

Ion-Neutralization Spectroscopy*

Homer D. Hagstrum

Bell Telephone Laboratories, Murray Hill, New Jersey 07974

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The ion-neutralization spectroscopy (INS) is discussed in comparison with other spectroscopies of solids. It is shown that INS probes the local density of states of the solid at or just outside the solid surface. It is believed that this accounts for the clear-cut differences between INS results and those of other spectroscopies. Because of its unique specificity to the surface region INS is particularly useful in studying the surface electronic structures of atomically clean surfaces and of surfaces having ordered arrays of known atoms adsorbed upon them. In the latter case INS determines a portion of the molecular orbital spectrum of surface molecules formed from the adsorbed foreign atom and surface atoms of the bulk crystal. Such spectra provide information on local bonding symmetry and structure and electrical charging within the surface molecule which is as yet unavailable by any other method. INS is the first attempt to base a spectroscopy of electronic states on a two-electron process. More recent work on experimental and mathematical problems which such a spectroscopy entails are also briefly mentioned in this paper.

Key words: Auger processes; autoionization; density of states; ion-neutralization; transition probability.

1. Introduction

In general, spectroscopies of electronic states have been based on the absorption or emission of electromagnetic radiation when the system under observation is excited or de-excited. In absorption spectroscopies one can observe the absorption of the photon or observe the electrons emitted when the photon is absorbed as in photoelectron spectroscopy. All of these spectroscopies are based on one-electron transition processes. The ion-neutralization spectroscopy (INS), on the other hand, is the first, but not the only spectroscopy, to be based on a two-electron process in which a band transition density function is obtained. It is like the photoelectron spectroscopies in that the spectroscopic information is obtained by measurement of the kinetic energy distribution of electrons ejected in the process. However, because INS employs a two-electron process, the kinetic energy distribution contains the "spectroscopic function" in folded or convolved form, making data reduction somewhat more in-

volved than for a spectroscopy based on a one-electron process.

INS is a relatively new spectroscopy of solids having its own unique set of characteristics, advantages, and limitations. It is the purpose of this paper to review these properties in comparison with other spectroscopies. We discuss the method and what it measures, its resolving power and operational limitations, and its unique contributions to our knowledge of electronic state densities.

2. The Nature and Method of INS

When an excited and/or ionized atom is projected at a solid surface, an excited solid-atom system is formed. The ion-neutralization process upon which INS is based is one of the processes of auto-ionization by which such an excited solid-atom system de-excites itself. Not all such processes are appropriate to INS, however. The autoionization processes can be divided into two principal classes depending upon whether unfilled electronic levels in the atom do or do not lie opposite filled electronic levels in the solid. These are in-

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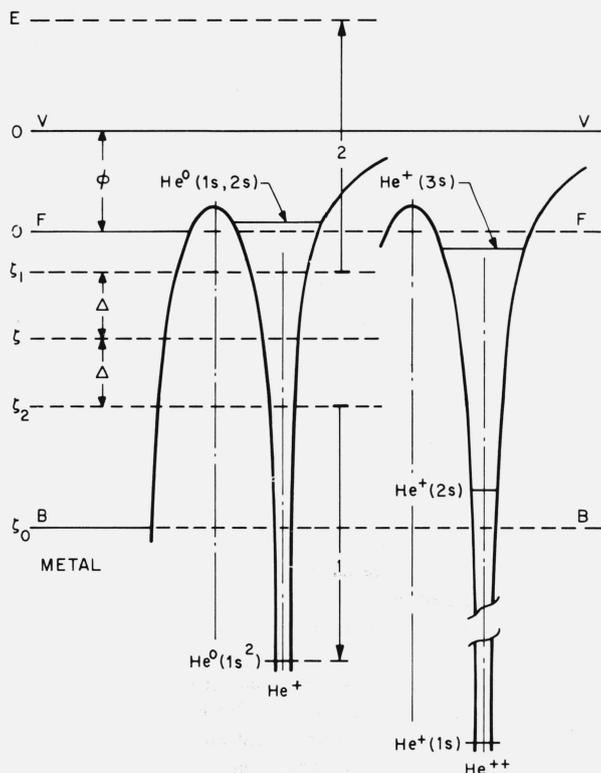


FIGURE 1. Electron energy diagram showing metal at left and two atomic wells for He^+ and He^{++} cores. V is the vacuum level, F the Fermi level and B the bottom of the filled band. Transitions 1 and 2 are those of the ion-neutralization process.

indicated schematically in figure 1. Here we show the electronic energy level diagram of a metal to the left and two atomic wells outside. One atomic well is that of the $\text{He}^+(1s)$ core in which the levels are those of He^0 . The second well is that of the He^{++} core in which the energy levels are appropriate to He^+ . We see that the two wells differ in that one (He^{++}) has two states [$\text{He}^+(2s)$ and $\text{He}^+(3s)$] lying in the energy range of the filled band of the metal, whereas the other (He^+) has no states in this energy range.

