Introduction

Due to the Coulomb interaction, an electron approaching a metal surface can excite a core electron into a state of the unoccupied bands. Above a threshold energy both the excited core electron and the deexcited primary electron are scattered into valence states just above the Fermi energy. Appearance-potential spectroscopy (APS) monitors the intensity of this radiationless transition as a function of the energy of the primary electrons by detecting the emitted x rays or Auger electrons of the subsequent core-hole decay. Since core-hole formation is involved, the method is element specific and local. Its comparatively simple experimental setup and its surface sensitivity qualify APS as a useful technique for surface analysis. For a ferromagnetic material, the spin dependence of the AP signal obtained by using a polarized electron beam reflects the surface magnetization, as has been demonstrated for the transition metals Fe and Ni.\(^5\)\(^6\)\(^9\) In a sense APS can be considered to be complementary to Auger-electron spectroscopy (AES).\(^10\) While the Auger line shape resulting from core-valence-valence (CVV) transitions yields information on the occupied part of the valence band, APS is sensitive to the unoccupied electronic structure. Unlike \textbf{k} resolved (inverse) photoemission, the AP transition is more or less localized in real space. This suggests employing APS as a quantitative probe for the unoccupied part of the spin-dependent local valence density of states (DOS).

In most cases the interpretation of appearance-potential spectra is still based on a simple independent-electron model suggested by Lander in 1953,\(^1\)\(^1\)\(^1\) where the line shape is given by the self-convolution of the unoccupied part of the DOS. The desired information can then be obtained by deconvolution techniques.\(^12\)\(^13\) Within the context of AES, however, it soon became clear that the self-convolution model is oversimplified. Powell\(^14\) discovered an "anomalous" shape of the CVV Auger line of Ag which has been attributed to electron-correlation effects. Correlations may be significant for APS also because of the direct interaction of the two additional valence electrons in the final state. This is demonstrated by the Cini-Sawatzky theory.\(^15\)\(^16\) Within the framework of the single-band Hubbard model, the two-particle (APS/AES) excitation spectrum is dominated by a pronounced satellite feature which is split off the bandlike part by a characteristic energy of the order of the on-site Coulomb interaction \(U\). For more realistic (multiband) Hubbard models the direct correlations give rise to very complex satellite structures.\(^17\)\(^21\)

A second shortcoming of the Lander model consists in the fact that transition-matrix elements are not taken into account. Modern theories for APS (AES) based on density-functional theory and the local-density approximation (LDA) have overcome this deficiency.\(^22\)\(^23\) Although the direct correlations are still neglected in these approaches, it seems that the AP spectra of Fe and Ni, for example, are well understood—serious indications of correlation effects have not been observed. This is surprising since it is well known that the Auger line shape of Ni cannot be explained within an effective independent-electron model.\(^23\)\(^24\) It is dominated by a strong spectral-weight transfer due to an on-site interaction of the order of \(U\approx2\)–3 eV to be compared with the effective \(d\)-band width \(\Delta=3\) eV.\(^10\)\(^26\)

Clearly, the question of what really determines the appearance-potential line shape of transition metals can only be answered \textit{a posteriori}—namely by comparison with a theory that realistically includes electron-correlation as well as matrix-element effects, orbital degeneracy, and \(sp\)-\(d\) hybridization from the very beginning. Analysis of the AP line shape of Ni, as a prototypical ferromagnetic 3\(d\) metal, is the purpose of the present paper. In the experiment spin-resolved spectra from excitation of the \(2p_{3/2} (L_{III})\) core level are recorded for different temperatures ranging from \(T=100\) K up to and slightly above the Ni Curie point \(T_C=624\) K.\(^27\)
Theoretical interpretation of the line shape is essentially based on a multiband Hubbard-type model with general onsite Coulomb interaction and a realistic parametrization of the (LDA) one-particle electronic structure as an input for a subsequent many-body calculation. Standard diagrammatic techniques are used to account for correlations. The transition-matrix elements are calculated within the usual intra-atomic approximation. The approach allows separate study of the DOS effect (bare self-convolution), the temperature-dependent effect of the (direct and remaining indirect) correlations, and the effect of the transition-matrix elements.

