X-Ray Absorption Near Edge Structure in Metals: Relativistic Effects and Core-Hole Screening

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A long standing theoretical problem "the absence of a white line in the L_2 x-ray absorption near edge spectrum of Pt metal" has been solved taking into account relativistic effects and the presence of a core hole. The photoabsorbing atom is treated as a single-site impurity in our theory of x-ray absorption near edge structure (XANES) based on the fully relativistic layer Korringa-Kohn-Rostoker Green-function method. Comparing the XANES of Al with those of Cu and Pt, it is found that for transition metals d electrons play a dominant role in deep core-hole screening, whereas in Al sp electrons are important.

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X-ray absorption near edge structure (XANES) or near edge x-ray absorption fine structure (NEXAFS) has been recognized as a valuable probe of studying the unoccupied electronic states in solids just above the Fermi level E_F. Since the first experiment in the 1920s on structural analysis of matter, the observed spectra have attracted a considerable amount of theoretical interest. Almost three decades ago, a model proposed by Mahan to explain the x-ray absorption threshold divergence [1] triggered successive theoretical studies on the many-electron response to a photocreated core hole in metals [2,3]. With the advent of polarized light from synchrotron sources, magnetic linear and circular dichroism (MLD, MCD) in XANES spectroscopy has become one of the most powerful techniques to study the magnetic structure of materials. In combination with a sum rule the MLD and MCD spectra reveal unique information such as the orbital magnetic moment in ferromagnetic systems [4].

Existing theories are based on either an atomic and molecular or a band-structure description. In the atomic picture, electron correlation effects can be explicitly treated using Hartree-Fock based configuration interaction methods, while multiple scattering by the surrounding atoms is crudely approximated by a parametrized crystal field [5]. The band-structure-based theory relies on the single-electron description in order to fully account for multiple scattering. Although XANES spectra of a number of metals have been reasonably well explained within the framework of these theories, there are still unsolved problems. The present work addresses the long standing problem of the absence of a strong peak at the L_2 absorption edge, the so-called white line (WL), of Pt metal. More than 40 years ago, Mott [6] proposed an explanation for this unusual feature in the L absorption spectrum of Pt: If the unoccupied d states in Pt are predominantly states with total angular momentum $j = 5/2$, then one expects transitions from L_3 ($j = 3/2$) but not from L_2 ($j = 1/2$) core states because of the atomic dipole selection rule $\Delta j = 0, \pm 1$. Several attempts were made to confirm Mott's explanation, but the theoretical L_2 WL never convincingly vanished [7–9]. In this Letter we show that the WL in the calculated L_2 spectrum for Pt automatically vanishes, if one takes into account relativity and the presence of a core hole *simultaneously*, even in the single-electron description. Comparing Pt with other fcc metals, Cu and Al, we discuss why the single-electron description or, equivalently, the band-structure-based theories explain the K-edge (but not the L-edge) spectra of transition metals very well [10], and why the atomic picture occasionally works so well, even in metallic (delocalized) systems.

The photoabsorption rate per unit time is generally given by the imaginary part of a photon self-energy [11]. The well-known lowest order diagram consists of two external photon lines connected by an electron-hole loop. Many-electron effects can be included by renormalizing the electron and hole lines separately, such that renormalized Green functions (GF) describe the propagation of the dressed particles. Since the deep core hole is tightly bound to the nucleus, one can safely assume that the interaction between the electron-hole pair does not affect the hole state (nonrecoil) but only the photoelectron. The correction for this interaction (vertex correction), therefore, can be imposed on the photoelectron GF. If the hole GF is decomposed into the spectral form [12] and the absorption rate is normalized by the photon flux c (the velocity of light), the total absorption cross section for a core-state photoexcitation can be written in the form

$$\sigma(\omega) = -\frac{4\pi c}{\omega} \int A_c(E_c)\, \mathrm{Im}\langle \phi_c | \Delta^\dagger G(\omega - E_c) \Delta | \phi_c \rangle \, dE_c, \tag{1}$$

where $|\phi_c\rangle$ is the core-state wave function and $G(E)$ the *renormalized* single-electron GF of the unoccupied states. Equation (1) is the relativistic generalization of Durham's formula [13] with energy $E = \omega - E_c > 0$ (E_c is the core-hole energy, $E_F = 0$). The electron-photon interaction is given by $\boldsymbol{\Delta} = \boldsymbol{\alpha} \cdot \boldsymbol{\varepsilon}$ with the Dirac matrix $\boldsymbol{\alpha}$ and complex photon polarization $\boldsymbol{\varepsilon}$ in the dipole approximation [14]. The core-hole spectral weight function $A_c(E_c)$, which predominantly determines the

