

The frequency-dependent dielectric function for long wavelengths obtained from the simulations is shown in Fig. 3(a). The dipolaron frequency, where $\epsilon^R \simeq 0$, is indicated by the arrow. Furthermore, the peak in $\epsilon^I(\omega)$, at a frequency ($\omega \sim 4.0$) roughly corresponding to the inverse of the dipolar relaxation time ($\omega \sim 3.6$), corresponds to a strongly damped transverse collective mode. An alternative and more traditional way of presenting this same dielectric response is the Cole-Cole plot⁷ in Fig. 3(b) which serves again to illustrate that the polarization autocorrelation function cannot be completely described by a single relaxation time since then the data would lie on the indicated semicircle. More closely related to experiment is the dispersion curve for transverse electromagnetic waves, Fig. 3(c),

$$ck_R = \omega \operatorname{Re}[\epsilon(\omega)]^{1/2}, \quad (10)$$

as calculated from this same dielectric function, showing the transition from the low-frequency, $\epsilon(\omega) \simeq \epsilon(0)$, to the high-frequency, $\epsilon(\omega) \rightarrow 1$, regime. The dipolaron may be identified with the

upper cusp in this curve where $\epsilon^R(\omega) \sim 0$. The finite wavelength here indicates the damping, $\epsilon^I(\omega) \neq 0$, of the dipolaron mode.

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L_3VV Auger-Electron Line Shapes and Peak Positions for Near-Threshold Electron Excitation in Nickel and Copper

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Measurements of L_3VV Auger-electron line shapes were made for Ni and Cu at incident electron energies near threshold for L_3 subshell ionization to reduce perturbing satellite effects. Large shifts were observed in the position of L_3VV features as the incident energy was varied. These shifts are comparable to those found in free atoms due to post-collisional interaction. Apparent inconsistencies in the calculated electronic properties of nickel are removed by a new value of $U_{\text{eff}} = 2.5$ eV, the effective energy of two d electrons on the same atom.

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The screened Coulomb interaction energy U_{eff} between two d electrons (or d holes) is a direct measure of electron localization which affects transition-metal properties as diverse as ferromagnetism and satellites in photoelectron spectra. Experimental values reported for U_{eff} in nickel have differed widely^{1, 2} (4.1 and 1.4 eV); this variation makes a considerable difference in theoretical models applied to the above phenomena.^{3, 4} U_{eff} can be determined by measuring the displacement downward in energy of a CVV (C = core, V = valence) Auger-electron spectral line below the

value predicted from the known core-electron binding energy and the one-electron density of states.

In many cases, however, features in experimental spectra due to different transition channels overlap and make unambiguous interpretation difficult.⁵ This complication is illustrated in the L_3VV Auger spectrum of Ni and Cu where L_3 holes are produced not only by direct ionization but by L_2L_3V Coster-Kronig transitions from L_2 holes. These different methods of L_3 -shell ionization lead to displaced and overlapping L_3VV spectra

due to the presence of a "spectator" valence-electron excitation following the Coster-Kronig process.

We report results of an experiment in which a technique has been used to eliminate the effects of L_2L_3V Coster-Kronig transitions on the L_3VV Auger spectra of Ni and Cu and determine what we believe is an accurate value of U_{eff} for nickel. We have measured these spectra as the energy of the incident electron beam was lowered to the vicinity of the L_2 -shell ionization threshold so that the fraction of L_3 -shell ionizations produced by the Coster-Kronig transitions could be significantly decreased. Our principal results are as follows:

(1) The L_3VV Auger spectrum of Ni at low incident electron energies can be seen to consist of two distinct features consistent with recent predictions.^{6, 7} One of these features is identified as being due to atomic final states (i.e., two d holes localized on the same atom) and the other related to the density of states in the valence band. The atomic feature is displaced by U_{eff} , the mutual interaction energy of the two holes. The value obtained for U_{eff} of nickel is 2.5 eV.