II. EXPERIMENT

Experiments were performed for a Ni(110) single-crystal surface with in-plane magnetization. The spin-polarized electron beam used for excitation is emitted from a GaAs photocathode irradiated by circularly polarized light. The longitudinal spin polarization of the emitted photoelectrons is changed to transverse by 90° electrostatic deflection. To correct for the incomplete polarization of the electrons ($P \approx 30\%$), all data have been rescaled to a 100% hypothetical state. The intensity asymmetry in the main peak gradually diminishes with increasing temperature and vanishes at $T_C$. For an incoming electron with spin $s$ and the Fermi energy and is mainly due to $d-d$ character of the two final-state electrons. Additional small $s-d$ contributions are present in the secondary peak at $E \approx 859$ eV as has been concluded from the analysis of the transition-matrix elements.


total spin polarization and the sample-magnetization vector. In the present setup the core-hole decay is detected via soft-x-ray emission. The detector arrangement consists of a multichannel plate with filters and a CsI layer acting as photon-to-electron converter. The APS signal is measured as a function of the primary energy of the electrons. Modulation of the sample potential together with a lock-in technique is employed to separate the signal from the otherwise overwhelming background. For the potential modulation a peak-to-peak voltage of $2$ V was chosen. This value ensures high APS signals for the $2p_{3/2}$ core level without modulation-induced broadening effects. Further details of the experimental setup and the sample preparation have been described elsewhere.

Figure 1 shows the differential AP intensity as a function of the energy of primary electrons with polarization parallel (minority, $\downarrow$) or antiparallel (majority, $\uparrow$) to the target magnetization. The displayed energy range covers the emission from the $L_{III}$ transition. The $L_{II}$ emission would be visible at higher energies shifted by the $2p$ spin-orbit splitting of about 17.2 eV.

For $T/T_C = 0.16$ the system is close to ferromagnetic saturation. The appearance-potential spectrum shows a strongly asymmetric intensity ratio as well as a spin splitting of the main peak at $E = 852.3$ eV (dotted line). Since Ni is a strong ferromagnet, there are only a few unoccupied $d$ states available in the majority spin channel, and thus $I_\uparrow < I_\downarrow$ holds for the (nondifferential) intensities. This is the dominant spin effect. The intensity asymmetry in the main peak gradually diminishes with increasing temperature and vanishes at $T_C$.

Note that only the position of the majority peak shifts with $T$ while the minority peak position remains unchanged.

The main peak is related to the high density of states at the Fermi energy and is mainly due to $d-d$ character of the two final-state electrons. Additional small $s-d$ contributions are present in the secondary peak at $E \approx 859$ eV as has been concluded from the analysis of the transition-matrix elements.

Theoretical interpretation of the line shape is essentially based on a multiband Hubbard-type model with general onsite Coulomb interaction and a realistic parametrization of the (LDA) one-particle electronic structure as an input for a subsequent many-body calculation. Standard diagrammatic techniques are used to account for correlations. The transition-matrix elements are calculated within the usual intra-atomic approximation. The approach allows separate study of the DOS effect (bare self-convolution), the temperature-dependent effect of the (direct and remaining indirect) correlations, and the effect of the transition-matrix elements.

III. THEORY

The theoretical approach is based on the usual two-step description assuming the lifetime of the core hole to be sufficiently long. The AP line shape is then unaffected by the cross section for the core-hole decay step but solely determined by the excitation step. According to Fermi’s golden rule, the intensity can be written as

$$I_{\sigma,\sigma'}(k|E) \propto \text{Im} \sum_{L_1, L_2} M_{\sigma \sigma'}^{L_1, L_2}(k|E) \times \langle \psi_{L_1, \sigma}^c \psi_{L_2, \sigma'}^c \psi_{L_1, \sigma} \psi_{L_2, \sigma'} \rangle \times \left[ M_{\sigma \sigma'}^{L_1, L_2}(k|E) \right]^*.$$
with $\sigma_c = \sigma_i$. Since the spin state of the final core hole is not detected, the intensities have to be summed incoherently:

$$I_{\sigma_f}(k_{\parallel}, E) = I_{\sigma_f, \sigma_i}(k_{\parallel}, E) + I_{-\sigma_f, \sigma_i}(k_{\parallel}, E).$$

(2)

Above the Curie temperature $I_{\sigma_f} = I_{-\sigma_f}$.

