Electron momentum distribution in vanadium: Compton scattering measurements and band-structure calculation

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The [100], [110], and [111] Compton profiles and reciprocal form factors have been derived from Compton scattering measurements made with 60-keV ^{241}Am γ rays on single-crystal samples of vanadium. The same quantities have also been obtained theoretically on the basis of a self-consistent linear-muffin-tin-orbital band-structure calculation, using the local-density approximation for the exchange-correlation potential. An r-space procedure was adopted to calculate the reciprocal form factor $B(\mathbf{r})$ directly from the wave functions. The experimental and theoretical results are compared with previous 412-keV Compton scattering measurements and other band-structure calculations. All calculations overestimate the Compton profile anisotropies at low momenta.

I. INTRODUCTION

Among the $3d$ transition metals, vanadium is the heaviest which does not order magnetically. As in niobium, its Fermi level (E_F) lies on a density-of-states peak, which causes anomalous elastic behavior. [1] However, its expected[2] superconducting transition temperature is substantially reduced due to spin fluctuations. At the Sagamore VI Conference[3] vanadium was chosen as a representative of the $3d$ transition-metal series for comparative electronic structure investigations. Cuts of the same single crystal have been distributed among a number of laboratories.

In this work we present results of Compton scattering measurements on vanadium using 59.54-keV γ rays from a ^{241}Am source along the [100], [110], and [111] crystal directions, and a theoretical analysis based on a self-consistent band-structure calculation. Within the impulse approximation,[4] the Compton scattering results yield the electronic directional momentum distribution ("Compton profile") $J(p_z)$, which is related to the momentum density $\rho(\mathbf{p})$ through

$$J(p_z)=\int\int \rho(\mathbf{p})dp_x dp_y \ . \tag{1}$$

It has been found fruitful[5,6] to analyze the Compton profile by considering its Fourier transform $B(\mathbf{r})$:

$$B(\mathbf{r})=\int \rho(\mathbf{p})\exp(i\mathbf{p}\cdot\mathbf{r})d^3p = \int J(p_r)\exp(ip_r r)dp_r \ , \tag{2}$$

where p_r is the $\mathbf{p}$ component parallel to $\mathbf{r}$. This function is sometimes called the "reciprocal form factor." It gives the r-space autocorrelation of the electronic wave function.

Contrary to previous works,[7,8] the present theoretical analysis is based on direct calculation of the autocorrelation function $B(z)$ [$\equiv B(z\hat{\mathbf{z}})$ in the notation of Eq. (2)] rather than $J(p_z)$. This way the results appear to be insensitive to small irregularities in the wave functions due to the approximations used. $J(p_z)$ is obtained from $B(z)$ by a one-dimensional Fourier transformation [Eq. (2)].

The wave functions are calculated in the independent-particle approximation using the linear-muffin-tin-orbital (LMTO) band-structure method.[9] The self-consistent potential is calculated using the local-density approximation (LDA).[10,11] This approximation lacks rigor when momentum densities are calculated; however, it is essential to have accurate momentum-density calculations within the LDA before analyzing corrections to the LDA.[12] Comparison is made with previous LDA results[7,8] in the augmented-plane-wave (APW) and the linear-combination-of-atomic-orbital (LCAO) band-structure methods. Our experimental and theoretical results are also compared with previous Compton profile measurements[13] made on cuts from the same single crystal as ours, but using higher-energy 412-keV γ rays from a ^{198}Au source.

II. EXPERIMENTAL PROCEDURE

The experimental Compton profile is derived from the energy spectrum of γ rays inelastically scattered from the sample to be investigated. A general review of Compton profile measurements has been given in Ref. 14. In the present work we use 59.54-keV γ rays from a 5-Ci ^{241}Am annular source. The scattering angle is 169.5°. The scattered γ rays are measured with an intrinsic Ge detector. The resolution of the spectrometer is 365-eV full width at half-maximum (FWHM) at 60 keV. This means a resolution of 0.53 a.u. of momentum near the peak of the profile.

