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Studies of total density of states of metals up to 70 eV above E_F

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We present bremsstrahlung-isochromat spectroscopy (BIS) measurements and density-of-states (DOS) calculations extending 70 eV above E_F. The BIS spectra show considerable structure, which is clearly seen to be dominated by total DOS effects. However, we find discrepancies between energy positions in the experimental and theoretical structures in many transition- and noble-metal elements, which are small below 10 eV, but typically 5—8 % at higher energies. We also compare BIS and x-ray absorption spectra up to 70 eV above threshold to clarify the influence of core-hole potential.

I. INTRODUCTION

Most bremsstrahlung-isochromat spectroscopy (BIS) studies have concentrated on the region 0—15 eV above E_F (although there are a few longer spectra in Refs. 1—4) because of the large collection times necessary to obtain good statistics with a small-solid-angle monochromator and because of the preconception that inelastic losses of the incident electrons would dominate any (weak) structure in the density of states (DOS) at higher energies.[5—7] In fact Refs. 1 and 2 even attempted to use BIS as a means to analyze characteristic losses of transition and noble metals. So far only Chu and Best[3,4] have stressed the importance of final-state effects in the bremsstrahlung process at higher energies but finally came to the conclusion "... that the thin target spectrum from aluminum and nickel respectively, explicitly do not represent the calculated density of vacant states of these metals."[4] The purpose of this paper is to present BIS data for many 3*d* and 4*d* transition and noble metals taken with a large-solid-angle (0.1-sr) monochromator, and DOS calculations using the local-density approximation of density-functional theory to show that total DOS features in fact dominate the spectra up to 70 eV above E_F. For Pd, Cu, and Ag we observe discrepancies between the energies of features in the BIS spectra and state-of-the-art DOS calculations over a wide energy range. We argue that these differences are probably not due to spurious effects like inelastic scattering or technical problems with the form of the potentials used in the calculations. They are more likely to be related to effects discussed in the literature under the keywords self-energies, nonlocal corrections to the potentials, and energy-dependent potentials. Whatever their cause the differences are important for problems in other areas.[8—17] The main use of BIS in this energy region is to study DOS effects but we also want to emphasize, already at this point, the use of BIS measurements at higher energies in relation with x-ray absorption spectroscopy (XAS) measurement. As BIS gives a picture related to the *total* DOS, this provides an extension of XAS, which probes only the local and *l*-projected DOS. Even more, as no core-level excitations are involved in the bremsstrahlung process this provides an experimental way to quantify the role of the core-hole potential in x-ray absorption, which has been a matter of debate for many years.[18,19]

II. EXPERIMENTAL

In BIS the intensity of light emitted when electrons impinge on a solid is measured at one frequency with respect to the variable kinetic energy of the electrons. Our measurements were made with an x-ray photoemission spectroscopy (XPS) monochromator similar in principle to that of Lang and co-workers[20] but with 54 quartz single crystals on a toroidal surface to increase the acceptance angle (by a factor of 10). The monochromator is set at 1487 eV (Al $K\alpha$ line) and we used an electron beam from a cylindrical Pierce gun of 300 μA with 260 meV energy spread.[21] The typical pressure during measurements was 2×10^{-10} Torr, mainly due to gas desorption induced by scattered electrons. Measurements were made on polycrystalline samples of high purity for many hours after careful checks on the region near E_F to ensure that the spectra did not change with time. The accumulation time for the data varied between 10 and 40 min for the different elements depending only on the rate of contamination.

III. DENSITY OF STATES CALCULATIONS

In our band-structure calculations we use the local density approximation of density-functional theory with the Korringa-Kohn-Rostoker (KKR) method. The calculations employ the first-principles self-consistent potentials of Moruzzi *et al.*[22,23]

Whereas the applicability of the single-particle interpretation of density-functional eigenvalues for the occupied states in transition metals has been widely investigated, there is no comparative study of the unoccupied states in the energy range of our BIS experiments. In general, it is agreed that below E_F discrepancies exist, and the d bands are calculated to be too weakly bound and too broad compared with experiment.[14,24,25] Recently, it has been claimed that these discrepancies might have their origin in inaccurate determinations of the band-state energies due to limited or fixed basis sets and linear energy expansion of the wave functions.[26] Instead of using one of the fast modern linear band structures, possibly affected by such criticism, we have calculated the band structure with the much more time consuming KKR method. For a muffin-tin potential this method gives an exact solution for the band-structure problem if the expansion of the wave functions into spherical harmonics is not truncated by a finite $l_{\max}$ value for which we have chosen $l_{\max}=4$ in our calculations. Both approximations, the muffin-tin form of the potential and the truncation by finite $l_{\max}$, are discussed in the following.

