

curves will be published elsewhere.

We also call attention to the dependence on $\omega\tau$ of the limiting value of attenuation at high fields ($X \rightarrow 0$):

$$S_{11}(X \rightarrow 0) = (1/15)(ql)^2/[1 + (\omega\tau)^2],$$

as shown in Ref. 3. In Fig. 1 it can be seen that the high-field attenuation for $\omega\tau = 1$ is one-half that for $\omega\tau = 0$. Experimental studies of l in very pure metals using high field-attenuation values must take into account the effects of finite $\omega\tau$.

We gratefully acknowledge the assistance of W. R. Cox in preparing the computer programs for these calculations.

*Work supported by the National Science Foundation.

†University Fellow.

¹We refer here to the usual geometry with magnetic field perpendicular to the direction of propagation. See, for example, G. N. Kamm and H. V. Bohm, Phys. Rev. 131, 111 (1963).

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ION-NEUTRALIZATION SPECTROSCOPY OF COPPER AND NICKEL

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(Received 11 January 1966)

In this Letter we present experimental results concerning the band structures of copper and nickel obtained by a new method of electronic spectroscopy of solids. There is considerable current interest in the band structures of the transition metals, particularly concerning the validity of the rigid-band model¹ and the existence of many-body resonances.² Our results relate to both of these matters. The new spectroscopy, which we call ion-neutralization spectroscopy (INS), extracts information concerning the state densities of solids from the measured kinetic-energy distributions of electrons ejected from the solid when an ion incident from outside is neutralized at the surface. Since the basic electronic transition is of an Auger type involving two electrons from the solid, it is necessary to unfold or deconvolute the energy distribution. The results involve not only state densities in the initial and final states but transition probability factors peculiar to the ion-neutralization process. There is promise of fruitful comparison with soft x-ray spectroscopy (SXS) and photoelectron spectroscopy (PES), each of which has its characteristic transition probability factors.

Since a detailed description of the method of INS is being written,³ we discuss it only briefly here. The method has developed out of an extended series of experimental and interpretive studies of the ion-neutralization process itself.⁴ Experimentally, a focused monoenergetic beam of slow ions (4-10 eV) is made to

strike a specific crystallographic face of the solid to be studied.⁵ Electrons ejected by ion neutralization are collected on a spherical collector which surrounds the target. The electron kinetic-energy distribution, $X_K(E)$, for ions of incident kinetic energy K , is obtained by differentiating the curve of sphere current versus retarding potential between collecting sphere and target. The target surface, which may also be examined by low-energy electron diffraction in the same apparatus, is cleaned by sputtering and is annealed. Background pressure in the apparatus is low enough (less than 10^{-10} Torr) to give monolayer times in excess of five hours. Thus data can be obtained for surfaces whose contamination is less than 2% of a monolayer of any foreign gas.

Energy broadening inherent in the electron transition process varies with incident ion kinetic energy, K .⁴ Energy distributions for electrons ejected by ions of two incident energies ($K = 5$ and 10 eV, say) are obtained and a linear extrapolation is made to obtain a distribution, $X_0(E)$, characterized by an amount of broadening estimated to be less than 0.1 eV. This procedure is carried out for electron energy distributions obtained using He^+ , Ne^+ , and Ar^+ ions.

Next the "debroadened" distribution, $X_0(E)$, is divided by a probability of electron escape from the solid, $P(E)$, to obtain the internal energy-distribution function $F(E) = X_0(E)/P(E)$. $P(E)$ is put in as a three-parameter function

