

High-Resolution Measurements of the $L_3M_{2,3}M_{4,5}$ Auger Transitions in Nickel and Copper*

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Measurements are reported (with ≈ 0.1 -eV resolution) of the $L_3M_{2,3}M_{4,5}$ Auger-electron energy distributions from evaporated Ni and Cu using electron-beam excitation. The data reveal new structure (over an ≈ 20 -eV range) that could be correlated in part with the final states (for atomic Cu) and in part with overall features of the $3d$ -band density of states determined by soft-x-ray emission spectroscopy and x-ray photoelectron spectroscopy.

Auger-electron spectroscopy has been extensively employed for the chemical characterization of solid surfaces.¹ This Letter describes measurements with improved energy resolution (≈ 0.1 eV) which were undertaken to assess the practicality of deducing density-of-states information from Auger-electron energy distributions, as suggested by Lander.² There are only a limited number of techniques³⁻⁵ for probing the occupied valence bands of solids, but it is known that energy-dependent transition probabilities and specific initial- or final-state effects can perturb the observed spectral distributions.⁶ In the absence of a complete theory describing each type of measurement, comparisons and contrasts of spectral data obtained for a material by different techniques are valuable in determining common features of the density of states and the importance of the possible perturbing effects.

Few attempts have been made to obtain density-of-states information from Auger-electron spectra.⁷ In contrast to this earlier work that was restricted to K -valence-valence or L -valence-valence transitions (which involve an integral self-convolution of the density of states times the transition probability), it was decided to measure here Auger transitions involving two relatively well-defined inner-shell levels and the valence band (for which no deconvolution of the experimental data is required). The $L_3M_{2,3}M_{4,5}$ Auger transitions of nickel and copper were selected for measurement, as features of the valence-band (predominantly $3d$) density of states have been determined by other techniques.^{4,5,8} The new measurements show evidence of final-state splitting (not apparent or considered in previous work⁷) that could be interpreted with the use of a simple atomic model. On the basis of this model calculation, one component of the Auger structure for each metal could be selected and compared with other experimental data. Tak-

ing into account the lifetime broadening of the L_3 and M_3 levels for Ni and Cu, the present results were similar to the results of x-ray photoelectron⁵ and soft-x-ray emission⁸ experiments that were obtained with comparable overall energy resolution.

Initial ionizations in the evaporated samples were created by 3-keV electrons and electron energy analysis was performed with a Kuyatt-Simpson analyzer system⁹; details of the experiment will be published elsewhere. Figure 1 shows the experimental data in the region of the

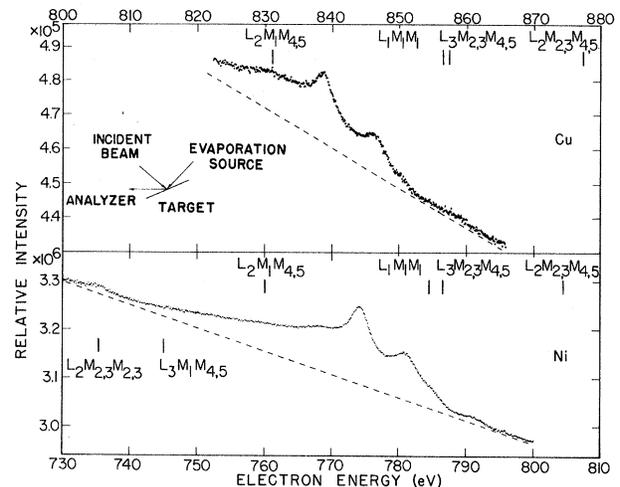


FIG. 1. Portions of the secondary-electron energy spectra for Ni and Cu obtained by excitation with 3-keV electrons. Dashed lines represent an assumed linear background (to compensate partially for inelastic scattering of the Auger electrons) to give the curves of Fig. 2. Vertical bars denote the positions of Auger transitions based on pure $j-j$ coupling and calculated with the ground-state electron binding energies [J. A. Bearden and A. F. Burr, *Rev. Mod. Phys.* **39**, 125 (1967)]. Auger peaks could be expected to be found at energies about 5 to 10 eV lower than those indicated as the emitting atom is left in a doubly ionized state following the specified transitions.

