Two-Electron Resonance at the 3p Threshold of Cu and Ni

M. Iwan
II Institut für Experimentalphysik, Universität Hamburg, Hamburg, D-2000, Federal Republic of Germany

and

F. J. Himpsel and D. E. Eastman
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598
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A sharp 3d-electron satellite excitation has been found for Cu which exhibits a strong resonant enhancement ($\sim \times 5$) at the Cu 3p-core-level threshold similar to the 6-eV resonant satellite observed previously in Ni. This satellite, which has two peaks at 11.8 and 14.6 eV below E_F, is identified as a quasiatomic two-electron excitation with two 3d holes plus one 4s electron ($3d^8 4s$). Present models for the Ni resonant satellite are not able to describe our Cu results.

A satellite structure observed at about 6 eV below the Fermi level E_F in Ni photoemission spectra[1-5] has gained interest since a resonance of the satellite intensity was observed at the 3p-core-level threshold.[1-3] At least three different explanations have been offered for this satellite: (a) Guillot *et al.*[1] propose an autoionization process which could qualitatively explain the resonance but fails to explain the existence of the satellite below the 3p threshold; (b) Tibbets and Egelhoff[2] invoke a configuration interaction (shakeup) mechanism where a 4p state becomes occupied concurrent with the creation of a 3d hole; and (c) Penn[3] proposed a shakeup process which involves the excitation of two-hole virtual bound states involving correlated d holes which resonantly interact with the 3$p \rightarrow$ empty-d-state transition at threshold. It has been stated that such satellites are associated with metals such as Fe, Co, and Ni which have partially filled d bands, but not with Cu.[1,3,4] In particular, the resonance enhancement of the Ni satellite has been related to the 3p-core-level $\rightarrow$ empty-d-state excitation.[1,3,4]

Contrary to these conclusions, we have found a satellite structure for Cu which has a resonance behavior similar to that of the 6-eV satellite previously reported for Ni.[1] For Cu, two sharp ($\sim$ 1.3 eV full width at half maximum) satellite peaks are observed at 14.6 and 11.8 eV below E_F, i.e., at 11.0 and 8.2 eV below the center of the 3d bands. They exhibit an approximately fivefold resonant enhancement at the 3p threshold. This double-peak resonant satellite in Cu cannot be explained by the previously proposed mechanisms for Ni, which require empty d states[1,3] or give the wrong satellite peak structures and energy separations.[2]

We have determined that the resonant satellite in Cu can be described by a quasiatomic shakeup state involving two correlated 3d holes plus a low-lying excited nl electron (nl mainly 4s) in the final state. Off resonance, this two-hole shakeup state for Cu is excited according to $3p^6(3d^{10})4s + h\nu \rightarrow 3p^6(3d^8 nl)4s + e^-$. At resonance, the excitation and simultaneous Auger decay of the 3p state creates a two-hole final state with the same configuration:

$$3p^6 3d^{10}4s + h\nu \rightarrow 3p^5 3d^{10}4snl \rightarrow 3p^6(3d^8 nl)4s + e^-.$$

Consequently, a Fano-type resonance between these two-electron excitations occurs which is analogous to the usual Fano resonance between the one-electron excitations (3p hole and 3d hole) at the 3p threshold. The 3p absorption edges for Cu and Ni are shown to be markedly affected by these resonant two-electron excitations.

The experiments were performed with a two-dimensional display-type spectrometer combined with a toroidal-grating monochromator using synchrotron radiation from Tantalus I. Counting rates were 2×10^6/s for the Cu 3d bands with an overall energy resolution of $\sim$ 0.3 eV and acceptance of an emission solid angle of 1.8 sr. The photon flux was determined by the photoyield of a clean Au film and published quantum yield data. Crystals were sputter annealed and characterized by low-energy electron diffraction, Auger spectroscopy, and photoelectron spectroscopy.

