though this theory was intended only for the region $T > T_M$, it is reasonable to extend the results into the region of spontaneous magnetization where there is still a large RE spin polarizability. If one therefore assumes that $ErRh_4B_4$ is a type-I superconductor at T_M, it is only necessary to compare the magnetic induction $B \cong 10$ kG assuming saturated magnetization with the thermodynamic critical field $H_c = 1.8$ kG calculated from the heat capacity of $LuRh_4B_4$[21] to conclude that orbital effects may also be important in the destruction of superconductivity in these magnetic superconductors.

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Effect of Bound Hole Pairs on the *d*-Band Photoemission Spectrum of Ni

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It is shown that the spectral density of the Ni *d* electrons contains a peak due to excitations of bound hole pairs. The spectral density is observed directly in photoemission experiments which show a satellite peak below the bottom of the *d* bands. The observed peak exhibits a strong resonance as a function of photon energy and this behavior is also explained by the present theory.

My purpose is to present a theory for the physical origin of the satellite that is observed at approximately 7 eV below the Fermi energy in photoemission experiments on Ni, and also to explain the observed resonance in the satellite intensity as a function of photon energy. The satellite has been observed[1-6] in both x-ray and ultraviolet photoemission spectroscopy (XPS and UPS), at a binding energy of roughly 7 eV.[7] The amplitude of the satellite has its maximum at a photon energy of 67 eV (Ref. 4) and is unobservably small below roughly 25 eV.[5,6] The *d*-band peak observed in both XPS and UPS is narrowed relative to the calculated *d*-band peak[8] and a narrowing is predicted by the present theory. However, Eastman, Himpsel, and Knapp[9] have also observed a band narrowing at photon energies below 20 eV where the satellite is not seen.

The simplest explanation for the satellite would be the excitation of a 5-eV Ni plasmon (the satellite is located at 6 eV below the main d-band peak). However, an examination of electron-scattering and optical data shows that this is not the answer. In this Letter, I show that the satellite is caused by a shake-up process which involves the excitation of two-hole virtual bound states following photoexcitation of d-band electrons. The states consist of two itinerant d holes that are correlated in such a way that there is a relatively high probability that they are located on the same atom. These holes have a higher energy than two uncorrelated holes because of the intra-atomic Coulomb interaction and consequently the satellite peak is at lower kinetic energy than the main d-band peak. The hole-pair states are derived mainly from the bottom of the d band and thus reduce its width.

This work supports earlier suggestions by Mott[10] and Hüfner and Wertheim[11] that the satellite is caused by photoexcitation of a d electron followed by the creation of a second hole on the same atom. However, the two-hole excitations are in fact resonances rather than well-defined modes; the itinerant correlated hole pairs decay into excitations that belong to the usual bandlike hole-pair continuum.

The enhancement of the satellite at a photon energy of 67 eV is related to the photoexcitation of a $3p$ core electron to an empty d state. The empty states in the d band are less than 0.3 eV in width so that this photoexcitation is only possible for photon energies near 67 eV. The 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. If the two d holes produced in the Auger event are left in a virtual bound state the excited electron will have an energy corresponding to the satellite. This process can be coherent with the direct d-band photoemission and consequently the total satellite intensity as a function of photon energy is asymmetric.[4] There is also an asymmetry due to photoexcitation of a core electron to an empty s-p state (followed by an Auger event) which can only occur for photon energies greater than 67 eV. The importance of the core-level photoexcitation in producing a resonance in the satellite was pointed out by Guillot *et al.*[4] using a model for Ni consisting of essentially noninteracting atoms.

