

## Quasiatomic Excitation in Bulk Nickel

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Ultraviolet photoemission spectra of nickel atoms vapor deposited on an amorphous carbon substrate show a characteristic energy-loss peak 6 eV below  $E_f$  for the full range of coverages from adsorbed nickel adatoms to bulk nickel. The quasiatomic excitation responsible for this energy-loss peak is the promotion of a nickel valence-shell electron to a  $4p$  level in the ionic final state.

The peak in the photoemission spectra of nickel which is located about 6 eV below the Fermi level has been the subject of much discussion in recent years. This Letter presents the first data which show that the structure at 6-eV binding energy is observed for dispersed nickel adatoms as well as for bulk nickel, implying that the 6-eV peak is a quasiatomic excitation in bulk nickel.

Spicer originally pointed out that this peak was well outside the region of direct photoemission from the nickel  $d$  bands and thus involved an energy-loss process.<sup>1</sup> Hüfner and Wertheim<sup>2</sup> found that similar energy-loss peaks are observed in conjunction with the x-ray photoemission peaks of the nickel  $2p$ ,  $3s$ , and  $3p$  core levels. They attributed this energy loss to photoionization with the simultaneous promotion of a  $3d$  electron to a higher-energy state. Ley *et al.*,<sup>3</sup> emphasized that the screening and quenching of valence-band holes plays a decisive role in determining which metals will exhibit loss peaks. Smith *et al.*,<sup>4</sup> attributed this 6-eV peak in nickel to direct interband transitions; however, the precise nature of the final state was not known. It was suggested by Mott,<sup>5</sup> that the 6-eV loss process in nickel could be due to the creation of an excitonic state. As Guillot *et al.*<sup>6</sup> point out, localized, atomic effects coexist with itinerant, metallic effects in nickel and this has long impeded better interpretation of experiments on bulk nickel. Nevertheless, the work of Kemeny and Shevchik,<sup>7</sup> provide some further insight into the origin of the peak. Their work on the alloy  $Ni_9Zn_1$  shows that such an energy-loss peak is observed in conjunction with the primary photoemission peaks of the nickel core levels but not with those of the zinc core levels. This demonstrates that the peak at 6 eV for bulk nickel is not an extrinsic loss feature exhibited by all photoelectrons traversing a nickel medium. Instead, it is an intrinsic excitation which has a high probability of excitation when a nickel level is photoionized.

We have used ultraviolet photoelectron spec-

troscopy (UPS) to study the development of the electronic structure and the 6-eV peak during the transition from isolated adatoms to bulk nickel. In order to study the electronic properties of dispersed Ni atoms, we have vapor deposited small concentrations of Ni atoms on amorphous carbon at 295 K. It is well known from the studies of Hamilton, Logel, and Baetzold,<sup>8</sup> and Mason, Gerenser, and Lee,<sup>9</sup> that transition-metal atoms deposited on amorphous carbon at coverages less than  $5 \times 10^{14}$  atoms/cm<sup>2</sup> (0.05 nm) are present as isolated adatoms. The experiments have been conducted under ultrahigh-vacuum conditions in the  $10^{-8}$  Pa ( $10^{-10}$  Torr) range. Surface cleanliness was monitored by x-ray photoemission and contamination was negligible at all times. The amorphous carbon substrate was produced by extensive Ar<sup>+</sup> ion bombardment ( $14 \mu\text{A}/\text{cm}^2$  at 2 kV for 3 h, plus annealing to remove implanted Ar) of the basal plane of pyrolytic graphite (Union Carbide). The nickel was evaporated from a tungsten filament and monitored with a quartz crystal microbalance. UPS data were recorded with a microwave discharge He resonance lamp, previously described,<sup>10</sup> and a commercial double-pass cylindrical-mirror analyzer and processed by an on-line minicomputer. The amorphous carbon substrate was tilted to achieve angle integration of the spectra.