The measurements are carried out on vanadium samples which were cut from the same single crystal along the [100], [110], and [111] symmetry directions. They are all 1 mm thick and about 1 cm in diameter.

The data are collected in 2048 channels. The channel width is approximately 0.06 a.u. About 1.5×10^5 counts are accumulated at the channel of the Compton peak for each sample. The data analysis includes background subtraction, absorption correction, and a Monte Carlo correc-

tion for multiple scattering.[15] Fourier deconvolution and filtering is done so that the data are still smeared with a Gaussian resolution function of 0.53 a.u. FWHM. Aikala[16] calculated the smearing contribution of the annular source geometry to the measured Compton profile anisotropies. By computer simulation he showed that the maxima and minima of the anisotropies are reduced by about 3% and 14% for scattering angles of 174.5° and 166°, respectively. For the present scattering angle of 169.5° we have made similar calculations and found a reduction of about 9% in the maxima and minima of the anisotropies. In order to compare our experiment with theory, the theoretical profile has to be smeared with the experimental resolution function of 0.53 a.u. as well as with the effect of the annular source geometry.

III. THEORETICAL PROCEDURE

The theoretical calculation is based on the LMTO band-structure method.[9] Within this method, the Bloch function of an electron of band j and wave vector $\mathbf{k}$ is expressed as a combination:

$$\psi_j^{\mathbf{k}}(\mathbf{r})=\sum_{l,m}[\phi_{lm}^{\nu}(\mathbf{r})\alpha_{lm}^{j\mathbf{k}}+\dot{\phi}_{lm}^{\nu}(\mathbf{r})\beta_{lm}^{j\mathbf{k}}]\ , \tag{3}$$

where ϕ_{lm}^{ν} are solutions of a single-particle spherically symmetric Schrödinger equation at energy E_ν in spheres around centers of approximate spherical symmetry (normalized within a sphere), and $\dot{\phi}_{lm}^{\nu}$ are the energy derivatives of such solutions at E_ν. In the present work one calculation has been performed taking one sphere per unit cell around the atom, and another calculation taking six additional interstitial spheres per unit cell around the corners of the bcc Wigner-Seitz (WS) cell. The $B(z)$ and $J(p_z)$ results of the two calculations are found to be very close to each other.

The exchange-correlation part of the self-consistent potential was calculated once in the Kohn-Sham approximation[11] and then in the von Barth—Hedin approximation,[17] and again the difference between the two results was found to be negligible.

Within the independent-particle approximation, the reciprocal form factor (2) can be expressed (at zero temperature) as

$$B(\mathbf{r})=\sum_{j,\mathbf{k}}\Theta(E_F-E_j^{\mathbf{k}})\int[\psi_j^{\mathbf{k}}(\mathbf{r}+\mathbf{r}_1)]^*\psi_j^{\mathbf{k}}(\mathbf{r}_1)d^3r_1\ , \tag{4}$$

where $E_j^{\mathbf{k}}$ are the band energies, and the function Θ assumes the value 0 or 1 for negative or positive arguments, respectively. The $\mathbf{r}$ integration in (4) is over a bcc unit cell. It has been found convenient numerically to take one-half the integral over a cube which contains two bcc unit cells. The $\mathbf{k}$ summation in (4) is over the Brillouin zone (BZ). Each point in the BZ is obtained from the irreducible BZ (IBZ) by one of the 48 cubic star transformations s, which satisfy

$$E_j^{s\mathbf{k}}=E_j^{\mathbf{k}},\quad \psi_j^{s\mathbf{k}}(\mathbf{r})=\psi_j^{\mathbf{k}}(s^{-1}\mathbf{r})\ . \tag{5}$$

Thus (4) can be expressed as

$$B(\mathbf{r})=\tfrac{1}{2}\sum_{j,s}\sum_{\mathbf{k}\text{ in the IBZ}}\Theta(E_F-E_j^{\mathbf{k}})\times\int_{\text{cube}}[\psi_j^{\mathbf{k}}(s(\mathbf{r}+\mathbf{r}_1))]^*\psi_j^{\mathbf{k}}(s\mathbf{r}_1)d^3r_1\ . \tag{6}$$