Figure 1 shows angle-integrated photoelectron spectra of Cu(100) normalized to the incident photon flux. The geometry (s-polarized light, collection in an $\sim 80^\circ$ cone around the surface normal) was chosen to minimize emission from the 4s4p bands which are degenerate with the Ni satellite but not with the Cu satellite. Indeed, we see only very weak emission in the sp-band re-

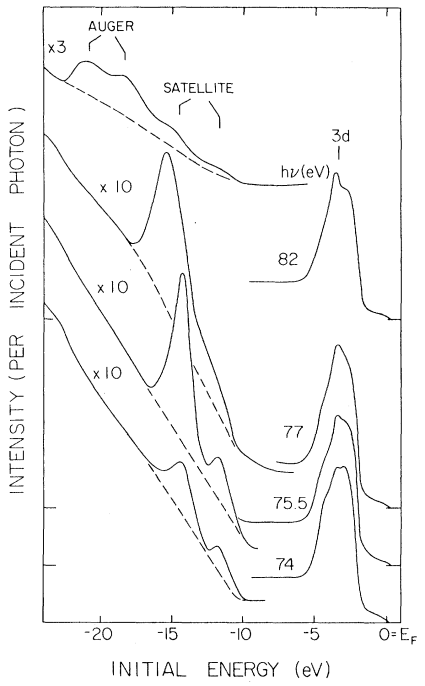

FIG. 1. Angle-integrated photoelectron energy distributions from Cu(100) for different photon energies ($h\nu$) with s-polarized light. Satellite peaks are seen at 14.6 and 11.8 eV below E_F which show resonant enhancement at the Cu $3p$ core-level threshold ($h\nu \sim 76$ eV).

gion of Cu (-9 eV $< E_i \leq -5$ eV). For Cu, we see two satellite peaks (14.6 and 11.8 eV below E_F) below the $3p$ threshold and an $M_{2,3}VV$ ($V = M_{4,5}$) Auger multiplet (two peaks at ~61.3 and ~63.7 eV above E_F and a shoulder at ~66.5 eV) which coincides with the satellite at the $3p$-core-level threshold and moves towards lower apparent initial energy when $h\nu$ is increased. The Cu satellite structure is visible far from resonance [$3p_{3/2}$ = 75.2 eV, $3p_{1/2}$ = 77.2 eV (Ref. 1)], e.g., at $h\nu$ = 50 eV with ~1% and at $h\nu$ = 100 eV with ~3% of the $3d$ emission intensity. The Cu satellites are not due to an energy-loss feature since there is no structure in the energy-loss function $\mathrm{Im}(1/\epsilon)$ at that energy. The main energy-loss peak is ~20 eV below the $3d$ peak (see Fig. 1 and Hagemann, Gudat, and Kunz[6]).

Figure 2 shows the line shape and energy of the satellite and Auger structures for Cu and Ni. They were obtained by subtracting a smooth background of secondary electron emission (deduced from spectra for photon energies far from resonance and taking into account secondary electron production by the $3d$ bands, the satellite, and the Auger multiplet). This figure also gives the

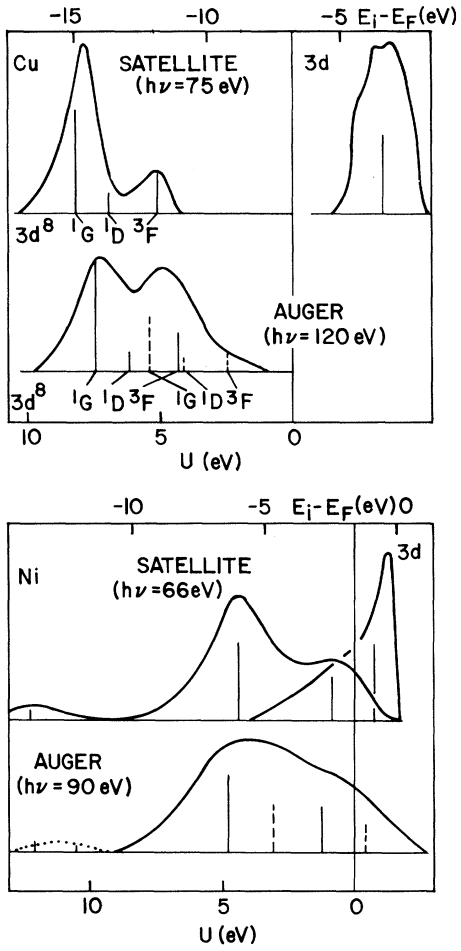

FIG. 2. Satellite and Auger ($M_{2,3}VV$) line shapes and energy positions for Cu and Ni. The excess binding energies U (effective Coulomb interaction, see Ref. 7) are measured relative to the energies expected in a one-electron model, i.e., an "initial" energy of $E_i = E(3d) - [E_F - E(3d)]$ ($E_i = E_F - 6.8$ eV for Cu, $E_i = E_F - 1.4$ eV for Ni) for the satellite and a final energy $E_f = E(3d) + [E(3d) - E(3p_{3/2})]$ ($E_f = E_F + 68.4$ eV for Cu, $E_f = E_F + 64.6$ eV for Ni) for the M_3VV Auger line. A decomposition into atomic d^8 multiplets is shown for Cu [the ^1S and ^3P states of the d^8 multiplet have negligible calculated intensity (Ref. 7) and have been omitted]. The dotted line is from Ref. 8.