expected positions of the $L_2M_{2,3}M_{4,5}$ Auger transitions for Ni and Cu. For each metal, the principal feature is a pair of peaks, as observed^{10,11} and discussed¹² previously. For reasons that will be detailed below, we identify the structure consisting of these two peaks (774.2 and 780.9 eV for Ni, and 838.8 and 846.4 eV for Cu), the weaker peak at lower energy (≈ 767.5 eV for Ni and ≈ 830 eV for Cu), and some fraction of the higher-energy shoulders located at ≈ 785.5 eV for Ni and ≈ 850.5 eV for Cu as comprising the $L_3M_{2,3}M_{4,5}$ Auger transition for each element. The structure at higher energies is due to initial ionizations in the L_2 shell. We identify the weak peak at about 735.5 eV for Ni as being due to the $L_3M_1M_{4,5}$ transition. The other possible transitions shown in Fig. 1 would be expected to be much weaker than those just discussed, mainly on account of Coster-Kronig transitions.¹³ The quasicontinuous general increase in intensity with decreasing energy seen in Fig. 1 can be attributed to inelastic scattering of the emerging Auger electrons. The structure of interest can be displayed more clearly by subtracting an arbitrary linear background, indicated by the dashed lines in Fig. 1, and the results of this partial correction for inelastic scattering are shown in Fig. 2. Some fine structure, defined by a sequence of points, is believed detectable in Fig. 1 and has been shown in Fig. 2, even though the amplitude

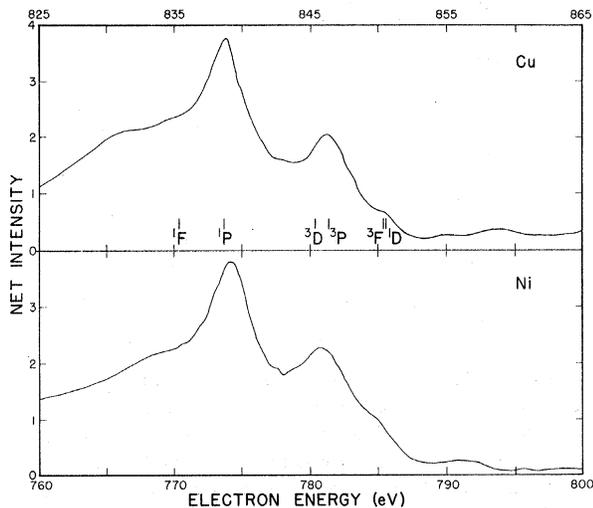


FIG. 2. Smooth curves showing $L_3M_{2,3}M_{4,5}$ and weak $L_2M_{2,3}M_{4,5}$ Auger transitions for Ni and Cu (data of Fig. 1 after subtraction of a linear background to correct partially for inelastic scattering). Vertical bars (top) denote the calculated *relative* energy separations of the designated final states for the copper configuration $3s^2 3p^5 3d^9$.

of this structure is comparable to the statistical uncertainty of a single point in Fig. 1.

