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Multielectron excitations in Ni and Cu metals observed with x-ray photoelectron spectroscopy

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High-energy x-ray photoemission spectra (XPS) can provide information on transitions due to multielectron excitations. The experimentally observed satellites in the XPS spectra of Ni and Cu are compared with the calculated transitions. The availability of calculated band structures for these metals has provided a framework for theoretical understanding of the electronic structure of metals having *d* bands.

INTRODUCTION

In recent years a debate has developed as to the nature of the phenomena connected with the presence of a satellite in the valence region of the Ni spectrum (subsequently observed also in Cu, Zn, Ga, etc.) which, at particular energy values (the $3p$ core-level threshold), undergoes a resonance phenomenon.

We will here briefly discuss this debate and then go on to demonstrate that further light can be shed on our knowledge of Ni and Cu *via* high-energy spectroscopy ($h\nu = 1486.6$ eV). Multielectron excitations become important at this energy, which is much higher than the energies at which the resonance effect is observed.

EXPERIMENTAL

A Vacuum Generators Ltd. model No. ESCA-3 photoelectron spectrometer with an Al $K\alpha_{1,2}$ radiation source ($h\nu = 1486.6$ eV) and pressure of 1.0×10^{-9} Torr was used for the x-ray photoemission spectra (XPS) measurements. Polycrystalline targets with the surface mechanically polished and cleaned *via* several cycles of Ar-ion sputtering and annealing at 600 °C (Ni) and 700 °C (Cu) were used as samples. The possibility of a little CO or O_2 contamination on the surfaces does not change the content of our discussion, because it can cause only a decrease in the satellite intensities. In the figures, the energy zero has been placed at the center of the main peaks for convenience.

RESULTS

Ni

For Ni the problems most discussed in the literature are essentially as follows:

(1) the width and position of the $3d$ bands;

(2) the appearance of a satellite (or envelope of satellites) at a $\Delta\epsilon \cong 6.0$ eV from the Fermi energy E_F in the valence region or from the center of the main core peaks;

(3) the appearance of a second satellite at ~ 12 eV as predicted by the calculations of Feldkamp and Davis[1] and clearly observable in our Ni $3p$ region. Furthermore, we give an interpretation of the Ni $3s$ satellite different from that proposed by Hüfner and Wertheim.[2]

The first problem to clarify is whether the local atomic ground-state configuration in Ni metal is "essentially" $3d^9 4s$ or $3d^{10} 4s$. To solve this problem, we will first consider this last point. From an analysis of the $3s$ XPS line in metallic Ni, Hüfner and Wertheim[2] deduced that the exchange splitting expected for the interaction of the $3s$ core hole state with an open d shell is absent; consequently, the local configuration must be $3d^{10} 4s$. Comparing the Ni $3s$ XPS spectrum with that of CuO (having configuration d^9) and Cu_2O (having configuration d^{10}) reveals considerable similarity between the Ni $3s$ and CuO $3s$ spectra (see Fig. 1), while no similarities with the spectrum of Cu_2O may be seen.

The presence of such a complex spectrum in CuO(d^9) which disappears in Cu_2O(d^{10}) has been attributed to the presence of an exchange splitting due to an open-shell configuration.[3] This exchange splitting also appears to be present in the Ni $3s$ spectrum, although it is partially covered by the simultaneous presence of the well-known satellite at ~ 6 eV found in all Ni spectral regions and discussed below.

It thus appears reasonable that the local atomic configuration of the Ni metal is "essentially" $3d^9 4s$. Apart from the exchange effect (shown by A and B in Fig. 1, in analogy with CuO) two other satellites are observed, each at $\Delta\epsilon = 3.0 \pm 0.2$ eV from A and B. Given that these cannot originate in $3s$ from multiplet splitting[4] they must be assigned to an intraband transition (e.g., $d \rightarrow d$). In the $2p_{3/2}$ region, a transition appearing at a $\Delta\epsilon$ from the main peak of 3.2 eV is also shown by an arrow.