We expect that atomic levels lying in the range of allowed levels of the solid will become resonances or virtual bound states and that of these allowed levels, those lying in the range of the filled band will fill. Thus the atomic levels should control the autoionization process in some energy ranges when they can fill by tunneling. Preliminary experiments with doubly-charged He^{++} ions and with metastably-excited $\text{He}^+(2s)$ ions appear to bear this out. Thus if we want the autoionization process to be dominated by initial state electrons whose state density is determined by the solid or its surface there should be no atomic levels lying in the energy range of the filled band as is the case in figure 1 for He^+ . This is a fundamental restriction on the ion-solid

systems to which INS can be applied. For He^+ ions the solid band should lie within the energy range from ~ 4.5 eV to ~ 22.5 eV below the vacuum level. Earlier work has shown that the effective ionization energy of He is about two eV less than its 24.5 eV free-space value [1].

The transitions (1 and 2) of the two-electron, Auger-type, ion-neutralization process are also shown in figure 1. Since ζ_1 and ζ_2 may vary over the entire filled band we expect the ejected electrons to have energies lying in a broad band. Experimentally the kinetic energy distributions are measured by regarding potential means using apparatus we shall not describe here [2,3]. Examples of recorder plots of several kinetic energy distributions, $X(E)$, are shown in figure 2. It is clear that the X distribution is sensitive to the nature of the solid and the preparation of its surface. The spectroscopic information obtained by INS resides in these distributions. In order to extract it we must understand the structure of these distributions in detail.

The distribution functions which we need to understand the ion-neutralization process are shown for an atomically clean copper face in figure 3. Suppose we start with the simplification of constant transition probability independent of the initial energy ζ . Then it

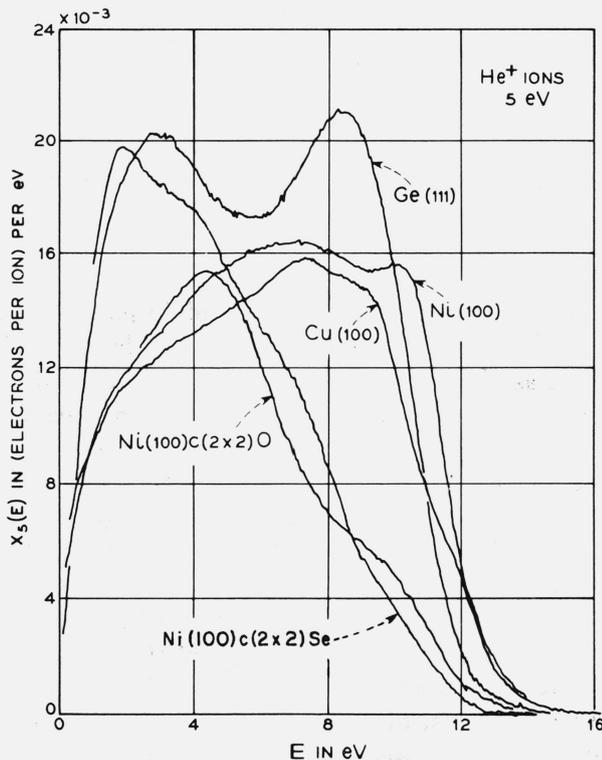


FIGURE 2. Kinetic energy distribution of electrons ejected by 5 eV He^+ ions from atomically clean surfaces of $\text{Ge}(100)$, $\text{Ni}(100)$, and $\text{Cu}(100)$ and from $\text{Ni}(100)$ surfaces having ordered $c(2 \times 2)\text{O}$ and $c(2 \times 2)\text{Se}$ structures upon them.

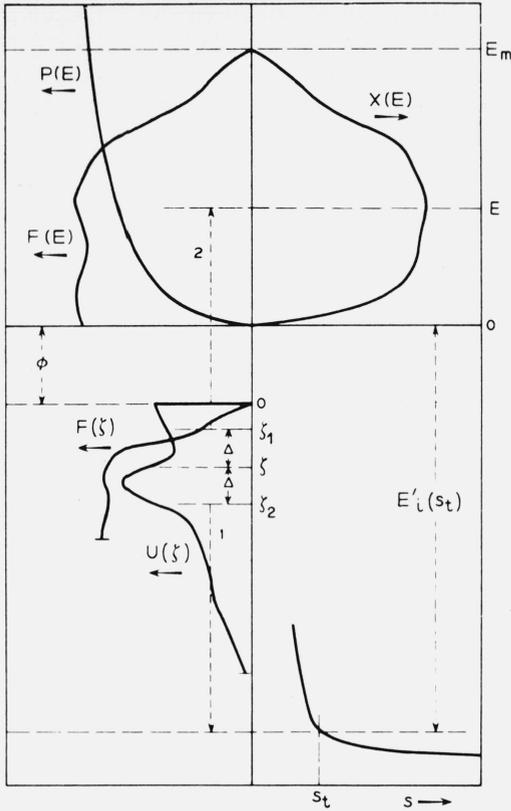


FIGURE 3. Electron energy diagram showing distribution functions appropriate to copper. The arrows under the functional labels indicate the direction in which the function is plotted. Shown also is the variation of ground state position $E_i'(s)$ in the lower right-hand quadrant of the figure.