(2) The position of the dominant peak in the L_3VV spectrum of both Ni and Cu changes systematically with incident energy near threshold. We attribute the peak shifts to a post-collisional interaction comparable to those found in the Auger-electron spectra of atoms⁸ and of several selenium compounds.⁹ The magnitude of the shift is similar to that predicted with use of an atomic model, a surprising result since metallic screening would be expected to reduce the effect. Our result also implies that there will be a corresponding shift in the measured minimum excitation energy of the L_3 -core level in Ni and Cu as the incident electron energy is varied in the same range. We thus expect that the apparent binding energy of core electrons will be different when measured under "sudden" and "adiabatic" conditions.

The experiments were performed on high-purity (99.999%) foils of Ni and Cu which were cleaned by argon-ion sputtering (as determined from conventional Auger spectra) but not annealed. The Auger-electron data were acquired with a double-pass cylindrical-mirror analyzer equipped with a coaxial electron gun. At incident electron energies near threshold for core-electron ionization, the Auger-electron signals are small and overlap features due to inelastic scattering (in the present case, excitation of valence and $3p$ elec-

trons) of the incident electrons. The Auger-electron signal of interest could be extracted by applying a small bias voltage (1.35 V) to the sample on alternate spectral sweeps and by storing data in a multichannel analyzer alternately additively and subtractively on successive sweeps.¹⁰ The resulting derivative of the desired Auger-electron spectrum was integrated to yield the $N(E)$ curves presented in Fig. 1. At low Auger-signal levels, within 40 eV of the L_3 -subshell threshold, data were accumulated in runs of up to 6 h; several such runs were compared and added to produce an Auger spectrum for a particular incident energy. Drifts caused some fluctuations of the background near the dominant L_3VV Auger feature and incomplete elimination of energy-loss features. Some of the spectra in Fig. 1 have been truncated to eliminate identified artifacts. The overall energy resolution was degraded to about 2 eV by the bias voltage on the sample.

Figure 1(b) shows a series of Auger-electron spectra of Cu for incident electron energies E between 965 and 1505 eV.¹¹ The spectrum for $E = 1505$ eV consists of the prominent L_3VV feature at about 919 eV and the much weaker L_2VV structures at about 939 eV; this spectrum is in agreement with published data.⁵ As the incident energy is reduced to 965 eV, the intensity of the feature at about 915 eV previously ascribed to the effects of Coster-Kronig transitions decreases. Although

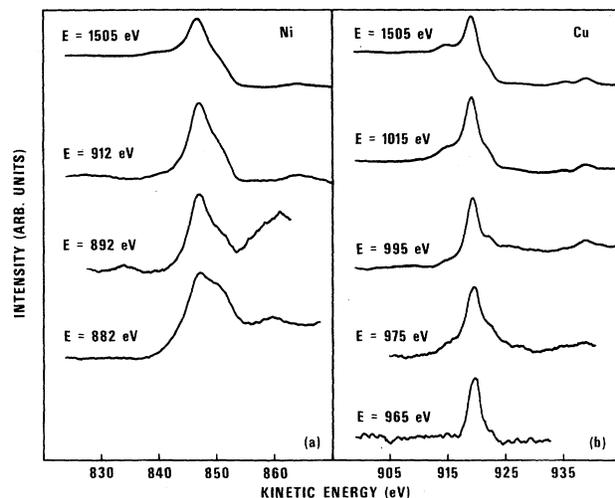


FIG. 1. Experimental Auger-electron spectra for (a) Ni and (b) Cu as a function of incident electron energy E . Binding energies of electrons in the L_2 and L_3 subshells are approximately 872 and 855 eV for Ni and 951 and 931 eV for Cu, respectively (Ref. 12).

the threshold energy of L_2 -subshell ionization is 951 eV,¹² the cross section for L_2 -subshell ionization decreases more rapidly than that for L_3 -subshell ionization for $965 < E < 1000$ eV. The spectrum for $E = 965$ eV is in close agreement with that obtained by a coincidence method to eliminate Coster-Kronig effects.¹³ We also find that the intensity in the 895–915-eV region relative to that of the 919-eV peak for $E = 1000$ eV is much reduced compared to that found for $E = 1505$ eV. This observation reflects the decreasing depth of L_3 -subshell ionization possible as the incident energy decreases to threshold.