When considering these approximations one has to distinguish the effects on the calculation of the band states and on the iterative construction of the self-consistent density-functional ground-state potential where the errors of the individual band states may accumulate or cancel during the iterations. MacDonald *et al.*[25] have shown that non-muffin-tin corrections lead to a ground-state potential for Cu which changes the energies of the occupied bands only by several mRy which is an order of magnitude smaller than the observed discrepancies. The reason for these small corrections is the high cubic symmetry of the fcc lattice. It is fair to assume similar small corrections also at the higher energies of our interest. This can be seen from perturbation theory or from the relevant augmented plane-wave (APW) or KKR equations[27] which show that the Fourier components of non-muffin-tin parts of the potential are weighted by $1/E$ which should therefore reduce their importance at higher energies.

The error introduced by truncating the spherical harmonic expansion of the wave functions increases considerably with energy. However, in the KKR method this has quite significantly different effects on the wave functions and on the band structure, a fact which is often not very well appreciated. The KKR band structure is only affected by the nonvanishing phase shifts which rapidly decrease for $l>2$ in transition metals and is not affected by the accuracy of the wave-function expansion. This clearly distinguishes the KKR method from other methods like the APW method or the cellular method which relay on accurate wave functions and therefore higher l values. However, also in the KKR method one needs accurate wave functions for energies below E_F to obtain accurate charge densities necessary to construct the ground-state potential in the self-consistent procedure. Since the Cu potential of Moruzzi *et al.*[22,23] calculated by the KKR method with $l_{\max}=4$ very well gives the same band energies as calculated by MacDonald *et al.*,[25] we consider the self-consistent potentials of Moruzzi *et al.* accurate enough for our purposes. With these potentials we have calculated the band structure and the resulting DOS shown in Figs. 2–4. To convince ourselves that a calculation with $l_{\max}=4$ is sufficient we have repeated the calculation also with $l_{\max}=3$ which leads to changes in the band energies of less than ~ 10 mRy for the highest states and to indistinguishable DOS pictures.

The DOS have been obtained by the tetrahedron integration method[28] with 6144 tetrahedra in the irreducible part of the Brillouin zone. The high number of tetrahedra reduces the weight of possible spurious peaks[29] which occur if band crossings in a tetrahedron are missed by interpolating the integrand from the values at the corner points of the tetrahedron. A comparison of our DOS for Cu with the very similar DOS for Ni[30] calculated by the different Gilat-Raubenheimer scheme[31] shows a one-to-one correspondence of all peaks and precludes any spurious peaks arising from our integration scheme in the same energy range. Our DOS shows more clearly the sharp van Hove singularities arising from critical points. This reflects the fact that we use approximately twice as many microvolumes in the irreducible part and 2 times better energy resolution.

In order to compare the theoretical density of states with the experimental spectra it is essential to include broadening due to the experimental resolution (for these measurements a Gaussian of width 0.7 eV) and the lifetime of the excited state. This lifetime is caused by the imaginary part of the self-energy and is included by convolution with an energy-dependent Lorentzian.[32]

IV. RESULTS AND INTERPRETATION

In Fig. 1 we present a survey of the BIS spectra of $3d$ transition metals and in Figs. 2–4 we present in more de-

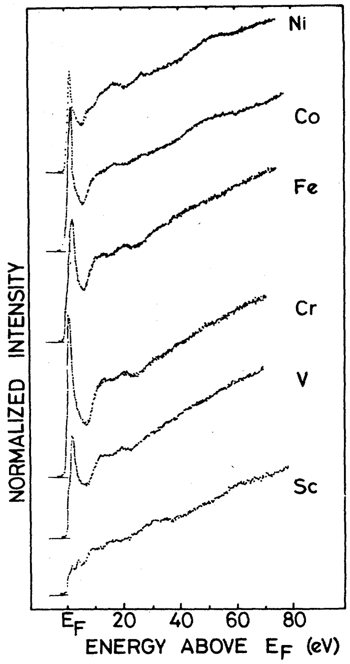

FIG. 1. BIS spectra for selected $3d$ transition elements up to 70 eV. The intensity could not be normalized on an absolute scale (Ref. 33).