Figure 1(a) presents the He I spectrum of the clean amorphous carbon surface. In order to display better the changes in the spectrum which accompany deposition of nickel atoms, the spectra for the various coverages of nickel have been plotted as difference graphs, i.e., the spectrum with nickel adatoms minus the clean surface spectrum. The results are presented in Fig. 1(b). Clearly the peak at 6-eV binding energy is observed continuously from the regime of isolated adatoms to the multilayer characteristic of bulk nickel. The slight shift in peak position and the modest broadening that occurs with increasing coverage indicate that the excitation is substan-

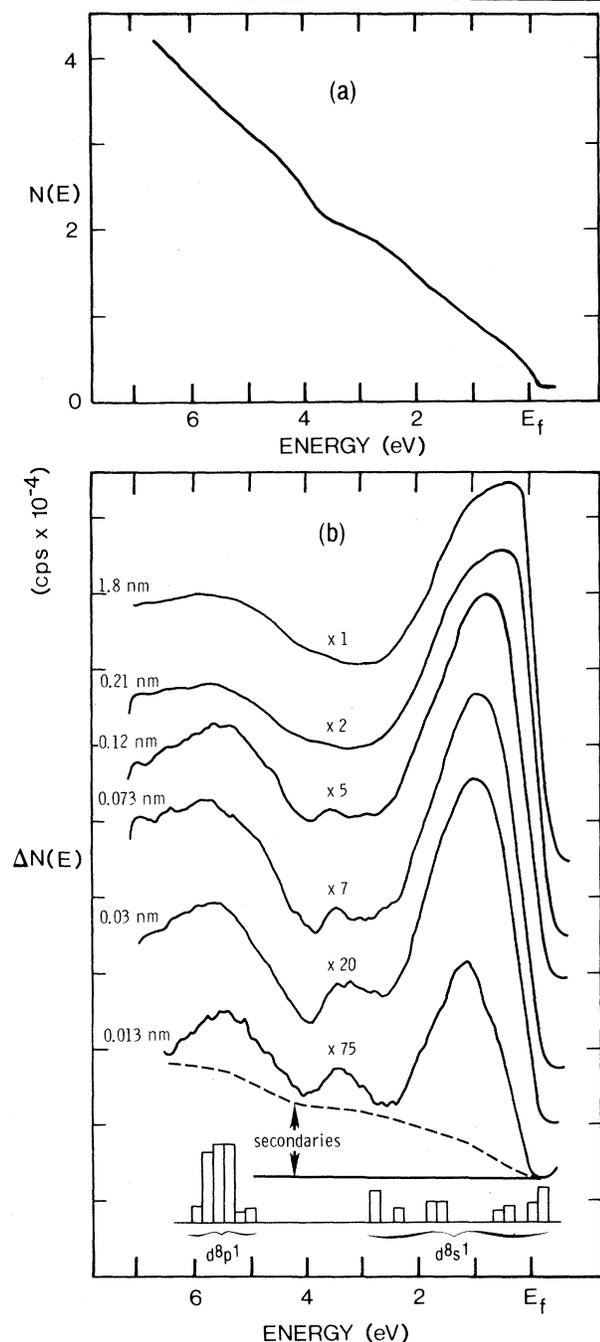


FIG. 1. (a) He I (21.2-eV photon energy) photoemission spectrum of clean amorphous carbon. (b) Difference spectra for Ni adsorbate layers on an amorphous carbon substrate. Each  $N(E)$  unit corresponds to  $10^4$  Hz for the 1.8-nm film. One monolayer equals approximately 0.2 nm.

tially the same in bulk nickel. The small peak observable at 3.5-eV binding energy at low coverage corresponds to energy to the only deviation

from linearity in the substrate spectrum in Fig. 1(a), and we can therefore not rule out the possibility that it is due to substrate subtraction.