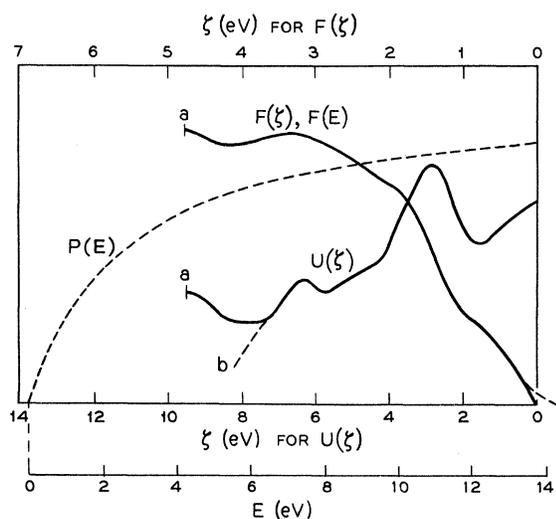


FIG. 1. Plots of the functions F , P , and U for He^+ ions incident on Cu (110). Two ζ scales are necessary if F and U are to be plotted so that related structure in the curves appears at the same point. Note that the data used are in the region where $P(E)$ is relatively flat.

of the proper general form, and its parameters are determined so that the forms of the function $F(E)$ obtained for the three ions are essentially the same except for a possible multiplicative normalizing constant. This is not a difficult requirement to meet since, as we shall see below, we use our data in the region $E > 4$ eV where the $P(E)$ function is quite flat. $F(E)$ and $P(E)$ functions are plotted in Figs. 1 and 2. E is the kinetic energy of the ejected electrons measured from the vacuum level. ζ is the band energy measured positively down into the filled portion of the conduction band from the Fermi level. $F(\zeta)$ is obtained from $F(E)$ by change of energy variable.

The end result of INS is a function $U(\zeta)$ which is related to $F(\zeta)$ by the integral relation

$$F(\zeta) = \int_0^{\zeta} U(\zeta + \Delta)U(\zeta - \Delta)d\Delta.$$

$F(\zeta)$ is thus the fold of $U(\zeta)$, and $U(\zeta)$ the unfold of $F(\zeta)$. If all matrix-element factors were equal for the two electrons involved in the process and independent of ζ , $U(\zeta)$ would be proportional to the state density in the filled portion of the conduction band. If we allow matrix-element factors to vary with ζ but still require that they be equal for the two participating electrons, $U(\zeta)$ is then what might be called the transition density, the probability that an

electron in $d\zeta$ at ζ will be involved in the ion-neutralization process. There are reasons for believing that matrix-element factors are not greatly different for the two electrons and that unfolding $F(\zeta)$ to obtain $U(\zeta)$ is justified. Matrix-element effects to be seen in the data are mentioned below.

In Figs. 1 and 2 the functions F , P , and U are shown for Cu (110) and Ni (111), respectively. The U functions are obtained from the F functions by a digital unfold procedure carried out on the IBM 7090 calculator. Inelastically scattered electrons should be produced by the excited electrons and are undoubtedly present at higher ζ values. However, they appear to be many times fewer in number than for incident photons. This we believe to result from the fact that the electrons ejected from the solid in the ion-neutralization process originate considerably closer to the surface than do photoelectrons. The photon energy for a one-electron photoemission process which is equivalent to a He^+ ion-neutralization process is about 18 eV. We have cut off the data as indicated at a in these figures thus avoiding the region of $P(E)$ which varies most rapidly with E and is not as accurately expressed by our three-parameter formula.

The U functions for Cu and Ni are compared in Fig. 3. Results for Ne^+ and Ar^+ ions agree quite well with the results shown here for He^+

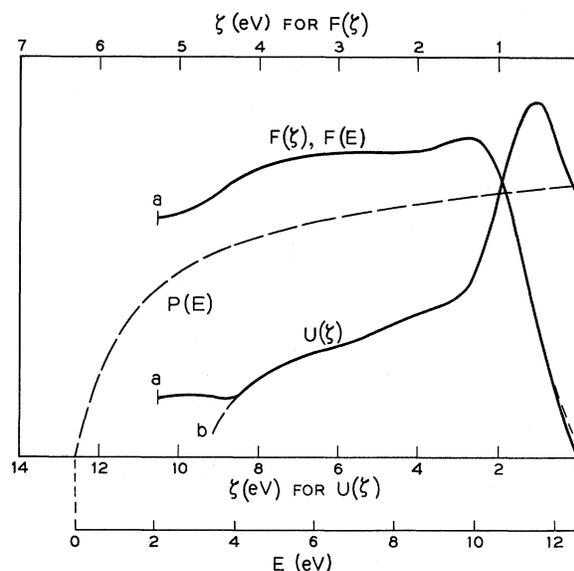


FIG. 2. Plots of F , P , and U functions for He^+ ions incident on Ni (111).