The raw spectrum resulting from an intra-atomic transition at the lattice site $i$ is given by the imaginary part of the retarded two-particle (Zubarev) Green function in Eq. (1). It describes the correlated propagation of the two additional final-state electrons at energy $E:

$$\langle \langle \langle c_{iL_1\sigma}^\dagger c_{iL_2\sigma}^\dagger c_{iL_2\sigma'} c_{iL_1\sigma'} \rangle \rangle \rangle_E = - \int_0^\infty dt e^{iEt} \langle \langle c_{iL_1\sigma}^\dagger(t) c_{iL_2\sigma}(t); c_{iL_2\sigma'}(0) c_{iL_1\sigma'}^\dagger(0) \rangle \rangle_E.$$ 

(3)

Here $\langle \cdot \rangle$ is the thermodynamic average, $\langle \cdot \rangle_0$ the commutator, and $O(t) = \exp(iHt)O\exp(-iHt)$ is the Heisenberg time dependence of an operator $O$. The Green function is expressed in terms of annihilators (creators) $c_{iL\sigma}^\dagger$ which refer to a tight-binding one-particle basis. Due to translational symmetry of the fcc lattice the $i$ dependence is only formal. $L = \{l, m\}$ characterizes the angular momentum of the localized $3d$, $4s$, and $4p$ basis functions. In total there are $2 \times 9$ orbitals $\{iL\sigma\} = c_{iL\sigma}^\dagger \{\text{vac}\}$ per site.

Because of the definite $L$ character of the basis orbitals, the orbitals on different sites are mutually nonorthogonal: $\langle iL\sigma | j' L' \sigma' \rangle = \delta_{L L'} \delta_{\sigma \sigma'}$. There are different advantages to developing the many-body formalism for a nontrivial overlap matrix $S \neq 1$ (see Refs. 31 and 32): A unique decomposition of the spectrum into $s$, $p$, and $d$ parts is possible, the basis orbitals are more localized, and in the interaction part of the Hamiltonian the on-site Coulomb interaction among the $3d$ electrons can be dealt with separately. Furthermore, the same basis states enter the definition of the transition-matrix elements, and their definite angular-momentum character implies helpful selection rules.

The transition-matrix elements in Eq. (1),

$$M_{L_1L_2}^{\sigma\sigma'}(k_{\parallel}, E) = \langle \langle \langle c_{iL_1\sigma}^\dagger c_{iL_2\sigma}^\dagger c_{iL_2\sigma'} c_{iL_1\sigma'} \rangle \rangle_k \rangle_{E} \langle \langle \langle c_{iL_1\sigma}^\dagger c_{iL_2\sigma}^\dagger c_{iL_2\sigma'} c_{iL_1\sigma'} \rangle \rangle_k \rangle_{E},$$

(4)

are calculated by assuming the transition to be intra-atomic as usual.\textsuperscript{10,22,23} The different wave functions as well as the Coulomb operator $1/|r_i - r_j|$ are expanded into spherical harmonics, the angular integrations are performed analytically, and the numerical radial integrations are cut at the Wigner-Seitz radius (see Ref. 33 for details).

Surface effects enter the theory via the high-energy scattering state $|k_{\parallel}E\sigma\rangle$. It is calculated as a conventional low-energy electron diffraction state\textsuperscript{24} with $k_{\parallel} = 0$ to describe the normally incident electron beam in the experimental setup.

At kinetic energies of the order of keV, however, the $k_{\parallel}$ dependence turns out to be weak. Furthermore, at high kinetic energies, multiple-scattering effects are small and may be neglected for convenience.

The (paramagnetic) LDA potential for Ni is determined by a self-consistent tight-binding linear muffin-tin orbital (LMTO) calculation.\textsuperscript{35} The $3d$, $4s$, and $4p$ valence orbitals $\{iL\sigma\}$ are taken to be the muffin-tin orbitals. The fourfold degenerate $2p_{3/2}$ core state is obtained from the LDA core potential by solving the radial Dirac equation numerically. Its (relativistically) large component is decomposed into a (coherent) sum of Pauli spinors $\langle 2p_{\sigma} \rangle$ with $\sigma_c = \pm 1$.

