PHYSICAL REVIEW B VOLUME 26, NUMBER 9 1 NOVEMBER 1982

Resonant valence-band satellites and polar fluctuations in nickel and its compounds

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(Received 8 March 1982)

The photon energy dependences of the valence-band photoemission spectra of the Mott insulator NiO, the Pauli paramagnetic metal NiTe, the diamagnetic metal NiSb, and the semiconductor Cu_2O have been measured in the vicinity of the transition-metal $3p$ threshold. Resonant satellites similar to those of Ni and Cu metal were found in all of these compounds. The resonance behaviors of the satellites and the main $3d$ emissions are also similar to those of the metals. From these data it is concluded that (1) the satellites and the resonance behaviors are in the first approximation of an atomic origin, (2) the Fano line shapes in the constant initial-state spectra of Ni and its compounds arise from the super-Coster-Kronig interaction between a discrete state $3p^5 3d^{n+1}$ and continuum states $3p^6 3d^{n-1}\epsilon l$ following the $3p \rightarrow 3d$ photoabsorption, (3) initial-state configuration mixing contributes significantly to the Ni "6-eV" satellite, and (4) the Ni metal main $3d$ band resonates strongly due to a $3d^8 4s$ final state. Different interpretations of the Ni "6-eV" satellite are critically assessed in the light of these findings, and it is argued that these conclusions imply an appreciable amount of polar fluctuation to the $3d^8 4s^2$ configuration in the Ni metal many-body ground state. The importance of Hund's-rule coupling for the ferromagnetism of Ni is also discussed in view of different interpretations of the Ni satellite.

I. INTRODUCTION

A problem which is not yet fully resolved but is central to a complete understanding of the electronic structure of transition metals is the extent to which correlation effects reduce polar fluctuations, i.e., fluctuations in the number of d-shell electrons on an atom, below the value predicted by a Hartree-Fock or other one-electron theory.[1] The distribution of valence states d^n in an uncorrelated wave function follows a binomial law,[2,3] from which one finds, for example, that in a half-filled d band the fractional number of d^n are 0.246 (d^5), 0.205 (d^4,d^6), 0.117 (d^3,d^7), 0.044 (d^2,d^8), and less than 0.01 (d^0,d^1,d^9,d^{10}). If the Coulomb repulsion between two electrons on a site is comparable to or larger than the single-particle bandwidth, the occurrence of valence states far from the average number of electrons is suppressed, extreme examples being the mixed- or single-valent rare-earth materials in which the number of $4f^n$ valence states is only two or one, respectively, and the single-valent transition-metal oxides. The number of highly probable valence states is also greatly suppressed, even in an uncorrelated wave function, if the band is nearly filled. For example, if the average number of d electrons is 9.4, as for nickel, the uncorrelated valence-state distribution is[2] 0.538 (d^{10}), 0.344 (d^9), 0.099 (d^8), 0.017 (d^7), and less than 0.002 (d^6-d^0). Thus in nickel the question of primary quantitative importance is the extent of correlation suppression of the d^8 configuration in the ground state.

It is relevant that the width of the valence-band photoemission spectrum of nickel is about 30% smaller than predicted by band-structure calculations and that there is a satellite structure at about 6 eV below the Fermi level which does not correspond to any feature in the calculated band structure.[4–6]

Although much progress toward understanding this "6-eV" satellite has been made through various experimental and theoretical studies, there remain unanswered questions and divergences of models. In this paper we report resonance photoemission studies of the valence-band and satellite structures of several nickel and copper compounds, and we assess critically various models for the nickel 6-eV satellite in the light of the experimental results. We also point out certain inferences that can be drawn concerning polar fluctuations and the origin of ferromagnetism in the nickel ground state, depending on the interpretation of the satellite. The remainder of the introduction summarizes previous work on the satellite, and poses the questions to be discussed.

The nickel 6-eV satellite has received much attention recently,[7–14] motivated by the discovery that it shows a Fano-type resonant enhancement in intensity when the incident photon energy is close to that of the Ni $3p$ binding energy.[7] (See Fig. 1.) Guillot *et al.*[7] interpreted this satellite and its resonance behavior in terms of an atomic configuration interaction picture, in which it was argued that the ground state of nickel can be thought of as being in a coherent superposition of $3d^9 4s$ and $3d^{10}$ configurations and upon $3d$ photoemission the $3d^9 4s$ configuration gives the satellite with a $3d^8 4s$ final state. The satellite can display a Fano resonance near the $3p$ threshold by the photoabsorption process

$$3p^6 3d^9 4s + h\nu \rightarrow 3p^5 3d^{10} 4s \ ,$$

followed by a super-Coster-Kronig decay into a continuum

$$3p^5 3d^{10} 4s \rightarrow 3p^6 3d^8 4s + \epsilon l \ .$$

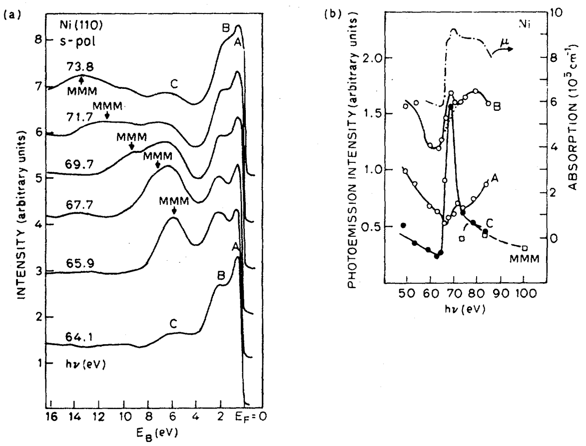

FIG. 1. (a) Energy-distribution curves (EDC's) for the valence band of Ni(100) excited by *s*-polarized photons with energies close to the $3p$ threshold. The peaks *A* and *B* represent the main $3d$ emissions and *C* represents the 6-eV satellite. *MMM* marks $M_{23}VV$ Auger emission (from Ref. 8). (b) Areas under the EDC structures of (a) vs photon energy. Curve *A* gives the contribution for $E_b < 1$ eV, curve *B* for 1 eV $< E_b < 4$ eV and curve *C* for $E_b > 4$ eV; curve *MMM* shows the area under the $M_{23}VV$ Auger emission. The scales are all comparable. For comparison, the absorption spectrum μ is included (from Ref. 8). Note the strong Fano-type enhancement of the 6-eV satellite (curve *C*) and the strong antiresonance of the main $3d$ emissions (curves *A* and *B*).