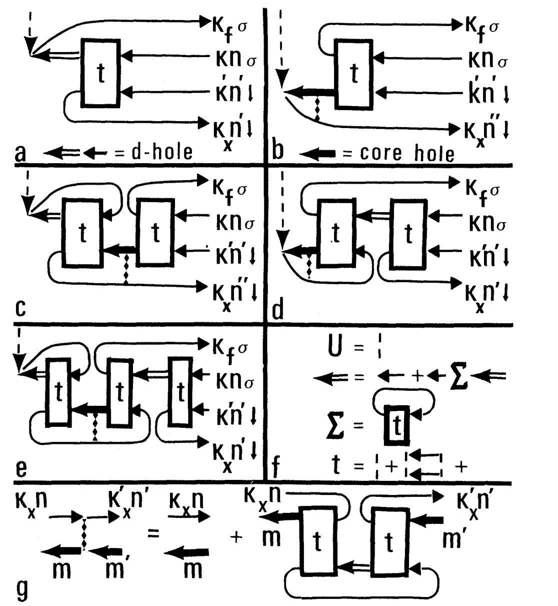

FIG. 1. (a) Diagram for d-band photoexcitation followed by scattering of the d hole. (b)–(e) Diagrams for photoexcitation which involve the creation and destruction of a core hole. These processes are important only near resonance. (f) Schematic representation of U, G, Σ, and t. (g) Diagram giving the meaning of the interaction line between a core hole and d electron that appears in diagrams (b)–(e).

The d-band electrons are assumed to obey the degenerate Hubbard Hamiltonian

$$H=\sum_{k,n,\sigma}\epsilon_{k,n}a_{k,n,\sigma}{}^{\dagger}a_{k,n,\sigma}+\tfrac{1}{2}\sum_{l,n,\sigma,n'}U(1-\Delta_{n,\sigma;n',\sigma'})n_{l,n,\sigma}n_{l,n',\sigma'}, \quad (1)$$

where $\epsilon_{k,n}$ is the band energy of a Bloch electron composed of a linear combination of atomic states with z component of angular momentum n, and $\epsilon_{k,n}$ is assumed to depend only on k. The second term is the intra-atomic Coulomb interaction between two electrons located on the lattice site l. The intra-atomic Coulomb interaction has strength U and the δ function represents the effect of the Pauli principle.

The diagram for d-band photoemission is shown in Fig. 1(a). An electron is photoexcited to a state of k_f leaving a hole. The hole is filled by an Auger event in which a second d electron is scattered into an empty d state, k_x, n'. This leaves two d holes which multiply scatter. The scattering is described by the t matrix and a pole in t yields the bound state responsible for the satellite peak. The t-matrix approach is valid[12,13] when the number of unfilled d states is small as in Ni. From Fig. 1(a) the photoemission current at energy ϵ is calculated by ordinary time-dependent perturbation theory to be[14]

$$I_a(\epsilon)=\frac{2}{\hbar}\sum_{k,n,\sigma,k_f}|\langle kn\sigma|\vec{A}\cdot\vec{P}|k_f\sigma\rangle|^2\operatorname{Im}G_{k,n,\sigma}(\epsilon-\hbar\omega_0)\delta(\epsilon-\epsilon_{k_f,\sigma}),\tag{2a}$$

where $\hbar\omega_0$ is the photon energy and the one-hole Green's function $G_{k,n,\sigma}(\epsilon)$ is determined by the hole self-energy

$$\Sigma_{k,n,\sigma}(\epsilon)=\sum_{K,k_x,n'}\frac{(1-f_{k_x,n',\downarrow})U(1-\Delta_{n,\sigma;n',\downarrow})\Delta_{K,k+k_x}}{1+UG_0^{n,\sigma;n',\downarrow}(\epsilon+\epsilon_{k_x,n',\downarrow}-\hbar\omega_0,K)},\tag{2b}$$

where the two-hole Green's function is

$$G_0^{n,\sigma;n',\sigma'}(\xi,K)=\sum_q f_{K/2+q,n,\sigma}f_{K/2-q,n',\sigma'}[\xi-\epsilon_{K/2+q,n,\sigma}-\epsilon_{K/2-q,n',\sigma'}-i\delta]^{-1}\tag{2c}$$

and $\epsilon_{k,n,\sigma}$ is the Hartree-Fock band energy.