Note that the Green function in Eq. (1) generally depends on four quantum numbers $L_1 - L_4$. In fact, for the present case each term in the sum gives a significant contribution to $I_{\sigma_f, \sigma_i}$. The usual characterization of the final state with two quantum numbers ($d-d$, $s-d$, etc.) is no longer valid if correlations are included. The orbital character may change by electron scattering.

Neglecting electron correlations altogether and assuming the matrix elements to be constant, Eq. (1) reduces to the Lander model. In this case the intensity $I_{\sigma_f}$ is given by the following sum of (singlet and triplet) self-convolutions:

$$I_{\sigma_f} \propto \sum_{L_1L_2} \int dE' \tilde{\rho}_{L_1\sigma_f}(E') \tilde{\rho}_{L_2-\sigma_f}(E-E')$$

$$+ \sum_{L_1L_2} \int dE' \tilde{\rho}_{L_1\sigma_f}(E') \tilde{\rho}_{L_2\sigma_f}(E-E').$$

(5)

Here $\tilde{\rho}_{L\sigma}(E) = [1 - f(E)] \rho_{L\sigma}(E)$ is the unoccupied part of the $L$-resolved and spin-dependent density of states $\rho_{L\sigma}(E)$, where $f(E)$ is the Fermi function. The prime in the second sum in Eq. (5) excludes the term $L_1 = L_2$, $\sigma_c = \sigma_i$, which is forbidden by the Pauli principle. Note that lattice symmetries require the on-site ($i = i'$) but off-diagonal ($L \neq L'$) DOS $\rho_{LL'\sigma}(E) = (-1/\pi) \text{Im} \langle c_{iL\sigma}^\dagger c_{iL'\sigma'} \rangle_E$ to vanish identically. This is a consequence of the choice of the (nonorthogonal) basis set $|iL\sigma\rangle$.

To estimate the significance of correlation effects, the two-particle Green function in Eq. (1) is calculated for a nine-band Hubbard-type model $H = H_{LDA} + H_{\text{int}} - \Delta H$ including $4s$, $4p$ orbitals and correlated $3d$ orbitals:

$$H = \sum_{i' L' \sigma} T_{i'i}^{LL'} \langle \langle c_{iL\sigma}^\dagger c_{i'L'\sigma'} \rangle \rangle_k \langle \langle \langle c_{iL\sigma}^\dagger c_{i'L'\sigma'} \rangle \rangle_k \rangle_{E}$$

$$+ \sum_{i\sigma'} \sum_{m\ldots m_4} U_{m_1\ldots m_4 \sigma} c_{im_1\sigma'} c_{im_2\sigma} c_{im_3\sigma'} c_{im_4\sigma} - \Delta H.$$

(6)

The hopping parameters $T_{i'i}^{LL'}$ of the one-particle term $H_{LDA}$ (and also the overlap $c_{i'i}^{LL'}$ parameters) are obtained from a Slater-Koster fit to the paramagnetic LDA band structure for Ni.\textsuperscript{32} Unlike in photoemission spectroscopy, this comparatively simple tight-binding parametrization appears to be suf-
cient in the case of APS since the two-particle spectrum does not crucially depend on the details of the one-particle DOS.

The on-site interaction among the 3d electrons is described by the second term $H_{\text{int}}$. The Coulomb matrix depends on four orbital indices $U_{m_1,m_2,m_3,m_4}$, referring to the MTO's for $l=2$. Using atomic symmetries the interaction parameters can essentially be expressed in terms of two parameters $U$ and $J$. Interactions involving delocalized $s$ and $p$ states are assumed to be sufficiently accounted for within the LDA. For the $d$ states, however, there is the well-known double-counting problem: The interactions are counted twice, once in $H_{\text{LDA}}$ (i.e., on a mean-field level) and once more in $H_{\text{int}}$. To avoid this double counting, a third term $\Delta H$ has been introduced by which the Hartree-Fock part of $H_{\text{int}}$ is subtracted.\[32,36\]