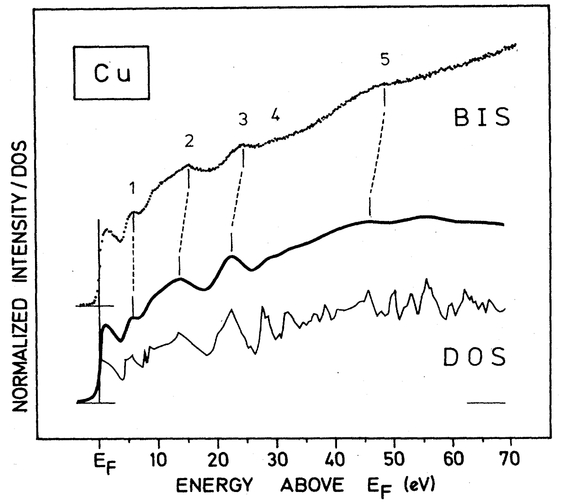

FIG. 2. Bremsstrahlung-isochromat spectrum and calculated density of unoccupied states for Cu. The correspondence of structures in the measured spectrum (dots) with features in the broadened DOS (solid line) is indicated. The energy positions show, however, drastic differences for the high-energy states as listed explicitly in Table I.

tail the spectra up to 70 eV above E_F for Cu, Ag, and Pd. In all the transition metals we see structure or peaks close to E_F which are linked to the transition metal d states as discussed elsewhere (see Ref. 9 and references therein). Above this, at 7—10 eV in the transition metals and 3—4 eV in the noble metals there is a step in the intensity due to critical points and the onset of p bands. Again, these have been discussed elsewhere.[8,9,34] At higher final-state energies we see a general increase in the BIS intensity with some additional weak structures extending in many cases up to ~70 eV which was the limit for this investigation. It is this region which is the subject of this paper. We shall associate the structure in the BIS curves up to ~70 eV with features in the density of states and be concerned with small differences between the calculated and observed peak positions.

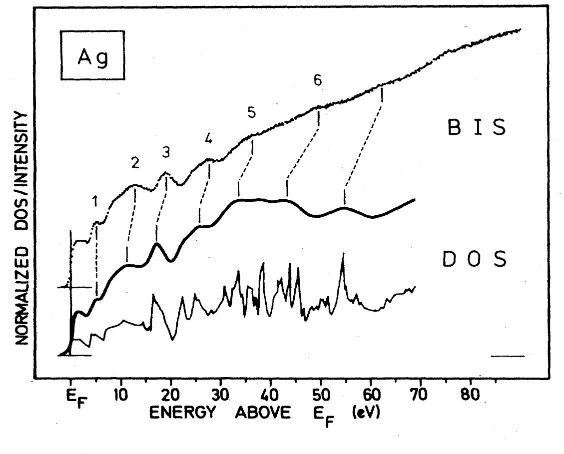

FIG. 3. Bremsstrahlung-isochromat spectrum and computed unoccupied DOS for Ag. Symbols as for Fig. 2.

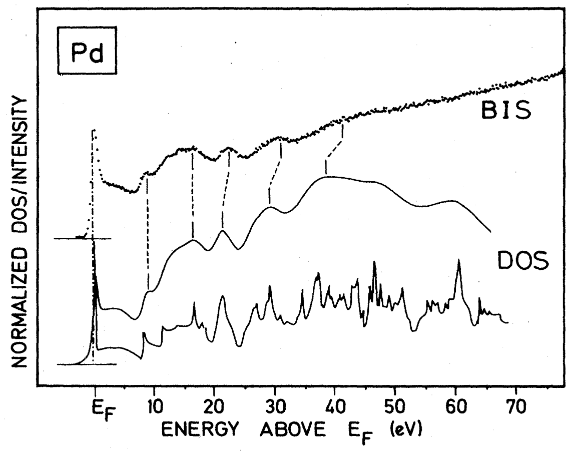

FIG. 4. Bremsstrahlung-isochromat spectrum and computed unoccupied DOS for Pd. Symbols as for Fig. 2.