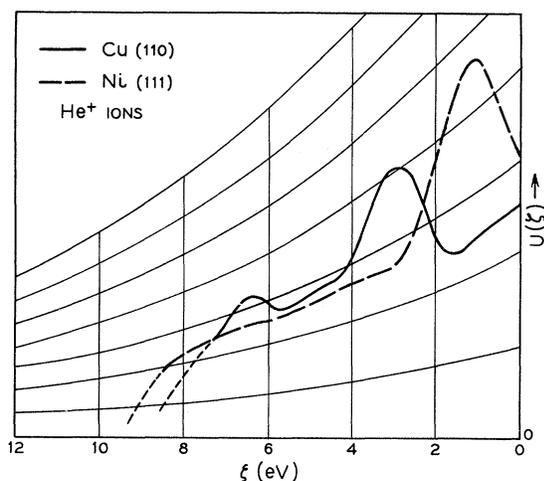


FIG. 3. Comparison of $U(\xi)$ for He^+ ions on Ni (111) and Cu (110). The constant ordinate lines are plots of $A \exp(-0.12\xi)$.

ions. Figures 1 and 2 indicate that the tail of the function $F(\xi)$ near $\xi=0$ has been cut off slightly. This is necessary if the unfold to $U(\xi)$ is to proceed properly. $F(\xi)=0$ defines the point $\xi=0$. Theory⁶ indicates that for Ni and Cu, the bottom of the s - p band should occur at $\xi=8$ -9 eV. This is indicated at b in Figs. 1 and 2. The electrons at greater ξ are in all probability the inelastically scattered component.

The functions $U(\xi)$ shown in Fig. 3 display several interesting features:

(1) Both curves show d -band peaks, for Cu in the range $\xi \sim 2$ -4 eV and for Ni in the range $\xi \sim 0$ -2 eV. These d bands appear to be derivable from each other according to the rigid band model. In this respect our results appear to differ from those of PES.¹

(2) The Cu d band differs from that predicted by theory⁶ and seen by PES from polycrystalline evaporated films⁷ in that it is narrower and does not show a double peak. At the moment we incline to the position that these results are not the result of poorer resolution in INS. Further investigation of this point is in progress, however.

(3) In $U(\xi)$ for Cu, a small peak appears at $\xi=6.5$ eV at the same position as that observed by PES.^{7,8} We are engaged in studying other crystallographic faces of Cu in an attempt to confirm the existence of this peak as a band-structure feature. On the other hand, we do not see a large peak in $U(\xi)$ for Ni at $\xi=4.5$

eV as has been observed by PES and attributed to a resonance.¹ Preliminary work on the (100) face of Ni also fails to show a peak in this region.

(4) Effects due to the matrix element are observed in our results. One is the strong discrimination against the participation of d electrons relative to s - p electrons in the ion-neutralization process. For Cu the ratio of s - p density above the d band to the maximum d -band intensity is at least an order of magnitude greater than for PES. Theory predicts an approximately constant state density in the s - p band above the d band. In Fig. 3 the s - p band for Cu appears to decrease in magnitude with increasing ξ . We attribute this to a tunneling effect whereby the wave-function magnitude in the atomic well outside the solid decreases as ξ increases. The ordinate lines in Fig. 3, which are plots of $A \exp(-0.12\xi)$, indicate a reasonable magnitude for this tunneling effect for s - p electrons. It is possible that this tunneling effect is different for d electrons. In fact the relative magnitudes of the d peaks above the s - p background for Ni and Cu in Fig. 3 would indicate a more rapid decrease of d -electron tunneling with increasing ξ .

We intend to publish detailed descriptions of the method of INS and the experimental results and conditions for each of the materials studied.

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