

ler's rule¹³ which normalizes d_{ijk} with the linear susceptibility.

In conclusion, we have calculated, for the first time, the AIOHG coefficients³ χ_{ijklm} for several III-V and II-VI zinc-blende semiconductors, and found excellent agreement with the measurements of Boyd, Nash, and Nelson² on GaAs.

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Shielding of Impurities as Measured by Extended X-Ray-Absorption Fine Structure

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A new theory of the extended x-ray-absorption fine structure (EXAFS) is presented which avoids the inaccurate approximations of previous ones. It is shown that, in addition to structure determination, EXAFS gives detailed information on the shielding of the singly ionized absorbing atom. Experimental verification of the theory is obtained from EXAFS data for Ge and Cu, explicitly showing shielding oscillations for Cu.

X-ray absorption in matter is characterized by absorption edges where a core electron can just be excited to above the Fermi energy, leaving the absorbing atom ionized. Careful measurements on the high-energy side of absorption edges reveal a fine-structure oscillation in the absorption versus energy. Recent work¹⁻³ has shown that one can perform a Fourier analysis of this fine structure in the high-energy side of x-ray absorption edges (up to several keV past the edge) to give the location of the atoms immediately surrounding the atom absorbing the x ray. This very important result indicates that this extended x-ray-absorption fine structure (EXAFS) is a valuable tool for determining structures, especially for amorphous materials and

complicated crystals composed of many different types of atoms. This Letter presents a new theoretical analysis which shows that, in addition to structural information, EXAFS also yields direct information on the screening of the ionized excited atom. An important new element in the analysis is that the perturbation of the surrounding atoms induced by the core hole of the absorbing atom is the dominant mechanism for producing EXAFS.

Based on a recent short-range order theory of the EXAFS,¹ Fourier transforms of the EXAFS data (called radial structure functions) from several semiconducting samples were made to determine the positions of the surrounding atoms,^{2,3} and reasonable agreement with the theory was

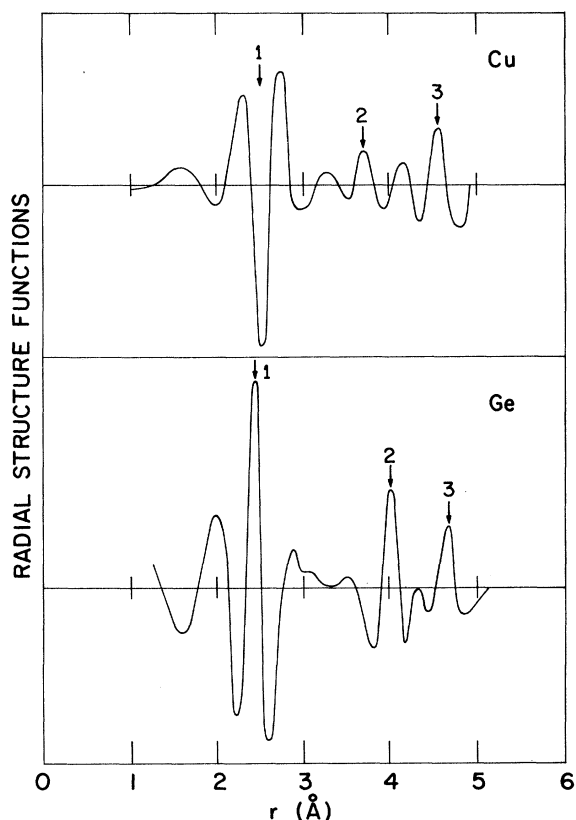


FIG. 1. Radial structure functions for the first three shells of crystalline Cu and Ge obtained by performing a Fourier analysis of experimental EXAFS data for these materials. The peaks corresponding to various shells are indicated by arrows.

found. However, when a radial structure function of copper was determined as shown in Fig. 1, not even qualitative agreement with the theory

was attained. The theory predicts that at the location of each shell of surrounding atoms a peak occurs as shown by the arrows in Fig. 1. Although the magnitude of the peak varies from shell to shell, the relative phase should not vary, i.e., the peaks should be all positive or all negative. It is clear from Fig. 1 that there is a definite change in phase between the first peak and the next two in copper. For comparison, the result for Ge is also shown in Fig. 1 and all peaks are of the same sign as found before.³ No previously proposed theory⁴⁻⁷ can explain this change in sign.

The new theory, which explains all the available data including the copper data, starts in zero order with the periodic solid instead of an isolated atom. Next, the perturbation by the ionized atom is introduced, including any distortion of the surrounding atoms, i.e., the perturbed problem is a single impurity one—the impurity being the atom which has absorbed the x-ray photon. The single-impurity problem is mathematically simpler to handle, permitting more exact solutions. This analysis gives new physical insight showing that the observed EXAFS is from the distortion of the surrounding atoms induced by the absorbing atom as it becomes ionized. This particular effect has been neglected in all previous theories of the EXAFS, explaining their inadequacy to explain copper.