The $L_3M_{2,3}M_{4,5}$ structure of Fig. 2 is distributed over about 20 eV and cannot be interpreted on the basis of pure $j-j$ coupling.¹² The observed structure can be understood with the use of $L-S$ coupling^{12,14} and with the following model which, for greater simplicity, will be applied only to Cu. Following the $L_3M_{2,3}M_{4,5}$ Auger transition a copper atom would have the configuration $1s^2 2s^2 2p^6 - 3s^2 3p^5 3d^9 4s$. The widths of the principal structure of Figs. 1 and 2 reflect mainly the $3d$ band (as discussed below), and we will ignore here, for simplicity, the contribution associated with the $4s$ electron ($L_3M_{2,3}N_1$) as this would be spread (with no significant features expected⁸) over a range of at least 9 eV. For the configuration $1s^2 2s^2 2p^6 3s^2 3p^5 3d^9$, there are then three possible final singlet and three possible final triplet states based on $L-S$ coupling.¹⁵ A. W. Weiss of the National Bureau of Standards has calculated the Slater integrals¹⁵ for CuIII in its ground state (using Clementi wave functions) to enable estimates to be made of the energy differences between the above six final states. The calculated *relative* energy separations of these final states are indicated in Fig. 2 in which it can be seen that the spread in final-state energies is comparable to that for the experimental data. The spin-orbit interaction in the $3p$ shell has been neglected here, but this splitting (≈ 2 eV)⁸ should not greatly modify the spread of final-state energies. It is reasonable to presume that for the Auger transition $2p^5 3p^6 3d^{10} ({}^2P) \rightarrow 2p^6 3p^5 3d^9 \epsilon l$, the most intense features correspond to $l=0$ and thus, by the Auger selection rules, to the 1P and 3P final states.¹⁶ The computed separation of these final states corresponds closely to the observed separation of the two more intense Cu peaks in Fig. 2.

Figure 3 shows the x-ray photoelectron spectra (XPS) of Fadley and Shirley,⁵ and the M_3 soft-x-ray emission spectra (SXS) of Cuthill *et al.*⁸ The top panels of Fig. 3 show the present Auger data (AES); we have here arbitrarily aligned each of the two prominent peaks for each element (Fig. 2) with the d -band peak positions found in the XPS and SXS experiments.¹⁷ The upper portions of the AES spectra for each element are broader than the lower portions, as would be expected from the overlapping contributions corresponding to the 3D and 3P final states indicated for Cu in Fig. 2, and it therefore appears reasonable to compare the lower AES curves with the SXS and XPS data.

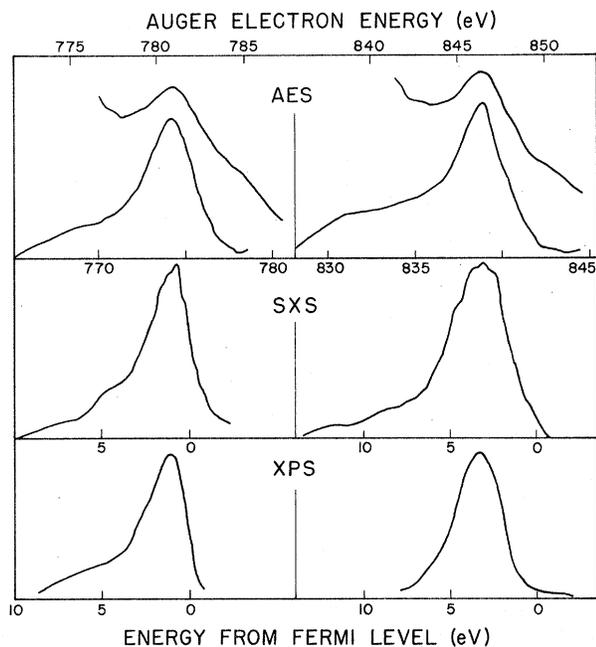


FIG. 3. Comparison of Auger-electron spectra with soft-x-ray emission spectra (Ref. 8) and x-ray photoelectron spectra (Ref. 5) for Ni (left) and Cu (right). The AES curves have been derived from Fig. 2 with each of the two prominent AES peaks for both Ni and Cu vertically aligned with the SXS and XPS $3d$ -band peak positions.