is clear that the probability of the elemental process involving valence band electrons initially at ζ_1 and ζ_2 is $N(\zeta_1)N(\zeta_2)$ where $N(\zeta)$ is the appropriate state density of the combined metal-atom system. If we ask the relative probability of producing excited electrons in dE at E we see that all elemental processes contribute in which the electrons are symmetrically disposed on either side of the level ζ which lies halfway between the level E and the ground level of the atom at $-E_i'(s_t)$. Thus we must integrate over Δ obtaining the restricted pair distribution function $F_c(\zeta)$ appropriate to the assumption of constant transition probability:

$$F_c(\zeta) = \int_{-\zeta}^{\zeta} N(\zeta - \Delta)N(\zeta + \Delta)d\Delta. \quad (1)$$

Relaxation of the restriction on transition probability to obtain a general $F(\zeta)$ function requires introduction into eq (1) of a factor proportional to the square of the matrix element. Thus:

$$F(\zeta) \propto \int_{-\zeta}^{\zeta} |H_{fi}|^2 N(\zeta - \Delta)N(\zeta + \Delta)d\Delta. \quad (2)$$

We shall sidestep questions of antisymmetrization of wave functions discussed elsewhere [4] and discuss only the one elemental matrix element:

$$H' = \iint u_g^*(1)u_v'(1)(e^2/r_{12})u_e^*(2)u_v''(2)d\tau_1d\tau_2 \quad (3)$$

in which u_v' and u_v'' are initial state functions in the band, u_g is the atomic ground state function, and u_e is the function for the excited electron. In eq (3) terms have been rearranged so that functions of the variables of the same electron are brought together.

We see that the matrix element may be viewed as a Coulomb interaction integral between two electron clouds of spatial extent $u_g u_v'$ and $u_e u_v''$. Since u_g is limited to the general vicinity of the atom the term $u_g u_v'$ varies in magnitude with u_v' . Thus the "down" electron makes a contribution to H' which varies with energy as $[u_v'(\zeta - \Delta)]_A$, the u_v' function evaluated near the atom position. If the "up" electron were also restricted to the vicinity of the atom we could make a similar argument relating to the energy variation of the contribution of the up electron to H' to the magnitude of $[u_v''(\zeta + \Delta)]_A$. This requires in addition that u_e' vary little and smoothly with energy as appears reasonable.

Several reasons can be adduced for believing that the up electron is excited near the atom position. These are listed here without really adequate discussion:

- (1) Experimentally the prominence of the molecular orbital peaks in the results for surface molecules indicates that the wave function magnitudes in the surface region are controlling.
- (2) Dominance of atomic level resonances in the results for ions in which atomic levels fill also points to the dominance of wave function magnitude at the atom in governing the autoionization process.
- (3) The difference between INS and photoelectric results for atomically clean surfaces can be understood only if INS is surface dominated.
- (4) Energy broadening in the $X(E)$ distribution is reduced by a factor 10 when an ordered monolayer of O, S, or Se is formed on the surface of Ni(100). This must be the result of reduction of the density of states just above the Fermi level. Since this reduction can occur only in and outside the monolayer we have evidence in this result that the INS process occurs predominantly in this region.
- (5) There appear to be many fewer inelastically scattered electrons in INS than for equivalent photon energy in photoelectric emission, again

suggesting a surface source of excited electrons.

- (6) Theoretical considerations by Heine [5] and Wenaas and Howsmon [6] lead to the conclusion that the up electron is excited predominantly outside and in the first layer of the solid.
- (7) Large momentum transfer between the two participating electrons means a close collision near the atom where we know the down electron is concentrated. Also viewing the Auger process as photoemission by the down electron followed by photoabsorption by the up electron points to the conclusion that the up electron is most likely excited in the rapidly-decaying near field of the dipole of the down electron transition.
- (8) If the up and down electrons made very different contributions to H_{fi} we could not conclude that F is the convolution square $U*U$ but must be the convolution product $V*W$ of two dissimilar factors. When $V*W$ is inverted as though it were a convolution square it can be shown that spurious features will be introduced into $U(\zeta)$ unless $V \cong W$. These are not found.

We are thus led to the general conclusion that:

$$H_{fi} \approx [u'_v(\zeta - \Delta)]_A [u''_v(\zeta + \Delta)]_A, \quad (4)$$

from which eq (2) becomes:

$$F(\zeta) \propto \int_{-\zeta}^{\zeta} [u'_v(\zeta - \Delta)]_A^2 N(\zeta - \Delta) [u''_v(\zeta + \Delta)]_A^2 N(\zeta + \Delta) d\Delta. \quad (5)$$

eq (5) may be written as:

$$F(\zeta) = \int_{-\zeta}^{\zeta} U(\zeta - \Delta) U(\zeta + \Delta) d\Delta = U*U, \quad (6)$$

defining the transition density function $U(\zeta)$ which thus includes both state density and transition probability factors. We see also from eqs (5) and (6) that $U(\zeta)$ is essentially the so-called local density of states in the vicinity of the atom, *i.e.*, the actual state density weighted by the local wave function magnitude at the atom position. This wave function magnitude must, of course, include the effect of the presence of the atom itself in this vicinity.