Turning to point (1) (width and position of $3d$ band), there is disagreement between experiment and theory as to the d-band width and the exchange splitting caused by ferromagnetic character of Ni. Previous XPS measurements showed there is a band narrowing in Ni (Ref. 5) which was subsequently verified by more accurate angle-resolved photoemission (ARP) measurements.[6] The experimental values of the d-band resonance width (~ 3.3 eV) and the exchange splitting (0.31 eV) are narrower than the self-consistent one-electron band theory estimates (4.5 and 0.7 eV, respectively).[7] Conversely, for Cu the same theoretical calculations are in good agreement with experimental re-

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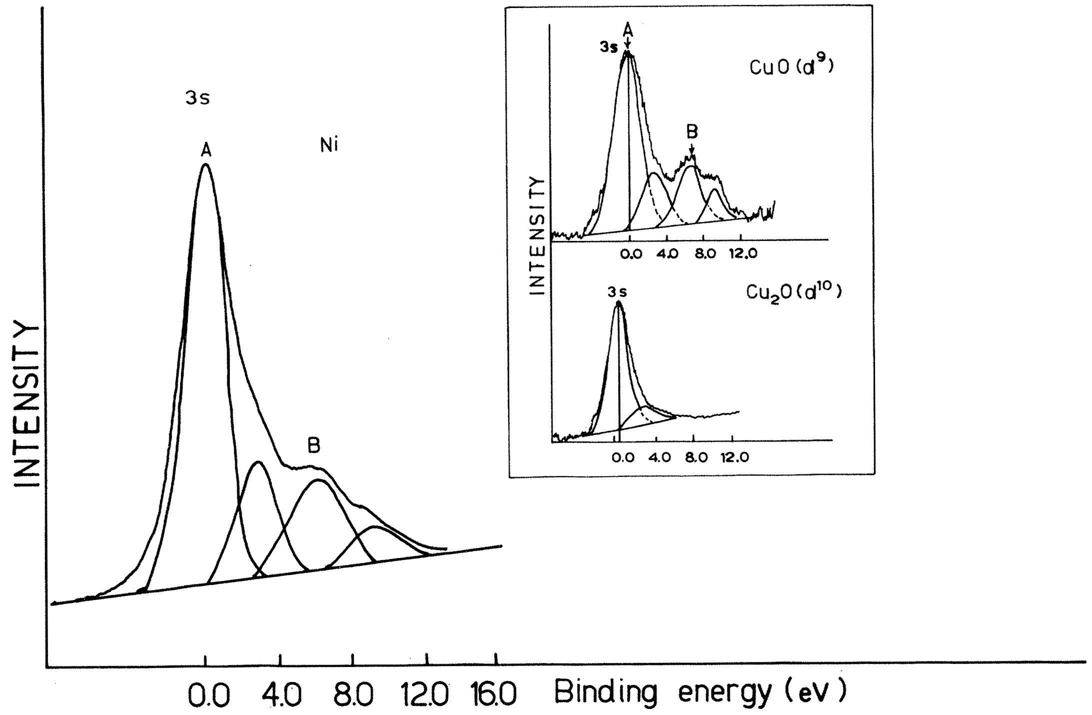

FIG. 1. XPS spectrum of Ni 3*s* band.

sults.

This difference in behavior between the two metals was attributed to the different *d*-band population. As the 3*d* bands are partially filled in Ni whereas they are full in Cu, this suggests that electron correlations in the 3*d* bands are responsible for the discrepancies. The Hubbard model, a simple approximation for the self-energy operator, is generally used to treat such correlations.[8–11] Recently Anisimov *et al.*[12] used an $X\alpha$ cluster approximation to calculate the orbitals relaxation in photoelectron spectra for systems having a continuous distribution of electron states. These authors concluded that relaxation effects lead to a narrowing of the occupied region of the Ni *d* band in accord with experimental results. The transitions observed in the Ni 3*s* and Ni $2p_{3/2}$ at $\Delta\epsilon = 3.0$–3.2 eV, and assigned by us to a $d \rightarrow d$ interband transition seem to confirm the other experimental results. We will not discuss this aspect further because it has been widely discussed in the literature.

In an XPS spectrum of the 3*d* band [Fig. 2(b)] carried out on a polycrystalline sample it is possible to observe narrowing of the 3*d* band, as reported in Ref. 5 and a broad envelope connected with the satellite found at a $\Delta\epsilon$ from E_F of ~ 6.0 eV and present also in the other spectral regions.[13] The presence of this satellite in the Ni 3*d* region (point 2) has become of interest since enhancement of the satellite intensity was observed by Guillot *et al.*[14] at the 3*p* core-level threshold.