The strong parallels between the structure in the BIS spectra in the region up to ~70 eV above E_F and the calculated DOS in Figs. 2—4 suggest that DOS effects dominate the BIS spectra here; but it should be remembered that there are three basic contributions to the intensity in a BIS measurement: the final density of states, inelastic electron energy loss prior to the bremsstrahlung transition, and matrix-element effects. Considering BIS matrix elements first, we note that these have not been treated in a consequent way for the solid state. However, when we break down the total DOS into its different l components we find the bands to be strongly hybridized. No systematic shifts would occur if, for example, the matrix element for one component was exceptionally high.

The inelastic energy-loss contribution to BIS is considered more fully in the Appendix. We find that, in general, it gives rise only to a smooth increase in the background, as illustrated for Ag in Fig. 6 which produces, at most, slight and insignificant shifts of peak positions to higher energies. The major structures in Figs. 1—4 do not arise from characteristic inelastic losses, but from direct transitions. There are three important points to be made in connection with Figs. 2 and 3 for Cu and Ag.

First we note that, in general, the BIS structures in the range 5—35 eV for elements with the same crystal structure are similar in form, scaling roughly with the Wigner-Seitz radius.[35] This is particularly obvious for the case of Cu and Ag illustrated in Figs. 2 and 3.

Second, the BIS spectra are influenced by the atomic potential and this becomes evident in the spectra more than 30 eV above E_F. For instance, there is only one broad peak at ~48 eV in copper, but in silver there are features at ~35, 48, 62, and 75 eV. The calculated density of states of silver also shows many features in this region and some of these have been attributed to the influence of the $4f$ states,[35] which are of course not a factor at these energies in the case of Cu.

Third, note that all the observed spectra show less structure in the region higher than 30 eV above E_F, in

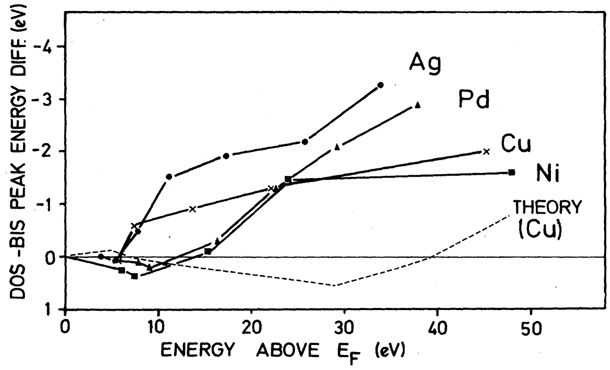

FIG. 5. Discrepancies in energy for structures between BIS spectra and DOS calculations. The energy axis for the structures is given by the theoretical values (Ref. 23). Also included is a theoretical self-energy correction for Cu based on the free-electron gas model by Hedin and Lundqvist taken from Ref. 15.

contrast to the broadened densities of states. This may be largely attributed to the influence of lifetime broadening, which is related to the electron inelastic mean-free path. This point is discussed in more detail in subsection V D.

Finally in this section we discuss the discrepancies between peak positions in theory and experiment. These are summarized in Fig. 5 for several elements and in Table I for Cu, Ag, and Pd. The early transition metals, like V and Cr, also show differences of 10% and more at about 20 eV [(theory) − (experiment) = −2 eV for a V BIS peak at 19.5 eV and −3.0 eV for a Cr BIS peak at 20.6 eV]. In addition we have reported differences between calculated and observed critical-point positions at 7–10 eV above E_F in almost all of the 3d and 4d transition metals we studied.[9] In general the differences between theory and experiment are quite small as percentages (up to ~10%) which illustrates an important point. Similar discrepancies (in percent of the binding energy) would not always be easily detected in photoelectron spectroscopy from valence bands but become quite obvious with the wider energy range available to BIS. Note also that the trends of the discrepancies in Fig. 5 are quite distinct for the different elements, but that the curves for elements in a similar position in the Periodic Table are similar (Ni and Pd, Cu and Ag). This point should be followed up in further work.

