface, can be understood simply in two ways. Firstly, for tight-binding bands Cyrot-Lackmann[5,6] has shown that the second moment μ_2 of $\mathfrak{N}_s(E)$ [or of $\mathfrak{N}(E)$ in the bulk] is proportional to the number of nearest neighbors z. This is rigorously true for a tight-binding band of s states and approximately so for d bands. Thus the rms width varies as $\sqrt{z}$, where $z=7$, 8, 9 for (110), (100), and (111) surfaces on face-centered cubic metals, compared with $z=12$ in the bulk. Secondly we have the behavior of $\mathfrak{N}_s(E)$ at the band maximum

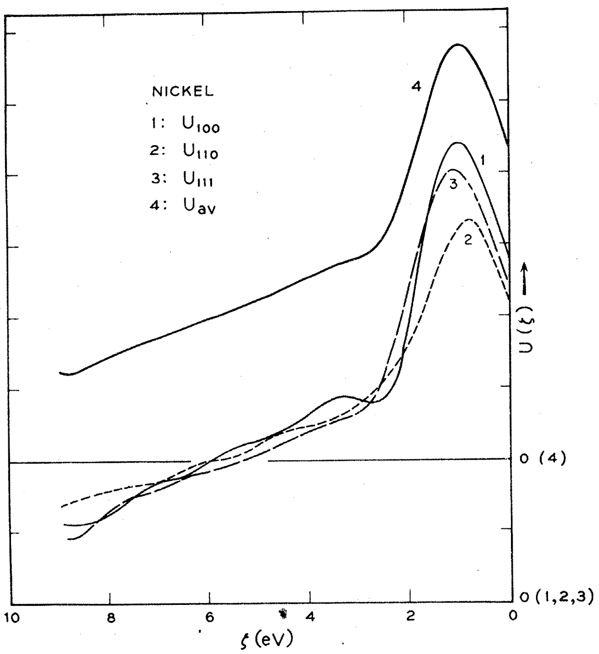

FIG. 1. The density of states, as measured by INS, at the three principal surfaces of Ni from experimental results of Hagstrum.

or minimum E_m. Whereas $\mathfrak{N}(E)$ rises rapidly proportional to $|E - E_m|^{1/2}$, at the surface $\mathfrak{N}_s(E)$ varies more slowly as $|E - E_m|^{3/2}$. This result, first asserted by Kalkstein and Soven,[7] can easily be proved for a tight-binding band.[8] The gist of the argument is to note that the wave functions tend smoothly to zero at the surface, which means that for long wavelengths ψ on the surface atom is reduced, being proportional to the wave vector k measured from the extremum in the Brillouin zone. The net effect is to suppress the edges of the band in $\mathfrak{N}_s(E)$ and correspondingly enhance the center.

Turning to the photoemission results, we note that only electrons generated within a distance λ of the surface escape from the specimen to be collected.[9] Here λ is the mean free path for electrons of the collecting energy, which can be obtained from an analysis of low-energy electron-diffraction measurements. Published work on Cu,[10] together with some further unpublished work, indicated that Σ_i, the imaginary part of the electron self-energy, has the value $\Sigma_i \approx -1$ eV for $5 < E - E_\mathrm{F} < 15$ eV and then a sharp increase to $\Sigma_i \approx -4$ eV for $20 < E - E_\mathrm{F} < 30$ eV for secondary electron energy and Fermi energy E_F. Quantitative values do not differ substantially for Ni. From a simple scattering picture, the relationship $\lambda \propto E^{1/2}/\Sigma_i$ can be interpreted as a value for λ of 15 Å at lower energies, decreasing to 4 Å at higher energies. Also as λ decreases, the surface part of the optical matrix element[9] will account for an increasing fraction of the total yield. We conclude therefore that secondary emission in the 20–40-eV range will sample only the surface layer, while at progressively lower energies the subsurface layers are sampled to a greater extent. We immediately have an explanation of the narrowing of the d-band contribution to the density of states for Ni in UPS, and the absence of narrowing in Cu at the lower incident energy ranges in which it is measured. We could expect that higher-energy incident light would show up this narrowing. We can further tentatively conclude that a decrease in λ for Cr at low energies would account for the band narrowing experimentally observed in UPS. Incidentally, λ increases again for $E - E_\mathrm{F} > 50$ eV and this might be observable with synchroton radiation. Of course other factors, such as the density of final states, also affect the measured yield of photoelectrons though we see no obvious reason why they should give a similar systematic variation with energy. In any case we believe the theory shows that the behavior of $\mathfrak{N}_s(E)$ must be considered as one factor contributing to the rms width of the d-band spectrum.