Penn,[9] on the other hand, considered an itinerant *d* band with intra-atomic Coulomb correlations described by the degenerate Hubbard Hamiltonian, and showed that the *d*-hole spectral density has contributions from the two-hole virtual bound states arising from multiple scattering of *d* holes due to the Coulomb interactions. The two-hole bound state then gives rise to the 6-eV satellite of Ni, and can resonate coherently at the Ni $3p$ edge ($\sim$67 eV) by the super-Coster-Kronig Auger decay following photoexcitation of $3p$ electrons to empty $3d$ states. In a related calculation, including multiplet splittings, Liebsch[10] suggested that for an almost filled *d* band, the two-hole bound state can be thought of as the remnant of the atomic d^8 multiplets. Mårtensson and Johansson[11] afterwards estimated the binding energy of the ^1G multiplet component of the d^8 configuration to be about 5.8 eV from the Fermi level. Recently a spin-polarized photoemission experiment[12] has been performed on Ni metal following the suggestion that the resonant two-hole bound state should be highly spin polarized,[13] and evidence was found that the 6-eV satellite is indeed spin polarized near resonance ($h\nu = \sim 67$ eV).

Both the models of Guillot *et al.* and Penn require the existence of *d* holes in the initial state to explain the occurrence of the satellite and its resonance behavior. However, contrary to these expectations, Iwan *et al.*[14] observed in Cu metal ($3d^{10}$ ground-state configuration) a satellite structure which shows a resonant enhancement at the Cu $3p$ edge ($\sim$77 eV). Consequently they proposed a quasiatomic shakeup mechanism involving two correlated $3d$ holes plus a low-lying excited $4s$ electron ($3d^8 4s^2$ final-state configuration) to be responsible for the satellite. Off resonance, this shakeup satellite is excited by the process

$$3p^6 3d^{10} 4s + h\nu \rightarrow 3p^6 3d^8 4s^2 + \epsilon l \ .$$

At resonance, the excitation of the $3p$ hole and subsequent Auger decay creates a two-hole final state with the same configuration

$$3p^6 3d^{10} 4s + h\nu \rightarrow 3p^5 3d^{10} 4s^2 \rightarrow 3p^6 3d^8 4s^2 + \epsilon l \,,$$

resulting in a Fano-type resonance. Similar resonant satellites are observed for Ga and GaP (Ref. 15) ($3d^{10}$ ground state), and they have been interpreted with the same model. One of the criticisms of this model is that the resonance of the satellite is rather sharp compared to the width of the Cu *s-p* band, and a possible mechanism to explain this was proposed by Davis and Feldkamp.[16] They considered a simple itinerant *s-p* band, but included interaction terms due to the potentials of the two-hole final state ($3d^8$ configuration) and the core-hole after photoabsorption, analogous to the x-ray edge problem. By numerical calculations they found a resonant satellite with a rather sharp resonance width, which persists for photon energies well above resonance. This can be interpreted as due to the singular transition probability to levels near the Fermi energy, as shown by Girvin and Penn's analytic calculations.[17] The atomic nature of the satellite in Cu metal has been supported by the experiment on Cu vapors,[18] which shows essentially the same satellites and resonance behaviors.

These interpretations of satellites as many-body effects were questioned by Kanski *et al.*[19] in the case of Ni. They calculated photoelectron energy distributions of Ni(100), and found a strong resonance due to interband transitions at 5-eV binding energy. They proposed, therefore, that the 6-eV satellite resonance is merely a conventional interband transition effect arising from an enhancement in the one-dimensional joint density of states. Still another interpretation was put forward by Dietz *et al.*,[20] who suggested that the resonant enhancement of the Ni 6-eV satellite at the $3p$ edge is mainly due to the overlap with the incoherent $M_{23}VV$ Auger emission following $3p \rightarrow 3d$ photoabsorption.

The essential differences that distinguish these models can be summarized by the following questions.

(1) Is the photoabsorption process responsible for the resonance at the threshold $3p \rightarrow 3d$,[7,9] or $3p \rightarrow 4s$?[14,15]

(2) Does the existence of a satellite and its resonance depend in an essential way on the valence-band electronic structure (metal or insulator), or are they basically of an atomic origin?

(3) Is the overlap of incoherent Auger emissions mainly responsible for the resonant enhancement of the satellite at the $3p$ edge?[20]

(4) Is the satellite a final-state shakeup effect, or does it represent ground-state mixing?

As reported in this paper, by studying the valence-band photoemission of several Ni and Cu compounds, we will try to answer these questions and thus understand better the origin of the Ni 6-eV satellite and its resonance behavior. In particular, we will show that the strong resonance which also occurs for the main band emission of Ni implies the presence of $3d^9 \rightarrow 3d^8$ spectral weight in the main band. This raises a question about the final state of the 6-eV satellite, because if it is a two-hole bound state relative to the resonating part of the main band then the satellite has a $3d^7 4s^2$ final state, whereas some models assume a $3d^8 4s$ final state for the satellite. We will also argue that the satellite for the most part represents ground-state configuration mixing, so that the interpretation of the satellite has important implications for the ground state of nickel metal and its ferromagnetism.

The remainder of this paper is organized as follows. Section II describes the samples and experimental procedures. In Sec. III the experimental data are presented and interpreted to answer the questions raised above. In Sec. IV we discuss whether the satellite is a final-state shakeup effect or an initial-state effect. In Sec. V possible interpretations of the Ni 6-eV satellite and the related theoretical and experimental results are discussed critically in the light of our new data and observations. In Sec. VI we discuss implications of our findings and the different interpretations of the 6-eV satellite for polar fluctuations in the ground state of nickel and the role of Hund's-rule coupling for its ferromagnetism. Finally Sec. VII summarizes the major conclusions of this work.