TABLE I. Peak energies in eV above E_F for density-of-states features in BIS and calculated DOS as indicated by numbers in Figs. 1 and 2. Also given are the differences, theory-experiment, from this work (Δ) and for Cu in the free-electron-gas model (δ_{FEG}) from Ref. 15.

Peak	no.	Experiment	Theory	Δ	δ_{FEG}
Cu	1	5.5	5.63	+0.1	~0
	2	14.7	13.6	−0.9	+0.01
	3	23.5	22.2	−1.3	+0.3
	5	47.2	45.2	−2.0	−0.5
Ag	1	5.3	5.15	−0.1	
	2	12.6	11.1	−1.5	
	3	19.2	17.3	−1.9	
	4	27.9	25.7	−2.2	
	5	37.1	33.8	−3.3	
	6	50.4	44.13	−6.3	
Pd	1	8.8	9.0	+0.2	
	2	16.6	16.3	−0.3	
	3	22.6	21.3	−1.3	
	4	31.2	29.1	−2.1	

V. DISCUSSION

A. BIS as a probe of the total DOS

The observation of density-of-states features in BIS up to ~70 eV above E_F has several important consequences. BIS opens the possibility to investigate *total* density of states over a wide energy range and is comparatively easy to handle due to the need of only polycrystalline samples. Our conclusion that BIS is related to the total DOS is based only on the experimental observation of the similarity between the spectra and DOS calculations. Unfortunately calculations of matrix elements do not exist for the solid state with realistic wave functions.

BIS is complementary to x-ray absorption of studies of the unoccupied density of states and BIS is not plagued by uncertainties concerning the role of the core-hole potential[18] as in XAS. An illustration of this is given by the Pd K XAS spectrum.[36,37] This shows features related to the density of p states above E_F. Just as in BIS, there is a 6–7% discrepancy between the XAS peak positions observed and calculated in the symmetry selected DOS calculated in the augmented plane-wave method. Similar effects have previously been found over a similar energy range in the 3d elements by Grunes.[38] Based on Materlik *et al.*[11] this was interpreted as the effect of the core-hole potential. However, we find the same effects in BIS where no core hole is created! We can therefore conclude that *these* discrepancies in XAS-DOS comparisons are not primarily due to the core-hole potential. A class of effects observed close to E_F which are related more or less directly to the effect of the core hole potential are discussed elsewhere.[39]

B. Differences between peak position in BIS and DOS calculations

There are several experiments pointing to a fundamental problem of relating measured and calculated density-of-states features both below and above E_F. In particular there have been many investigations directed towards the differences in calculated and observed positions in photoemission.[14,40,41] Similar effects are also observed above E_F in low-energy electron diffraction (LEED) (Refs. 13, 42, and 43), where one must know the average potential felt by an electron (the inner potential) in order to estimate the electron kinetic energy and the interatomic distances. The inner potential is known to be dependent on the electron kinetic energy. Thus when we discuss below the energy dependence of the potential felt by an electron in a solid we are not introducing new physics but introducing a new and more versatile and faster probe of the effect over a wider energy range. However, before we proceed to that point, we ask "are there 'technical problems' with the calculations employed or the particular experiment involved?"

It is unwise to be too dogmatic on this point but we think the discrepancies do not arise because of technical problems. As discussed in Sec. II the KKR method was chosen to minimize possible problems. However, the same results can be obtained by other methods if they are properly tailored for DOS calculations at high energies. This was discussed for the case of augmented plane-wave calculations of Pd in subsection V A, where the same discrepancies appeared as with the KKR method.

Considering the particular experiment, the major problems could arise from energy-loss effects (considered in the Appendix) and matrix elements. In principle matrix elements could cause problems if the matrix elements for partial waves with different l were quite different and if the peaks in the distribution of the high matrix-element component were consistently to one side of the major DOS peaks. We examined the partial wave character of the states to check for such effects and found that the states high above E_F were very strongly mixed. We find no conceivable mechanism for matrix element effects to consistently shift peaks appreciably.

C. Energy dependence of the electron potential

We follow the work of Janak *et al.*[41] and Hedin and Lundqvist[44] and attribute the differences between peak energies in DOS calculations and BIS measurements to the need to use an energy-dependent $V(E)$ and *not* an energy-independent potential. The physical reason for this is that the high-energy, final-state electrons move through the crystal for the valence electrons too fast to adjust to its movement.[44] DOS calculations do not take account of this properly for the excited states. They thus overestimate correlation and the "binding" of the electrons. In other words, an electron near E_F can be more efficiently screened than one at higher energies for which the screening electrons are too slow.