As regards the ion neutralization data, the ejected electrons originate largely from the surface atomic layer.[2,11] It is therefore not surprising that the d band has a smaller rms width than expected from the bulk density of states. Before proceeding to our detailed calculations of this effect, it is necessary to explain briefly the new theoretical method[12] we have used.

One of the central assumptions of Bloch's theorem, namely, the infinite extent of the regular lattice, clearly has to be removed to obtain a realistic theory of many surface phenomena. Our method is therefore formulated in terms of some chosen atom, atom 0 say, and its local atomic environment. We consider a tight-binding band of d states, ignoring the hybridizing plane-wave band for present purposes. Let $|m,j\rangle$ with $m = -2$ to $+2$ be a d orbital on atom j. Then $\mathfrak{N}_0(E)$, the density of states on atom 0, can be written in terms of the Green's function:

$$\mathfrak{N}_0(E) = -\frac{1}{\pi}\sum_m \lim_{\epsilon\to\infty} \operatorname{Im} G_{m0}(E + i\epsilon), \tag{1}$$

$$G_{m0}(E) = \langle m, 0|(E - H)^{-1}|m, 0\rangle, \tag{2}$$

where H is the Hamiltonian. We consider the basis states on different atoms orthogonal though there is no difficulty in removing this restriction if desired. Our method[12] consists of writing Eq. (2) as an infinite continued fraction

$$G_{m0}(E) = \cfrac{1}{E - a_0 - \cfrac{b_1^2}{E - a_1 - \cfrac{b_2^2}{E - \cdots}}}, \tag{3}$$

the coefficients a_n and b_n being obtained from a set of normalized basis states $|n\}$, $n = 0, 1, 2, \cdots$, defined by a recursion formula,

$$N_{n+1}|n+1\} = H|n\} - a_n|n\} - b_n|n-1\}. \tag{4}$$

In this formula $|n+1\}$ is obtained from $H|n\}$ by orthogonalizing the latter to $|n\}$ and $|n-1\}$, the N_{n+1} then being the extra normalizing constant: $H|n\}$ is automatically orthogonal to $|r\}$ for $r < n - 1$. The recursion process is started off by choosing $|0\}$ as $|m, 0\rangle$, which can be taken at a surface, or in the bulk or elsewhere. By taking the matrix elements of Eq. (4) with $\{n|$, $\{n-1|$, $\{n-2|$, etc., we see that H has tridiagonal form in terms of this basis set, from which Eq. (3) follows easily.[13] A more complete description of the process will be published elsewhere.[12,14] The

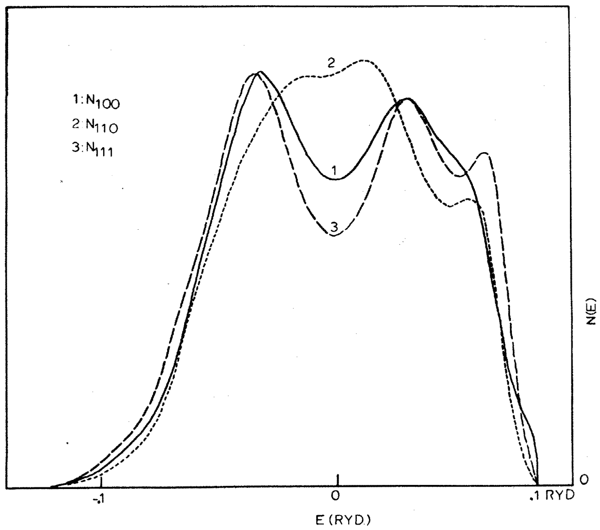

FIG. 2. Surface density of states for the three principal surfaces of a model fcc d-band resonance.

functions $|n\}$ are stored in the computer as column vectors in terms of the $|m,j\rangle$ basis states.