The lower AES curves are very similar in overall appearance to the SXS and XPS data. The lifetime broadening associated with the $L_3M_{2,3}M_{4,5}$ Auger transition for Ni and Cu is estimated^{8,18} to be 0.6 eV, and it thus appears that the overall features of the $3d$ bands for these metals are being determined, with comparable overall energy resolution,^{3,5,8} by the SXS, XPS, and AES techniques. There is weak structure in the lower AES curves at the expected position of the Fermi level but this and the other fine structure, if real, might be due to overlapping final-state components as well as to structure in the density of states. The detailed differences in the spectra for each metal in Fig. 3 are believed due to the perturbing effects described in the first paragraph; multiple initial- or final-state effects have already been observed in AES of gases¹⁹ and in SXS²⁰ and XPS^{14,21} of solids. It appears that AES can be a useful complement to SXS and XPS in determining the magnitude of these effects and in elucidating features of the density of electronic states.

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Electric-Field-Dependent Conductivity for Hopping-Type Charge Transport

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Measurements of the electric field dependence of the conductivity have been made on the transition-metal oxide $\text{Ni}_{0.6}\text{Mn}_{2.4}\text{O}_4$. It is found that the conductivity is a linear function of field to fields of 3×10^5 V/cm after corrections for thermal response are made. The observed effect cannot be explained in terms of current theory of field-dependent hopping transport.

An electric-field-dependent conductivity has been observed in the spinel-structured transition-metal oxide $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$. Both the magnitude of the effect and the functional field dependence are in disagreement with current theoretical treatments of high-field charge transport in localized hopping materials.

In the papers by Éfros,¹ Bagley,² and Emtage³ an electric-field-dependent conductivity was derived for charge transport by thermally activated hopping of localized charge carriers. These authors included the additional energy difference between neighboring atomic sites, eFl , in a calculation of the hopping frequency of a localized charge carrier (e is the electronic charge, F the field strength, and l is the intersite or hopping distance). Bagley, in terms of a diffusion model, and Éfros and Emtage, in terms of the Holstein small-polaron model, arrived at the same expression for a field-dependent conductivity. This expression is

$$\sigma = (A/F) \sinh(eFl/2kT), \quad (1)$$

where A contains the carrier concentration and the hopping parameters which are assumed to be field independent. This expression is an analytic function of the field with no unknown parameters and is therefore readily compared with experiment.

The compound $\text{Ni}_x\text{Mn}_{3-x}\text{O}_4$ was selected for study because it has been established that the charge-transport mechanism is thermally acti-

vated hopping. Charge transport in this system has been studied by Larson *et al.*⁴ over the composition range $1 > x > 0$. From measurements of the thermoelectric power and conductivity, they conclude that the charge-transport mechanism is a local and thermally activated valence exchange between +3 and +4 manganese ions on the octahedrally coordinated lattice sites. The carrier concentration is constant and determined by the relative concentration of +3 and +4 octahedral manganese ions and is on the order of 10^{20} cm^{-3} . The charge carrier mobility is thermally activated with an activation energy of 0.35 eV and has a room-temperature value of about 10^{-4} $\text{cm}^2/\text{V sec}$. Similar conclusions have been reached in other manganese spinel compounds such as $\text{ZnLi}_x\text{Mn}_{2-x}\text{O}_4$ ⁵ and $\text{Cu}_x\text{Ni}_{1-x}\text{Mn}_2\text{O}_4$,⁶ in all of which the $\text{Mn}^{+3}\text{-Mn}^{+4}$ valence states exist on the octahedral sites and provide the charge carriers.

The experimental procedures employed in measuring the field dependence of the conductivity must be carefully chosen so that extraneous changes in conductance at high fields due to contact barriers and Joule self-heating can be either eliminated or accounted for. Details of the experimental procedures employed are described in this Letter in order fully to substantiate the results presented below.

The samples were prepared in polycrystalline form by sintering the appropriate mixture of NiO and Mn_2O_3 . The composition $\text{Ni}_{0.6}\text{Mn}_{2.4}\text{O}_4$, which has a room-temperature resistivity of approxi-