II. EXPERIMENTAL

The compounds we have studied are NiO, NiTe, NiSb, and cuprous copper oxide Cu_2O. NiO is an antiferromagnetic Mott-Hubbard insulator at room temperature with a filled O $2p$ band and a $Ni^{2+}(3d^8)$ ionic configuration having localized Ni $3d$ electrons.[21] NiTe is a paramagnetic metal with an almost filled Ni $3d$ band having itinerant Ni $3d$ electrons.[22] NiSb is also a metal with an almost filled itinerant Ni $3d$ band, but is diamagnetic. It is believed that these metallic compounds have fewer *d* holes in the ground state than Ni metal.[22] Cu_2O is a semiconductor with filled O $2p$ and Cu $3d$ shells[23] ($3d^{10}$ configuration). This set of compounds enables us to study the effects on the satellites and their resonance behaviors of (1) the number of $3d$ holes in the initial state, and (2) the valence-band electronic structure and the degree of localization of 3*d* electrons, and thus to assess critically the various models proposed for the Ni 6-eV satellite.

The experiments were performed at the 4° branches of beam lines I and III (Refs. 24 and 25) at the Stanford Synchrotron Radiation Laboratory using a vacuum chamber with a base pressure of less than 2×10^{-10} Torr. A commercial double-pass cylindrical mirror analyzer (CMA) was used as an electron-energy analyzer. This CMA has an energy resolution of 1.6% relative to the analyzer pass energy which normally was kept at 25 eV in the measurement to be presented. The resulting 0.4-eV resolution is the dominant contribution to the total resolution for the range of photon energies employed.

A clean surface of NiO was prepared by cleaving a single crystal (NaCl structure) *in situ* along the (100) plane. This surface is fairly inert and stayed clean for at least ~ 8 h under the vacuum conditions quoted above. No appreciable charging effect was detected during the measurement. The polycrystalline NiTe and NiSb crystals were fractured *in situ* to obtain clean surfaces. The Cu_2O film was prepared by heating a clean Cu sample ($>500\,^{\circ}C$) in the presence of oxygen gas ($\sim 10^{-3}$ Torr), and its photoemission spectra were compared with published x-ray photoelectron spectroscopy (XPS) data[23,26] to ensure that Cu_2O had been obtained.

We have made two types of photoelectron spectroscopy measurements. One was the conventional electron-energy-distribution curve (EDC) with fixed photon energy, and the other consisted of scanning both the incident photon energy and the kinetic energy of the collected electrons so as to keep $h\nu$-E_k constant, thus producing constant-initial-state spectra (CIS).[27]

III. EXPERIMENTAL INTERPRETATIONS AND DISCUSSIONS

Figure 2 shows the EDC's of the NiO valence band for various incident photon energies. The spectrum at $h\nu=150$ eV is essentially the same as the published XPS data by Hüfner and Wertheim,[23] but has better resolution of the peaks. The double peaks near the Fermi level (labeled *A*) are due to the Ni 3*d* electron emission, and can be well described by the $3d^7$ final-state multiplets calculated from ligand-field theory.[28] This confirms the localized nature of the Ni 3*d* electrons in NiO. O 2*p* states give a small peak *B*, while peak *C* has been interpreted as a multielectron satellite.[23,28,29] This satellite is generally attributed to a monopole charge-transfer transition from the O 2*p* level to the Ni 3*d* level ($O\,2pe_g \rightarrow Ni\,3de_g$) accompanying Ni 3*d* photoionization.[29] Hence the final state of this satellite peak is ($Ni\,3d^{8*}O\,2p^5$), where * denotes an excited state. Similar satellites also appear in the XPS core-level spectra of NiO,[23] and other transition metal oxides's spectra as well.[30] As we change the photon energy in the vicinity of the Ni 3*p* binding energy (~ 67 eV), it is clear from the figure that the satellite peak *C* grows in intensity (resonant enhancement) while the main Ni 3*d* band emission (peak *A*) goes through some kind of an "antiresonance" (interference dip).

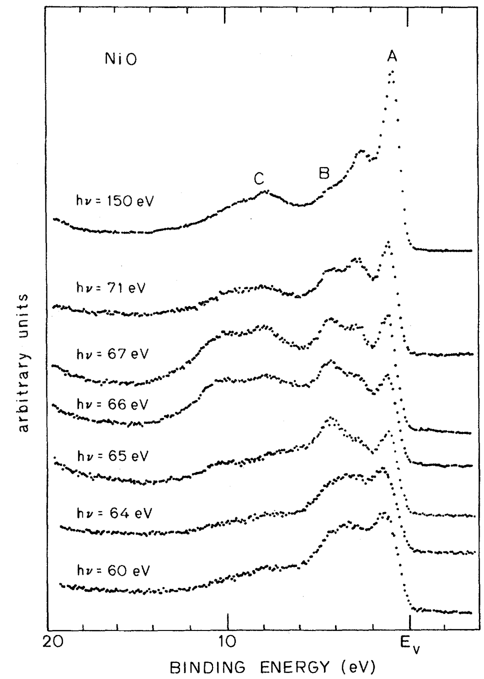

FIG. 2. Electron-energy-distribution curves (EDC's) for the valence band of NiO(100) at various incident photon energies. The binding energy is measured from the top of the valence band.

The CIS spectra of Fig. 3 show this more clearly. Figures 3(a) – 3(c) correspond to peaks *A* (main 3*d* emission), *B* (O 2*p*), and *C* (satellite), respectively. Comparing with Fig. 1 for the Ni metal case, we find surprising similarities—i.e., a Fano-type resonant enhancement of the satellite and a characteristic interference dip of the main band—in spite of the quite different electronic structures of Ni (metal with itinerant 3*d* electrons) and NiO (insulator with localized 3*d* electrons). This suggests that the satellite and its resonance behavior are mainly

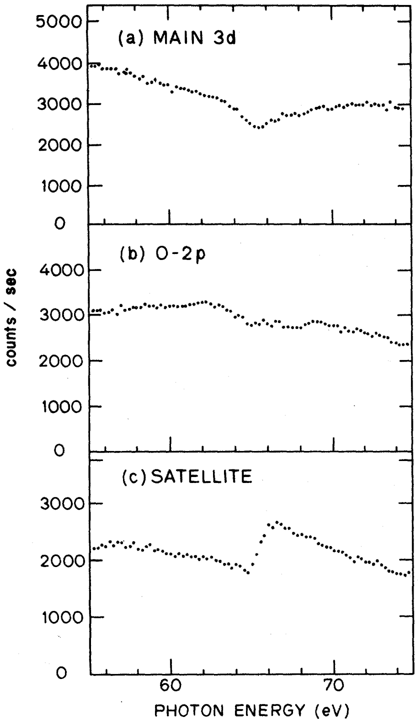

FIG. 3. Constant initial-state spectra (CIS) of various peaks in the NiO valence-band photoemission of Fig. 2. (a) Main Ni 3*d* emission (peak *A*). (b) O 2*p* (peak *B*). (c) Charge-transfer satellite (peak *C*).

