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## Correlation correction on Compton profiles of V and Cr

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**Abstract.** Anisotropic electron–electron correlation effects in the directional Compton profiles of vanadium and chromium, which cannot be described within the local density approximation, are successfully modelled by introducing an energy-dependent, correlated, occupation function into an APW band calculation of the electron momentum density.

### 1. Introduction

One of the most fundamental comparisons between theory and experiment on the electronic structures of transition metals is that of the Compton profiles. In the 1970s band-theoretical calculations of Compton profiles of vanadium and chromium were published [1–3], and were compared with the available experimental Compton profiles. Although solid state detectors were being used at that time, the treatment of multiple-scattering effects on experimental data by a Monte Carlo simulation [4] had not yet been established. Although the agreement between theory and experiment was thus limited, the correlation correction was expected to be necessary [1].

Recent experimental multiple-scattering profiles of vanadium [5, 6] and chromium [7, 8] have been processed by the Monte Carlo method as for some other transition metals. Their single-scattering profiles are, therefore, very reliable. The difference between the experiment and the theory which is estimated via the band-theoretical one-electron approximation shows a significant feature: around the origin of the momentum axis the theoretical values are greater than the experimental ones, and in the higher momentum region the opposite is true. The general features have been ascribed to electron–electron correlation, which was not taken into account in the one-electron scheme. In the one-electron approximation at zero temperature, the occupation probability of the individual particle energy levels is equal to one for levels below the Fermi energy, and zero for levels above the Fermi level. Migdal [9] introduced the correlation into a Fermi gas system and found that the occupation probability of the energy levels is less than one even for levels below the Fermi level and finite for levels even above the Fermi level, and that the characteristic discontinuity (the Migdal discontinuity) at the Fermi level in the occupation probability still existed. This situation corresponds to the configuration interaction which allows the mixing of energy levels above and below the

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Fermi energy. Daniel and Vosko [10] also showed that a large discontinuity in the momentum distribution function  $n(p)$  of an interacting electron gas still remains.

Until now, correlation effects on Compton profiles have been estimated by using the Lam–Platzman correction [11]. Very roughly speaking, the correction moves some amount of momentum density from the lower momentum region to the higher. This is an inherent characteristic of the momentum distribution function  $n(p)$  in a correlated electron gas system [10, 12]. In the case of a nearly free electron system, like a simple metal, the energy dependent occupation probability function  $n(E)$ —hereafter called the energy occupation function—and the momentum distribution function  $n(p)$  have almost the same meaning, since they are related to each other through parabolic energy dispersion. In fact, Rennert [13] estimated a correlation correction using  $n(p)$  for beryllium and obtained a reasonable result. Correlation effects on the Compton profiles for some transition metals have been estimated by using the Lam–Platzman correction within the local density approximation [5, 7, 14–16]. In this estimation method, the correlation correction is defined as follows:

$$\Delta J_{\text{LDA}}(p) = \int_{\text{unit cell}} \Delta J(p, \rho(r)) \, dr. \quad (1)$$

Here,  $\Delta J(p, \rho(r))$  is a Lam–Platzman correction at a point  $r$  whose local density is  $\rho(r)$ . Although Rennert obtained fairly good results, there are two weak points in that treatment. The first is that although the real correlation correction should be anisotropic, the correction is isotropic. The second is that the correction is based on the local density approximation and the density includes the core electron contributions whose correlation effect should be very small.

The momentum distribution function  $n(p)$  defined by Cardwell [7] is as follows:

$$n(p) = \begin{cases} 1 - a_\rho p^2/p_F^2 - d(1 - p/p_F) & \text{for } p < p_F \\ a_\rho (b_\rho - p)^2/(b_\rho - p_F)^2 & \text{for } p > p_F. \end{cases} \quad (2)$$

where  $a_\rho = 1.7/\pi^2 p_F$ ,  $p_F = (9\pi/4)^{1/3}/r_s$ ,  $r_s$  is the Wigner radius, i.e.  $4\pi/3r_s^3$  is the volume for one electron, and  $b_\rho$  is the upper bound of the distribution, determined by the following normalisation condition:

$$\int n(p) \, d^3p = (4\pi/3)p_F^3. \quad (3)$$

Together  $a_\rho$ ,  $b_\rho$  and  $d$  characterise the momentum distribution with the former two being functionals of the charge density.

