ELECTRON MOMENTUM DENSITY OF TITANIUM

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The Compton profile of polycrystalline titanium has been measured at Mo $K\alpha$ ($\lambda = 0.709$ Å). The valence-electron momentum density evidences significant 4s character, and the discontinuity in momentum density associated with the Fermi surface is at 1.08± 0.06 a.u. compared with the free-electron value of 1.01 a.u. for four electrons per atom. Band-momentum wave functions are unavailable for comparison with theory.

Compton profile measurements have been reported[1] for many substances of low atomic number ($Z \leq 13$). The very rapid increase in photoelectric absorption with atomic number makes difficult Compton profile measurements for heavy elements. We have extended the range of measurements to Ti ($Z = 22$), the first measurement on a transition element done with sufficient accuracy to determine the momentum density.

The technique is identical to that reported previously.[1] Mo $K\alpha$ x rays ($\lambda = 0.709$ Å) collimated to ±1.5° and scattered ~118° from a compact of titanium powder were analyzed with a LiF crystal (400). The entire spectrum from $\lambda \cong 0.700$ to $\lambda \cong 0.800$ Å, encompassing both the elastic and inelastic components, was recorded in intervals of 0.0003 Å. Sixteen runs were taken, each of several days duration, so that at least 10 000 photons per point were accumulated near the Compton peak. The Compton-peak-to-background ratio was approximately 2.5 to 1. The α_1 component of the Compton profile was separated by the Rachinger method[2] after subtracting background, and the data on the long-wavelength side of the Compton profile were converted to an electron-momentum scale z from the relation

$$z = \frac{mc}{2\lambda_0 \sin\theta} \times \left[\frac{\lambda-(\lambda_0+2h\sin^2\theta/mc)}{[1+\Delta\lambda/\lambda_0+(\Delta\lambda/\lambda_0)^2(\frac{1}{4}\sin^2\theta)]^{1/2}}\right], \qquad (1)$$

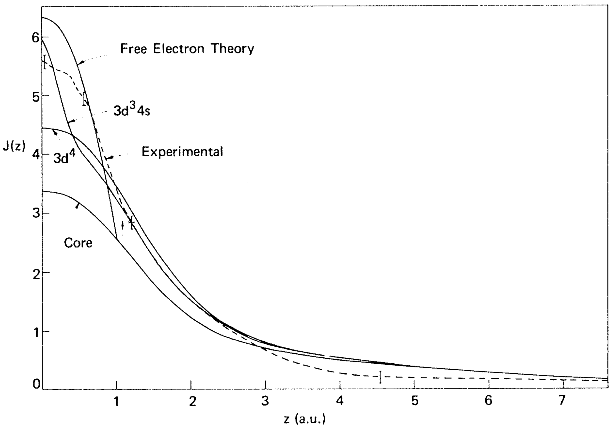

FIG. 1. The measured Compton profile of polycrystalline titanium. The curves marked $3d^4$ and $3d^34s$ are calculated from Hartree-Fock wave functions including the $2s^22p^63s^23p^6$ core. The curve marked free-electron theory is calculated for four electrons per atom plus a Hartree-Fock core $2s^22p^63s^23p^6$. The lowest curve is calculated for the core alone.

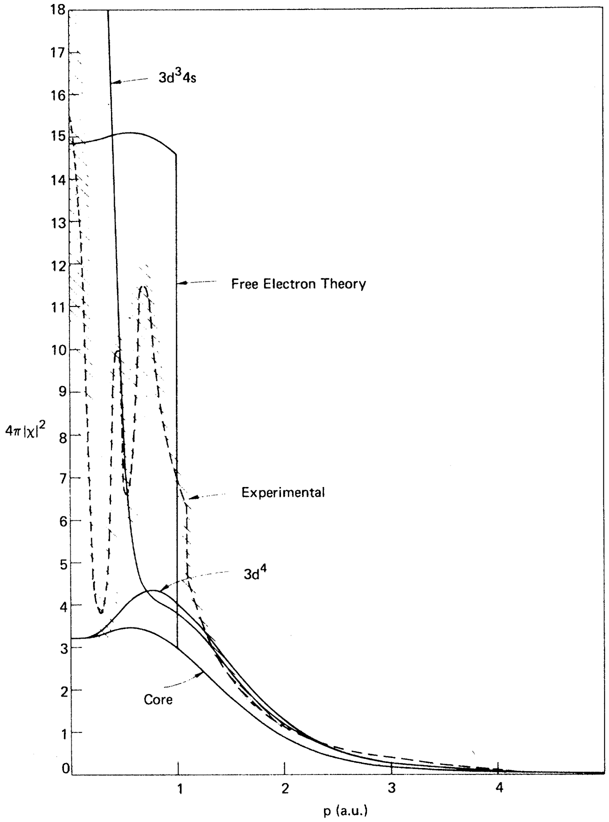

FIG. 2. The normalized momentum density $4\pi|\chi|^2$ per unit volume in momentum space determined from the measured Compton profile of titanium. The momentum p is in atomic units. The curves calculated from free-atom Hartree-Fock wave functions are shown for the core alone $2s^22p^63s^2p^6$ and for the core plus the valence-electron configurations $3d^34s$ and $3d^4$ and valence-electron free-electron theory. The value of $4\pi|\chi|^2$ at $p = 0$ for the $3d^34s$ configuration is 90 (a.u.).