Some of our calculations for Ni are shown in Fig. 2. The d-band density of states at the surface was calculated using the Slater-Koster[15] overlap parameters as determined by Pettifor[16] from his resonance model claimed to be similar to the d band in Ni. The first four pairs of coefficients a_n, b_n in Eq. (3) were obtained from Eq. (4) which means that the first eight moments of our density of states are exact.[17] Subsequent coefficients were put equal to the asymptotic values a_∞, b_∞ determined by the band extrema.[12,17] Our bulk density of states agrees well with Pettifor's,[12,16] giving us confidence in our surface results. We are well aware, however, that we have ignored the important effect that surface dilation of interatomic spacing may have on the local overlap parameters. In Fig. 2 we present the results for the surface density of states at the (100), (110), and (111) surfaces for our model fcc d band. One is immediately faced with the problem that the scale on which these results are presented is of the same order of magnitude as the resolution of most experimental techniques. A more detailed account of the relation of this fine structure to the corresponding structure in the bulk will be published elsewhere.[14] In order to proceed we decided to smooth out the detail by using an Edgeworth series[18] approximation which is of the form of a polynomial in the first four moments, modulated by a single Gaussian whose half-width is related to the second moment. We consider this a reasonable guess at representing the lifetime broadening of the final d-hole states. The effect of this smoothing is to give $\mathcal{N}_s(E)$ a single central peak similar to the observed spectra. To locate the Fermi level E_{F} we assumed the d band of Ni contained 9.5 d electrons per atom at the surface as well as in the bulk. The peak position E_p relative to E_{F} is listed in Table I, together with the experimental data of Hagstrum and Becker[2] and their ratio. The agreement of the ratio for the (100) and (111) faces could be interpreted as meaning that our model resonance width is a bit too narrow. The anomalous result for the (110) face (which has the lowest coordination number) suggests that the accumulation of our approximations has become too severe. The experimental data for Cu indicate that the (110)-face results are also anomalous in terms of peak position.

TABLE I. Nickel surface densities of states; peak position with respect to the Fermi level in eV.

Face	Experiment (INS)	Theory	Ratio
(110)	−0.77	−0.83	0.94
(100)	−1.0	−0.85	1.18
(111)	−1.07	−0.91	1.18

We conclude that there are strong theoretical reasons for the density of states at a surface to differ from $\mathcal{N}(E)$ in the bulk, and that detailed calculations can be made for a tight-binding band using our new method. We believe the effect is a contributing factor to the narrowed band shapes by ion neutralization spectroscopy and photoemissions.

We are indebted to P. W. Anderson, H. D. Hagstrum, and D. E. Eastman for stimulating conversations and to the last for making available his unpublished results. Two of us gratefully acknowledge financial support, R. H. from The Atomic Energy Research Establishment, Harwell, and M. J. K. from a Unilever Scholarship and a New Zealand Postgraduate Scholarship.

---

[1] D. E. Eastman, in Proceedings of the International Conference on Electron Spectroscopy, Asilomar—Pacific Grove, California, 1971 (North-Holland, to be published).

[2] H. D. Hagstrum and G. E. Becker, Phys. Rev. 159, 572 (1967). For the most recent extensive article see H. D. Hagstrum and G. E. Becker, J. Chem. Phys. 54, 1015 (1971).

[3] L. Hodges, H. Ehrenreich, and N. D. Lang, Phys. Rev. 152, 505 (1966).

[4] C. Kittel, *Quantum Theory of Solids* (Wiley, New York, 1963), p. 339.

[5] F. Cyrot-Lackmann, Advan. Phys. 16, 393 (1967).