The pair distribution function $F(\zeta)$ of eq (6) becomes the distribution in energy of excited electrons, $F(E)$, when band variable ζ is replaced by the outside energy variable E according to the relation:

$$E = E'_i(s_i) - 2(\zeta + \varphi). \quad (7)$$

This equation is obtained by equating magnitudes of the energy transitions 1 and 2 in figures 1 or 3. The externally observed electron energy distribution $X(E)$ is related to $F(E)$ by the equation:

$$X(E) = F(E)P(E), \quad (8)$$

where $P(E)$ is the probability of escape over the surface barrier and includes any other dependences on E such as variation in density of final states.

The method of INS consists in reversing the above development to obtain $U(\zeta)$ from measured $X(E)$. It proceeds in the following steps:

- (1) Experimental determination of two $X_K(E)$ at ion energies $K = K_1$ and K_2 . Usually $K_1 = 5$ eV and $K_2 = 10$ eV.
- (2) Linear extrapolation of X_{K_1} and X_{K_2} to X_0 to reduce the natural broadenings present in the X_K distributions. This is done by use of the relation:

$$X_0(E) = X_{K_1}(E) + R[X_{K_1}(E) - X_{K_2}(E)]. \quad (9)$$

Since it has been shown that broadening varies with ion velocity, it is possible to write R_{K_1, K_2} as

$$R_{K_1, K_2} = (K_2/K_1)^{1/2} - 1. \quad (10)$$

- (3) Division of $X_0(E)$ by a $P(E)$ function, reversing eq (8), to obtain $F(E)$. This step is really not necessary since replacement of $P(E)$ by a constant merely changes the intensity level of $U(\zeta)$ progressively as ζ increases without disturbing the structure. However, we have usually divided by a parametric $P(E)$ whose parameters are chosen so that the pieces of $F(\zeta)$ obtained by He^+ , Ne^+ , and Ar^+ ions are essentially coincident.
- (4) After change of variable, $F(\zeta)$ is inverted by a sequential deconvolution procedure. The formulas used are:

$$U_0 = (F_1/2\Delta\zeta)^{1/2},$$

$$U_2 = (1/U_0) (F_2/2\Delta\zeta),$$

$$U_{2n-2} = (1/2U_0) [(F_n/2\Delta\zeta)$$

$$- \sum_{p=1, n-2} U_{2n-2p-2} U_{2p}], \quad n \geq 2, \quad (11)$$

in which F and U are digitalized as $F_n = F(n\Delta\zeta)$, $n = 1, m$; $U_{2n-2} = U[(2n-2)\Delta\zeta]$, $n = 1, m$.

- (5) Tests of the mathematical uniqueness of $U(\zeta)$ by variation of its origin and by comparison with $F'(\zeta)$, the derivative of the fold function. These steps cannot be discussed in this paper

but will be discussed extensively in a forthcoming publication [7]. Suffice it to say that, although deconvolution is in general a difficult procedure, the sequential unfold works extremely well for the general class of $F(\zeta)$ functions we have for which $F(0) = 0$, $F'(0) = k$, and $F(\zeta)$ does not depart drastically from $F(\zeta) = k\zeta$.

The procedure we now use is essentially that given when the INS method was first discussed [4]. However, in the interim we have learned a good deal about the mathematical side of the data reduction, particularly the unfolding procedure. We have derived all possible digital sequential unfold formulations which invert directly or with the independent calculation of no more than the first data point U_0 . We have also studied the noise characteristics and shown that the step-mid-point formulation given above in eq (11) not only is the only one which inverts directly without independent calculation of the first point but also has by far the best stability characteristics with respect to noise in the data. We have also faced up to the problems involved in the possibility that we are inverting as a convolution square (U^*U) a function which is in reality a convolution product (V^*W) and have devised tests to determine if any spurious structure could possibly be introduced in this way. The data reduction procedures, although more complicated than for a one-electron spectroscopy, proceed smoothly on the digital computer and produce unique and correct answers. We shall discuss further some of the properties and limitations of INS in section 4.

3. Examples of INS Results

We turn now to the presentation of INS results. These are in two categories: (1) results for atomically clean surfaces of the transition metals Cu and Ni [8], and (2) results for the Ni(100) surface with ordered monolayers of O, S, and Se adsorbed upon it [9]. Some unpublished results for Si and Ge will be mentioned in the discussion of item (1).

In figure 4 we reproduce figure 6 of reference 8 showing $F(\zeta)$ and $U(\zeta)$ for Cu(111). Also shown in the correct relative position is the $P(E)$ function used, indicating how flat it is over the energy range of the data. The average $U(\zeta)$ function for (100), (110), and (111) faces of Cu (fig. 15 of ref. 8) is compared in figure 5 here with the optical density of states curve (ODS) of Krolikowski and Spicer [10]. In figure 6 the $U(\zeta)$ curve for atomically clean Ni(100) from INS is shown and compared with Eastman's ODS curve for a nickel film obtained by photoemission [11].