Many workers have treated this problem. It can be divided into two aspects: (a) the presence of a satellite (or convolution of satellites) at ~ 6.0 eV from the main peaks in all the spectral regions; (b) enhancement of this satellite when the photon energy is close to the binding energy of the 3*p* core electrons.

The presence of this satellite in all the spectral regions suggests that these satellites have the same origin. Hüfner and Wertheim[2] and Penn[10] used a Hubbard model to propose a two-hole virtual bound state in the 3*d* band (d^8 configuration) following photoexcitation of the *d*-band electrons. As explained by Penn, far from resonance the satellite is due to an intra–*d*-shell Auger transition occurring simultaneously with the 3*d* photoexcitation to produce a two-hole virtual bound state in the 3*d* band. In this model, the process predicts that two electrons are excited simultaneously, one of them into the continuum and

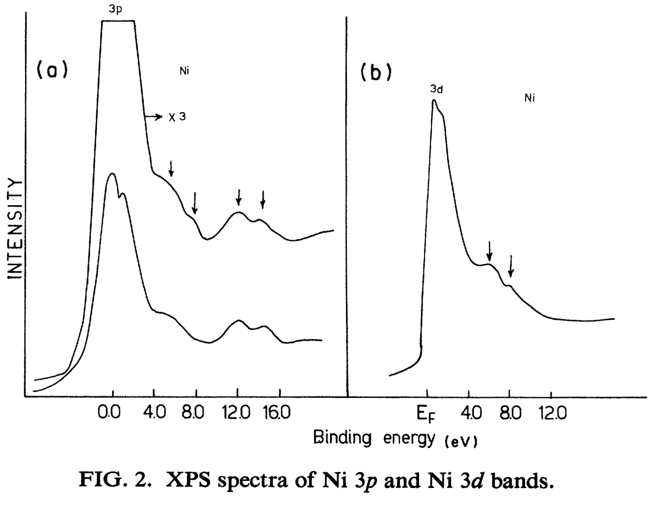

FIG. 2. XPS spectra of Ni 3*p* and Ni 3*d* bands.

the other into the empty *d* state immediately above the Fermi level.

Eberhardt and Plummer[15] criticized this interpretation, pointing out that if this shakeup occurs within the *d* band (i.e., an excitation from the bottom of the 3*d* band to the empty *d* state at the Fermi level) where the maximum expected energy spread is only ~3.3 eV,[6] the energy of the transition would be too low to explain the satellite at 6.0 eV. Recent experimental results on Cu (see below) and analysis in terms of atomic energy levels[16–18] associate the Ni 6.0-eV peak with a $3d \rightarrow 4s,p$ shakeup. Tibbetts and Egelhoff[16] compared the ultraviolet photoelectron spectra of Ni atoms (vapor deposited on an amorphous carbon substrate) with those of bulk nickel. They concluded that (a) the 6.0-eV peak appears continuously with coverage from nickel atoms up to bulk nickel (this implies that there is a quasiatomic excitation in bulk nickel), (b) the 3*d* shell is not dispersed and the observed states are well described by the d^8 atomic multiplet terms, and (c) the photoemission process producing the 6.0-eV peak in the bulk-nickel spectrum depends on the valence "shell" of the ionized atom being more tightly bound than the valence "band" of the surrounding metal. These results lead to the conclusion that the valence to 4*s*,*p* excitations are quasiatomic and may be compared with that of atomic nickel.

Given the narrowness of the *d* band (3.3 eV) and the consequent high localization of the 3*d* wave functions (almost like core electrons) this atomiclike interpretation of the shakeup process appears highly probable. The problem is to assign the correct ground-state configuration. Three ground-state configurations are possible: $3d^84s^2$, $3d^94s$, and $3d^{10}$. There exists a large probability that the dominant configuration, as discussed at the beginning of this paragraph, is $3d^94s$.

After excitation of a *d* electron, the Ni^+ configuration becomes $3d^84s$. From Moore's tables[19] the excited $3d^74s^2$ or $3d^74s\,4p$ states above the ground state of Ni^+ have an energy of ~6.3 eV. This is in line with the atomiclike nature suggested above.

