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Directional Compton Profiles and Energy Bands of Palladium

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The directional Compton profiles of palladium along [100] and [110] directions have been measured using 100 mCi 241Am Compton spectrometer. The theoretical Compton profiles and energy bands have been computed using hybridisation of Hartree-Fock and density functional theory. Except some fine structures, the energy bands are in good agreement with the available data. The measured anisotropy is found to be smaller than the present calculations and the available augmented plane wave and linear combination of Gaussian type orbitals based profiles. The experimental profiles are interpreted in terms of energy bands of Pd and Fermi surface topology.

Key Words: X-ray or γ-ray scattering, Electronic structure and band structure calculations, Fermi surface topology

INTRODUCTION

Within the impulse approximation, the Compton profile $J(p_z)$ is a projection of $\rho(\vec{p})$ and can be deduced from the spectral distribution of Compton scattered photons[1]. The spherical part of $\rho(\vec{p})$ can be isolated by forming direction difference profiles as:

$$\Delta J(p_z) = J_{hkl}(p_z) - J_{h'k'l'}(p_z) \quad (1)$$

Pd is a 4d transition metal and has technological importance. Regarding earlier studies on Pd, Papanicolaou *et al.*[2] and Chen *et al.*[3] have reported electron momentum densities and directional Compton profiles of Pd using self-consistent augmented plane wave (APW) within the local density formalism and linear combination of Gaussian type orbitals (LCGO) methods, respectively. We present the directional Compton profiles of Pd measured along [100] and [110] directions using our first ever lowest intensity 100 mCi ^{241}Am Compton spectrometer[4]. To compare our experimental data, we have also computed

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Compton profiles using B3PW (hybridisation of Hartree-Fock and density functional theories) scheme of CRYSTAL03 code[5].

EXPERIMENT

For the present measurements, we have employed 100 mCi ^{241}Am Compton spectrometer[4]. For each individual measurement, identical single crystal of Pd (length 2 mm, dia 5 mm) along [100] and [110] directions were held vertically in the scattering chamber. The γ-rays (59.54 keV) scattered at an angle 165±1.5° were analysed by a high purity Ge detector. The overall momentum resolution of the spectrometer was 0.55 a.u. Gaussian full width at half maximum (FWHM). The raw data have been measured for 700 and 585 h for [100] and [110] directions, respectively. The raw Compton data were corrected for several systematic corrections like background, instrumental resolution (limited to stripping off the low energy tail), sample absorption, detector efficiency, Compton scattering cross-section and multiple scattering, etc.[6] Finally, the experimental profiles were normalised to have an area of 18.33 electrons which is equal to that of the free atom profile area in the momentum range 0 to 7 a.u.[7].

THEORY

To compute the theoretical directional Compton profiles and energy bands, we have used linear combination of atomic orbitals method as embodied in CRYSTAL03[5]. We have employed the B3PW scheme, which is basically the hybridisation of density functional theory (DFT) and the Hartree-Fock (HF) scheme. In the B3PW, the exchange correlation density functional energy E_{XC} is defined as[5]:

$$E_{XC} = 0.80*\left(E_X^{LDA} + 0.90*\Delta E_X^{BECKE}\right) + 0.20*E_X^{HF} + 0.19*E_C^{VWN} + 0.81*E_C^{PWGGA} \quad (2)$$

where E_X^{LDA}, ΔE_X^{BECKE} and E_X^{HF} are the exchange energies of Dirac-Slater[5], Becke[8] and HF[5] while E_C^{VWN} and E_C^{PWGGA} are the correlation functional energies due to Vosko-Wilk-Nusair[9] and Perdew and Wang[10], respectively. The self-consistent field calculations have been performed at 29 **k** points in the irreducible Brillouin zone (BZ) with default tolerances (truncation criteria). Both the theoretical directional Compton profiles were normalized to corresponding free atom Compton profile area as mentioned above.

RESULTS AND DISCUSSION

In Fig. 1, we have reported the energy bands using B3PW scheme of CRYSTAL03 code in the energy range –0.50 to 0.25 Hartree. Except some fine structures, the overall features of bands are found to be in good agreement with

the data of Chen *et al.*[3]. From the energy bands (Fig.1) a strong hybridisation is quite evident, particularly along the Δ and Λ directions. The s-d bandwidth defined as $\Gamma_{25'} - \Gamma_1$ is found to be 0.125 Hartree while the occupied d-band width measured by $E_F - X_1$ is 0.228 Hartree. These data are in good agreement with the data reported by Chen *et al.*[3]. Separately, it is seen that the Fermi surface of Pd consists of a large closed region of electrons centered at Γ, small closed ellipsoidal region of holes at X and a multiply connected region of holes passing through the points X and W. The Fermi surface features (not shown here) are also reproduced by the energy bands (Fig. 1). In Fig. 2, we have plotted the

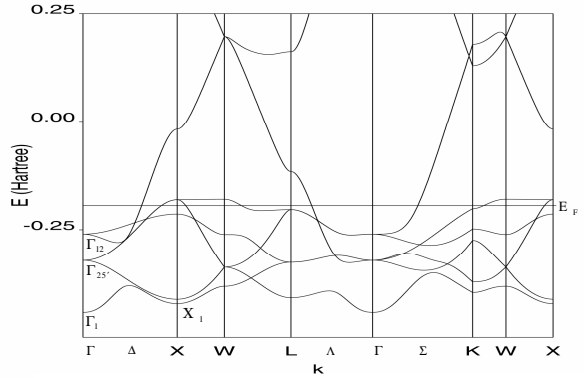

Fig. 1: Selected energy bands (E-k relation) of Pd along high symmetry directions of the first Brillouin zone using HF+DFT (B3PW) approach.

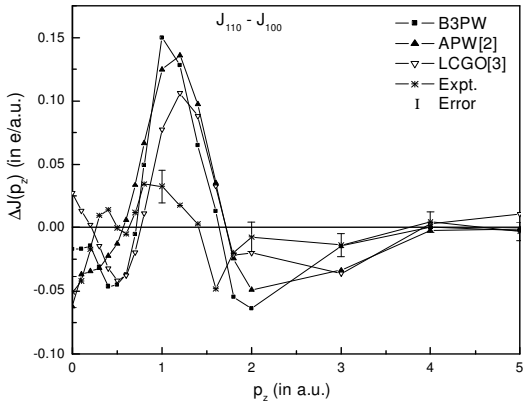

Fig. 2: Difference in directional Compton profiles of Pd. The theoretical profiles are convoluted with the instrumental function.

theoretical (B3PW, APW and LCGO) and experimental anisotropies in the momentum densities of Pd. It is seen that the amplitude of the oscillation in the experimental data is lower than the theoretical data.

The periodicity in the anisotropic Compton profiles, particularly in theory, is consistent with the energy bands of Pd. For example, the cross-overs of E_F by energy bands (Δ branch) coming from degenerate states Γ_{12} and $\Gamma_{25'}$ contribute to opposite trend of anisotropy in the momentum densities near p_z=0.8 a.u. Trend in the experimental anisotropy is found to relatively in better agreement with our B3PW calculations.

Conclusion

Experimental Compton profiles of Pd along [100] and [110] directions are reported. A comparison of experimental data with different theoretical calculations (B3PW, APW and LCGO) shows that the B3PW calculations give a relatively better agreement with the anisotropy in momentum densities. The present disagreement between theory and experiment in the low momentum region warrants the incorporation of anisotropic electron-electron correlation effects in 4d transition metals. The anisotropy in momentum densities are found to be consistent with E–k relations of Pd.

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