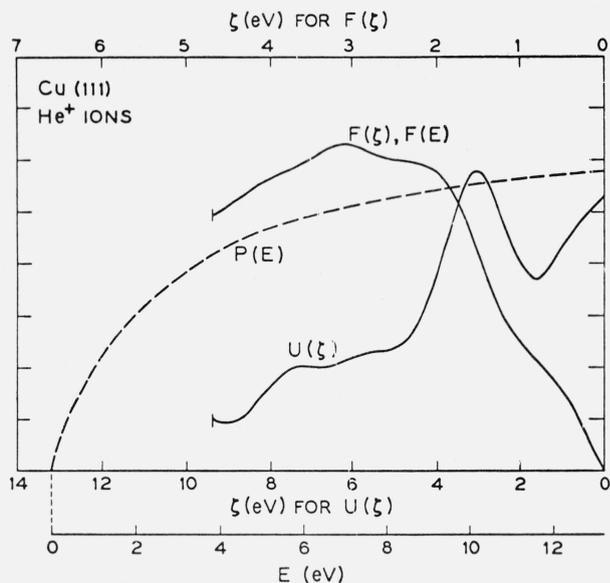


FIGURE 4. F and U functions for atomically clean Cu(111) and He^+ ions [fig. 6 of ref. 8]. The probability of electron escape used in the data processing is also shown.

First, it is evident that the INS results show a peak in the general vicinity of the bulk d -band in both Cu and Ni. However, it is equally evident that this peak does not have the shape or width to be expected from band theory or measured by ultraviolet photoelectron spectroscopy (UPS). A strong case can be made that the differences evident in figures 5 and 6 are due to the fact that the two spectroscopic methods are sensitive to different things. Although the energy resolving power of INS is somewhat poorer than that of UPS, one cannot by any stretch of the imagination consider the INS $U(\zeta)$ curve as a smeared out version of the ODS curves. In reducing the Ni data of figure 6 very little digital

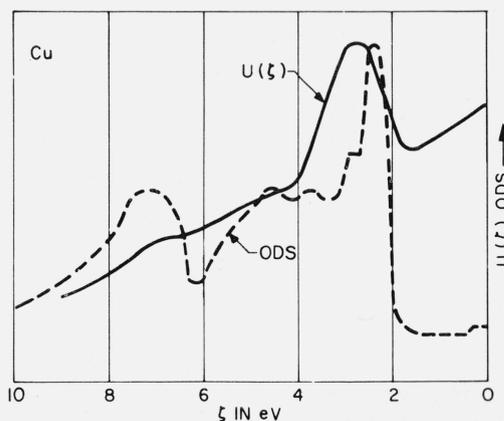


FIGURE 5. Comparison of the average $U(\zeta)$ function for (100), (110), and (111) faces of Cu [fig. 15 of ref. 8] compared with the optical density of states curve (ODS) of Krolikowski and Spicer (ref. 10) obtained by photoelectron spectroscopy.

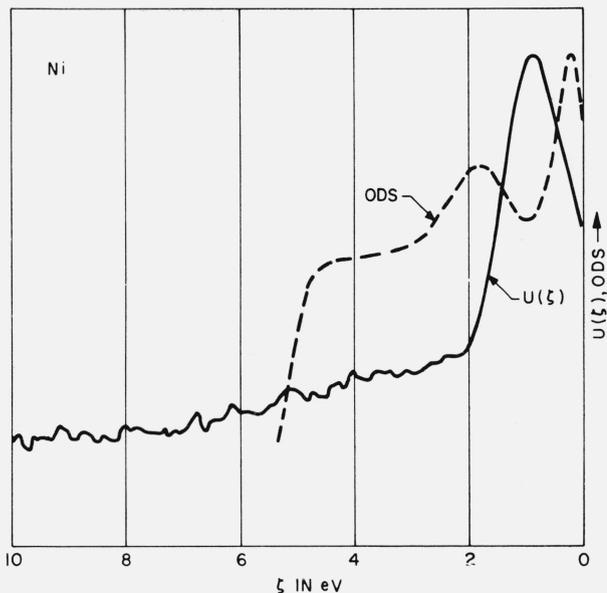


FIGURE 6. $U(\zeta)$ for Ni(100) compared with the ODS curve of Eastman (ref. 11) also obtained by photoelectron spectroscopy. The amount of smoothing used in the INS data reduction was deliberately reduced to the point of leaving in the data the noise seen in an attempt to demonstrate the best resolving power of the INS method.

smoothing of the data was used in an attempt to increase the resolving power at the expense of letting through low-frequency noise. Some increase in resolving power (about 20%) is evident when comparison with similar curves in reference 9 are made. The sharpness of the peak in $U(\zeta)$ at $\zeta = 1$ eV is an indication of the INS resolving power. In view of the characteristics of INS discussed above it is believed that the $U(\zeta)$ curve is in fact the local density of states at or just outside the surface whereas the UPS results are characteristic of the bulk.

Why the local density of states for d bands of transition metals outside the surface differs from the bulk band is an interesting question in surface physics. The reduction in number of nearest neighbors as well as a probable small dilatation of the lattice at the surface could narrow the tight-binding d band and make it more like an atomic level. Tight-binding bands are particularly vulnerable to such modification in the surface region. Unpublished work on Si and Ge appears to indicate that the INS results will much more closely mirror what is expected from bulk theory [12]. This is probably attributed to the fact that the s and p wave functions of the semiconductor valence bands overlap more strongly at the surface even though the surface atoms may be displaced from their "bulk positions" by larger amounts than are surface atoms of the transition metals. Another interesting suggestion to account for the INS results in Cu and Ni arises in the

work of Pendry and Forstmann [13] who predict that on some faces of transition metal crystals a new type of surface state appears which should clearly modify the surface local density of states from the bulk density.