The Hamiltonian $H$ constitutes an involved many-body problem. Due to the low density of 3d holes in the case of Ni, however, it appears to be reasonable to employ the so-called ladder approximation\[59\] which extrapolates from the exact (Cini-Sawatzky) solution for the limit of the completely filled band.\[15,16\] For finite hole densities the ladder approximation gives the two-particle Green function \(\langle cc; c'^{\dagger} c' \rangle\) as a functional of the one-particle Green function \(\langle c; c' \rangle\). The one-particle Green function of the type \(\langle c; c' \rangle\) corresponds to the (inverse) photoemission spectrum, which itself is renormalized by $H_{\text{int}}$ ("indirect correlations"). It is calculated self-consistently within second-order perturbation theory (SOPT) around the Hartree-Fock solution.\[32\] For a moderate $U \sim \Delta$ and a low hole density, a perturbational approach can be justified.\[30\] A resummation of higher-order diagrams is important to describe bound states ("Ni 6 eV satellite")\[37\] which, however, are relevant for AES only. The numerical values for the direct and exchange interactions, $U = 2.47$ eV and $J = 0.5$ eV, are taken from Ref. 23, where they were fitted to the ground-state magnetic properties of Ni. Since spin-wave excitations are neglected in the approach, the calculated Curie temperature $T_C = 1655$ K is about a factor 2.6 too high compared with experiment. Using reduced temperatures $T/T_C$ however, the temperature trend of the magnetization is well reproduced.\[32\]

IV. RESULTS AND DISCUSSION

The solid lines in Fig. 1 (left) show the spectra as calculated from Eq. (1) using the ladder approximation. To account for apparatus broadening, the results have been convoluted with a Gaussian of width $\sigma = 0.6$ eV (see Ref. 23). The calculated data are shifted by 852.3 eV such that onset of the unbroadened spectrum for $T/T_C = 0.16$ coincides with the maximum of $L_{\text{III}}$ emission in the experiment (dotted line).

What are the signatures of electron correlations? To estimate first the effect of the direct interaction between the two additional final-state electrons, Fig. 1 (right) also displays the results of the self-convolution model for comparison (still including matrix elements as well as the fully interacting one-particle DOS). Figure 1 and also a more detailed inspection show that the secondary peak at $E \approx 859$ eV is not affected by correlations at all. This is consistent with the observed temperature independence of the peak and with the fact that the DOS has mainly $s$-$p$ character at the discontinuity deriving from the $L_\gamma$ critical point. The maximum of the secondary peak is therefore used as a reference to normalize the measured spectra for each $T$. Looking at the results of the ladder approximation, the overall agreement with the measurements is rather satisfying. Except for the lowest temperature the intensity, the spin splitting, and the spin asymmetry of the main peak are well reproduced and, consistent with experiment, a negligibly small intensity asymmetry and spin splitting is predicted for the secondary peak. Switching off the direct correlations (Fig. 1, right) results in a strong overestimation of the main peak structure. Within the Cini-Sawatzky theory this has a plausible qualitative explanation. For low hole density the main effect of the direct correlations is known to transfer spectral weight to lower energies inaccessible to APS. This weight shows up again in the Auger spectrum. Recall that in fact a considerable weight transfer is seen in AES,\[10,26\] and that hypothetically for $U \rightarrow \infty$ all weight would be taken by a satellite split off at the lower boundary of the Auger spectrum.\[15,16\]

The indirect correlations manifest themselves as a renormalization of the one-particle DOS. Thus, in the first place they are responsible for the correct temperature dependence of the intensity asymmetry of the main peak in the AP spectrum. In particular, the indirect correlations result in a narrowing of the DOS, which near the Fermi energy $E_F$ is given by the (almost spin-independent) quasiparticle weight $\approx 0.88 < 1$, and in an intrinsic lifetime broadening $\Gamma \propto (E - E_F)^2$. For $T = 0$ the latter turns out to be smaller than $\Gamma \approx 0.01$ eV for $E - E_F < 1$ eV.\[32\] The discrepancy between experiment and theory for $T/T_C = 0.16$ is possibly due to an underestimation of $\Gamma$ within the SOPT: With decreasing $T$ the increase of the exchange splitting leads to the appearance of a strong peak just above $E_F$ in the minority DOS. A larger lifetime broadening of this peak would imply a less pronounced feature in the differential AP spectrum—mainly in the minority channel.