basic explanation for the satellite and Auger structures in an atomic picture. The satellites are shakeup features, i.e., the atom is left in an excited state after ejection of a $3d$ photoelectron. For Cu, the splitting and the intensity ratio of the two satellites are characteristic of a $3d^8$ configuration (see, for example, atomic-energy levels given for $3d^8 4s^1$ as well as for $3d^8 4s^2$ by Moore[9] and atomic calculations for d^8 multiplet splittings and intensities of the $L_{2,3}M_{4,5}M_{4,5}$ Auger

multiplet in Antonides, Janse, and Sawatzky[7] and references therein). In an analogous way, the Cu $M_{2,3}VV$ Auger structure is decomposed into two d^8 multiplets which are split by the spin-orbit splitting of the $3p_{1/2}$ and $3p_{3/2}$ holes (2.0 eV) and weighed according to their multiplicity. For Ni we see three resonant satellite structures (~ 14, ~ 6, and ~ 2–3 eV below E_F). The $M_{2,3}VV$ Auger structure can be decomposed into the satellite multiplet for Ni as well as for Cu. We note that the effective Coulomb interaction U (see Fig. 2) is about the same for the satellite lines as for the Auger lines in both Cu and Ni.

For the strongest satellite we observe a separation of 11.3 eV from the center of the $3d$-emission peak (which is 3.4 eV below E_F). This separation is close to the energy difference of 10.9 eV between the corresponding $^2G(3d^8(^1G)4s^1)$ and $^2D(3d^9)$ levels[9] in atomic Cu^{++} (itinerant $4s$ screening electrons), but not far from the difference of about 9 eV between the $3d^84s^2$ and $3d^94s$ levels in atomic Cu^+ (atomic $4s$ screening electron). If we apply the atomic model proposed for Ni by Tibbetts and Egelhoff[2] to Cu, we obtain an incorrect multiplet structure, i.e., a single narrow (< 1 eV full width) peak for the satellite ($3d^94p^1$ configuration) and a separation of only ~ 6 eV from the $3d$-emission peak ($3d^94s^1$ in this model). The Ni satellite and Auger line shapes cannot be described by an atomic model unambigously. At least two different shakeup final states are expected [$3d^94s + h\nu \rightarrow (3d^74s)4s + e^-$ and $\rightarrow 3d^84s + e^-$ for shakeup into empty $4s$ and $3d$ levels, respectively]. Also, it has been shown that the Auger final state has substantial itinerant character,[7,10] with consequent line broadening as observed.

In Fig. 3 we sketch the ionization processes which contribute to the spectra of Fig. 1. An autoionization interaction between the $3d \rightarrow e^-$ continuum and the quasidiscrete core-hole excitation $3p \rightarrow nl$ has been used previously[11-13] to explain the shape of the Ni $3p$ absorption edge assuming $nl = 3d$. The two-electron resonance that we find involves excitation of two $3d$ electrons. The shakeup continuum and the $M_{2,3}VV$ Auger semicontinuum interact with a discrete transition which can be described as the coherent Auger decay of the $3p \rightarrow nl$ excitation at threshold.

In Fig. 4, the partial cross sections for the two-electron resonant satellite channels as well as for the Auger channels are shown. The spectra were decomposed using the line shapes and energy positions given in Fig. 2. The resonant satellite cross sections contribute significantly to the $3p$ absorption edge. In particular, the double structure in the Ni $3p$ edge[12] is mainly due to the resonant satellite. The shape of the resonance curve for the satellite cross section (Fig. 4) is very similar for Cu and Ni, e.g., considering the resonant enhancement (× 5) and the width (~ 3 eV) which is much narrower than the total absorption

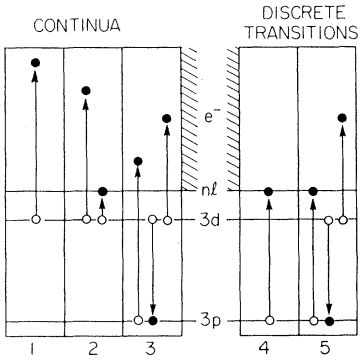

FIG. 3. Schematic representation of the photoionization processes discussed in the text. 1 denotes $3d$ excitation, 2 denotes nonresonant shakeup, 3 denotes $M_{2,3}VV$ Auger, 4 denotes core-hole threshold, 5 denotes resonant shakeup or resonant Auger. Discrete transitions interact with continua (autoionization), e.g., process 1 with process 4 ($1\text{-}e^-$ resonance) and processes 2 and 3 with process 5 ($2\text{-}e^-$ resonance).