In this paper correlation effects on the Compton profiles of vanadium and chromium are estimated by using real band wave functions and an empirical energy occupation function which is defined as follows:

$$n(E) = \begin{cases} 1 - A(E - E_1)/(E_F - E_1) - D & \text{for } E < E_F \\ B(E - E_b)^2/(E_F - E_b)^2 & \text{for } E_F < E < E_b. \end{cases} \quad (4)$$

Here, values of coefficients  $A$ ,  $B$  and  $D$  should be determined empirically.  $E_1$  is a reference energy like the  $\Gamma_1$  point, and  $E_b$  is the upper bound energy of the distribution, determined by a normalisation condition similar to equation (3). The first equation of (4) is derived approximately from that of (2) using the relation  $E \propto p^2$ , and the second one is obtained if  $E$  is close to  $E_F$ .

Finally, it should be mentioned that similar procedures which employ energy dependent enhancement factors have been used to estimate the positron–electron correlation effects [17–19].

## 2. The Compton profiles determined by one-electron band calculations

The effective potentials used for the band calculations are the modified  $X_\alpha$  potentials [20] determined so as to reproduce the observed Fermi surfaces determined by the de Haas–van Alphen effect. The energy values and the wave functions are calculated by the APW method at 55  $k$  points in the one-48th of the Brillouin zone. There are about 50 APWs, and the maximum number of angular-momentum quantum numbers,  $l$ , is six. The wave functions within the inscribed sphere are calculated up to  $l = 4$ . From the Bloch functions thus obtained, the momentum density distribution  $\rho_b(\mathbf{q}, E)$  is determined for 767 reciprocal lattice vectors, which include more than 99% of the total number of band electrons. The Compton profiles in three major orientations are calculated for the band electrons in vanadium and chromium via the following formula:

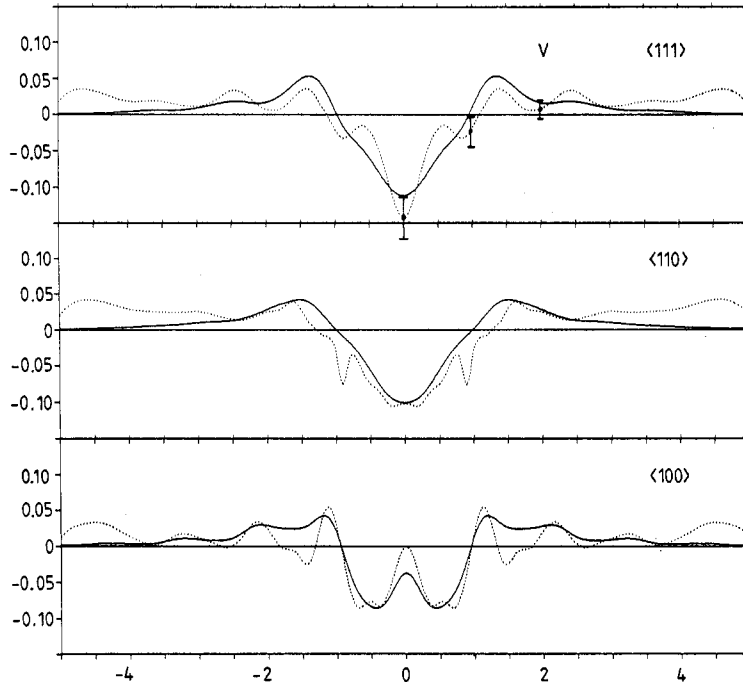
$$J_k(q_z) = \sum_b \int \int \int \rho_b(\mathbf{q}, E) \theta(E_F - E) dq_x dq_y dE \quad (5)$$

where  $\theta(E)$  is a step function,  $b$  denotes a band index and  $\mathbf{k}$  is the direction of the scattering vector parallel to  $q_z$ .