Equation (1a) is the usual expression for the photoemission current. The self-energy is normally taken to be the small-U limit of Eq. (2b), the Hartree-Fock self-energy. However, the hole-hole interaction is $t=U/(1+UG_0)$ rather than the Hartree-Fock approximation of U. The denominator of t represents multiple scattering and results in a strong energy dependence of t and consequently of $\Sigma_{k,n,\sigma}(\epsilon)$, an effect which is neglected in the Hartree-Fock approximation but which gives rise to the satellite. Figure 1(f) shows schematically U of Eq. (1), the diagrams giving G and Σ of Eq. (2b), and t.

The Ni band is almost filled, so that it is reasonable to expect that its two-hole excitation spectrum is similar to that of Cu. The two-hole spectrum for materials with filled d bands has been discussed by Sawatsky[15] and by Cini[16] in reference to valence-band Auger spectra. In the limit of large U they show that the two d holes excited in the Auger process are left in a correlated atomiclike state and consequently the Cu Auger spectrum is atomiclike as is observed experimentally. However, in the case of materials with filled d bands, the two-hole state is not coupled to the single-hole excitation spectrum because there are no empty d states to scatter into and thus the Cu photoemission spectrum does not exhibit a satellite. A d electron could be scattered into an empty s-p state but this has relatively low probability and in any case would lead to a tailing of the d spectra rather than a satellite because of the width of the s-p band.

In order to account for the dependence of the satellite intensity on photon energy it is necessary to include photon or Auger excitation of a $3p$ core level to an unfilled d state. All the relevant diagrams for the photoexcitation probabilities are shown in Figs. 1(b)–1(e). The standard t-matrix approximation that there is at most one electron in an unfilled d state (because of the small number of such states) has again been made. A solid arrow pointing to the left denotes a renormalized core hole; the self-energy is given by essentially the same diagrams as those for a d hole except that, when a core hole interacts with a d electron via t, it is understood that the first scattering event is governed by an Auger event whereby the core hole is scattered into a d hole. Diagram 1(g) shows the meaning of the interaction line between a core hole and a d electron residing in an initially unoccupied d state. This type of interaction appears in Figs. 1(b)–1(e).

Diagrams 1(b) and 1(c) are not coherent with the other diagrams for the case $n'\neq n''$ and correspond to a "normal" Auger process with a photoemission current

$$I_{b,c}(\epsilon)=(2/\hbar)F(\hbar\omega_0)\sum_{k,n,\sigma,k_f}\Delta_{k,k_f}\operatorname{Im}\Sigma_{k,n,\sigma}(\epsilon-\hbar\omega_0)\delta(\epsilon-\epsilon_{k_f})\sum_{\substack{n',n''\\ n'\neq n''}}(5-\Delta_{\sigma,\downarrow})^{-1}$$
$$\times\Big|\sum_m[\langle m|\vec{A}\cdot\vec{P}|n''\rangle]_{ab}\langle n\sigma,n'\downarrow|V|k_f\sigma,m\downarrow\rangle/U\Big|^2,\tag{3}$$

where $F(\hbar\omega_0)=[(\hbar\omega_0-\bar{\epsilon}_c)^2+\Sigma_c^2]^{-1}$, $\bar{\epsilon}_c$ is the $3p$ to unfilled-d-state excitation energy, and Σ_c is the core-hole self-energy. $|m\rangle$ is the core-state wave function with azimuthal quantum number m, $|n''\rangle$ is a d-state atomic wave function on the same atom, and the average over the matrix element of $\bar{A}\cdot\bar{P}$ indicates there is an additional contribution to $\langle m|\bar{A}\cdot\bar{P}|n''\rangle$ from diagram 1(c) (which is numerically small). V is the Coulomb interaction in the Auger process.