The second category of INS experimental result to be mentioned in this paper is found for metal surfaces upon which ordered monolayers of adsorbed atoms are present. In figure 7 is reproduced the $U(\zeta)$ functions from reference 9. Here in curve 1 is repeated the transition density for atomically clean Ni(100). Curves 2, 3, 4 are for $c(2 \times 2)$ structures of O, S, Se, respectively, and curves 2', 3', and 4' are for $p(2 \times 2)$ structures involving these same adsorbed atoms, respectively. We note a very interesting increase in complexity of the U functions for the covered surfaces. These appear now

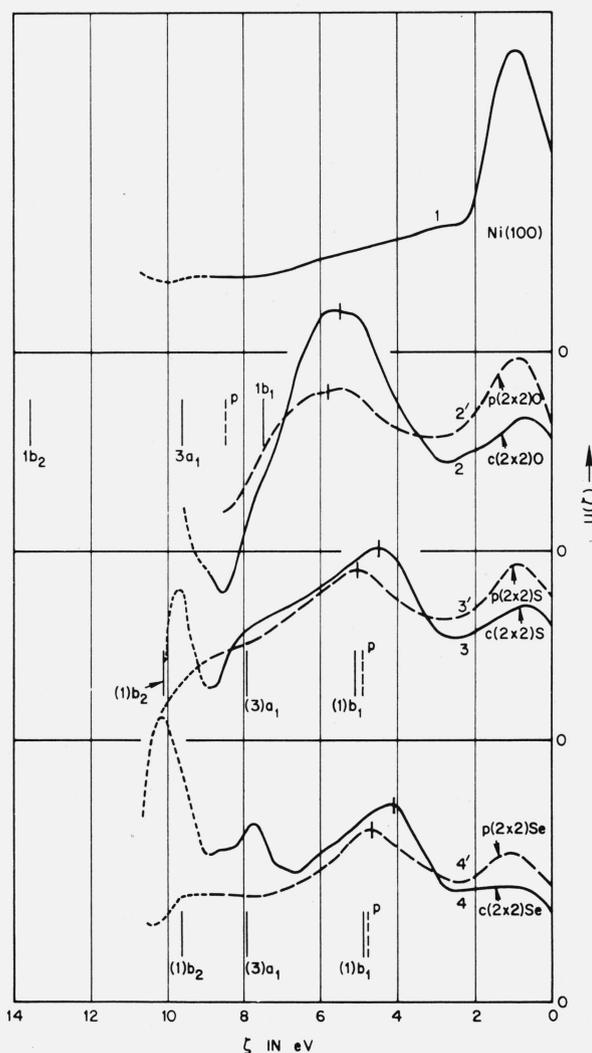


FIGURE 7. Transition density functions, $U(\zeta)$ for atomically clean Ni(100) (curve 1) and for the surface with $c(2 \times 2)$ structures of O, S, Se (curves 2, 3, 4, respectively) and with $p(2 \times 2)$ structures of O, S, Se (curves 2', 3', 4', respectively). Energies labelled p, $1b_1$, $3a_1$, and $1b_2$ are identified in the text.

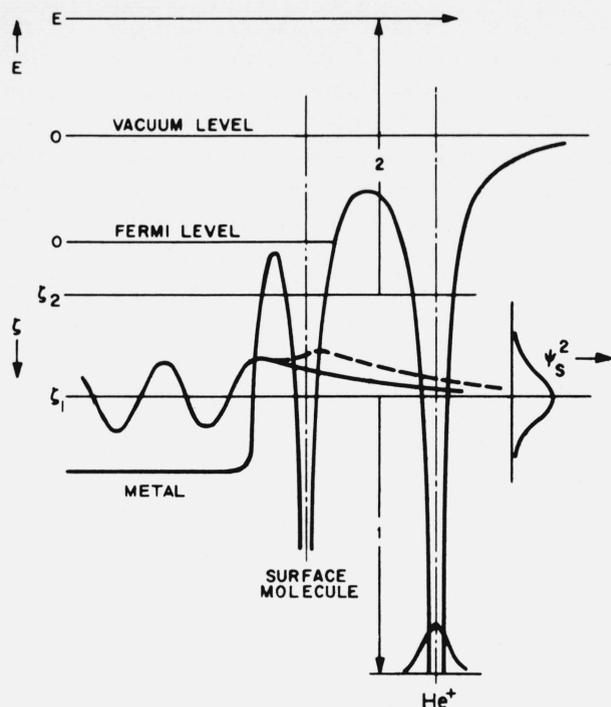


FIGURE 8. Electron energy diagram illustrating the effect on INS of a resonance or virtual bound state of a surface molecule formed on a metal surface. The bond resonance in the surface molecule is assumed to lie at ζ_1 (which is also the initial energy of the down electron) and to increase the magnitude of the surface wave function ψ_s over a broadened energy range as indicated on the right-hand side of the diagram. The increase in wave function outside the solid in this energy region is indicated by the dashed-line modification of the electronic wave function at ζ_1 .

to indicate the energy spectra of electronic orbitals of electrons in the bonds of so-called "surface molecules" formed from the adsorbed atom and atoms of the substrate.