A calculation of this effect for the *K* edge, using a similar analysis as used previously,¹ but now on the single-impurity Hamiltonian and with Bloch states as the unperturbed states, leads to the formula for the oscillatory part of the EXAFS, $\chi(k)$, in a one-component system,

$$\chi(k) = \frac{\mu(k)}{\mu_0(k)} - 1 = \frac{1}{k} \sum_j \frac{N_j}{r_j^2} E(r_j) g_j(2\vec{k}) \exp(-2\sigma_j^2 k^2) \sin[2kr_j + 2\eta(k)]. \quad (1)$$

Here $g_j(2\vec{k})$ is the backward-scattering amplitude from the surrounding atoms in the j th shell of the excited p -state electron of wave number k per unit electric field. The direction of \vec{k} is radially out from the excited atom to the center of an atom in the j th atomic shell; $E(r_j)$ is the average electric field induced at r_j , the position of the j th shell of atoms, by the ionized atom at $r=0$; $\mu(k)$ is the total measured absorption coefficient, including fine structure, and $\mu_0(k)$ is the structureless absorption coefficient of the unperturbed material. N_j is the total number of atoms in the j th shell and σ_j^2 is a measure of the fluctuations of the actual positions of the atoms in the j th

shell about their average position r_j . The exponential containing σ_j^2 is a Debye-Waller-type factor.

To compare this theory with data taken in crystalline Ge and Cu, the assumption was made that the $E(r_j)$ can be approximated as constant over the dimensions of the atom at r_j , but still varying from shell to shell. The data were consistent with this assumption since $g(2\vec{k})$ was found, to a good approximation, to be independent of j . We note that with $g(2k)$ independent of j , the Fourier transform of (1) with respect to $\sin(2kr + 2\eta)$ is peaked at $r=r_j$ with an area under the peak pro-

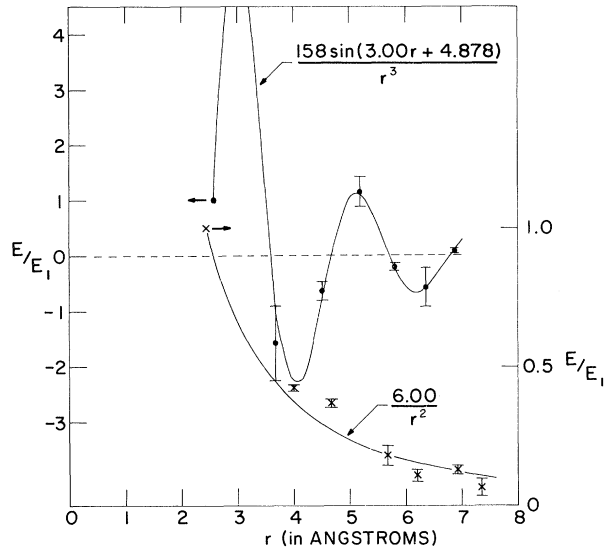


FIG. 2. Electric field $E(r_j)$ relative to the electric field at the first shell of atoms, $E(r_1)$, versus r for seven shells in Cu (dots) and Ge (crosses). The solid line through the copper data has the theoretically predicted asymptotic form. The solid line represents a $1/r^2$ electric field in Ge (r in angstroms). The ordinate for the Cu data is on the left, while it is on the right for the Ge data.

portional to $E(r_j)$. By this means we obtain from the experimental EXAFS data on Ge and Cu the values for the ratio for $E(r_j)$ of the j th shell to that of the first shell shown in Fig. 2.

The data are in striking contrast for the two solids. The oscillation in the shielded electric field in Cu is obvious, while in Ge the shielded electric field is all of one sign. Also plotted in Fig. 2 are two curves, an r^{-2} dependence for Ge and a sinusoidal variation divided by r^3 for Cu. The data for Ge follow the r^{-2} trend with a small deviation which may be significant. The curve plotted for Cu has the form of the theoretically predicted asymptotic behavior for an electron gas,⁸ $\sin(2k_F r)/r^3$, except that a phase shift is added and k_F is about 10% larger than the free-electron value of 1.35 \AA^{-1} . The Fermi surface of Cu is appreciably distorted from a sphere, with eight necks in the $\langle 111 \rangle$ directions, which may account for the 10% difference from the electron gas value. Another possible explanation for the difference is that the assumed asymptotic form is not adequate to describe the data over the complete range. For the smaller values of r the neglected portions of the asymptotic form which vary as r^{-4} , etc., are not negligible, and we should not expect the assumed asymptotic

form to agree with these points. We can fit the larger r points by using the free-electron value for k_F , $\sin(2.7r + 0.35)/r^3$ (r in angstroms), and assume that the deviation from the low r points can be corrected by the neglected terms in the asymptotic form. This form still shows a phase shift of 20° from the electron gas case.