The $\mathbf{r}_1$ and $\mathbf{r}+\mathbf{r}_1$ integration points can be obtained by star transformations s_1', s' and lattice translations $\mathbf{R}_1,\mathbf{R}$ from points in the irreducible WS (IWS) cell:

$$\begin{aligned}&\mathbf{r}_1=\mathbf{R}_1+s_1'\mathbf{r}_1'\ \text{ for } \mathbf{r}_1' \text{ in the IWS cell,}\\ &\mathbf{r}+\mathbf{r}_1=\mathbf{R}+s'\mathbf{r}'\ \text{ for } \mathbf{r}' \text{ in the IWS cell.}\end{aligned} \tag{7}$$

So, by Bloch's theorem, one can express $B(\mathbf{r})$ as

$$B(\mathbf{r})=\tfrac{1}{2}\sum_{k\text{ in the IBZ}}\int_{\text{cube}}d^3r_1\sum_{j,s}e^{i\mathbf{k}\cdot s(\mathbf{R}_1-\mathbf{R})}[\psi_j^{\mathbf{k}}(ss'\mathbf{r}')]^*\times\psi_j^{\mathbf{k}}(ss_1'r_1')\ . \tag{8}$$

The functions $\psi_j^{\mathbf{k}}(ss'\mathbf{r}')$ and $\psi_j^{\mathbf{k}}(ss_1'\mathbf{r}_1')$ are obtained from $\psi_j^{\mathbf{k}}(\mathbf{r}')$ and $\psi_j^{\mathbf{k}}(\mathbf{r}_1')$ by appropriate transformations.

Further analysis shows that of the 48 star operations s, it is sufficient to take the 24 operations which do not include inversion (and take the real part of the result). Also, for points $\mathbf{r}$ on a symmetry axis it is sufficient to take one member from each class of operations which all have the same effect on the axis. Thus, one is left with three operations for the [100] axis, six operations for the [110] axis, and four operations for the [111] axis.

The $\mathbf{k}$ summation is based on the tetrahedral linear interpolation method:[18] The wave functions are calculated at the centers of mesh cubes in the IBZ, whose corners are used to construct the tetrahedra. Convergence is achieved for 55 mesh points in the IBZ. The $\mathbf{r}$ integration is performed by the Simpson method on the x,y,z cubic axes. As mentioned, the values of the wave functions at the $\mathbf{r}$ points are obtained from the values at the IWS cell by the appropriate star and translation transformations. Convergence is achieved for 89 points in the IWS cell. Special care has been taken for the strong nodes of the wave functions close to the nuclei.

By the above procedure we calculated the contribution of the valence electrons to $B(z)$. The contribution of the core electrons is based on the Hartree-Fock free-atom calculation of Biggs *et al.*[19] By a one-dimensional Fourier transformation of $B(z)$ [Eq. (2)] the directional momentum distributions $J(p_z)$ along the axes are obtained.

The LMTO method has been applied before for Compton profile calculation,[20,21] but differently from the present approach of calculating $B(z)$ directly. In Ref. 21 it was shown that accuracy is significantly improved when the $\mathbf{r}$ integration is carried out on the real WS cell, as in the present work, rather than on a WS sphere, as in Ref. 20.