The curves showing the difference between the experimental and theoretical results (experiment – theory) are shown by dotted curves in figures 1 and 2 for vanadium and chromium respectively. The theoretical one-electron profile is the sum of the band contribution described before, and the core contribution calculated by Biggs *et al* [21], and has been convoluted with a Gaussian of FWHM 0.4 au corresponding to the width of the resolution function for the experiments on vanadium [5] and chromium [7, 8]. In the case of vanadium, the experimental data used here are only from the high energy side of the profile, and so the difference profiles are symmetrical. In the case of chromium, on the other hand, the experimental data from both high and low energy sides are used, and so the difference curves are not necessarily symmetrical. Although the effective one-electron potentials (modified  $X_\alpha$  potentials) used by the APW band calculations include some correlation effects like the local density functional (LDF) approximation [22], the APW band theoretical Compton profiles do not include any dynamical correlation effects. Therefore, the difference between experiment and theory should be due to the correlation effect, and the dotted curves in figures 1 and 2 may be called experimental correlation profiles.

## 3. Correlation correction

In order to explain the experimental correlation profiles, so far, the Lam–Platzman correction has been used. The correction is only isotropic and there is no distinction between correlation effects due to 3d electrons and core electrons. In the case of vanadium and chromium, the density distributions should be strongly anisotropic.



**Figure 1.** Directional Compton profile difference curves ( $\gamma$ -ray experiment minus APW theory) shown as full curves for the three principal orientations in vanadium: the error bars refer to experimental uncertainties. The dotted curves show the anisotropic correlation corrections calculated from equation (7) and convoluted with the experimental resolution function.

Therefore, realistic band structures should be used to estimate the correlation effects. A theoretical correlation profile is defined as follows:

$$\Delta J_k^{\text{corr}}(q) = - \int_{\Gamma_1}^{E_F} (1 - n(E)) J_k(q, E) dE + \int_{E_F}^{\infty} n(E) J_k(q, E) dE. \quad (6)$$

Here,  $n(E)$  is an energy occupation function and  $J_k(q, E)$  is a partial Compton profile contributed from the states whose energy is  $E$ . In the actual calculation each integration is replaced by a summation as follows:

$$\Delta J_k^{\text{corr}}(q) = - \sum_{i=1}^{n_F} (1 - n(E_i)) J_k(q, E_i) \Delta E + \sum_{i=n_F+1}^{n_{\text{max}}} n(E_i) J_k(q, E_i) \Delta E. \quad (7)$$

Here,  $J_k(q, E_i)$  is an energy average partial Compton profile contributed from the states whose energies are between  $E_{i-1}$  and  $E_i (= E_{i-1} + \Delta E)$ .

In figures 3, 4 and 5, the  $J_k(q, E_i)$  for vanadium along the  $\langle 100 \rangle$ ,  $\langle 110 \rangle$  and  $\langle 111 \rangle$  scattering axes are shown, respectively. In each figure the right-hand axis is for the momentum  $q$  in atomic units and the left-hand axis is for the energy denoted by the number  $i$  ( $E_i$ ) in units of  $\Delta E$ . In these units  $E_0 = -0.6179$  Ryd, the Fermi energy  $E_F = E_{n_F=22} = -0.899$  Ryd and  $\Gamma_1 = -0.5799$  Ryd. The energy width,  $\Delta E$ , is 0.024 Ryd. (Hereafter, energy values are referred to in units of  $\Delta E$ .) When  $J_k(q, E)$  is