Diagrams 1(a), 1(d), and 1(e) and diagrams 1(b) and 1(c) for $n'=n''$ are coherent. The corresponding expression for their contribution to the photoemission current will be given elsewhere[14] since the largest contribution to the satellite is from the incoherent part of diagram 1(b) near resonance and diagram 1(a) far from resonance. The coherent terms will produce a resonant behavior of the main d-band peak and this is currently under study.

In order to evaluate the various contributions to the photocurrent, the dependence of the current on the final-state band structure is neglected by replacing $\delta(\epsilon - \epsilon_{k_f})$ in Eqs. (2a) and (3) by $\rho(\epsilon)$, the density of final states. Also, G_0 of Eq. (2c) is replaced by its average over κ and the small exchange splitting is ignored. In this approximation G_0 depends only on the Hartree-Fock d-band density of states, ρ_0.

The Ni spectrum for d-band photoemission (no core contribution) is calculated from Eq. (1). ρ_0 is taken from the work of Wang and Callaway.[8] Figure 2 shows the experimental spectrum[1] after a background subtraction as the solid curve marked XPS. The XPS spectrum predicted by band calculation[2] in the absence of correlation effects ($U=0$) is shown by circles; it is determined by ρ_0 which is normalized so that there is good agreement between theory and experiment near the Ni Fermi energy. The results of the present calculation of $I_a(\epsilon)$ for $U=2.0$ eV are given by the squares marked XPS. For larger values of U, the satellite moves to lower energies and removes more weight from the main d-band spectrum. For $U \simeq 5$ eV the satellite peak is predicted to be roughly 13 eV below ϵ_F.

The magnitude of the diagrams 1(b)–1(e) has all been estimated and 1(b) is found to dominate for the satellite (although not for the main peak). The ratio of the total intensity produced by Fig. 1(b) to that from Fig. 1(a) is approximately[14]

$$\frac{I(1(\mathrm{b}))}{I(1(\mathrm{a}))} = \frac{\Sigma_c}{F(\hbar\omega_0)} \left| \frac{\langle c|\vec{A}\cdot\vec{P}|d\rangle}{\langle d|\vec{A}\cdot\vec{P}|k_f\rangle} \right|^2 \frac{N_x}{2\pi\rho}, \qquad (4)$$

where $N_x = 0.6$ is the number of d holes, and ρ is the density of states at energy $\hbar\omega_0$ above the d bands. Diagrams 1(a) and 1(b) have most of their intensity in the main peak and in the satellite, respectively, thus $I(1(\mathrm{b}))/I(1(\mathrm{a}))$ is an estimate of the observed satellite to main peak intensity I_s/I_0. In order to estimate $I(1(\mathrm{b}))/I(1(\mathrm{a}))$, $|c\rangle$ and $|d\rangle$ are taken to be atomic wave functions, $|k_f\rangle$ is approximated by an orthogonalized plane wave, and Σ_c is taken from experiment. Equation (4) yields $I(1(\mathrm{b}))/I(1(\mathrm{a})) \simeq 2$ for $\hbar\omega_0 = \bar{\epsilon}_c = 67$ eV