Previous photoemission studies of gaseous Hg<sup>11</sup> and Ba<sup>12</sup> have been successfully interpreted by using optical data for the energy levels of the excited ionic final state. The energies of photoelectrons from dispersed Ni atoms may be calculated by a similar procedure.<sup>13</sup> The density of final states [Fig. 1(b)] is calculated by giving each electronic state its statistical weight of  $2J+1$  and summing over each 0.2-eV interval. The energy scale is adjusted by using our measured analyzer work function, the first ionization potential of Ni, and an extra-atomic relaxation of 3.9 eV associated with adsorption on a carbon substrate. The initial state of the Ni adatoms is expected to be  $d^9s^1$  rather than  $d^8s^2$ , with which it is almost degenerate, because the  $d^9s^1$  will be stabilized by bonding with the surface. The extremely high density of final states of type  $d^8p^1$  of the Ni<sup>+</sup> ion creates an especially large transition probability for the 6-eV loss peak. The  $d^8s^1$  final states appear in Fig. 1 to cover a wider energy range in the free atom than the  $d$  band (1-eV peak) at lowest coverage. However, the unpaired spins of the free atom will be quenched in the adsorbed atom thereby reducing the multiplet splittings and yielding better agreement.

Considering that precise calculation of peak positions using atomic data is impossible without knowing exact values for relaxation and binding energy shifts due to the carbon substrate, these values show good agreement with the shakeup peak of the He II spectrum. The spectra show that the final-state spectrum associated with the energy-loss peak at 6-eV binding energy ( $d^8p^1$ ) is little affected by the transition from atomic to bulk nickel.

In further support of the data of Fig. 1 are the corresponding spectra taken with He II radiation ( $h\nu = 40.8$  eV). It is important to establish that the 6-eV energy-loss feature is not photon-energy dependent and thus not simply due to a direct transition. Figure 2(a) presents the He II data for dispersed nickel adatoms at a coverage of 0.02 nm ( $2 \times 10^{14}$  cm<sup>-2</sup>) and for a 1.8-nm-thick film of nickel. Clearly the 6-eV feature is observed with about the same intensity relative to the 3d-band peak, both in the adsorbed-atom limit and in the bulk-metal limit.

Figure 2(b) presents an interesting correspondence in the x-ray ( $h\nu = 1253.6$  eV) photoelectron spectrum of the  $2p_{3/2}$  level of dispersed nickel