IV. RESULTS AND DISCUSSION

The present theoretical LMTO results of the valence-electron contribution to the Compton profile of vanadium are shown in Table I for the directions [100], [110], and

TABLE I. LMTO-calculated contribution of the valence electrons to the Compton profile of vanadium along the [100], [110], and [111] directions. No convolution is made.

p_z (a.u.)	[100]	[110]	[111]	p_z (a.u)	[100]	[110]	[111]
0.0	1.790	2.163	2.258	2.6	0.192	0.155	0.138
0.1	1.876	2.174	2.245	2.7	0.155	0.132	0.131
0.2	2.016	2.157	2.182	2.8	0.131	0.118	0.121
0.3	2.036	2.051	2.055	2.9	0.118	0.103	0.108
0.4	1.934	1.879	1.892	3.0	0.108	0.090	0.092
0.5	1.790	1.707	1.709	3.1	0.091	0.085	0.076
0.6	1.657	1.551	1.526	3.2	0.070	0.080	0.067
0.7	1.560	1.398	1.397	3.3	0.060	0.070	0.062
0.8	1.456	1.263	1.330	3.4	0.068	0.061	0.054
0.9	1.233	1.153	1.227	3.5	0.079	0.058	0.045
1.0	0.910	1.043	1.024	3.6	0.076	0.053	0.040
1.1	0.681	0.911	0.797	3.7	0.063	0.044	0.038
1.2	0.647	0.766	0.644	3.8	0.052	0.040	0.037
1.3	0.679	0.626	0.560	3.9	0.046	0.039	0.036
1.4	0.638	0.510	0.504	4.0	0.041	0.034	0.034
1.5	0.538	0.433	0.466	4.1	0.036	0.029	0.031
1.6	0.444	0.390	0.438	4.2	0.030	0.028	0.026
1.7	0.376	0.351	0.394	4.3	0.021	0.027	0.022
1.8	0.335	0.307	0.340	4.4	0.016	0.023	0.018
1.9	0.307	0.276	0.305	4.5	0.020	0.021	0.016
2.0	0.257	0.264	0.285	4.6	0.025	0.021	0.015
2.1	0.194	0.253	0.256	4.7	0.024	0.019	0.015
2.2	0.170	0.234	0.212	4.8	0.021	0.015	0.016
2.3	0.198	0.220	0.171	4.9	0.019	0.014	0.019
2.4	0.231	0.210	0.148	5.0	0.017	0.014	0.021
2.5	0.226	0.187	0.140				

TABLE II. 60-keV measurement and LMTO calculation of the Compton profile of vanadium along the [100], [110], and [111] directions. The theoretical results which include calculated core contribution, have been convoluted with the experimental 0.53-a.u. FWHM Gaussian resolution function and smeared for the effect of annular source geometry.

	Experiment			Theory		
p_z (a.u.)	[100]	[110]	[111]	[100]	[110]	[111]
0.0	5.178	5.296	5.330±0.022	5.133	5.309	5.354
0.1	5.172	5.270	5.293	5.124	5.284	5.326
0.2	5.132	5.198	5.211	5.093	5.211	5.245
0.3	5.050	5.079	5.095	5.029	5.092	5.115
0.4	4.919	4.914	4.936	4.925	4.931	4.946
0.5	4.743	4.715	4.735	4.777	4.738	4.748
0.6	4.523	4.489	4.506	4.588	4.523	4.531
0.7	4.279	4.251	4.265	4.363	4.294	4.301
0.8	4.023	4.006	4.006	4.108	4.056	4.060
0.9	3.757	3.753	3.728	3.835	3.813	3.807
1.0	3.488	3.493	3.453±0.017	3.557	3.565	3.546
1.2	2.986	2.991	2.976	3.049	3.068	3.033
1.4	2.569	2.558	2.543	2.627	2.604	2.588
1.6	2.197	2.185	2.196	2.251	2.210	2.223
1.8	1.888	1.890	1.896	1.915	1.893	1.914
2.0	1.637	1.644	1.641±0.011	1.637	1.640	1.648
2.5	1.197	1.184	1.192	1.202	1.191	1.167
3.0	0.904	0.899	0.897	0.904	0.894	0.889
3.5	0.737	0.736	0.732	0.733	0.723	0.715
4.0	0.631	0.626	0.623	0.618	0.612	0.609
5.0	0.477	0.479	0.470±0.008	0.458	0.456	0.460

[111]. These results were found insensitive to a finer treatment of the electronic wave functions in the interstitial region. Since these results are based on a direct calculation of $B(\mathbf{r})$, small details of wave functions there have effect mainly for small $\mathbf{r}$ values and are hardly noticed in a Fourier transformation to $J(p_z)$. These results were also found to be almost insensitive to whether the LDA exchange-correlation potential was calculated in the von Barth–Hedin[17] or the Kohn-Sham[11] approximation.