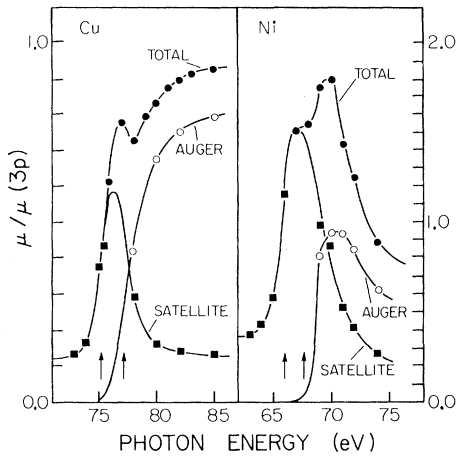

FIG. 4. Partial cross sections for the two-electron resonance channels (total denotes Auger plus satellite) described in Fig. 3, normalized to the step height of the absorption coefficient at the $3p$ threshold [$\mu_{(3p)} = 3.6 \times 10^5$ cm^{-1} for Ni (Ref. 13) and $\mu_{(3p)} = 1.4 \times 10^5$ cm^{-1} for Cu (Ref. 6) using the area under the $3d$-emission peak below the $3p$ threshold for calibration].

edge. This narrow resonance indicates that a discrete ($3d^8 4s$) final state exists for Cu with the $4s$ electron localized at the site of the $3d$ holes. This calls into question models treating the shake-up electron (nl in Fig. 3) as itinerant.[3] The magnitude of the satellite cross sections is ~ 7 times larger in Ni than in Cu. This indicates the contribution of extra shakeup levels due to empty d states ($nl = 3d$), for Ni compared with Cu.

We expect that the two-electron resonance observed for Cu and Ni occurs for d levels in other materials, especially for higher-Z atoms where atomic effects become important.[7] Compared with Ni, Cu is a simpler test case for studying many-electron effects at the $3p$ threshold because of its sharp atomiclike[7,10] satellite and Auger multiplets and the simple filled-d-shell ground state.

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Anomalous Magnetoresistance of Quasi One-Dimensional $Hg_{3-\delta}AsF_6$

D. P. Chakraborty, R. Spal, A. M. Denenstein, K.-B. Lee, and A. J. Heeger
Department of Physics and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104

and

M. Ya. Azbel
Department of Physics, Tel Aviv University, Ramat-Aviv, Israel
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Resistivity and magnetoresistance data in the field range 0–180 kG at low temperatures are presented. The temperature dependence (T^3), suppression of residual resistance, and large magnetoresistance are understood as resulting from the unusual Fermi surface. In spite of the large number of defects and the relatively weak interchain coupling ($\Delta\epsilon/E_F \sim 10^{-2}$) inferred from the magnetoresistance, the states near E_F are extended over distances greater than 100 μm.

The incommensurate linear chain structure of $Hg_{3-\delta}AsF_6$ leads to unique one-dimensional (1d) lattice dynamics[1] and highly anisotropic electronic properties.[2-4] Transport studies showed metallic behavior with $\rho_{ab}(300\ \mathrm{K}) \simeq 10^{-4}\ \Omega$-cm and no sign of residual resistivity,[3] a result of particular interest since the unusual structure[1,5] contains approximately 6% anion vacancies.[6] The magnetoresistance[4] is large in low fields, and the increment, $\Delta\rho(T,H) \simeq \Delta\rho(H)$, is insensitive to temperature. These magnetoresistance data were described in terms of a magnetic-field-induced residual resistivity.[4]

We present new data on the resistivity and magnetoresistance in the extended field range 0–180 kG at low temperatures. Low-field studies show that $\Delta\rho/\rho(0)$ approaches quadratic behavior only for $H \lesssim 1$ G. The high-field results show no satu-