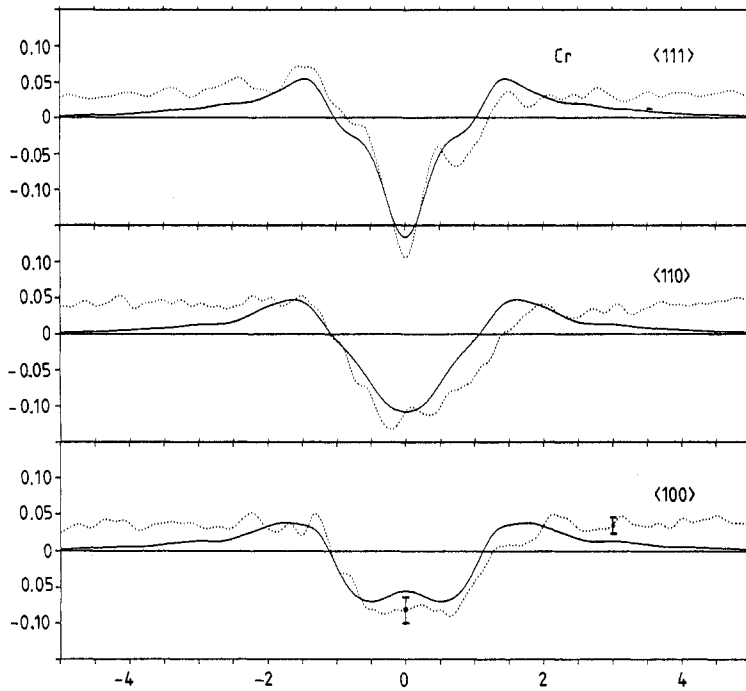


Figure 2. As for figure 1 except for Cr.

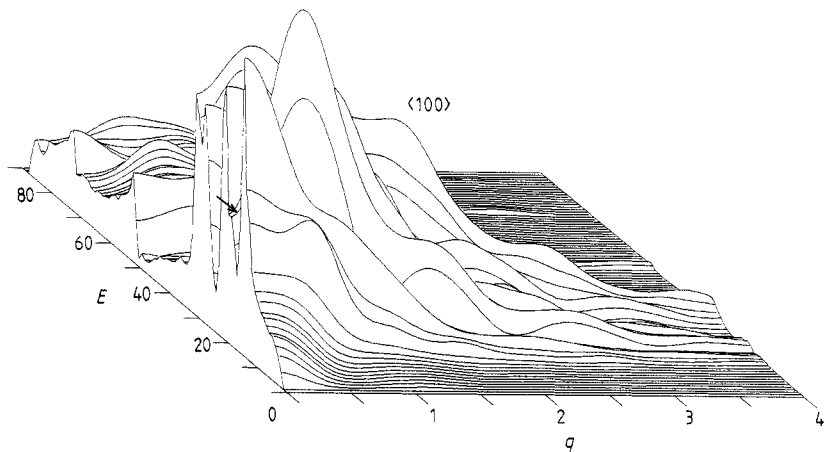
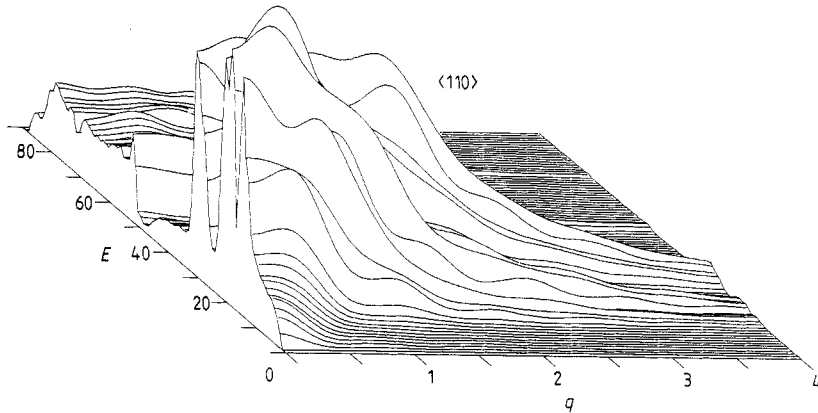
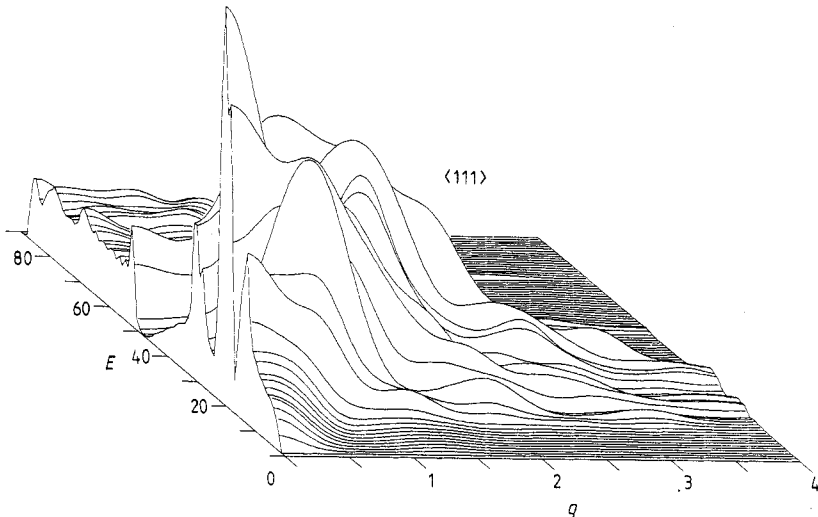