of an atomic origin with little band-structure effect, which contradicts the model of Kanski *et al.*[19] that the resonance arises from a conventional interband transition. The CIS's of the main 3*d* bands and the satellites can be fit by Fano line shapes with comparable parameters for both Ni metal and NiO. The CIS of the O 2*p* peak in Fig. 3(b) has only a weak structure near the Ni 3*p* edge, which we believe is due to some inseparable overlap with the satellite structure and also to some inelastically scattered electrons from the Ni 3*d* main band emissions. This nonresonance of the peak *B* confirms the assignment of this peak as due to O 2*p* emission, and implies that the interatomic Auger interaction between O 2*p* and Ni 3*d* electrons does not contribute significantly to the resonance behaviors. We also note here that no $M_{23}VV$ Auger emission could be detected in the NiO valence band near the resonant photon energy, in contrast to the Ni metal case. This argues against the model by Dietz *et al.*,[20] who suggested that the resonant enhancement of the satellite is mainly due to the overlap with the Auger emission. The fact that $M_{23}VV$ Auger emission is present in metals and absent in insulators near the resonant photon energy seems to be generally true for all the transition-metal compounds.[31]

The EDC's of NiTe at $h\nu = 110$, and 63 eV (off resonance) and at $h\nu = 66$ eV (on resonance) are shown in Fig. 4(a). We see again a resonant satellite *B* at about 7 eV below the Ni 3*d* main peak *A*. The resonances of this satellite and the main band shown in Fig. 4(b) are weaker than those of Ni and NiO, but the qualitative features are again quite similar. From these data, we can conclude that the occurrence of satellites and the resonance behaviors of valence-band structures are not much dependent upon valence-band electronic properties (whether it is a metal or an insulator, whether 3*d* electrons are itinerant or localized), so in the first approximation they can be thought to have an atomic origin. The EDC's and CIS's of NiSb shown in Fig. 5 are similar to those of NiTe, which supports this conclusion.

The other important question of whether the photoabsorption process $3p \rightarrow 3d$ or $3p \rightarrow 4s$ is responsible for the resonance behaviors can be answered by the data on Cu_2O ($3d^{10}$ ground-state configuration) in Fig. 6. The EDC's in Fig. 6(a) show a satellite at ~12 eV below the main 3*d* peak,

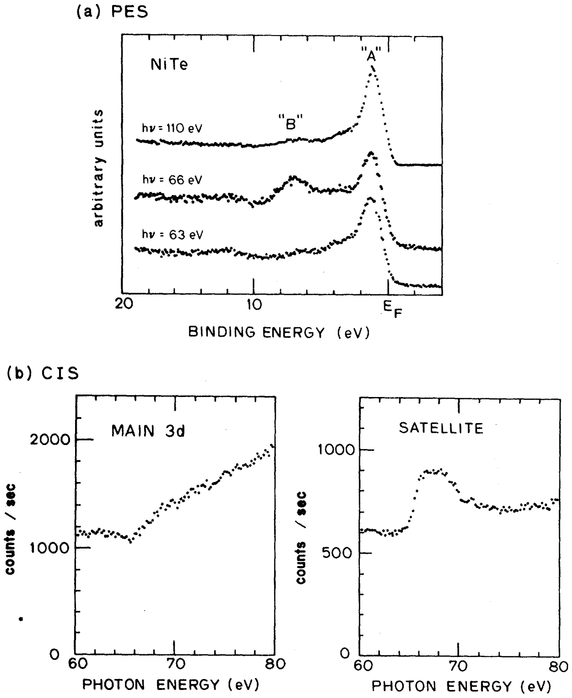

FIG. 4. (a) EDC's for the valence-band photoemission of NiTe at three different incident photon energies. (b) CIS's of the main 3*d* peak and the satellite in the vicinity of the Ni 3*p* threshold ($h\nu$ equal to ~67 eV).

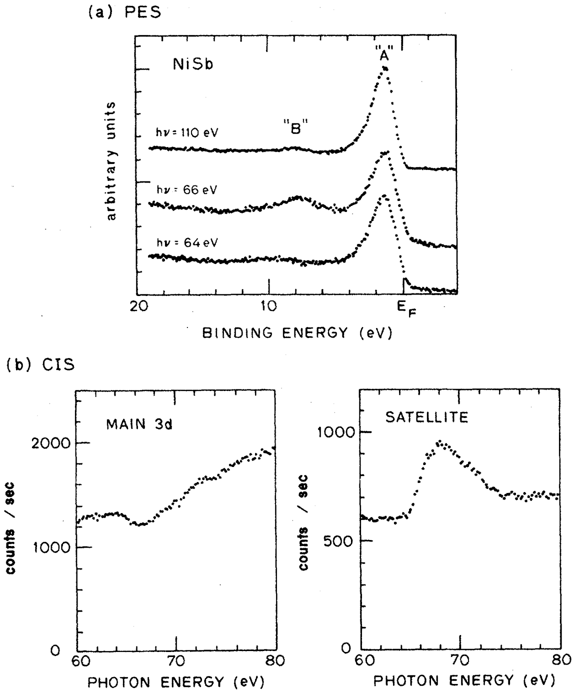

FIG. 5. (a) EDC's for the valence-band photoemission of NiSb at three different incident photon energies. (b) CIS's of the main $3d$ peak and the satellite in the vicinity of the Ni $3p$ threshold.

