

Extended X-Ray Isochromat Fine Structure of Cu

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We have measured fine structure extending 400 eV above the Fermi energy in the x-ray bremsstrahlung isochromat spectrum of Cu. This spectrum is shown to be extremely similar at high energies to an extended x-ray-absorption fine-structure (EXAFS) spectrum of Cu. We conclude that the EXAFS model for high-energy conduction-electron propagation in solids is applicable to bremsstrahlung isochromat spectroscopy and that an EXAFS-like procedure is suitable for the quantitative analysis of extended-range bremsstrahlung isochromat spectral data.

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Use of bremsstrahlung isochromat spectroscopy (BIS) to study the unoccupied electronic states of solids has increased greatly in the past five years, with applications ranging from the surface^{1,2} and bulk^{2,3} states of semiconductors to highly correlated *d* and *f* states of transition metals,^{4,5} rare earths,⁶⁻⁸ and actinides.^{9,10} Analysis of BIS data at low final-state electron energies E_f has traditionally relied on the assumption that the transition matrix elements vary so slowly with E_f that spectral structure can be attributed completely to variations in the density of electronic states (DES). We show in this Letter that BIS data can be analyzed in quite a different way for E_f exceeding a few tens of electronvolts above the Fermi energy. The states available to the final-state electron in BIS have many features in common with those available in core-level x-ray absorption. Furthermore, x-ray-absorption spectra exhibit extended oscillatory fine structure known as EXAFS which resembles the structure that we observe in BIS spectra, as reported here. The EXAFS is understood to arise predominantly from single-event backscattering of the final-state electron wave in the potential of the surrounding atoms, and there are well-developed techniques for quantitatively analyzing EXAFS spectra to obtain the distances between the excited atom and its neighbors.¹¹ If applicable, such techniques would be powerful tools for the analysis of extended-range BIS data to obtain meaningful physical quantities of general interest, as discussed below.

We have measured fine structure in the BIS spectrum of Cu extending 400 eV above the Fermi energy, a range of energies substantially greater than in previous studies.¹² Cu is a prototypical material for EXAFS measurements and calculations. We have employed EXAFS techniques to analyze our BIS data and have compared the results of those to conventional analysis of the EXAFS on the *K*-edge x-ray-absorption spectrum of Cu.¹¹ These

reduced spectra are very similar in shape, providing strong support for the applicability for BIS analysis of the EXAFS model for high-energy conduction-electron propagation. The principal differences are that the BIS oscillations have a smaller amplitude and are shifted slightly to higher energies. While numerically significant, they present no barrier to the quantitative analysis of extended-range BIS data using EXAFS-like procedures. We explore below the origins of the differences and the underlying reasons for the success of this analysis. Further, we discuss the relationship between an EXAFS and a DES approach to the analysis of BIS data.

The BIS spectrum of Cu was measured at ~ 350 K both at Kernforschungsanlage Jülich and at Xerox Palo Alto Research Center by use of high-vacuum electron spectroscopy instruments described in detail elsewhere.^{7,8} The spectra obtained at the two laboratories are essentially identical. The surfaces of pure polycrystalline Cu samples were cleaned by argon-ion bombardment or scraping with a ceramic file, and checked for cleanliness with x-ray-photoelectron spectroscopy. With the detector for the emitted x-ray photon fixed at an energy of 1486.7 eV, the incident electron energy E was scanned from 1480 to 1890 eV. The detected photon intensity is plotted as a function of $(E - E_0)^{1/2}$ in Fig. 1. The onset of the spectrum corresponds to $E = E_F + 1486.7$ eV, where E_F is the Fermi energy. E_0 is chosen to be 7 eV below that threshold, corresponding approximately to the bottom of the conduction band in Cu. The spectrum has been normalized to the number of incident electrons. The signal I_b contributed by incident electrons which scatter inelastically before emitting a photon has been removed by taking¹² $I_b(E)$ to be proportional to the convolution of the primary spectrum with the inelastic loss spectrum, which is approximated here by a step function at E . The resulting $I_b(E)$ is linearly proportional to the integral between