Figure 3. Partial Compton profiles  $J_k(q, E_i)$  along the  $\langle 100 \rangle$  scattering direction for vanadium convoluted with a Gaussian of FWHM 0.4 au. The right-hand axis  $q$  is in atomic units and the left-hand axis is energy  $E$  (see the text). The  $\Gamma_1$  energy is around 1 and the Fermi energy is at 22. An arrow indicates an area of relatively small density which causes the deep concave on the Compton profile along the  $\langle 100 \rangle$  direction.

integrated along the energy axis from the bottom of the band to the Fermi energy, the conventional Compton profile  $J_k(q)$  is obtained. These three figures reveal a stronger anisotropy in the momentum density than is expected, and this causes a very strong

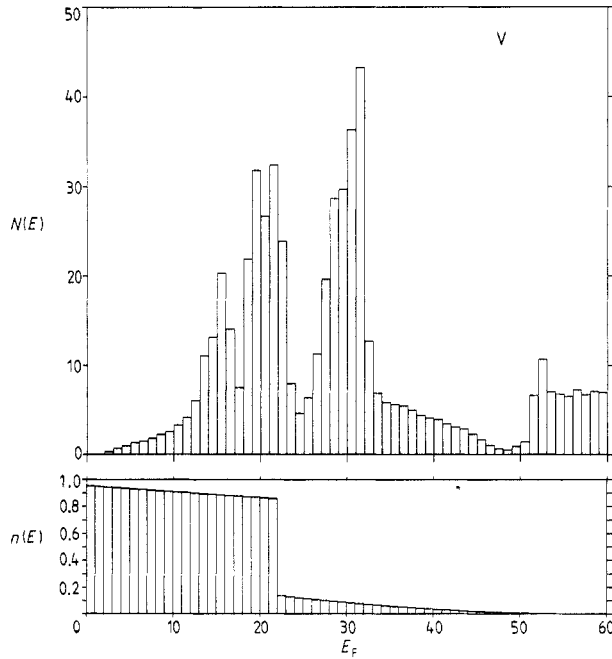


**Figure 4.** Partial Compton profiles  $J_k(q, E_i)$  along the  $\langle 110 \rangle$  scattering direction for vanadium convoluted with a Gaussian of FWHM 0.4 au.