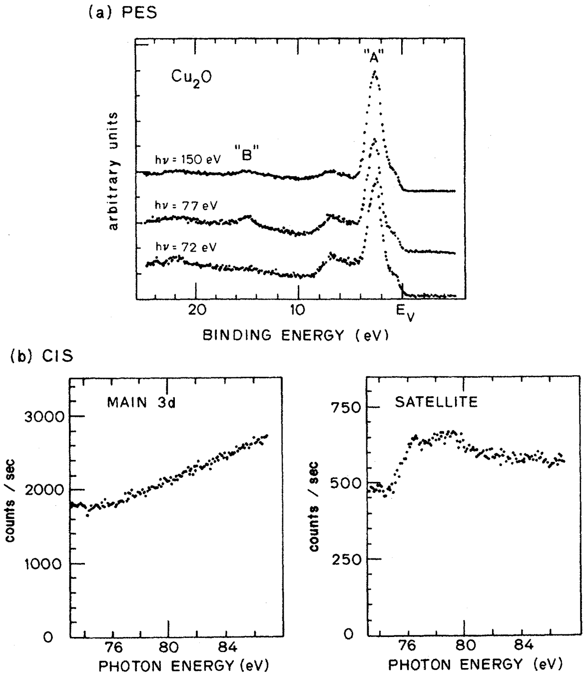

FIG. 6. (a) EDC's of the valence-band photoemission of Cu_2O at three different incident photon energies. (b) CIS's of the main $3d$ peak and the satellite in the vicinity of the Cu $3p$ threshold ($h\nu$ equal to ~ 77 eV).

which is resonantly enhanced at the Cu $3p$ threshold (~ 77 eV). The CIS's of the main peak and the satellite are shown in Fig. 6(b). These data are similar to the published data on Cu metal by Iwan *et al.*,[14] again suggesting an atomic effect. But here we see two major differences from the case of Ni. First, the intensity of the satellite compared to that of the main peak and its resonance at the $3p$ edge are much weaker than in the case of Ni and its compounds. Second, the main $3d$ emission shows only a very weak and broad resonance at the $3p$ threshold, in contrast to the case of Ni and its compounds. Hence, it can be concluded that the initial $3d$ hole is necessary for a strong resonance effect, and consequently that $3p \rightarrow 3d$ photoabsorption is mainly responsible for the strong resonance behaviors of Ni and its compounds. The dominant decay mechanism of this intermediate state is the super-Coster-Kronig Auger transition involving two $3d$ electrons.[32,33] The Fano line shapes in the CIS's therefore arise from the interference between a discrete state $3p^5 3d^{n+1}$ and continuum states $3p^6 3d^{n-1} \epsilon l$, where $3p^6 3d^n$ is the ground-state configuration and ϵl represents a continuum photoelectron.

From the strong resonance (interference dip) in the main $3d$ emission of Ni metal and the fact that the intermediate and final states must differ by two $3d$ electrons, we deduce that the Ni main band has strong contributions from a $3d^9 4s$ initial state ($3d^8 4s$ final state). This is in contrast to the cases of Cu and Cu_2O, whose main band emissions cannot resonate strongly because $3p \rightarrow 3d$ photoabsorption is not possible for the $3p^6 3d^{10}$ initial-state configuration. The above-mentioned fact that the resonances of satellites and main $3d$ bands are weaker for NiTe and NiSb compared with Ni metal can also be explained by the smaller number of d holes in these compounds. This conclusion that the $3d^8 4s$ final state contributes strongly to the Ni metal main band photoemission has an important implication for the interpretation of the 6-eV satellite, as discussed later in Sec. V.

We have used, so far, a localized picture to describe the satellite and its resonance behavior, although $3d$ electrons in Ni form a band. This is justified because the intermediate state $3p^5 3d^{n+1}$ is probably localized due to the strong core-hole Coulomb potential, and the subsequent super-Coster-Kronig Auger process is also local. It appears that we can use the localized description for the final state of the satellite as well, although the main band photoemission of Ni shows a bandlike dispersion.[4,5] One justification is the angle-resolved photoemission data by Eberhardt and Plummer,[5] which shows no dispersion for the Ni 6-eV satellite. We can also find an analogous situation in the $M_{23}VV$ Auger spectra of Cu and Zn, where in spite of the bandlike properties of $3d$ electrons, the two-hole final states of the $M_{23}VV$ Auger spectra are quite atomiclike. This has been understood by the theoretical work of Sawatzky[34] and Cini,[35] in which they showed that if the electron correlation energy between $3d$ electrons is larger than or comparable to the conduction bandwidth, then the strong "on-site" correlation effects cause the two final-state d holes to remain localized on one atom, and therefore we see corresponding Auger spectral weights in atomiclike final states. A similar situation may also apply to the Ni 6-eV satellite.

IV. FINAL-STATE SHAKEUP VERSUS INITIAL-STATE CONFIGURATION MIXING

We now address the important question of whether these photoemission satellites are final-state shakeup structures or whether they represent initial ground-state mixing of different configurations. To begin, it is necessary to define the terms "initial-state effect" and "final-state effect" more precisely. We note first that the distinction is meaningful only in the context of a specific choice of single-particle basis, because in general the degree of configuration interaction required to represent a particular many-body state depends strongly on the single-particle basis utilized. The physical question of interest determines the basis in which the question is posed. For example, to discuss valence effects in a solid, in which we are interested in this paper, a localized (Wannier) basis is appropriate rather than an extended (Bloch) basis.

Now let us consider the case of atomic Cu. The ground-state many-body wave function can be well described by a single Slater determinant $|\Psi_0\rangle$ ($|3d^{10}4s\rangle$ in this case) in a suitably chosen basis set of single-particle eigenstates (e.g., Hartree-Fock wave functions). The final eigenstate after photoionization of a $3d$ electron will be given by, in the same basis set,

$$|M\rangle = |3d^9 4s\rangle + \epsilon_1 |3d^8 4s^2\rangle + \cdots ,$$

where the ellipsis denotes other configurations which we neglect here. The coefficient of the $3d^8 4s^2$ configuration ϵ_1 may be nonzero (even though it is usually small) either because of the change of the final-state single-particle orbital wave functions due to the potential of a hole created by photoionization (orbital relaxation effect), or because of the configuration interaction in the final state due to the residual Coulomb interaction.[36] These two effects are in fact basically of the same nature, since the change of the final-state single-particle eigenfunctions is just an attempt to get the optimum single Slater determinant with minimum residual Coulomb interaction. In a similar way, the final state corresponding to the satellite is

$$|S\rangle = \epsilon_2 |3d^9 4s\rangle + |3d^8 4s^2\rangle .$$

Usually, $|\epsilon_1|$ and $|\epsilon_2|$ are of similar magnitude. (They are equal if we have only two configurations.) The intensity of the satellite in the sudden approximation is given by the overlap $|\langle S|\hat{d}|\Psi_0\rangle|^2 = |\epsilon_2|^2$ which may be nonzero, where $\hat{d}$ is the destruction operator for the $3d$ electron and $|\Psi_0\rangle$ is the ground-state wave function ($|3d^{10}4s\rangle$). Therefore, we see that even though the ground-state wave function is well described by a single Slater determinant, we can have in photoemission a satellite due to an apparent two-particle excitation because of the Coulomb interaction in the final state. We call this a final-state effect, and the occurrence or the intensity of the satellite in this case does not reflect the ground-state configuration of the system.