The theoretical efforts made since the 1960s have not been in proportion to the importance of knowing $V(E)$. Janak *et al.*[41] used a linear scaling of the energy scale to take account of variations in V. This is acceptable for small energy ranges but, as indicated by Fig. 5, not over the energy range we investigate. In their original papers Kohn and Sham indicated that local density theory would present problems when applied to excited states.[45] Hedin and Lundqvist formulated an approach to the energy dependence of V for free-electron metals which pointed out that plasmons or other excitations could produce structure in the energy dependence. We can confirm the appearance of structure in the curves of Fig. 5, but the calculations of Nilsson and Larsson for Cu (Ref. 15) based on Ref. 44 do not reproduce the experimental effects well, as shown in Fig. 5. For instance for Cu in Table I and Ref. 15, the predicted differences Δ have the incorrect sign up to ~ 30 eV and even at 45 eV the estimate is a factor of 4 too low. A rigorous density-functional correction for single-particle energies has to include self-energy effects which can be approximated by a complex energy-dependent potential. Thus potential is neither well-known nor easily incorporated into existing codes for DOS calculations. Being complex it can be treated presently by band-structure methods only in an approximate manner.[15]

D. Lifetime broadening and mean-free-path effects

We noted in previous sections that the calculated DOS must be broadened to account for the energy uncertainty due to the short lifetime of the electrons in states high above E_F. This is in accord with the short inelastic mean-free path of the *final-state* electrons in this energy range[46] and with the treatments of electron lifetime effects in, for example, LEED.[12] The electron inelastic mean-free path leads to lifetime broadening rising to 4—10 eV in the region of interest to us, which in itself greatly smears out the observed BIS structure. In addition more subtle effects become possible if the electron-electron interactions leading to inelastic scattering are explicitly taken into account in the imaginary part of the self-energy in a band-structure calculation. Then it is possible that flat bands disappear and band gaps may be closed.[47] Furthermore, as the inelastic mean free path takes on such small values it becomes debatable whether a standard DOS approach or a more local scattering approach similar to that used for extended x-ray adsorption fine structure (EXAFS), is the more appropriate starting point for discussion. There have been few detailed studies of lifetime broadening in the energy range up to 70 eV above E_F, and, clearly, spectra such as those we present here would give a better basis for such studies. For the moment, suffice it to say that the large lifetime broadening does not smear out the DOS structure completely.

VI. CONCLUDING REMARKS

We have found structure in BIS spectra up to 70 eV above E_F and shown it to be dominated by DOS effects. We have found differences in energy between observed and calculated DOS features for which a qualitative explanation in terms of the energy dependence of the electron potential exists. However, a quantitative description is not available and our observations indicate the need to go beyond the free-electron gas treatment of Hedin and Lundqvist in the search for understanding of the energy dependence of the electron potential. Also, quantitative descriptions of BIS matrix element effects in solids and lifetime broadening are necessary. The needs are all the more pressing because of the growing importance of studies of unoccupied DOS by BIS and x-ray absorption and uses for determination of interatomic distances and coordination spheres.[48]

ACKNOWLEDGMENTS

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fects in solids. We thank M. Campagna for discussions and support and J. Keppels, R. Otto, and F. U. Hillebrecht for cooperation in development of the BIS technique. Other work on XAS (Ref. 39) done in cooperation with J. Fink, G. A. Sawatzky, and J. Zaanen has greatly helped us to get this study in perspective. The investigations were supported (in part) by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands organization for the Advancement of Pure Research (ZWO).

APPENDIX: ENERGY LOSSES IN BIS

Just as in photoemission, the BIS transitions carrying the information about the state densities do occur near the surface and those transitions with an inelastic scattering tend to happen deeper in the solid. The inelastic contribution in BIS becomes more important at higher energies in BIS, and not at lower kinetic energies as in photoemission. Our arguments against dominance of energy-loss processes in high-energy BIS, which we will expand at a later date, are as follows:

(1) The similarity between calculated DOS and BIS spectra up to 70 eV can only be explained if electron energy loss processes to do not dominate BIS (see Figs. 2—4).