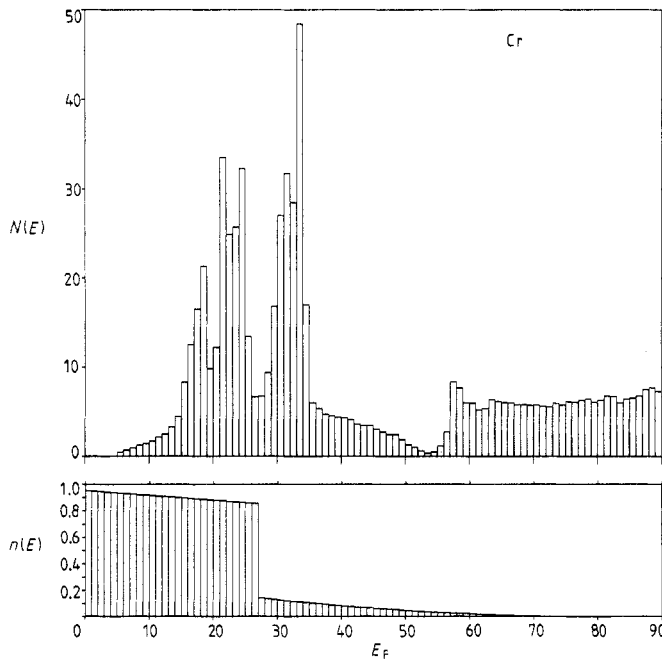


**Figure 5.** Partial Compton profiles  $J_k(q, E_i)$  along the  $\langle 111 \rangle$  scattering direction for vanadium convoluted with a Gaussian of FWHM 0.4 au.

anisotropy in the Compton profiles without correlation effects. In figure 3 an arrow indicates an area of relatively small density which originates from the jungle-gym structure in the Fermi surfaces of vanadium and is the origin of the deep concave on the Compton profile along the  $\langle 100 \rangle$  direction. When  $J_k(q, E)$  is integrated along the momentum axis, the density-of-states curve  $N(E)$  shown in figure 6 is obtained. In figures 3–6 the states at energies from 1 to 12 are predominantly due to s electrons, those at energies from 13 to 33 are due to d electrons, those from 34 to 51 are due to sp electrons and those from 52 to 85 are due to f electrons. At the bottom of figure 6, the energy occupation function is also shown in order to give a measure of the mixing of the higher energy states into the lower in the correlation effect. The function determined empirically for vanadium is as follows:



**Figure 6.** Density-of-states curve  $N(E)$  (top) and the empirical energy occupation function  $n(E)$  (bottom) for vanadium that gives the best agreement between theory and experiment.



**Figure 7.** Density-of-states curve  $N(E)$  (top) and the empirical energy occupation function  $n(E)$  (bottom) for chromium that gives the best agreement between theory and experiment. The  $\Gamma_1$  energy is around 4 and the Fermi energy is at 27.



$$n(E) = \begin{cases} 0.95 - 0.091 (E/E_F) & \text{for } E < E_F \\ 0.141 (E - E_b)^2 / (E_F - E_b)^2 & \text{for } E_F < E < E_b. \end{cases} \quad (8)$$

Energies are relative to the lowest energy  $E_0$ . The lower and upper energy parts of the function  $n(E)$  have been adjusted using the following normalisation condition:

$$\sum_{E=\Gamma_1}^{E_F} N(E)(1 - n(E)) = \sum_{E=E_F}^{E_b} N(E)n(E) \quad (9)$$

where  $E_b$  is determined to be at  $E_{60}$ . The numerical value of each side of equation (9) is 0.59. As the total number of band electrons is five, about 12% of those below the Fermi level are replaced by ones from above it. As equation (8) has not been obtained by a first-principles approach, it is not rigorous, and it is only empirical.

The theoretical correlation profiles are obtained from equation (7) using the energy occupation function (8) and  $J_k(q, E_i)$ . They are shown by full curves in figure 1.