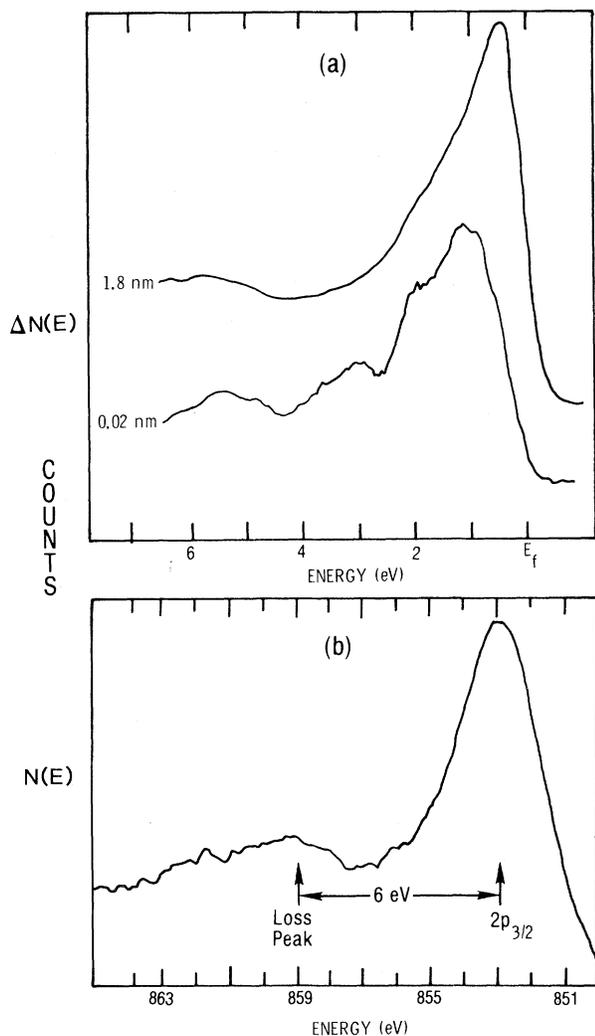


FIG. 2. (a) He II (40.8-eV photon energy) photoemission difference spectra for thin and thick layers of Ni on carbon substrates. (b) Mg  $K\alpha$  (1253.6-eV photon energy) photoemission spectrum for electrons ejected from  $2p_{3/2}$  core level for a 0.036-nm layer of Ni.

adatoms. An energy-loss peak is observed 6 eV below the primary photoelectron peak. This implies that a two-electron process can occur in which one electron is photoemitted from a core level and another is promoted from the valence band to the  $4p$  level. Of course, this peak has previously been observed for bulk nickel.<sup>2,7</sup> The significant point is that we report its observation for dispersed nickel adatoms. This implies that a quasiatomic excitation in bulk nickel can also occur in conjunction with photoemission from a core level. The present observations have an intriguing similarity to the Auger spectra of  $3d$ -series metals. Sawatzky<sup>14</sup> and Baro, Salmeron,

and Rojo<sup>15</sup> recently noted that all of the essential features of the  $L_{23}M_{45}M_{45}$  Auger spectra of Ni, Cu, Zn, Ga, Ge, As, and Se can be explained using an atomic model. In this model the final state consists of two  $3d$  holes localized on the same metal atom. The  $3d$  shell of the atom is thus not dispersed in any band sense and the observed states are well described by the  $d^8$  atomic multiplet terms. Although the quasiatomic phenomena observed in the present work for both valence and core ionization arrive at the final state in a completely different manner from the Auger mechanism, there is a close correspondence in the final states as both have two holes localized on the same metal atom. Thus we conclude that the photoemission process which produces the 6-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 so that the concurrent valence-to- $4p$  excitation can be localized as a quasiatomic excitation similar to that of atomic nickel. In order for the quasiatomic peak to be observed the two holes involved must remain localized on the same nickel atom for a finite time. From the observed peak width and the uncertainty principle, the localization must persist for at least  $10^{-16}$  s.

Not all two-electron processes contributing to the spectrum have energies as precisely defined as those which contribute to the 6-eV loss peak. In most cases the two holes will be at least partially dispersed in the nickel valence band. The resulting photoelectrons thus exhibit a continuous range of energies and appear as the secondary background shown in Fig. 1(b).

Another feature in Fig. 1 is noteworthy. At the lowest coverages of nickel, the density of states at the Fermi level is very small. At higher coverages an increase in the density of states at the Fermi level is observed during the development of bulk nickel. The  $3d$  band moves to lower binding energy until its upper edge is above the Fermi level. Most of the increase in the intensity at the Fermi level occurs as the coverage increases from half a monolayer to one monolayer. These observations provide insight into the evolution of the valence electronic structure from adsorbed nickel atoms to bulk nickel.

In conclusion, our experiments show that the 6-eV energy-loss peak appears continuously with coverage from Ni adatoms up to bulk Ni. The phenomenon responsible for this peak in bulk nickel is a quasiatomic excitation. The quasi-

atomic character is retained even in the bulk because nickel has a significant probability of forming an atomlike final state with two holes localized on the same atom. Thus we have found a new case in which a property of atomic nickel is manifest in bulk nickel.

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<sup>1</sup>W. E. Spicer, in *Optical Properties and Electronic Structure of Metals and Alloys*, edited by F. Abelès (North-Holland, Amsterdam, 1966).

<sup>2</sup>S. Hüfner and G. K. Wertheim, *Phys. Lett.* **51A**, 299, 301 (1975).

<sup>3</sup>L. Ley, S. P. Kowalczyk, F. R. McFeely, R. A. Pollak, and D. S. Shirley, *Phys. Rev. B* **8**, 2392 (1973).