Figure 1(a) shows a similar series of Auger-electron spectra of Ni for different incident energies. As for Cu, the weak peak at about 840 eV decreases in intensity; this feature is likewise associated with Coster-Kronig transitions from initial L_2 -subshell ionizations rather than an intrinsic process (i.e., shakeup) associated with initial L_3 -subshell ionizations.

We observed a significant, systematic shift in the positions of the main L_3VV peak for both Cu and Ni as a function of E , as shown in Fig. 2. The

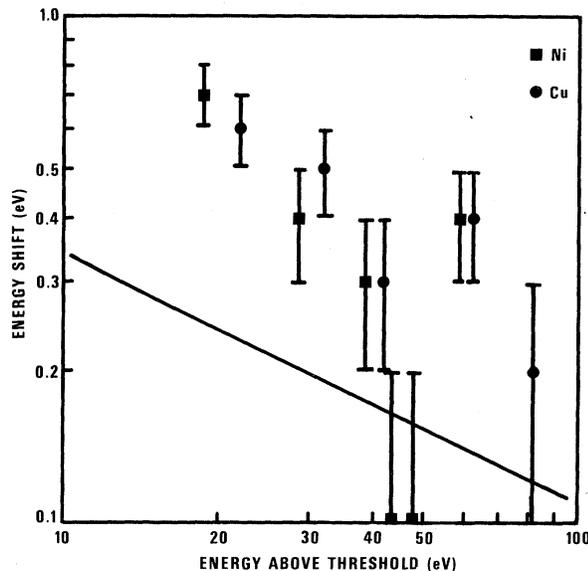


FIG. 2. Plot of the shift in the measured position of the dominant peak in the L_3VV Auger spectra of Cu (solid circles) and Ni (solid squares) as a function of incident energy above the L_3 -subshell binding energy for each metal. The shift is measured with respect to the peak position found with $E = 1505$ eV and the error bars indicate the imprecision in peak location. The solid line is the result of a model calculation for a free atom (Ref. 14) with a L_3 -subshell lifetime corresponding to 0.6 eV (Ref. 18).

dependence of the shift on E is similar to the dependence $\Delta E \propto (E - E_c)^{-1/2}$, where E_c is the core-electron binding energy, that has been observed previously.^{8,9} The latter shifts have been interpreted as a Coulomb interaction often referred to as post-collision interaction (PCI). The result of a free-atom PCI model calculation¹⁴ is shown in Fig. 2 as a solid line; this calculation neglects the effect of the excited core electron and thus underestimates the expected energy shift.

Figure 3 shows a comparison of the Ni L_3VV spectrum (curve *b*) measured at $E = 912$ eV with self-convolutions of a calculated¹⁵ density of states (curve *a*) and of a measurement¹⁶ of the valence-band x-ray photoemission spectrum (curve *c*). The convolutions have been performed with use of 852.4 eV as the binding energy of electrons in the L_3 subshell.¹⁶ The displacement of the measured Auger peak in curve *b* from either the theoretical (curve *a*) or the empirical (curve *c*) peak positions indicates the degree of correlation effects. In Fig. 3, curve *b* shows two compo-