The electronic states to be associated with bond orbitals in surface molecules form resonances or virtual bound states. These will evidence themselves in the transition density for reasons we attempt to make clear by figure 8. The presence of the electronic orbital at the surface will increase the wave-function magnitude in the vicinity of the surface molecule as indicated by ψ_s^2 in the figure. This will in turn increase the tunneling probability for band electrons into the He^+ well. The dashed line indicates how a band wave function in the absence of the surface molecule (full line) is increased in the presence of the surface molecule (dashed line). These wave function increases in the He^+ well will result in peaks in the local density of states and hence the $U(\zeta)$ transition density function observed by INS.

This paper is not the place to discuss the results in figure 7 in any great detail. A preliminary discussion is to be found in the original publication [9] and an exten-

sive paper is in preparation [7]. However, it is essential to an understanding of the scope of INS as a spectroscopy of electronic states to mention briefly the principal results for these cases of chemisorption. Several energies are indicated in figure 7. These are the levels of the atomic p orbitals in free O, S, and Se, labelled p in the figure. In the figure the second, third, and fourth panels from the top refer to adsorbates O, S, and Se respectively. The lines labelled $1b_1$, $3a_1$, and $1b_2$ are molecular orbital energies in the free molecules H_2X where X is O, S, or Se in the second, third, or fourth panels of the figure, respectively.

Three types of molecular orbital spectrum are to be found among the six curves for adsorbed species in figure 7. Curves 3 and 4 are the most complex spectra having peaks near the orbitals indicated for the free H_2X molecule. These have been attributed to the bridge-type bonding illustrated in figure 9(a) and (b). Relatively small negative charging of the $X = \text{S, Se}$ end of the surface molecule is indicated by the fact that the lone-pair orbital peak near $(1)b_1$ also lies near the atomic p orbital energy as for free H_2X .

When the structure is changed from the $c(2 \times 2)$ [fig. 9(b) to the $p(2 \times 2)$ [fig. 9(d)] by removal of half of the adsorbate we see that the molecular orbital spectra change completely to those of curves 3 and 4 in which there is a single peak below the Ni d -band peak indicating a change in the local bonding structure. The only other reasonable alternative is the π -type symmetrical bonding as shown in figure 9(c) and (d) for which we expect a nonbonding orbital in this energy range. Removal of the "center atom" in the $c(2 \times 2)$ structure removes the agent which distorts the square of Ni atoms of C_{4v} symmetry below each X atom into a rhombus of C_{2v} symmetry. C_{2v} symmetry is essential if the molecular structure is to resemble H_2X . Reversion to C_{4v} symmetry when the center atom is removed demands change of the molecular structure and spectrum as is indeed found.

Finally, both $c(2 \times 2)\text{O}$ (curve 2) and $p(2 \times 2)\text{O}$ (curve 2') show a single peak shifted by a much larger amount toward the Fermi level from the atomic p level than is the case for either S or Se. This orbital spectrum (single peak in the available energy range) and larger negative charge (orbital energy shift) together with small work function change on adsorption can be shown to be consistent with a reconstructed surface in which the adsorbed atom is incorporated into the top layer of substrate atoms where relatively large charge will not result in large work function change. Although the above account of the data in figure 7 is admittedly

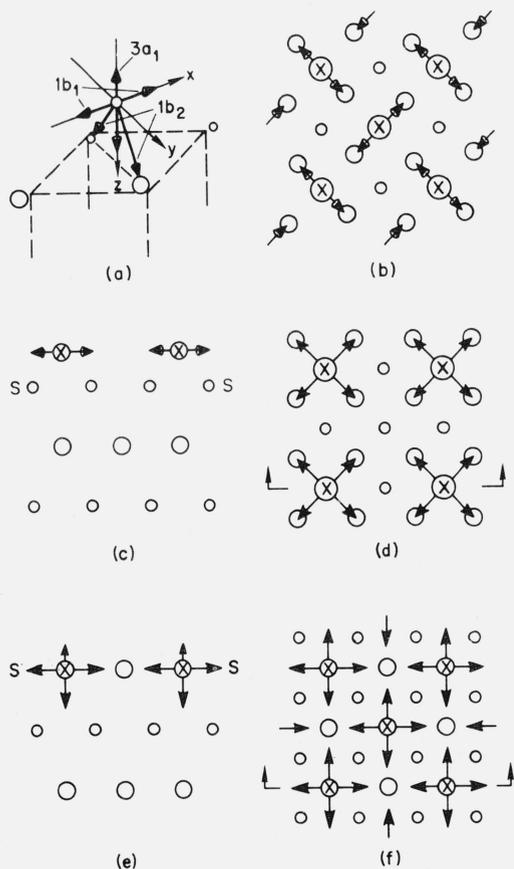


FIGURE 9. Surface structures suggested (ref. 9) to account for the molecular orbital spectra of figure 7. (a) and (b) are for a bridge-type Ni_2X -type structure repeating over the surface in a $c(2 \times 2)$ pattern to account for curves 3 and 4 of figure 7. (c) and (d) illustrate a $p(2 \times 2)$ structure adequate to account for curves 3' and 4' of figure 7. (e) and (f) illustrate a reconstructed $c(2 \times 2)$ structure to account for curve 2 of figure 7. Simple removal of the "center atom" in (f) without other change produces the $p(2 \times 2)$ reconstructed surface thought to account for curve 2' of figure 7. In these figures bond orbitals are indicated by the heavy arrows with conical arrowheads.

sketchy, it does indicate how INS determines a portion of the molecular orbital spectrum of a surface molecule and the power such information has in elucidating symmetry and bonding character.