In the valence region of the spectrum a resonance effect is also observed on this satellite when the photon energy is close to the 3*p* binding energy. At this energy, two phenomena overlap: (a) a $3d \rightarrow 4s$ transition (the 6.0-eV satellite), and (b) a photoexcitation of a 3*p* core electron to an empty *d* state. This photoexcitation is followed by an Auger process in which a *d* electron fills the core hole, while another *d* electron is excited to higher energy (Penn[10]). Because this model is operative only in metals with unfilled *d* bands, Davis and Feldkamp[20] propose a more general mechanism which, involving a super-Coster-Kronig (sCK) decay process, also covers cases of metals having filled *d* bands such as Cu, Zn, Ga, etc.

To further clarify these mechanisms, other experiments have been attempted to check cases in which the Ni atoms are isolated, e.g., nickel phtalocyanine.[21] The same resonance behavior at 6.0 eV was found, indicating that it is a strongly localized atomic effect. The authors[21] interpreted the enhancement as a resonance (of quasiatomic nickel) caused by a configuration interaction between $3p \rightarrow 3d$ and continuum transitions. Kanski *et al.*[22] then calculated the photoelectron energy distribution in Ni(100) and found that the resonance structures can be well understood in terms of normal interband excitations. They suggested that the strong enhancement at $h\nu = 66$ eV arises when the final electron energy band approaches the Brillouin-zone boundary at point *X* and is caused by a corresponding enhancement in the one-dimensional joint density of states.

Our XPS measurements are outside the range of this phenomenon because of the high incident photon energy in electron spectroscopy for chemical analysis (ESCA) ($h\nu = 1486.6$ eV). At these photon energies, transitions to empty *s*-*p* states become allowed. Because of the width of the *s*-*p* band and the possibility that multiplet splitting occurs, the experimental satellite appears as a broad envelope, suggesting that more than one transition is present. From our XPS spectra (Figs. 2 and 3) we observe the following.

(1) In all regions of the Ni spectrum, the satellite appearing at $\Delta\epsilon \simeq 6$ eV from the main peak (or from E_F in the valence region) is clearly split by ~2.2 eV in the 3*d* and 3*p* regions and ~1.3 eV in $2p_{3/2}$.

(2) In the 3*p* region, a further pair of satellites is observed at a $\Delta\epsilon$ from the main peak of 12.3 and 14.6 eV.

In the Ni 2*p* region the satellite at ~6.0 eV is found at different $\Delta\epsilon$ as regard the two main $2p_{3/2}$ and $2p_{1/2}$ peaks. In the $2p_{3/2}$ region, it lies at $\Delta\epsilon = 6.0$ eV and in the $2p_{1/2}$ one at $\Delta\epsilon = 4.6$ eV (Fig. 3). This $\Delta\epsilon$, differing from

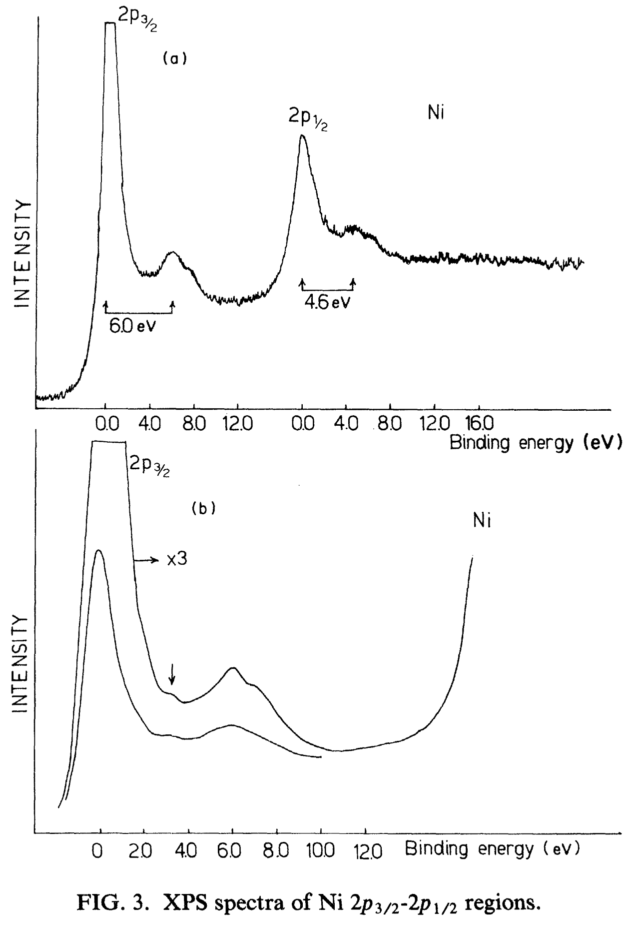

FIG. 3. XPS spectra of Ni $2p_{3/2}$-$2p_{1/2}$ regions.

the two components of the Ni $2p$ transition, is discussed by Martensson and Johansson[23] in terms of a complete screening picture of the final states. The main core line corresponds to a d-electron final-state screening while the satellite is due to s-electron screening.