In Table II we show the present experimental Compton profiles along these directions, compared with the LMTO theory after adding to it the core contribution,[19] convoluting it with the 0.53-a.u. FWHM Gaussian resolution function of our experimental apparatus, and smearing it with the effect of our annular source geometry. The agreement between theory and experiment in the total profiles is about 1% in the vicinity of the peak.

In order to observe the crystalline effects, it is convenient to check the anisotropies $\Delta J(p_z)$ in the Compton profiles (namely the differences between the profiles in the three orientations). In order to provide a basis for comparison between the various theories and experiments, we convoluted, in addition to our LMTO results, the LCAO (Ref. 8) results with our 0.53-a.u. FWHM Gaussian resolution function and smeared them with the annular source effect. A similar treatment was performed on the experimental results of Rollason *et al.*,[13] which contain a resolution of 0.40 a.u. FWHM and were convoluted further to 0.53 a.u. and also smeared with our annular source ef-

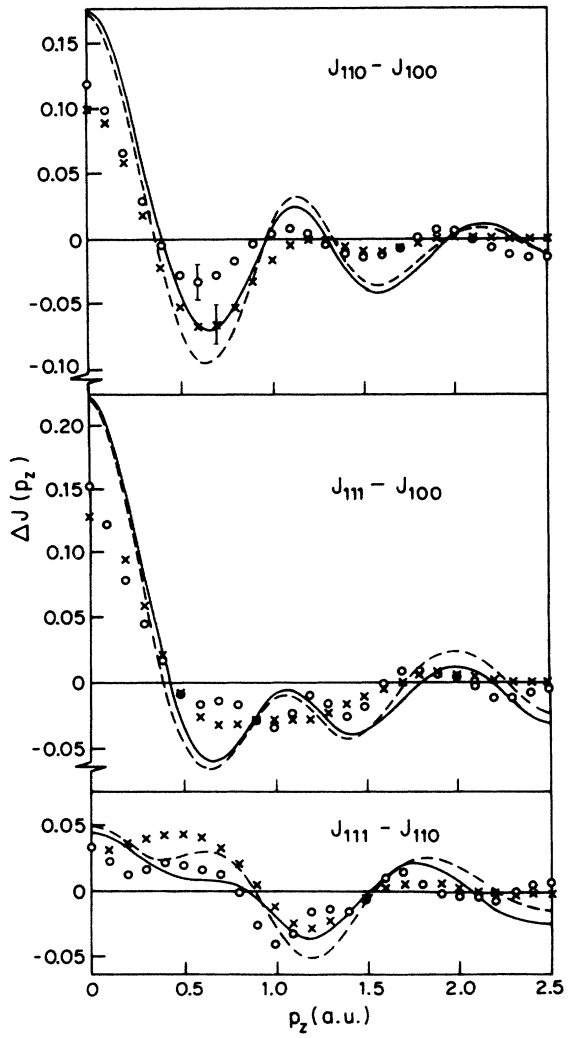

FIG. 1. Experimental and theoretical anisotropies in the Compton profile of vanadium. The circles are the present 60-keV measurement. The crosses are the 412-keV measurement from Ref. 13. The solid line is the present LMTO calculation. The dashed curve is the LCAO calculation from Ref. 8. All curves contain a convolution with a Gaussian of 0.53 a.u. FWHM and a smearing due to the annular source geometry.