<sup>4</sup>R. J. Smith, J. Anderson, J. Hermanson, and G. J. Lapeyre, *Solid State Commun.* **21**, 459 (1977).

<sup>5</sup>N. F. Mott, in *Optical Properties and Electronic*

*Structure of Metals*, edited by F. Abelès (North-Holland, Amsterdam, 1966), p. 314.

<sup>6</sup>C. Guillot, Y. Ballu, J. Paigné, J. Lecante, K. P. Jain, P. Thiry, R. Pinchaux, Y. Pétrouff, and L. M. Falicov, *Phys. Rev. Lett.* **39**, 1632 (1977).

<sup>7</sup>P. C. Kemeny and N. J. Shevchik, *Solid State Commun.* **17**, 255 (1975).

<sup>8</sup>J. F. Hamilton, P. C. Logel, and R. C. Baetzold, *Thin Solid Films* **32**, 233 (1976); J. F. Hamilton and P. C. Logel, *Thin Solid Films* **23**, 89 (1974), and *J. Catal.* **29**, 253 (1973).

<sup>9</sup>M. G. Mason, L. J. Gerenser, and S.-T. Lee, *Phys. Rev. Lett.* **39**, 288, 1372(E) (1977).

<sup>10</sup>G. G. Tibbetts, J. M. Burkstrand, and J. C. Tracy, *Phys. Rev. B* **15**, 3652 (1977).

<sup>11</sup>D. C. Frost, C. A. McDowell, and D. A. Vroom, *Chem. Phys. Lett.* **1**, 93 (1967).

<sup>12</sup>D. A. Shirley, to be published.

<sup>13</sup>C. E. Moore, *Atomic Energy Levels as Derived from Analysis of Optical Spectra* (U. S. GPO, Washington D. C., 1971).

<sup>14</sup>G. A. Sawatsky, *Phys. Rev. Lett.* **39**, 504 (1977).

<sup>15</sup>A. M. Baró, M. Salmeron, and J. M. Rojo, *J. Phys. F* **5**, 826 (1975).

## Pseudopotentials in Density-Functional Theory

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The ability of a local pseudopotential to describe accurately core effects in energy calculations is demonstrated. If the pseudopotential is properly chosen, excitation energies of the silicon atom and binding-energy curves of the Si<sub>2</sub> dimer agree well with calculations using the full density functional and the pseudo charge density is virtually identical to the real charge density outside the core region.

Pseudopotential schemes have been used widely in calculations of the electronic properties of semiconductors and their interfaces<sup>1</sup> in order to eliminate numerical difficulties arising from the core electrons and the requirement of orthogonality. The replacement of the core by a local effective potential is, however, an approximation which is difficult to test against *ab initio* calculations, so that questions such as the relationship between the pseudo charge density and the correct charge density are not yet settled. Recently, Wendel and Martin<sup>2</sup> used the density-functional scheme of Hohenberg, Kohn, and Sham<sup>3</sup> to calculate structural energies in silicon using the Si<sup>4+</sup> pseudopotential of Appelbaum and Hamann.<sup>4</sup> They noted that this potential leads to a substantial underestimate of the lattice constant, necessitating an additional *ad hoc* repulsive force.

Since the full density functional reproduces the lattice constants of many bulk materials remarkably accurately,<sup>5</sup> this error is probably a consequence of the pseudopotential approximation rather than the functional scheme itself.

In this Letter, we consider the relation between the full density functional (DF) and the pseudo density functional (PDF). We show that if the pseudopotential is chosen to maximize the similarity between valence orbitals and pseudo orbitals for the Si atomic ground state, a criterion different from that of Appelbaum and Hamann, both schemes give similar results for atomic excitation energies and for binding-energy curves of the Si<sub>2</sub> dimer. In addition, the pseudodensity and the correct density are virtually indistinguishable outside the core region. To our knowledge, this is the first quantitative comparison of