According to this model, the calculated position of the $2p$ satellite should be at 4.6 eV. The difference in the satellite positions with respect to $2p_{3/2}$ and $2p_{1/2}$ main peaks may then be ascribed to different multiplet splitting for the two $2p_{3/2}$-$2p_{1/2}$ holes.[24] This different position of the satellites is clearly evident in our spectra [Fig. 3(a)]. However, as mentioned above, the satellite spectrum clearly shows that we do not have a single transition but a series of two (or more) giving a rather broad band which does not arise from multiplet splitting alone (Figs. 2 and 3). Indeed, in the $2p$ region, i.e., multiplet splitting between p and d hole is relatively small.[25] There is, probably, a series of multielectron excitations which arise because of the width of the s-p band.

Conversely, in the $3d$ and $3p$ regions the dispersion connected with the multiplet splitting effect is much more extensive and there is a kind of continuity between main peak and satellite. In the $3p$ region, a convolution of satellites centered at ~ 13 eV is also clearly visible. This is also formed by more than one transition, which seems to confirm the suggestion that they are multielectron excitations. Feldkamp and Davis[1] calculate that this satellite (13 eV) corresponds to an unoccupied two-bound level, i.e., the d^8 configuration. According to Moore's tables[19] the transitions $3d^8 4s \rightarrow 3d^7 4s\,5s$ (or $5p$) or $3d^8 4s \rightarrow 3d^8 5p$ can be energetically compatible.

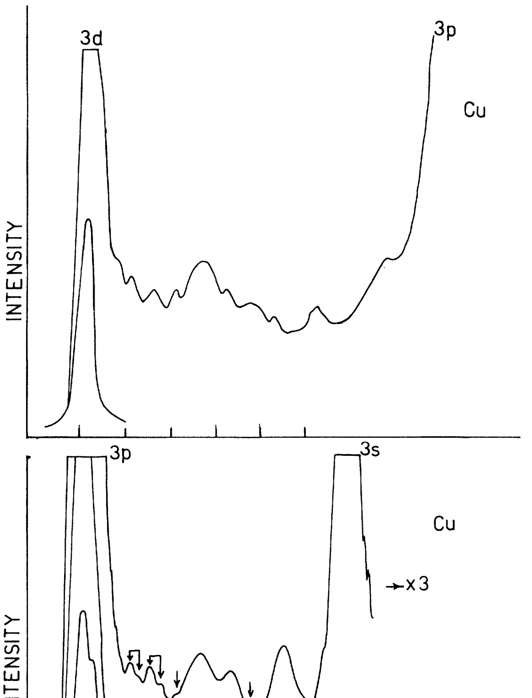

FIG. 4. XPS spectra of Cu $3d$ and Cu $3p$ regions.

Copper

For copper and other metals having full d bands (Zn, Ga, etc.) the phenomena involved are somewhat different. For example, the narrowing of the d-d bandwidth is no longer present. However, even in these metals a satellite similar to that observed for Ni (at ~ 6.0 eV) is again observed[18] and a similar—but weaker—resonance enhancement at the metal $3p$ core-level threshold. The latter is unexpected since the Cu d bands are (nominally, at least) full and the Penn mechanism requires that holes be present in the d bands.

Iwan *et al.*,[18] using an atomic notation, propose that the satellite observed off-resonance is produced by a two-electron excitation with two holes plus one $4s$ electron ($3d^8 4s$). At resonance, the excitation and simultaneous Auger decay of the $3p$ states creates a two-hole final state with the same configuration. A Fano-type resonance thus occurs between these two excitations.

Using solid state notation, Davis and Feldkamp proposed a model for the same problem in which the sequence of events is slightly different.[20] When a photon is absorbed, a $3p$ core electron is excited to the $4s$-$4p$ conduction band and the $3p$ hole state decays *via* a super-Coster-Kronig transition into the continuum state. Given that the Auger peak moves with photon energy (the Auger line is at constant kinetic energy but nonconstant binding energy) near the photon threshold energy the two effects combine and become indistinguishable. This produces a broad resonance peak in the spectrum consisting of (a) a satellite at constant binding energy and (b) an Auger line.