On the other hand, there are cases when the initial-state configuration mixing is responsible for the satellite. Suppose we have two lowest-energy configurations that are very close to each other in energy and have non-negligible interaction matrix elements between them. Then the configuration interaction in the ground state is important, and we should write the ground-state wave function as (in this hypothetical Cu atom case)

$$|\Psi_0\rangle = a|3d^{10}4s\rangle + b|3d^9 4s^2\rangle .$$

The photoemission spectrum will show a "satellite" with the $3d^8 4s^2$ configuration, and its intensity will be $|b|^2$ in the absence of the final-state effect, which gives directly the amount of the $3d^9 4s^2$ configuration mixing in the ground state. This satellite is then said to arise from an initial-state effect, and its occurrence or its intensity gives information about the ground state of the system, analogous to the two-valence spectra of mixed-valent rare-earth materials.[37] Usually both initial- and final-state effects are present, and the intensity of the satellite in that case is given by $|a\epsilon_2 + b|^2$. A more detailed discussion on this point can be found in Ref. 36.

The satellites in the spectra of Cu vapors and Cu metal are probably due mostly to the final-state effect since: (1) the lowest $3d^9 4s^2$ configuration of the Cu atom is energetically 1.39 eV above the

$3d^{10}4s$ ground-state configuration,[38] which suggests that the initial-state configuration mixing is not appreciable; and (2) the intensity of the satellite is weak (10–15 % of the main peak intensity at resonance, less than 3% off resonance), and it does not vary much from Cu vapor to Cu metal (not much influence from different initial states).

The satellites in Ni and its metallic compounds, however, are expected to be different. In atomic Ni the configurations $3d^9 4s$ and $3d^8 4s^2$ are quite close to each other in energy (0.025 eV between lowest multiplets according to Moore's atomic table[38]), and the energy of the $3d^{10}$ state is not much greater. In addition, the $3d$ wave functions of Ni are more spread-out than those of Cu, which gives stronger interactions between these configurations. Therefore we expect stronger mixing of various configurations in the ground state of Ni metal and its metallic compounds, which can give rise to the satellite structure. This contention is further supported by the facts that the intensities of the satellites in Ni compounds are generally stronger than that of Cu, and that among Ni and its compounds the satellite in Ni metal is stronger than those of NiSb and NiTe, which can be explained by the initial-state effect because these compounds are expected to have a smaller number of d holes than Ni metal in the ground state. These considerations argue strongly that initial-state contributions dominate in the 6-eV satellite of Ni metal, although there should be inevitably some contributions from the final-state effect as well.

In fact, existing theoretical models of the Ni satellite are initial state models in a Wannier basis. Consider, for example, the numerical calculation of Davis and Feldkamp[39] for a more than half-filled, fully spin-polarized, s-band Hubbard model. In the Bloch basis the ground state is a single Slater determinant, because the filled majority-spin band prevents the Coulomb term from causing any scattering. However, the states obtained by removing a majority-spin electron must be described by configuration interaction because the Coulomb term causes scattering between up- and down-spin electrons when the majority-spin band is not full. It is found that the majority-spin spectral weight is split by the Coulomb interaction into a main band and a satellite, and the satellite appears as a final-state effect in the Bloch basis. In the Wannier basis, on the other hand, the ground state is represented by a linear combination of Slater determinants, each of which has some doubly occupied sites and some singly occupied majority-spin sites. In this basis the splitting of the spectral weight for removing a majority-spin electron is seen to correspond to whether the electron is removed from a singly occupied or a doubly occupied site. From this point of view, it is expected that for the Coulomb interaction U large compared to the single-particle bandwidth, the splitting is given by U and the division of spectral weight corresponds merely to the numbers of the two kinds of sites, an expectation fully confirmed by the large-U numerical results of Davis and Feldkamp. For smaller U comparable to the bandwidth, the purity of the labeling of the spectral weight according to valence will diminish, the splitting will not be $\sim U$, but will also depend on the bandwidth, and the weights will not correspond to the number of sites. Similar considerations apply to the Penn model,[9] although not in such a simple form because the model has orbital degeneracy and employs a t-matrix approximation, the precise meaning of which is difficult to assess for the questions posed here.

V. INTERPRETATION OF THE Ni 6-eV SATELLITE

Since we have argued that the 6-eV satellite of Ni metal is dominantly due to the initial-state effect, it is even more interesting to understand its nature, because it tells something about the ground state of Ni metal. In this section we point out that two interpretations of the Ni 6-eV satellite which are widely taken to be equivalent are in fact quite distinct, and discuss critically various theoretical and experimental results trying to decide which of the two models is correct.

Penn,[9] based on the degenerate Hubbard Hamiltonian model of Ni d bands, assigned the satellite as arising from the two-hole virtual bound state. The satellite has a higher binding energy than the main band because of the intra-atomic Coulomb repulsion between two holes on the same atom. If we follow this interpretation, and if, as discussed above, the purity of spectral weight labeling according to valence is not completely lost, we should assign the satellite to the $3d^7 4s^2$ final-state configuration, since the resonance of the one-hole spectrum (main band) of Ni must be due to the $3d^8 4s$ final-state configuration, as discussed in Sec. III. In fact, Mott[40] suggested the possibility of exciting the $3d^7 4s^2$ final state in photoemission from the $3d^8 4s^2$ configuration in the ground state of Ni some time ago.

However, the degenerate Hubbard Hamiltonian Penn used is oversimplified for describing the d band of Ni in that, among other things, it does not include multiplet splittings of the $3d^8$ configuration. If multiplet splittings are included, as in Liebsch's calculation of the d-hole self-energy,[10] the $3d^8$ configuration would have a range of binding energies, and it is possible that some of the $3d^8$ multiplets with lower energy (e.g., ^3F) contribute to the main $3d$ band, while others with higher energy (e.g., ^1G) are pushed out of the main band and retain atomic character to give the satellite. In this model the energy difference between the main band and the satellite final states is not due to a differing number of d holes, but to the multiplet structures of the $3d^8$ configuration. The correlation energy U responsible for the energy separation between the main and the satellite emissions is determined by the Slater integrals $F^{(2)}$ and $F^{(4)}$ in this case, rather than $F^{(0)}$ as would be the case with differing numbers of d electrons (Penn's model). It should be noted that if the $3d^8$ multiplets can actually be identified in the spectrum, as claimed by some authors,[10,11] then the valence purity of the satellite must be quite good. On the other hand, fits of two-hole models to the spectrum are found to be good in the regime where the splitting is not equal to U, implying, as discussed above, that the valence purity may not be particularly good. However, the fact that the Ni 6-eV satellite shows no dispersion in the angle-resolved photoemission spectra[5] suggests that the purity of spectral weight labeling according to valence is not completely lost and that it is meaningful to discuss atomic final-state configuration for the satellite.