The density-of-states curve for chromium and the energy occupation function are also shown in figure 7. The function determined empirically is as follows:

$$n(E) = \begin{cases} 0.95 - 0.095 (E/E_F) & \text{for } E < E_F \\ 0.145 (E - E_b)^2 / (E_F - E_b)^2 & \text{for } E_F < E < E_b \end{cases} \quad (10)$$

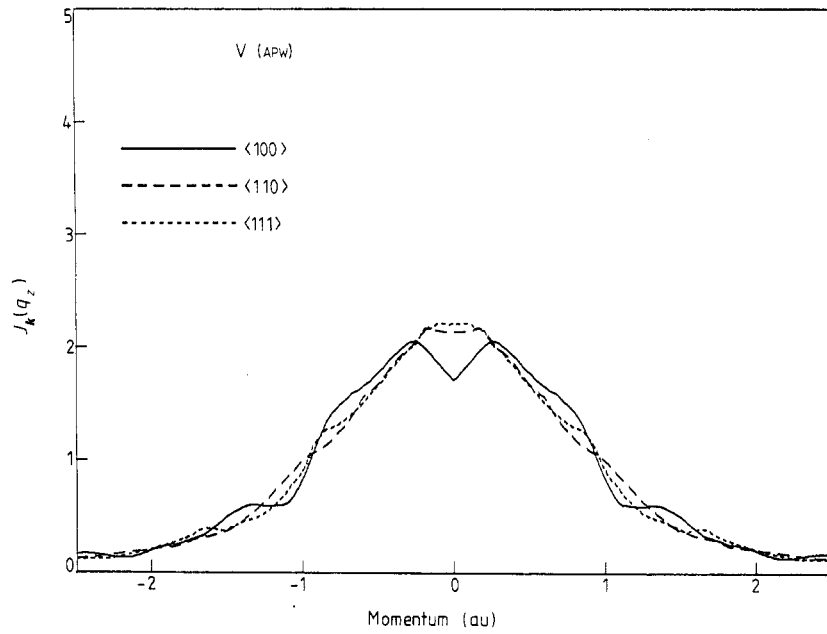
where  $E_b$  is determined to be at  $E_{82}$ . The numerical value obtained from equation (9) is 0.69. Also, in the case of chromium the amount of mixing is again about 12%. The theoretical correlation profiles of chromium are shown by full curves in figure 2. This figure has already been published together with error bars and the Lam-Platzman correction by Cardwell *et al* [8].

When individual experimental Compton profiles were less reliable, more reliable directional difference profiles were used to investigate the discrepancy between theory and experiment. It has already been shown for chromium [8] how the correlation correction improved the agreement between theory and experiment. Now it is no longer necessary to use directional differences—they are not shown in this paper.