In this model, the satellite is due to the strong interaction of the $4s$-$4p$ conduction electrons with $3d^8$ configuration in the final state. Enhancement at resonance occurs in the satellite because the sCK decay process preferentially goes to d^8 final states. The width of the satellite peak (actually two peaks due to multiplet splitting) is governed by the lifetime of the $3d^8$ configuration. Far from resonance—as in our case— the same satellite final state can be reached if a $3d \rightarrow 4s\,4p$ shakeup transition accompanies the photoexcitation of a $3d$ electron.

The band structure of copper has been extensively studied both theoretically[26–28] and experimentally in ARP spectroscopy[29–34] with, in general, good fit between theory and experiments. The d band is narrow and lies somewhat below the Fermi level, the top of the band having a binding energy of ~ 2.0 eV. Near E_F and above the d band there is also a broad s-p band with some d character.

One problem in directly comparing theory and experiments[34] is that the photoemission results (which by definition are excited state) cannot be directly compared with ground-state band-structure calculations without relaxation corrections that are, generally, difficult to estimate. For their experimental results on the occupied states, Courth *et al.*[34] find better agreement with the oldest non-

TABLE I. Experimental values of the separation energy $\Delta\epsilon$ (eV) of the satellites relative to the main Cu 3*d* and 3*p* peaks. The error limit can be evaluated as ±0.2 eV.

	3*d*	3*p*	Janak (Ref. 27)	Assignment[a]
Main peak	0.0	0.0		
Satellite	5.2	4.8	5.0	$L_2'^{v} \rightarrow L_1^c$
	8.0	8.8		
	12.0	12.0		
	16.0	16.8	16.3	$X_5^v \rightarrow X_5^c$
	21.0	21.2	20.9	$X_5^v \rightarrow X_3^c$
	25.0		24.5	$L_3^v \rightarrow L_2'^{c}$
		26.8	26.3	$L_3^v \rightarrow L_3'^{c}$
	29.6	29.4	29.6	$\Gamma_{12}^v \rightarrow \Gamma_{25}'^{c}$
	34.0		34.1	$\Gamma_1^v \rightarrow \Gamma_{15}^c$
	41.2			$\Gamma_1^v \rightarrow \Gamma_{ex}^c$

[a] Band labels are from Burdick (Ref. 26).

self-consistent augmented plane wave band-structure calculation of Burdick[26] than with more sophisticated self-consistent theories.[28]

Here, we are particularly interested in the multielectron excitation phenomena because of the high energy of our source. XPS spectra contain detailed information about the excitation of individual final states which are not evident in absorption spectroscopy.

In Fig. 4 we report our spectra of the 3*d* and 3*p* zones where the satellite structure appears more evident. In both these zones two sharp satellites are present at a $\Delta\epsilon$ from the main peak of 8.0 and 12 eV (from 3*d*) and 8.8 and 12.0 eV (from 3*p*). The satellite appearing in the 3*p* zone clearly shows also the spin-orbit splitting of the two $p_{3/2}$-$p_{1/2}$ components of the 3*p* level (shown in the figure by two coupled arrows).

We describe this double peak (8.0 and 12 eV), observed far from resonance energy, as $3d \rightarrow 4s\,4p$ shakeup transitions accompanying the photoexcitation of a 3*d* electron.

At lower $\Delta\epsilon$ (5.5 eV from 3*d* and 4.8 eV from 3*p*) we observe another transition corresponding to the interband transition observed by Johnson and Christy[35] by means of reflection and transmission measurements. Their experimental value (5.0 eV) corresponds with the calculated *L* gap ($L_{2'}^{v} \rightarrow L_1^c$) reported by Janak *et al.*,[27] by Burdick[26] (4.56 eV), and by Jepsen *et al.*[28] (4.6 eV).

In addition to the described transitions, we also observe a series of other satellites at a $\Delta\epsilon > 15.0$ eV which we ascribe to multielectron excitations. These transitions may be compared with the calculated[26,27] band structure. Table I lists our experimental data in comparison with some transitions drawn from the calculations of Janak *et al.*

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