4. Comparative Critique of INS

A comparative critique of INS is perhaps best carried out by listing its characteristics and attempting to assess them as advantages or disadvantages in comparison with other spectroscopies of solids. The other spectroscopies are the two forms of photoelectron spectroscopy, ultraviolet photoelectron spectroscopy UPS [10,11] and x-ray photoelectron spectroscopy XPS [14]; soft x-ray spectroscopy SXS [15], and the surface Auger spectroscopy SAS [16].

In the first place INS is a two-electron spectroscopy as is SAS whereas UPS, XPS, and SXS are one-electron spectroscopies. SAS is based on a two-electron Auger process similar to that underlying INS except that the vacant ground level in the excited system is an inner level of a surface atom rather than the ground level of the parent atom of an incoming atomic ion. The SAS process has been used extensively in the identification of surface impurities but Amelio and Scheibner [16] were the first to attempt to separate the Auger distribution from the large background of secondary electrons and to unfold it to obtain spectroscopic information as has been done in INS.

The fact that INS, like SAS, is a two-electron spectroscopy must in itself be considered a drawback since it necessitates unfolding of the data. However, in INS the data are of such quality that unfolding now offers no significant problem. We have learned much about unfolding methods and possible errors since the last discussion of these matters in the literature [4].

A second characteristic of INS is its surface specificity and hence surface sensitivity. This means, as we have seen, that INS results can be compared with the results of bulk spectroscopies only in special cases. However, INS gives us a tool to study variation of electronic band structure from bulk to surface, to study surface states on both metals and semiconductors, and, perhaps most importantly, to measure molecular orbital spectra of surface molecules formed in chemisorption. Some recent UPS work [17] with 21.2 eV radiation and grazing incidence has shown the possibility of detection of large molecules adsorbed on surfaces. Whether surface molecules of the type discussed here can be observed in this manner has yet to be demonstrated.

The transition probability factors of INS arise from its surface specificity and the tunneling character of the electronic transitions. Four types can be listed: (1) a tunneling factor which decreases with depth in the band, (2) a symmetry factor arising from extent of the surface wave function which decreases as the character proceeds from s to p to d , etc., (3) a second tunneling factor which favors bulk states whose k vector is normal to the crystal face used, and (4) the enhancement in certain energy ranges caused by the surface resonances of adsorbed atoms. Although they are distinctive, there appears to be no particular disadvantage associated with these transition probability factors. It is the last one which makes possible the study of surface molecules and this must be listed as an advantage.

The energy range which can be explored in the solid is $E_i' - 2\phi$ where E_i' is the effective neutralization ener-

gy of the incident ion near the surface (effective ionization energy of the parent atom) and φ is the work function of the solid. This means that INS is the equivalent of a photoelectric process for which $h\nu = E_i' - \varphi$. For He, $E_i' \sim 22.5$ eV and for a representative solid $\varphi \sim 4.5$ eV. Thus $E_i - \varphi \sim 18$ eV. To equal this range with UPS one must use the 21.2 eV He resonance radiation. XPS, SXS, and SAS, on the other hand, have essentially no energy range limitation with respect to the valence bands of solids. Like UPS, INS is limited by vacuum level cutoff making it difficult to extract data near the vacuum level because of the rapid variation of escape probability there.

Energy resolving power of INS is undoubtedly somewhat less than that of UPS but as figure 6 indicates not greatly less. It is in all probability better than that of SXS, XPS, or SAS since each of these involve the relatively broad inner level of an atom at one point or other.

Finally, we shall mention a series of side effects which must be considered in evaluating any spectroscopy. There appear to be fewer inelastically scattered electrons to contend with in INS than in UPS at higher energies. SAS has a serious background problem unknown to INS. Plasma losses, which can be a complicating interpretive factor, apparently play no role in INS results. SXS has a serious spectral superposition problem unknown to INS. The signal intensity in INS is adequate which sometimes cannot be said for SXS or SAS. INS has the possibility of variation of natural broadenings by variation of a controllable experimental parameter, namely incident ion velocity, making it possible to extrapolate out broadenings admittedly greater than those of UPS.

In conclusion it is possible to state that ion-neutralization spectroscopy is a viable spectroscopy of solids having its own peculiar set of characteristics. It appears that its most important area of application at present is to the study of the molecular orbital spectra

of surface molecules formed in chemisorption. Here it holds promise of extending our knowledge of surface structure beyond what low-energy electron diffraction (LEED) now can do. LEED tells us how a given adsorption or bonding structure repeats itself over the surface. INS yields information about bonding symmetry, orbital energy-levels, and electric charging within the surface molecular structure, which in many cases, using LEED and work function data, will permit the specification of bonding structure. Surface state and surface modifications of band structure also promise to be interesting fields in which INS can make a contribution.

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