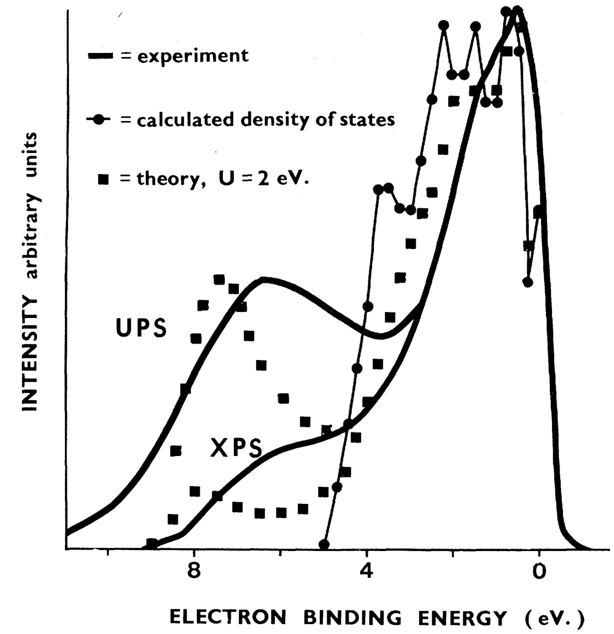

FIG. 2. The solid curve marked XPS is the experimental XPS photoemission current. The solid curve marked UPS is the experimental spectrum *at resonance*, $\hbar\omega_0 = 67$ eV. The relatively small differences in the d-band portion of the curves have not been shown for the sake of clarity. The dots represent the spectrum predicted by band theory. The squares marked XPS are the results of the present theory for $U=2$ eV. The squares marked UPS are the results of the theory with $U=2$ eV and the Auger matrix elements normalized so that the experimental and theoretical satellite curves are the same height.

compared to the observed value[4,5] of $I_s/I_0 \simeq 1$. In view of the many approximations made, this is quite reasonable agreement.

$I_{b,c}(\epsilon)$ is calculated from Eq. (3) at resonance, $\hbar\omega_0 = 67$ eV, assuming constant matrix elements. In Fig. 2, $I_a(\epsilon) + I_{b,c}(\epsilon)$ for $U=2$ eV is shown as the upper set of squares and is compared to the experimental results (the solid line marked UPS). The matrix elements in Eq. (3) have been normalized so that the peak heights of the theoretical and experimental curves are equal. It can be seen from Eqs. (3) and (2b) that in the Hartree-Fock approximation the calculated UPS peak would be located at the bottom of the d bands. The coherent terms mentioned above are estimated to contribute roughly 20% to the satellite intensity at resonance.

With respect to other metals I note the following: (a) The satellite cannot be excited in metals with filled d bands and has not been observed in such materials. (b) Fe and Co show evidence of similar but weaker satellites; this is consistent with the present theory but requires further study. (c) A satellite has not been observed in Pd despite a value of U similar to that for Ni; however, Pd has fewer $3d$ holes and a calculation predicts a lifetime tailing of the main d-band peak but no satellite.

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Spectrum of the Cosmic Background Radiation

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New measurements of the emission spectrum of the night sky have been made in the frequency range from 1.7 to 40 cm^{-1} using a fully calibrated, liquid-helium–cooled, balloon-borne spectrophotometer. The results show that the spectrum of the cosmic background radiation peaks at 6 cm^{-1} and is approximately that of a 3-K blackbody out to several times that frequency. However, the data show deviations from a simple blackbody curve.

Previous measurements[1] of the cosmic background radiation (CBR) have shown that its spectrum is approximately that of a 3-K blackbody over the frequency range from 0.02 to 17 cm^{-1}. These observations have been instrumental in establishing the big-bang theory of cosmic expansion as the accepted model of the Universe. In its most elementary version this theory predicts a blackbody spectrum for the CBR. The experimental results reported to date, however, have lacked the accuracy required to detect deviations from a Planck curve as large as 20%. We report in this Letter an observation of the CBR in the frequency range from 2.5 to 24 cm^{-1} with a flux accuracy of better than 10% of the peak flux of a 3-K blackbody at 6 cm^{-1}.

The apparatus used for this experiment was an improved version of the liquid-helium–cooled balloon-borne Fourier spectrophotometer developed for our previous measurement of the near-millimeter CBR, which is described in Woody *et al.*[2] and Mather, Richards, and Woody.[3] The sensitivity was increased by one order of magnitude over that of our previous system by the use of a ^{3}He-cooled composite bolometer.[4] Improvements were also made to the antenna by the use of a Winston concentrator[5] to define the $\approx 7°$ field of view on the sky and by the addition of a large earthshine shield.

The cryostat containing the antenna and the spectrometer was mounted in a gondola with the required telemetry and launched from Palestine,