where θ is one-half the scattering angle, λ the final wavelength, λ_0 the initial wavelength, and $\Delta\lambda = \lambda - \lambda_0$. The area under this curve was normalized to ten electrons, i.e., one-half the total number of excited electrons $[2s^2 2p^6 3s^2 3p^6 (3d4s)^4]$. (The $1s^2$ are too tightly bound to be excited.)

The final normalized profile $J(z)$ is shown in Fig. 1, together with the Compton profiles calculated from Hartree-Fock free-atom wave functions[3] for $3d^3 4s$ and $3d^4$ valence-electron configurations. Included also are the calculated core profile ($2s^2 2p^6 3s^2 3p^6$) and the profile in free-electron theory (4 free electrons per atom).

Since the data were taken on a polycrystalline sample, it is a straightforward procedure to determine the spherically averaged momentum density $|\chi|^2$ from the slope of the $J(z)$ curve since[1]

$$4\pi|\chi|^2 = |(2/z)(dJ/dz)|. \tag{2}$$

The momentum density is shown in Fig. 2 together with the calculated momentum densities from Hartree-Fock free-atom wave functions for the configurations $3d^3 4s$ and $3d^4$ and that calculated from free-electron theory.

To establish the position of the metallic discontinuity in momentum density (which appears as a discontinuous change in slope in Fig. 1 and a discontinuity in Fig. 2 at $z \cong 1.1$), a large number of additional runs were taken at intervals of 0.000 15 Å over a limited range of wavelengths in the vicinity of the free-electron value of Fermi momentum. The corresponding momentum range examined was approximately 0.7 to 1.5 a.u. The discontinuity in slope was observed at 1.08 ± 0.06 a.u. which is close to the free-electron value of 1.01 a.u. for titanium.

It is interesting that the calculated free-atom Compton profile is so sensitive to the relative $4s$ and $3d$ character in the valence band. A shift of one $3d$ electron to $4s$ produces over a 30% change in $J(z)$ at $z = 0$ (Fig. 1). Until band calculations for titanium are evaluated in momentum space or the space wave functions transformed to momentum space, no comparison with band theory is possible. Free-electron behavior and free-atom (Hartree-Fock) behavior for the four valence electrons, however, represent the two extremes, and the experimental data lie somewhere between the two. It does appear, though, that something between 0.5 and 1.0 $4s$ electron occupies the band in titanium. The observed structure in the momentum density at $p \sim 0.45$ and $p \sim 0.70$ (Fig. 2) is presumably a solid-state effect.

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[1] W. C. Phillips and R. J. Weiss, Phys. Rev. 171, 790 (1968).

[2] W. A. Rachinger, J. Phys. E: J. Sci. Instr. 25, 254 (1968).

[3] R. J. Weiss, W. C. Phillips, and A. Harvey, Phil. Mag. 17, 146 (1968).

CONFIGURATION COORDINATES OF Tl^+ IN KCl FROM RAMAN SCATTERING

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Raman scattering data for KCl:Tl^+ crystals are reported. The dominant scattering amplitudes are attributed to vibrations having E_g and T_{2g} symmetry about the Tl^+ ion. Comparison of the data with theory suggests a small change in interatomic force constants which can be understood in terms of Coulomb and repulsive forces. The Tl^+-Cl equilibrium spacing in the electronic ground state appears to be consistent with the value computed by Williams.

Although Seitz[1] had, in 1938, given an essentially correct analysis of the optical absorption bands of Tl^+ in KCl, research interest in this ion continues to the present. As a prototype of a series of ions, including In^+, Pb^{++}, Sn^{++}, and Sb^{+++}, Tl^+ represents an important class of phosphor sensitizers. In addition, it possesses an electronic simplicity which has made it and continues to make it extremely attractive for fundamental studies.

The ultraviolet absorption bands of Tl^+ are associated with transitions from a ${}^1S_0$ ($6s^2$) ground state to the ($6s6p$) manifold of states derived from ${}^1P_1$, ${}^3P_2$, ${}^3P_1$ atomic states. The relative widths and intensities of these three bands have been discussed in terms of lattice interactions and spin-orbit splittings, using configuration-coordinate curves to describe the lattice interaction, although the precise nature of the coordinates have, of necessity, been unspecified until