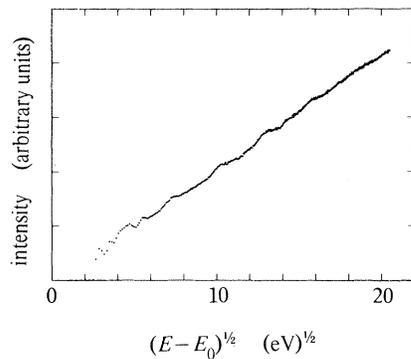


FIG. 1. The BIS spectrum of polycrystalline Cu at ~ 350 K plotted against $(E - E_0)^{1/2}$, where E_0 corresponds approximately to the bottom of the conduction band. Note that the spectrum is a straight line on the average, as one would expect for a "free-electron" density of states.

the threshold of the spectrum and E of the difference between the total intensity and I_b (i.e., the primary spectrum). Adjusting the single constant of proportionality, we obtain a primary spectrum which is proportional to $(E - E_0)^{1/2}$ on average over its entire range, the leading term expected from simple arguments.¹³ This self-consistency supports our approach. The energy dependence has been quantified by fitting the reduced spectrum with a low-order Chebyshev polynomial in $(E - E_0)^{1/2}$. The coefficients of terms of higher order than $(E - E_0)^{1/2}$ are at least a factor of 90 smaller than that of the $(E - E_0)^{1/2}$ term.

Clearly evident in the data are oscillations about the fit which are nominally periodic in $(E - E_0)^{1/2}$. These are the extended x-ray-isochromat fine structure (EXIFS). They bear a very strong resemblance to those found in the EXAFS spectrum of Cu. Viewing the fine structure as a modulation of a smooth, free-atom-like spectrum, we extract the oscillations as a fraction of the total signal. This is accomplished by dividing the BIS spectrum by the fitted polynomial and subtracting unity. The resulting EXIFS spectrum is multiplied by electron momentum $k \propto (E - E_0)^{1/2}$, in analogy with EXAFS procedures, and is shown in Fig. 2(a) as a function of k . For comparison the well-known Cu EXAFS obtained from the K -shell x-ray spectrum¹¹ of a polycrystalline sample at room temperature is shown as a dashed line. These data were treated analogously (e.g., E_0 was chosen to be 7 eV below the K -edge threshold). Both spectra have been smoothed in the following manner, frequently practiced in EXAFS data analysis¹¹: The entire spectrum is Fourier transformed to r space, where $2r$ is the variable complementary to k ; the result is truncated beyond $r \approx 10.5$ Å and transformed back into k space. This removes all the high-frequency noise in the spectra, but very little proper signal (the BIS spectrum in r space has dropped to $< 6\%$ of its nearest-neighbor value by $r = 11$ Å). The amplitude of the EXAFS oscillations is greater than the BIS oscilla-

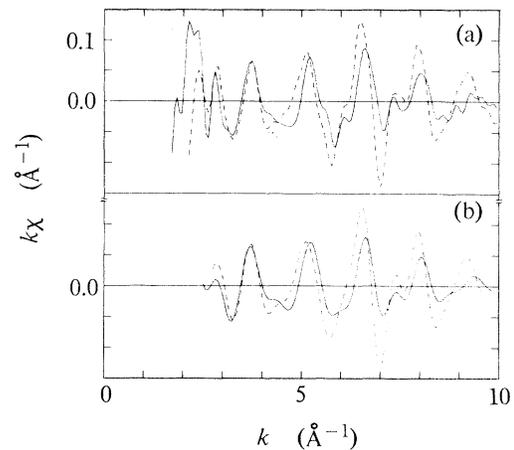


FIG. 2. (a) The fine structure is the BIS spectrum of Fig. 1 extracted as described in the text, multiplied by electron momentum k , and shown as a function of k (solid line). For comparison we have also shown the analogous function, $k\chi$, obtained from the K -edge EXAFS spectrum of polycrystalline Cu at room temperature (dashed line). The EXAFS data have been reduced by a factor of 2 to facilitate comparison. (b) The same two spectra after the contributions from atoms beyond fourth nearest neighbors have been removed as discussed in the text.

tions, for reasons discussed below, so that the EXAFS spectra in Fig. 2 have been reduced by a factor of 2 for comparison.

It is apparent that the oscillations in the two spectra are very similar, apart from a small phase shift and stronger higher-frequency components in the BIS spectrum. In Fig. 2(b) these same spectra are shown, except that the r -space range of the $r \rightarrow k$ transform is roughly 2 to 5.4 Å. This eliminates more of the high-frequency oscillations in the BIS spectrum (i.e., contributions from atoms beyond fourth nearest neighbors), and increases the similarity between these spectra. The r -space spectra are also extremely similar, differing only as anticipated from the observed slight differences in k space.