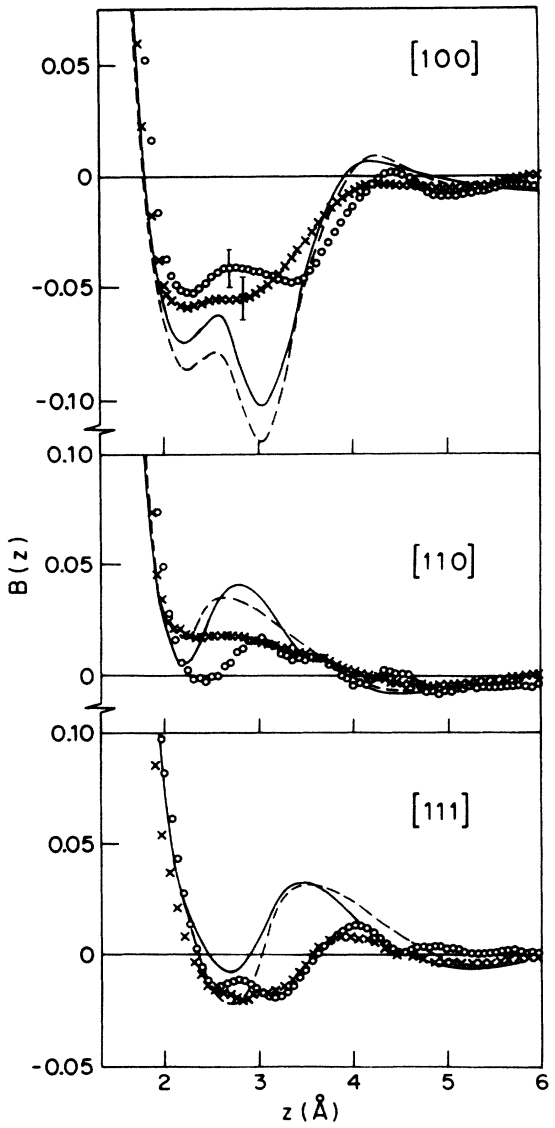

FIG. 2. Directional autocorrelation functions of vanadium along the [100], [110], and [111] directions. The circles are the present 60-keV measurement. The crosses are the 412-keV measurement from Ref. 13. The solid line is the present LMTO calculation. The dashed curve is the LCAO calculation from Ref. 8. All curves contain a convolution with a Gaussian of 0.53 a.u. FWHM and a smearing due to the annular source geometry.

fect. The anisotropies $\Delta J(p_z)$ in the two experiments and the two theories are shown in Fig. 1, and the reciprocal from factors $B(z)$ are shown in Fig. 2.

It is noticed that all the experimental and theoretical results show similar features. It is clear, however, that in general there is better agreement between the measurements themselves and between the calculations themselves than there is between theory and experiment. The theoretical results also agree qualitatively with the earlier APW (Ref. 7) calculations, which are not shown in the figures here. The theoretical oscillations in $\Delta J(p_z)$ are somewhat larger than the experimental ones, in particular, the values of $\Delta J(0)$. Corrections to the LDA (used in the theoretical calculations), of the type applied in a recent calculation of the Compton profile of copper,[12] are expected to reduce such discrepancies between theory and experiment. Such a calculation is especially worthwhile now, when experimental and theoretical results of different groups, using different techniques, seem to converge.

The structure of the $B(z)$ and $\Delta J(p_z)$ curves is determined by wave-function and Fermi-surface (FS) effects. The latter have important effects on the oscillation of $B(\mathbf{r})$. For an insulator, $B(\mathbf{r})$ has zeros when $\mathbf{r}$ equals a lattice point $\mathbf{R}$.[6] In vanadium the smallest $\mathbf{R}$ values are 2.62, 3.03, and 4.29 Å in the [100], [110], and [111] directions, respectively. We do not observe correlation between the zeros of $B(\mathbf{r})$ and these points, which indicates the significance of the FS effect on the $B(\mathbf{r})$ oscillations. The high resolution necessary for accurate FS studies is achieved in the electron-positron momentum distribution obtained by positron annihilation measurements. Such measurements for vanadium have been carried out recently[22] using a two-dimensional apparatus.

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