This distinction between these two models, i.e., the model that the main band has a $3d^8 4s$ final state while the satellite is a two-hole bound state with a $3d^7 4s^2$ final-state configuration, or that both the main band and the satellite have $3d^8 4s$ final states but originating from different multiplets, has not been pointed out previously, because most models for the satellite have implicitly assumed that the main band spectral weight is largely from the $d^{10} \rightarrow d^9$ transition.[7,13] However as pointed out in Sec. III, the Ni metal main band also has strong contributions from $3d^9 \rightarrow 3d^8$ spectral weight, and therefore these two models are in fact quite distinct. It is important to understand the nature of the 6-eV satellite since it has some bearing on the ground state, but unfortunately it seems difficult at present to decide which of them is correct, as we will now discuss.

We can try to estimate the energy separations between the $3d^8$ and $3d^7$ configurations, or among various multiplets of the $3d^8$ state, and compare with the experimental value of 6 eV. Recently, Mårtensson and Johansson[11] applied their method of calculating core-level binding energies in metals[41] to the Ni valence-band $3d^8$ state, and estimated that the binding energy of the ^1G multiplet component of the $3d^8 4s^2$ state is about 5.8 eV from the Fermi level. The ^3F multiplet is estimated to have ~ 3.0-eV binding energy, which is within the main $3d$ emissions. Their method is based on the assumption that the photoionized atomic site is totally screened by a lowest-lying valence electron to give a neutral configuration. (Note that our prior discussion has assumed unscreened singly ionized $3d$ configurations in the final state and perfectly screened $3d$ configurations in the ground state.) Although this gives quite good estimates of core-level binding energies,[41] screening of the valence hole may be different than for a core hole, which is cause for caution. If, on the other hand, we compare peak positions of the unscreened valence hole (Ni^+ ion), the separation between the main peak and the satellite should be the energy difference between $3d^8 4s$ (main band) and $3d^7 4s^2$ (satellite) configurations. Although Moore's atomic table[38] does not list the energies of these configurations, it does list the separation between the $3d^8$ and $3d^7 4s$ configurations (Ni^{2+}) as $6.5-9.3$ eV, depending on multiplet energies. Since another $4s$ electron will make this value smaller through atomic screening and the more effective metallic screening would probably make it even smaller, it will be close to the experimental value of 6 eV. We note, however, that Mårtensson and Johansson[11] estimated the binding energies of the $3d^7$ multiplet to be about $10-18$ eV from the Fermi level. These higher values come mainly from the fact that the screening charge to make the site neutral is $4s^2 4p$, and the $4p$ level is ~ 7 eV higher than the $4s$ level in the atomic $3d^7$ configuration. This may be an overestimation, because $4p$ levels form a band with $4s$ levels in the metal, and their energies are probably comparable. At any rate, since at present a complete understanding of the valence-hole screening process is lacking, it seems difficult to give a convincing argument one way or the other.

We can also try to compare the line shape of the Ni 6-eV satellite at resonance with the calculated line shapes of the $3d^8$ or $3d^7$ configurations. Iwan *et al.*[14] fit the Cu metal satellite line shape (which has a $3d^8$ final state) with atomic $3d^8$ multiplet structure of the $L_{23}M_{45}M_{45}$ Auger spectrum calculated by Antonides *et al.*[42] [Fig. 7(a)]. We can fit the line shape of the NiO satellite (which also has a $3d^8$ final-state configuration) at resonance with the same $3d^8$ multiplet structures [Fig. 7(b)], but the energy separations between multiplets in this case are a little smaller than in the case of Cu, because Ni has one less nuclear charge than Cu. The case of the Ni metal satellite, however, is not so clear-cut. Iwan *et al.*[14] extracted the line shape of the Ni satellite assuming the structure at 2–3 eV from the Fermi level is a part of the satellite structure [dashed line in Fig. 7(c)]. We can try to fit this line shape with the $3d^8$ multiplet structures, assigning ^1G to the 6-eV satellite and ^3F to the peak at 2–3 eV from the Fermi level. However, this structure at 2–3 eV is within the main $3d$ emission and may be simply due to the peak of the $3d$ density of itinerant states. Further, the separation between the ^3F and ^1G multiplets is larger than the corresponding separation of the Cu $3d^8$ multiplets, which is opposite to what we expect. Shown in Fig. 7(c) in solid line is the line shape of the Ni 6-eV satellite which can be extracted assuming that the structure at 2–3 eV from the Fermi level is part of the main band. This is quite different from the $3d^8$ multiplet structures. In this connection, it would be very useful to know the theoretical line shape of the $3d^7$ final state at resonance, but to our knowledge it has not been calculated.

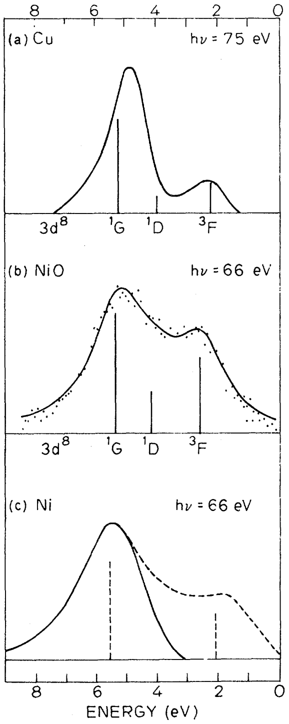

FIG. 7. Line shapes of satellites at resonance and their fit with the atomic $3d^8$ multiplet calculations. (a) Cu metal (from Ref. 14). (b) NiO. (c) Ni metal (solid line is from Ref. 8 assuming the peak at 2–3 eV from the Fermi level is part of the main band, and dashed line is from Ref. 14 including the peak at 2–3 eV as a part of the satellite structure.)