It should be emphasized that the agreement between the predicted theoretical variation of the shielding fields in Cu and Ge and the analysis of the experimental data using Eq. (1) is strong confirmation of the validity of the ideas that led to Eq. (1). The change in phase between the peaks in Cu in Fig. (1), which does not occur for Ge, is a direct consequence of the shielding oscillations in metals which does not occur in semiconductors or insulators.

The form of the shielding found in Ge and Cu gives a lower limit to the lifetimes of the ionized atom and the excited photoelectron state. The appropriate dielectric function to shield the ionized atom depends on the lifetimes of both the ionized atom and the excited photoelectron. If the shorter of the two lifetimes is called τ , then the frequency-dependent dielectric function $\epsilon(\omega)$ is required for shielding, where $\omega \approx \tau^{-1}$. In Ge, if $\hbar\omega \gg 0.67 \text{ eV}$, the gap energy, but still less than the plasma frequency of a free-electron gas of the same electron density as Ge ($\sim 15 \text{ eV}$), the shielding will be metalliclike with oscillations as in Cu. If $\hbar\omega \ll 0.67$, the shielding will be like static shielding in a semiconductor, i.e., it will vary like r^{-2} . The data in Fig. 2 show that $\hbar\omega \ll 0.67$, and the lifetimes of both the ionized atom and the photoelectron in Ge are such as to each give an energy uncertainty of less than 0.67 eV . It should be pointed out that the lifetime of the ionized atom is larger than that of the K -shell hole. The K -shell hole is usually de-excited by L - and M -shell states dropping down to fill it. Such de-excitation still maintains an ionized atom. In Cu the fact that the oscillations are seen means that $\hbar\omega \ll 7 \text{ eV}$, the approximate value of the plasma frequency.

In summary, an improved theory of the EXAFS is presented which shows that, in addition to obtaining structure information from EXAFS, it is also possible to determine (1) the average electric field induced by the excited atom at each surrounding site, and (2) the k dependence of the scattering amplitude induced by the excited atom in its surroundings. The theory has been verified by experimental data on Cu and Ge, which show the expected shielding oscillations in Cu directly

for the first time and the ν^{-2} shielding behavior in Ge. A more detailed version of the theory is in preparation.

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Photoemission Observations of Resonant d Levels and d -Band Formation for Very Thin Overlayers of Cu and Pd on Ag†

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Photoemission studies of very thin overlayers of Cu and Pd on Ag substrates show resonant bound d states with half-widths $\Gamma \approx 0.5$, and 0.8 eV centered at 2.5 and 1.2 eV below the Fermi energy E_F , respectively, for depositions ≈ 2 average monolayers, and show the formation of bulk band structure for deposition $\gtrsim 4$ monolayers. The d -resonance position for Pd on Ag (1.2 eV below E_F) is markedly different from that of dilute Pd in AgPd alloys (2 eV below E_F), while the level widths are comparable.

We report photoemission measurements of electronic energy level positions and level widths for very thin overlayers of Cu and Pd deposited on Ag substrates. Recently, there have been a number of spectroscopic measurements of adsorbates on metal surfaces. These include field-emission spectroscopy (FES) studies of alkaline-earth adsorbates on tungsten,¹ for which the ionization potential of the adsorbate I^{ads} is less than that of the substrate (i.e., $I^{\text{ads}} < I^{\text{sub}}$) and electrons tend to be transferred to the substrate, and ion neutralization spectroscopy (INS) and photoemission electron spectroscopy (PES) studies of chalcogen adsorbates² and gaseous adsorbates (O, CO, etc.) on metal surfaces,³⁻⁵ for which $I^{\text{ads}} > I^{\text{sub}}$ and electrons tend to be transferred to the adsorbate.

In this work, we have essentially neutral adsorption ($I^{\text{ads}} \approx I^{\text{sub}}$), and for average adsorbate coverages of ≈ 1 monolayer we observe the relatively simple situation in which the adsorbate d -state resonances for Cu and Pd lie above the

d bands of the Ag substrate and are degenerate with the Ag "s" bands. For Cu and Pd, respectively, we observe occupied resonant bound state d levels of half-width $\Gamma \approx 0.5 - 0.8$ eV centered at about 2.5 and 1.2 eV below the Fermi level E_F . Our observed level widths appear to be consistent with the Anderson model as applied to chemisorption,^{6,7} and are similar to observed level widths for dilute Pd in AgPd alloys.^{8,9} Quantitatively, a recent Korringa, Kohn, and Rostoker (KKR) calculation by Cooper¹⁰ for a 1-monolayer film of Cu embedded in a simple metal predicts a Cu d state of half-width $\Gamma \approx 0.50$ eV centered at -2.7 eV.

As the adsorbate deposition was increased from about 1 to 4 average monolayers for Cu and Pd (the deposited mass was monitored), the adsorbate energy distributions were observed to change in shape from asymmetric Lorentzian-like shapes to shapes characteristic of the bulk metal. Also, adsorbate-induced emission characteristic of nondirect optical transitions is observed for de-