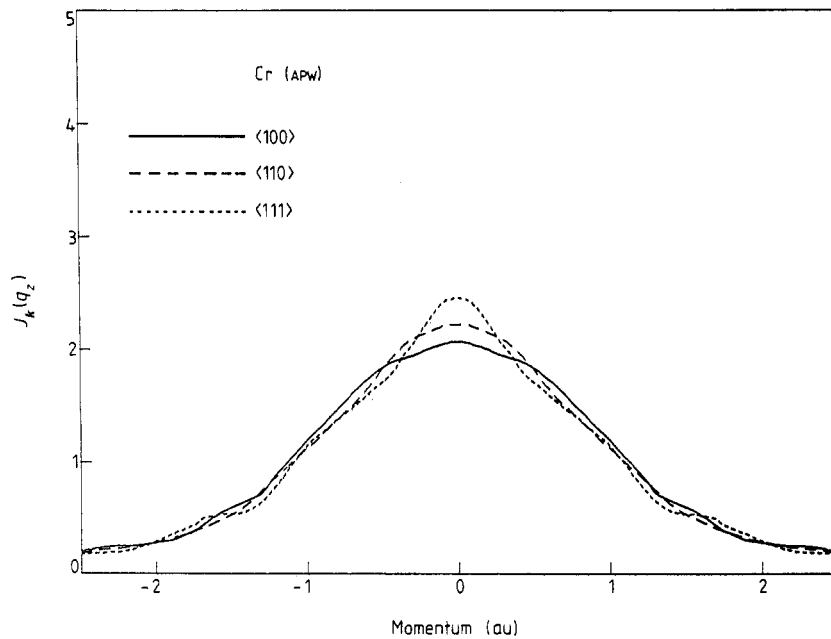
#### 4. Discussion and conclusion

As the values of the total Compton profiles of vanadium and chromium are about 5 at the origin ( $q = 0$ ), and those of the correlation effect are about 0.1, the correlation correction is a very small proportion of the profiles. Still, the agreement between the theoretical correlation curves and the experimental ones is very good. It can be said that the correlation effects are reproduced very well by introducing the energy occupation function. Although the theoretical correlation lines are almost zero in the higher momentum regions, the experimental ones are not. This fact may be due to a problem encountered in processing the experimental data. When the values of the experimental correlation curves in the higher momentum region tend to zero, the values around the origin should also be reduced a little, since the positive and negative areas of the curves should always cancel out.

Although the underlying band structure calculation is based on the use of only 55  $k$  points in the irreducible part of the Brillouin zone, and the Compton profiles are estimated by a linear interpolation procedure, this corresponds to a much finer sampling interval in momentum space than the experimental resolution width (0.13 au compared



**Figure 8.** One-electron theoretical Compton profiles due to the five band electrons in vanadium for three major scattering directions (from [3]).



**Figure 9.** One-electron theoretical Compton profiles due to the six band electrons in chromium for three major scattering directions (from [3]).

with 0.4 au). A finer mesh for the calculation will only be required if higher resolution experiments are ever performed.

Now some features of the correlation profiles of vanadium and chromium are analysed.

Firstly some of the momentum density around the origin is moved to the region where the momentum is larger than one atomic unit. This feature is common to the curves for vanadium and chromium and is also similar to the Lam-Platzman correction for the electron gas system. In the case of vanadium and chromium, the energy occupation function shifts about 12% of the electron density from below the Fermi level to energy states higher than the Fermi level. Within the d band, the radial wave functions of d components in the higher energy states are more contracted than those in the lower energy states, and the momentum distributions for the higher energy states ( $\approx 22-40$ ) are more extended than those for the lower energy states ( $\approx 10-22$ ). The situation can be seen from figures 3, 4 and 5. Therefore, introduction of the energy occupation function moves some amount of momentum density from the lower momentum region to the higher one.

Secondly, it can be seen from figures 1 and 2 that although the shapes of the theoretical correlation curves are different from each other, they are very similar to those of the corresponding experimental ones. The origin of the overall shapes is basically the Lam-Platzman correction, but the structures in the curves can be understood as follows. In the case of vanadium, the structures in the Compton profiles are predominantly due to the jungle-gym structure of the Fermi surface in the third band [1]. The structures are seen in the curves in figure 8 [3], which are obtained by a one-electron band theoretical calculation. As the energy occupation function without correlation is a step function, the jungle-gym Fermi surface gives rise to very remarkable structures in the curves. The correlation effect should weaken the structures. It is clearly seen that the peaks at the origin and at about 1 au in the  $\langle 100 \rangle$  correlation curve for vanadium in figure 1 correspond to the concaves on the  $\langle 100 \rangle$  profile shown in figure 8. The relatively sharp concave at the origin in the  $\langle 111 \rangle$  correlation curve for chromium in figure 2 corresponds to the sharp peak at the origin in the  $\langle 111 \rangle$  profile shown in figure 9 [3].

From these facts we may conclude that the effects of correlation on the Compton profiles of vanadium and chromium, whose Fermi levels are located in the middle of the d bands, are predominantly due to the energy occupation function  $n(E)$  for the d bands. In the case of iron, nickel and copper, however, the situation should be more complicated, because in those metals the Fermi level is very close to the top of the d bands.

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