A good reason to expect that similar explanations will apply to both BIS and EXAFS spectra is that the electron final states available to both processes are very similar. In BIS, a high-energy electron (1.5 to 2 keV) decays into an unoccupied state by emitting an x-ray photon. The spectrum is generated by variation of the initial-state energy and detection of photons of fixed energy. In K -edge EXAFS, an energetic x ray (~ 10 keV) is absorbed through excitation of an electron from the Cu K shell to an unoccupied state. The spectrum is generated by variation of the photon energy and monitoring of the absorption cross section. Both final states include an excited electron with energy up to several hundred electronvolts above the Fermi energy.

The short lifetime of such a high-energy electron, corresponding to a short mean free path, is known to reduce greatly the contributions of high-order terms in the Born

series for the x-ray—absorption cross section, so that the term linear in the scattering matrix for individual atoms dominates (i.e., the single-scattering term). The same result is expected for the BIS cross section. Note further that the localized initial state in x-ray absorption affects the dominant linear term so as to produce spectral structure. (The DES has no significant structure coming from the linear term in its Born series, so that it is common to refer to EXAFS as a matrix-element effect.¹⁴) As a consequence, the Cu EXAFS spectrum is well understood to arise predominantly from single-event backscattering from the near neighbors of each excited Cu atom. The only significant effects of multiple-atom scattering arise from a few *short* multiple-scattering paths with lengths corresponding to the fourth-nearest-neighbor distance.¹⁴ The excitation process in BIS is arguably quite localized as well because the incident electron is more likely to emit a photon when it is “accelerating” near the core of an atom than when it is passing between atoms. The similarity of the spectra of Fig. 2 is strong but circumstantial evidence that EXAFS and EXIFS have the same origin and analogous descriptive equations.

On the other hand, the two spectra of Fig. 2(b) are not identical. The principal differences between them are that the BIS oscillations are (1) smaller in amplitude than the EXAFS by a factor of 0.4 to 0.5 and (2) shifted to higher k by 0.15 to 0.20 \AA^{-1} for $k > 4.5 \text{\AA}^{-1}$ (and by a very small amount for $k < 4.5 \text{\AA}^{-1}$). While we do not have a ready explanation for the apparent coincidence of these two spectra at $k \simeq 3.7 \text{\AA}^{-1}$, we present below an explanation for the differences at high k based on our understanding of the EXAFS equations and of the physical differences between the two phenomena.

An EXAFS spectrum can be expressed as the superposition of many phase-shifted and amplitude-modulated sine waves, one for each scattering path i beginning and ending at the excited atom¹¹:

$$k\chi(k) = \sum_i A_i(k) \sin[kd_i + P_i(k)], \quad (1)$$

where d_i is the path length, equal to twice the distance between the atoms for single-atom scattering. Distant atoms yield high-frequency contributions in k space. A_i depends on the number, type, and distribution of atoms, while the phase shift P_i depends principally on the type of the excited and scattering atoms. A_i depends on the electron mean free path $\lambda(k)$ through a factor similar to $\exp(-d_i/\lambda)$, which reduces the contributions of long paths due to multiple scattering or distant-neighbor single scattering.

The major differences in the two excitation processes must arise directly from the fact that the initial electron state in EXAFS is a deep core state rather than the high-energy extended state of BIS, leading to features special to EXAFS: (1) Angular momentum is a good quantum number l in the EXAFS initial state, so that the dipole selection rule leads to a final state containing $l' = l \pm 1$;

and (2) the Coulomb potential and the finite lifetime of the localized core hole in the EXAFS final state both modify the wave function of the excited electron. We show below that these two effects are capable of explaining the differences seen at high k between the spectra in Fig. 2.

The core hole contributes a term of $P_i(k)$. The observed shift between the BIS and EXAFS spectra at high k corresponds to 0.7 to 0.9 rad in the argument of the nearest-neighbor contribution to Eq. (1). Teo and Lee¹⁵ have calculated the $l=1$ phase shift for a Cu atom in two configurations: $3d^{10}4s^1$ and $3d^94s^2$. They differ by ~ 0.5 rad at $k \simeq 6.6 \text{\AA}^{-1}$. We expect this to be a lower bound on the phase shift added by a core hole. An upper bound might be half of the difference between Ca and Ca^{++} , which is ~ 1.8 rad at $k \simeq 6.6 \text{\AA}^{-1}$. Consequently we expect the core-hole phase shift to be in the range of 0.5 to 0.9 rad for $k \simeq 6.6 \text{\AA}^{-1}$. This is of the correct sign and approximate magnitude to account for the phase differences at high k in Fig. 2. In addition, the slightly weaker high-frequency components in the EXAFS spectrum would be an expected effect of the finite lifetime of the core hole (which reduces further the range of near-neighbor distances seen in the spectrum).