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line shape for photoelectrons in x-ray photoemission spectroscopy (XPS), normally is asymmetric with respect to a spectral peak [15]. Since we expect that the main features of $\sigma(\omega)$ should be attributed to $G(\omega - E_c)$ rather than $A_c(E_c)$, we approximate the functional form of A_c by a symmetric Lorentzian with a natural core level width Γ_c describing hole-lifetime broadening [16].

While we obtain the core-state wave functions in an established way [17], we employ the fully relativistic layer Korringa-Kohn-Rostoker GF method in the construction of the single-site GF for the unoccupied states [18]. In view of the long lifetime of the photoexcited states just above E_F it is important to account for multiple scattering by the infinite lattice. This is treated only approximately in atomic-cluster-based theories. The GF can be written in terms of bra and ket solutions, $\langle J_K^L|$ and $|J_K^R\rangle$, of the Dirac equation as [19]

$$G(E) = G_a^+(E) + \sum_{K,K'} |J_K^R\rangle D_{K,K'}(E) \langle J_{K'}^L| , \qquad (2)$$

where $G_a^+(E)$ is the atomic outgoing-wave GF and the quantum number K stands for the angular momentum $[\kappa(j), \mu]$. $D_{K,K'}$ determines the multiple-scattering correction. Correspondingly the absorption cross section can be expressed as a free-standing atomic cross section plus a contribution due to backscattering by the crystal, $\sigma(\omega) = \sigma_0(\omega) + \sigma_B(\omega)$.

Assuming a strong metallic screening, the potential change for the photoelectron due to the core hole is accounted for at the site of the photoabsorbing atom only. This reduces the problem to that of a single-site impurity, and the GF of the photoabsorbing atom can be written in a form analogous to Eq. (2) with $D^{(\mathrm{hole})} = \{1 - D(T^{(\mathrm{hole})} - T)\}^{-1} D$, where the $D^{(\mathrm{hole})}$ and D are matrices with elements labeled by (K, K'). $T^{(\mathrm{hole})}$ and T are the atomic single-site t matrices with and without the core hole [20].

In our specific crystal model, we employ spherically symmetric atomic potentials that are obtained from a scalar relativistic linearized muffin-tin orbital (LMTO) calculation, including the effect of spin-orbit coupling. Energy dependence of the exchange-correlation potential for unoccupied states is included by superimposing spatially uniform complex potentials (the optical potential), obtained from low-energy electron diffraction (LEED) studies [21], on the LMTO-derived potentials. Thermal vibration effects are included for the lighter atoms Cu and Al by renormalizing the atomic t matrix [22]. To model the potentials with the core hole, we performed three different self-consistent LMTO band-structure calculations imposing charge neutrality: (i) the $Z + 1$ approximation [23] using the crystal structure of the element with atomic number Z, (ii) the core-hole calculation adding one electron per atom to the valence band, and (iii) the supercell calculation in which 1 of every 32 atoms has a core hole. These potentials are good representatives of the electronic states fully relaxed in response to the core hole. In order to account for incomplete relaxation we shift the potential by a constant. The supercell calculation was particularly informative since it was found that the core-hole screening is complete at the absorbing atom site. The above three model potentials give practically identical results in the calculation of the photoabsorption cross section. Therefore, we show the results in the $Z + 1$ approximation, which is most easily achieved by standard band-structure codes.