[6] F. Cyrot-Lackmann, J. Phys. Chem. Solids 29, 1235 (1968).

[7] D. Kalkstein and P. Soven, Surface Sci. 26, 85 (1971).

[8] V. Heine and M. J. Kelly, to be published; V. Heine, to be published.

[9] W. L. Schaich and N. W. Ashcroft, Phys. Rev. B 3, 2452 (1971).

[10] J. B. Pendry, J. Phys. C: Proc. Phys. Soc., London 4, 2514 (1972).

[11] V. Heine, Phys. Rev. 151, 561 (1966).

[12] R. Haydock, V. Heine, and M. J. Kelly, to be published.

[13] The standard cofactor inversion of a matrix leads to the development of a continued fraction.

[14] R. Haydock and M. J. Kelly, to be published.

[15] J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).

[16] D. G. Pettifor, J. Phys. C: Proc. Phys. Soc., London 2, 1051 (1969), and 3, 367 (1970).

[17] J. A. Shohat and J. D. Tamarkin, *The Problem of Moments* (American Mathematical Society, New York, 1943).

[18] We follow the procedure of F. Ducastelle and F. Cyrot-Lackmann, J. Phys. Chem. Solids 31, 1295 (1970), who quote M. G. Kendall and A. Stuart, *The Advanced Theory of Statistics* (Charles Griffin, London, 1963), Vol. 1.

Spherical-Wave Neutron Propagation and Pendellösung Fringe Structure in Silicon*

C. G. Shull and J. A. Oberteuffer
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

(Received 11 August 1972)

We have studied neutron Pendellösung fringe patterns within the Bragg reflection from perfect silicon crystals. The patterns as obtained with a full-spectrum incident beam show that the coherent wave front of the neutron radiation must be considered as spherical rather than planar, and also that the crystals under study possess a uniformly curved distortion. The extended fringe patterns permit a precision determination of the coherent nuclear scattering amplitude for silicon of $0.414\,91(10)\times 10^{-12}$ cm per nucleus.

An earlier study[1] has demonstrated the appearance of Pendellösung fringe structure within the Bragg reflection of neutrons from perfect crystals of silicon under suitably controlled physical conditions. This interference-fringe structure arises from the coherent addition of different traveling waves in the crystal while under Bragg reflecting conditions. It was assumed in the above study that the coherent neutron wave field was to be described as a plane wave, and accordingly the Pendellösung fringe characteristics were interpreted quantitatively on the basis of plane wave (PW) theory. It has been shown, however, by Kato[2] that the treatment of dynamical diffraction theory with spherically coherent wave fields, spherical-wave theory (SW), leads to small but not insignificant differences relative to the PW treatment in the interference characteristics. Moreover, a series of x-ray diffraction experiments have been performed by Kato and by others which demonstrate the applicability of either SW or PW theory, depending upon experimental conditions. Accordingly, the earlier neutron study has been extended to test the applicability of the theory and to improve materially the quantitative interpretation of the fringe structure, leading to a precision determination of the silicon scattering amplitude. It has been found that, under the conditions of the experiment, indeed SW theory must be used to describe the neutron fringe characteristics.

The experiments have been performed with collimated neutron radiation being delivered to a symmetrically transmitting crystal (Laue geometry) as described in the inset of Fig. 1. An exit slit opening placed on the back side of the parallel-faced crystal plate can be used to scan over the linear width of the Bragg reflection. With PW theory, the distribution of intensity across the band of Bragg reflection as a function of the parameter $\gamma=\tan\epsilon/\tan\theta$ is given by

$$I_{\mathrm{PW}}(\gamma)=C(1-\gamma^2)^{-1/2}\sin^2[A(1-\gamma^2)^{-1/2}\tan\theta], \quad (1)$$

where $A=2tNF_{hkl}d$, with t the crystal thickness, d the interplanar spacing, N the unit cell density, θ the Bragg angle, and F_{hkl} the crystal structure factor per unit cell. F_{hkl} depends upon the atomic scattering amplitude b, and for the silicon (111) reflection characteristic of all of the present re-