(2) We have observed extended x-ray isochromat fine structure (EXIFS) up to $\sim$400 eV (Ref. 49), which is fully analogous to EXAFS. EXIFS could not be observed if the energy-loss processes dominated or produced structure in the spectrum.

(3) The general trend of the spectral intensity is near to the $E^{1/2}$ dependence expected for the DOS of a free-electron-like metal, e.g., for Cu a polynomial fit to the first 400 eV of the spectrum has coefficients for the E^1 and $E^{1.5}$ terms less than 5% of the $E^{1/2}$ term.[50] This is difficult to explain if energy-loss terms dominate the BIS spectrum.

(4) In one of our previous papers on Cu and Ag critical points it was shown that a good fit to the BIS spectrum can be obtained by addition of only 30% intensity to the calculated DOS in the form of a fold of the DOS with an energy-loss function taken from energy-loss spectroscopy (ELS).[8] This 30% does not dominate or change the DOS structure significantly.

(5) In Fig. 6 we have plotted the Ag DOS, the energy-loss spectrum of Ag obtained in reflection for 1500 eV electrons, and the result of a fold of the loss function thus obtained with the DOS. In normal circumstances the reflection energy-loss function (RELS) is not appropriate for comparison with BIS spectra, because the electrons "interact with the surface twice" in RELS and only "once" in BIS. Thus in for instance Al, the surface plasmons play a stronger role in RELS.[50] However, for Ag the bulk and surface plasmons are pinned at $\sim$3.6 eV by the *d*-band edge so an RELS loss function is appropriate here.

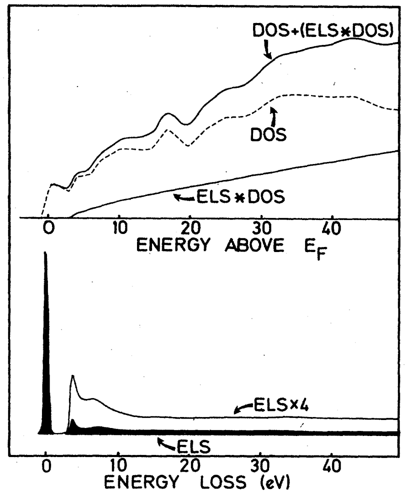

FIG. 6. Lower half; electron energy-loss spectrum of Ag taken in reflection mode with 1500 eV primary beam energy. Upper half; from bottom up. Result of a fold of the loss function (ELS minus primary peak) with the calculated and broadened DOS of Ag (DOS*ELS). The middle curve is the broadened DOS. The top curve is the broadened DOS + (DOS*ELS) with the latter normalized to give a 33% loss contribution at $\sim$45 eV.

The loss spectrum of Ag shows a strong peak at $\sim$3.6 eV but it is not strong with respect to the elastic line, or with respect to the integrated loss function. Thus it does not introduce strong replicas or new structure into the fold between the loss function and the density of states which is shown in Fig. 6. The result of the fold is an almost monotonic rise in intensity at energies away from the high-energy limit (E_F). We thus see that the energy-loss contribution cannot introduce new structure. A rising background can shift the positions of peaks in the BIS spectrum to higher energy above E_F but subtracting the function in Fig. 6 from the BIS spectrum in Fig. 3 shows that the maximum shifts involved are certainly less than $\sim$20% of the average discrepancies indicated in Fig. 6. We come to essentially the same conclusion for all the other elements in the *d*-metal rows.

We are fully cognizant that low-energy BIS, or inverse photoemission, probably has a stronger energy-loss contribution[6] and hence low-energy BIS is not suitable for investigations of the type reported in the main paper here.

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[33] It is difficult to normalize the BIS spectra on an absolute scale because of the extreme dependence of intensity on sample position. In Fig. 1 the spectra are roughly normalized to the intensity 70 eV above E_F. However, it is noteworthy that the intensity at this point scales with the intensity at the minimum above the d band, and not with the d-band intensity itself, which is at a maximum in the middle of the transition metal series (see Ref. 11). If the slope were dominated by the inelastic BIS contribution it should scale with the d band intensity and the slope should increase at higher energies where the multiple-loss contribution increases.

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