In Fig. 1, we present L-edge spectra for Pt together with the density of states (DOS) above E_F as obtained

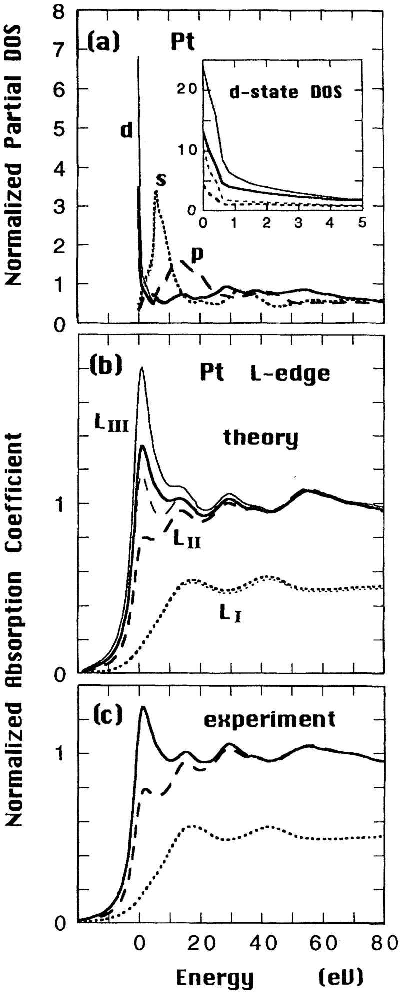

FIG. 1. Pt L-edge XANES spectra. (a) Angular momentum projected normalized partial DOS of the unoccupied states in Pt, with (thick lines) and without (thin lines) the core hole. The curves are normalized according to the degeneracy of 5 for d states (solid), 3 for p states (dashed), and 1 for s states (dotted). In the inset, the d DOS is projected further onto $d_{5/2}$ (solid) and $d_{3/2}$ (dashed) states. (b) Theoretical normalized Pt L-edge XANES spectra with (thick) and without (thin) core-hole correction: L_1 (dotted), L_2 (dashed), and L_3 (solid). The L_3 spectra are divided by the statistical value 2. The atomic part $\sigma_0(\omega)$ contributes to a smoothed step-function background for both the cases with and without a core hole. (c) Experimental Pt L-edge XANES spectra. The L_3 spectrum is divided by a factor of about 2 to facilitate comparison with the L_2 spectrum.

from the imaginary part of $G(E)$. The theoretical spectra are plotted without the denominator ω in Eq. (1), and an absorption cross section ratio of $2(\omega_{L_2}/\omega_{L_3}) \sim 2.3$ between L_3 and L_2 is recognized in this energy range. Here the factor 2 is the statistical weight from the p-d transition (negligible p-s contribution). Since the ratio is in good agreement with the hitherto reported experimental value 2.2 [24], we conclude that matrix-element effects in the transition probability are quite small. The agreement between theory and experiment is excellent. In order to achieve this agreement, however, it is necessary to shift the model potential upward by 1 eV (0.2 eV for the supercell potential). This was to be expected since the fully relaxed potentials are very deep, and too many electrons are gathered to screen the core hole. Strong core-hole effects as observed in the L_2 and L_3 spectra (but not L_1) can be attributed to the following core-hole screening mechanism. For the excited atom a strong reduction of the local d DOS at E_F is observed while no change is found in the s and p DOS, in accordance with theoretical XANES spectra. The d electrons play a dominant role in deep core-hole screening through a mechanism whereby the core hole attracts mainly d electrons rather than the s and p electrons. Screening charge is accommodated in d states at the excited atom, and consequently the d DOS at E_F decreases. An s-d mixing, which may be introduced by the core hole, seems to be quite small in our DOS calculation. This fact and a short core-hole lifetime [$< (5\ \text{eV})^{-1}$] explain the absence of the threshold divergence [25]. In the sense of the $Z + 1$ approximation, where the unoccupied d-state wave function of Pt fits nicely to the uppermost occupied d state of Au and the main difference between Pt and Au ground-state band structures is the position of d band relative to E_F, one can argue that it is energetically more favorable to screen the deep core hole by adding one localized d electron (intra-atomic) instead of attracting delocalized sp electrons (interatomic). The atomic picture works reasonably well, since a relatively small number of electrons participates in the core-hole screening. For the transition metals, the band-structure-based calculations excellently explain the K-edge but not the L-edge spectra. In photoexcitation from s-type core states, only p states are the dipole-allowed final states which are much less responsive to the core hole.

In a scalar relativistic calculation [26] that we performed (not shown), the L_2 and L_3 spectra are almost identical in shape since the DOS ratio $d_{5/2}/d_{3/2} = 3/2$ is energy independent and only reflects the degree of degeneracy. Therefore, we identify both relativistic and core-hole effects as the origin of the L_2-spectrum anomaly since both effects are pronounced in the low-energy region (<20 eV). Because the ratio $d_{5/2}/d_{3/2}$ as determined from measured WL heights does not reflect the degeneracy of the final states calculated without the core-hole correction, the XANES analyses as well as those of MCD based on band-structure calculations [27] should be revised.