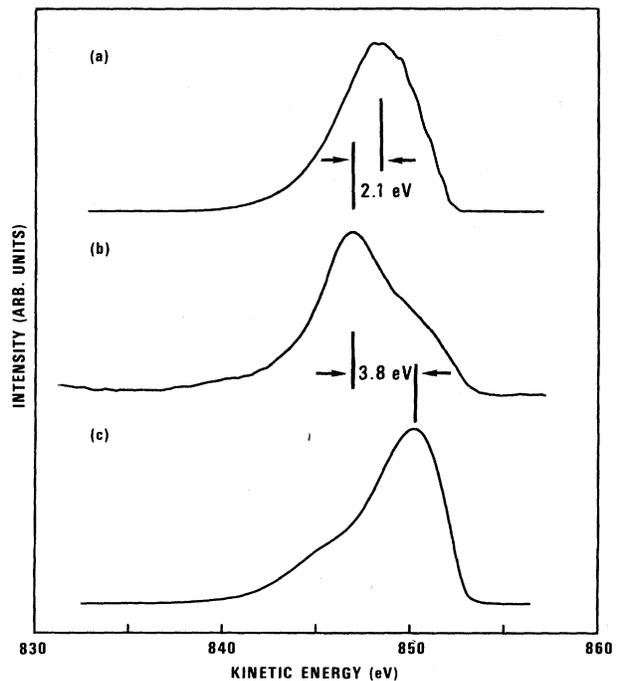


FIG. 3. Comparison of L_3VV Auger-electron spectrum of Ni measured with $E = 912$ eV (curve *b*) with self-convolution of a calculated density of states (curve *a*) and of an experimental (Ref. 16) valence-band x-ray-photoemission spectrum (curve *c*). The calculated density of states resulted from use of the spin-polarized exchange-correlation potential of von Barth and Hedin (see Ref. 15).

nents in the Auger line: a main peak which is displaced by 2.1 eV from the theoretical or 3.8 eV from the empirical line-position estimates and a shoulder attributed to a second peak with a displacement less than 1 eV. The estimated experimental uncertainty is 0.3 eV.

We take the displacement between the main peaks in Fig. 3, curves *a* and *b*, of 2.1 eV as providing a nominal value of U_{eff} . The larger displacement between the peaks of Fig. 3, curves *b* and *c*, is related to many-electron effects that modify the measured photoemission spectrum from the calculated one-electron density of states.

The criterion for atomic or bandlike behavior is associated, respectively, with $U_{\text{eff}} \gg W$ or $U_{\text{eff}} \ll W$, where W is the width of the valence band.⁶ A value of U_{eff} intermediate between these extremes should result in an Auger line whose shape exhibits both broad bandlike and narrow atomic features. The nominal U_{eff} is comparable to the calculated width of the Ni *d* band, 4.5 eV.¹⁵ We therefore identify the main peak in our Auger spectrum at 846 eV as due to atomic final states and the undisplaced shoulder at ~850 eV as associated with bandlike final states.

The nominal value of U_{eff} for Ni of 2.1 eV has to be increased by 0.4 eV because of the PCI effect shown in Fig. 2. Our final value is $U_{\text{eff}} = 2.5$ eV. This value is significantly lower than the value of 4.1 eV obtained by a similar technique¹ and significantly higher than the value of 1.4 eV obtained from photoemission satellites.² Calculated electronic properties of Ni are sensitive to U_{eff} ; variations in U_{eff} of ± 1 eV can have a large effect on photoemission line shapes, satellite intensities, and the exchange gap.^{3, 4} Our experimental value of 2.5 eV is consistent with the analyses of Treglia, Ducastelle, and Spanjaard and of Kleinman who have deduced values of ~2.3 and 3.2 eV, respectively.

The fact that the shifts of Auger-electron lines in Fig. 2 are comparable to free-atom PCI shifts indicates that metallic screening apparently has a small effect. Our results also indicate that measurements of binding energies of core electrons under "adiabatic" conditions (i.e., near-threshold excitation) as obtained, for example,

in appearance-potential spectroscopy (APS) will always be less than those measured under "sudden" conditions as obtained, for example, in x-ray photoemission spectroscopy (XPS). A systematic difference¹⁷ between binding energies measured by APS and XPS is therefore expected and is not necessarily associated with possible experimental artifacts.

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