Recent spin-polarized photoemission data by Clauberg *et al.*[12] are, in our opinion, also not conclusive on this point. They reported that the Ni 6-eV satellite is 57±15% spin-polarized near resonance ($h\nu = 67$ eV), which they claimed is in good agreement with the theoretical prediction by Feldkamp and Davis.[13] However, the peak of which they measured spin polarization is usually attributed to the ^1G component of the $3d^84s$ configuration[10,11] which should show 100% spin polarization, whereas the theoretical prediction of 60% by Feldkamp and Davis[13] is an average value over all the multiplets of the $3d^8$ configuration. The fact that the satellite is spin polarized does not by itself rule out the $3d^74s^2$ assignment to the satellite, because we expect some spin polarization for the $3d^74s^2$ final state as well.[43] It is also not clear that we can safely neglect the interaction with magnons carrying spin moments in a high-energy probe such as photoemission.

VI. POLAR FLUCTUATIONS AND FERROMAGNETISM IN THE GROUND STATE OF Ni

The extent of polar fluctuations is particularly important in nickel for assessing assertions by Van Vleck[2] and Slater[44] that intra-atomic Hund's-rule coupling is crucial in stabilizing the ferromagnetic ground state.[1] For this mechanism to be operative, two circumstances are certainly required. First, there must be an appreciable fraction of d^8 configurations admixed into the many-body ground state, i.e., the electron correlation effect should not suppress too strongly the extent of polar fluctuations into d^8 configurations below the value of 9.9% (Ref. 2) in an uncorrelated wave function. Second, the d^8 singlet cannot be admixed to the same extent as the triplet.

Regarding the first criterion, the suppression of d^8 configurations in the ground state depends on the ratio of the mixing matrix element, which is of order of the d-band width, to the polar fluctuation energy $d^9 \rightarrow d^8$. Herring,[1] and others[2,40] have argued that the Coulomb repulsion between two $3d$ holes is substantially reduced from the Slater integral $F^0(3d,3d)$ by the screening effect of the 4s-4p electrons. Depending on whether the photoemission final state is perfectly screened or not, the energy of a screened polar fluctuation $3d^9 4s \rightarrow 3d^8 4s^2$ is equal to or less than the energy below the Fermi level in the photoemission spectrum at which the $3d^9 \rightarrow 3d^8$ spectral weight occurs. Therefore the fact that the nickel main band contains some $3d^9 \rightarrow 3d^8$ spectral weight shows the importance of *s-p* screening, and implies that the fraction of d^8 configurations in the ground state should not be much reduced below the uncorrelated value of 9.9%.

Regarding the second criterion, the two different interpretations of the Ni satellite discussed in Sec. V have different implications. If the satellite is due to the ^1G component of the $3d^8 4s$ configuration and the ^3F component is in the main band, then it is energetically favorable for the mixing of the triplet state into the ground state to be greater than that of the singlet. However, if the satellite locates the energy of the $d^8 \rightarrow d^7$ spectral weight, it follows that all the components of the $d^9 \rightarrow d^8$ spectral weight, i.e., all the multiplets of the $3d^8 4s$ final states, are part of the main band and hence that the mixing of the triplet and singlet states into the ground state can be nearly equal.

To summarize, the contribution of some $d^9 \rightarrow d^8$ spectral weight to the main band is inferred from the strong main band resonance for photon energies at the $3p \rightarrow 3d$ absorption edge, and this in turn implies d^8 configurations are not excluded from the ground state. Thus $d^8 \rightarrow d^7$ spectral weight is expected at some energy in the valence band. If the $d^9 \rightarrow d^8$ and $d^8 \rightarrow d^7$ spectral weights have the energies estimated by Mårtensson and Johansson,[11] then Hund's-rule coupling is probably important in nickel. If, on the other hand, the satellite marks the $d^8 \rightarrow d^7$ spectral weight, then the Hund's-rule energy is probably overwhelmed by some combination of screening and the single-particle bandwidth. Thus there is strong motivation to remove the ambiguities in the interpretation of the satellite.

VII. SUMMARY

We have shown by studying resonant satellites of various Ni and Cu compounds that:

(1) These satellites and their resonance behaviors are not much dependent upon valence-band electronic properties, and hence are mainly of an atomic origin;

(2) strong resonances of the satellites and the main bands of Ni and its compounds are due to the photoabsorption process $3p \rightarrow 3d$ followed by a super-Coster-Kronig Auger decay involving two 3*d* electrons;

(3) the overlap with incoherent Auger emissions is not primarily responsible for the resonant enhancement;

(4) the satellites in the photoemission of Cu vapors and metals are probably due to final-state shakeup effects, whereas the initial-state configuration-mixing effect contributes to the Ni metal 6-eV satellite; and

(5) the strong Ni metal main 3*d* band resonance is due to the $3d^8 4s$ final state ($3d^9 4s$ initial state).

Based on these observations, we discussed two alternative interpretations of the origin of the Ni 6-eV satellite; one being a two-hole bound-state model in which the satellite with the $3d^7 4s^2$ final state is separated from the main band by the hole-hole correlation energy; and the other mechanism in which both the main band and the satellite have $3d^8 4s$ final states but are separated from each other by multiplet splittings. We argued that it is difficult to decide which model is correct from energy estimates without a complete understanding of the screening process, and that neither the line-shape analysis nor the spin-polarized photoemission data is conclusive in this respect. We also argued that the fact we have $d^9 \rightarrow d^8$ spectral weight in the main band emission of Ni metal implies that polar fluctuation into $3d^8$ configurations is not strongly suppressed in the ground state, and then pointed out that depending on the interpretation of the satellite, one draws different conclusions about the importance of Hund's-rule coupling for ferromagnetism in nickel.

Note added in proof. Dr. L. C. Davis pointed out that the spin-orbit interaction will reduce the ^1G spin polarization below 100% (private communication).

ACKNOWLEDGMENTS

We would like to thank S. Doniach, B. Johansson, R. M. Martin, C. Herring, and W. E. Spicer for helpful discussions, and J. Keem for providing the NiO single crystal. This work is supported in part by the National Science Foundation under Contract No. DMR 79-13102. The experiments were performed at the Stanford Synchrotron Radiation Laboratory which is supported by the National Science Foundation through the Division of Materials Research in cooperation with the Department of Energy.

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