The angular momentum content of the final state affects P_i in two ways: a term $\pi L/2$, where L is the sum of the angular momenta of the outgoing and incoming waves, l' and l'' ; and an l -dependent phase shift coming from the excited atom. For a highly symmetric configuration of nearest neighbors, such as is found in face-centered-cubic Cu, the incoming wave will be predominantly $l'' = l'$, so that the first effect contributes $\pi l'$. The l -dependent phase shift coming from the excited atom may be estimated from the Ni phase shifts calculated by Teo and Lee.¹⁵ Taking both of these contributions into account, we estimate that the oscillations due to $l=0$ will be shifted by -0.7 rad (for $k \simeq 6.6 \text{\AA}^{-1}$) from the $l=1$ contribution present in the EXAFS spectrum, and those due to $l=2$ by 1.2 rad. Such contributions are also clearly able to account for the observed phase shift at high k . The interference between oscillations with slightly different phases might also account for the observed amplitude reduction of the BIS spectrum. For example, an equal mixture of sine waves differing in phase by 1.2 rad would shift the phase by 0.6 rad and reduce the amplitude by $\sim 20\%$.

Finally, the applicability of an EXAFS-like expression was tested directly for each spectrum through quantitative analysis as follows¹¹: The nearest-neighbor signal is extracted and used as a scattering signature to fit the signal from the next two shells of neighbors. The resultant near-neighbor distances agree with crystallographic data within 0.01 \AA for both EXAFS and EXIFS. It follows that the high-energy BIS spectrum may be analyzed in analogy with the procedures used for EXAFS analysis,¹¹ yielding detailed information about not only the separa-

tion but also the number and atom species of close atom pairs. The principal difference from this perspective is that BIS would not provide a partial separation of the individual pair correlation functions in a material with more than one atom species, as does EXAFS, since all close pairs will contribute to each spectrum.

It is also possible to analyze extended-range BIS data (and EXAFS data as well) from a conventional band-structure viewpoint,¹² provided that care is taken with two aspects. Firstly, it is essential to incorporate the transition matrix elements, which most certainly vary importantly over such a large energy range. Secondly, one must account for the finite lifetime of the final state, an effect which is less important for states near E_F . The simplest approximation is to include an energy-dependent but spatially constant imaginary part to the electron scattering potential. The effects of this on a calculated DES can be accounted for by convoluting it with a Lorentzian of energy-dependent width. It is not clear, however, how to modify the transition matrix elements analogously. Müller and co-workers¹⁶ have used a band-structure approach to calculate x-ray-absorption spectra with good results. They have approximated the effects of finite lifetime by convoluting the computed absorption spectrum (not simply the DES) with a Lorentzian of energy-dependent width.

An EXAFS calculation properly incorporates transition probabilities from the outset. Furthermore, this multiple-scattering approach lends itself to the incorporation of finite-lifetime effects. This has led to calculated Cu EXAFS spectra¹⁴ which are in excellent agreement with the measured EXAFS and, by implication, BIS for energies exceeding a few tens of electronvolts above E_F . Equally good agreement would necessarily result from a DES treatment wherein transition matrix elements and finite-lifetime effects are incorporated properly, but a striking difference between these "two means to the same end" is the computational complexity of the DES approach. This has been discussed by many authors in connection with EXAFS theory, most extensively by Schaich.¹⁷ Unless the energy dependence of the transition matrix elements is negligible, by far the most direct (and economical) approach to calculating either EXIFS or EXAFS well above E_F is the single- or multiple-atom scattering treatment commonly used in EXAFS applications.

In summary, we have shown that fine structure occurs in the extended BIS spectrum of Cu and that it has the same origin as the fine structure appearing in an x-ray-absorption spectrum. We have discussed the differences between the measured spectra in the context of EXAFS theory and have shown that the EXAFS model for

high-energy electron propagation accounts for the major features of actual BIS spectra for energy exceeding a few tens of electronvolts above E_F , and that extended BIS spectra can be quantitatively analyzed in analogy with EXAFS spectra.

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