A further test was done on Cu and Al where the d states are completely occupied or absent in the simple atomic picture. In fcc Cu, contrary to atomic Cu, there is significant d character in the DOS at E_F, and these states with d character play a main role in intra-atomic screening. Accordingly the theoretical K-edge spectrum for Cu metal [10] is slightly improved upon inclusion of the core-hole correction since the p DOS is slightly changed (not shown).

Theoretical and experimental [28] Al K-edge spectra and the corresponding DOS of the unoccupied states are shown in Fig. 2. Although the reduction of the d DOS at E_F due to the core hole is seen both in Pt and Cu, its origin in Al must be attributed to a different screening mechanism. For fcc Al, a part of the d-projected DOS below E_F is moved into the unoccupied region above E_F so that the core hole can gather s and p electrons more effectively. This accounts for the major part of the core-hole screening. As a result of the change in the

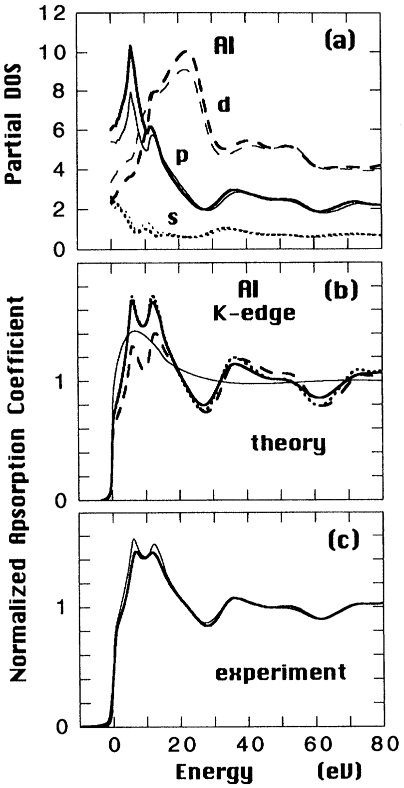

FIG. 2. Al K-edge XANES spectra. (a) Angular momentum projected partial DOS for fcc Al unoccupied states with (thick lines) and without (thin lines) the core hole: s (dotted), p (solid), and d (dashed). (b) Theoretical normalized Al K-edge XANES spectra with (dotted) and without (dashed) core-hole correction. Thermal vibration effects are taken into account in addition to the core-hole correction (solid). The absorption spectrum for a free-standing crystal atom is also shown (thin solid). (c) Experimental Al K-edge XANES spectrum at room temperature (thick) and the theoretical spectrum simulating time-dependent response effects (thin).

p DOS in Al due to the presence of a core hole, the theoretical K-edge spectrum is significantly improved in the low-energy region. However, the agreement is not as satisfactory as for Pt and Cu spectra. Regarding the fact that the necessary upward potential shift of 3.8 eV (3.3 eV for the supercell calculation) is larger than that used in the Pt calculation, the response to the core hole is slower than intra-atomic relaxation by the relatively localized d electrons [29]. Apart from the absorption threshold divergence, which depends on the asymptotic limit of the time evolution of the core hole [3], time-dependent screening effects are important in the response to the core hole as well. The electron emitted from the photoabsorbing atom and the backscattered electron may experience different potentials. In panel (c) we simulate this effect in a crude way by multiplying $\sigma_0(\omega)$ by a factor of 1.5. This time-evolution effect will be a future challenge, since the s and p electrons are likely to be of importance in shallow core-hole screening.

In conclusion, we have successfully explained the absence of the L_2-edge WL of Pt metal XANES spectrum. Relativity and the effects of a core hole are unambiguously identified as the main cause of the anomaly of the Pt L_2 edge. We expect that the L-edge difficulty of transition metals in the band-structure-based theories, which has been attributed to many-body effects, can be quite generally removed in accounting for the effect of the core hole, even within the single-electron description [30]. Comparing Cu, Pt, and Al XANES spectra, it was found that d electrons play an important role in the on-site screening in transition metals. In Al metal sp electrons, instead of d electrons, take part in the core-hole screening, and the K-edge spectrum is accordingly affected.

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