Setting $M_{L_1 L_2}^{\alpha \beta}(k_1,E) = \pm 1 = \text{const}$ for $L_1 \geq L_2$ or $L_1 < L_2$, respectively (see below), and comparing with the results of the full theory, demonstrates the importance of the transition-

![Fig. 2. Ni AP spectrum for $T=0$. (a) Full theory. (b) As (a) but matrix elements taken to be constant (see text).](image-url)
matrix elements. Their energy dependence (via \( |k| E \sigma_{l} \)) is weak over a few eV at energies of the order of keV and cannot explain the difference between (a) and (b) in Fig. 2. The main difference is rather a consequence of the fact that the radial 2p core wave function has a stronger overlap with the (more localized) 3d as compared to the (more delocalized) 4s/4p radial wave functions. This implies a suppression of the s-p contributions to the orbital sum in Eq. (1) as already found by Ebert and Popescu.\(^2\) The features above

\[ E = 860 \text{ eV} \]

originate from additional discontinuities of the s-p-like DOS (as for the peak at \( E \approx 859 \text{ eV} \)).

For \( T < T_C \) the spin asymmetry of the spectrum is mainly due to the spin dependence of the Green function in Eq. (1). If the calculation of the matrix elements (4) starts from the spin-polarized L(S)DA potential, an additional spin asymmetry is observed resulting from the spin dependence of the states in Eq. (4). This, however, is small and has essentially no influence on the results. On the other hand, Fig. 2 shows a strong suppression of the intensity asymmetry at high energies when taking matrix elements into account. This effect is controlled by the symmetry of the matrix \( M_{L_1L_2}^{s_i,s_j}(k_L,E) \). In the antisymmetric case, \( M_{L_1L_2}^{s_i,s_j} = -M_{L_2L_1}^{s_j,s_i}(L_1 \neq L_2) \), there is a maximum spin asymmetry (Fig. 2) while, even for a ferromagnet, there is no spin asymmetry at all for the symmetric case. The results of the full calculation by Eq. (4) are neither fully symmetric nor antisymmetric with respect to \( L_1, L_2 \).

V. SUMMARY

In conclusion, the AP line shape of a typical ferromagnetic 3d transition metal results from a rather complex interplay of different factors. The present study has shown that a quantitative theoretical analysis of the temperature- and spin-dependent spectrum must be based on three ingredients at least.

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(i) ‘‘Indirect’’ correlations: A realistic Hubbard-type model including s-p-like states is a proper starting point to describe the magnetism and the temperature-dependent renormalization of the one-particle DOS.

(ii) ‘‘Direct’’ correlations: While s-p-derived features at higher energies appear to be sensitive to the geometrical structure only, the main peak is strongly affected by the direct interaction between the two additional final-state electrons. Consistent with the Cini-Sawatzky model, the dominant effect is a considerable spectral-weight transfer to energies below the threshold.

(iii) Matrix elements: Spin-resolved APS cannot be described theoretically without calculating orbital-dependent matrix elements. The spin asymmetry is mainly determined by their transformation behavior under exchange of the orbital quantum numbers \( L_1 \leftrightarrow L_2 \).

An open question concerns the importance of core-hole effects in APS. Future work will be concerned with the scattering at the core-hole potential in the final state and will include the edge effects known from the studies of simple metals. A generalized ladder approximation including the valence-core interaction was proposed in Ref. 20. Previous work has shown that one should not expect the effects due to scattering at the core-hole potential to be strong for the case of Ni. However, core-hole effects will become more important for systems with a smaller 3d occupancy. For Co and Fe one also expects stronger effects of d-d correlations. This work has shown that these d-d correlations cannot be neglected even for a system with low d-hole density such as Ni, and that deconvolution techniques to extract the unoccupied local DOS have to be questioned seriously.

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